

Werner Freyland

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Coulombic Fluids

Bulk and Interfaces



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Coulombic Fluids

Bulk and Interfaces

With 117 Figures



Springer

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*To my wife Beate and our children Laura,
Felix, and Moritz*

Preface

During the last decade, the number of publications on ionic liquids has increased nearly exponentially. Obviously, this reflects an enormous interest in these liquids and their potential applications. Among their most striking characteristics are the low melting points near room temperature and the extremely low vapour pressures in the liquid state. Furthermore, a large variety of ionic liquids can be synthesized and so their properties can be tailored depending on the chemical demands. Generally, they are composed of an organic cation and an inorganic or organic anion. Therefore, their bulk and interfacial properties are dominated by Coulomb or Coulombic interactions. By focusing on this characteristic, one expects some similarities with their classical counterpart, the molten salts such as alkali halides that have been studied intensively for quite some time. So, the question arises: What can we learn from molten salts which could help improving our understanding of ionic liquids? Such a comparison is one of the main motivations for writing this book. Points of particular interest in the bulk phase concern their microscopic structure, the phase behaviour and critical phenomena, solubilities and solvation characteristics, transport, and other physicochemical properties. Interfacial phenomena comprise adsorption, wetting, and spreading characteristics, the problem of the electric double layer in ionic media, and, more generally, the electrified ionic liquid/electrode interface as well as potential electrochemical applications, for instance, in electrocrystallization or electrowetting. With regard to interfaces, in particular, a reversal of the above question is of similar attraction for molten salts. Due to their low vapour pressures, several interfacial investigations employing ultrahigh vacuum can be performed with ionic liquids, but are difficult or not possible with molten salts at elevated temperatures. So, there is a productive influence in both directions. This potential for interface studies has been realized only recently.

A further objective of this book deals with the change of the interionic interaction and electronic structure in systems such as metal–molten salt solutions or fluid metals. By expansion of a fluid metal or its dilution by adding salt, the electronic screening of the Coulomb potentials can be reduced to such an extent that electrons become localized or trapped in the Coulomb well and a metal–nonmetal transition occurs. The characteristics of this electronic transition in the fluid state are treated for selected examples.

The focus of this book is on a comparative study of molten salts and ionic liquids and their bulk and interfacial physicochemical properties. Special attention is drawn to recent experimental work and results of computer simulations. In addition, the topic of electronic transitions in fluids has been included, which bridges the way from electron to ion conducting liquids. All these systems have in common a dominating Coulomb interaction and so may be classified as Coulombic fluids. The first book entitled ‘Coulomb Liquids’ appeared in 1984 by March and Tosi. Its main focus was on different theoretical aspects of liquids, especially liquid metals and molten salts. In this book, the emphasis is on experimental research of molten salts and ionic liquids and their possible electrochemical applications in nanotechnology. It addresses to scientists and engineers working in the field, to physicists and chemists, as well as to material scientists interested in soft condensed matter. An introduction into the basic concepts and a detailed description of some of the main experimental methods assist the interested graduate student to get a direct access to these new and promising liquids.

Many of the results presented in the following chapters are based on investigations by the author’s research group mainly over the last two decades. So, I am pleased to acknowledge gratefully the valuable contributions of my former research students and co-workers. For outstanding collaboration over several years, I am particularly indebted to D. Nattland and Th. Kosłowski, C.L. Aravinda, V. Halka, G.B. Pan, R. Tsekov, and A. Turchanin. Special thanks are due to F. Hensel who introduced me to the fascination of fluid metals. During the preparation of the text and figures of this book, I got valuable assistance by D. Rohmert-Hug and J. Szepessy to whom I am especially grateful. Last, but not least, it is my pleasure to thank my brother Max and my good friend Helmut who always kept an eye on my health.

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Werner Freyland

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Acronyms

CV	Cyclic voltammetry
DC	Direct current
DL	Double layer
EC-STM	Electrochemical scanning tunnelling microscopy
EC-SPM	Electrochemical scanning probe microscopy
EMF	Electromotive force
ESR	Electron spin resonance
EXAFS	Extended X-ray absorption fine structure
FFT	Fast Fourier transform
GCS	Gouy–Chapman–Stern
HOPG	Highly oriented pyrolytic graphite
IR-VIS	Infrared-visible
MC	Monte Carlo simulation
MD	Molecular dynamics simulation
ML	Monolayer
NFE	Nearly free electron
NMR	Nuclear magnetic resonance
OCP	Open circuit potential
OPD	Overpotential deposition
PZC	Potential of zero charge
QMD	Quantum molecular dynamics
SHG	Second harmonic generation
STM	Scanning tunnelling microscopy
STS	Scanning tunnelling spectroscopy
UHV	Ultrahigh vacuum
UPD	Underpotential deposition
XPS	X-ray photoelectron spectroscopy

Chapter 1

Introduction

Generally, liquids are an intermediate between the solid and vapour phase and merge in the fluid state at supercritical conditions. In a first approach to understanding the liquid state, its intermolecular interactions, and properties, a comparison with the characteristics of the neighbouring coexisting solid and vapour phases is of interest.

On melting, crystalline solids – metals or salts – exhibit drastic changes in some properties; in others, they do not. Ionic crystals such as the classical inorganic salts (e.g. NaCl and KCl) undergo a transition from insulators to ionic conductors with conductivities in the range of $1 \Omega^{-1} \text{ cm}^{-1}$. A similar change occurs with the so-called room temperature molten salts or ionic liquids – composed of an organic cation and an organic or inorganic anion – although these melts have lower conductivities of about $10^{-2} \Omega^{-1} \text{ cm}^{-1}$ (e.g. imidazolium-based ionic liquids). With metals, the electronic conductivity is only slightly reduced on melting, which is consistent with the nearly free electron (NFE) model and a strong screening of the Coulomb potential by these electrons. Thus, at conditions near the normal melting point, the electrical conductivity of Coulombic fluids spans a range of nearly seven orders of magnitude.

The structural properties vary significantly on fusion. The structure transforms from a periodic lattice into a disordered liquid. In the liquid state, only a local structure or ordering persists, which reflects the nature of interatomic interactions and is described by average interparticle distribution or correlation functions. In Coulomb liquids, such as the classical molten salts, local charge cancellation leads to nearest neighbour ordering of positive and negative ions. In ionic liquids, such as the imidazolium-based melts, this effect, in general, is less pronounced as the ions are relatively bulky and polarization forces and steric effects come into play. In simple liquid metals, such as the alkalis, structural ordering can extend up to third nearest neighbour distances. To understand this microscopic structure and the cohesive energies of liquid metals, a proper description of the screening of the ions by the electron fluid is essential. Specific differences among Coulomb liquids are also seen in the density variation on melting, which is related with the structural changes. Most metals expand only slightly, by 2–4%, whereas molten salts exhibit a relatively large volume increase of up to $\sim 25\%$ (e.g. NaCl).

The few properties considered so far represent the thermodynamic conditions near the melting point. Unusual and peculiar characteristics can be induced if one

varies the thermodynamic state of a Coulombic fluid over a larger range of density and temperature. With respect to this, the thermodynamic critical point is of particular interest. At supercritical conditions, the density can be reduced continuously from liquid-like to gas-like values, which has a strong impact on the intermolecular interactions. For instance, a molten salt can be transformed continuously from an ionic conductor into an insulating molecular fluid characterized by ion pairing. This was shown first for the example of bismuth chloride by Tödheide and Treiber in 1973. In a similar manner, a metal–nonmetal transition occurs in supercritical metals, which was initially studied for fluid mercury by Kikoin and Sechenkov, and Hensel and Franck in the 1960s. Reducing the mass density and thus the number density of nearly free electrons of expanded fluid metals, a limit is reached where screening of the ions by the electron fluid is no longer sufficient, so electron localization and nonmetallic behaviour set in. A continuous variation of the electron density can also be achieved in metal–molten salt solutions at elevated temperatures, as was shown originally by Bredig and co-workers. Again, a metal–nonmetal transition is observed as a function of metal mole fraction. An advantage of these systems in comparison with solids such as highly doped semiconductors is that the electronic phase transition can be investigated in a permanent thermal equilibrium state. Continuous research on this subject and, more generally, on metal–insulator transitions in condensed matter is focusing on the interplay of disorder and electronic correlation. Distinct aspects of such metal–nonmetal transitions in Coulombic fluids are presented in this book.

In recent years, significant progress has been made in the experimental and theoretical investigation of fluid interfaces. This includes phenomena such as equilibrium wetting and wetting transitions, dynamics of liquid spreading, electrowetting, and also surface freezing transitions. They play an important role in many fields, on both the macroscopic and microscopic or nanoscopic scale. The technological interest ranges from processes such as soldering, coating, or development of new battery electrodes with higher efficiency and also includes self-cleaning surfaces. These interfacial phenomena have attracted the interest of scientists and engineers in such diverse disciplines as material science, physics, chemistry, and biology. A central part of this book focuses on the wetting phenomena and interfacial phase transitions in different Coulombic fluids. Experimental observations of their peculiar interfacial behaviour are described and discussed in comparison with those of simple liquids of the van der Waals type.

The aim of this book is to cover selected topics of actual research on different Coulomb liquids, their bulk, and interfacial phenomena. First, an introduction into some basic features and theoretical concepts of liquid metals, molten salts, and room temperature ionic liquids is given. This includes a comparative description of the microscopic structures and their relation with the interatomic potentials, a brief survey of the bulk phase behaviour and possible extensions of the liquid range, and a comparison of the electrical transport properties. Some basic interfacial characteristics such as wetting and electrowetting are introduced, and specific properties such as layering at liquid metal surfaces and charge ordering at electrified liquid/solid interfaces of ionic media are presented in detail. In Chap. 3, the problem

of metal–nonmetal transition in expanded fluid alkali metals, alkali metal alloys, and alkali metal–alkali halide solutions is addressed, with emphasis on the latter. This chapter is introduced by a brief summary of the important theoretical approaches and concepts necessary for the interpretation of the experimental results. A major part of the book deals with interfacial phenomena of Coulombic fluids including wetting transitions at the solid/liquid and liquid/vapour interface, interfacial oscillatory instabilities, and surface freezing transitions. This is presented in Chap. 4 on the basis of experimental investigations and simple thermodynamic model calculations. The first part of Chap. 5 deals with the problem of the electrical double layer in molten salts and ionic liquids in comparison with aqueous electrolytes. In the remaining sections of this chapter, the focus is on the electrified ionic liquid/solid interface. They deal with 2D electrochemical phase formation and phase transitions such as spinodal decomposition and describe nanoscale electrodeposition of metals and semiconductors for a few selected examples. In the final chapter (Appendices), a few techniques and their experimental adaptation to the specific measurement conditions that are necessary for the study of Coulombic fluids are described. For those contemplating future experimental studies of such systems, this information can prove to be of value.

Chapter 2

Liquid Metals, Molten Salts, and Ionic Liquids: Some Basic Properties

Abstract In the second chapter, some basic concepts of statistical thermodynamics of liquids and of the nearly free electron model are introduced including quantities such as the pair distribution function $g(r)$, the structure factor $S(q)$, and the dielectric function of electronic screening. This is followed by a more detailed description of intermolecular potentials and microscopic structures of liquid metals, molten salts, and ionic liquids, both their theoretical foundation and experimental determination. A summary of the bulk phase behaviour of Coulombic fluids with emphasis on the liquid range is given. Specific thermodynamic characteristics such as undercooling, the vapour pressures of ionic liquids, or their criticality in binary mixtures are discussed. The mechanisms of electronic and ionic transport are briefly described. In the final section on interfacial characteristics, a few fundamental relations such as the Gibbs adsorption equation and the basic equations of wetting and electrowetting together with the scenario of wetting transitions are introduced. Furthermore, topics such as the stratification at liquid metal/vapour interfaces and charge ordering at electrified liquid/solid interfaces of molten salts and ionic liquids are presented. All sections contain tables with representative numbers for the properties considered.

2.1 Distribution Functions and Statistical Thermodynamics: A Brief Introduction

For the calculation of thermodynamic quantities of simple classical fluids, by either statistical thermodynamics or computer simulation methods, configurational distribution functions play a key role. They describe the microscopic structure of a fluid on the same distance scale as the intermolecular interactions. Considering a system of uniform number density, $n = N/V$, with a specific distribution of the coordinates of N molecules, $\underline{r}^N = \underline{r}_1, \underline{r}_2, \dots, \underline{r}_N$, and of their momenta, $\underline{p}^N = \underline{p}_1, \underline{p}_2, \dots, \underline{p}_N$, the N -particle probability density distribution function, $p_N(\underline{r}^N, \underline{p}^N)$, is defined by

$$p_N(\underline{r}^N, \underline{p}^N) = \frac{\exp(-H_N \cdot \beta)}{Q_N}. \quad (2.1)$$

Here, $\beta = 1/kT$, with k being the Boltzmann constant, T the absolute temperature, and H_N and Q_N denote the total energy or Hamiltonian and the partition function of the system, respectively. The Hamiltonian has the usual form,

$$H_N(\underline{r}^N, \underline{p}^N) = \sum_{i=1}^N \underline{p}_i^2/2m + \phi(\underline{r}^N), \quad (2.2)$$

where $\phi(\underline{r}^N)$ is the total potential energy of the system. It is assumed that all particles have the same mass m . With the constraints that the number of molecules, N , the temperature, T , and the volume, V , are constant, the canonical partition function Q_N is given by – see e.g. [2.1]:

$$Q_N = \frac{1}{N!h^{3N}} \int \cdots \int \exp(-\beta \cdot H_N(\underline{r}^N, \underline{p}^N)) d\underline{r}^N d\underline{p}^N, \quad (2.3)$$

with h being the Planck constant. Knowing the distribution function p_N , the ensemble average of any property $X = X(\underline{r}^N, \underline{p}^N)$, in principle, can be calculated according to

$$\langle X \rangle = \int \cdots \int X(\underline{r}^N, \underline{p}^N) \times p_N(\underline{r}^N, \underline{p}^N) d\underline{r}^N d\underline{p}^N. \quad (2.4)$$

A solution of integrals like those in (2.3) or (2.4) requires an analytical form for $\phi(\underline{r}^N)$. To this end, numerous approaches have been developed; see e.g. [2.1]. A simple and often used approximation is that by pair potentials $\phi_{ij}(r_{ij})$,

$$\phi(\underline{r}^N) = \sum_{i>j=1}^N \phi_{ij}(r_{ij}) + \Delta\phi, \quad (2.5)$$

where $r_{ij} = r_i - r_j$ and the correction term $\Delta\phi$ summarizes all higher order contributions to the potential energy.

In the discussion of the local microscopic structure of simple liquids – i.e. liquids composed of identical particles with no internal structure and where the force between two particles 1 and 2 depends only on the distance $r_{12} \equiv r$ – the radial pair distribution function, $g(r)$, is of special interest. It is derived from $p_N(\underline{r}^N, \underline{p}^N)$, (2.1), by integrating the momenta out and averaging over the positions of the remaining $N - 2$ molecules; this yields the two-particle distribution function, see also [2.2],

$$g_2(\underline{r}_1, \underline{r}_2) = V^2 \int \cdots \int \frac{\exp(-\beta \cdot \phi(\underline{r}^N))}{Q_N^C} d\underline{r}_3 \cdots d\underline{r}_N, \quad (2.6)$$

where Q_N^C is the configurational partition function. It is obtained from (2.3) after integration of the momenta p^N and dividing Q_N by this integral. The distribution function $g_2(r_1, r_2)$ defines the relative probability of two molecules 1 and 2 being found simultaneously at r_1 and r_2 .

According to the definition in (2.6), g_2 is dimensionless. If spherical symmetry can be assumed, the radial pair distribution function, $g(r)$, results,

$$g(r) = \frac{n(r)}{4\pi nr^2 dr}. \quad (2.7)$$

Here, $n(r)$ is the number of molecule centres in a spherical shell of radius r and thickness dr surrounding an arbitrary molecule at the centre. Within the pair potential approximation, another simple relation for $g(r)$ results from (2.6):

$$g(r) = \exp(-\beta\phi(r)), \quad (2.8)$$

where $\phi(r)$ stands for $\phi_{ij}(r_{ij})$. Strictly speaking, this equation only holds in the limit of low densities where $\Delta\phi \rightarrow 0$ in (2.5). On the other hand, for dense fluids with $\Delta\phi \neq 0$, the effect of higher order interactions can be taken into account by introducing the so-called potential of mean force, $\phi_{\text{eff}}(r)$. The corresponding radial pair distribution function is as follows:

$$g(r) = \exp(-\beta \cdot \phi_{\text{eff}}(r)), \quad (2.9)$$

which, in first approximation, describes contributions of nearest and second nearest neighbours. An illustration of the behaviour of the radial pair distribution function of a dilute fluid (gas) in comparison with that of a dense liquid is presented in Fig. 2.1.

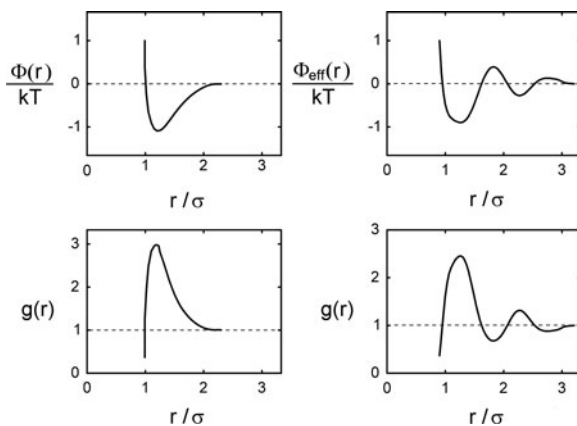


Fig. 2.1 *Upper panel:* Schematic drawing of pair potential, $\phi(r)$, and potential of mean force, ϕ_{eff} , vs. distance in units of the hard-sphere diameter σ ; *lower panel:* corresponding radial pair distribution functions, $g(r)$

Experimentally, the pair distribution function $g(r)$ can be determined from X-ray or neutron diffraction measurements of the structure factor, $S(q)$; see Sect. A.1. These quantities are related by Fourier transformation according to:

$$S(q) = 1 + 4\pi \cdot n \int_0^\infty (g(r) - 1) \frac{\sin qr}{qr} r^2 dr. \quad (2.10)$$

In the limit $q \rightarrow 0$ the structure factor obeys the relation,

$$S(0) = \kappa_T n k T, \quad (2.11)$$

where κ_T is the isothermal compressibility. This thermodynamic limit is often used as an independent check of the correction of scattering data.

In this chapter, some basic relations of statistical thermodynamics and microscopic structure of simple liquids have been summarized, which are of interest in the following. For a detailed presentation of *the theory of simple liquids*, reference is given to the classical book by Hansen and McDonald [2.3].

2.2 Interatomic Interactions and Microscopic Structures

2.2.1 Liquid Metals

The physics of metallic matter, in the solid and liquid state, is described in many monographs and textbooks, of which the following references are especially recommended for further studies [2.4–2.7]. Here, we confine to a short introduction of simple characteristics of the metallic state and briefly sketch the main approximations leading to screened effective pair potentials in metals.

Metals, in general, may be considered as a two-component system made up of ions and delocalized conduction electrons, whereby the latter originate from the valence electrons of the metal atoms. The volume fraction occupied by the ion cores is usually small so that most of the space in simple metals is available for the conduction electrons – for example, in solid or liquid alkali metals at conditions near their normal melting point only about 15% of the specific volume is taken by the ion cores. In the simplest approximation, the conduction electron states are treated as a gas of free and independent electrons – free electron (FE) model. Thus, the eigenstates of these electrons are the solutions of the time-independent Schrödinger equation,

$$\frac{-\hbar^2}{2m_e} \nabla^2 \Psi(\underline{r}) = E \Psi(\underline{r}), \quad (2.12)$$

with the periodic boundary conditions:

$$\Psi(x + L, y, z) = \Psi(x, y, z), \quad (2.13)$$

and similar for y , z . Here, the electron of mass m_e is contained in a 3D cube of volume $V = L^3$. The eigenfunctions are running plane waves,

$$\Psi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{V}} \exp(i \underline{k} \cdot \underline{r}), \quad (2.14)$$

with energy

$$E(\underline{k}) = \frac{\hbar^2 k^2}{2m_e}. \quad (2.15)$$

Since $\Psi_{\underline{k}}(\underline{r})$ is also a solution of the momentum operator, $\hbar \underline{k}$ has the meaning of a momentum. Due to the boundary conditions, the wave vector $\underline{k}$ has only certain discrete values of the form: $k_x = 2\pi n_x/L$, $k_y = 2\pi n_y/L$, and $k_z = 2\pi n_z/L$, with $n_i = \text{integers}$. For the ground state ($T = 0\text{K}$) of N noninteracting electrons, we begin by placing two electrons in the lowest energy state of $E = 0$ with $\underline{k} = 0$ and continue up to the highest electron level with energy E_F (Fermi energy) and wave vector k_F (Fermi wave vector). The factor 2 results from the Pauli exclusion principle, i.e. for each $\underline{k}$ there are two states, one for each spin direction. Within a sphere of radius k_F , the number of occupied states is $N = 2(4\pi k_F^3/3)/(2\pi/L)^3$ and thus k_F can be expressed by

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}. \quad (2.16)$$

In a similar way, the number of states per energy unit or the density of states, $n(E)$, can be derived; see e.g. [2.4]:

$$n(E) = \frac{3}{2} \left(\frac{n}{E_F} \right) \left(\frac{E}{E_F} \right)^{1/2}, \quad (2.17)$$

where $n = N/V$.

At finite temperatures, the occupation of the electronic energy levels is determined by the Fermi–Dirac distribution function,

$$f(E) = \left(\exp \left(\frac{(E - \mu)}{kT} \right) + 1 \right)^{-1}, \quad (2.18)$$

where μ is the chemical potential of electrons with $\mu \equiv E_F$ for $T = 0$. With the aid of $n(E)$ and $f(E)$ the internal energy U of the free electron gas is given by

$$U = V \int E n(E) f(E) dE, \quad (2.19)$$

which yields for the average energy per electron in the ground state: $\langle E \rangle = (3/5) \cdot E_F$.

The free electron or Sommerfeld theory of metals successfully accounts for some metallic properties including the temperature dependence of the specific heat at low temperatures and the high metallic conductivities, at least qualitatively. In this theory, the ions play no role with exception of maintaining overall charge neutrality. However, in many respects, this model is unrealistic! In the neighbourhood of the ion cores, the conduction electrons clearly interact with the positively charged ions. Nevertheless, for the following reasons, the electrons do not experience the full Coulomb attraction, but only a weak potential that may be approximated by a weak, nearly constant pseudopotential – nearly free electron (NFE) model. The first argument is that due to the Pauli exclusion principle the conduction electrons are expelled from the region of core electrons where the Coulomb attraction would be strongest. Secondly, outside the ion core the Coulomb interaction a conduction electron experiences is strongly screened by the rest of electrons. So the interactions between the ions and the conduction electrons can be treated as a weak perturbation (NFE model). In the following, the effect of screening is discussed in more detail; see also [2.4].

We first consider a positively charged particle with charge density $\rho_+(\underline{r})$ at a fixed position inside the electron gas. The electrostatic potential, $\phi_+(\underline{r})$, resulting from ρ_+ itself is given by Poisson's equation:

$$\nabla^2 \phi_+(\underline{r}) = -4\pi \rho_+(\underline{r}). \quad (2.20)$$

The Fourier transform of (2.20) is as follows:

$$q^2 \phi_+(\underline{q}) = 4\pi \rho_+(\underline{q}). \quad (2.21)$$

Very similar relations hold for the total potential $\phi(\underline{r})$ produced by both the positively charged particle and the induced cloud of screening electrons, $\rho_-(\underline{r})$. If the positive charge is an ion, the system of ion plus screening cloud of electrons sometimes is called a *pseudoatom*, though the screening electrons are not bound to the ion. To quantify the effect of screening, a linear relation between the Fourier components of $\phi(\underline{r})$ and $\phi_+(\underline{r})$ is assumed,

$$\phi(\underline{q}) = \varepsilon(\underline{q})^{-1} \phi_+(\underline{q}), \quad (2.22)$$

where the reduction of ϕ_+ is described by the wave vector dependent dielectric function, $\varepsilon(q)$. For sufficiently weak ϕ , the linear relation of (2.22) should hold. The problem of screening is now the determination of $\varepsilon(q)$. In quantum theoretical calculations, the quantity that is more directly accessible is the charge density $\rho_-(\underline{r})$ induced in the electron gas by $\phi(\underline{r})$. Assuming again a linear relation between ρ_- and ϕ , their Fourier transforms satisfy the equation:

$$\rho_-(\underline{q}) = \chi(\underline{q}) \phi(\underline{q}). \quad (2.23)$$

From (2.21) and the corresponding Fourier transform of $\nabla^2 \phi(\underline{r}) = -4\pi (\rho_+(\underline{r}) + \rho_-(\underline{r}))$, the following relation between $\varepsilon(\underline{q})$ and $\chi(\underline{q})$ results:

$$\varepsilon(\underline{q}) = 1 - \left(\frac{4\pi}{q^2} \right) \chi(\underline{q}) = 1 - \frac{(4\pi/q^2)\rho_-(\underline{q})}{\phi(\underline{q})}. \quad (2.24a)$$

The determination of $\chi(\underline{q})$ and thus of $\varepsilon(\underline{q})$ now concentrates on the calculation of $\rho_-(\underline{q})$. This, in principle, can be obtained from the electron pseudowave functions using ϕ as the potential in the Schrödinger equation. Here, we consider two approximate solutions. In the Thomas–Fermi approximation, the dielectric constant is as follows:

$$\varepsilon(\underline{q}) = \frac{1 + k_{\text{TF}}^2}{q^2}, \quad (2.24b)$$

where $k_{\text{TF}} = 0.815(r_s/a_B)^{1/2} \cdot k_F$ is the Thomas–Fermi screening length, $r_s = (3/4\pi n)^{1/3}$, and $a_B = \text{Bohr radius}$. Since r_s/a_B is about 2–6 for metals, k_{TF} is of the order of k_F . To illustrate the effect of $\varepsilon(\underline{q})$ on $\phi_+(\underline{r})$, we consider as an example a point charge with $\phi_+(\underline{r}) = Q/r$ and with the Fourier transform $\phi_+(\underline{q}) = 4\pi Q/q^2$. The total potential $\phi(\underline{q})$ is then as follows:

$$\phi(\underline{q}) = \varepsilon(\underline{q})^{-1} \phi_+(\underline{q}) = \frac{4\pi Q}{(q^2 + k_{\text{TF}}^2)}, \quad (2.25)$$

which has the inverse Fourier transform

$$\phi(\underline{r}) = \left(\frac{Q}{r} \right) \cdot \exp(-k_{\text{TF}} \cdot r), \quad (2.26)$$

i.e. in the Thomas–Fermi approximation, the Coulomb potential is exponentially screened over a distance of the order of k_F^{-1} .

The second approximation, first given by Lindhard [2.8], is a first-order perturbation calculation of $\rho_-(\underline{r})$ within the Hartree model. In this case, the screening of a point charge at large distances takes the following form:

$$\phi(r) \sim W(2k_F)^2 \cdot (2k_F r)^{-3} \cos(2k_F r). \quad (2.27)$$

The amplitude of the so-called Friedel oscillations of $\phi(r)$ is determined by the magnitude of the screened pseudopotential $W(\underline{q})$ at $q = 2k_F$. It may also be noted that the screening in the Lindhard approximation decays more weakly with r in comparison with the Thomas–Fermi approximation. With the knowledge of electronic screening, the construction of the effective interionic or pair potential $\phi(R)$ ¹ in pure metals is straightforward. Effective here means that the interionic interaction

¹ In the following, we also use R for the intermolecular distance in the pair potentials.

is mediated by the electron gas. It is assumed that at low R a Thomas–Fermi type repulsion prevails, whereas at intermediate and large R the attraction is given by an oscillatory potential. Thus, $\phi(R)$ can be approximated by

$$\phi(R) = \frac{2Z^2}{R} \exp(-k_{\text{TF}}R) + W(2k_{\text{F}})^2 \frac{\cos(2k_{\text{F}}R)}{(2k_{\text{F}}R)^3}, \quad (2.28)$$

i.e. the ion core is approximated by a point charge. It is worth noting that this pair potential, unlike, for instance, a conventional Lennard–Jones potential, depends on the volume V , because k_{F} is a function of V . Therefore, a better specification of ϕ should be $\phi(R; V)$, which implies that in metals a state-dependent potential has to be considered. The characteristic behaviour of $\phi(R; V)$ is shown in Fig. 2.2 for the examples of Na and Al. The respective potentials have been calculated using the same empty-core pseudopotentials but with different screening of the Coulomb repulsion – for further details see [2.5].

A first test of effective pair potentials of metals was performed by Rahman [2.9]. By employing a potential of Price et al. [2.10], he calculated the static structure factor of liquid Rb by molecular dynamic simulations and found good agreement with experimental results from neutron diffraction [2.11]. This is shown in Fig. 2.3.

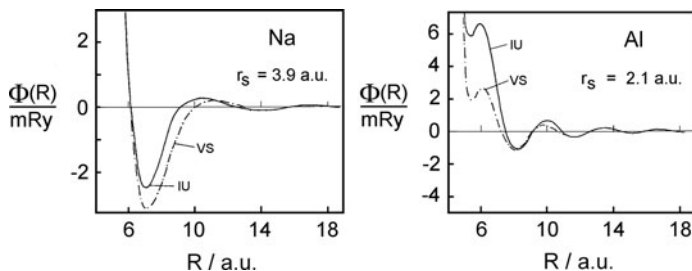


Fig. 2.2 Effective pair potentials for Na (*left*) and Al (*right*); the respective different curves correspond to different screening of the Coulomb repulsion – see Hafner [2.5]. Copy right permission (2010) by Springer Publishers

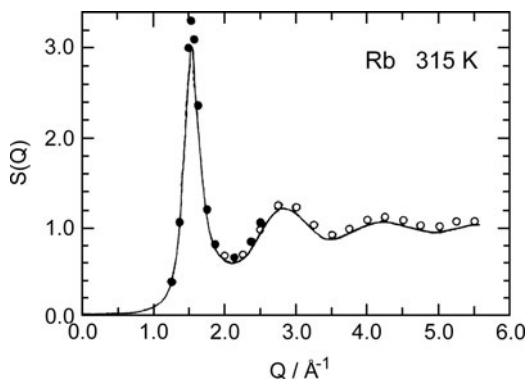


Fig. 2.3 Structure factor, $S(Q)$, of liquid Rb as obtained from MD calculations (*full line*) and neutron diffraction (*full and open symbols*). Figure adopted from [2.11] with permission from Copley and Rowe; copyright permission (2010) by the American Physical Society

2.2.2 Molten Salts and Ionic Liquids

In this section, we concentrate on the characteristic structural properties of molten salts and ionic liquids. They consist of oppositely charged species, but the character of these species varies from classical ions in the typical molten salts to charged polyatomic molecules in ionic liquids. The prototype of molten salts are fused alkali halides that contain closed-shell alkali and halogen ions and which exhibit high melting temperatures around 1,000 K. On the other hand, most ionic liquids have a polyatomic organic cation and an inorganic or organic anion. They typically melt near room temperature and, therefore, in the beginning, were also named room temperature or ambient temperature molten salts [2.12, 2.13]. The first ionic liquids, which were synthesized and characterized around 1980, were based on pyridinium [2.14] and imidazolium [2.15], [2.16] cations; see Fig. 2.4; mixtures of their chlorides with AlCl_3 become liquid over a wide range of compositions below room temperature; see e.g. Fig. 2.13 in Sect. 2.3. Over the last two to three decades, a large variety of ionic liquids have been synthesized, including so-called air and water stable melts, and have been applied in different fields such as organic, inorganic, or polymer synthesis, electrochemistry, catalysis, and various industrial processes – for a comprehensive description of properties, synthesis, and applications, see [2.13].

On melting of an alkali halide crystal, the ionic short-range order essentially remains. This is demonstrated by the partial pair distribution functions $g_{+/-}(R)$ for the example of molten RbCl in Fig. 2.5, which have been obtained from neutron diffraction experiments with isotopic substitution [2.17]. On comparing the coordination of unlike and like ions, a remarkable short-range order, i.e. alternation of charges, in the ionic melt is apparent. This also implies that ionic screening is oscillatory rather than monotonously decaying as in concentrated electrolytes. The first peak in $g_{+/-}(R)$, which marks the correlation of unlike ions, is rather pronounced and the first minimum is quite deep. This last observation suggests a slow exchange rate of ions between the first-neighbour shell and the bulk liquid. From MD calculations, a displacement time of two unlike ions of the order of several picoseconds has been estimated; see also [2.18]. The nearest neighbour distance, $R_{+/-}$, defined by the sharp maximum in $g_{+/-}(R)$, is slightly smaller than in the solid; see Table 2.1. This peak is asymmetrically broadened so that the corresponding coordination number $N_{+/-}$ is not clearly defined. If one mirrors the left part of the peak at $R_{+/-}$, this yields an average number of unlike ions in close contact of ~ 4 [2.18]. On the other hand, integration of the peak up to the first minimum yields an average nearest neighbour coordination number of ~ 6 , which is comparable with the crystal value;

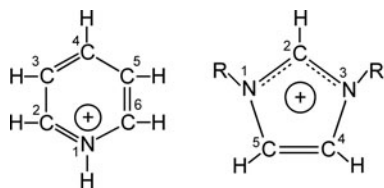


Fig. 2.4 Pyridinium (*left*) and imidazolium cation

Fig. 2.5 Smoothed partial pair distribution functions of molten RbCl obtained by neutron diffraction. Reprinted with permission from [2.17]; copyright permission (2010) by Taylor & Francis

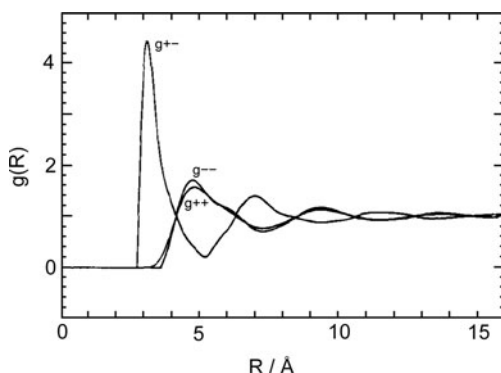


Table 2.1 Structural properties of solid (s) and liquid (l) alkali halides near the melting temperature, T_m , at atmospheric pressure: $R_{+/-}$ = nearest neighbour distance; $N_{+/-}$ = coordination number of nearest neighbours; $\Delta V/V$ = fractional volume change

	T_m/K	$R_{+/-}^{(s)}/\text{\AA}$	$N_{+/-}^{(s)}$	$R_{+/-}^{(l)}/\text{\AA}$	$N_{+/-}^{(l)}$	$\Delta V/V\%$
NaCl	1,081 (a)	2.814 (a)	6	2.78 (b)	~ 5.8 (b)	25 (e)
KCl	1,045 (a)	3.139 (a)	6	3.06 (c)		17.3 (e)
RbCl	990 (a)	3.27 (a)	6	3.18 (d)	~ 6.9 (d)	14.3 (e)

References in brackets: a = [2.19]; b = [2.20]; c = [2.21]; d = [2.18]; e = [2.22]; the $R_{+/-}^{(s)}$ values are taken at room temperature, the uncertainty of the liquid values is $\pm 0.05 \text{ \AA}$

see Table 2.1. Possibly, the reduced number of 4 can explain the relatively large expansion of the alkali halides on melting. The characteristic structural changes described here for the example of RbCl agree with further neutron diffraction studies of NaCl [2.20] and KCl [2.21] at conditions near the melting point.

Starting from the close similarity in the local microscopic structures of crystalline and molten alkali halides, this suggests the use of similar interionic model potentials to calculate the structural and thermodynamic properties of molten metal halides. The most widely applied form is the Born–Mayer potential, see e.g. [2.23], which is given by

$$\phi_{ij}(R) = A_{ij} \exp((R_i + R_j - R)/\alpha_{ij}) + Q_i Q_j / R - C_{ij} R^{-6} - D_{ij} R^{-8}. \quad (2.29)$$

Here, the indices i and j refer to a cation or an anion and ϕ_{ij} is the potential energy of a pair of ions i and j . It is a pairwise additive potential where the first term in (2.29) describes the short-range Born–Mayer type repulsion due to overlapping orbitals on neighbouring ions, which increases nearly exponentially with decreasing interionic distance. The Coulombic part describes the attraction between oppositely charged ions i and j . For an analysis of the parameters R_i , R_j , and α_{ij} , see the article by Fumi and Tosi [2.24]. The R_i for a given crystal structure have the meaning of ionic radii. The van der Waals terms with negative signs represent dipole–dipole and

dipole–quadrupole interactions and typically give a small correction of the cohesive energy.

Starting in the 1970s, numerous calculations of the microscopic structure and thermodynamic properties of molten salts have been performed employing pair potentials of the type in (2.29) including rigid and polarizable ions; see also references [2.18] and [2.22]. In general, the calculated internal energies of alkali halide melts agree well with experimental results, often within $\pm 1\%$ [2.25]. Theoretical work on the local ionic structures includes computer simulation studies – molecular dynamics (MD) and Monte Carlo (MC) simulations – as well as hypernetted chain (HNC) and mean spherical (MSA) approximations; see also [2.22]. One of the first MD simulations was reported by Woodcock and Singer for molten KCl [2.26, 2.27]. Good agreement with experimental data was found for both the partial radial distribution functions and the thermodynamic quantities such as internal energy, compressibility, and molar heat capacity. As an example, Fig. 2.6 shows for molten NaCl a comparison of experimental $g_{ij}(R)$ from neutron diffraction [2.28] with theoretical studies, both simulation results with a rigid ion model [2.29] and HNC calculations [2.30]. Although the agreement between the different datasets is satisfactory, there is a slight discrepancy between experiment and theory as for the position and width of the first peak in $g_{+/-}(R)$. Yet, in general, calculations based on a Born–Mayer type interionic potential give satisfactory results for the local ionic structures and thermodynamic functions of molten alkali halides.

Proceeding to other metal halide melts, more complex binding characteristics and variations in the microscopic ionic structures have to be considered. First, we discuss the example of liquid CuCl. In the solid state, CuCl crystallizes in the zincblende structure at lower temperature with fourfold coordination. This low number is also found in the liquid state from pair distribution functions determined by neutron diffraction with isotopic substitution; see Fig. 2.7 and [2.31]. On comparing the

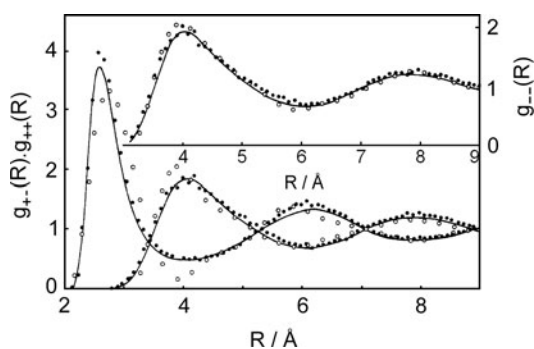
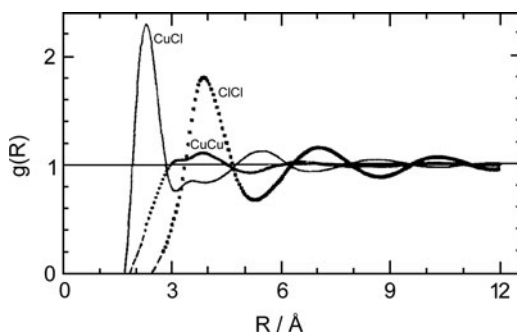


Fig. 2.6 Partial pair distribution functions of molten NaCl at conditions near the melting point, from neutron diffraction measurements (*open symbols*), simulation calculations (*full symbols*), and HNC theory (*full lines*). Reprinted with permission from [2.18]; copyright permission (2010) from IOP Publishing Ltd

Fig. 2.7 Smoothed data of the partial pair distribution functions, $g_{ij}(R)$, of liquid CuCl at 500°C from neutron diffraction experiments with isotopic substitution. Reprinted with permission from [2.31]; copyright permission (2010) by Taylor & Francis



$g_{ij}(R)$ with those in a typical alkali halide melt, the following differences are apparent: (1) There is an asymmetry between charge ordering in g_{ClCl} and g_{CuCu} at larger R . (2) Most striking is the observation that Cu^+ ions penetrate deeply into the coordination shell of unlike first neighbours; the shortest Cu – Cu distance is comparable with the shortest Cu – Cl distance. These observations are not consistent with simple ionic interactions and are explained as follows. The monovalent Cu^+ ion has an outer subshell of ten d -electrons, a small ionic radius and large electronic polarizability in comparison with an alkali ion such as K^+ . In contact with a highly polarizable Cl^- anion, covalent contributions in the $\text{Cu}^+ - \text{Cl}^-$ interaction have to be taken into account accompanied by a low coordination. Thus, the electronic structures of the ions can play an important role. Similar considerations apply for the interpretation of the structure of silver halide melts; see also [2.18].

In the case of divalent metal halides – metal ions of group IIA and IIB – a classification of the bonding characteristics has been predicted based on valence electron orbital radii [2.32]. Accordingly, bond ionicity should increase going from the lighter metal ions such as Zn^{2+} or Mg^{2+} to the heavier ones. This trend is supported by the results of neutron diffraction measurements of molten chlorides: For Ba^{2+} containing salts, the coordination number of closest contact of unlike ions is reported as 6.4 ± 0.2 , whereas for Zn^{2+} systems it is given by 4.3 [2.33]. For ZnCl_2 , different diffraction studies in the liquid and glassy state have been published, [2.33–2.36], including a more recent analysis of the partial structure factors from total scattering data [2.37], which all agree on the following structural model. The occurrence of a prepeak in $S(Q)$ clearly indicates intermediate range ordering. This is explained by a random close packing of Cl^- ions with a coordination number of N_{ClCl} of 8–10 with the Zn^{2+} ions occupying tetrahedral holes. Corner sharing of the resulting ZnCl_4^{2-} tetrahedrons enables a maximum distance between Zn^{2+} ions and thus a minimum of the Zn – Zn repulsion. Further evidence for a network-like melt with bridged tetrahedral ZnCl_4^{2-} species comes from Raman spectroscopy; see e.g. [2.38], but see also the interpretation of these spectra by MD simulations [2.39]. Consistent with this structural model are also the low electrical conductivity and high viscosity of molten ZnCl_2 – see Sect. 2.4.

Recently, the structure of liquid ZnCl_2 has been studied over a wide range of pressure and temperature (up to 4.5 GPa and 1,300 K), both by X-ray diffraction

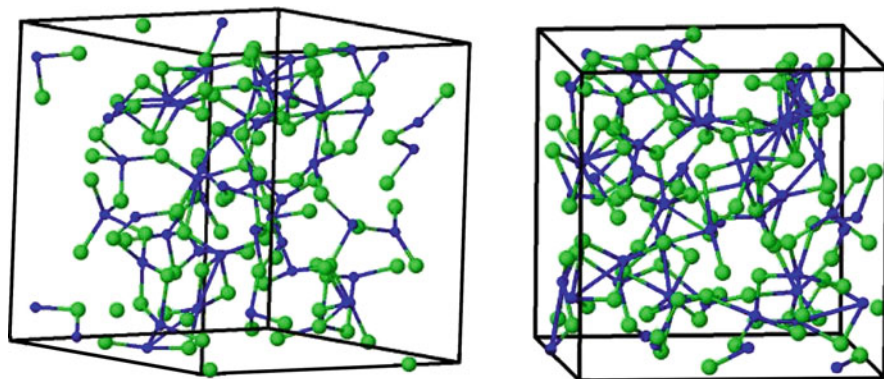


Fig. 2.8 Snapshots of MD simulations of liquid ZnCl_2 at 1,273 K; (*left*) covalent network regime at low pressure; (*right*) ionic liquid regime at high pressure. Reprinted with permission from [2.41]; copyright permission (2010) by Elsevier

[2.40] and by MD simulations [2.41]. The main findings of these investigations are that with increasing pressure a liquid–liquid transition occurs at higher temperatures, whereby the structure transforms from a covalent network of Cl^- ions to a dissociated ionic liquid. This structural transition is illustrated in Fig. 2.8 by two snapshots of the MD calculations.

With respect to the following discussion of the microscopic structure of ionic liquids and their mixtures with chloroaluminates, a comment on the structure of AlCl_3 melts is of interest. Aluminium trichloride melts at a relatively low temperature of 192°C (under pressure) [2.19] and exhibits an enormous expansion on melting of $\Delta V/V_s \sim 80\%$ [2.18]. The specific electrical conductivity is very low ($\sim 10^{-7} \Omega^{-1} \text{ cm}^{-1}$), comparable with that of a molecular liquid. First evidence that the melt is composed of molecular Al_2Cl_6 units came from Raman spectroscopy [2.38]. Recently, Madden et al. [2.42] have performed MD calculations of the liquid structure of AlCl_3 using an interaction model of polarizable ions. They found edge-sharing of tetrahedral structural units leading to the formation of charge neutral Al_2Cl_6 dimers, which they explain by the strong polarization of the Cl^- ions. Mixing of AlCl_3 with molten alkali halides leads to the formation of complex ion species in equilibrium, i.e. AlCl_4^- and Al_2Cl_7^- . Raman measurements indicate that at compositions of $x_{\text{AlCl}_3} < 0.5$, the AlCl_4^- tetrahedral species predominate [2.38]. These ionic species also form in mixtures of AlCl_3 with ionic liquids. This was shown first by Osteryoung et al. [2.14] who measured the Raman spectra of aluminium chloride-1-butyl-pyridinium melts. ^{27}Al NMR studies of the same system showed that the AlCl_4^- and Al_2Cl_7^- ions have lifetimes up to milliseconds [2.43].

Finally, for further information on the microscopic structure of metal halide mixtures and transition metal and rare earth metal halide melts, reference is given to the comprehensive reviews by Brooker and Papatheodorou [2.38] and Tosi et al. [2.44].

In comparison with molten salts, experimental research on the structural properties of ionic liquids is less advanced. In recent years, however, various computational

methods have been employed to study the structure and dynamics of pure ionic liquids and their mixtures with organic solvents, inorganic salts and gases such as CO_2 . Computational modelling of ionic liquids includes methods such as classical MD and MC simulations, ab initio quantum chemical, and ab initio or Car–Parrinello MD calculations. A very recent review by Lynden-Bell et al. [2.45] covers results on ionic liquids obtained by these methods. So, we concentrate here on a few topics of these computations on the structural properties. They have been performed predominantly for imidazolium-based ionic liquids and their mixtures.

The first simulation study of chloride and hexafluorophosphate salts of dimethylimidazolium and 1-ethyl-3-methylimidazolium $[\text{C}_2\text{mim}]^+$ was reported by Lynden-Bell and coworkers [2.46]. The interionic potential they used is similar to the Born–Mayer pair potential – see (2.29) – but without the quadrupolar term. Partial charges at each atomic centre were determined from ab initio calculations of individual cations and anions. Bond lengths and angles were kept fixed except those formed between the $\text{N} - \text{C} - \text{H}$ atoms in the methyl groups. Calculations were performed both with an explicit atom model and with a so-called united atom model where the carbon atoms and the hydrogen atoms are lumped. This potential model or force field was tested on the crystal structures of the respective compounds. Results of these calculations for the liquid structures at 400 K are shown in Fig. 2.9. A pronounced first peak is visible in the cation–anion radial pair distribution function $g_{+/-}(R)$, which is similar for the explicit atom and united atom model calculations for the chloride melts. In the case of the PF_6^- salt, this peak is shifted towards larger distances corresponding to the bigger anion size. The data also indicate a long-range charge ordering up to distances of $\sim 1.5\text{ nm}$. A more detailed picture of the anion distribution around the imidazolium cation is given by the 3D distribution functions in Fig. 2.9b, c. Apparently the highest probability for the chloride ion is near the C_2 hydrogen, which is the most acidic site and the region of highest positive charge. A view along the molecular symmetry axis down the $\text{C} - \text{H}$ bond (Fig. 2.9c) illustrates that the highest probability of the Cl^- ion is above and below the plane of the molecule.

In the years following 2001, various force fields with essentially the same functional form but with different parameters have been developed and critically analyzed for imidazolium-based ionic liquids; see [2.45]. The corresponding simulations essentially confirm the structural results described above. In several publications, Voth and coworkers have studied the effect of various alkyl side-chain lengths on the mesoscopic structure of imidazolium nitrate melts [2.47, 2.48]. For this aim, they have developed an effective force coarse-graining (CG) method, whereby atoms are grouped together to form several CG sites. In this way, MD simulations at a very large scale are possible. Figure 2.10 shows typical results of such calculations for the example of imidazolium nitrate [2.48]. Figure 2.10 (upper left) presents a snapshot of the tail groups of the alkyl chain with a length of four carbon atoms (C_4), whereas the upper right gives the corresponding snapshot for the anions. As can be seen, the ions are distributed relatively homogeneously, whereas the tail groups aggregate together and form several spatially heterogeneous domains. Increasing the alkyl chain length, this tail aggregation gets more pronounced, which

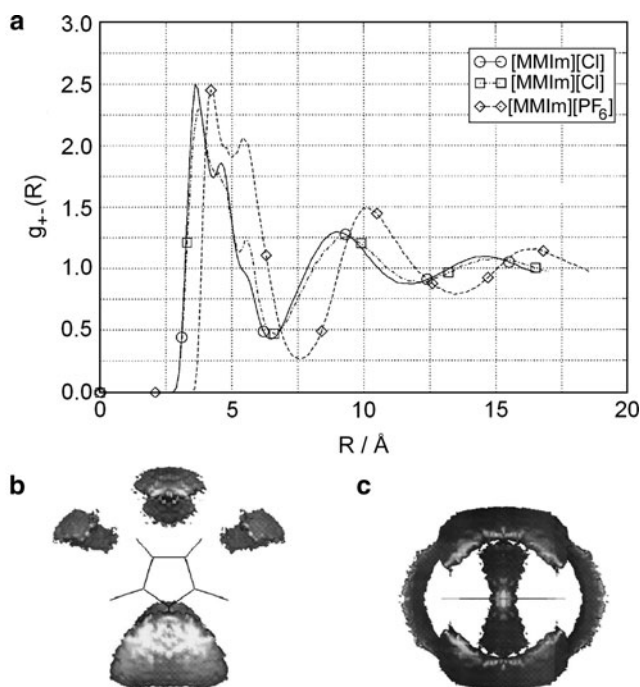


Fig. 2.9 (a) Pair distribution function $g_{+/-}(R)$ of liquid [MMIm][Cl] and [MMIm][PF₆] at 400 K calculated with the united (*dashed line open circles and full line open diamonds*) and explicit (*full line squares*) atom model; (b) view from above of the 3D probability distribution of Cl⁻ ions around the [MMIm]⁺ cation (united methyl model); (c) same as in (b), but viewed along the molecular symmetry down the C–H bond. Reprinted with permission from [2.46]; copyright permission (2010) by Taylor and Francis

is indicated by the pair distribution function in Fig. 2.10 (the lower left panel). In parallel, the diffusion of ions is clearly reduced with increasing tail aggregation; see Fig. 2.10 (lower right panel). On the basis of these results, it is concluded that for long enough side chains of the cations domain formation and liquid crystal-like structures should result. This is not restricted to imidazolium-based ionic liquids, but should occur in most organic ionic liquid systems [2.47].

The solubility and solvation of organic and inorganic compounds and of gases in ionic liquids is a crucial question, in both fundamental and applied research. Several of these aspects are treated in the book by Wasserscheid and Welton [2.13]. So, we may focus here on a few more recent theoretical investigations. Several groups have studied the solvation of imidazolium-based ionic liquids in mixtures with water, alcohols, acetonitrile, or DMSO [2.49–2.55]. The solvation of [C₂mim][Cl] in a cluster of 60 water molecules has been studied by Spickermann et al. with Car–Parrinello MD simulations. The authors could demonstrate that the structure of the hydration shell around the ion pair differs significantly from bulk water and that no ion pair dissociation occurs on the timescale of the simulation [2.50]. In MD simulations of 1-*n*-decyl-3-methylimidazolium bromide, [C₁₀mim][Br], in aqueous

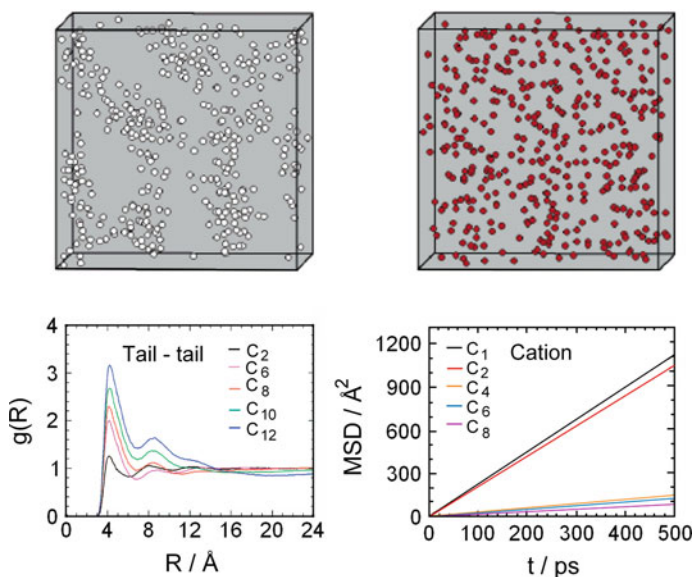


Fig. 2.10 Coarse-grained MD simulation of imidazolium nitrate with 400 ion pairs at $T = 700$ K: (upper left) snapshot of alkyl tail groups (alkyl chain length: C_4); (upper right) snapshot of anions only; (lower left) radial distribution function for tail–tail sites for different alkyl chain lengths C_i ; (lower right) mean square displacements of cations. Reprinted with permission from [2.47]; copyright (2010) by American Chemical Society

solutions, it is found that cations spontaneously form small micellar aggregates where the decyl chains are buried inside the micelle and the polar head groups are exposed to water [2.49]. In their NMR and MD investigations of $[C_4mim][Cl]$ in water and DMSO, Remsing et al. [2.53] find evidence of aggregation of butyl chains in aqueous environment. On the other hand, they show that $[C_4mim][Cl]$ behaves as a typical electrolyte in water i.e. both ions are completely solvated at low concentrations. This seems to be not the case in DMSO [2.53]. The solvation of lanthanide cations ($Ln = La, Eu, Yb$) in imidazolium-based ionic liquids with different anions has been studied with MD simulations by Chaumont and Wipff [2.56, 2.57]. A main result of these studies is that in all cases the first solvation shell of $Ln(III)$ is found to be purely anionic, with 6–8 coordinated ligands, and that this shell is surrounded by 13–14 $[C_4mim]^+$ cations leading to an *anion type* solvation of $Ln(III)$.

As mentioned above, the experimental elucidation of the microscopic structure of room temperature ionic liquids employing diffraction methods is a complex problem and knowledge is rather limited. A review covering the literature up to 2006 has been written by Hardacre [2.58]. In general, a complete set of partial structure factors or distribution functions is not accessible. A specific complication in neutron scattering experiments is due to the large incoherent scattering cross section of hydrogen, which typically dominates the coherent contributions of other elements in the scattering function. In principle, this problem can be significantly

reduced by deuterium isotope substitution. In X-ray diffraction, on the other hand, light elements such as hydrogen or deuterium are barely visible since the atomic form factors are proportional to the atomic number. So, the determination of the local structures in ionic liquids often requires further information, e.g. from the crystalline structures, MD simulations, or from NMR and Raman spectroscopy or EXAFS spectra. As an example of the experimental limitations, one may consider a recent study of Fujii et al. on the liquid structure of 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide, $[\text{C}_2\text{mim}][\text{NTf}_2]$ [2.59]. For the structural characterization, the authors have chosen X-ray measurements of the total scattering function, MD simulations of the conformers of $[\text{C}_2\text{mim}]^+$ and $[\text{NTf}_2]^-$, and NMR measurements of the ^1H , ^{13}C , and ^{19}F chemical shifts. Figure 2.11 presents the experimental total scattering intensity, $I(Q)$, in comparison with the contribution of intramolecular scattering calculated for a 1:1 mixture of the conformers. As can be seen, the intensity function at large Q ($Q > 4 \text{ \AA}^{-1}$) solely reflects the intramolecular scattering. So all the information on the intermolecular structure at larger R is contained in the small section of $I(Q)$ at low $Q < 40 \text{ nm}^{-1}$. To resolve the structure from this part alone is not possible, i.e. independent results e.g. from MD simulations are needed. For the present example, the authors suggest the following model for the intermolecular structure: A nearest neighbour distance of $6 \text{ \AA}$ for the $[\text{C}_2\text{mim}]^+[\text{NTf}_2]^-$ correlation and a distance of $9 \text{ \AA}$ for the like ions correlation. From the NMR results, it is concluded that the C2 proton of $[\text{C}_2\text{mim}]^+$ strongly interacts with the O atom of the $-\text{SO}_2(\text{CF}_3)$ group of $[\text{NTf}_2]^-$ [2.59].

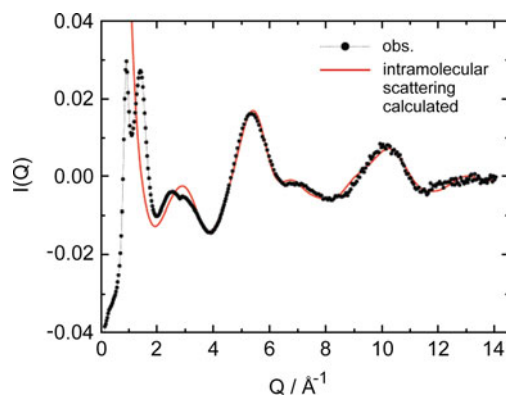


Fig. 2.11 X-ray scattering from liquid $[\text{C}_2\text{mim}][\text{NTf}_2]$ at 298 K: (symbols) total scattering intensity from X-ray measurement; (—) calculated intramolecular scattering contribution assuming a 1:1 mixture of $[\text{C}_2\text{mim}]$ and $[\text{NTf}_2]$ conformers. Reprinted with permission from [2.59]; copyright permission (2010) American Chemical Society

2.3 Bulk Phase Behaviour

Coulombic fluids span a wide range of temperatures extending from the low melting points of ionic liquids down to 200 K up to the critical temperatures of expanded fluid metals with that of tungsten being above 15,000 K. A representative collection of melting, boiling (decomposition temperatures in the case of ionic liquids) and critical temperatures is given in Table 2.2. Mainly for two reasons, the elements and compounds in this table have been chosen: First, they represent the typical range of melting points of the respective class of materials, and second, their thermophysical data are of interest in the following chapters.

The liquid range of a substance commonly is defined by the difference of the boiling and melting point temperatures. Accordingly, alkali metals and alkali halides have a high liquid range of the order of 600–700 K. Exceptionally high values of about 2,000 K are observed for Ga and W. In comparison with alkali halides, the liquid range of ionic liquids is rather reduced lying typically between 200

Table 2.2 Characteristic temperatures and thermodynamic data of Coulombic fluids: T_m = melting point, $T_b(T_{dec})$ = boiling point (decomposition temperature in the case of ionic liquids), T_c = critical temperature, ρ_m = liquid density at melting point, p_c = critical pressure

Coulombic fluids:	$\rho_m/\text{g cm}^{-3}$	T_m/K	$T_b(T_{dec})/\text{K}$	T_c/K	p_c/bar
Metals					
Cs	1.84 (a)	301.8 (a)	963 (a)	1,924 (b)	92.5 (b)
Rb	1.47 (a)	312.1 (a)	975 (a)	2,017 (b)	124.5 (b)
K	0.83 (a)	336.4 (a)	1,031 (a)	2,198 (c)	155 (c)
Hg	13.54 (a)	234.3 (a)	629 (a)	1,751 (b)	1,673 (b)
Ga	6.04 (a)	302.9 (a)	2,217 (a)	—	—
Bi	9.99 (a)	544.5 (a)	1,391 (a)	—	—
W	19.26 (a) (at 298 K)	3,650 (a)	5,808 (a)	15,227 (h)	—
Molten salts					
KCl	1.52 (d)	1,045 (d)	1,680 (d)	3,200 (d)	~200 (d)
BiCl ₃	3.92 (d)	505 (d)	714 (d)	1,178 (e)	~120 (d)
AlCl ₃	2.48 (f)	465 (d) (at 2.5 bar)	453 (d) sublimates	626 (f)	26 (f)
Ionic liquids					
[C ₂ mim][BF ₄]	1.26 (i)	288 (g)	≈ 520	—	—
[C ₂ mim]Cl:	1.29 (g)	283 (g)	—	—	—
[AlCl ₃](1:1)	(at 298 K)				
[C ₄ mim][Cl]	1.08 (g)	338 (j)	≈ 520	—	—
	(at 298 K)				
[C ₄ mim][BF ₄]	1.14 (g)	257 (g)	≈ 630	—	—
	(at 298 K)				

Letters in brackets denote the following references: (a) = [2.60], (b) = [2.61], (c) = [2.62], (d) = [2.19], (e) = [2.63], (f) = [2.64], (g) = [2.13], h = [2.65], (i) = [2.66], (j) = [2.67]

and 300 K, whereby the upper limit is determined by thermal decomposition. In principle, the liquid range of matter can be extended in two ways: By undercooling into a metastable state or by expanding the liquid at supercritical pressures up to the liquid–vapour critical region. For Coulombic fluids of interest, these variations shall be considered in detail here.

Most liquid metals can be undercooled below their melting point T_m ; see e.g. [2.68]. For that purpose, it is necessary that the liquid is free of solid particles or intrinsic solid nuclei where the latter usually can be dissolved by heating the melt up to $\sim 1.2T_m$ [2.68]. In large systems, undercooling is almost always limited by nucleation at extraneous interfaces. However, extreme levels of undercooling can be achieved by emulsification of liquid droplets ($\sim 10\ \mu\text{m}$ radii) in an inert carrier fluid, which was reported for the first time by Turnbull [2.69]. Employing the droplet emulsion technique, Perepezko and coworkers have studied a number of liquid metals and alloys and have elucidated the effects of size and surface coating on undercooling [2.70–2.72]. For low melting point metals such as Ga and Bi, they found a lower limit of undercooling in the range of $0.3\text{--}0.4T_m$. The idea behind the dispersion technique is that the nucleation probability is strongly reduced because the catalytic effect of heterogeneous nucleants may be restricted to a small fraction of droplets. The technique is not limited to low melting metals, where carrier fluids such as alcoholic sodium oleate or silicon oils have been used, but can be extended to high melting point materials such as Ge if proper molten salts are employed as dispersion medium [2.73].

The second possibility to extend the liquid range of matter is that by expansion at elevated temperature and pressure. This is illustrated in Fig. 2.12 for the example of expanded fluid caesium [2.74]. The coexisting liquid and vapour densities up to the critical point and the density variation along different isobars between 60 and 200 bar are presented. It is worth to note that in the limits between the melting and critical point the coexisting liquid density expands by nearly a factor of 5 and that the temperature range from boiling to critical temperature, T_c/T_b , is extended by a factor of ~ 2 . These two values are typical of fluid alkali metals; see also Table 2.2 and reference [2.61]. In the case of a molten salt such as BiCl_3 , the corresponding values are $\rho_m/\rho_c \sim 3$ and $T_c/T_b = 1.65$, which are comparable with those of typical molecular fluids; see e.g. [2.75]. Such a large expansion of fluids raises several fundamental questions: (1) Up to what density and temperature do the characteristic liquid properties such as the metallic or ionic conductance persist? (2) How do they transform to different states of condensed matter? These topics are discussed in detail in Chap. 3.

The bulk phase behaviour of molten salts and ionic liquids is dominated by Coulomb attraction between ions, which depends on the ion charges, the interionic distances and the coordination number, or the Madelung constant in the corresponding crystals. With this knowledge, some characteristic trends of the melting points are immediately understandable: For instance, the decrease in melting temperatures of the alkali halides with increasing anion or cation size. In particular, this explains the strong reduction of the melting points in room temperature ionic liquids due to the large size of the organic cations. Qualitatively, this also accounts

Fig. 2.12 Density variation of expanded fluid Cs at liquid–vapour coexistence and along different isobars between 60 and 200 bar at sub- and supercritical conditions. See also [2.74]

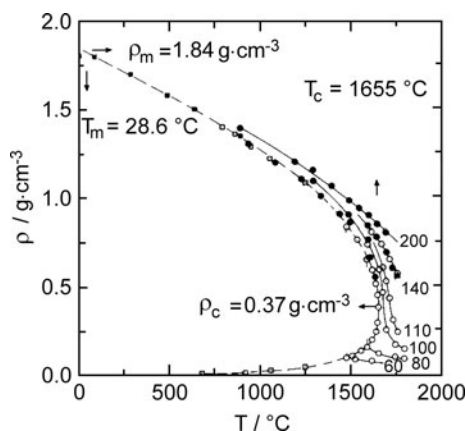
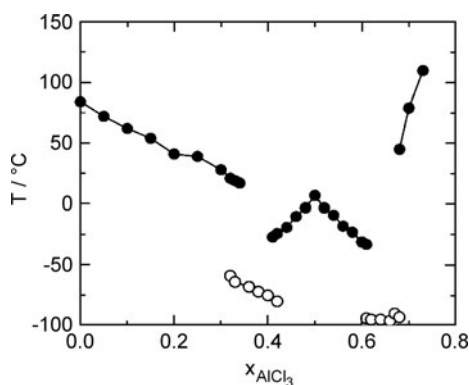


Fig. 2.13 Solid–liquid phase diagram for [C₂mim]Cl–AlCl₃ as a function of AlCl₃ mole fraction; *full symbols*, melting and freezing points, *open circles*, glass transition points. Adapted with permission from [2.16]; copyright permission (2010) by American Chemical Society



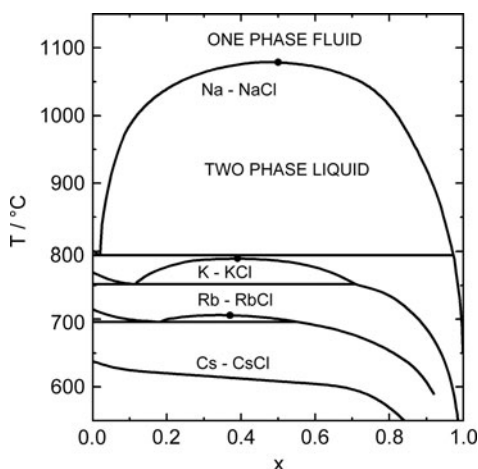
for the variation of the melting temperatures with changing the anion size, the trend being: $T_m(\text{Cl}^-) > T_m(\text{PF}_6^-) > T_m(\text{BF}_4^-) > T_m(\text{NTf}_2^-)$; see also [2.76]. A significant effect on the low temperature phase behaviour of ionic liquids is induced by varying the alkyl chain length C_n in e.g. $[\text{C}_n\text{mim}]^+$ salts; see also [2.77]. Increasing the length from $n = 2$ to $n = 10$, the melting point is reduced with a trend for glass transition on cooling. For $n > 10$, the melting point increases again and liquid crystalline phases occur [2.13, 2.76]. The tendency to strong undercooling and low glass transition temperatures is especially pronounced in binary mixtures of imidazolium-based salts with AlCl₃ or with other Lewis acidic melts such as ZnCl₂ [2.16, 2.78]. This behaviour is similar to mixtures containing simple inorganic salts such as KI + ZnCl₂ [2.78]. An illustration is given in Fig. 2.13 for the phase diagram of [C₂mim]Cl + AlCl₃ [2.16].

Investigation of the high-temperature phase behaviour of ionic liquids is rather complicated due to thermal decomposition. The onset temperatures of decomposition are generally not well defined and reproducible. They depend on a number of influences such as impurities (especially water), wall reactions, and prolonged exposure at elevated temperatures; see also [2.13]. Therefore, the numbers in Table 2.2 may be considered as an average upper bound.

Near and slightly above the melting point, ionic liquids exhibit exceptionally low vapour pressures in their pure state ($<10^{-8}$ mbar according to the author's own experience with UHV experiments [2.79]), which for the first time enabled ultrahigh vacuum measurements such as XPS with a fluid system; see e.g. [2.80]. It is mainly this unusual property to which ionic liquids owe the name *green solvents*. Various attempts have been made to determine or estimate the thermodynamic properties, in particular, the vapour pressures, of different ionic liquids at elevated temperatures [2.81–2.84]. Rebelo et al. have tried to predict the boiling and critical point of a number of imidazolium-based ionic liquids on the basis of measured surface tension data and by extrapolation of the critical points with the use of the empirical Eötvös and Guggenheim relations. Such predictions have some severe uncertainties, not only because of the extrapolation over a wide temperature range, but also because it is not clear if these empirical laws apply to ionic liquids where charge ordering at the liquid/vapour interface should be considered – see also Sect. 2.5.2. Only recently, reliable measurements of the thermodynamic properties at elevated temperatures have been reported [2.83, 2.84]. By Knudsen effusion and transpiration measurements, Heintz and coworkers obtained the vapour pressure curves of $[\text{C}_2\text{mim}][\text{NTf}_2]$ and $[\text{C}_2\text{mim}][\text{DCA}]$ at temperatures up to 528 K and 480 K, respectively. They also could determine the gaseous enthalpy of formation of $[\text{C}_4\text{mim}][\text{DCA}]$ from combustion measurements and found good agreement with results from ab initio calculations. On the basis of these calculations, they conclude that the vapour phase is composed of ion pairs, i.e. $[\text{C}_4\text{mim}]^+[\text{DCA}]^-$, with a negligible degree of dissociation at the highest measured temperatures. This last result is supported by a recent mass spectroscopic study of several imidazolium-based salts. As for the nature of the vapour phase, these observations demonstrate the close similarity between ionic liquids and conventional molten salts. With the vapour pressure data of Heintz et al., finally, a more realistic extrapolation of two interesting quantities is possible: The vapour pressure near room temperature and the boiling point. For $[\text{C}_2\text{mim}][\text{NTf}_2]$ these are $p \sim 10^{-12}$ mbar, which is barely measurable, and $T_b \sim 1,200$ K, which is almost 600 K above the decomposition onset of this salt [2.85].

For a long time, criticality in Coulombic fluids has attracted the interest in theory and experiment alike; see e.g. [2.86–2.96]. Detailed knowledge of the thermodynamic properties near a liquid–vapour or liquid–liquid demixing critical point gives insight into the scaling behaviour and the nature of the dominant intermolecular interaction potential. In fluid alkali metals (Cs and Rb), Hensel and Warren [2.61] present a careful analysis of the coexisting liquid and vapour densities, ρ_l and ρ_v , and the diameter $\rho_d = (\rho_l + \rho_v)/2$ as a function of reduced temperature $\tau = (T_c - T)/T$ approaching the critical point up to $\tau \sim 10^{-3}$. From a single power law fit of $\Delta\rho/2\rho_c = (\rho_l - \rho_v)/2\rho_c$ vs. τ they find for the critical exponent β of the order parameter ρ a value of $\beta = 0.35\text{--}0.36$, which is close to the value of 0.325 predicted for the 3D Ising model. Therefore, these authors conclude that the critical behaviour of these fluid metals – despite the metal–nonmetal transition near the critical region, see Sect. 3.1 – can be described by short-range interactions, but it is not dominated by long-range Coulomb interactions. For binary liquid mixtures exhibiting a metal–nonmetal transition as a function of composition and a miscibility gap with an

Fig. 2.14 High-temperature section of the phase diagrams – temperature T vs. metal mole fraction x – of alkali metal–alkali chloride melts; the *full dots* indicate the critical or consolute point of the respective system. See also [2.96]



upper critical point, differences in the critical behaviour have been reported. As an example of such systems, Fig. 2.14 shows the phase diagrams of alkali metal–alkali chloride melts.

Precise determinations of the liquid–liquid coexistence curve in Na–NH₃ solutions show a change of the critical exponent β from 0.502 to 0.34 at ~ 2 K below the consolute point [2.97]. Small-angle neutron scattering investigations of the concentration fluctuations in the critical region of K – KBr melts indicate a behaviour corresponding to the 3D Ising model [2.98].

Research of the critical demixing of ionic liquid solutions at ambient conditions was started by Weingärtner and coworkers [2.99]. They studied systems of tetraalkylammonium salts dissolved in different aqueous and nonaqueous solvents, and also the system ethylammonium nitrate + *n*-octanol, which has an upper critical point of 315.2 K. From an experimental point of view, these systems are especially attractive for investigations of critical phenomena since the critical temperatures near ambient conditions allow temperature stabilization and control with a high precision. A systematic investigation of the coexistence curves of tetra-*n*-butylammonium picrate, N₄₄₄₄ Pic, solutions in 1- and 2-alkanols has been reported by Schröer, Weingärtner, and coworkers, whereby the dielectric constant at T_c varied from $\epsilon = 16.8$ –3.6 and the critical temperatures ranged from 315.87 to 351.09 K [2.100]. Figure 2.15 shows a typical example of the liquid–liquid miscibility gap in N₄₄₄₄ Pic in 1-tetradecanol. For the uncertainty of the critical temperatures, the authors give a value of ± 10 mK and that of the order parameter, the mass fraction w_c , is ± 0.004 . From a detailed analysis of the scaling laws, the following conclusions are drawn. The critical exponent β for the coexistence curves lies near the Ising value, but shows systematic deviations with varying ϵ , from $\beta = 0.315$ at $\epsilon = 16.8$ to $\beta = 0.36$ at $\epsilon = 3.6$. For larger reduced temperatures $\tau > 0.01$ and using the mole fraction scale as order parameter, the critical exponent is near the mean field value of $\beta_{\text{eff}} = 0.5$. The authors do not draw a final conclusion on the problem of crossover to mean-field criticality, which is discussed in several of the earlier publications [2.95–2.97].

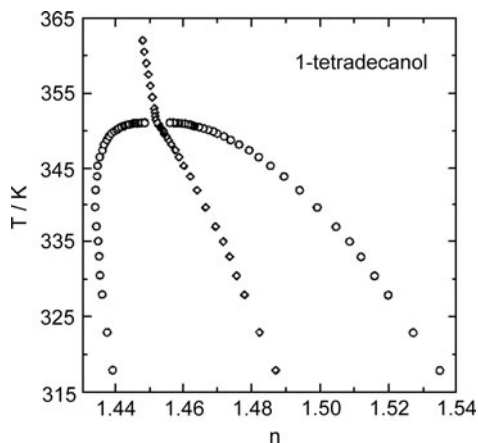


Fig. 2.15 Coexistence curve of solutions of N_{4444} Pic in 1-tetradecanol with an upper critical temperature of 351.09 K; plotted is the temperatures T vs. measured refractive index n as composition variable along the coexistence curve (*open circles*) and the coexistence curve diameter and an extension into the homogeneous liquid phase (*open diamonds*). Remarkable is the deviation of the diameter from the simple rectilinear diameter rule. Reprinted with permission from [2.100]; copyright permission (2010) from American Institute of Physics

Finally, assuming Ising criticality and the applicability of the rectilinear diameter rule, an empirical state behaviour of ionic liquid solutions seems possible, where all phase diagrams map on one master curve [2.101].

2.4 Transport Properties

Transport in fluid systems encompasses energy (thermal conductivity), momentum (viscosity) and particle transfer (diffusion) and, in Coulombic fluids, includes charge transfer characteristics (electrical conductivity). This is a broad field and, therefore, we content ourselves with a brief description of the electrical transport properties that are relevant to the discussion in later chapters and give reference to reviews for further details.

The theoretical basis of the electron transport in liquid metals is described in the monographs by Ziman [2.6] and Cusack [2.7]. Within the NFE model for metals, the DC conductivity is given by

$$\sigma(0) = n e \mu_e = \frac{n e^2 \tau_e}{m_e} = \frac{n e^2 \lambda_e}{m_e v_F}. \quad (2.30)$$

Here, μ_e is the mobility, τ_e is the relaxation time, and λ_e is the mean free path of conduction electrons; the other symbols have their usual meaning, v_F being the Fermi velocity. For a calculation of τ_e , the scattering of conduction electrons by

the pseudopotentials is treated as a weak perturbation and the positions of screened ions are taken into account by the structure factor $S(Q)$ of the liquid. This yields the Ziman formula for $\sigma(0)$ of liquid metals [2.6] as follows:

$$1/\sigma(0) = \frac{3\pi n}{e^2 \hbar v_F^2} \cdot \frac{1}{4k_F^4} \int_0^{2k_F} Q^2 S(Q) \phi(Q)^2 dQ, \quad (2.31)$$

where $\phi(Q)$ is the Fourier transform of the pseudopotential. There are two further transport properties that within the NFE model are independent of τ_e : The Hall coefficient, R_H , which characterizes the electronic transport in a magnetic field vertical to the electric current, and the thermoelectric power, S , which is defined by the Thomson coefficient, σ_T , i.e. $S = \int_0^\Gamma (\sigma_T/T) dT$. In the NFE model, these quantities are as follows:

$$R_H = -(\text{nec})^{-1}, \quad (2.32)$$

and

$$S = -\frac{\pi^2}{6} \cdot \frac{k_B}{e} \left(\frac{k_B T}{E_F} \right) \quad (2.33)$$

Intuitively, one expects that the distance λ_e between two scattering events is large in comparison with the interatomic distance, which is of the order of $r_s = (3/4\pi n)^{1/3}$ i.e. $\lambda_e \gg r_s$ – for alkali metals r_s is several Å. In this way, the conduction electrons can wander nearly freely through the metal and their wave functions can be approximated by plane waves. On the other hand, if the electrons were localized within an atomic distance, i.e. their uncertainty in position would be $\Delta x \sim r_s$, then the uncertainty in momentum – since $k_F \sim 1/r_s$ – would be $\hbar k_F$. Thus, a classical NFE model is impossible. The data in Table 2.3 give an overview how well the criterion $\lambda_e \gg r_s$ holds for liquid metals near their melting point.

Table 2.3 Experimental data of electronic DC conductivity, $\sigma(0)$, electron mean free path, λ_e , Hall coefficient, R_H , divided by the NFE value according to (2.32), and conductivity ratio $\sigma/\sigma_{\text{calc}}$; σ_{calc} has been determined according to (2.31) with pseudopotentials from phase shift analysis and with experimental $S(Q)$ data [2.102]

Metal	$\sigma/10^5 \Omega^{-1} \text{cm}^{-1}$	$\lambda_e/\text{\AA}$	R_H/R_{NFE}	$\sigma/\sigma_{\text{calc}}$
Na	1.04	157	0.98 (b)	1.77 (d)
K	0.77	176		2.1 (d)
Rb	0.45	118		1.2 (d)
Cs	0.27	82	1.0 (c)	1.1 (d)
Cu	0.47	34	1.0 (b)	
Al	0.41	18	1.0 (b)	
Ga	0.38	17	0.97...1.04 (b)	
Bi	0.078	4	0.7...0.95 (b)	

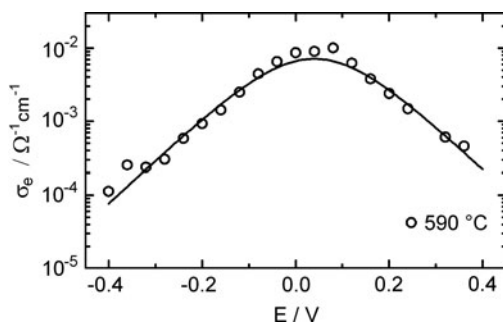
All data for liquid metals near the melting point; conductivities from (a) = [2.60]; (b) = [2.103], (c) = [2.104], (d) = [2.102]

In the liquid state, electronic conduction is not restricted to metals, but is also known to occur in mixtures with molten salts, possibly also in ionic liquids, although this has not been studied yet. In molten salts, two situations are of interest. At elevated temperatures salts such as the alkali or bismuth halides exhibit continuous miscibility with the respective metals and thus, as a function of added metal, undergo a nonmetal–metal transition. In this context, one of the fundamental questions is, what is the electronic structure in the nonmetallic salt-rich melts and how does it change towards the metal-rich solutions? With these problems, we will be concerned in Sect. 3.5. Another important mechanism of electron conduction in molten salts prevails in systems that contain two valence states of the same metal element. Typical examples are mixtures of $\text{NdI}_2 - \text{NdI}_3$ [2.105–2.107], $\text{CuCl} - \text{CuCl}_2$ [2.108], or solutions of transition metal halides such as TaCl_5 or NbCl_5 in molten salts such as NaCl or CsCl [2.109]. The composition in these mixtures can be varied by changing the ratio of the salt components of different valency, by adding metal to the salt of higher valency, or, in electrochemical experiments, by changing the applied electrochemical potential in an electrochemical cell with a solution of e.g. $\text{TaCl}_5 - \text{NaCl}$ [2.109]. The electronic transport in these systems is thermally activated, which can be explained by intervalence charge transfer in a simple two-site model [2.107, 2.109]. As a function of composition, the electronic conductivity exhibits a parabolic dependence with a clear maximum, whereby the conductivities at the maximum range from $\sim 10^{-2} \Omega^{-1} \text{cm}^{-1}$ [$\text{Ta(IV)} - \text{Ta(V)}$ in $\text{CsCl} - \text{NaCl}$] to $10 \Omega^{-1} \text{cm}^{-1}$ ($\text{CuCl} - \text{CuCl}_2$ at a temperature near 1,000 K); see Fig 2.16. The parabolic concentration dependence is easy to understand if one takes into consideration that for a successful intervalence charge transfer two ions of different valency have to be nearest neighbours; the probability for this is proportional to the product of the respective mole fractions, e.g. $x(\text{Ta IV}) \cdot x(\text{Ta V})$. In applications, where optimization of current efficiencies matters, knowledge of the electronic conduction component is very valuable.

The ionic DC conductivity in molten salts and ionic liquids can be described by the following equation:

$$\sigma_{\text{ion}}(0) = \sum_i n_i q_i \mu_i, \quad (2.34)$$

Fig. 2.16 Impedance measurements of the electronic DC conductivity vs. electrochemical potential E in a $\text{CsCl} - \text{NaCl} - 3 \text{ mol\% Ta (IV, V) oxychloride}$ melt at 863 K; (*open circles*) experimental points; (*full line*) fit with a parabolic function. See also [2.109]



where n_i is the number density, q_i the charge, and μ_i the mobility of ions i ($i = +, -$). The mobility is given by the Einstein relation,

$$\mu_i = \frac{D_i q_i}{k_B T}, \quad (2.35)$$

where D_i is the self-diffusion coefficient of ion i . Thus, the ionic conductivity is directly related with the self-diffusivity of the ions; the molar conductivity, $\Lambda = \sigma/c$, is then determined by

$$\Lambda = \left(\frac{F^2}{RT} \right) (D_+ + D_-). \quad (2.36)$$

Here, F is the Faraday constant, R is the gas constant, and c is the molar concentration. Conductivities calculated from (2.36) with independently measured ion diffusion coefficients may deviate from measured ionic conductivities. Both in molten salts [2.110] and in ionic liquids [2.111, 2.112], these deviations are explained by short-lived ion pairs. These pairs can contribute to diffusion, but not to the electrical conductance. Via the Stokes–Einstein relation, there is a strong coupling between the viscosity, η , and the diffusion, and thus between viscosity and ionic conductivity. So, in many cases, the temperature dependence of the ionic conductivity follows a Vogel–Tammann–Fulcher (VTF) relation,

$$\sigma_{\text{ion}}(T) = \sigma_0 \exp \left(\frac{-B}{(T - T_0)} \right) \quad (2.37)$$

and correspondingly for η , which is inversely proportional to σ_{ion} . In (2.37), B is referred to as a pseudo-activation energy and T_0 is the zero-mobility temperature or glass transition temperature. Typical values of conductivities, viscosities, and self-diffusion coefficients of a few ionic liquids in comparison with molten salts are given in Table 2.4.

Table 2.4 Ionic DC conductivity σ_{ion} , diffusion coefficients D_+ and D_- , and viscosity η , of selected molten salts and ionic liquids

Ionic melt	T_m/K	$\sigma_{\text{ion}}/\Omega^{-1}\text{cm}^{-1}$	$D_+/10^{-7}\text{cm}^2\text{s}^{-1}$	$D_-/10^{-7}\text{cm}^2\text{s}^{-1}$	η/c Poise
NaCl	1,081	3.61	962	673	1.43
KCl	1,045	2.2	—	—	1.34
CsCl	918	1.09	350	380	1.60
BiCl ₃	505	0.38	—	—	42.2
ZnCl ₂	556	0.02	—	—	18,000
[C ₂ mim][BF ₄]	288 (b)	0.14 (c)	5.0 (d)	4.0 (d)	35(c)/43 (c)
[C ₂ mim][NTf ₂]	258 (b)	0.008 (c)	5.0 (d)	3.0 (d)	33 (b)
[C ₄ mim][BF ₄]	192 (c)	0.005	1.8 (c)	1.8 (c)	75 (c)

Data of molten salts are from reference (a) at conditions near their respective melting points, those of ionic liquids correspond to 298 K and, for σ_{ion} , to 303 K; (a) = [2.19], (b) = [2.111], (c) = [2.67], (d) = [2.112]

With regard to these data, it is striking that the conductivities of molten salts near their melting points are of the same order of magnitude, $\sim 1 \Omega^{-1} \text{ cm}^{-1}$. Exceptions are melts such as ZnCl_2 , which are characterized by a network structure (see Sect. 2.2.2) and so are not completely dissociated molten salts. On comparing the conductivities and diffusion coefficients of the high-temperature molten salts with those of room temperature ionic liquids, they differ by roughly two orders of magnitude. However, if one extrapolates the values of ionic liquids to high temperatures near 1,000 K with the aid of (2.37) – for instance, for $[\text{C}_2\text{mim}][\text{BF}_4]$ B is $\sim 720 \text{ K}$ and $T_0 \sim 150 \text{ K}$ [2.112] – these hypothetical conductivities and diffusivities would be comparable with the values of molten salts. So, the essential difference between both classes of ionic media is less in their transport properties, but in their thermal stability and, of course, in the large chemical variability of ionic liquids.

2.5 Interfacial Characteristics

The behaviour of fluids at surfaces² and interfaces is a classical area of physical chemistry. It includes a variety of topics such as surface thermodynamics, adsorption phenomena, catalysis, tribology, micro- and nanofluidics, or processes at electrified liquid/solid interfaces; to name some of the most important subjects; see also [2.113]. Phenomena at fluid interfaces are not only of fundamental interest, but also of great practical importance in different fields. In many respects, surface science is also the basis for nanoscience and technology, since nano-objects – for which the number of atoms on the surface and in the interior are of comparable magnitude – are strongly determined by their surface characteristics and by interfacial phenomena. In recent years, research of fluid interfaces has made considerable progress based on new developments of microscopic theories and experimental techniques. For instance, with X-ray reflectivity measurements at high flux synchrotron sources and scanning probe microscopy, two powerful tools became available to probe the microscopic structure of surfaces and interfaces. In consequence, novel interfacial phenomena such as wetting and prewetting transitions, surface melting and freezing, or electrochemical nanostructuring have attracted special interest in physics, chemistry, and material science. With respect to liquid metals and molten salts or ionic liquids, studies of these topics at elevated temperatures are also of special practical interest. This covers applications in soldering, metal–metal or metal–ceramic bonding, and liquid metal embrittlement – see e.g. [2.114] – and also problems of thin film stability in integrated circuits or electrochemical 2D and 3D phase formation and growth. Some of these interfacial phase transitions of Coulombic fluids, at the liquid/vapour, the liquid/solid, and the electrified liquid/solid electrode interfaces, are dealt with detail in Chaps. 4 and 5. In the following, some basic characteristics are introduced from a more phenomenological point of view.

² The term surface often is used for interfaces where one of the neighbouring phases is a vapour phase or vacuum.

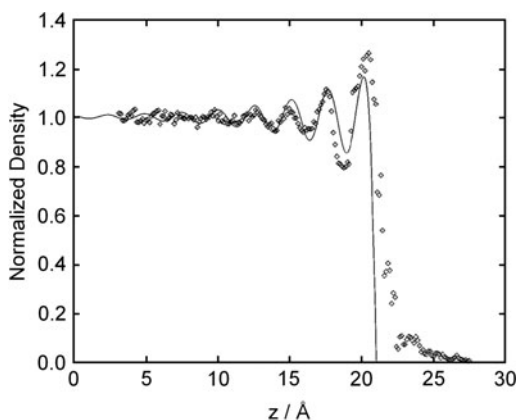
2.5.1 Liquid Metals

Across the liquid/vapour interface, metals exhibit a singular variation of their electronic structure: They undergo a metal–nonmetal (M – NM) transition and so, at temperatures well below the critical one, the character of the interatomic interaction changes abruptly from screened Coulomb interaction in the liquid to a Lennard–Jones type potential in the insulating vapour phase. The effect of this electronic transition on the microscopic structure of a liquid metal surface was first studied by Rice and coworkers [2.115]. Their Monte Carlo simulations of the inhomogeneous interfacial region indicated that the liquid/vapour interface of metals is stratified, i.e. a layered structure exists at the interface that decays over several atomic diameters into the bulk liquid. Experimental evidence of this stratification was obtained by X-ray reflectivity measurements on different liquid metals [2.116–2.118]. Figure 2.17 shows a comparison of theoretical with experimental results of the density distribution normal to the liquid/vapour interface of Ga at conditions near the normal melting point. The calculations are based on self-consistent quantum Monte Carlo simulations with pseudopotential representation of the electron–ion and ion–ion interactions [2.119], the experimental curve results from X-ray reflectivity measurements [2.117]. It is interesting to add that at the solid/vacuum interface of metals the electron distribution exhibits a similar oscillatory behaviour decaying into the bulk after several atomic layers; see e.g. [2.120].

For a description of the macroscopic interfacial properties, the Gibbs adsorption equation is fundamental. We consider a multicomponent system with two bulk phases, α and β , in equilibrium and separated by a plane located near a planar interface. Then the Gibbs equation is [2.113] as follows:

$$d\sigma_{\alpha\beta} = -S^{(\sigma)}dT - \sum_i \Gamma_i^{(\sigma)}d\mu_i. \quad (2.38)$$

Fig. 2.17 Normalized density distribution along the normal to the liquid/vapour interface of Ga near its melting point; (*open diamonds*) from quantum Monte Carlo simulations; (*full line*) from X-ray reflectivity measurements. Adapted with permission from [2.119]; copyright permission (2010) by American Physical Society



It relates the interfacial free energy per unit area, $\sigma_{\alpha\beta}$ – which is numerically equal to the surface tension – to the relative interfacial entropy per unit area, $S^{(\sigma)}$, and the relative adsorption or interfacial excess per unit area, $\Gamma_i^{(\sigma)} = n_i^{(\sigma)}/A$, with A being the area of the interface, T the temperature, and μ_i the chemical potential of component i . The mole number is $n_i^{(\sigma)} = n_i - n_i^\alpha - n_i^\beta$. Since the $\Gamma_i^{(\sigma)}$ are defined relative to an arbitrarily chosen Gibbs dividing surface, the surface can be placed such that one $\Gamma_j^{(\sigma)} = 0$. For a binary system of solvent 1 and solute 2, one can choose $\Gamma_1^{(\sigma)} = 0$, so that at constant temperature the interfacial excess of 2 relative to 1 is $\Gamma_{2(1)}^{(\sigma)} = -(\partial\sigma_{\alpha\beta}/\partial\mu_2)_T$. If the slope of $\sigma_{\alpha\beta}$ vs. μ_2 is negative, then there is an actual excess or enrichment of solute at the interface. In the opposite case, there is a deficiency of solute. In the case of solid/vapour interfaces, $\sigma_{\alpha\beta}$ is not generally equal to the surface tension because of crystallographic anisotropy and of changes in the state of surface stress on increasing the surface area. However, at temperatures near the melting point, these effects are reduced due to the relatively high atomic mobility. Similar considerations apply if a solid α is in contact with its own liquid – for instance, at nucleation in supercooled melts – or with a second solid having a negligible solubility in α .

Representative values of the interfacial free energies of pure metals are listed in Table 2.5 for the liquid/vapour, the solid/vapour, and the solid/liquid interface at conditions near the respective melting points. Also given are the temperature coefficients, $-\partial\sigma_{lv}/\partial T = S^{(\sigma)}$.

A careful analysis of the σ_{lv} data from the literature obtained by different methods has been performed by Allen [2.121], who suggests the following reliability limits: $\pm 5\%$ for the surface tensions σ_{lv} and $\pm 50\%$ for the temperature coefficients. Several attempts have been made to correlate the surface tension of liquid metals with bulk thermodynamic properties. Qualitatively, the data in Table 2.5 suggest that σ_{lv} increases with the melting temperature T_m , Ga being an exception. A quantitative fit of most experimental data is obtained by the empirical relation: $\sigma_{lv} = 3.6 T_m \cdot V_m^{-2/3}$, where V_m is the molar volume of the liquid and the prefactor has the dimension 10^{-7} J K^{-1} [2.121]. This correlation is consistent with the temperature dependence of σ_{lv} of liquid metals that follow the simple Eötvös law: $\sigma_{lv} = k_E(T_c - T)V_m^{-2/3}$, with $k_E \sim 0.64 \times 10^{-7} \text{ J K}^{-1}$ and $T_c \sim 6.6 T_m$.

Table 2.5 Representative selection of surface free energies, $\sigma_{\alpha\beta}$, of metals at the liquid/vapour (l/v), solid/vapour (s/v), and solid/liquid (s/l) interface at conditions near the melting point; the σ_{sv} – data correspond to polycrystalline surfaces

Metal	$\sigma_{lv}/\text{mJ m}^{-2}$	$\sigma_{sv}/\text{mJ m}^{-2}$	$\sigma_{sl}/\text{mJ m}^{-2}$	$\partial\sigma_{lv}/\partial T/\text{mJ m}^{-2} \text{ K}^{-1}$
K	115 ± 10 (a)	–	–	–0.08 (a)
Ga	730 ± 10 (b)	767 ± 6 (c)	82 (d)	–0.09 (b)
Bi	375 ± 10 (b)	501 ± 4 (c)	99 (d)	–0.11 (b)
Au	$1,140 \pm 50$ (a)	$1,410 \pm 30$ (c)	128 (d)	–0.5 (a)
Fe	$1,900 \pm 100$ (a)	$2,170$ (c) γ -Fe	269 (d)	–0.5 (a)
W	$2,500 \pm 150$ (a)	$2,690 \pm 22$ (c)	436 (d)	–0.3 (a)

(a) = [2.121], (b) = [2.122], (c) = [2.123], (d) = [2.124]

With these data, the above prefactor results. Further correlations that take into account the atomic bond strengths by the corresponding enthalpies of phase transition and consider the number of broken bonds at the interface have been tested. This yields the relation: $\sigma_{lv}(T_m) = 0.174 \times 10^{-8} \text{ mol}^{1/3} \Delta H_v V_m^{-2/3}$, where ΔH_v is the molar enthalpy of evaporation at T_m . It gives a very good fit of experimental σ_{lv} data with a correlation coefficient of 0.998 [2.125]. On the same basis of a broken bond model, a relation has been derived between σ_{sv} and σ_{lv} of the form [2.115]: $\sigma_{sv} = (Z - Z^{(\sigma)})/\Delta H_f V_{m,s}^{-2/3} + (\rho_s/\rho_l)^{2/3} \sigma_{lv}$; here, Z denotes the coordination number in the bulk solid, $Z^{(\sigma)}$ that at the surface, ΔH_f is the molar heat of fusion, $V_{m,s}$ is now the molar volume of the solid, and ρ_s and ρ_l are the solid and liquid density, respectively, at T_m . The main simplifying assumption is that the bond energies of surface and bulk atoms are equal. Depending on the packing of atoms in the surface planes – corresponding to hcp, bcc, and fcc crystal structures – lower and upper bounds for the ratio σ_{sv}/σ_{lv} can be estimated from the above relation [2.121]: $1.1 \lesssim \sigma_{sv}/\sigma_{lv} \lesssim 1.3$. Thus, an anisotropy of about 20% is estimated for the surface tension of crystalline metals. Theoretical determinations of the surface tension anisotropy in transition metals yield the following results [2.126]: For fcc crystals such as Ni cleaved with different surface orientations, it is found that $\sigma_{sv}(110) > \sigma_{sv}(110) > \sigma_{sv}(111)$ with $\sigma_{sv}(110)/\sigma_{sv}(111) = 1.3$; likewise, for bcc crystals with half band filling the corresponding inequality is $\sigma_{sv}(100) > \sigma_{sv}(111) > \sigma_{sv}(110)$ with $\sigma_{sv}(100)/\sigma_{sv}(110) = 1.4$. In both cases, a relatively strong anisotropy is predicted. Experimental values for different noble and transition metals amount to $\sim 10\%$ [2.121]. The data given in Table 2.5 for the solid/liquid interfacial free energies σ_{sl} have been determined from homogeneous nucleation rates in strongly undercooled liquid metals and are compiled in [2.124]. For metals, Turnbull found the following rule: $\sigma_{sl}(T_m) = 0.45 \Delta H_f V_{m,s}^{-2/3}$ [2.127], which has been verified on simple thermodynamic grounds [2.128].

Wetting phenomena of liquid metals are of particular interest in various metallurgical applications such as soldering, brazing, and welding and in problems with heat transfer or floatation. Wetting, generally, describes the spreading of a liquid deposited on a solid or liquid substrate. In order to simplify, consider a liquid drop on top of a clean, smooth, non-deformable, and horizontal solid surface. Then, three configurations are of particular interest, which can be distinguished by the magnitude of the contact angle Θ – this is defined by the angle between the solid surface and the tangent to the liquid surface at a point on the three phase contact line, taken in a plane vertical to the solid surface. The three distinct wetting configurations are as follows: (1) non-wetting for $\Theta > 90^\circ$; (2) partial wetting for $0 < \Theta \leq 90^\circ$; and (3) complete wetting in the limit $\Theta = 0$. The contact angle depends on the surface free energies of the three phases in contact: Solid (s), liquid (l), and vapour (v). At three-phase equilibrium, the total surface free energy, $\Delta F^{(\sigma)}$, has a minimum, $\partial \Delta F^{(\sigma)} / \partial A = 0$ from which the Young equation follows (see also [2.113]):

$$\sigma_{lv} \cos \Theta = \sigma_{sv}^0 - \sigma_{sl}. \quad (2.39)$$

It is important to note that the three phases are in mutual equilibrium and so the solid surface must be in equilibrium with the saturated vapour at pressure p_0 . Consequently, there must be an adsorbed film with a film pressure π_0 , i.e. $\sigma_{sv}^0 = \sigma_{sv} - \pi_0$, where σ_{sv} is the surface free energy of the pure solid substrate. In the limiting case $\Theta = 0$, (2.39) does not hold any longer and $\Theta = 0$ is not defined. This situation corresponds to the condition of a wetting transition.

Further insight into the distinct wetting configurations may be obtained by the spreading coefficient S , which is defined by

$$S = \sigma_{sv}^0 - (\sigma_{lv} + \sigma_{sl}). \quad (2.40)$$

It measures the difference between the surface free energy of the substrate when *dry and wet*. If $S > 0$, the liquid spreads completely and thus lowers the surface free energy. The opposite case, $S < 0$, corresponds to partial or non-wetting. Very similar considerations hold for spreading of a liquid over another liquid [2.113].

Research on wetting phenomena during the last decades was stimulated by a seminal paper of J. W. Cahn on *Critical point wetting* [2.129]. He could show that *in any two phase mixture of fluids near their critical point, contact angles against any third phase become zero in that one of the critical phases completely wets the third phase and excludes contact with the other critical phase. . . At some temperature below the critical, this perfect wetting terminates in what is described as a first-order transition of the surface*. The situation is illustrated in Fig. 2.18, which shows the phase diagram of a binary fluid mixture of components A and B exhibiting a miscibility gap. This is defined by the coexistence curve of phases α and β with an upper critical temperature T_c . In order to describe the characteristic wetting transitions in this system, let us focus on two specific variations of the thermodynamic states indicated by paths (1) and (2) in the figure. If at coexistence along path (1) the surface excess Γ_A ($\Gamma_B \equiv 0$) has a low and finite value, but diverges at some temperature T_w , this is the signature of a first-order, critical wetting transition, with T_w being the wetting temperature. Connected with this first-order wetting transition are so-called prewetting transitions, where a discontinuous jump from microscopically thin to thick adsorption films occurs and which can be observed off of coexistence along path (2) in the homogeneous B-rich fluid phase. The loci of these prewetting transitions define the prewetting line that leaves the coexistence curve tangentially at T_w and ends in a critical prewetting point at T_{cpw} – see the dashed line in Fig. 2.18. Along path (2) the distance to the coexistence curve is measured by the difference in the chemical potential, $\Delta\mu$, relative to μ_0 at coexistence. Following $\Gamma_A(\Delta\mu)$ along path (2) all the way to two phase coexistence, the surface excess continuously increases and diverges at coexistence. This is denoted a complete wetting transition. So, for $T_w < T < T_c$ along the coexistence curve, a macroscopically thick wetting film of the A-rich phase α separates the β phase from the vapour phase – or the container wall with T'_w . For an in depth presentation and discussion of the theory of wetting transitions, reference is given to the review article by Dietrich [2.131]. Wetting phenomena in nanofluidics have been treated recently in a review by Rauscher and Dietrich [2.132]. A very recent review on

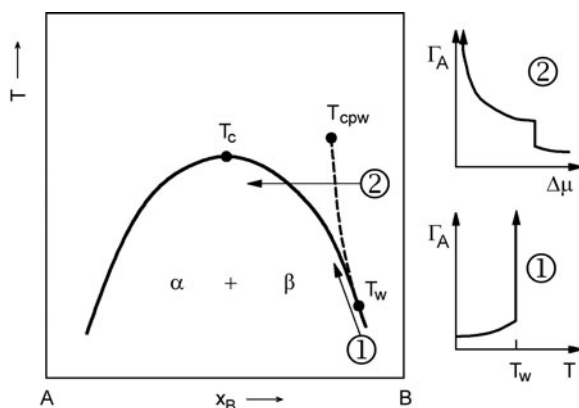


Fig. 2.18 Schematic bulk phase diagram of a binary fluid mixture exhibiting a miscibility gap, which is defined by the coexistence curve of phases α and β with an upper critical temperature T_c (full line in the temperature–mole fraction plane). Included in this figure is the surface phase diagram with a critical wetting transition at T_w and prewetting transitions along the prewetting line (dashed line). Changes in the surface excess Γ_A accompanying the distinct wetting transitions along paths (1) and (2) are depicted in the figures to the right. See also [2.130]

wetting and spreading covering various fundamental aspects and applications, with a high number of nearly 600 references, is that by Bonn et al. [2.133].

2.5.2 Molten Salts and Ionic Liquids

Various theoretical investigations have focused on the interfacial structure of molten salts. Evans and coworkers have calculated the equilibrium density profile and surface tension for the liquid/vapour interface within the restricted primitive model of a molten alkali halide. In this model, the anions and cations are represented by hard spheres of equal diameter and opposite charges. Using a square gradient approximation to calculate the free energy of the inhomogeneous charged fluid, they find differences in the shape of the density profile in comparison with a Lennard–Jones fluid, in particular, a sharper thickness of $\sim R - R$ being the radius of hard spheres – near the melting temperature. The theory gives a reasonable description of both the magnitude and the temperature dependence of surface tensions of alkali halides and other salts of nearly equal ionic radii [2.134, 2.135]. A number of molecular dynamics simulations of solid and liquid interfaces of salts have been performed by Heyes et al. [2.136, 2.137]. Of particular interest are the results obtained for a liquid/rigid wall and the corresponding electrified interface. A Born–Mayer–Huggins potential was used to model the ionic interactions with parameters for KCl [2.136]. It is found that close to and in a direction perpendicular to the wall there is substantial structural ordering. Oscillations in the density profile indicate a tendency towards layering of the ions near the liquid/wall interface; these oscillations die away rapidly towards

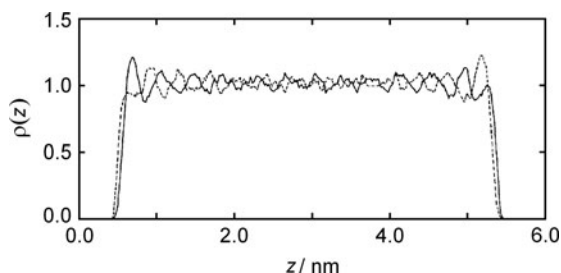


Fig. 2.19 MD simulation of the ion density profile, $\rho(z)$, vertical to the electrified liquid/wall interface of KCl at 1,075 K; (*full line*) corresponds to K^+ , (*dashed line*) to Cl^- ; densities are relative to the bulk liquid value. The formation of alternating K^+ - and Cl^- -rich layers is apparent. Adapted with permission from [2.136]; reproduced by permission (2010) of The Royal Society of Chemistry

the bulk. Similar effects are known from MD calculations of hard-sphere fluids against a repulsive wall and are predicted by theory; see e.g. [2.138]. Applying an electric field of $\sim 10^9 \text{ V m}^{-1}$ perpendicular to the liquid KCl/wall (electrode) interface, evidence is found of charge separation and ordering, whereby the oscillations of charge densities now penetrate much further into the bulk – see also Fig. 2.19. In relation to the double layer problem of electrified interfaces of ionic fluids, these findings are of special importance. Finally, it must be noted that experimental investigations of the microscopic structure of the liquid/vapour interface of molten salts such as alkali halides are still missing. Such experiments are complicated due to the fact that alkali halides have a relatively high vapour pressure near their melting point, which makes the use of ultrahigh vacuum techniques difficult.

Most metals – and other solid systems such as rare gases or ice – exhibit the phenomenon of surface melting approaching the melting point from below T_m during which the solid is wet by its own liquid – see e.g. [2.139]. It seems that this is not the case in salts such as the alkali halides. Indications of partial wetting connected with a contact angle of $\sim 48^\circ$ have been observed in an experiment of an Ar bubble captured at a crystalline NaCl/melt interface [2.140]. In a recent theoretical study, this problem of incomplete wetting of alkali halide crystal surfaces by their own melt at the triple point has been tackled by Tosatti and coworkers [2.141]. Using classic Born–Mayer–Huggins–Fumi–Tosi two-body potentials, these authors have performed extensive simulations for NaCl and have calculated the solid/liquid, liquid/vapour and solid/vapour interfacial free energies. They could show that NaCl(100) is a nonmelting surface with $\sigma_{sv} < \sigma_{sl} + \sigma_{lv}$. This behaviour is explained by mainly three factors (1) Surface anharmonicities stabilize the solid surface and thus reduce σ_{sv} ; (2) A large density jump on melting causes bad liquid – solid adhesion; (3) Incipient NaCl molecular correlations at the liquid/vapour interface lead to a reduction of the surface entropy of liquid NaCl below that of solid NaCl(100) and thus raise σ_{lv} . These are interesting predictions, waiting for an independent experimental confirmation.

The structure and composition of liquid/vapour or liquid/vacuum interfaces of room temperature ionic liquids have been studied quite intensively in recent years. In a first atomistic simulation of dimethylimidazolium chloride, Lynden-Bell found indications of charge ordering and a region of enhanced density immediately below the interface in which the cations are oriented with their planes perpendicular to the surface [2.142]. Similar conclusions were drawn from a more recent MD simulation study of $[\text{C}_4\text{mim}][\text{PF}_6]$ melts, where the butyl chains are observed to project outside the liquid surface and the imidazolium ring plane is found to lie parallel to the surface normal [2.143]. These findings have been supported by direct recoil spectroscopy measurements [2.144] and also by sum frequency generation (SFG) spectroscopy [2.145]. Seemingly conflicting propositions were derived from X-ray reflectivity measurements where it was claimed that these data are not consistent with a model in which the butyl chains protrude from the air/liquid interface [2.146]. However, this conflict could be solved unambiguously by a combined SFG and X-ray reflectivity study of imidazolium-based ionic liquids with different anions such as BF_4^- , PF_6^- , and I^- by Jeon et al. [2.147]. From a careful analysis of their reflectivity data in conjunction with the SFG spectra, these authors give evidence that the gas/liquid interface of these melts consists of a topmost layer of loosely packed butyl chains, while the densely packed imidazolium cores and anions form a layer in contact with the bulk liquid. Furthermore, the surface composition of various 1,3-dialkyl-imidazolium ionic liquids was studied by X-ray photoelectron spectroscopy [2.80]. Again, a clear enrichment of the alkyl chains at the outer surface is found; it is further concluded that both anions and cationic head groups are located approximately at the same distance from the outer surface [2.80].

It is known for a long time that charged walls in contact with an electrolyte solution strongly affect the interfacial structures and properties. This was first demonstrated by Langmuir in explaining the capillary rise of a dilute KCl solution in a quartz or glass tubing [2.148]. This effect can also explain a strong enhancement of the wetting film thickness at the molten KCl/sapphire interface due to charging of Al_2O_3 and double layer formation at the interface [2.149]; see also Sect. 4.3. The microscopic structure of an ionic liquid/charged wall interface has been elucidated, for the first time experimentally, for an ionic liquid at a charged sapphire (0001) surface [2.150]. This interface was probed by high energy X-ray reflectivity measurements spanning a momentum transfer range up to $q = 1.4 \text{ \AA}^{-1}$. In a temperature range from -15°C up to 110°C , three ionic liquids with different cations and the common $[\text{FAP}]^-$ anion have been studied, where $[\text{FAP}]^-$ stands for bis(pentafluoroethyl)trifluorophosphate. Charging of the Al_2O_3 surface was independently measured with a Kelvin probe. One of the main observations is that all reflectivity curves in the temperature range studied show a clear dip around $q_0 \sim 0.8 \text{ \AA}^{-1}$. This is a strong indication of interfacial layering with a layer spacing of $d = 2\pi/q_0 \sim 8 \text{ \AA}$ comparable in size with the thickness of an anion-cation double layer. A detailed analysis of the Fresnel-normalized reflectivity curves by fits with different models of the interfacial electron density profiles yields a layering structure of alternating cation and anion strata, which decays exponentially into the bulk with a decay length of $\sim 16 \text{ \AA}$ at the lowest temperature; see Fig. 2.20. In

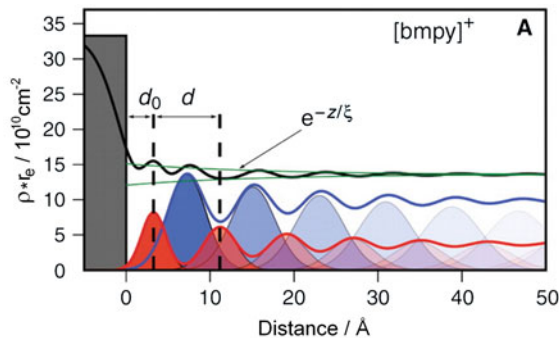


Fig. 2.20 Molecular layering in a fluorinated ionic liquid at a charged sapphire (0001) surface: Electron densities obtained from the best fit of the X-ray reflectivity measurement for the [C₄mpy] [FAP]–Al₂O₃ interface at –15°C; red and blue lines indicate cation and anion Gaussian distributions contributing to the respective partial electron density profiles; *black line*, total electron density profile, *grey bar*, electron density of sapphire substrate without roughness. From [2.150], reprinted with permission from the American Association for the Advancement of Science (2010)

conclusion, there is a close similarity in charge ordering at an electrified solid/liquid interface between an ionic liquid and a molten salt such as KCl; see Fig. 2.19.

Electrocapillarity and electrowetting phenomena have attracted considerable interest in recent years; see e.g. the review by Mugele and Baret [2.151]. Strong motivations result from potential applications in *lab-on-a-chip* devices or new kinds of electronic displays. Electrowetting enables the manipulation of tiny amounts of liquids on surfaces. The basic equation behind this is the Young–Lippmann equation; see [2.151]:

$$\cos \Theta = \cos \Theta_0 + \left(\frac{C}{2\sigma_{lv}} \right) \cdot U^2, \quad (2.41)$$

which describes the variation of the contact angle Θ of a liquid droplet of a conducting fluid on top of a thin dielectric film with capacitance C as a function of voltage U applied across the droplet and film. The liquid/vapour surface tension of the droplet is denoted by σ_{lv} . So far, electrowetting experiments have been mainly performed with droplets of aqueous electrolyte solutions on polymer coated dielectric films [2.151]. Only recently studies with ionic liquids have been reported [2.152–2.154]. Essentially, they exhibit the same electrowetting features of a parabolic dependence of $\cos \Theta$ vs. U^2 as is observed in electrolyte solutions. However, at higher voltages – ≥ 50 V in [C₄mim][PF₆] and [C₄mim][NTf₂] melts on a 100 nm SiO₂–Si dielectric substrate – decomposition of these ionic liquids sets in [2.79]. This is presumably caused by an electric breakdown and a corresponding discharging. The decomposition has been observed by the formation of large bubbles under UHV conditions that result from decomposition products such as HF. An example is given in Fig. 2.21.

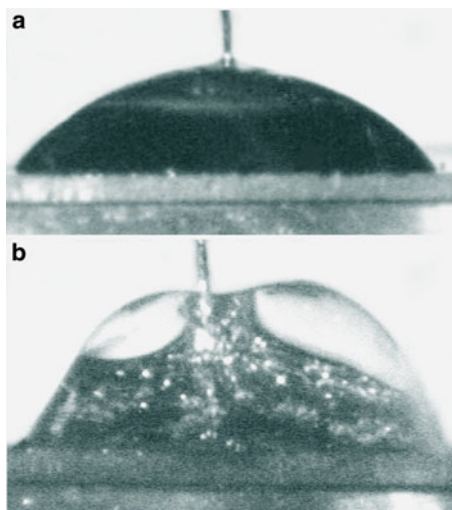


Fig. 2.21 Typical droplet shape of a $[\text{C}_4\text{mim}][\text{PF}_6]$ ionic liquid on a 100 nm thick SiO_2/Si substrate with a contact line diameter of ~ 2.60 mm at 298 K; **(a)** for an applied voltage below 50 V, **(b)** above 50 V where decomposition occurs indicated by small and large bubbles. These measurements have been performed under UHV conditions. Adapted from [2.79]

Table 2.6 Interfacial free energies or surface tensions, σ_{lv} , and their temperature dependence at the liquid/vapour interface of selected molten salts and ionic liquids near their respective melting points

Compound	$\sigma_{\text{lv}}/\text{mJ m}^{-2}$	$-\partial\sigma_{\text{lv}}/\partial T/\text{mJ m}^{-2} \text{K}^{-1}$
NaCl	1,138 (a)	0.07 (a)
KCl	98 (a)	0.07 (a)
BiCl_3	73 (b)	0.139 (b)
$[\text{C}_4\text{mim}][\text{Cl}]$	47.5 (c)	0.04 (c)
$[\text{C}_4\text{mim}][\text{Cl}]-\text{AlCl}_3$ (1:1)	46.5(c) (300 K)	0.055 (c)
$[\text{C}_4\text{mim}][\text{PF}_6]$	43.5 (d)	0.035 (d)

(a) = [2.135], (b) = [2.19], (c) = [2.155], (d) = [2.156]

In concluding this section, a selection of representative values of liquid/vapour surface tensions of molten salts and ionic liquids at conditions near their respective melting points is given in Table 2.6.

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Chapter 3

Bulk Peculiarities: Metal–Nonmetal Transitions

Abstract Metal–nonmetal transitions in fluid systems are the subject matter of this chapter. It first deals with the limits of the metallic regime as given by the Ioffe–Regel rule and the Mott criterion for the breakdown of electronic screening. Then various mechanisms of electron localization and types of metal–nonmetal transitions are discussed. This includes phenomena such as localization by disorder (Mott–Anderson transition), polaron and F-centre formation, intra-atomic electron correlation (Mott–Hubbard transition), and percolation transitions. The main part of this chapter deals with electronic phase transitions in expanded fluid alkali metals, liquid alkali metal alloys, and metal–molten salt solutions based on experimental investigations of their electronic transport, magnetic, and structural properties. In fluid alkali metals, strong indications of a highly correlated, nearly antiferromagnetic electron gas exist, which is the signature of a Mott–Hubbard transition. The nature of localized electronic states in alkali metal alloys depends on chemical bonding in the nonmetallic regime. Liquid semiconducting behaviour is found in alkali metal–antimony alloys and the transition to metallic states can be consistently described by crossing of a pseudogap. Some alkali metal–gold alloys exhibit predominantly ionic bonding near M–Au stoichiometry and thus behave very similar to alkali metal–alkali halide melts. The nonmetallic regime of the latter is characterized by polaronic defects leading to a metal–nonmetal transition of the Mott–Anderson type.

Transitions from metal to nonmetal – semiconductor or insulator – are driven by basic changes in the electronic structure of condensed matter. They can be induced by varying physical parameters such as pressure, temperature, density, composition, or external fields. In crystalline materials, a sharp division into metals and nonmetals is given by the Bloch–Wilson band model taking into account the occupation of band states by electrons according to Fermi–Dirac statistics. If the Fermi energy E_F lies in a band gap so that the density of states $n(E_F)$ is zero, then the dc conductivity $\sigma(0)$ is thermally activated, $\sigma = \sigma_0 \exp(-\Delta E/kT)$, and tends to zero with T . This is the characteristic of nonmetals. In a metal, the Fermi energy lies in a partially filled conduction band and $n(E_F)$ is finite. Thus, electron transport is not thermally activated and $\sigma(T = 0)$ should be finite.

However, in some cases, the simple band model of non-interacting electrons fails, which was first discussed by Mott [3.1–3.3]. A classical example is nickel oxide in

which the Ni^{2+} ions have the electronic configuration $3d^8$. According to the band model, one of the $3d$ subbands is partially empty and so NiO should be metallic. But this is not the case; pure nickel oxide is an insulator. Another example, which aroused the special interest of Mott, is that of a crystalline array of monovalent atoms with a hypothetical variable lattice constant d . Again, the band model predicts metallic characteristics even at large d , since half-filling of the conduction band should be independent on d . However, this is against intuition. At strong expansion of the “lattice”, approaching densities comparable with a dense vapour phase, one expects atomic like states and nonmetallic behaviour. In the discussion of such problems – which was pioneered by the work of Mott – it became clear that electronic correlations play an important role for the understanding of metal–nonmetal transitions in condensed phases – both long-range Coulomb interactions and intra-atomic electron–electron correlations, e^2/r_{12} . This is described in detail in the following chapters.

Considering metal–nonmetal transitions in non-crystalline materials and fluids, the effect of disorder on the electronic structure is a crucial problem. Among non-crystalline materials are highly doped semiconductors, glasses, amorphous or rapidly quenched films, and quenched metal–rare gas mixtures. Fluid systems of interest comprise expanded fluid metals, liquid semiconductors, some liquid metal alloys, and metal–nonmetal solutions such as metal–ammonia or metal–molten salt solutions. For the characterization of the electronic structure of these systems, the density of states plays a key role. However, due to disorder and the resulting random potentials, states in the band tails, at lower values of $n(E)$, drastically change their character. They become localized, i.e. their wave functions decay exponentially in space, and a critical energy E_c separates localized from extended states. If by some external parameter E_F is moved across E_c , a metal–nonmetal transition occurs. This situation is depicted schematically in Fig. 3.1. The mechanism is explained in detail in Sect. 3.2. A comprehensive description of the basic theoretical concepts of metal–nonmetal transitions in various systems is given in Mott’s last book [3.4]. Furthermore, there are several reviews that cover recent progress in the field of disordered electronic systems and which have been collected in two books edited by Edwards and Rao [3.5, 3.6].

3.1 Limits of the Metallic Regime

On melting of metals, both the mass density ρ and the conductivity $\sigma(0)$ change little; ρ typically is reduced by about 2%, and σ by less than a factor of 2; see e.g. [2.60]. The small change in ρ implies that there is no significant modification in the electronic screening. Considering, for instance, the Thomas–Fermi approximation, the change of the screening length is negligible, $k_{\text{TF}} \sim k_F \sim n^{1/3}$. The electron mean free path λ_e in liquid metals near the melting point is still large; in many cases $\lambda_e/r_s > 10$; an exception is the semimetal Bi (see Table 2.3). The Hall coefficient often shows NFE behaviour. All these observations give evidence that

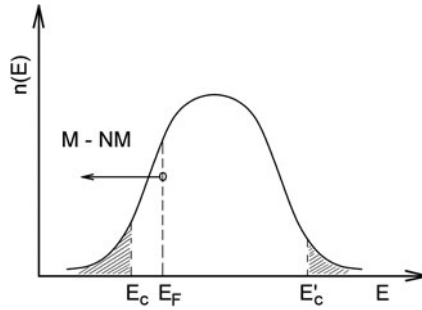


Fig. 3.1 Schematic drawing of the density of states, $n(E)$, across a band where tail states are localized (hatching) by disorder; the mobility edges at E_c and E'_c separate localized from extended band states. If the Fermi energy E_F is moved beyond E_c or E'_c a metal–nonmetal (M–NM) transition induced by disorder occurs (see arrow)

the loss of long-range order on melting is insufficient to cause major changes in the electronic structure of metals. The NFE picture still applies in dense liquid metals, and the electronic transport properties are only limited by weak scattering similar to the solid.

The question arises by how much can one reduce $\sigma(0)$ before the simple NFE model fails? As was first suggested by Ioffe and Regel [3.7], a weak scattering approximation based on nearly free electrons should break down, at the latest, once the limit of $\lambda_e \sim r_s$ is reached. For the liquid metals in Table 2.3, this corresponds to a conductivity of the order of $10^3 \Omega^{-1} \text{cm}^{-1}$. In fluid alkali metals (Rb and Cs), this conductivity belongs to a volume expansion by a factor of $\sim 2\rho_m/\rho \sim 2$ at conditions near liquid–vapour coexistence; see Sect. 3.3. Nominally, for $\lambda_e = r_s$, the wave function of a conduction electron changes its phase in a random way from atom to atom. Such behaviour surely is not consistent with the NFE model. If, in this limit, one chooses the proper wave function and calculates the dc conductivity with the Kubo–Greenwood formula, this yields [3.4]:

$$\sigma(0) = \frac{e^2}{3\hbar a}, \quad (3.1)$$

where $a \sim r_s$ is comparable with the mean interatomic distance. This is the limiting Ioffe–Regel conductivity, which for $a \sim 1 \text{ \AA}$ has a value of $\sim 10^3 \Omega^{-1} \text{cm}^{-1}$ [3.4].

Another limitation of the metallic regime is due to the breakdown of electronic screening, a problem addressed by Mott in several of his publications. Starting from a metallic system with a high density of conduction electrons, the Coulomb potential of metal cations is completely screened, for instance, in the form of a Thomas–Fermi potential or by Lindhard screening; see Sect. 2.2. Next, a continuous reduction of the valence electron density, e.g. by expansion of a fluid metal or by dilution of the metal concentration in a metal–nonmetal solution is considered. There must be a limiting electron density n_c below which screening is insufficient and electrons

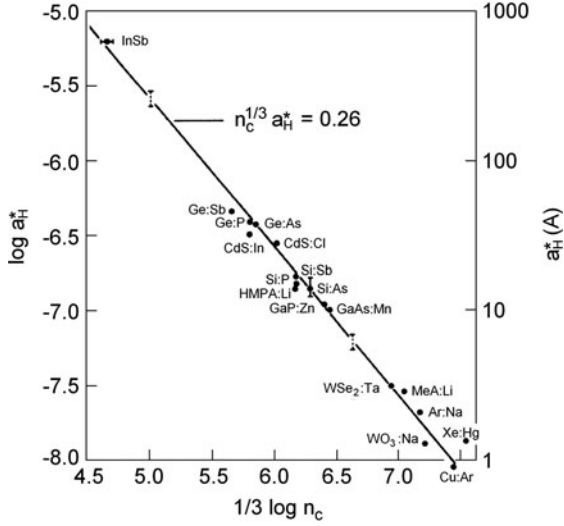


Fig. 3.2 Log–log plot of the Mott criterion, $n_c^{1/3} \cdot a_B^* = \text{const}$, determined from experimental data for highly doped semiconductors, metal–ammonia solutions, tungsten bronzes, and metal–rare gas systems. Reprinted with permission from [3.8]; copyright permission by American Physical Society

become bound or localized by the cation potentials. This metal–nonmetal transition is known as Mott transition. For the critical density n_c of charge carriers, Mott derived the following relation [3.1, 3.3]:

$$n_c^{1/3} \times a_B^* \approx 0.25. \quad (3.2)$$

Here a_B^* is the effective Bohr radius of a bound state, $a_B^* = \hbar^2 \epsilon / m_e e^2$, with ϵ being the dielectric constant of the medium. Edwards and Sienko [3.8] have shown that this Mott criterion holds for a number of different systems over a wide variation in n_c (see Fig. 3.2).

The Mott criterion can be derived by different arguments leading to a very similar result; see also [3.9]. A relatively general and simple estimate is the following [3.9, 3.10]. In a general view, a metal–nonmetal transition is due to a competition between potential and kinetic energy. The former tends to localize states and the latter to delocalize them. For an atomic state, the energy scales with $\text{const} (e^2/\epsilon) n^{1/3}$; for a degenerate electron gas, the kinetic energy can be approximated by $(\hbar^2/2m_e) n^{2/3}$. Assuming that at the transition the potential and kinetic energy are of comparable magnitude, this yields for n_c :

$$n_c^{1/3} \times a_B^* \sim 2 \text{ const}, \quad (3.3)$$

where the constant of the Mott criterion corresponds to $\text{const} \sim 1/8$.

3.2 Mechanisms of Electron Localization and Types of Metal–Nonmetal Transitions

3.2.1 Localization by Disorder

In non-crystalline materials, the electronic properties cannot be treated properly without taking into account the effect of disorder. To illustrate this influence, Fig. 3.3 shows a comparison of the main features of the crystalline band model of non-interacting electrons in comparison with the situation in a disordered system with random potentials. This model was first treated by Anderson [3.11]. A main characteristic of a crystalline arrangement of atoms is a distribution of extended states over a band of width B . The corresponding density of states $n(E)$ is continuous, but in crystalline materials may exhibit kinks at specific symmetry points in the Brillouin zone. Within the tight binding approximation, the band width for an s -band in a simple cubic lattice is $B = 2N_1 I$, where N_1 is the coordination number of nearest neighbours and I is the energy overlap integral; see e.g. [2.4]. In contrast, in a disordered system, the potential is considered random within limits $\pm(1/2)V_0$ (see Fig. 3.3). For large values of V_0 and corresponding large fluctuations of the electron energies at different sites, electrons will be trapped in deep potential wells. These electrons cannot escape by admixing states with another one, since nearby electrons are unlikely to be close in energy and states of similar energy are far apart. Overlap of such states is exponentially reduced. If disorder is strong enough, the envelopes of the wave functions of localized electrons decay exponentially with the so-called localization length ξ , which in the limit of strong localization is of the order of an atomic length. According to numerical calculations, this limit is reached when $(V_0/B) \sim 2$; see [3.4]. In general, one expects that states near the band edges are those that are localized most easily. Thus, at a given disorder near the critical value of $(V_0/B) \sim 2$, a situation occurs where states in the tails of $n(E)$ are localized up to an energy E_c or E'_c ; see Figs. 3.1 and 3.3. These energies separate localized from extended states and thus define a so-called mobility edge. If, by increasing disorder or reducing $n(E_c)$, the Fermi energy crosses the mobility edge, a metal–nonmetal transition of the Mott–Anderson type occurs.

The Anderson model described so far is that of a *frozen* disorder, appropriate for non-crystalline materials at low T . The question arises in how far these results apply to fluid systems at elevated temperatures. Liquid metals at high densities are characterized by a well-defined short-range order extending over first and second nearest neighbours. So, a description of the electronic energies by a tight binding approximation defining a range of band states is reasonable. With increasing expansion or reducing electron density of the metallic fluid, the number of nearest neighbours decreases – see Sect. 3.3 – and so does the band width or its equivalent for the fluid state. At the same time, thermal fluctuations and local microscopic inhomogeneities grow, which leads to a continuous increase in topological disorder and potential fluctuations. These considerations show that (V_0/B) clearly gets larger towards the

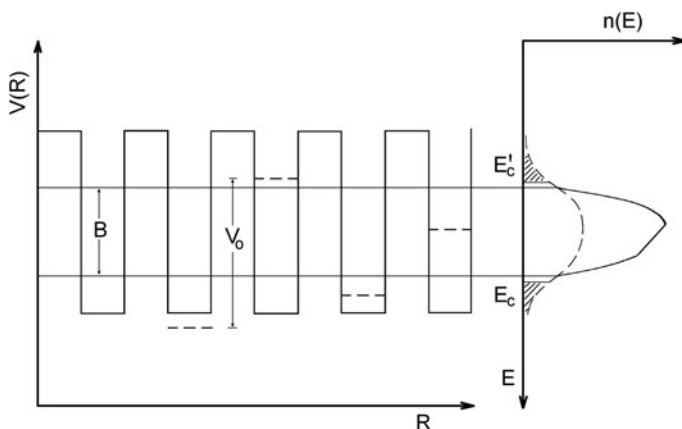


Fig. 3.3 Sketch of crystalline potential $V(R)$ together with a band of width B and the density of states, $n(E)$ (full lines); same for a random potential (dashed lines), where localized states below E_c and above E'_c are hatched

metal–nonmetal transition so that the mechanism of electron localization according to the Anderson model should also apply in fluid systems.

3.2.2 Electronic Defects and Polarons

Ionic crystals such as alkali halides belong to the best-known insulators. Their optical gaps are large – for instance, that of KCl is ~ 9 eV near 298 K – and so thermal excitation of electrons into the conduction band can be neglected at ambient temperatures. But the ionic conductance of these crystals is relatively high and ranges from 10^{-8} to $10^{-2} \Omega^{-1} \text{ cm}^{-1}$ at room temperature; see e.g. [2.4]. This is caused by highly mobile ion vacancies, anion and cation Schottky defects, which exist at thermal equilibrium. When excess electrons are introduced, either by additive doping of the crystal in contact with an alkali metal vapour or by high-energy irradiation, they are trapped or localized by anion vacancies. These defects give the crystal a characteristic colour, the most prominent colour centre being the F-centre (*Farbzentrum*). Colour centres can aggregate – e.g. in the form of M or R centres – where two or three neighbouring ion vacancies bind two or three electrons. A common characteristic of colour centres is that electrons are localized in deep traps and that the ground and excited state energies are located inside the crystal energy gap.

In ionic or semiconductor materials, another mechanism of electron localization is of interest: self-trapping of electrons or polaron formation. An electron in the conduction band can polarize and deform the surrounding medium, thus lowering its energy by the polarization energy, $W_p = 1/2(e^2)/\epsilon_p r_p$, where r_p is the polaron radius and $\epsilon_p^{-1} = \epsilon_\infty^{-1} - \epsilon^{-1}$, with ϵ_∞ and ϵ being the high frequency and static

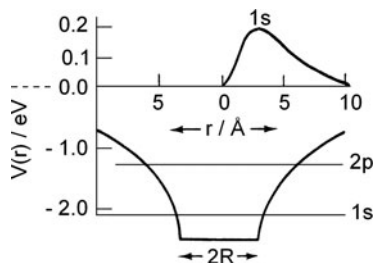


Fig. 3.4 Potential well of a solvated electron in ammonia according to the model of Jortner; also shown are the energies of the $1s$ ground and $2p$ excited state of the polaron and the $1s$ radial electron density (*upper panel*). Adapted from [3.15]; copyright permission (2010) by American Institute of Physics

dielectric constants; see also [3.12]. Through polaron formation the electron, so to say, *digs its own potential well* where it is trapped. For small polarons, the radius is of the order of an interatomic distance so that W_p in practical cases reaches a value of ~ 0.5 eV [3.12]. At elevated temperatures, polarons can move by thermally activated hopping with an activation energy of $\Delta E = 1/2(W_p)$. The energy gained by polarizing the medium is proportional to the square of the electric field of a polaron. Thus, a configuration with two electrons in the same potential well forming a bipolaron can be more stable than two separated polarons, provided the energy gain is greater than the Coulomb repulsion.

In the liquid state, atoms or ions are less rigidly bound, and for this reason, the formation of small polarons can be promoted. This idea was first suggested by Landau [3.13]. A prototype is the solvated electron in metal–ammonia solutions; see e.g. [3.14]. A model potential used by Jortner [3.15] to calculate the optical absorption and electron density of a self-trapped electron in ammonia is shown in Fig. 3.4. The polaron binding energy is found to be ~ 1.6 eV, its radius is about 3.2 Å [3.15]. In molten alkali halides, electron localization by F-centre-like defects – similar to the solid – has been confirmed by different MD calculations. Using a discretized version of the Feynman path integral method Parrinello and Rahman found highly localized states of excess electrons in liquid KCl, which they consider a justification of the F-centre model [3.16]. Similar results were obtained in a theoretical study of liquid K–KCl solutions by Selloni et al. where the authors applied for the first time the now well-known Car–Parrinello ab initio MD method [3.17]. Again, strongly localized F-centre-like states are observed, which in the liquid have a lifetime in the picosecond range [3.17]. These phenomena are discussed in detail in Sect. 3.5.

3.2.3 Intra-atomic Electron–Electron Correlation

A different mechanism of a metal–nonmetal transition due to short-range electronic correlation was first discussed by Hubbard [3.18]. For an ordered array of

one-electron atoms, he considered the following Hamiltonian:

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3.4)$$

The first term is characterized by a kinetic energy t_{ij} describing the hopping of an electron from site i to its nearest neighbour j ; it is assumed to be the same for all nearest neighbour pairs and zero else. The $a_{i\sigma}$ denote the creation operators for sites i , and σ refers to the spin direction. For $U = 0$, the first term is just a tight binding Hamiltonian and the nearest neighbour overlap $t_{ij} = B/2N_1$, with B being the band width and N_1 the coordination number. The second term in (3.4) describes the extra energy cost U of putting two electrons with spin up and down on the same site. Here, U can be written as follows:

$$U = \left\langle \frac{e^2}{r_{12}} \right\rangle = \iint \left(\frac{e^2}{r_{12}} \right) \varphi(\underline{r}_1)^2 \varphi(\underline{r}_2)^2 d\underline{r}_1 d\underline{r}_2, \quad (3.5)$$

where $\varphi(r_i)$ are the wave functions of electron $i = 1, 2$ on a site. For a hydrogen $1s$ state, the value of U is $U = 3/8 (e^2 a_B^{-1})$; see also [3.4]. In the atomic limit of a large distance R between the atoms, U has the limiting value $I - A$, where I is the ionization potential and A is the electron affinity. The Hubbard model does not take into account long-range Coulomb interactions, lattice–electron coupling, or disorder. So, one cannot expect that it describes real systems in detail. Still, it contains some principle consequences for the electronic structure of condensed matter, which are described in the following. In particular, the predictions of the Hubbard model are of relevance to expanded fluid alkali metals, which in some respect are the direct realization of an array of one-electron atoms with variable R .

Starting from the Hubbard model and considering monovalent atoms at large interatomic distance R , the energy to produce an electron pair and a hole is $U = I - A$. Reducing R and increasing the overlap at neighbouring sites, a lower and an upper Hubbard band are formed with band widths B_l and B_u , respectively. The upper band corresponds to the energy states of the excited electron pairs; the lower band is that of electron holes. The distance between the bands is now $\Delta E = U - 1/2(B_l + B_u)$, called the Hubbard gap. This situation is depicted schematically in Fig. 3.5. On further compression of the system, there must be a distance R_{M-NM} , where $\Delta E = 0$. This marks the transition from a Mott–Hubbard insulator to a metal; see Fig. 3.5. As regards the magnitude of R_{M-NM} , the following estimate is given by Mott; see [3.4]. Approximating U and B for the case of hydrogen atoms and assuming $R_{M-NM}/a_B^* \sim 4$, he finds a value of $n_c^{1/3} \times a_B^* \sim 0.2$. So, both for the intra-atomic electronic correlation of the Hubbard type and the breakdown of screening of long-range Coulomb interaction, the same Mott criterion results for the critical concentration n_c of carriers at the metal–nonmetal transition.

On the metallic side of the transition, the Hubbard model has specific consequences for the magnetic properties. For a highly correlated electron gas, where a small fraction of atomic sites contains two electrons or holes, Brinkman and

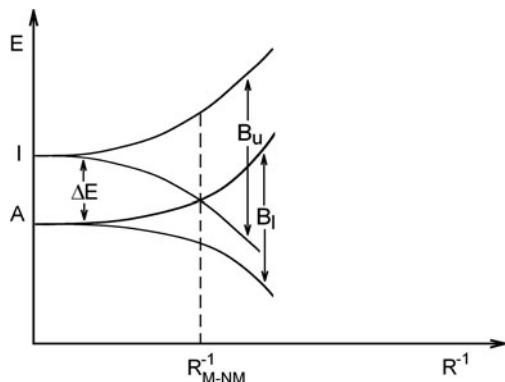


Fig. 3.5 Schematic sketch of the Mott–Hubbard transition in a system of one-electron atoms; plotted are the lower and upper Hubbard bands as a function of the reciprocal interatomic distance R^{-1} . The transition at band crossing occurs at R_{M-NM}^{-1}

Rice showed that both the Pauli susceptibility and the electronic specific heat are strongly enhanced [3.19]. The enhancement is inversely proportional to the fraction f of doubly occupied states, which is roughly given by $f = (I - U/B)$ with $B = 1/2(B_u + B_l)$; see [3.4].

3.2.4 Percolation Transition

Percolation, in general terms, describes the passage of information through a disordered system. Specific examples of a more physical interest are as follows: The flow of a liquid through a porous medium or current flow through a network of resistors randomly distributed on a lattice. Disorder may be introduced in different ways. The most common statistical assumptions are known as *bond percolation* and *site percolation* models. In the first, some fraction of bonds is missing from the lattice; in the latter, a known fraction of sites is missing. Two quantities are of particular interest in classical percolation theory: The percolation threshold, x_c , and the percolation probability, $P(x)$. Here, we focus on site percolation. If the concentration of allowed sites, x , increases, larger clusters containing allowed sites occur and at x_c the mean cluster size diverges for $N \rightarrow \infty$, N being the total number of sites. This definition of x_c implies, that for any finite N there is a complete path of adjacent allowed sites through the system. For $x > x_c$ and large N , only one large cluster will exist. The ratio of the number of allowed sites in the large cluster to the total number of sites on the lattice ($N \rightarrow \infty$) defines the site percolation probability, $P(x)$. Computer simulations of $P(x)$ for different common 3D lattices show that $P(x)$ above x_c rises sharply from zero and then approaches x for $x \gg x_c$ [3.20]. Near the threshold, $P(x)$ is characterized by a simple power law,

$$P(x) \sim (x - x_c)^S, \quad (3.6)$$

with $0.3 \leq S \leq 0.4$ [3.20]. Various numerical studies of the electrical conductivity employing resistor networks with site and bond percolation models have been performed [3.20]. In general, a distinct scaling behaviour is found near x_c :

$$\sigma(x) \sim (x - x_c)^\nu \quad (3.7)$$

with $1.5 \leq \nu \leq 1.6$. For $x \gg x_c$ these models generally agree with the predictions of classical effective medium theories such as the Bruggeman 3D model [3.21]. The calculations for bond and site percolation on a simple 3D cubic lattice yield a threshold value $x_c \sim 0.3$ [3.20].

3.3 Expanded Fluid Alkali Metals

Fluid metals have been treated in the book by Hensel and Warren, which covers various electronic, structural, and thermodynamic properties [2.61]. The electronic transitions in these systems are discussed in detail approaching the critical point region both from the expanded liquid and the dense vapour phase. In addition, there is a review on *The metal–nonmetal transition in expanded metals*, which presents several physico-chemical characteristics of expanded fluid metals [2.74]. Here, we confine to a few characteristic changes that occur during expansion of fluid alkali metals towards their critical point. Aspects of particular interest are as follows: The limit of the metallic regime as defined by the transport properties, the change in the microscopic structure on expansion, and the electronic correlation problem in relation with the magnetic properties. These themes have also been selected because they are of relevance for the discussion in later chapters.

3.3.1 Electronic Transport Properties

Figure 3.6 shows simultaneous measurements of the electrical conductivity and Hall coefficient of liquid cesium for temperatures between the melting point and $1,400^\circ\text{C}$ at a constant pressure of 99 bar [2.104]. Near coexistence, the density at $1,400^\circ\text{C}$ is $\sim 0.9 \text{ g cm}^{-3}$ (see Fig. 2.12) so that this temperature variation corresponds to an expansion of the liquid by almost a factor of 2. In this experiment, the conductivity was measured by a four-probe technique and the Hall voltage by the double ac method, that is, the magnetic field and the current had different frequencies ω_1 and ω_2 and the Hall signal was detected at $\omega_1 \pm \omega_2$; see also [3.22]. Liquid Cs was contained in a cylinder of quadratic cross section ($5 \times 5 \text{ mm}^2$) made from a thin $75 \mu\text{m}$ thick W–Re foil, so that corrosion at elevated temperatures was excluded. Measurements were performed inside a high pressure vessel with argon gas as pressurizing

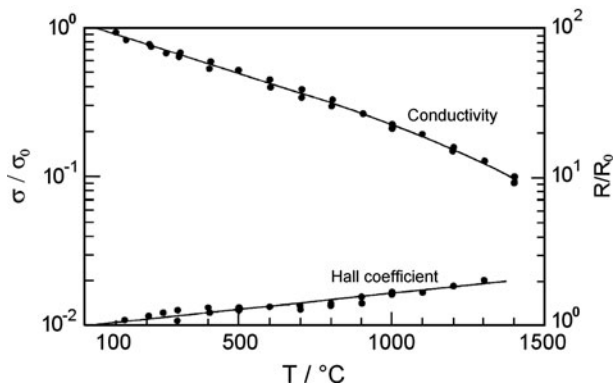


Fig. 3.6 Electrical conductivity, $\sigma(0)$, and Hall coefficient, R_H , of liquid Cs as a function of temperature at constant pressure of 99 bar; $\sigma(0)$ and R_H are given relative to the values σ_0 and R_0 at 30°C. See also [2.104]

medium. The accuracy of the Hall coefficient data was estimated to be $\pm 15\%$, that of conductivity $\pm 5\%$.

An interesting information of these results is that the Hall coefficient increases only slightly with temperature and reaches a value of $R_H/R_0 \approx 2$ at 1,400°C. This value is in good agreement with the prediction of the NFE model where $R_H \sim n^{-1}$. This observation strongly indicates that metallic transport characteristics consistent with the NFE model exist in liquid cesium even for an expansion by a factor of nearly 2. Over the same temperature and density range, the electrical conductivity decreases by a factor of ~ 10 , reaching a value of $\sim 3 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$ – see also Table 2.3. This is still above the Ioffe–Regel limit of $\sim 10^3 \Omega^{-1} \text{ cm}^{-1}$ where the NFE approximation should break down. In this context it is interesting to note that the temperature coefficient of the conductivity, $(\partial \ln \sigma / \partial \ln T)_v$, changes sign at a density of $\rho \sim 1 \text{ g cm}^{-3}$ [3.23]. For densities above 1 g cm^{-3} , the temperature coefficient of σ possesses low negative values, which is consistent with the predictions of the Ziman theory for weak scattering of electrons in monovalent liquid metals. By reducing the density below 1 g cm^{-3} , $(\partial \ln \sigma / \partial \ln T)_v$ exhibits clearly positive values indicative of thermally activated transport [3.23].

A general view of the variation of the electrical conductivity $\sigma(0)$ and, in parallel, the absolute thermoelectric power, S , of fluid cesium at sub- and supercritical conditions is presented in Fig. 3.7. Again, both quantities have been measured simultaneously using a W–Re cylinder with a wall thickness of $\sim 100 \mu\text{m}$, which enabled determination of liquid conductivities down to $\sim 10^2 \Omega^{-1} \text{ cm}^{-1}$ with an accuracy of about $\pm 20\%$ [3.23, 3.24]. On comparing the graphs in Fig. 3.7, it is apparent that both $\sigma(0)$ and S are weakly pressure dependent up to $\sim 1,500^\circ\text{C}$, which corresponds to a liquid density at saturation of $\sim 0.8 \text{ g cm}^{-3}$; see Fig. 2.12. The conductivity and thermopower at this temperature reach values of $\sim 2,000 \Omega^{-1} \text{ cm}^{-1}$ and $-50 \mu\text{V K}^{-1}$ near saturation. Above the temperature of 1,500°C, both $\sigma(0)$ and S change significantly as a function of temperature and pressure and drop to values

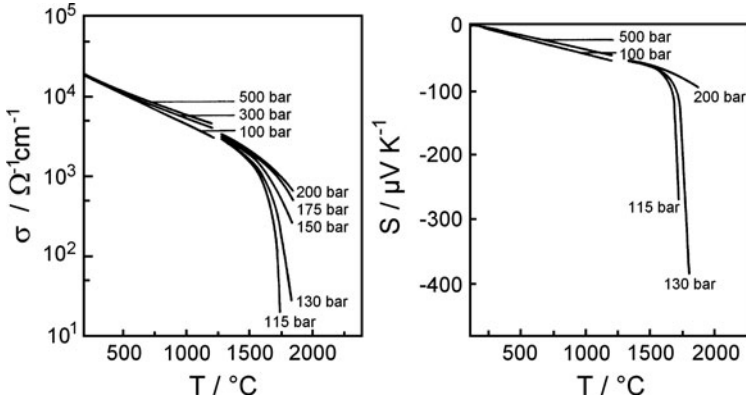


Fig. 3.7 Electrical conductivity, $\sigma(0)$, and absolute thermoelectric power, S , of fluid cesium at sub- and supercritical conditions. See also [3.24]

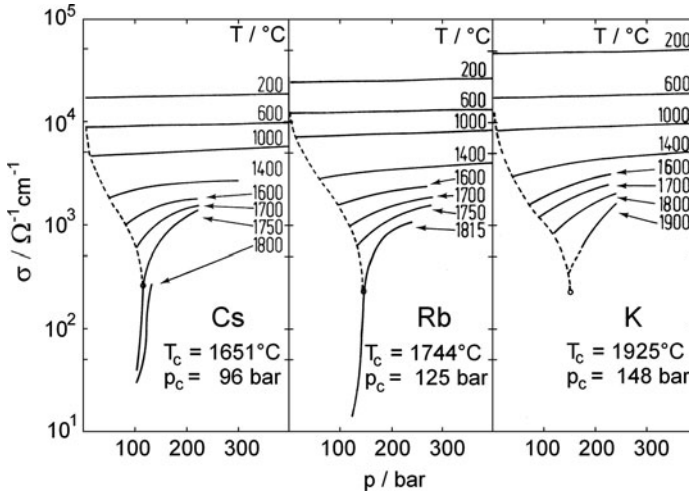
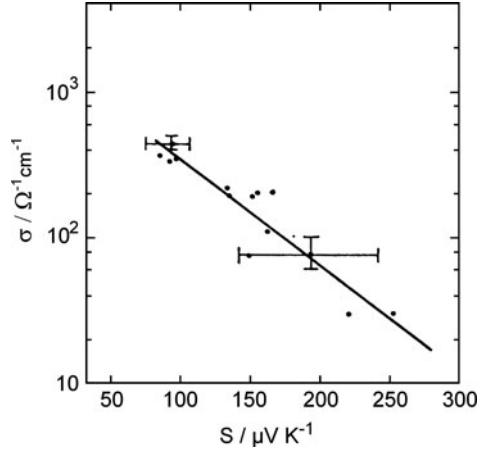


Fig. 3.8 Pressure and temperature dependence of the electrical conductivity, $\sigma(0)$, of fluid alkali metals at sub- and supercritical conditions. See also [3.25]

that are clearly outside the NFE metallic regime. The strong pressure and temperature dependence of both quantities above $1,500^\circ\text{C}$ reflect the corresponding strong density variation at conditions near the critical point; see also Fig. 2.12.

With respect to the electrical conductivity, fluid alkali metals exhibit a very similar behaviour going from the melting towards the critical point. This is demonstrated in Fig. 3.8. Above $\sim 2,000 \Omega^{-1} \text{cm}^{-1}$ the pressure dependence of σ is relatively small, whereas it gets strong below this limit. Near the critical point, the electrical conductivity reaches a value of the order of $\sim 10^2 \Omega^{-1} \text{cm}^{-1}$ [3.25].

Fig. 3.9 Logarithmic plot of conductivity, $\sigma(0)$, vs. thermopower, S , for expanded fluid cesium. See also [3.23]



In summary, these results of the electronic transport properties of expanded fluid alkali metals show that metallic characteristics consistent with the NFE model exist for conductivities above $\sim 2,000 \Omega^{-1} \text{cm}^{-1}$, in qualitative agreement with the Ioffe–Regel limiting law. Below this limit, strong deviations from metallic behaviour occur.

In the nonmetallic regime, approaching the critical point, the temperature coefficient of σ indicates thermally activated transport properties. Assuming – as was first suggested by Mott – that $\sigma(0)$ and S have the same activation energy, then the following relation should hold [3.4]:

$$\ln \sigma(0) = \ln \sigma_0 - \left(\frac{e}{k_B} \right) S + \alpha. \quad (3.8)$$

Here, σ_0 is Mott’s minimum metallic conductivity, $\sigma_0 = 0.03 e^2 / \hbar a_B$, and α is a constant [3.4]. Plotting the data of Fig. 3.7 near the critical point according to (3.8) yields a linear relation which is shown in Fig. 3.9. The slope of the straight line is $(-1.7 \pm 0.4) 10^4 \text{KV}^{-1}$ in comparison with the theoretical value $-e/k_B = -1.2 \times 10^4 \text{KV}^{-1}$. Taking $\alpha = 1$ and $e/k_B \cdot S = 1$ – the latter corresponds to $S = -80 \mu\text{VK}^{-1}$ – in (3.8) the minimum metallic conductivity is fixed, which yields $\sigma_0 \sim 400 \Omega^{-1} \text{cm}^{-1}$ for fluid Cs.

3.3.2 Microscopic Structure

Several experimental studies have been carried out of the static structure factor, $S(Q)$, of expanded fluid alkali metals, rubidium and cesium, at temperatures between the melting and critical point and corresponding densities near liquid coexistence. Both neutron [3.26, 3.27] and X-ray diffraction techniques [3.28] have been

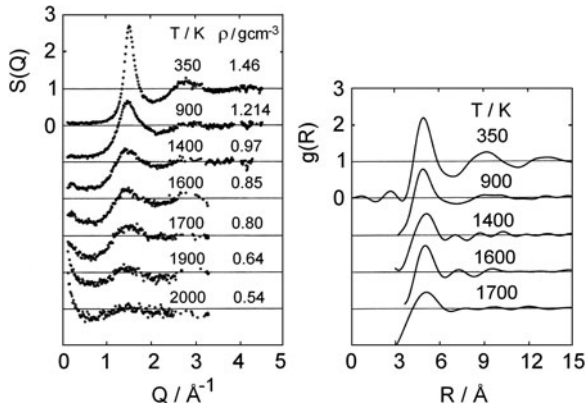


Fig. 3.10 Neutron scattering results of the static structure factor, $S(Q)$ (left), and pair distribution function, $g(R)$ (right), of fluid rubidium at different temperatures and densities approaching the critical point ($T_c = 2,017$ K, $\rho_c = 0.29$ g cm $^{-3}$). See also [3.26]

employed. In addition, the dynamic structure factor, $S(Q, \omega)$, of Rb has been determined from inelastic neutron scattering for an expansion up to about twice the critical density [3.29, 3.30]. In the following, we focus on the neutron diffraction results of Rb, which have been obtained in a specially constructed high temperature – high-pressure set-up [3.31] – for details see Sect. A.1. From the neutron point of view, rubidium has especially favourable properties; it is a good coherent scatterer with low absorption and incoherent scattering cross section.

Results of $S(Q)$ and its Fourier transform $g(R)$ of Rb are shown in Fig. 3.10. Near the melting point, both $S(Q)$ and $g(R)$ are well structured; a first and second nearest neighbour shell is well defined in $g(R)$. The scattering of data points in $S(Q)$ around $2.8 \text{ \AA}^{-1}$ is due to incomplete correction of the Bragg scattering of the solid container materials that are in the way of the neutron beam. In $g(R)$ at 350 K, weak oscillations of a short period are visible at small R below $3 \text{ \AA}$ where $g(R)$ per definition is zero. This wiggling line extends over the whole R range and is caused by truncation errors in the Fourier transform – see also the curves at higher temperatures. For this reason only the first peak in $g(R)$ is left for a reasonable interpretation. Without going into details the following gross features can be deduced from $S(Q)$ and $g(R)$ as a function of temperature and density approaching the critical point: (1) Up to 1,700 K the position of the first peak in $S(Q)$ and $g(R)$ stays nearly constant, whereas the intensity is reduced continuously; and (2) around 1,600 K smallangle scattering is clearly visible which is pronounced at densities near twice the critical density. These observations give valuable information on the change of the microscopic structure and interatomic interaction with expansion of the fluid.

As already indicated, the nearest neighbour distance R_1 of Rb is almost constant; it rises slightly from $4.9 \pm 0.1 \text{ \AA}$ at 350 K to $5.1 \pm 0.1 \text{ \AA}$ at 1,700 K. In this temperature interval, the number of nearest neighbours, N_1 , – determined from integration

of the first peak of $g(R)$ – decreases linearly as a function of density; it drops from 9 to about 4 near 1,700 K [3.26]. Comparable results have been obtained for fluid Cs [3.27]. As for this variation of N_1 and R_1 , expanded liquid alkali metals behave very similar to simple liquids such as argon – see e.g. the structural investigation of fluid Ar by Mikolaj and Pings [3.32]. Yet, the differences in the interatomic interactions become evident if one tries to describe $S(Q)$ by the hard-sphere model, which is presented in Fig. 3.11. This comparison shows that a qualitative fit by a *hard-sphere* model is only possible if one allows for a decrease of the hard-sphere diameter by $\sim 10\%$ between 350 and 1,700 K. This together with a stronger damping of $S(Q)$ at larger Q -values indicates that the repulsive part of the Rb potential is softer than that of Ar, where σ_{hs} is nearly constant with varying density or temperature. At low Q values, strong deviations of $S(Q)$ from the hard-sphere model occur above $\sim 1,400$ K; see Fig. 3.11. This is plotted in detail for the limit $Q = 0$ in Fig. 3.12. Qualitatively, this difference reflects changes in the attractive part of the interatomic potential at larger R values that can be argued as follows. Using thermodynamic perturbation theory, the long wavelength limit $S(0)$ can be approximated by [3.33]:

$$S(0) = S_{\text{hs}}(0)(1 + n S_{\text{hs}}(0)/k_{\text{B}}T \cdot \phi_1(Q = 0))^{-1}. \quad (3.9)$$

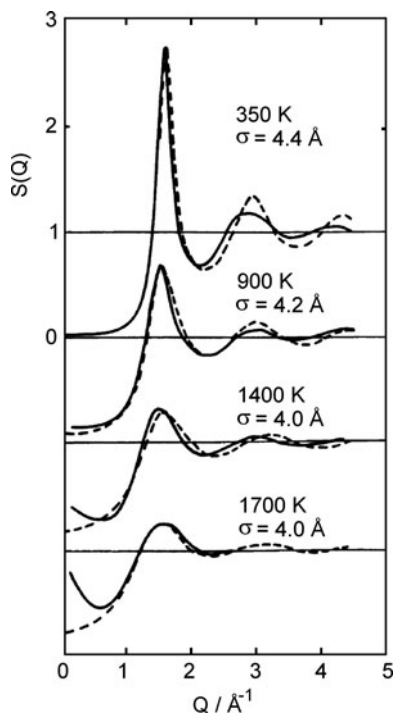
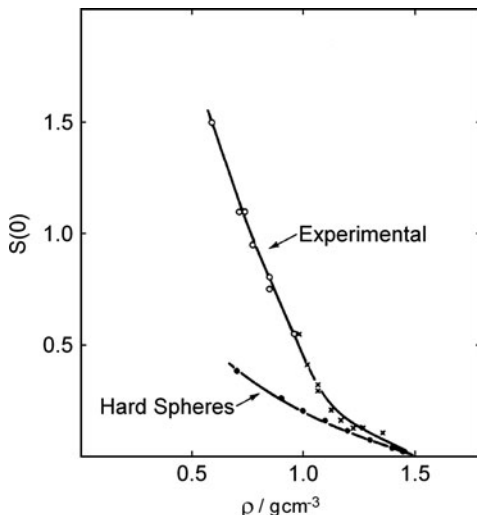


Fig. 3.11 Experimental (*full lines*) and calculated by the hard sphere model (*dashed lines*) $S(Q)$ of expanded liquid rubidium at different temperatures; the hard-sphere diameter, σ_{hs} , has been fitted to the first maximum of $S(Q)$. See also [3.26]

Fig. 3.12 Long wavelength limit $S(0)$ of Rb vs. density along liquid coexistence in comparison with hard-sphere model calculations. See also [3.31]



Here $S_{\text{hs}}(0)$ is the long wavelength limit of the hard-sphere reference system and $\phi_1(Q = 0)$ is the Fourier transform of the attractive, negative part of the potential at $Q = 0$, i.e.:

$$\phi_1(Q = 0) = \int_0^\infty \phi_1(R) 4\pi R^2 dR, \quad (3.10)$$

where, $\phi_1(R)$ is treated as a perturbation [3.33]. In this approximation, the strong increase of $S(0)$ of Rb with expansion can be explained by a stronger attraction of $\phi_1(R)$, due to a deepening of the potential minimum, a change towards a potential of longer range, or both. These changes are expected if electronic screening of the Coulomb potential gets weaker with reducing the density and the pseudopotential is no longer a weak perturbation. According to the small-angle behaviour of $S(Q)$ and the strong rise of $S(0)$, this effect in rubidium sets in when the density falls below $\sim 1 \text{ g cm}^{-3}$, i.e. roughly at triple the critical density; see Fig. 3.10. A very similar behaviour is observed for expanded liquid cesium [3.27]. Kahl and Hafner have calculated $S(Q)$ of fluid Rb using the optimized random phase approximation and effective interatomic pair potentials derived from pseudopotential perturbation theory [3.34]. For temperatures up to 1,400 K, they find good agreement with the neutron diffraction results. At higher temperatures, these calculations do not reproduce the strong increase of $S(0)$ observed experimentally. The authors explain this by the breakdown of electronic screening and conclude that below a density of about 1 g cm^{-3} in Rb the true potential is much more attractive than the one given by the linear response calculations [3.34]. A systematic investigation of the microscopic structure of expanded liquid alkali metals has been performed by Matsuda et al. [3.35]. They employed both a modified hypernetted chain (MHNC) approximation and MD simulations with local empty core pseudopotentials. Good agreement

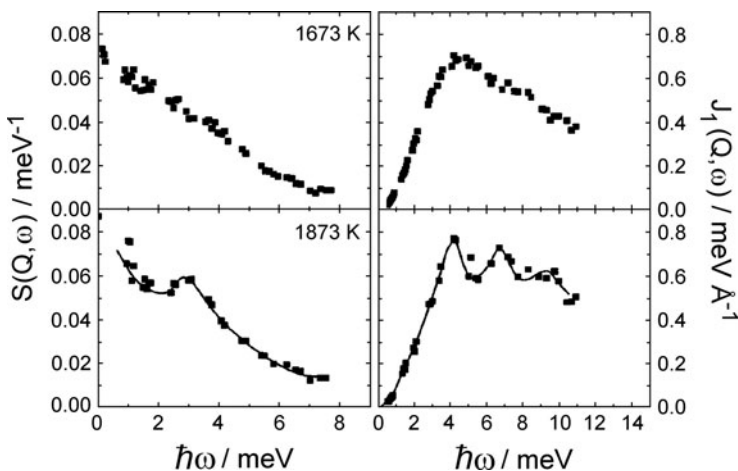


Fig. 3.13 Dynamic structure factor, $S(Q, \omega)$ (left panel), and current correlation function, $J_1(Q, \omega) = \omega^2/Q^2 S(Q, \omega)$, at $Q = 1.3 \text{ \AA}^{-1}$ of fluid Rb measured along the liquid–vapour coexistence curve at 1,673 K ($\rho = 0.87 \text{ g cm}^{-3}$) and 1,873 K ($\rho = 0.61 \text{ g cm}^{-3}$). Reprinted with permission from [3.30]; copyright permission (2010) by American Physical Society

is found between experimental data and MHNC calculations, both for $S(Q)$ and $S(0)$, for temperatures up to 1,700 K and an expansion down to 0.8 g cm^{-3} at coexistence in rubidium. Molecular dynamics calculations of $g(R)$ of Rb together with a detailed comparison with Ar have been reported by Tanaka at conditions between the melting and critical point [3.36]. On approaching the critical point, discrepancies in $S(Q)$ and $S(0)$ between Rb and Ar are clearly seen.

In conclusion, both experimental and theoretical investigations of the static structure factor of expanded liquid alkali metals indicate changes in the interatomic interaction towards a stronger attractive potential in the density range $3\rho_c$ to $2\rho_c$ at coexistence. This is the density range where the Ioffe–Regel limit is approached. Further information on the structural changes under these conditions has been obtained from inelastic neutron scattering measurements of the dynamic structure factor, $S(Q, \omega)$, of fluid rubidium; see Fig. 3.13 [3.29, 3.30]. Up to 1,673 K $S(Q, \omega)$ shows a behaviour that is characteristic of collective excitations. At 1,873 K and a corresponding density of nearly twice the critical density, a separate excitation appears at an energy of $\sim 3.2 \text{ meV}$. It has been assigned to the vibration energy of Rb_2 dimers, which is supported by density functional theory calculations. At a density of $\sim 0.6 \text{ g cm}^{-3}$, these calculations predict a vibrational energy of 3.2 meV, a dissociation energy of 90 meV, and a fraction of Rb_2 dimers in the fluid of $\sim 25\%$ [3.30]. Accordingly, the microscopic structure of alkali metals in the neighbourhood of the critical point may be described by that of an inhomogeneous fluid with fluctuating monomeric and dimeric configurations, and possibly, higher aggregated clusters.

3.3.3 Magnetic Properties

In discussing the magnetic properties of fluid alkali metals, the static paramagnetic spin susceptibility, $\chi^{e,p}$, is of particular interest.¹ In general terms, this is given by [2.4]:

$$\chi^{e,p} = -\mu_B^2 \int_0^\infty n(E) \left(\frac{\partial f}{\partial E} \right) dE. \quad (3.11)$$

Here, μ_B is the Bohr magneton, $n(E)$ is the density of states, and $f(E)$ is the distribution function for the occupation of states.

We consider first the case of the low-density vapour phase. This is predominantly composed of isolated atoms that carry a localized magnetic moment μ_B . The total susceptibility is given by

$$\chi^{\text{total}} = \chi^{i,d} + \chi^{e,d} + \chi^{e,p}. \quad (3.12)$$

In this expression, the different contributions are: $\chi^{i,d}$ is the diamagnetism of electrons in closed shells of the ion cores, $\chi^{e,d}$ and $\chi^{e,p}$ are diamagnetic and paramagnetic contributions of bound valence electrons, respectively. The first two terms present the Larmor diamagnetic susceptibility, which is proportional to the sum over the mean square ionic or atomic radii; see e.g. [2.4]. With exception of very high temperatures and pressures, $\chi^{i,d}$ in good approximation is constant. The last term in (3.12) is described by the Curie law, which characterizes the alignment of the spin magnetic moment μ_B in the magnetic field opposed by thermal disorder.

For localized $s = 1/2$ electron states, it is calculated from (3.11) with $f(E) \sim \exp((E - \mu)/k_B T)$ for non-degenerate electron states,

$$\chi_{\text{Curie}}^{e,p} = \frac{n\mu_B^2}{k_B T}. \quad (3.13)$$

Next, we consider the case of a liquid alkali metal near its melting point. The ion core diamagnetism remains the same, but the electron contributions $\chi^{e,p}$ and $\chi^{e,d}$ change significantly. By neglecting, for the moment, the orbital motion of conduction electrons in the magnetic field H , the spin susceptibility is strongly reduced due to quantum statistics for highly degenerate electrons. Only a fraction $\mu_B H/E_F$ contributes to the electron paramagnetism. Thus, $\chi^{e,p}$ is now replaced by the Pauli spin susceptibility, which is obtained from (3.11) by employing Fermi–Dirac statistics for $f(E)$:

$$\chi_{\text{Pauli}}^{e,p} = \mu_B^2 n(E_F), \quad (3.14)$$

¹ The magnetic susceptibility χ or volume susceptibility χ_V is dimensionless in cgs units; it is related to the mass, χ_g , and molar, χ_m , susceptibility by $\chi = \chi_g \cdot \rho$ and $\chi_m = \chi_g M$ with ρ = mass density and M = atomic mass.

where $n(E_F)$ is the density of states at the Fermi level. Within the NFE model, $n(E_F) = 3/2(n/E_F)$ and thus the ratio of $\chi_{\text{Pauli}}^{e,p}/\chi_{\text{Curie}}^{e,p} = 3/2(T/T_F)$, where the Fermi temperature is $T_F \sim 2 \times 10^4$ K for Cs and Rb at densities near the melting point. Coming back to the diamagnetism of conduction electrons, this results from the coupling of the electron orbital motion with the field H which leads to quantized Landau levels. For free electrons, this yields the Landau diamagnetism with [2.4]:

$$\chi_{\text{Landau}} = -\frac{\chi_{\text{Pauli}}}{3}. \quad (3.15)$$

So far the effects of electron–electron correlation and exchange have not been taken into account. As for the Landau diamagnetism, the theory of Kanazawa and Matsudawa gives the following correction [3.37]:

$$\chi_{\text{corr}}^{e,d} = x^{e,d} (1 + 0.028 \cdot r_s (\ln r_s + 1.51)). \quad (3.16)$$

With respect to the electronic paramagnetism these effects are discussed below in relation with the interpretation of the experimental results.

The static spin susceptibilities of fluid alkali metals have been determined in several experiments by two different methods. By employing the conventional Faraday technique, the total susceptibility of cesium and rubidium has been measured both in the dense vapour and the thermally expanded liquid phase along the liquid–vapour coexistence curve [3.38, 3.39]. In these experiments, the liquid sample was contained in a cylindrical W–Re pressure vessel of about 10 mm diameter and 25 mm length, which was hanging from a sensitive balance connected with a vacuum furnace inside the magnetic field gradient. By varying the amount of sample in different measurements, the liquid and vapour contributions to χ^{total} could be separated. Representative error bars are given in the figures below. The second method used was nuclear magnetic resonance (NMR). In metals, nuclear magnetic moments interact with the spin polarization of conduction electrons via the hyperfine interaction. In alkali metals, the valence electrons have predominantly s -character with a non-zero probability amplitude, $\langle \varphi(0)^2 \rangle$, at the nucleus. Thus, the observed nuclear resonance frequency, ω_{obs} , is shifted with respect to the nuclear Zeeman frequency, ω_0 , yielding the Knight shift K [3.40]:

$$K = \frac{\omega_{\text{obs}} - \omega_0}{\omega_0} = \left(\frac{8\pi}{3} \right) \langle \varphi(0)^2 \rangle_F V_m \chi^{e,p}, \quad (3.17)$$

where V_m is the atomic volume and $\langle \varphi(0)^2 \rangle_F$ denotes average over electrons at E_F . Warren and coworkers succeeded in a comprehensive study of the ^{133}Cs Knight shift and nuclear relaxation rate in expanded liquid cesium at temperatures up to $1,590^\circ\text{C}$ covering a density range from 1.93 to 0.70 g cm^{-3} [3.41]. In these measurements, the liquid sample was contained in a sapphire cell on which the NMR coil was wound. The cell with surrounding dc heating elements and thermal insulation was

Fig. 3.14 Electronic part of the magnetic gram susceptibility, χ_g^e , of fluid caesium vs. density along the liquid–vapour coexistence curve; the numbers indicate temperature in degree celsius. See also [2.74]

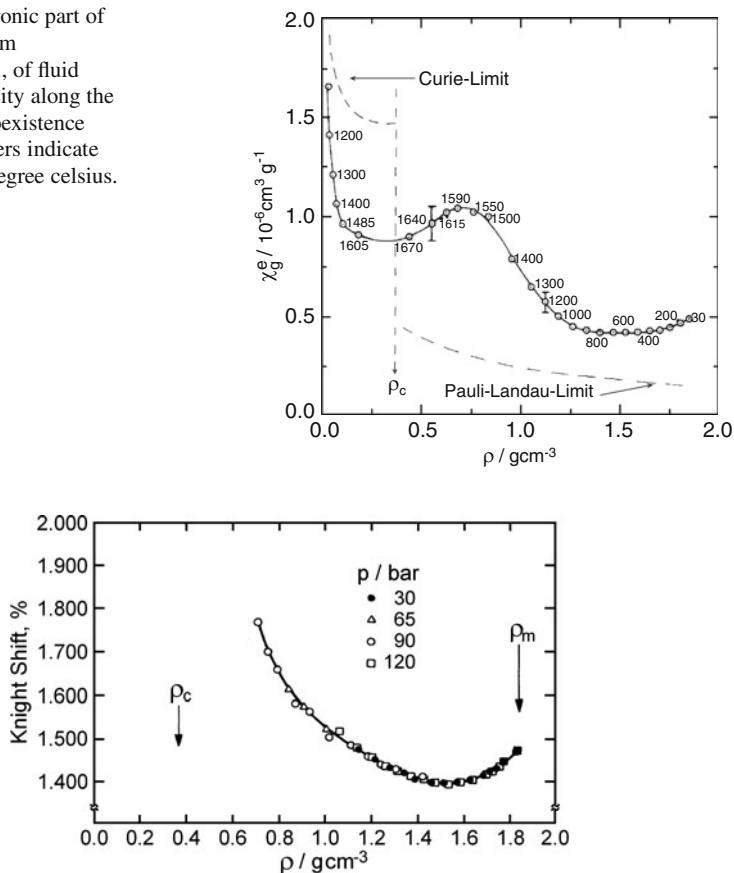


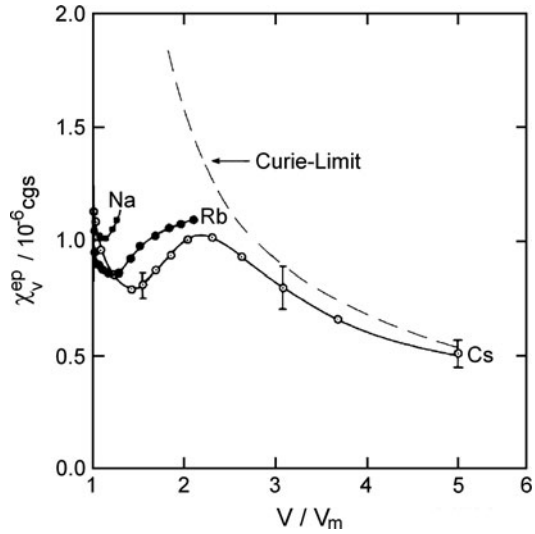
Fig. 3.15 Isobaric ^{133}Cs Knight shifts vs. density at various pressures; the density scale corresponds to conditions near liquid–vapour coexistence. ρ_m , density at melting point; ρ_c , critical density. Reprinted with permission from [3.41]; copyright permission (2010) by American Physical Society

mounted in a copper–beryllium autoclave that fitted inside the magnet poles. For further details of the set-up and the applied technique, see [3.41, 2.61].

Results of the electronic part of the magnetic gram susceptibility, χ_g^e , of fluid caesium are presented in Fig. 3.14. They have been determined from the measured values of χ_g^{total} after subtraction of the constant core diamagnetism of $\chi_g^{i,d} = -0.26 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. Plotted are the susceptibilities at different densities and temperatures along the liquid–vapour coexistence curve ranging from the melting point to the low-density vapour phase. For comparison, the Knight shift of liquid caesium as a function of density along the coexistence curve is shown in Fig. 3.15.

In the following, we discuss these results in detail and begin with the expanded liquid phase. As can be seen in Fig. 3.14, clear differences exist between the experimental values and the prediction of the NFE model presented by the Pauli–Landau

Fig. 3.16 Spin susceptibility of fluid alkali metals vs. reduced volume (V_m = volume at melting point). See also [2.74]



limit. The latter has a weak density dependence $\sim \rho^{-2/3}$. Starting at the melting point, the experimental χ_g^e is slightly reduced, passes a shallow minimum around 1.5 g cm^{-3} , and then increases significantly up to a maximum near 0.8 g cm^{-3} corresponding to $\sim 2\rho_c$. A very similar trend is observed in the Knight shift in Fig. 3.15; it is also found for other alkali metals as shown in Fig. 3.16 above. At the melting point, the spin susceptibility $\chi^{e,p}$ of Cs is enhanced by a factor of ~ 2.5 taking into account the Kanazawa and Matsudawa correction of the electron diamagnetism. This enhancement can be explained by exchange–correlation effects as calculations by Vosko et al. [3.42] and Moruzzi et al. [3.43] have shown; see also [2.74]. Near the density of $\sim 2\rho_c$, the enhancement of the spin susceptibility amounts to a factor of 3 relative to the Pauli–Landau limit. In accordance with the predictions of the theory of Brinkman and Rice [3.19], this increase of the spin susceptibility has been interpreted by an enhancement of the density of states relative to its free-electron value $N_0(E_F) : N(E_F)/N_0(E_F) = m_e^*/m_e$, where m_e^* is the effective mass of electrons [3.38]. As was first pointed out by Warren [3.44], the maximum in $\chi^{e,p}$ near $2\rho_c$ is due to Curie law limitations at high temperatures and reduced densities; see also Fig. 3.16. Taking $x_{\text{Pauli}}/x_{\text{Curie}} = 1$ and correcting E_F for the expansion between $\rho = 1.85$ and $2\rho_c \sim 0.8 \text{ g/cm}^3$, in the case of Cs, this yields

$$\frac{3}{2} (k_B T E_F^{-1}) = \left(\frac{T}{T_F} \right) 2.5 \left(\frac{m_e^*}{m_e} \right) = 1, \quad (3.18)$$

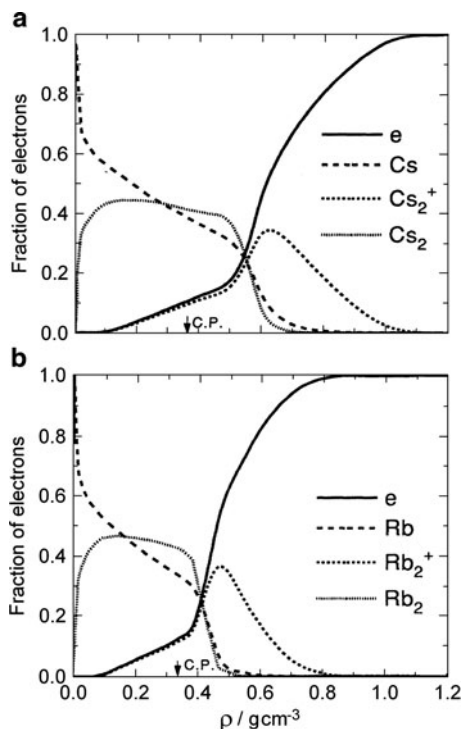
from which results an enhancement of $m_e^*/m_e = 4$ for $T/T_F \sim 0.1$ at 2,000 K. According to Mott's estimate for the fraction of doubly occupied states, $f = 0.5/(m_e^*/m_e)$, this corresponds to a fraction of $f = 1/8$. Thus, the magnetic properties of expanded alkali metals exhibit the characteristics of a nearly antiferromagnetic, highly correlated electron gas.

Turning next to the dense vapour phase, a discrepancy between the experimental data and the Curie limit of isolated atoms is apparent in Fig. 3.14. The same observation has been made for rubidium [3.39]. In first approximation, we have considered a simple chemical equilibrium of neutral atomic and diatomic species whereby the susceptibility of the first was described by the Curie law and the diamagnetism of the molecule was estimated to be $\sim -90 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Cs_2 [3.38]. This simple model yielded a fraction of Cs_2 molecules of $\sim 10\%$ at $1,100^\circ\text{C}$ and 10 bar increasing to $\sim 25\%$ at $1,600^\circ\text{C}$ and 80 bar; similar results were obtained for rubidium [3.39]. At this point, it was suggested [3.38] that charged species such as Cs^+ , Cs_2^+ or Cs^- , Cs_2^- and higher aggregated clusters M_n must be considered, since the ionization potential decreases and the electron affinity increases with rising n [3.45]. It was also conjectured that these species should exist above the critical density, which would explain the symmetric minimum in the spin susceptibility around ρ_c ; see Fig. 3.14 [3.25]. Hernandez [3.46] and Redmer and Warren [3.47] systematically investigated these suggestions by statistical thermodynamic calculations. They started from a weakly ionized, low-density plasma model and determined the equation of state and the composition of the fluid in a quantum statistical approach taking into account interaction corrections between different species. They found good agreement with the magnetic susceptibility of Cs and Rb for the dense vapour and the expanded liquid region near ρ_c [3.47]. Results of these calculations for the fraction of free electrons and electrons localized in different species are shown in Fig. 3.17. In this approach, the dominating species in the dense vapour phase are neutral monomers and dimers in agreement with the interpretation of the vapour susceptibility given above. The strong increase of the dimer fraction in the density range $\rho_c < \rho < 2\rho_c$ is consistent with the shallow minimum of the susceptibility near ρ_c ; see Fig. 3.14. A relatively high fraction of ionized dimers is predicted around $2\rho_c$, which may contribute to the spin susceptibility enhancement.

3.3.4 Metal–Nonmetal Transition

During thermal expansion of fluid alkali metals in the density range between the melting and the critical point all quantities presented, the electrical, magnetic and structural properties, undergo significant changes at a density of about twice the critical density ρ_c , which is roughly half way between the melting and critical point density. Above this density the electronic transport properties are consistent with the predictions of the nearly free-electron model as demonstrated by the magnitude of the Hall coefficient, the thermopower, the conductivity, and the temperature dependence of the latter. The electron mean free path is still larger than the mean interatomic distance. The local microscopic structure exhibits a nearly constant nearest neighbour distance and a continuous reduction of the number of nearest neighbours by about a factor of 2. Approaching $2\rho_c$ from above, the spin susceptibility is enhanced indicating the characteristics of a highly correlated electron gas. In this context, it is interesting to note that all the characteristic variations

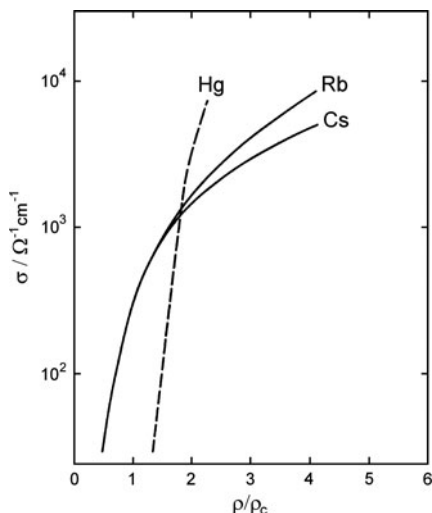
Fig. 3.17 Fractions of free electrons and electrons localized in monomeric and dimeric species in Cs(a) and Rb(b) for densities at liquid–vapour coexistence according to the weakly ionized plasma model of Redmer and Warren. Reprinted with permission from [3.47]; copyright permission (2010) by American Physical Society



of these quantities still can be described and understood within the concept of a simple band model.

Near $2\rho_c$, the Ioffe–Regel limit is reached, at the latest. The temperature coefficient of conductivity changes sign and achieves clearly positive values; both conductivity and thermopower drop significantly on further expansion. At $2\rho_c$, the spin susceptibility goes through a maximum in accordance with Curie law limitation. From the susceptibility maximum results a mass enhancement of $m_e^*/m_e \sim 4$, which, according to the Brinkman and Rice theory, corresponds to a fraction of $f \sim 10\%$ of doubly occupied states; this also means that about 10% of the atomic sites contain two or no electrons. Independently, a very similar value of f is obtained from Mott’s estimate of $f = (2(N_1 + 1))^{-1}$ [3.4], taking for the nearest neighbour number the experimental value of $N_1 \sim 4$, which was determined from neutron diffraction for Cs and Rb at $2\rho_c$. This analysis shows that fluid alkali metals near $2\rho_c$ possess the main characteristics of a highly correlated, nearly antiferromagnetic electron gas, which is the signature of a Mott–Hubbard transition. This implies that the density of states including all excitations is enhanced, but that of the current carriers is reduced. In this way, a pseudogap may form that exhibits a minimum in the density of states where states are localized around E_F [3.4]. In how far an interplay between electronic interaction and disorder has to be considered is open, but see [3.48].

Fig. 3.18 Electrical conductivity, $\sigma(0)$, vs. reduced density, ρ/ρ_c , at a constant supercritical temperature $T/T_c = 1.05$ for alkali metals in comparison with fluid mercury. See also [3.49]



Below $2\rho_c$ and approaching the critical point, electronic screening more and more breaks down. This can be concluded from the long wavelength limit of the static structure factor. It indicates a continuous increase of the strength of the attractive part of the interatomic potential. This may lead to an increasing electron localization. The condition of the classical Mott criterion for a limiting concentration n_c of screening electrons, $n_c^{1/3} a_B^* \sim 0.25$, seems to be fulfilled at densities near the critical point. This coincides with a conductivity of $\sim 300 \Omega^{-1} \text{ cm}^{-1}$, comparable with Mott's minimum metallic conductivity. Below this limit, nonmetallic characteristics become evident, which is demonstrated by the dependence of $\ln \sigma$ vs. S . It is interesting to note that the calculations of Redmer and Warren predict a large fraction of electrons localized in atomic and molecular states at densities around the critical point. It seems that the plasma approach gives an adequate description of the critical region and that the concept of ionized clusters merges the band model at higher densities. In concluding this section, it should be pointed out that the peculiarities described here for expanded fluid alkali metals do not generally apply to other fluid metals. To stress this point, Fig. 3.18 shows the different behaviour of the electrical conductivity of mercury in comparison with fluid Rb and Cs as a function of reduced density.

3.4 Liquid Alkali Metal Alloys

A number of liquid binary alloys of alkali metals with metal elements of larger electronegativity exhibit clearly nonmetallic characteristics at specific compositions. The most prominent examples are Cs–Au and Rb–Au alloys that undergo a metal–nonmetal transition in the liquid state near the compound compositions CsAu

Table 3.1 Electrical conductivity, $\sigma(0)$, and molar magnetic susceptibility, χ_m , of liquid M–Au and M–Sb alloys at the stoichiometric compositions MAu, MSb, and M_3Sb and at temperatures T given in brackets (M = alkali metal)

Compound composition	$\sigma/\Omega^{-1}\text{cm}^{-1}(T/\text{K})$	$\chi_m/10^{-6}\text{emu mol}^{-1}(T/\text{K})$	References
RbAu	5 (873)	–70 (873)	[3.51, 3.52]
CsAu	4 [50] (858)	–81 (923)	[3.53, 3.54]
NaSb	70 [1.5] (750)	–26 (973)	[3.55]
KSb	30 [1.5] (850)	–	[3.55]
CsSb	20 [1.0] (870)	–30 (870)	[3.55]
Na ₃ Sb	300 (1,300)	–72 (1,173)	[3.55, 3.56]
K ₃ Sb	200 (1,127)	–72 (1,073)	[3.55, 3.57]
Cs ₃ Sb	200 (1,073)	–89 (1,073)	[3.55, 3.57]

The σ -data given in square brackets refer to the solid compounds at temperatures near the melting point

or RbAu [3.50]. The electrical conductivity of liquid CsAu is comparable to that of a molten salt; see Table 3.1. Similarly, liquid alloys of some alkali metals with metals or semimetals of groups 13–15 show strong deviations from simple metallic characteristics at specific compositions; see also [3.58]. In many cases, the conductivity reaches values near or below the Ioffe–Regel limit. Semiconducting transport properties have been observed in alkali metal–antimony alloys near the compound compositions MSb and M_3Sb (M = alkali metal); see Table 3.1. In this chapter, we focus on the two prototype systems, alkali metal–gold and alkali metal–antimony alloys, and discuss the changes of the microscopic and electronic structure in these melts during the metal–nonmetal transition.

3.4.1 Caesium Gold Alloys

The phase diagram of the Cs–Au system exhibits a congruent melting compound of stoichiometry CsAu, which melts at 858 K [3.59]. Crystalline CsAu has a CsCl-type structure with a lattice constant of 0.4261 nm corresponding to $\text{Cs}^+ \text{Au}^-$ distance of 0.3691 nm [3.60]. In the following, we first consider the bonding characteristics in molten CsAu and then proceed with the discussion of the microscopic structure and electronic properties of these melts with excess caesium.

As mentioned above, the magnitude of the electrical conductivity of liquid CsAu is indicative of that of a molten salt. Further direct evidence of the ionic character

of CsAu melts has been obtained from the following experimental investigations. Using the Faraday method, a value of $-81 \times 10^{-6} \text{ emu mol}^{-1}$ has been obtained for the static molar magnetic susceptibility. Taking for the Cs^+ ion the literature value of $-36 \times 10^{-6} \text{ emu mol}^{-1}$ [3.61], a value of $-45 \times 10^{-6} \text{ emu mol}^{-1}$ results for the Au^- ion. This is consistent with the value of $-(50 \pm 5)10^{-6} \text{ emu mol}^{-6}$, which can be estimated from an extrapolation of the isoelectronic series Bi^{3+} , Pb^{2+} , and Tl^+ [3.54]. The comparison indicates a predominantly ionic bonding in liquid CsAu. Further evidence of the nonmetallic characteristics of solid and liquid CsAu was found by measurements of the IR–VIS optical absorption of μm thick samples embedded between two sapphire windows. Results of this experiment are shown in Fig. 3.19 where the absorption constant K is plotted versus the photon energy at different temperatures of the solid compound CsAu and in the melt at 900 K, [3.62]. The lower part of the figure presents the change of the optical gap E_g with temperature. In the solid state, the optical gap – taken at the highest measured K -values – decreases from 2.52 eV at room temperature to 2.10 eV at the melting point. The value of $E_g = 2.52 \text{ eV}$ found here at room temperature is in good agreement with the minimum value of 2.6 eV of Spicer et al. for the direct optical gap [3.63]. The discontinuous jump of the optical absorption edge by 0.8 eV on melting is remarkable; see Fig. 3.19. Such a behaviour is typically observed in alkali halides [3.64]. For CsAu, the relatively large red shift on melting has been explained by fluctuations in the distribution of the Madelung potentials that typify the liquid [3.65]. So, the optical characteristics of CsAu are consistent with an ionic interaction in the melt.

The microscopic structure of liquid $\text{Cs}_x\text{Au}_{1-x}$ alloys ($0.5 \leq x \leq 1$) has been investigated by neutron diffraction [3.66]. Results of the static structure factor $S(Q)$ and the corresponding pair distribution function $g(R)$ are given in Fig. 3.20. Focusing first on the molten CsAu compound, its $g(R)$ exhibits the typical molten salt feature of charge cancellation at larger distances R ; cf. Fig. 2.5. From the first peak in $g(R)$, the nearest neighbour $\text{Cs}^+ - \text{Au}^-$ distance is found to be 0.357 nm, which is lower by 0.012 nm in comparison with the corresponding crystalline value. The reduction of the nearest neighbour distances in alkali halides on melting is presented in Table 2. Thus, the structural data support the ionic model for pure CsAu melts. A weak prepeak or shoulder is visible in $S(Q)$ for $\text{Cs}_{0.5}\text{Au}_{0.5}$ at $Q = 1.2 \text{ \AA}^{-1}$. This, presumably, can be explained by concentration fluctuations; see also [3.66].

Turning next to the evolution of the microscopic structure in $\text{Cs}_x\text{Au}_{1-x}$ melts with $x > 0.5$, the following observations are of particular interest. At all compositions with $0.53 \leq x \leq 0.8$, the pair distribution function is dominated by the peak corresponding to the $\text{Cs}^+ \text{Au}^-$ nearest neighbour correlation. Besides this, a separate contribution of the first coordination sphere of pure Cs can be resolved, which disappears below $x_{\text{Cs}} = 0.7$, where the conductivity reaches the Ioffe–Regel metallic limit of $\sim 10^3 \Omega^{-1} \text{ cm}^{-1}$. In parallel to this behaviour of $g(R)$, the static structure factor exhibits a clearly enhanced small-angle scattering at composition in the metallic regime. So, the structural data show a clear tendency towards microscopic segregation into metallic Cs and nonmetallic $\text{Cs}^+ \text{Au}^-$ domains. A detailed investigation of the small-angle scattering and the corresponding concentration fluctuations shows that the critical temperature of the concentration fluctuations

Fig. 3.19 Optical absorption in solid and liquid CsAu: absorption constant, $K(\omega)$, at different temperatures (*upper panel*) and temperature dependence of the optical gap E_g (*lower panel*). See also [3.62]

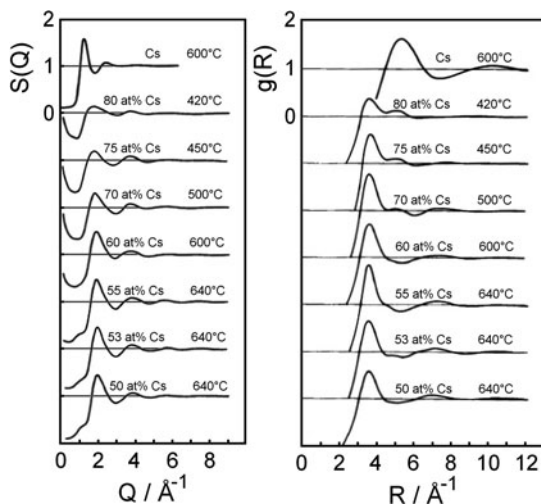
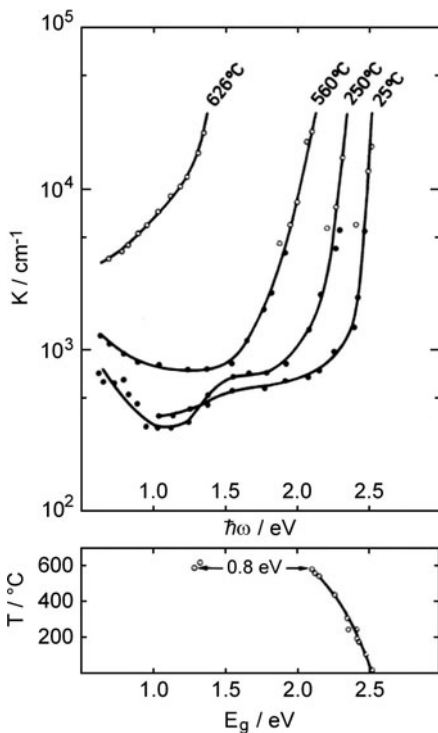
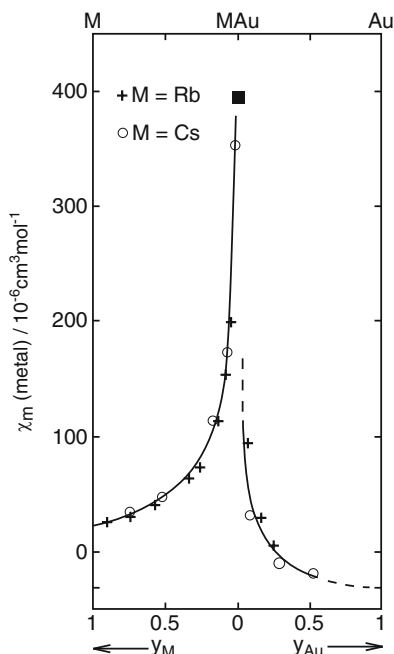


Fig. 3.20 Static structure factor, $S(Q)$, and corresponding pair distribution function, $g(R)$, of liquid $\text{Cs}_x\text{Au}_{1-x}$ alloys from neutron diffraction measurements. See also [3.66]

Fig. 3.21 Molar magnetic susceptibility, χ_m , of dissolved metal vs. mole fraction y_M and y_{Au} , respectively, in liquid ($T = 600^\circ\text{C}$) pseudobinary alloys $M_y(\text{MAu})_{1-y}$ and $\text{Au}_y(\text{MAu})_{1-y}$ ($M = \text{Rb}, \text{Cs}$). The Curie law limit of $s = 1/2$ electrons is indicated by the *full square*, calculated for 600°C . See also [3.52]



in Cs–Au liquid alloys lies below the liquidus line, which is very similar to the caesium–caesium halide system [3.66, 3.67].

In the nonmetallic alloys, insight into the electronic structure and, in particular, the nature of localized electronic states was obtained from investigations of the magnetic properties. The concentration dependence of the static magnetic susceptibility, both in Cs–CsAu and Rb–RbAu melts, very much resembles that in alkali metal–alkali halide solutions [3.52]. On approaching the stoichiometric composition MAu ($M = \text{Cs}, \text{Rb}$) from both sides, a strong paramagnetic deviation from simple metallic characteristics is observed. This is shown in Fig. 3.21 for the pseudobinary systems $M_y(\text{MAu})_{1-y}$. Near the compound composition MAu, the molar paramagnetic susceptibility of dissolved excess metal extrapolates to the Curie susceptibility of $s = 1/2$ electrons – see the full square in Fig. 3.21. This indicates that electron localization in the form of either atomic or polaronic F-centre-like states has to be considered.

Further information on the nature of electron localization has been obtained from ^{133}Cs NMR investigations. These results for liquid Cs–Au alloys at 600°C are presented in Fig. 3.22, [3.68]. The ^{133}Cs resonance or Knight shift decreases continuously in the metallic regime, down to a conductivity of $\sim 10^2 \Omega^{-1} \text{ cm}^{-1}$, and then drops rapidly below about 20% excess Cs reaching a minimum value of $750 \pm 20 \text{ ppm}$ for stoichiometric CsAu. On the Au-rich side, the shift is nearly constant. The variation of the shift in the metallic regime can be explained with the use of a simple free-electron gas model approximating the electron paramagnetism

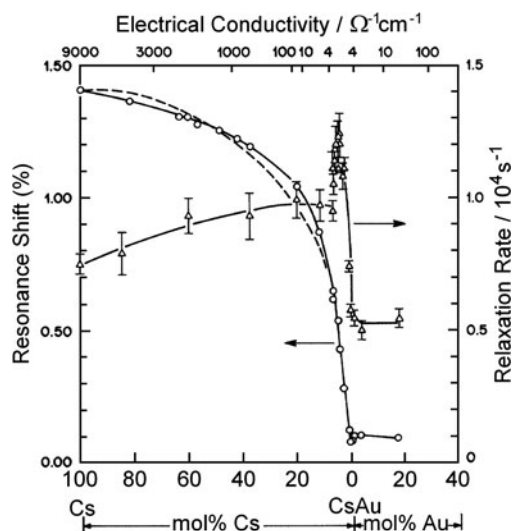


Fig. 3.22 ^{133}Cs NMR resonance shift (circles) and nuclear relaxation rates (triangles) vs. composition in liquid Cs—CsAu and Au—CsAu alloys at 600°C . Broken curve shows variation of the shift using the free-electron Pauli volume susceptibility normalized to the shift data for pure Cs. Upper scale shows the variation of the dc electrical conductivity from [3.53]. See also [3.68]

by the Pauli susceptibility; see the dashed line in Fig. 3.22. Direct evidence for the onset of electron localization is signalled by the concentration dependence of the relaxation rate T_1^{-1} ; see Fig. 3.22. It exhibits a clear break in slope around 10% excess Cs followed by a sharp peak near 5% excess Cs in CsAu. As the shift varies smoothly at these compositions, the drastic change of T_1^{-1} can only be associated with a sharply increased lifetime of the hyperfine field due to localized electrons. Assuming a Curie law susceptibility for localized $s = 1/2$ electrons, the relaxation rate is given by

$$T_1^{-1} = 1/2c \langle (A/\hbar)^2 \rangle \tau, \quad (3.19)$$

where c is the concentration of localized electrons, $\langle (A/\hbar)^2 \rangle$ is the mean square value for the hyperfine coupling, and τ is the correlation time characterizing fluctuations of the local hyperfine field. Calculations of τ from the experimental rates show that a consistent description of τ is only obtained if $\langle A^2 \rangle$ is about one sixth of the free-atom value. This is a typical magnitude for the first neighbour hyperfine field around an F-centre in alkali halide crystals [3.69]. This finding strongly indicates that localized electronic states close to stoichiometry in Cs—CsAu alloys are most likely to be analogous to F-centres.

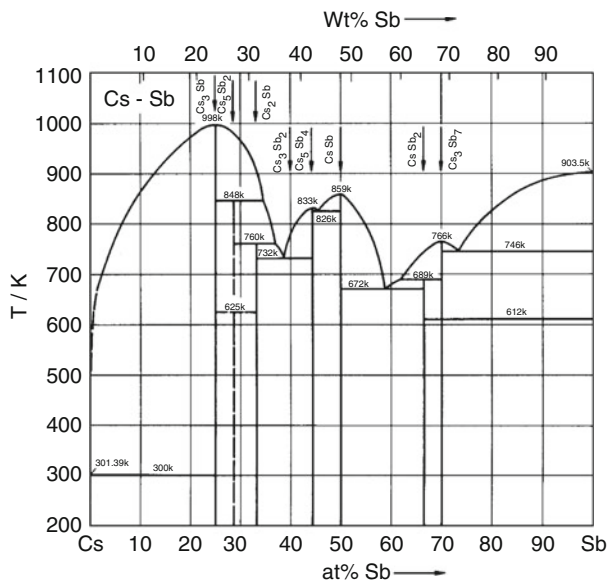
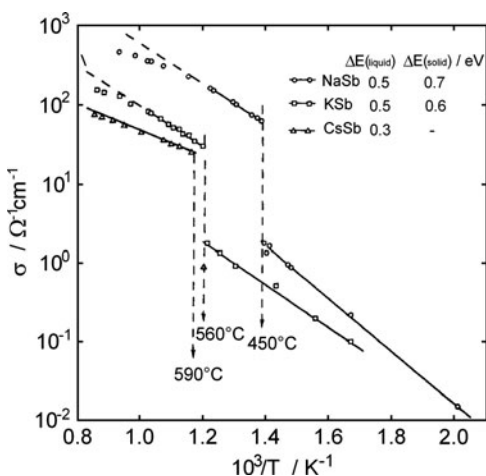


Fig. 3.23 Phase diagram of the Cs–Sb alloy system. From [3.70]; copyright permission (2010) by Springer Publishers

3.4.2 Alkali Metal–Antimony Alloys

The phase diagrams of binary alkali metal–antimony alloys are rich in intermetallic compounds. This is demonstrated in Fig. 3.23 for the example of the Cs–Sb system [3.70]. The most prominent compounds are those with stoichiometries M_3Sb and MSb , respectively. The congruently melting octet compounds M_3Sb crystallize with a $NaAs_3$ structure or, in the case of Cs_3Sb , a distorted $NaTl$ structure [3.71]. The relatively low melting monoantimonides MSb have a NaP or $LiAs$ -type structure, which is characterized by spiral Sb chains [3.71]. On the basis of this structure, a covalent bonding model with strong (pp σ) bonds along the chains has been proposed [3.72]. The structures of the numerous compounds with intermediate stoichiometry are largely unknown. Both the octet and the monoantimonide compounds are narrow gap semiconductors in the solid state, which have been widely investigated; see e.g. [3.73]. Calculations of the electronic structure based on self-consistent linear muffin-tin orbitals show that the electronic states are dominated by a deep anion potential [3.72]. In the octet compounds, the valence states are very close to those of the free Sb ions. The bonding is predominantly ionic, but distinct covalent contributions are found in compounds formed by the lighter alkali metals. In the equiatomic compounds, the valence band is very similar to that of chalcogenides such as Te, which is isoelectronic with Sb^- . The bonding characteristics are clearly covalent [3.72].

Fig. 3.24 Logarithmic plot of the DC conductivity, $\sigma(0)$, vs. reciprocal temperature of different MSb compounds ($M = \text{Na}, \text{K}$, and Cs) in the solid and liquid state. See also [3.55]



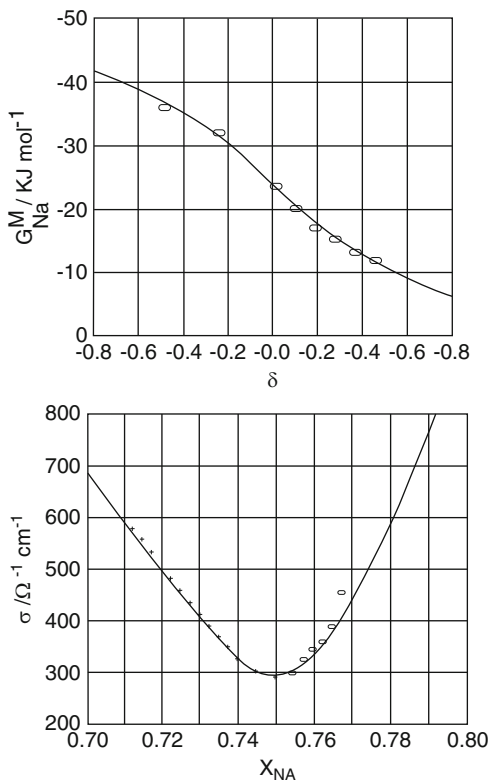
On melting, the octet and the equiatomic compounds retain their nonmetallic transport characteristics; see Table 3.1. The electrical conductivities of the molten M_3Sb compounds² are of the order of $10^2 \Omega^{-1} \text{cm}^{-1}$, whereas those of the MSb compounds lie below this limit at conditions near the melting point; see Table 3.1. For the latter it is interesting to note that the activation energy ΔE of the conductivity is only slightly reduced in the melt, which is shown in Fig. 3.24. Semiconducting behaviour in liquid $\text{Na}_{3+\delta}\text{Sb}$ alloys was found by simultaneous measurements of the electrical conductivity $\sigma(0)$ and the partial molar Gibbs energy of Na, G_{Na}^m , at small deviations $\delta = (4x_{\text{Na}} - 3)/(1 - x_{\text{Na}})$ from exact stoichiometry [3.56]. In these experiments, G_{Na}^m has been determined by an EMF technique and the composition of the alloy was accurately controlled in situ by coulometric titration; see also Sect. A.2. The observed concentration dependence of both quantities quantitatively agrees with the predictions of the model of a doped compound semiconductor assuming an equal number of electrons and holes at stoichiometry [3.74]; see also [2.4]. The corresponding equations for G_{Na}^m and σ are as follows:

$$G_{\text{Na}}^m(\delta) = G_{\text{Na}}^{m,o} + RT \times \sinh^{-1} \left(\frac{\delta}{2x_e^o} \right), \quad (3.20)$$

where the index ^{o} refers to exact stoichiometry and x_e^o denotes the ratio of the number of electrons to the number of Sb atoms at stoichiometry. Similarly, the conductivity is given by

² The lower values of $\sim 5 \Omega^{-1} \text{cm}^{-1}$ for Na_3Sb and $\sim 3 \Omega^{-1} \text{cm}^{-1}$ for Cs_3Sb in an earlier publication [3.55] have been erroneously attributed to the liquid state; in the case of Na_3Sb , it was shown later [3.56] that the melting point of this compound is $1,015^\circ\text{C}$ instead of 856°C as given in the literature.

Fig. 3.25 Relative partial molar Gibbs energy of Na, G_{Na}^{m} (*upper panel*), and electrical DC conductivity (*lower panel*) of liquid semiconducting $\text{Na}_{3+\delta}\text{Sb}$ alloys at 1,030°C; the full curves are fits of the experimental data by the corresponding equations for compound semiconductors; see text and also [3.56]



$$\sigma = \sigma_{\min} \cosh \left((E_{\min} - E) \frac{F}{RT} \right), \quad (3.21)$$

where F is the Faraday constant and $\sigma_{\min}$ and $E_{\min}$ are the conductivity and EMF, respectively, at stoichiometry. The EMF E and the sodium activity and mole fraction x_{Na} are related by the Nernst equation. Figure 3.25 presents the experimental results together with the fits according to (3.20) and (3.21). This comparison gives evidence for semiconducting transport behaviour in the liquid Na–Sb alloy near the compound composition Na_3Sb .

In the following, we concentrate attention upon experimental investigations of the bonding characteristics of nonmetallic liquid alkali metal–antimony alloys near the stoichiometric compositions M_3Sb and MSb . A first insight is obtained from the magnitude of the magnetic susceptibilities at both stoichiometries; see Table 3.1. For purely ionic interaction between 3 M^+ and Sb^{3-} ions, the molar susceptibilities should be more negative, by roughly a factor of 2, in comparison with the experimental data. A similar argument holds for the MSb stoichiometry. Measurements of the microscopic structure give the following picture; see Fig. 3.26. Two interesting features are observed in the structure factor $S(Q)$ [3.75]: (1) At a composition of $\text{Cs}_{0.85}\text{Sb}_{0.15}$, a clear small-angle scattering is visible, which indicates – similar to

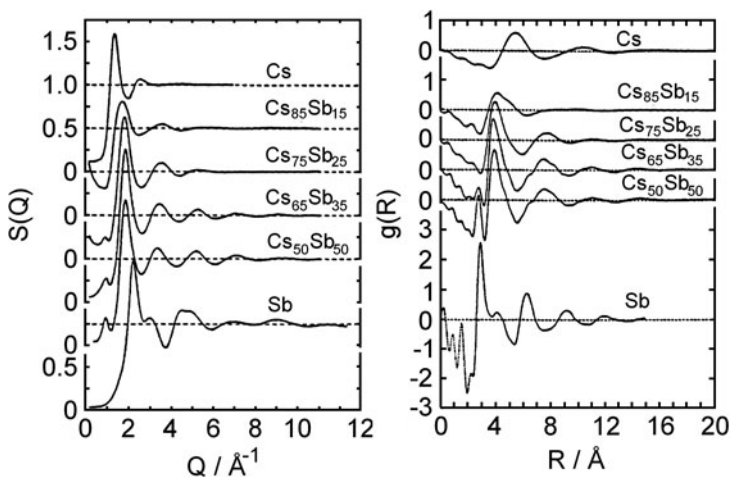


Fig. 3.26 Total structure factors, $S(Q)$, and corresponding pair distribution functions, $g(R)$, for Cs–Sb alloys at temperatures ranging from 600°C (Cs) up to 750°C ($\text{Cs}_{0.75}\text{Sb}_{0.25}$). See also [3.75]

the Cs–Au system – microscopic inhomogeneities or a tendency towards microscopic segregation; (2) for compositions with $0.65 \geq x \geq 0.5$, a prepeak near $Q \sim 0.95 \text{ \AA}^{-1}$ occurs with a width of $\Delta Q \sim 0.25 \text{ \AA}^{-1}$; using the Scherrer formula, an intermolecular distance correlation of $\sim 25 \text{ \AA}$ is estimated, indicating relatively large molecular units. The pair correlation of $\text{Cs}_{0.75}\text{Sb}_{0.25}$ has a first main peak at $4.01 \text{ \AA}$, which compares well with the nearest neighbour distance of $3.96 \text{ \AA}$ of the solid compound. For a predominantly ionic bonding, a nearest neighbour distance of $R_{\text{Cs}^+} + R_{\text{Sb}^{3-}} = 4.12 \text{ \AA}$ would be expected. For the CsSb compound, $g(R)$ exhibits a sharp first peak at $2.84 \text{ \AA}$, which is smaller than the Sb–Sb distance in liquid Sb, but is in good agreement with the covalently bonded Sb–Sb distance of $2.85 \text{ \AA}$ in the solid compound semiconductor of orthorhombic structure. So, it may be concluded that in both solid and liquid CsSb very similar bonding exists and, possibly, also in Cs_3Sb .

An NMR study of the changes in bonding and of the metal–nonmetal transition has been performed in liquid Cs–Sb alloys for the concentration range $0 \leq x_{\text{Sb}} \leq 0.62$ [3.76]. In this investigation, information has been obtained on (1) the density of states at the Fermi level in the M–NM transition region; (2) the electronic localization via the electron correlation time; and (3) the change in bonding for excess Sb in liquid Cs_3Sb . Results of the ^{133}Cs nuclear resonance shift and spin–lattice relaxation rate, T_1^{-1} , are shown in Fig. 3.27 for liquid $\text{Cs}_x\text{Sb}_{1-x}$ alloys. For $x < 0.75$, the atomic mole fraction scale is used, for $x > 0.75$ the excess mole fraction scale is plotted, i.e. $y_{\text{Cs}} = (4x_{\text{Cs}} - 3)/(1 - x_{\text{Cs}})$. In contrast to the Cs–Au system, a rapid initial decrease occurs both in the ^{133}Cs shift and relaxation rate with addition of Sb. This can be interpreted in terms of bound or virtual bound impurity states as is detailed in [3.76]. Assuming that each Sb atom added removes three electrons from the conduction band and that $\langle |\varphi(0)|^2 \rangle > E_F$ remains

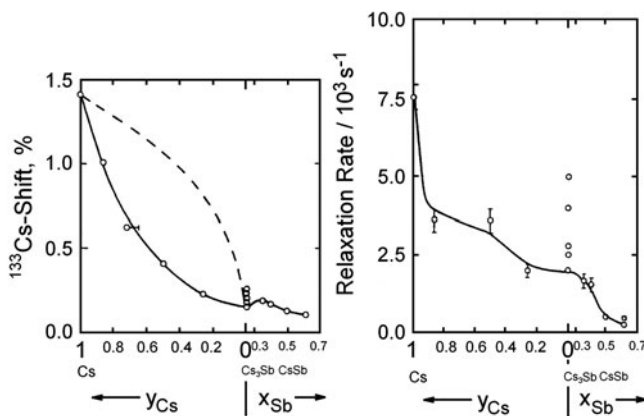
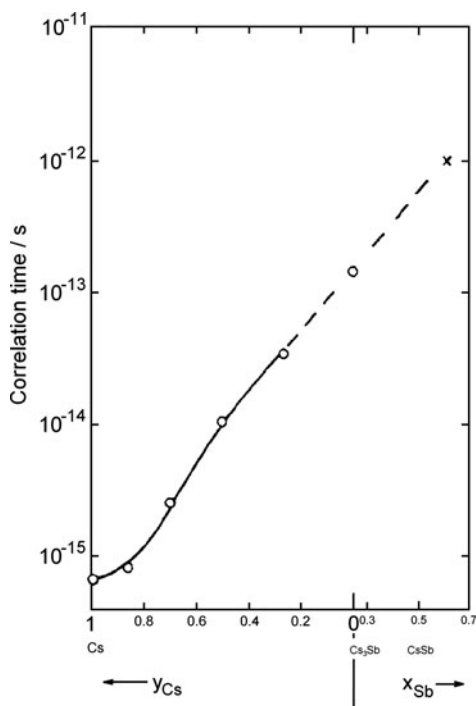


Fig. 3.27 ^{133}Cs resonance shift and ^{133}Cs relaxation rates (T_1^{-1} , $\circ$, T_2^{-1} open square) in liquid $\text{Cs}_x\text{Sb}_{1-x}$ alloys vs. composition at 750°C . For $x > 0.75$, the excess mol fraction scale y is used (left-hand scale). The errors in the shift are less than the size of the symbols. The dashed line in the left panel gives the calculated free-electron shift assuming a purely ionic model; see text. See also [3.76]

constant, the shift has been calculated with the free-electron Pauli susceptibility; see the dashed line in Fig. 3.27. This model description gives excellent agreement with experiments for Cs–Au alloys (see Fig. 3.22), but obviously does not hold in the case of metallic liquid Cs–Sb. By the time the antimony concentration has reached 10 at. % ($y_{\text{Cs}} = 0.66$), the limit of the NFE regime is approached, i.e. the electron mean free path and the mean interatomic distance are comparable. Below this limit, a linear relation between shift and the measured electron paramagnetic susceptibility $\chi^{e,p}$ has been found over an excess concentration range of $0.2 \leq y_{\text{Cs}} \leq 0.9$ [3.76]. This implies that $\langle \varphi(0) |^2 > E_F$ stays constant in this concentration range. The most important result is that the density of states, $n(E_F)$, is strongly reduced and, relative to the free-electron value, reaches a value of $n(E_F)/n(E_F)^0 \sim 0.2\text{--}0.3$ near $y_{\text{Cs}} \sim 0.2$. In the same concentration range, a linear relation between shift and the square root of the electrical conductivity has been established [3.76]. The electronic correlation time τ determined from the measured T_1^{-1} data – see (3.19) – increases by more than two orders of magnitude reaching a value of $\sim 4 \times 10^{-14}$ s near $y_{\text{Cs}} \sim 0.2$ and $\sim 10^{-13}$ s at the stoichiometric composition; see Fig. 3.28.

All these variations of shift and relaxation rate quantitatively correlate with the predictions of the pseudogap model, where a mobility gap of localized states forms approaching the compound composition Cs_3Sb from the Cs-rich side. This behaviour is not found in the Cs–Au system, but is characteristic of liquid chalcogenide semiconductors; see also [3.77]. Near the composition Cs_3Sb both shift and relaxation rate are sensitive to small deviations from stoichiometry; see Fig. 3.27. So it cannot be excluded that there is a narrow peak in both quantities for slight excess caesium.

Fig. 3.28 ^{133}Cs hyperfine-field correlation time τ in liquid $\text{Cs}_x\text{Sb}_{1-x}$ vs. composition at 750°C ; for the definition of the different concentration scales, see Fig. 3.27. See also [3.76]



On the Sb-rich side, there is only a small variation in shift, whereas the relaxation is further decreased by a factor of 4 near CsSb. At these compositions a strong reduction of the hyperfine field from, for example, 1.1 GHz at $x_{\text{Sb}} = 0.35$ to 0.6 GHz at $x_{\text{Sb}} = 0.5$ occurs [3.76]. The corresponding decrease in the s -electron density at the Cs nucleus demonstrates a change in bonding going from Cs_3Sb to CsSb and is consistent with the structural model of covalently bonded Sb^-Sb^- chains stabilized by surrounding alkali ions.

3.4.3 Metal–Nonmetal Transition in Liquid Alkali Metal Alloys

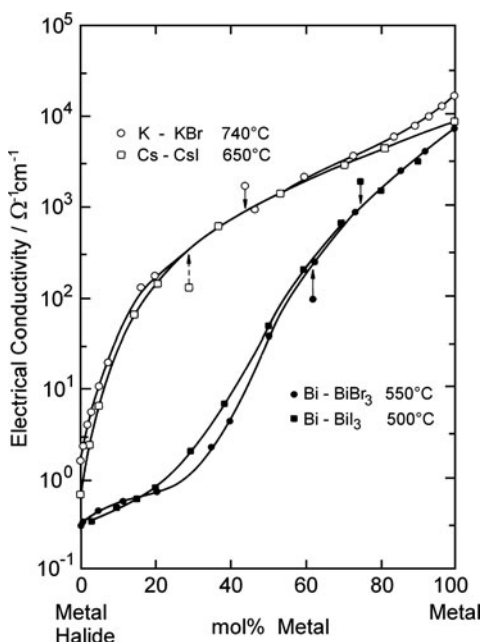
On comparing the nonmetallic properties of liquid alkali metal–gold and alkali metal–antimony alloys, striking differences become evident. Liquid CsAu is characterized by predominately ionic bonding of separated Cs^+ and Au^- ions. This is deduced from the magnitude of the diamagnetic susceptibility, the microscopic structure, and, indirectly, the optical absorption properties and the magnitude of the electrical conductivity of $\sim 3\Omega^{-1}\text{cm}^{-1}$. The NMR data indicate that with excess Cs in liquid CsAu localized electronic states similar to F-centres form. Thus, the nonmetallic alloys $\text{Cs}_x\text{Au}_{1-x}$ have several features in common with metal–molten salt solutions, which are discussed in detail in the following chapter.

In contrast to this, liquid alkali metal–antimony alloys near specific stoichiometries exhibit properties typical of liquid semiconductors such as the chalcogenides Se, Te, and their alloys. At the M_3Sb stoichiometry, both the conductivity and the partial molar Gibbs energy in the Na–Sb system show the typical behaviour of an extrinsic semiconductor. On the basis of the NMR data, it is very likely that semiconductivity in liquid Cs_3Sb is not caused by predominantly ionic bonding, but arises from the formation of molecular units with intramolecular bond satisfaction. This is consistent with the band structure calculations of the solid compounds [3.72]. With excess alkali metal, the transition from semiconductor to metal probably occurs via crossing of a pseudogap. This model is supported by the variation in the density of states and the strong change of the electron correlation time τ as deduced from the NMR results. Probably, electron localization in the pseudogap is of the Anderson type. At the MSb stoichiometry semiconducting transport characteristics persist on melting. The same is true for the type of chemical bonding that consists of covalently bonded Sb^-Sb^- helical chains stabilized by surrounding M^+ ions. This interpretation is particularly supported by the neutron diffraction results for $g(R)$.

3.5 Metal–molten Salt (M–MX) Solutions

Metals, including transition and post-transition metals, have a high solubility in their molten metal halides [2.19]. In systems such as alkali metal–alkali halide or bismuth–bismuth halide solutions, complete miscibility in a homogeneous fluid phase can be achieved at elevated temperatures. This is exemplified by the phase diagrams of alkali metal–alkali halide melts in Fig. 2.14. Solutions of light alkali metals such as Na–NaCl or K–KCl exhibit a well-defined liquid–liquid miscibility gap with an upper critical temperature of the order of 10^3 K; in the caesium solutions this gap is suppressed [3.78]; only a trend towards demixing is indicated in the thermodynamic mixing functions and in the long wavelength limit of the concentration–concentration structure factor, $S_{cc}(0)$, which has a peak at specific concentrations [3.67]. In the case of polyvalent metal solutions such as Bi– BiX_3 , the existence of lower oxidation states broadens the nonmetallic range and shifts the miscibility gap to more metal-rich concentrations [3.79]. The continuous transition from metallic to nonmetallic states in both types of systems, the M–MX and the Bi– BiX_3 solutions, is illustrated in Fig. 3.29. Taking as an upper limit of nonmetallic behaviour a conductivity of $\sim 10^2 \Omega^{-1} \text{ cm}^{-1}$, nonmetallic transport in the alkali halide solutions occurs over a relatively large concentration range up to ~ 20 mol% excess metal. In the bismuth halide solutions, this value is further extended to nearly 60 mol% metal. Metallic conductivities above $\sim 10^3 \Omega^{-1} \text{ cm}^{-1}$ occur only in the metal-rich solutions, in Bi– BiX_3 melts above ~ 80 mol% Bi. For the understanding of the M–NM transition in these systems, the peculiarity of the electrical conductivity raises a number of questions. Starting with the pure molten salts it obviously makes a difference if the melt is fully dissociated like in the alkali halides or retains a substantial part of its molecular structure like in many polyvalent

Fig. 3.29 DC electrical conductivity vs. composition for some metal–molten salt solutions; *arrows* indicate the critical concentrations at the consolute point; for Cs–CsI this corresponds to the composition where $S_{cc}(0)$ has a maximum. Reprinted with permission from [3.80], copyright permission (2010) by Taylor and Francis



metal halides. In the nonmetallic solutions, the crucial question concerns the state of dissolved metal. Different possibilities may be considered: (1) The metal is dissolved as neutral atoms; (2) the metal valence electron is released and is trapped in a polaronic or F-centre-like state, the lifetime of these traps being determined by the dynamics of the ions in the melt; (3) with increasing metal excess aggregation of localized electrons (bipolarons or dimers) may occur thus expanding the non-metallic concentration range; and (4) in polyvalent metals formation of metal ions of lower oxidation state has to be considered. In the following, we first concentrate on the problem of electron localization in alkali metal–alkali halide solutions. Subsequently, the changes in the microscopic structure are considered in the metallic solutions. On the basis of these results, the possible mechanisms that induce the metal–nonmetal transition are discussed. The bismuth halide solutions are treated in the context of quenched M–MX systems in the last section of this chapter.

3.5.1 Electron Localization in Alkali Halide Melts

Before discussing localization of excess electrons in alkali halide melts, it is worth remembering the main features of the electronic structure in pure liquid alkali halides. This is illustrated in Fig. 3.30 for the example of KCl [3.81]. Shown are the electronic density of states for both the crystalline solid and the liquid consisting of a filled valence band (anion states) and an empty conduction band (cation

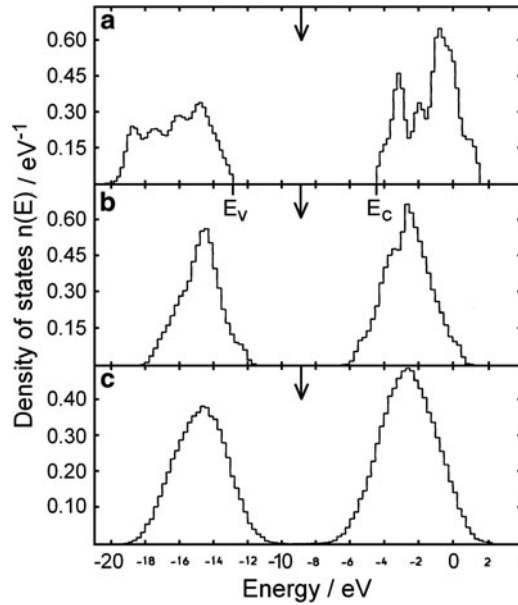


Fig. 3.30 Numerical study of the density of states of solid and liquid KCl using the primitive model of charged hard spheres to simulate the structure and a tight-binding Hamiltonian to describe the electronic structure; (a) solid, (b) liquid with topological disorder, and (c) liquid including topological disorder and Madelung potential fluctuations ($T \sim 10^3$ K). The arrows indicate the position of the Fermi level. Reprinted with permission by Kosłowski from [3.81]; copyright permission (2010) by Bunsengesellschaft für Physikalische Chemie

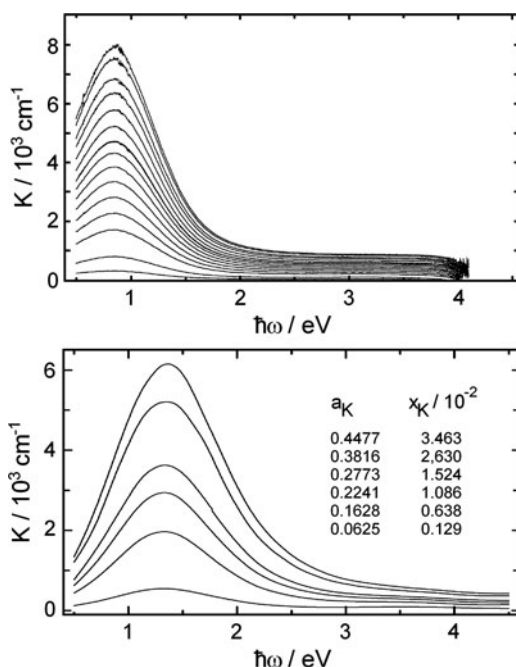
states) separated by the gap energy $\Delta E_g = E_c - E_v$. On melting, topological disorder and fluctuations in the Madelung potentials with a nearly Gaussian distribution prevail [3.65]. This has two significant consequences for the electronic structure: (1) The effective electronic site energies have a Gaussian distribution (see Fig. 3.30); and (2) the distance of the average valence and conduction band energies is clearly reduced, by ~ 2 eV for KCl [3.81]. The Gaussian random potentials can also explain the characteristic behaviour of the fundamental UV absorption edge in alkali halides, known as Urbach's rule [3.82]. This is given by

$$K(\omega, T) = K_0 \exp\left(\frac{-\gamma \hbar(\omega_0 - \omega)}{k_B T}\right), \quad (3.22)$$

where K_0 is the absorption constant at the band maximum ($K_0 \sim 10^6 \text{ cm}^{-1}$), $\hbar\omega_0$ is the fundamental optical absorption energy, and γ is a constant (~ 0.8 for KX melts). For alkali halide melts, $\hbar\omega_0$ ranges from ~ 6 eV for chlorides to ~ 4.5 eV for NaI, see also [2.96].

Various spectroscopic methods have been employed to elucidate the nature of localized electronic states in M_xMX_{1-x} melts. This includes optical absorption

Fig. 3.31 Optical absorption spectra of liquid $\text{Cs}_x\text{CsCl}_{1-x}$ ($10^{-3} \leq x \leq 4 \times 10^{-2}$) and liquid $\text{K}_x\text{KCl}_{1-x}$ (*lower panel*) at 800°C . The compositions have been varied in situ by Coulometric titration; the metal activities a_K for $\text{K}_x\text{KCl}_{1-x}$ have been measured simultaneously with the spectra by an EMF technique. See also [3.82, 3.83]



spectroscopy [3.83, 3.84], electron spin resonance (ESR) [3.85], spectroscopic ellipsometry [3.86, 3.87], and nuclear magnetic resonance NMR [3.88, 3.89]. In the first two methods, the composition was varied in situ by Coulometric titration over a wide range of compositions from dilute to concentrated solutions ($10^{-5} \leq x \leq 5 \times 10^{-2}$). This ensures a precise control of changes in the spectra as a function of x . Details of this technique are described in Sect. A.2. A further advantage of this technique is that simultaneously with the spectra the alkali metal activity and thus the thermodynamic properties can be measured. We start with a survey of the absorption spectroscopy results. Figure 3.31 shows a selection of spectra of liquid $\text{Cs}_x\text{CsCl}_{1-x}$ ($10^{-3} \leq x \leq 4 \times 10^{-2}$) and $\text{K}_x\text{KCl}_{1-x}$ ($10^{-3} \leq x \leq 3 \times 10^{-2}$) solutions recorded in the near-infrared-visible spectral range [3.83, 3.84]. There are two main features in the spectra, which shall be pointed out: a broad absorption band with a maximum near 0.85 eV ($\text{Cs}_x\text{CsCl}_{1-x}$) and 1.25 eV ($\text{K}_x\text{KCl}_{1-x}$) and, in addition, a background absorption, which is clearly visible towards higher energies and increases with x . These two contributions are discussed in detail in the following.

It has been shown that the energy, E_m , of the absorption band maximum scales with the interionic distance, $R_{+/-}$, according to $E_m \propto R_{+/-}^{-\alpha}$; here, α has the same value for alkali halide melts, exceptions, possibly, are the $\text{Na}_x\text{NaX}_{1-x}$ solutions, but see also [2.96]. This dependence, for MX crystals known as the Mollwo–Ivey rule, is the optical signature of the crystalline F-centre. As the same relation holds in the melt, too, the absorption band has been assigned to the liquid state analogue of the

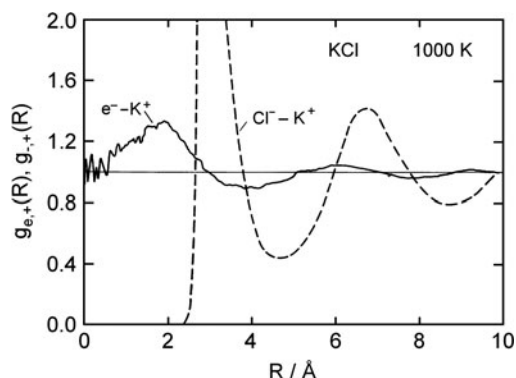


Fig. 3.32 Molecular dynamics and Feynman path integral calculations of the electron–cation, $g_{e+,+}(R)$, and anion–cation, $g_{-,+}(R)$, radial pair distribution functions in K–KCl [3.16]. Adapted from [3.91] with permission from: Fois et al. (1988); copyright permission (2010) by American Chemical Society

F-centre band [3.90]. In the simple model of the potential well of a solvated electron in Fig. 3.4, the F-centre absorption corresponds to an excitation from a $1s$ to a $2p$ state. As was shown by MD calculations of Parrinello and Rahman [3.16] and later confirmed by further theoretical studies using the Car–Parrinello method [3.17], solvation in a molten salt means that the electron is strongly correlated with, on an average, four cations. The mean electron–cation separation is substantially less than the anion–cation distance, which explains a strong polaron effect; see Fig. 3.32. With respect to the crystalline F-centre excitation at room temperature, the E_m values in the melt are reduced by roughly 1 eV [3.90]. This is comparable in magnitude with the reduction of the fundamental optical excitation energy in the pure salts on melting. This and the relatively large half width of the absorption band of ~ 1 eV can be explained by Madelung potential fluctuations in the ionic melt, which have a typical value of the root mean square fluctuation of the distribution function of ~ 1 eV [3.65].

For the interpretation of the background absorption, a closer analysis of the dynamics of localized electrons in molten salts is of interest. Warren et al. have measured the nuclear spin relaxation rate in several alkali metal–alkali halide melts. From these studies, they have determined the electronic correlation time τ characteristic of the fluctuations of the local hyperfine field produced by nearby paramagnetic electrons [3.88, 3.89]. For nonmetallic $\text{Cs}_x\text{CsX}_{1-x}$ solutions they find a value $\tau \sim 10^{-12}$ s near $x \sim 0.01$ [3.89]. This shows that the electron localization times in dilute solutions are comparable with the diffusion-limited lifetime of a local configuration of ions. A deeper insight into the F-centre dynamics and localization has been obtained by the quantum molecular dynamics calculations of Parrinello and coworkers [3.17, 3.91, 3.92]. In dilute K–KCl solutions, they find a value of $\tau \sim 0.3 \times 10^{-12}$ s for the average lifetime of the F-centre. The mechanism of electron diffusion according to these calculations is illustrated in Fig. 3.33. During a jump

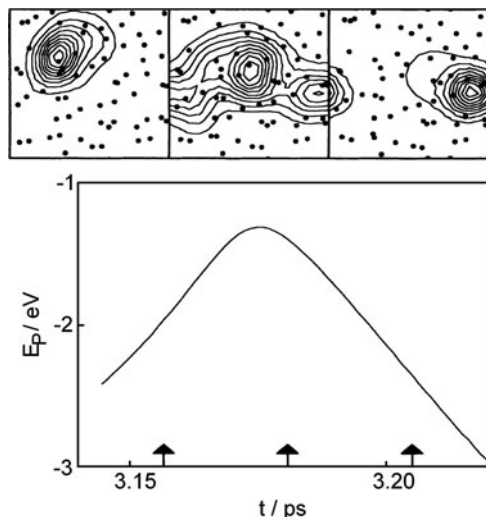
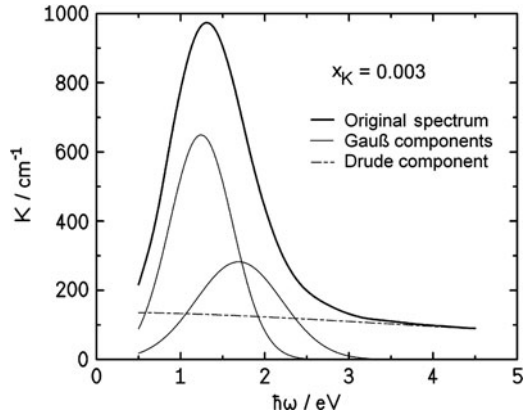


Fig. 3.33 *Top panel:* Contour plots of the electronic density at three successive times: just before, during, and just after a hopping event; see the *arrows* in the *lower panel*; the *dots* refer to the ions of the molten salt. *Lower panel:* Time evolution of the corresponding electron potential energy E_p . Reprinted with permission from [3.17]; copyright permission (2010) by American Physical Society

of an F-centre electron between two spatially separated sites the electron potential energy, E_p , varies significantly with a rms fluctuation of ~ 1 eV – typical of the Madelung potential fluctuations. As a consequence, the $1s$ ground state energy is strongly increased and the fundamental $1s - 2p$ excitation energy is reduced. The electron density at intermediate times is no longer strongly localized as in the F-centre ground state, but is extended over the size of the simulation box; see upper panel in Fig. 3.33. This suggests that these states contribute to the optical conductivity, $\sigma(\omega)$, and, thus, to the background absorption similar to weakly localized or nearly free-electron states; see below. If this is the case, their number density should be equal to that of the F-centres. With increasing metal excess – but still in the nonmetallic regime – the QMD calculations give evidence that bipolaronic structures form, where two spin-paired electrons are trapped in the same liquid cavity [3.91, 3.92]. Both the bound and dissociated bipolaron diffuse on an ionic time scale. On approaching the transition towards metallic states – $x \sim 0.11$ in K_xKCl_{1-x} ; see also below – the QMD calculations predict clustering of bipolarons with an elongated percolating structure indicating extended states [3.92].

In order to analyse the optical absorption spectra in Fig. 3.31, the following contributions have been taken into account as depicted in Fig. 3.34. Two Gaussians have been allowed for, one for the F-band absorption and a second describing the asymmetry of the absorption bands towards higher energies where the bipolaron excitations are expected. The background absorption was approximated by a simple Drude term for nearly free electrons [3.83]:

Fig. 3.34 Deconvolution of a typical optical absorption spectrum of liquid K_xKCl_{1-x} ($x = 0.003$, $T = 800^\circ\text{C}$) by two Gaussians and a Drude component; see text. See also [3.83]



$$\sigma(\omega) = \frac{\sigma(0)}{1 - i\omega\tau_e/2\pi}, \quad (3.23)$$

where $\sigma(0)$ is the DC conductivity of electrons and τ_e their relaxation time. The number density of electrons n_e and their mobility μ_e are then defined by (2.30). A typical deconvolution of the measured spectra by these three terms is shown in Fig. 3.34, which corresponds to a fit of a K_xKCl_{1-x} spectrum at $x = 0.003$ and 800°C [3.83]. The main results of such an analysis can be summarized as follows. For all systems studied, the energy and half width of the F-band stay nearly constant for $x \leq 0.04$; representative values of the energy E_m are 1.64 ± 0.02 eV (Na–NaBr), 1.25 ± 0.01 eV (K–KCl), 0.84 ± 0.01 eV (Cs–CsI). The half widths are ~ 0.85 eV (K–KCl, $x \leq 0.01$) and 0.9 eV (Cs–CsI, $x \leq 0.06$). There is no indication of a second Gaussian in the Cs–CsX systems, whereas this is clearly distinguished in the lighter alkali metal halides indicative of bipolaron excitation – for example, at 1.7 ± 0.1 eV in K–KCl for $10^{-3} \leq x \leq 3.5 \times 10^{-2}$ with a half width of ~ 1.1 eV [3.83, 3.84]. According to these numbers, the bipolaron in comparison with two separated F-centres is stabilized by ~ 0.5 eV. This is in reasonable agreement with the bipolaron binding energy of ~ 0.7 eV from QMD calculations [3.91]. The absence of bipolaronic states in the Cs–CsX systems may be explained by a lower polarization energy in these systems in comparison with the lighter alkali metal halides. Most interesting are the results obtained by fitting the background absorption with a Drude term. The mobility of these electrons is found to be of the order of $10^{-1} \text{ cm}^2 (\text{Vs})^{-1}$ and their number density is comparable to that of F-centres at different x . The electronic conductivity $\sigma(0)$ calculated from these data, within experimental errors, is in very good agreement with results from independent measurements using the Wagner polarization technique [3.93]. It gives directly the electronic component separated from the ionic conductivity [3.94, 3.95]. This comparison of the electronic conductivities, $\sigma_e(0)$, derived from the optical spectra and independent polarization measurements, is given in Fig. 3.35 for the example of K_xKI_{1-x} [3.84].

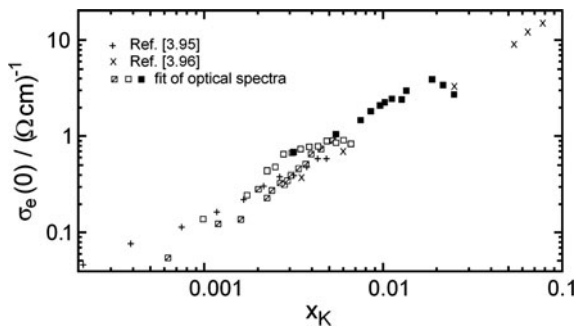


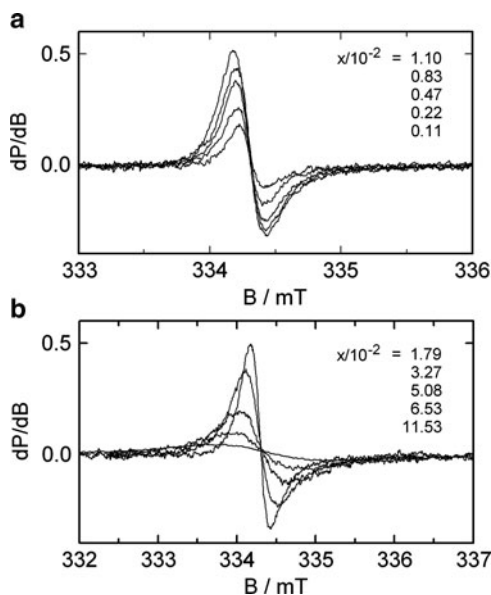
Fig. 3.35 Comparison of DC electronic conductivities, $\sigma_e(0)$, in liquid $\text{K}_x\text{Kl}_{1-x}$ at 800°C obtained from Drude fits of the optical spectra and measured directly with the Wagner polarization method. See also [3.84]

In concluding this part, the optical absorption spectra give valuable information on electronic localization in nonmetallic alkali metal–alkali halide melts. They give evidence for the occurrence F-centre-like states whereby an electron is localized in a cavity surrounded by on average four cations. With increasing metal excess in the lighter alkali metal halides, F-centres can coalesce into an energetically more favourable bipolaronic state. The bipolaron in its ground state contains two spin-paired electrons in an ionic cavity. These localized states dissociate on a timescale of $\sim 10^{-12}$ s, typical of the ion diffusion. During this process the electrons can acquire a relatively high mobility of $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ comparable to electrons in band gap states. However, it is still far below the metallic value of $\sim 10^1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These excitations contribute to a nearly constant background absorption, which could be identified undoubtedly by in situ metal addition with the Coulometric titration technique. All these findings are in complete accordance with the results of QMD calculations.

Further confirmation of these conclusions results from ESR investigations in $\text{K}_x\text{KCl}_{1-x}$ melts [3.85]. ESR spectra have been recorded over a wide range of concentrations ($10^{-4} \leq x \leq 10^{-1}$) again with in situ metal addition employing the Coulometric titration technique; see Sect. A.2 for more details. Typical ESR spectra, shown in Fig. 3.36, have been reproduced in the same run by titrating metal in and out. The main characteristics of the spectra are (1) the g-factor of 1.994 is slightly smaller than that of the crystalline F-centre (1.996) [3.69], it is nearly constant at all x ; and (2) the ESR signals up to $x \sim 0.05$ exhibit a narrow half width of ~ 0.2 mT, indicating extreme exchange narrowing with $\omega_0 \tau \ll 1$; here ω_0 is the Larmor frequency and τ the electron–nuclear correlation time ($\omega_0 \sim 10$ GHz). On approaching the composition $x \sim 0.1$, the line width increases by nearly a factor of 5. The spin susceptibility, χ_s , has been determined from the spectra according to, see also [3.40],

$$\chi_s = (2/\pi)\omega_0 \int_0^\infty \chi''(\omega) d\omega. \quad (3.24)$$

Fig. 3.36 ESR spectra of liquid K_xKCl_{1-x} at 815°C taken in one experimental run with in situ x -variation by Coulometric titration; sequence of spectra corresponds to sequence of x -values in the figures. See also [3.85]



Here, χ'' denotes the imaginary part of the susceptibility that has been obtained from fits of the spectra by Lorentzians. The variation of χ_s over the whole composition range studied is presented in Fig. 3.37. In this plot, two observations are especially remarkable. First, only in the dilute concentration limit ($x \leq 10^{-3}$) the spin susceptibility approaches the Curie law paramagnetism of isolated $s = 1/2$ electrons as expected for F-centres. At higher metal concentrations, the ESR spin susceptibility shows a clear diamagnetic deviation from the Curie law, which should be the case if bipolarons coexist with F-centres. On the other hand, the steep increase of χ_s towards $x \sim 0.1$ agrees well with the Pauli susceptibility calculated for a rigid band model – see the full dots in Fig. 3.37. In this calculation, the density of states of pure liquid KCl has been used (Fig. 3.30) and $n(E_F)\chi_s \propto n(E_F)$ was determined at different $E_F(x)$; see [3.81]. So, it may be concluded that at high $x > 0.01$, the variation of the spin susceptibility within experimental errors is consistent with electrons occupying conduction band tail states.

A main result of the different spectroscopic investigations of nonmetallic M_xMX_{1-x} melts is the occurrence of localized electronic states that are similar in character to their solid-state counterparts, such as F-centres, F-centre dimers, and dimer clusters or n -mers. This, very early, led to the question if thermodynamic defect models of solid-state chemistry also apply to liquid metal–salt solutions [3.96]. Hereby, it is assumed that dissolution of metal leads to the formation of electronic defect species that react in chemical equilibrium. The equilibrium constants and thus the concentrations of the respective species can be obtained from fits of the thermodynamic properties under investigation by the respective equations of a defect model. Considering, for instance, the thermodynamic metal activity, a_K , in liquid K_xKCl_{1-x} , the following variation of defect species is evident; see Fig. 3.38. If only F-centres would exist ($\delta_K = n_F \propto a_K$, [3.98])

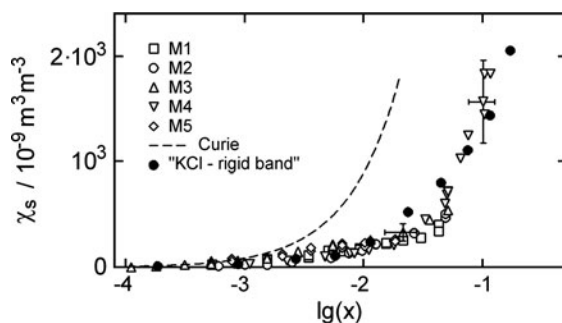


Fig. 3.37 Semilogarithmic plot of the spin susceptibility of liquid K_xKCl_{1-x} at 815°C determined from ESR spectra corresponding to different experimental runs M1–M5; also included are the limiting Curie law behaviour (*dashed line*) and calculated values of the Pauli spin susceptibility for a simple rigid band model (*closed circles*). See also [3.85]

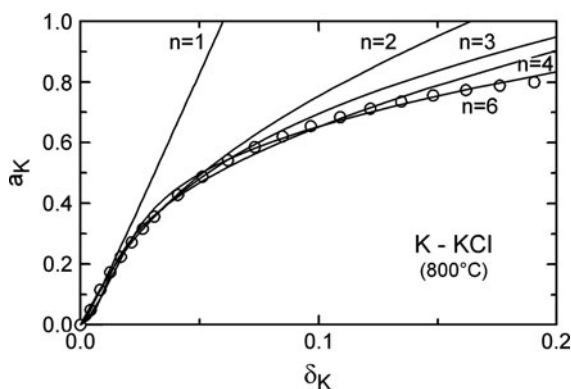


Fig. 3.38 Comparison of measured thermodynamic metal activity, a_K , of liquid K_xKCl_{1-x} (*open circles*) with predictions of a thermodynamic defect model (*full lines*) for the concentrations of F-centres ($n = 1$) or F-centre aggregates or clusters (n -mers), $\delta_K = x/(1 - x)$. See also [3.97]

and then δ_K should vary linearly with a_K , which only holds in the dilute limit ($x_K < 0.01$). Allowing for an equilibrium with higher aggregated species such as n -mers ($\delta_K \propto n_F + n_n \propto a_K + K(T)a_K^n$, [3.98]), a reasonable description of the experimental metal activity is possible up to high metal excess $x \sim 0.1$, where bipolaron clustering has been predicted by the QMD calculations. In a similar way, the concentrations of different defects have been determined from optical absorption, ESR, and electronic conductivity measurements and, in general, a reasonable correspondence of the distinct datasets was obtained; see also references [3.83, 3.84]. This indicates that thermodynamic defect models can be used in the liquid state, too, to describe electronic defect equilibria.

So far the discussion has concentrated on the properties of K_xKCl_{1-x} melts, which raises the question in how far these are representative of all alkali metal halides. For the heavier alkali metals, it was demonstrated that F-centre-like states

occur; in systems such as $\text{Cs}_x\text{CsX}_{1-x}$ melts, the equilibrium between F-centres and bipolarons seems to be shifted to higher metal concentrations in comparison with e.g. $\text{K}_x\text{KCl}_{1-x}$. However, in the lighter alkali metal halides such as the Na–NaX systems systematic deviations have been observed, for instance, of the optical excitation energies from the Mollwo–Ivey rule; see above. With the smaller cation radius of Na^+ – and even more for Li^+ – localization of excess electrons in atomic like states can be favoured. This was first concluded from MD calculations of Parrinello and Rahman [3.16] employing the Feynman path integral method and was later confirmed in independent QMD calculations [3.98]. At higher metal excess, the latter predict the formation of various spin-paired species, the most probable being Na^- and Na_2 [3.98].

3.5.2 Transition to Metallic States

In the concentration range $0.1 \leq x \leq 0.2$, significant changes in the electronic properties of alkali metal–alkali halide melts occur: (1) The spin susceptibility rapidly increases and reaches a value of $\sim 2 \times 10^{-6}$ at $x = 0.1$ corresponding to $n(E_F) \sim 2 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$; see Fig. 3.37; (2) the DC conductivity near $x = 0.2$ approaches a value of $\sim 10^2 \Omega^{-1} \text{ cm}^{-1}$ comparable with Mott’s minimum metallic conductivity $\sigma_{\min}$; see Fig. 3.29; near this composition, the temperature coefficient of conductivity changes sign [3.99]; and (3) the electronic mobility near $x = 0.2$ is about $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; see Fig. 3.39. From the magnitude of these quantities, it must be concluded that a transition to conduction in extended states sets in at a composition of $x \sim 0.2$. In this case, the mobility is given by

$$\mu_{\text{ext}} = eD/k_B T = 1/6v_e a^2 e/k_B T, \quad (3.25)$$

where v_e is an electron frequency, $v_e \sim \hbar/m_e a^2$, and a is now the distance in which phase coherence is lost. Thus, μ_{ext} at 1,100 K is estimated by

$$\mu_{\text{ext}} \sim \frac{1}{6} \left(\frac{e}{k_B T} \right) \frac{\hbar}{m_e} \sim 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \quad (3.26)$$

which is comparable in magnitude with the experimental value. Assuming that with increasing x and $E_F(x)$ a mobility edge is crossed in the range $0.1 \leq x \leq 0.2$, the number density of electrons at E_c is approximately given by (see p. 219 in [3.12])

$$n(E_c) \sim \frac{\sigma_{\min}}{(e\mu_{\text{ext}}k_B T)}. \quad (3.27)$$

With $\sigma_{\min} \sim 10^2 \Omega^{-1} \text{ cm}^{-1}$ and $\mu_{\text{ext}} \sim 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, this yields at 1,100 K a value of $n(E_c) \sim 3 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$. This, again, is comparable to the result of $n(E_F) \sim 2 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$ determined from the spin susceptibility near $x \sim 0.15$.

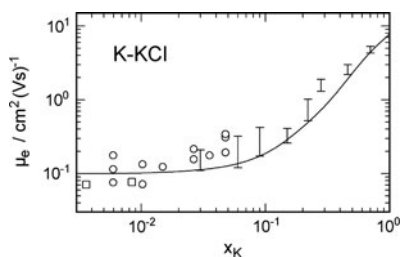


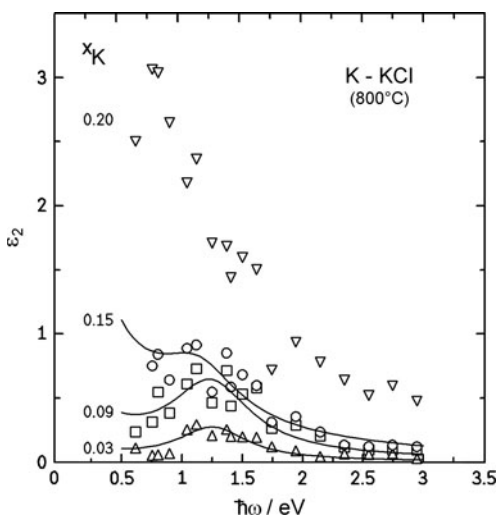
Fig. 3.39 Electronic mobility μ_e vs. x in liquid K_xKCl_{1-x} at 800°C determined by different methods: polarization measurements (*open squares*), Drude fits of optical absorption (*open circles*), and Drude fits of spectroscopic ellipsometry data (*bars*); the *full line* has been calculated from the DC conductivity by dividing it by the number density of excess electrons. See also [3.100]

In conclusion, these considerations show that the transition to metallic behaviour in alkali metal–alkali halide melts exhibits some of the characteristics of a Mott–Anderson transition, whereby a mobility edge at E_c is crossed with increasing metal excess in the range $0.1 \leq x \leq 0.2$. This is schematically depicted in Fig. 3.1. Localization of electrons at energies below E_c is driven by topological disorder and Madelung potential fluctuations with an rms value of ~ 1 eV – see the situation in Fig. 3.3. An interesting finding is the coexistence of Curie moments and Pauli spins in the nonmetallic regime. This behaviour evidently extends into the metal–nonmetal transition region, which is demonstrated in Fig. 3.40 for liquid K_xKCl_{1-x} by the optical conductivity or the imaginary part, ε_2 , of the dielectric function determined by spectroscopic ellipsometry [3.87]. Here, a simple two-component model, a combination of a Gaussian and a Drude term, is sufficient to describe the essential characteristics of the spectra. At $x = 0.2$, the Drude term, $\sigma(\omega) \propto \sigma(0)\omega^{-2}$, prevails, which is expected if transport by carriers excited to extended states near or above E_c takes over. Finally, with respect to the two-component model, a close similarity is noticed with the change of the electronic structure during the metal–nonmetal transition in highly doped semiconductors [3.101].

In the discussion so far, the onset of metallic behaviour was defined by the characteristic changes of the electronic structure according to a Mott–Anderson transition. Another approach to identify the transition is that by the so-called Herzfeld criterion [3.102]. It predicts a divergence of the dielectric polarization or susceptibility on approaching the metal–nonmetal transition from the nonmetallic side. In liquid K_xKCl_{1-x} the concentration dependence of the refractive index was measured at a wavelength of $1.5 \mu\text{m}$ approaching the transition [3.103]. From a power law fit of the corresponding dielectric susceptibility enhancement the metal concentration at the dielectric divergence was found to be $x_c = 0.1 \pm 0.03$, which is comparable to the concentration range where the Mott–Anderson transition sets in.

It is clear from the phase diagrams (Fig. 2.14) that most metal–salt solutions separate into a metal- and salt-rich phase at temperatures below T_c . This tendency of demixing persists at conditions far away from the miscibility gap that was shown by neutron diffraction studies of the microscopic structure in various M–MX melts.

Fig. 3.40 Imaginary part of the dielectric function, $\varepsilon_2(\omega)$, vs. photon energy in liquid $\text{K}_x\text{KCl}_{1-x}$ determined by spectroscopic ellipsometry; the *full curves* correspond to fits of the spectra by the two-component model; see text. See also [3.87]



In metal-rich $\text{Rb}_{0.8}\text{RbCl}_{0.2}$ melts, Chabrier et al. [3.104] find the same pattern in the pair correlation function as that shown in Fig. 3.20 for liquid Cs–CsAu alloys: Peaks characterizing the first coordination sphere of liquid Rb metal and RbCl molten salt coexist. This clearly indicates a tendency towards microscopic segregation into metal- and salt-rich domains. On the other hand, the extent of concentration fluctuations in the near critical region in K–KBr and K–KCl melts was studied by small-angle neutron and X-ray scattering [3.105, 3.106]. A main result of these investigations is that concentration fluctuations with a correlation length of $\geq 20 \text{ \AA}$ extend over a range of $\sim x_c \pm 0.1$. Taking these microscopic inhomogeneities into account, Senatore and Tosi have investigated another approach for the metal–nonmetal transition in these melts [3.107]. They have used a volume percolation model from which they estimated the percolation threshold for potassium-based solutions to occur at $x \sim 0.5 x_c$. The main conclusion is that the nonmetal–metal and the thermodynamic demixing transition are well separated [3.107].

Before ending this section, a brief comment is timely on the metal–nonmetal transition in liquid ionic alloys of the Cs–Au type. The comparison of their properties (Sect. 3.4) with those of liquid alkali metal–alkali halides shows close similarities. This ranges from electron localization by F-centre-like states in the nonmetallic alloys to microscopic segregation as evidenced by neutron diffraction in the metallic liquids. Therefore, it is suggested that the metal–nonmetal transition in both systems is based on the same mechanism, a Mott–Anderson transition.

3.6 Rapidly Quenched M–MX Melts

Almost all liquids, when cooled fast enough or in small enough sample sizes – for instance, nanoscale droplets in microemulsions – can be vitrified in bulk. Current research on the glassy state of matter concentrates on the mechanisms and, in particular, the dynamic processes of the glass transition – for reviews see e.g. [3.108–3.110]. Among the best known and widely studied glassy materials are ionic and metallic glasses. The ionic case includes inorganic glasses such as metal halide and oxide mixtures and also the more recently investigated glass forming ionic liquids. With respect to the glass transition mechanism, the latter are similar to molecular liquids, which is also seen in the empirical law for the glass transition temperature, $T_g/T_m \sim 2/3$ [3.110]. Research on metallic glasses, discovered over 50 years ago [3.111], has made enormous progress that led to applications in different fields [3.112]. In comparison with these systems, investigations of glassy or amorphous materials with properties intermediate between metal and nonmetal are rare. There are a few examples of amorphous metal–rare gas mixtures rapidly quenched at low temperatures (see e.g. [3.113]), but to our knowledge there is only one report on the vitrification of a metal–molten salt solution, the Bi–BiCl₃ system, which was achieved by rapid quenching from the melt [3.114]. In the following, the specific properties of this glass shall be described, but first the characteristics of the corresponding melt are briefly summarized.

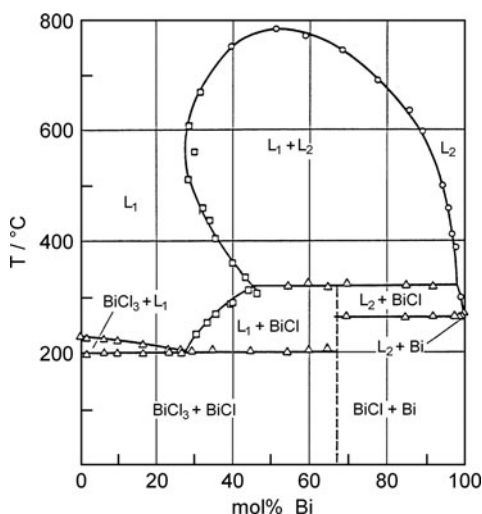
The phase diagram of the Bi–BiCl₃ system is shown in Fig. 3.41, taken from [3.115]. Measurements were performed with samples sealed in quartz tubes that could withstand the elevated pressures of the Bi_x(BiCl₃)_{1–x} mixtures at high temperatures, the boiling point of pure BiCl₃ being $T_b = 714$ K; see Table 2.2. At elevated temperatures, the phase diagram exhibits a wide liquid–liquid miscibility gap with a consolute point at $x_c = 0.52$ and $T_c = 1,053$ K. The solubility of metal in the salt first decreases with increasing temperature from $x = 0.45$ at 593 K to $x = 0.28$ at 823 K, and then increases. This is the so-called *retrograde solubility* behaviour.

In the salt-rich melts, the electronic structure is dominated by the complex chemistry of bismuth: Both monomers of differing valence (Bi⁺ and Bi³⁺) or polymers of the general form Bi_{*n*}^{*m*+} may form, extending up to Bi₉⁵⁺ [3.116]. At low metal excess, intervalence charge transfer based on Bi⁺–Bi³⁺ nearest neighbour ions has been discussed, whereas at higher metal concentrations an equilibrium of Bi⁺ with one or more polyatomic species is considered; see also [3.80]. The latter suppress electronic conduction and are the reason for the shift of the metal–nonmetal transition towards higher metal concentrations; see Fig. 3.29. It is assumed that polyatomic Bi species also exist in the transition region towards metallic behaviour [3.80].

Experiments on rapid cooling of Bi_x(BiCl₃)_{1–x} melts were performed with a splat-cooling device (anvil–piston principle) inside a glove-box filled with pure argon gas [3.117]. The samples were sealed in thick-walled quartz tubings and were heated at a temperature above T_c for several hours. Afterwards, they were quenched to room temperature with the metal-rich phase at the bottom end of the

Fig. 3.41 Phase diagram of the Bi–BiCl₃ system.

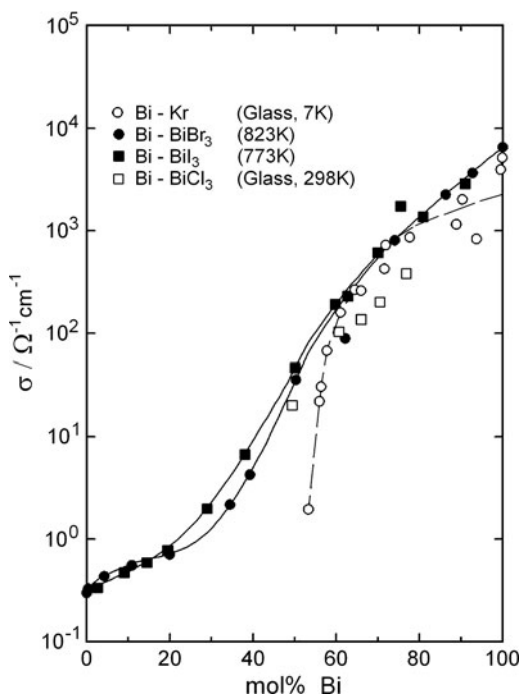
Different symbols refer to different detection methods: (*open circles*) visual, (*open squares*) decantation, (*open triangles*) thermal analysis. Reprinted with permission from [3.115]; copyright permission (2010) by American Chemical Society



quartz capillary. After opening of the quartz tubing at the bottom end it was reheated at high speed in an induction furnace. The first liquid droplet that left the capillary passed a laser beam and thus triggered the anvil–piston apparatus, which was equipped with two polished Cu pistons. The quenched splats had a typical size of 1 cm diameter and 50 μm thickness. The cooling rates achieved in these experiments were of the order of 10^6 K s^{-1} [3.117]. The amorphous structure of the quenched samples was checked by X-ray diffraction and their composition was analysed by atomic absorption spectrometry, ion chromatography, and gravimetry. The uncertainty in the composition was estimated to be $\leq \pm 7\%$. Further characterization of the X-ray amorphous samples included (1) measurements of the electrical conductivity by ESR; and (2) investigation of their microscopic structure by small-angle X-ray (SAXS) scattering and by extended X-ray absorption fine structure (EXAFS) measurements.

Results of the electrical DC conductivity of glassy $\text{Bi}_x(\text{BiCl}_3)_{1-x}$ ($20 \leq \sigma/\Omega^{-1} \text{ cm}^{-1} \leq 400$) in comparison with corresponding melts and glassy Bi–Kr mixtures are shown in Fig. 3.42. With reference to the latter systems, the conductivities of glassy Bi–BiCl₃ are systematically shifted to lower values, by nearly a factor of 2 in comparison with the data of the melts. It is also interesting to note that the conductivity of liquid $\text{Bi}_x(\text{BiBr}_3)_{1-x}$ up to $x \sim 0.8$ has a positive temperature coefficient [3.118], whereas that of the $\text{Bi}_{0.61}(\text{BiCl}_3)_{0.39}$ glass is negative [3.117]. Interesting is the comparison with the concentration dependence of conductivity in glassy Bi–Kr mixtures. In this system, a scaling law of the form $\sigma \propto (x - x_c)^\nu$ has been found with a threshold $x_c = 0.55$ and an exponent $\nu \sim 1.1$ [3.113]. This is not consistent with a simple site or bond percolation model for which $1.5 \leq \nu \leq 1.6$ is expected; see Sect. 3.2. A similar plot for glassy $\text{Bi}_x(\text{BiCl}_3)_{1-x}$ yields a threshold $x_c \sim 0.47$ and an exponent $\nu \sim 1 \pm 0.2$ [3.117]. Although this is based on only five data points, it indicates that in both glassy systems the metal–nonmetal transition

Fig. 3.42 Electrical conductivity vs. mol% Bi of glassy Bi–BiCl₃ quenched from the melt in comparison with conductivities in different melts and in glassy Bi–Kr mixtures at low temperatures. See also [3.114]

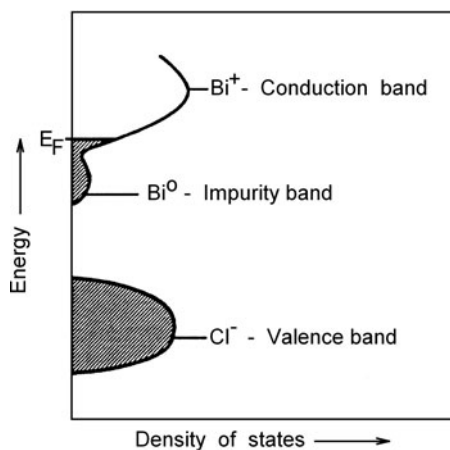


cannot be explained by a classical percolation mechanism. This conclusion is supported by small-angle X-ray scattering measurements, which can be described by a scaling law of the intensity of $I(q) \propto q^{-P}$, where the exponent P lies in the range of $3.3 \leq P \leq 3.6$. These exponents are not consistent with scattering by mass fractals such as aggregated clusters for which $P \leq 3$, but they are typical of scattering by internal interfaces or pore fractals; see also [3.119]. The existence of small Bi clusters, neutral or charged, has been indirectly derived from EXAFS investigations on glassy Bi_x(BiCl₃)_{1-x}. They give evidence for a nearest neighbour Bi–Bi distance of 3.11 ± 0.03 Å in comparison with 3.06 ± 0.03 Å measured on a Bi foil. This distance was observed in all glasses with $0.3 \leq x \leq 0.8$ [3.120].

In summary, the example of Bi–BiCl₃ shows that M–MX melts can be quenched into the glassy state with properties intermediate between a metal and a salt. The M–NM transition in this glass is not consistent with a simple classical percolation model. Instead, the critical exponent of the electrical conductivity of $\nu \sim 1$ is indicative of a disorder-driven Mott–Anderson transition, in accordance with the scaling theory of Abrahams et al. [3.121] and observations in amorphous Bi–Kr at low temperatures. In this context a suggestion for the change of the density of states in liquid and glassy Bi–BiX₃ systems near the M–NM transition is of interest; see Fig. 3.43 (Kosłowski, personal communication, 1995). It is assumed that an impurity band of Bi atoms or clusters exists and that the following chemical equilibrium prevails:



Fig. 3.43 Sketch of a qualitative model for the density of states in the metal–nonmetal transition range of liquid and glassy Bi–BiX₃; occupied states are hatched. Reprinted with permission from [3.117], Koslowski, personal communication, 1995



At high temperatures, the equilibrium is shifted to the right and so E_F is lifted into the conduction band. In this way, the positive temperature coefficient of the conductivity in the melts can be explained. At lower temperatures, the equilibrium lies on the left side, which is consistent with the lower conductivities in the glassy material. However, further experimental investigations are needed to test this model.

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Chapter 4

Interfacial Phase Transitions

Abstract The chapter on phase transitions at interfaces of conducting fluids includes phenomena such as prewetting and complete wetting, oscillatory wetting instabilities, and surface freezing. Systems of interest comprise fluid metals, alloys, and metal–molten salt solutions. Experimental investigations and model calculations of the last decade are presented. Among the surface and interfacial sensitive probes employed and developed in these measurements at elevated temperatures are capillary wave spectroscopy, spectroscopic ellipsometry, X-ray reflectivity and grazing incidence diffraction, and electron spectroscopies.

4.1 Wetting Transitions at the Liquid/Vapour Interface of Ga-Based Alloys

The main characteristics of the bulk phase diagram of Ga-based alloys of interest here are presented in Fig. 4.1. They are defined by a wide liquid–liquid miscibility gap with an upper critical temperature T_C , a monotectic point of four-phase coexistence at T_M , and a deep eutectic at T_E near room temperature on the Ga-rich side. The spinodal region of unstable fluid inside the miscibility gap is indicated by the dashed curve. Underneath the liquidus line – which connects the monotectic and eutectic points – is drawn the metastable extension of the liquid–liquid coexistence curve into the liquid–solid two-phase region (dashed black line). Its separation from the liquidus line at constant temperature is given by the difference of the respective chemical potentials $\Delta\mu$.

The surface free energy of liquid Ga is almost a factor of two higher than that of liquid Bi or Pb at conditions near their respective melting points (see Table 2.5). In addition, the temperature coefficients of the liquid/vapour interfacial energies of these metals are comparable and small. So, for simple energetic reasons, it can be expected that the Bi or Pb component is enriched at the surface of Ga-rich alloys. An interesting question is: How does this surface excess change with composition and temperature and, in particular, under what conditions do singularities or phase transitions occur at the interface? As the bulk phase behaviour of Ga-based alloys very much resembles the situation depicted in Fig. 2.18, the occurrence of prewetting

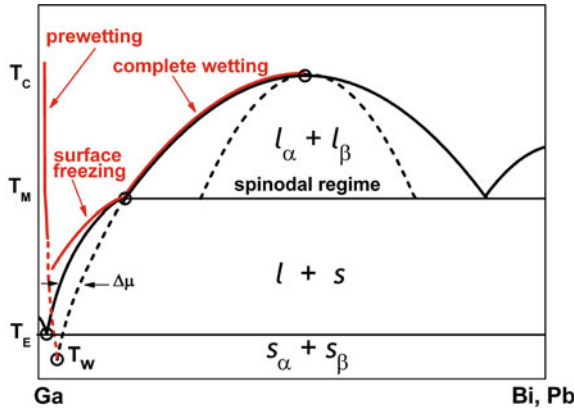


Fig. 4.1 Schematic drawing of the bulk (black full line) and the surface (red line) phase diagram of Ga-based alloys, Ga–Bi and Ga–Pb. The temperatures on the abscissa are as follows: Eutectic (T_E), monotectic (T_M), and the critical temperature (T_C). For the selected alloys, the (x, T) coordinates are as follows: (Ga–Bi) $x_E = 0.002$, $T_E = 29.5^\circ\text{C}$; $x_M = 0.085$, $T_M = 222^\circ\text{C}$; $x_C = 0.3$, $T_C = 262^\circ\text{C}$; (Ga–Pb) $x_E = 0.0006$, $T_E = 29.5^\circ\text{C}$; $x_M = 0.02$, $T_M = 313^\circ\text{C}$; $T_C = 610^\circ\text{C}$. For further details of the bulk phase diagrams, see Ref. [4.1]

and complete wetting transitions in these alloys must obviously be considered. The corresponding surface phase diagram is represented in Fig. 4.1 by the red lines. In the following section, the experimental evidence for the respective interfacial phase transitions is presented. Measurements in all the cases were performed under UHV conditions, thus ensuring clean surfaces. As the vapour pressures of the respective liquid metals are extremely low up to 500 K ($<10^{-10}$ mbar), evaporation and resulting compositional changes of the alloys did not cause a problem.

Prewetting transitions are defined by discontinuous jumps of the surface excess $\Gamma_i^{(\sigma)}$ at temperatures above the wetting temperature T_W (see Fig. 2.18). In the Ga-rich alloys, at conditions off of liquid–liquid coexistence, the second liquid phase X ($X = \text{Bi, Pb, Tl, etc.}$) is thermodynamically not stable, and so only a jump from microscopically thin to thick wetting films can occur. The loci of these discontinuities define the prewetting line that ends at higher temperatures at the critical prewetting temperature, $T_{c,\text{pw}}$. The “thin–thick transitions” are manifested by clear breaks in slope in the Gibbs adsorption isotherms,

$$d\sigma_{lv} = \Gamma_{X(\text{Ga})}^{(\sigma)} \cdot d\mu_X, \quad (4.1)$$

where $\Gamma_{X(\text{Ga})}^{(\sigma)}$ is the surface excess of X relative to Ga and μ_X is the chemical potential of component X in the bulk liquid alloys. Typical adsorption isotherms of liquid Ga–Bi and Ga–Pb alloys are shown in Fig. 4.2, where $\Delta\mu_X$ is approximated by the ideal solution model, $\Delta\mu_X^{\text{id}} = RT \ln x_X$, which is sufficient in the dilute limit considered here [4.2]. The data plotted in this figure have been determined from detailed measurements of $\sigma_{lv}(x, T)$ using capillary wave spectroscopy

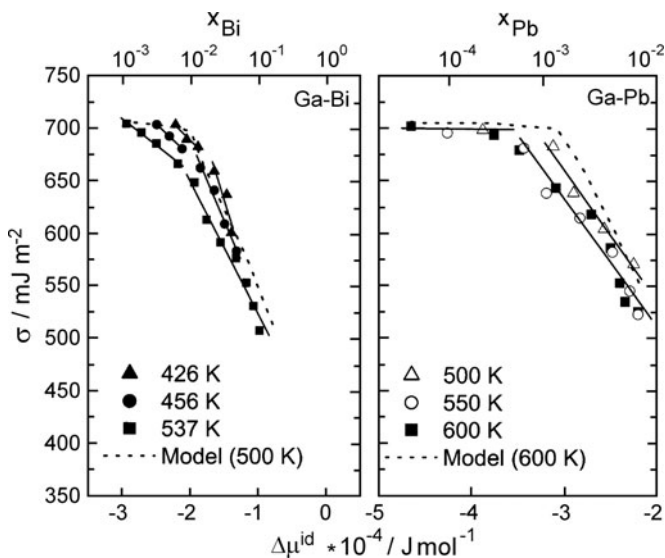


Fig. 4.2 Gibbs adsorption isotherms of liquid Ga–Bi and Ga–Pb alloys. See also [4.6]

at elevated temperatures; see also Sect. A.3. The isotherms exhibit distinct breaks in slope at very Ga-rich compositions, i.e. near $x_{\text{Bi}} \sim 10^{-2}$ and $x_{\text{Pb}} \sim 10^{-3}$, respectively, leading to the prewetting line as indicated in Fig. 4.1. Taking, for instance, the isotherm of Ga–Bi at 537 K, the change in slope at $x_{\text{Bi}} = 0.009$ corresponds to a jump from low Bi adsorption ($\Gamma_{\text{Bi(Ga)}}^{(\sigma)} = 0.5 \pm 0.05 \times 10^{-5} \text{ mol m}^{-2}$) to high adsorption ($\Gamma_{\text{Bi(Ga)}}^{(\sigma)} = 1.3 \pm 0.01 \times 10^{-5} \text{ mol m}^{-2}$), whereby the latter is comparable with a pure Bi monolayer. It is interesting to note that similar changes in slope are obtained if one describes the interfacial region by the Prigogine layering model and approximates the thermodynamic properties of the layers by a regular solution model [4.3]. Calculations of this kind have been made for the Ga–Pb system by Wynblatt et al. [4.4]. The dashed lines in Fig. 4.2 correspond to such calculations [4.5].

Complete wetting transitions connected with the formation of macroscopically thick wetting films occur if the liquid–liquid coexistence curve in Ga-rich alloys is approached. For a quantitative discussion of the thickness dependence on the distance from the coexistence curve, $\Delta\mu$, we consider the following configuration. At coexistence, the Ga-rich liquid (α), the X-rich liquid (β), and the vapour phase (γ) are considered in thermal equilibrium. It is also assumed that the interfacial free energies are related by

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \quad (4.2)$$

i.e. a macroscopic phase (β) wets or spreads at the α/γ interface. At conditions off of coexistence, β is no longer in stable equilibrium with α and γ and therefore does not form a macroscopic film. In order to determine its thickness d as a function of the distance $\Delta\mu$ from coexistence, we consider the effective interfacial potential

$\Omega^{(\sigma)}(T, \mu; d)$ per unit area of the interface, which in mean field approximation is given by [2.131]:

$$\Omega^{(\sigma)}(T, \mu; d) = \sigma_{\alpha\beta} + \alpha_{\beta\gamma} + \Delta\mu \cdot d + w^{(\sigma)}(d) + w^{(g)}(d). \quad (4.3)$$

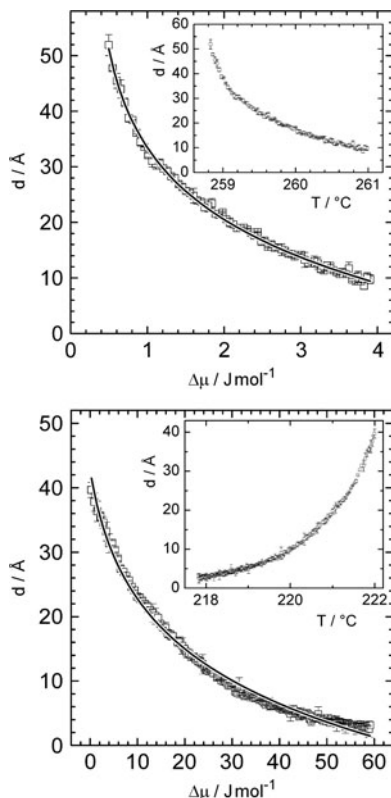
Here, $\Delta\mu \cdot d$ describes the excess free energy of the wetting film [4.7], $w^{(\sigma)}$ is a correction to the surface free energy, which results from the finite thickness d of the wetting film, and $w^{(g)} = g \Delta\rho Ld$ is the gravitational energy necessary to lift the wetting film across the height L of the non-wetting phase, where the density difference between phases α and β is $\Delta\rho$. The last contribution matters only in the limit $\Delta\mu \rightarrow 0$, when the film gets macroscopically thick. In this limit, the thickness scales as $d \propto \xi \ln(L/\xi)$, where ξ is the correlation length of composition fluctuations [4.7]. Far away from the critical point of $\alpha - \beta$ or $\beta - \gamma$ coexistence, these are of molecular dimensions. In the case of screened Coulomb interactions, an appropriate approximation of the surface correction term $w^{(\sigma)}$ is $w^{(\sigma)} = \sigma_0 \exp(-d/\xi)$, where σ_0 is of the order of a typical interfacial free energy. Thus, the thickness d that minimizes $\Omega^{(\sigma)}$ is as follows:

$$d = \xi \ln \left(\frac{\sigma_0}{\Delta\mu \xi} \right). \quad (4.4)$$

According to this model, a logarithmic divergence of the wetting film thickness approaching coexistence is expected, i.e. $d \propto \ln(\Delta\mu^{-1})$.

The first observation of complete wetting at the liquid/vapour interface of a metal alloy has been reported for the Ga–Bi system employing ellipsometric measurements [4.8, 4.9]. This was followed by an Auger spectroscopic investigation of the liquid/vapor interface of Ga–Pb alloys [4.10]. In both experiments, the monotectic point was approached along the liquidus line, i.e. on a special path off of liquid–liquid coexistence. The Auger results clearly indicated a logarithmic divergence of the thickness of a Pb-rich wetting film approaching the monotectic point. Subsequent investigations of the liquid/vapor interface in Ga–Bi alloys by X-ray reflectivity [4.11] and spectroscopic ellipsometry [4.12] have focused on the composition and microscopic structure of the Bi-rich wetting films and, in particular, on the evolution of its thickness approaching coexistence along different paths in the bulk phase diagram. Figure 4.3 shows results of the wetting film thickness d determined from ellipsometric measurements. The upper figure corresponds to cooling of the sample at constant bulk composition of $x_{\text{Ga}} = 0.8$ to a temperature of 258.8°C, very near coexistence (see inset); the lower one corresponds to cooling along the liquidus line below the monotectic temperature of 222°C. In both cases, the wetting film thickness increases to values of about 50 Å at conditions near liquid–liquid coexistence. The variation of d with the distance $\Delta\mu$ from coexistence follows a logarithmic dependence, $d \propto \ln(\Delta\mu^{-1})$, demonstrated by the full lines in the figures, which represent the corresponding fits of the experimental data points. In the ellipsometric investigations, both single-wavelength ellipsometry and spectroscopic ellipsometry have been employed; for further details see Sect. A.4.

Fig. 4.3 Variation of wetting film thickness d as a function of distance $\Delta\mu$ from liquid–liquid coexistence in Ga–Bi alloys; *upper panel*: cooling of a sample with constant composition $x_{\text{Ga}} = 0.8$ towards the coexistence curve; see inset for the T -dependence; *lower panel*: cooling along the liquidus line below the monotectic temperature of 222°C ; see inset for T -dependence. The *solid lines* in both figures represent fits of d proportional to $\ln(\Delta\mu^{-1})$. See also [4.12]



In order to complete the wetting diagram in Ga-based alloys as sketched in Fig. 4.1, the location of the wetting temperature T_W has to be defined. This problem was first addressed by Dietrich and Schick in a paper on “tetra point wetting” [4.13]. In analogy with triple point wetting in a one-component system [4.14], they described wetting at the monotectic point in two-component Ga-based alloys as complete wetting at a tetra point of four-phase coexistence, comprising the X-rich solid, X-rich liquid, Ga-rich liquid, and the vapour phase. Focusing on the metastable extension of the liquid–liquid coexistence curve below this tetra point – see the dashed line in Fig. 4.1 – a first-order wetting transition at T_W is expected where the prewetting line and the metastable extension merge. Obviously, for Ga-based alloys, this happens at low temperatures below the eutectic T_E . From adsorption measurements of Pb at the surface of single-phase Ga-rich liquid Ga–Pb alloys, Wynblatt et al. have estimated a value of $T_W \sim 240\text{ K}$ [4.15].

Surface phase transitions in liquid metallic alloys can be predicted by simple thermodynamic model calculation, which has been exemplified for the Ga–Bi system [4.16]. In the case of complete wetting, the chemical potential of the Bi-rich liquid film adsorbed at the Ga–Bi liquid/vapour interface can be approximated by

$$\mu_F = \mu_0 + RT \ln x_F - \Delta\mu_F, \quad (4.5)$$

where $\Delta\mu_F$ is the excess chemical potential due to the finite thickness of the film ($\Delta\mu_F = 0$ for $d \rightarrow \infty$). The mole fraction x_F of Bi in the film can be assumed as constant – at least for a small range of T and x_{Bi} in Ga-rich alloys – and can be estimated from the cryoscopic effect of freezing of the Bi-rich bulk phase at the monotectic point, see [4.16], which yields a value of $x_F \sim 0.8$. Off of coexistence, it is assumed that the thin liquid films are essentially stabilized by repulsive interactions. In the case of liquid metals, these can be described by screened Coulomb potentials and have been approximated by Thomas–Fermi potentials $\phi_{\text{Bi,Bi}}$ and $\phi_{\text{Bi,Ga}}$. Thus, the correction $\Delta\mu_F$ of the chemical potential can be estimated by

$$\Delta\mu_F = N_A^2 \rho_F \int_d^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty (x_F \phi_{\text{Bi,Bi}}(r) + (1 - x_F) \phi_{\text{Bi,Ga}}(r)) dx dy dz, \quad (4.6)$$

where N_A is the Avogadro number and ρ_F is the mass density of the liquid film. The integration limits in (4.6) follow from the definition in (4.5). Finally, if the Bi-rich liquid film is in equilibrium with the Ga-rich bulk liquid, the corresponding chemical potentials are equal, i.e.

$$\mu_F(d, T; x_F) = \mu_B(x_{\text{Bi}}, T). \quad (4.7)$$

From this relation, the dependence of $d = d(x_{\text{Bi}}, T)$ can be determined. The results of such calculations of complete wetting in liquid Ga–Bi alloys are shown in Fig. 4.4. Plotted are the equilibrium thicknesses d of an interfacial Bi-rich liquid film as a function of the Bi mole fraction in the bulk at various constant temperatures. As is seen, the thickness increases with increasing x_{Bi} , while it decreases with rising temperature. The $d(x_{\text{Bi}})$ isotherms diverge at compositions near liquid–liquid coexistence and along the metastable extension of the coexistence curve – see the inset in Fig. 4.4. This comparison shows that the model calculations reproduce the typical trend of complete wetting transitions in liquid Ga–Bi alloys. The deviation visible in the inset for $x_{\text{Bi}} > 0.1$ is due to the fact that the Bi chemical potential in the bulk has been fitted to the liquidus line and so is not a good approximation at higher $x_{\text{Bi}} > 0.1$; see also [4.16].

4.2 Interfacial Oscillatory Wetting Instabilities in Fluid Binary Alloys

Transforming a binary or multicomponent fluid – for instance, by slow cooling or heating – from a homogeneous one-phase into a two-phase demixing region, periodic oscillations of the bulk properties can occur. This was first observed in water-in-oil microemulsions where temperature-induced phase separation leads to nearly periodic oscillations in turbidity and specific heat, with periods of the order of several minutes [4.17]; see Fig. 4.5. Further examples are methanol–hexane or ethanol–oil mixtures and also polymer solutions [4.18–4.20]. Qualitatively, it is

Fig. 4.4 Thermodynamic model calculation of thickness d as a function of bulk Bi mole fraction x_{Bi} at various temperatures for Bi-rich wetting films in liquid Ga–Bi alloys. The divergence of $d(x_{\text{Bi}})$ indicates the respective complete wetting transitions. Their loci in the bulk phase diagram are shown by the *full line* in the *inset* in comparison with experimental points of the coexistence curve (*open circles*) and its metastable extension below the monotectic temperature (*filled circles*). Adapted from [4.16]

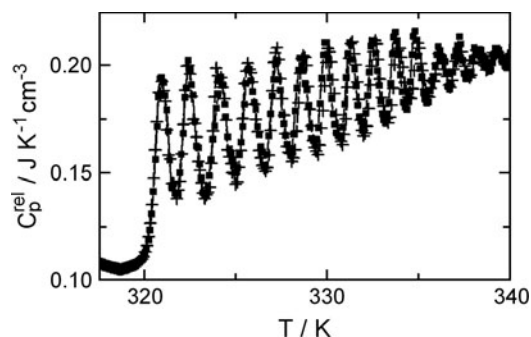
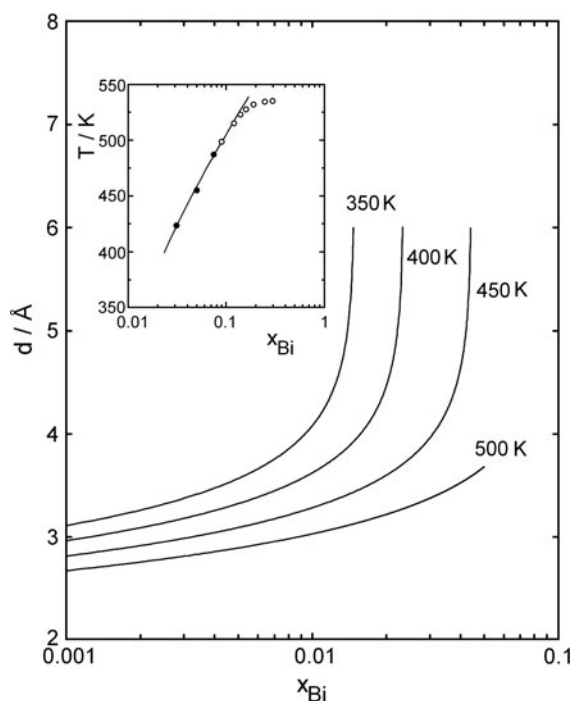


Fig. 4.5 Oscillating phase separation in a water-in-oil microemulsion: Temperature-dependent variation of the relative specific heat after passing the emulsification boundary at 319.3 K. Results of two independent measurements, *squares* and *crosses*, on the same sample are shown for heating at a constant rate of 21 K h^{-1} . Reprinted with permission from Ref. [4.17] copyright permission (2010) by American Institute of Physics

generally assumed that oscillatory phase separation proceeds as follows [4.20]: Crossing the binodal or coexistence curve, supersaturation of the homogeneous mixture induces nucleation, which is followed by droplet growth and coarsening; once the droplets have reached a critical size, gravity causes their sedimentation and the

system changes from turbid to transparent. Continuous change of temperature in the two-phase fluid leads to repeated supersaturation, and further cycles of droplet growth, coarsening, and sedimentation follow. This may be repeated several times until the two-phase region is left at constant heating or cooling.

Different model calculations have been performed to account for the phase separation dynamics and its oscillatory behaviour. Vollmer et al. have suggested a “minimal theoretical model”, which stresses the role of supersaturation by the temperature ramp at subsequent nucleation and coagulation of droplets. Within this model, which is of thermodynamic origin, these authors predict an oscillatory phase separation where the oscillation frequency depends on the diffusion constant and the temperature ramp rate [4.19]. In a more recent paper, the same authors used the Cahn–Hilliard equation for phase separation coupled with a gravity–volume exchange term at continuous cooling. Again, an oscillatory instability of droplet formation is found. These calculations are at variance with the general understanding that phase separation in fluid mixtures originates from two transport mechanisms, diffusion and hydrodynamic flow, which are generally coupled in a complicated manner; see also [4.21].

Among liquid metal alloys, oscillatory instabilities during phase separation were detected for the first time in Ga-based alloys [4.22–4.24]. At (x, T) conditions inside the miscibility gap – on slow cooling, heating, and even at constant temperature – they show up with periodic changes of the properties at the liquid/vapour interface, coupled with temperature oscillations in the bulk fluid. An example is given in Fig. 4.6 for a $\text{Ga}_{0.95}\text{Pb}_{0.05}$ alloy, the surface of which has been probed by second

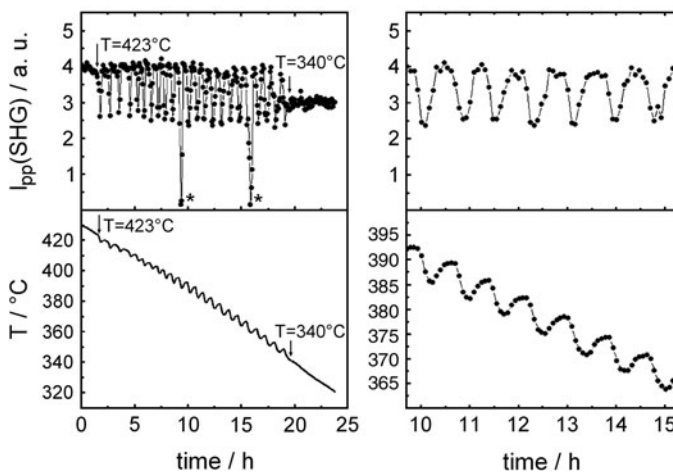


Fig. 4.6 Oscillations of SHG intensities at the liquid/vapour interface coupled with periodic changes of sample temperature of a liquid $\text{Ga}_{0.95}\text{Pb}_{0.05}$ alloy cooled with a constant rate of 7 K/h across the miscibility gap. The panels to the *right* show an enlarged section of the curves to the *left*. See also [4.22]

harmonic generation (SHG) on cooling across the miscibility gap at a constant rate of 7 K/h [4.22]. Crossing the phase boundary near 423°C, the SHG intensity drops to a value typical of pure Pb, which is expected if a Pb-rich macroscopic wetting film forms. This is accompanied by a drop of ~ 5 K in the sample temperature. On further cooling, the SHG signal rises to its original value, representing a Ga-rich surface. This has been interpreted by a “dewetting” process (see below). With a time lag of 3–4 min, the sample temperature increases again to a value that is extrapolated from the cooling curve above 423°C. These oscillations with a period of ~ 40 min persist down to $\sim 340^\circ\text{C}$, the monotectic temperature being 313°C .

In comparison with mixtures of molecular liquids, oscillatory phase separation in fluid metallic alloys exhibits several peculiarities. First, there is a strong correlation between formation and decay of complete wetting films at the interface and temperature oscillations in the bulk. Taking into account that the emissivities of both liquid Bi or Pb are higher than that of liquid Ga, radiation losses at the interface increase and the bulk temperature decreases if Bi-rich or Pb-rich wetting films grow to macroscopic thickness. Second, oscillatory instabilities also occur at constant temperature. This last observation is especially remarkable and is demonstrated in Fig. 4.7 for a $\text{Ga}_{0.8}\text{Bi}_{0.2}$ liquid alloy [4.24]. The upper panel shows the temperature oscillations in the bulk; the two lower panels represent the time evolution of the

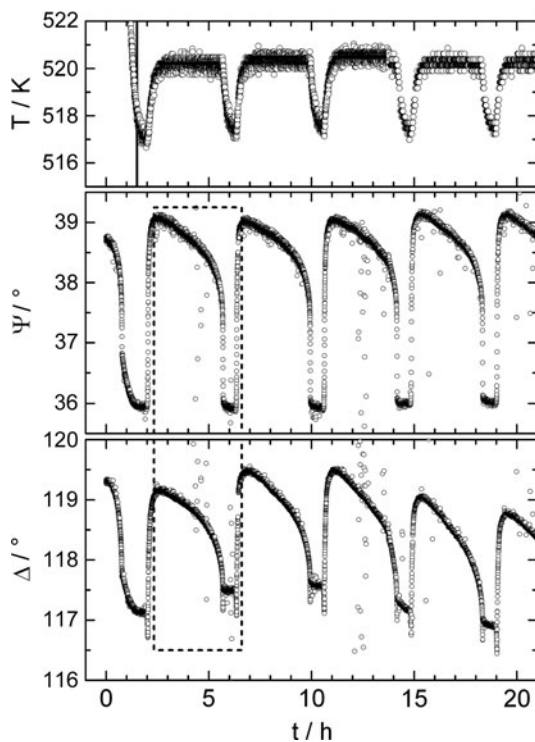


Fig. 4.7 Oscillatory instability in a liquid $\text{Ga}_{0.8}\text{Bi}_{0.2}$ alloy at constant average temperature of 520 K. *Upper panel:* variation of bulk temperature with time. *Lower panels:* time evolution of the ellipsometric angles ψ and Δ measured at the liquid/vapour interface at a photon energy of 2.75 eV. See also [4.24]

ellipsometric parameters ψ and Δ measured at the liquid/vapour interface. They are related with the complex reflection ratio, ρ , of the parallel and normal component of the polarized light by $\rho = \tan \psi \cdot \exp(i\Delta)$; see also Sect. A.4. The sample in Fig. 4.7 was cooled down from the homogeneous phase. After the furnace temperature reached 552.5 K, it was set at a constant level – see the vertical line at 1.5 h on the time scale of Fig. 4.7 – and the sample temperature approached an average value of 520 K. For the $\text{Ga}_{0.8}\text{Bi}_{0.2}$ alloy, this corresponds to a point well inside the miscibility gap. Considering the first cycle marked by a dashed frame, the following changes are of interest. In the first 2 h, Ψ and Δ decrease only slowly and then drop to plateau values of $\psi = 36^\circ$ and $\Delta = 117.5^\circ$, respectively. As these plateaus are reached, the sample temperature decreases exponentially to 517 K with a time constant of $\tau \sim 0.25$ h. The plateau is stable for about 0.6 h, before ψ and Δ jump back to their initial values and the temperature returns to its average value of 520 K. More than eight oscillations with a period of 4.26 h were observed before the experiment was stopped [4.24].

From the analysis of the ellipsometric data, ψ and Δ information can be obtained on the variation of the interfacial structure during a cycle. For this purpose, a three-phase model representing the vapour phase, the liquid Bi-rich wetting film, and the Ga-rich bulk phase has been used – see also Sect. A.4. The necessary complex dielectric functions, $\varepsilon = \varepsilon' - i\varepsilon''$, have been determined as follows: For the film, the (ψ, Δ) data points in the plateau region have been used, yielding $\varepsilon_F = -14.2 - 12.0i$, whereas the bulk value $\varepsilon_B = -18.41 - 9.88i$ has been determined from the (ψ, Δ) couples at the beginning of the cycle, representing the bulk liquid phase before complete wetting sets in. Keeping ε_F and ε_B constant, the only parameter in the three-phase model is the film thickness d . This has been obtained at different times from nonlinear fits of the respective (ψ, Δ) pairs by the three-phase model. The result of this analysis is given in Fig. 4.8 for the period of one cycle. In the first hours, the film thickness increases only slowly up to about 50 Å, which is comparable to complete wetting at coexistence; see Fig. 4.3. Then it shoots to macroscopic values above 500 Å, stays in this state for ~ 0.6 h, and dewets completely within a period of 0.1 h.

On combining the different observations in Ga-based liquid alloys, the following interpretation of the oscillatory interfacial instabilities inside the miscibility gap emerges. For simplicity, we consider the case of Ga–Bi at constant average temperature – see also Fig. 4.9. On entering the two-phase region, a complete wetting film forms at the liquid/vapour interface. This is a slow process. Once an equilibrium thickness of ~ 50 Å is reached, the bulk temperature begins to decrease. This can be explained by the higher emissivity of Bi in comparison with Ga, which becomes effective as soon as a macroscopically thick Bi-rich wetting film exists at the surface – for further details of this effect, see also [4.23]. As a consequence of the temperature reduction, the Ga-rich bulk phase becomes purer in Bi according to the x – T -dependence along the coexistence curve. So, excess Bi diffuses and nucleates at the film/Ga-rich bulk liquid interface at the top and at the Ga-rich liquid/Bi-rich liquid interface at the bottom of the crucible. As nucleation at these interfaces occurs without thermal activation, these are fast processes, only limited by diffusion. In

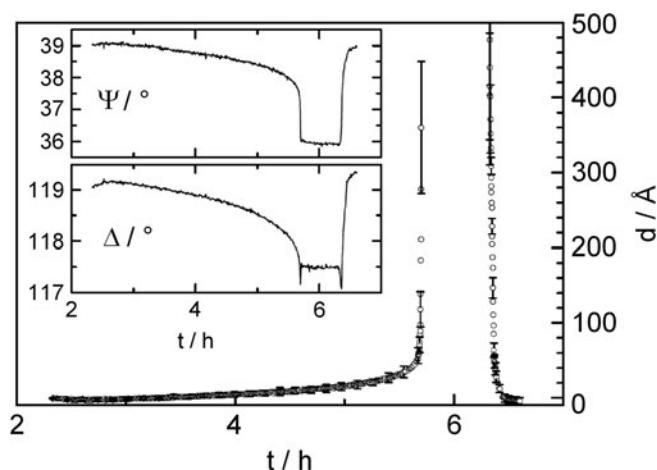


Fig. 4.8 Variation of the wetting film thickness during one cycle of interfacial oscillations in liquid $\text{Ga}_{0.8}\text{Bi}_{0.2}$ at conditions inside the miscibility gap. The corresponding ellipsometric angles ψ and Δ , from which the thickness has been determined with a three-phase model, are given in the *inset*. See also [4.24]

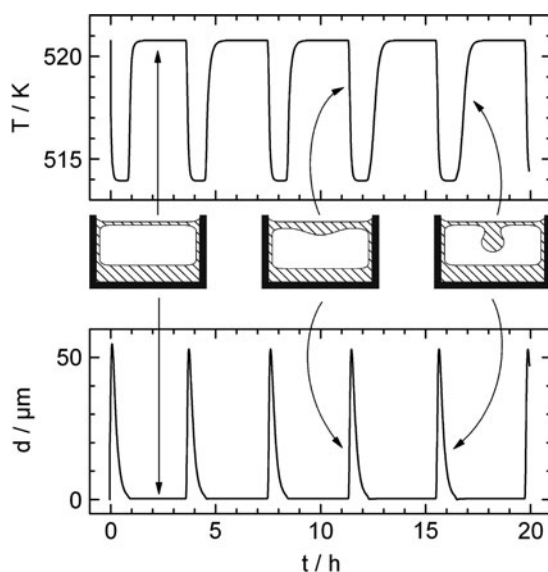


Fig. 4.9 Oscillations of temperature T and Bi-rich wetting film thickness d in a $\text{Ga}_{0.8}\text{Bi}_{0.2}$ alloy at conditions inside the miscibility gap as calculated by a hydrodynamic model (see text). The *middle row* shows sketches of the liquid sample with three specific configurations of the liquid/vapour interface: complete wetting film (*left*), wetting film growing due to temperature drop and corresponding bulk supersaturation (*middle*), and unstable film with falling drop (*right*). See also [4.24]

any case, the wetting film can now grow beyond its equilibrium thickness, well above 50 Å. At some thickness, it becomes unstable against gravitation as the mass density of the Bi-rich liquid is larger than that of the Ga-rich liquid; nearly circular flat lenses become visible at the interface, which grow and drop to the bottom. As a result, the Ga-rich surface is reformed in a completely dewetted state. At this moment, the bulk temperature returns to its initial value. In this sequence of steps, the most important parts are the interplay of complete wetting with bulk temperature variation and the interfacial instability, leading to dewetting. Both phenomena are linked with the occurrence of spinodal decomposition or liquid–liquid demixing.

For a quantitative description of the oscillation dynamics, a model that is based on hydrodynamic equations within the Reynolds approximation has been developed [4.23]. In the main, the following effects have been taken into account. As the radius of the liquid sample is much larger than its height, only the normal balance of the heat flow has been considered where energy loss due to radiation is an essential component. The dependence of the integral emissivity on the thickness of the wetting film has been included explicitly in the calculations; see also [4.25]. The composition evolution in the bulk liquid is described by diffusion. The equation from which the film thickness variation during wetting and dewetting is obtained has two main contributions: One accounts for the increase or decrease of the film thickness driven by diffusion and for the corresponding normal temperature gradient, and the second describes the relaxation of the film thickness as a result of the collecting and falling down of droplets of the unstable wetting film. As for the latter, the Fourier transform of the thickness perturbations, Δdq , is governed by the following equation [4.23]:

$$\frac{\partial(\Delta dq)}{\partial t} = \frac{H h_D^2 \eta^{-1} q^2 (\Delta \rho g - \sigma_{FB} q^2) \Delta dq}{4}. \quad (4.8)$$

Here, H is the sample height, h_D is the mean thickness of a local droplet lens, η is the viscosity of the bulk liquid underneath the wetting film, q is the wave number, $\Delta \rho$ is the difference between the mass densities of the coexisting liquid phases, $g = 9.81 \text{ ms}^{-2}$, and σ_{FB} is the tension at the film/bulk liquid interface. In (4.8), the expression in brackets describes a competition between gravity and interfacial energy. It can be seen from (4.8) that a critical wave number $q_c = (\Delta \rho g / \sigma_{FB})^{1/2}$ exists, below which $\partial/\partial t(\Delta dq) > 0$, so that the local perturbations in the film thickness become unstable and grow exponentially in time. This is the signature of a capillary–gravitation or Rayleigh–Taylor instability. In the range of unstable Fourier components, the most rapidly propagating ones dominate. Their wave number is calculated from the maximum of the expression in brackets in (4.8) with respect to q : $q_m = (\Delta \rho g / 2\sigma_{FB})^{1/2}$. The corresponding wavelength for Ga-based alloys is of the order of mm, which means that the perturbations are not limited by the dimensions of the sample crucible of $R = 26 \text{ mm}$. In the final analysis of the thickness evolution, only the mode with q_m has been taken into account. Typical results of these calculations for the film thickness and temperature oscillations of

a Ga–Bi liquid alloy at constant average temperature inside the miscibility gap are shown in Fig. 4.9. Also included in this figure are sketches of the interfacial changes during wetting–dewetting processes.

4.3 Wetting Transitions at the Liquid/Solid Interface in Coulombic Fluids

Spreading of a liquid drop on a solid substrate is one of the most common wetting phenomena, which is of key importance for many applications. In comparison with wetting properties at fluid interfaces as discussed in previous chapters, the solid surface may induce additional effects and complications for wetting and dewetting. An important one is the surface structure. Surface defects and impurities may lead to frustration so that the equilibrium state of spreading is not reached. Rough or microscopically patterned surfaces have a strong influence on the wetting behaviour; prominent examples are biological surfaces such as superhydrophobic Lotus leaves. The chemical interactions at the liquid/solid interface are generally determined by long-ranged van der Waals and short-ranged electrostatic forces. Their effect on the thickness d of thick wetting films can be derived from the effective interfacial potential approximation yielding $d \propto (\Delta\mu)^{-1/3}$ for van der Waals interaction and $d \propto \log(\Delta\mu^{-1})$ in the case of screened Coulomb interaction; see Sect. 4.1.

Wetting transitions at fluid/solid interfaces have been studied experimentally for rare gas/alkali metal systems at low temperatures, see e.g. [4.26], and in various binary solutions with hydrocarbons near room temperature [2.133]. At high temperatures, only a few experimental investigations have been reported so far, and they are the subject of this chapter. They are binary alkali metal–alkali halide solutions, in particular, K–KCl melts, and expanded fluid Hg. At elevated temperatures, both systems exhibit a continuous transition from metallic to nonmetallic states in the bulk phase, which can be induced by composition and density changes, respectively; see Sects. 3.3 and 3.5. In both cases, a first-order wetting transition has been found, which is necessarily associated with prewetting transitions for $T > T_w$. In fluid Hg, the prewetting line lies wholly in the nonmetallic dense vapour phase, whereas in K–KCl melts, a salt-rich wetting film intrudes between the solid substrate and the metallic liquid phase. In these systems, the wetting behaviour has been investigated by different spectroscopic methods at the interface of the fluid with a single crystal sapphire window. Although the temperatures are high, metal–molten salt solutions – and similar for expanded fluid metals – offer a special advantage for experimental interfacial investigations: the metallic and nonmetallic phases have extremely different electronic properties so that the nature of the wetting phase can be clearly distinguished spectroscopically.

The bulk phase diagram of K–KCl is shown in Fig. 4.10 with the metal-rich end expanded logarithmically. Qualitatively, it is similar to that of Ga-based alloys; see Fig. 4.1. A liquid–liquid miscibility gap (α) exists at high temperatures with a critical temperature $T_c = 790^\circ\text{C}$ and a monotectic temperature $T_M = 751^\circ\text{C}$ [3.78]. Below T_M , the liquidus line separates the homogeneous liquid metallic phase

(γ) from the two-phase region of solid KCl coexisting with liquid K–KCl (β). At elevated temperatures ($T > T_c$), a continuous metal–nonmetal transition occurs in the salt-rich fluid near $x_{\text{KCl}} \sim 0.8$; see Sect. 3.5.

The first indication of a wetting transition in metal-rich $\text{K}_x\text{KCl}_{1-x}$ solutions was obtained by optical reflectivity and ellipsometry measurements [4.27]. On heating along the liquidus line, discontinuous changes of the optical properties were observed near 480°C . Analysis of these measurements showed that a salt-rich wetting film with a composition of roughly $\text{K}_{0.1}\text{KCl}_{0.9}$ had intruded between the sapphire window and the metal-rich bulk phase. The thickness of this film was estimated to be ~ 200 nm at a temperature of $\sim 770^\circ\text{C}$ near coexistence. In a subsequent experiment, the interface was probed by SHG as a function of temperature at different metal-rich compositions. If a salt-rich wetting film is enriched at the interface, the F-centre excitation at 1.3 eV with a half-width of ~ 1 eV should be in resonance with the exciting fundamental of 1.2 eV. Thus, a strong enhancement of the SHG intensity is expected when crossing the wetting transition. This was indeed observed above the apparent wetting temperature, T'_w , near 500°C along the liquidus line and at different x , T points in the homogeneous metal-rich phase [4.28]. These points, marked as open black circles in Fig. 4.10, define the prewetting line, which is

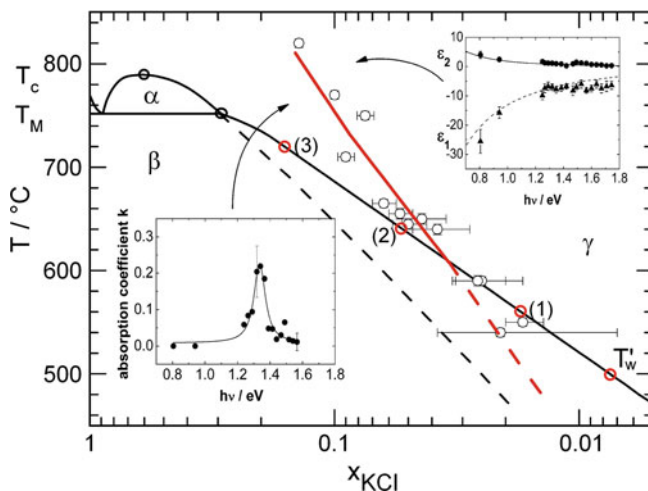


Fig. 4.10 Bulk (black) and surface (red) phase diagram of liquid $\text{K}_x\text{KCl}_{1-x}$ solutions in a semilogarithmic plot. The bulk phase regions of special interest are as follows: (α) KCl-rich liquid coexisting with K-rich liquid (liquid–liquid miscibility gap with an upper critical temperature T_c); (β) two-phase region of solid KCl coexisting with liquid K–KCl; (γ) homogeneous liquid K–KCl. The black dashed line indicates the metastable extension of the liquid–liquid coexistence curve extrapolated towards lower temperatures. The prewetting line (red) refers to the fluid/sapphire interface; the apparent wetting temperature, T'_w , near 500°C corresponds to the first observation of wetting on heating along the liquidus line. The numbered red circles along this line denote loci with the following wetting film thicknesses: 30 ± 20 nm (1), 200 ± 100 nm (2), 300 ± 100 nm (3); see also [4.31]. The insets show typical ellipsometric spectra observed above (upper right) and below the prewetting line (lower left). Adapted from [4.6]

accessible at equilibrium above the liquidus line. Further spectroscopic evidence of the wetting characteristics in metal-rich K_xKCl_{1-x} melts was obtained from spectroscopic ellipsometry [2.149], [4.29]. At conditions to the right of the prewetting line, the interface is characterized by typical metallic Drude-like behaviour of the optical constants; see the upper right inset in Fig. 4.10. Below the prewetting line, the ellipsometric spectra exhibit the F-centre band near 1.3 eV, which is the signature of the salt-rich liquid. An example is given by the inset in the lower left end in Fig. 4.10. The clearly reduced half-width of the F-band in the film in comparison with bulk K–KCl is remarkable and has been interpreted by charge ordering at the film/sapphire interface. This effect reduces the Madelung potential fluctuations in the bulk liquid [4.30]. From ellipsometry data and simultaneously measured optical reflectivities at normal incidence, the following values of the wetting film thickness d have been estimated [2.149]: Near the prewetting line, unusually high values of $d \sim 30 \pm 20$ nm appear; along the liquidus, they increase from $\sim 30 \pm 20$ nm at 500°C to 300 ± 100 nm near the monotectic point at 751°C ; see the red circles in Fig. 4.10.

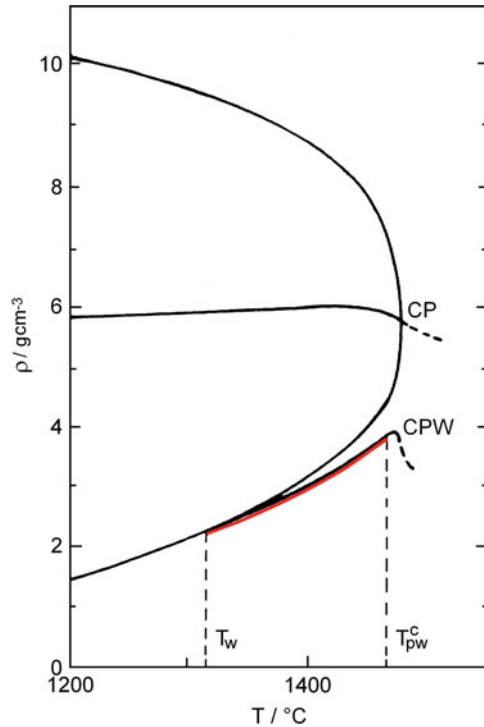
When discussing the wetting behaviour in K–KCl melts and, more generally, in alkali metal–alkali halide solutions, a number of peculiarities and open questions have to be pointed out. Similar to Ga-based alloys, the wetting characteristics summarized in Fig. 4.10 strongly indicate a tetra point wetting scenario in K–KCl melts. Accordingly, it must be assumed that the true wetting temperature T_w lies at low temperatures – outside the temperature range of Fig. 4.10 – where the metastable extension of the liquid–liquid coexistence curve and the dashed extrapolation of the prewetting line meet tangentially. The apparent wetting temperature T'_w should then be located near 600°C , where the prewetting and liquidus line cross, instead of $\sim 500^\circ\text{C}$, where on heating along the liquidus line, a wetting transition was observed for the first time. Here, there is a discrepancy, although the uncertainty in the composition of the wetting transition near 500°C is relatively large. In the context of tetra point wetting, the relevant distance $\Delta\mu$ in the chemical potentials is that with respect to the metastable extension, which is not well known. Yet, on heating along the liquidus line, it must decrease continuously, which explains, at least qualitatively, the increase of the wetting film thickness up to ~ 300 nm near T_M . The observation of the F-centre band at 1.3 eV gives evidence that the salt-rich wetting films are liquid – the crystalline F-center excitation in KCl occurs near 2.2 eV at 298 K. However, the monotectic temperature is 751°C . So, wetting films observed below this temperature must be in an undercooled liquid state. Another problem concerns the magnitude of the wetting film thicknesses $\gtrsim 30 \pm 20$ nm. Using (4.4) – which is valid for screened Coulomb interactions – and taking $\xi \sim 1$ nm, $\sigma_0 \sim 0.1 \text{ J m}^{-2}$ (typical of molten KCl), and $\Delta\mu \sim 10^7 \dots 10^8 \text{ J m}^{-3}$ (representing the distance from the prewetting line) a value of the thickness of $d \sim 3$ nm is obtained, which is an order of magnitude off. A possible reason for this difference may be due to charging of the sapphire surface, an effect that was first considered by Langmuir when describing the capillary rise of an aqueous electrolyte in a charged quartz tubing [2.148]. For alumina in contact with alkali metals, it was found that electrons from the metal are transferred into surface states of alumina, leading to surface charging [4.32]. Assuming

a fully ionized surface, this amounts to a surface charge density of $\sigma_C \sim 1 \text{ C m}^{-2}$; see also [4.33]. From this, a potential drop of $\sim 1 \text{ V}$ results at the charged interface, leading to an additional free energy density of $\sim 1 \text{ J m}^{-2}$; see also [2.149]. Taking this value for σ_0 in (4.4), the estimated wetting film thickness increases to $d \sim 10 \text{ nm}$, which is comparable in magnitude with the experimental results near the prewetting line for $T \gtrsim T'_w$. A final remark concerns the wetting behaviour in other alkali metal–alkali halide melts. The ratio of the liquid/vapour interfacial tensions of salt and metal at their respective melting points shows the following trend: $\sigma_{MX}/\sigma_M = 0.95$ (Na–NaCl), 1.6 (K–KCl), and 2.8 (Cs–CsCl). Although these numbers are restricted to the pure components – there are no measurements of the interfacial tensions for salt-rich or metal-rich solutions – from the trends one can expect that in the Na–NaCl system, adsorption of the salt at the interface with a wall is favoured, whereas this should not be the case in the Cs–CsCl system. Indeed, this has been observed in earlier ellipsometric investigations [4.34].

Wetting in dense mercury vapour has been studied by different methods on chemically distinct substrates: On sapphire by optical reflectivity [4.35] and also ellipsometry [4.36], and on molybdenum and niobium container walls by velocity of sound measurements [4.37]. In both cases, a first-order wetting transition at coexistence has been observed, which is associated with a prewetting line, and a prewetting critical temperature $T_{c,pw}$ of $1,468^\circ\text{C}$ on sapphire and $1,587^\circ\text{C}$ on molybdenum/niobium. The bulk critical temperature of Hg is $1,478^\circ\text{C}$ [2.61]. Fig. 4.11 presents the wetting diagram of fluid Hg together with the bulk liquid and vapour densities at coexistence [4.38]. Evidently, the prewetting line lies completely in the dense vapour phase. At T_w , the coexisting liquid density is near 9 g cm^{-3} , which marks the onset of the metal–nonmetal transition in expanded liquid mercury [4.39]. This indicates that complete wetting films of fluid Hg on sapphire have a nonmetallic character.

At high temperatures, dense mercury vapour has the properties of a dilute plasma [2.61], and therefore the dominant interactions should be exponentially decaying forces rather than algebraic ones of the van der Waals type. So, for an estimate of the wetting film thickness, (4.4) should apply. Considering, for instance, a point on the prewetting line at $1,400^\circ\text{C}$, this has a distance $\Delta\mu$ from the coexistence curve of $\Delta\mu = V_m \Delta p \sim 3 \times 10^6 \text{ J m}^{-3}$, where V_m is the molar volume of the vapour phase at $1,400^\circ\text{C}$ and $\Delta p \sim 25 \text{ bar}$; see also [4.36]. Taking the same values of the parameters ξ and σ_0 as used for K–KCl above yields a prewetting film thickness of $d \sim 6 \text{ nm}$ for fluid Hg at $1,400^\circ\text{C}$. It is comparable in magnitude with the experimental results, which have been determined from optical reflectivities using a homogeneous slab model [4.36]. For $1,400^\circ\text{C}$, a thickness $d \sim 10 \text{ nm}$ is found. These values are an order of magnitude larger than the thick prewetting films, for example, in He on Cs, which is a weak binding substrate [4.40].

Fig. 4.11 Vapour and liquid densities ρ of fluid Hg along the coexistence curve. The prewetting line (red) corresponds to the fluid/sapphire interface and ranges from $T_W = 1,310^\circ\text{C}$ to the prewetting critical point at $T_{c,pw} = 1,468^\circ\text{C}$. Reprinted with permission from Ref. [4.38]



4.4 Surface Freezing in Binary Liquid Alloys

Phase transitions of systems in reduced dimensions have attracted interest in theoretical and experimental research for a long time, and they still do, motivated also by nanoscale systems. This includes phenomena such as 2D melting, surface alloying, grain boundary, and surface melting, as well as surface freezing or surface-induced crystallization. The first rigorous computation of the thermodynamics of a true 2D crystal can be traced back to Onsager [4.41]. Within the Ising model, he found an order–disorder transition at a specific critical temperature characterized by a logarithmic singularity in the specific heat. In the 1970s, Kosterlitz, Thouless, Halperin, Nelson, and Young developed the so-called KTHNY theory of *dislocation-mediated melting in two dimensions* [4.42–4.44]. Applied to a 2D crystal supported on a substrate, they essentially distinguish two configurations: (1) Melting on a smooth substrate, e.g. crystal or film in contact with a liquid; and (2) melting of a film adsorbed onto a crystalline substrate where the strength and periodicity of the substrate potential have to be considered. In both cases, the theory of 2D melting makes specific predictions for the structural changes. On a smooth substrate, the transition should take place in two steps, from a low-temperature solid phase into a *liquid crystal* or hexatic phase that transforms into an isotropic fluid at higher temperature. The hexatic phase is characterized by exponential decay of

translational order, but power-law decay of sixfold orientational order. On a periodic substrate, the hexatic phase should not exist. Depending on the strength of the substrate potential and its mesh, a transition from a commensurate solid to a floating solid film and to a fluid phase occurs with rising temperature. On the other hand, for an incommensurate potential with small strength only the floating solid and fluid phase should exist [4.43].

During the last few decades, numerous experimental investigations and computer simulations have dealt with the problem of 2D melting in different systems such as adsorbed gases on graphite, hard disk fluids, granular and colloidal monolayers, and metal monolayers on oriented metal single crystals – see also the review by Strandburg [4.45]. Instead of summarizing these works, we present vicariously the results of very recent publications of two groups who have studied in detail the structural changes on 2D melting by in situ microscopic methods in two systems that are of direct relevance to the KTHNY theory. The first example has to do with melting of a monolayer of colloidal particles investigated by Maret and coworkers [4.46–4.48]. The system consists of $\sim 3 \times 10^5$ spherical colloidal particles of 4.5 μm diameter, which segregate at the water/air interface. The cores of the particles contain paramagnetic F_2O_3 nanoparticles, so their magnetic interaction can be controlled via an external magnetic field. The ratio of this magnetic energy and the thermal energy $k_{\text{B}}T$ defines an inverse effective temperature scale that can be varied with high precision. With an optical microscope (CCD camera), the positions of all particles have been recorded every 0.25 s over long periods. In this way, a detailed picture has been obtained of the translational and orientational correlation functions and, for the first time, of the topological defects as a function of temperature. It is found that the 2D colloidal crystal melts in two steps, with the hexatic phase being intermediate. The decay of the correlation functions in the separate phases quantitatively agrees with the predictions of the KTHNY theory for 2D melting on a smooth substrate. Furthermore, the microscopic mechanisms of melting including the formation and dissociation of topological defects have been elucidated directly. From the temperature dependence of the elastic moduli, it is concluded that both the crystalline–hexatic and the hexatic–fluid transition are of second order. The second example concerns 2D melting of Ce adatom superlattices stabilized by long-range substrate-mediated electronic interactions on Cu (111) and Ag (111) surfaces [4.49]. This has been investigated by low-temperature scanning tunnelling microscopy (STM), density functional calculations, and kinetic Monte Carlo simulations. Again, the pair correlation and bond-angular correlation functions at variable temperature have been determined with high resolution. The scaling behaviour of these quantities clearly indicates that melting in this system occurs directly from the solid into the fluid phase, without transition through the hexatic phase. This is in accordance with the KTHNY theory for a fine mesh periodic substrate potential [4.43]. Before continuing, it should be noted that other theories of defect-mediated melting and also the theory of grain boundary melting predict first-order transitions [4.50, 4.51].

At liquid/vapour interfaces 2D or quasi-2D phase transitions may occur by surface freezing or surface-induced crystallization. In dielectric liquids such as alkanes

or liquid crystals, these phenomena have been studied quite intensively over the last two decades; see the more recent review by Lang [4.52]. While focusing on liquid metals and their alloys, essentially two situations can be distinguished. If in a binary alloy a liquid layer with composition different from that of the bulk segregates at the surface – for instance, a prewetting film – surface freezing may take place independent of bulk solidification. This case is treated in detail below for the example of Ga-based alloys. On the other hand, if surface layering is pronounced or surface nucleation is strongly enhanced as predicted for liquid Si or Ge [4.53], then surface-induced crystallization can be favoured. We will come back to this later.

As shown in Sect. 4.1, Ga-based liquid alloys are characterized by a first-order wetting transition. Consequently, at the liquid/vapour interface, Bi-rich or Pb-rich wetting films reside on the Ga-rich bulk liquid. At conditions off of liquid–liquid coexistence and at compositions between the prewetting and liquidus line (see Fig. 4.1), these liquid films are in a metastable state and have a thickness of about 1–2 monolayers; this thickness has been derived from the slopes of the Gibbs adsorption isotherms. With reference to the monotectic temperature, the films at lower temperatures exist in an undercooled state. According to classical nucleation theory, the rate of nucleation is strongly increased with the degree of undercooling; see also [2.113]. So, a critical value exists for the temperature of solidification of these wetting films, the so-called surface freezing temperature T_{sf} . Considering the difference $\Delta\sigma$ between the free energies of the surface covered by liquid and by solid films, T_{sf} or the corresponding surface melting temperature, T_{sm} , can be defined by $\Delta\sigma = 0$. This aspect is further detailed below. The surface freezing films should consist of pure Bi or Pb since there is no solubility of Ga in Bi or Pb in the solid state according to the bulk phase diagram.

We begin with experimental investigations of surface freezing in liquid Ga–Bi alloys. Figure 4.12 shows the surface tension of a eutectic $\text{Ga}_{0.9978}\text{Bi}_{0.0022}$ alloy measured by capillary wave spectroscopy at temperatures above the eutectic temperature of 29.5°C [4.54]. Measurements were performed under UHV conditions with liquid samples contained in a molybdenum crucible of 42 mm diameter. The liquid alloy was first equilibrated at temperatures above the monotectic one, the liquid surface was cleaned by Ar-ion sputtering to get rid of spurious oxide impurities, and was cooled with a rate of 8 K h^{-1} . The temperature error was estimated to be $\pm 1\text{ K}$. Capillary wave spectra were recorded at several wave numbers ($215 \leq q/\text{cm}^{-1} \leq 645$) using optical heterodyne detection; for further details, see Sect. A.3. The results in Fig. 4.12 correspond to several cooling and heating cycles on different samples. In the temperature interval from 70°C down to 52°C , the temperature dependence of σ is weak, which is consistent with the literature data. A striking change occurs below 52°C , where the temperature coefficient $\partial\sigma/\partial T$ is clearly positive. This signifies that the surface excess entropy, $S^{(\sigma)} = -\partial\sigma/\partial T$, undergoes a discontinuous change at 52°C , indicating a first-order surface phase transition. A positive value of $S^{(\sigma)}$ – as exists for most liquids – indicates a greater freedom of molecules at the surface than in the bulk. A clearly negative surface excess entropy corresponds to a marked reduction in the available degrees of freedom. Thus, the discontinuity in $S^{(\sigma)}$ observed for the eutectic liquid Ga–Bi alloy leads to the conclusion that at

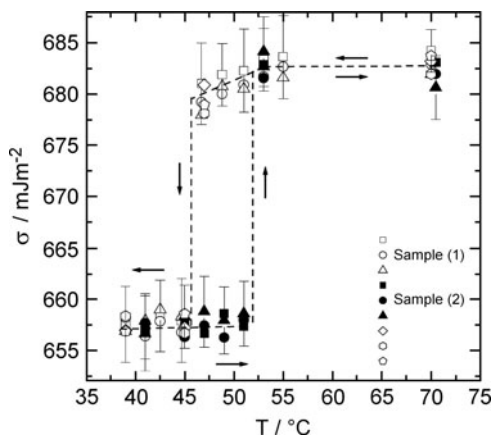


Fig. 4.12 Surface tension σ vs. temperature T of a liquid eutectic Ga–Bi alloy measured by capillary wave spectroscopy; the *open symbols* refer to cooling, the *full ones* to heating, the *dashed lines* are drawn to guide the eye; the surface freezing temperature is $46 \pm 2^\circ\text{C}$, and the eutectic one is 29.5°C . See also [4.54]

52°C , a transition from a bare liquid surface to a more ordered surface structure sets in. It is worth mentioning that a very similar observation has been made for the surface freezing transition in liquid Ga–Pb alloys and in pure liquid alkanes [4.55]. Continuing with Fig. 4.12, near 46°C , the surface tension drops by $\sim 25 \text{ mJ m}^{-2}$ and then stays constant on further cooling down to $\sim 38^\circ\text{C}$. The sharp drop in σ marks the onset of the surface freezing transition at $T_{\text{s,f}} \sim 46^\circ\text{C}$, whereby a thin solid-like film forms at the interface. The mere fact that capillary waves could be detected down to $\sim 38^\circ\text{C}$ strongly indicates that the surface freezing films have a microscopic thickness. This is further supported by the magnitude of the surface excess elastic modulus and shear viscosity of the films, which have been determined from the q -dependence of capillary wave spectra [4.2, 4.54]. On further cooling to below 38°C , the films grow in thickness so that they become invisible for capillary wave spectroscopy well before bulk freezing at T_{E} . In summarizing the observation in Fig. 4.12, it is found that the surface freezing transition in a eutectic liquid Ga–Bi alloy occurs in two steps. With a reduction in temperature, there is first a jump in the surface excess entropy, indicating a transition from a liquid to an ordered surface structure; this is followed by a first-order surface freezing transition with a pronounced hysteresis, whereby surface freezing films form with a microscopic thickness.

Further investigations of surface freezing in Ga–Bi alloys at various compositions have been performed by SHG and plasma generation methods [4.56]. It has been found that the SHG signal with parallel polarized incoming and parallel polarized outgoing second harmonic light, $I_{\text{pp}}(2\omega)$, is especially sensitive to interfacial changes from liquid to solid. A selection of such measurements across the surface freezing transition at different compositions is presented in the upper part of Fig. 4.13. A pronounced hysteresis loop is observed whose width is reduced towards

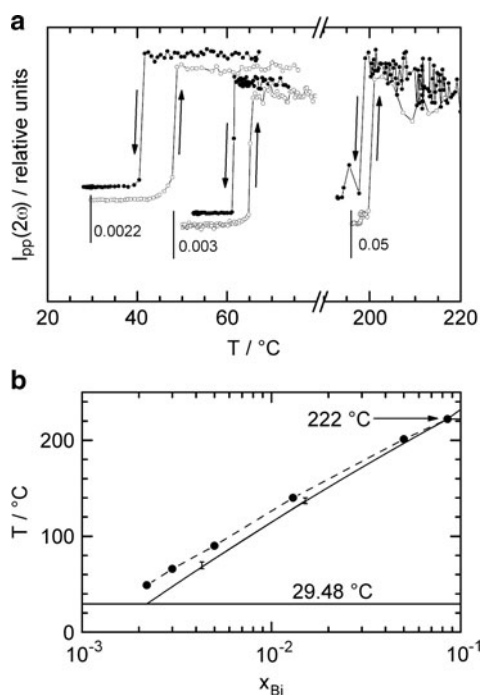


Fig. 4.13 Surface freezing in liquid Ga–Bi alloys at different compositions: (a) variation of SHG signal, $I_{pp}(2\omega)$, and hysteresis behaviour during cooling and heating across the surface freezing transition; the numbers below the heating curves give the Bi mole fractions; the vertical lines indicate the corresponding liquidus temperatures; (b) surface freezing line (*dashed line*) in comparison with liquidus line in the limits between the eutectic and monotectic points; note the error bars in the liquidus curve taken from [4.59]. Adapted from [4.56] and [4.58]

higher temperatures. The round shape of the heating curve during melting of the surface freezing films observed in some cases is remarkable. Such continuous melting has also been reported in ultrathin Bi films deposited on highly oriented graphite with a coverage of 1–10 ML of Bi [4.57]. It is explained by a size distribution of crystallites in the films and a corresponding size-dependent melting. For a Bi film with coverage of ~ 10 ML, melting spans over a temperature range of ~ 10 K [4.57]. A summary of the surface freezing temperatures as obtained by SHG measurements in comparison with the liquidus line [4.58] is plotted in the lower part of Fig. 4.13. Within a temperature uncertainty of ± 2 K, this surface freezing line agrees with that obtained from capillary wave spectroscopy [4.2]. At all compositions, the surface freezing temperatures lie clearly above the liquidus line. The surface freezing and liquidus line seem to merge on approaching the monotectic point. Despite several attempts, no surface freezing transition was detected for compositions below the eutectic. Since the prewetting line should be located near the eutectic point – see the extrapolation in Fig. 4.1 – this result indirectly confirms the assumption that a

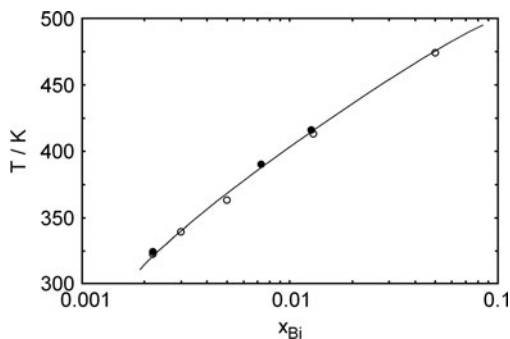


Fig. 4.14 Surface freezing line in Ga–Bi alloys from thermodynamic model calculations (*solid line*) in comparison with experimental results from SHG (*open circles*) [4.56] and capillary wave (*filled circles*) [4.2] measurements. See also [4.16]

liquid prewetting film is the necessary prerequisite for the occurrence of a surface freezing transition in these alloys.

The thermodynamic model described in Sect. 4.1 has also been applied to calculate the surface freezing transition in Ga–Bi alloys [4.16]. In order to find out if at a given composition and temperature a liquid (l) wetting or a solid (s) surface freezing film is preferred at the interface, the difference, $\Delta\sigma$, of the respective interfacial free energies has been analyzed. Using the Gibbs adsorption isotherms, this difference is given by

$$\Delta\sigma = \sigma_l - \sigma_s = -RT \int (\Gamma_{Bi,l}^{(\sigma)} - \Gamma_{Bi,s}^{(\sigma)}) d \ln x - C, \quad (4.9)$$

where $\Gamma_{Bi,l}^{(\sigma)} = x_{F,l} \rho_{F,l} d_l$ and $\Gamma_{Bi,s}^{(\sigma)} = \rho_{Bi,s} d_s$ are the corresponding adsorptions of bismuth at the Ga–Bi liquid/vapour interface. The integration constant C accounts for the difference of the chemical potentials of the two bulk phases composing the films. Calculating the excess chemical potentials of the films according to (4.6) and applying the corresponding equilibrium conditions – equality of Bi chemical potentials in the films and the Ga-rich bulk liquid – yields the thicknesses d_l of the wetting film and similarly for d_s of the surface freezing film. For $\Delta\sigma = 0$, the surface freezing or melting line is obtained. Results of this calculation for the Ga–Bi system are plotted in Fig. 4.14. The agreement between the calculated surface melting curve and experimental data from SHG and capillary wave spectroscopy is remarkable.

Further characterization of surface freezing films has concentrated on their thickness and topology. For the thickness determination, X-ray photoelectron (XPS) and Auger electron spectroscopy (AES) have been used. Experiments were conducted with a commercial Omicron Multiprobe P spectrometer at a base pressure below 10^{-10} mbar. The liquid samples were contained in a cylindrical molybdenum container of 13 mm inner diameter and 8 mm height. These dimensions caused a relatively strong curvature of the liquid surface, which affected the Auger intensity measurements. The necessary corrections, including the shadow effect of the crucible wall, led to an uncertainty of $\sim 30\%$ in the thickness determination by

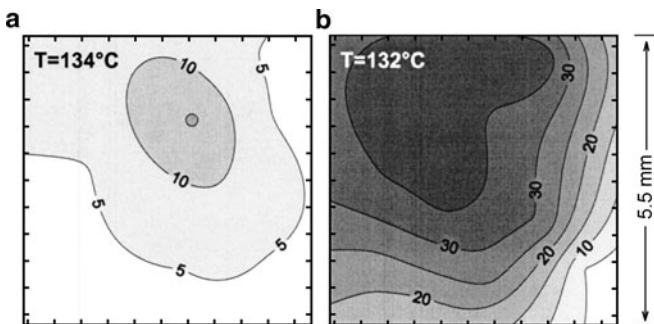


Fig. 4.15 Thickness profiles of Bi-rich surface films on top of a $\text{Ga}_{0.989}\text{Bi}_{0.011}$ alloy determined by Auger spectroscopy: (a) liquid wetting film at 134°C and (b) surface freezing film at 132°C . The numbers give the thickness in Å. See also [4.61]

Auger measurements. In the thickness determinations by XPS and AES, a simple slab model has been used, which relates the thickness d of a surface film to the intensities of the peaks of the spectra. For XPS spectra of a Ga–Bi alloy, the relation is – see also [4.60],

$$\frac{I_{\text{Bi}}/I_{\text{Bi},0}}{I_{\text{Ga}}/I_{\text{Ga},0}} = \left(1 - \exp\left(-\frac{d}{\lambda(E_{\text{Bi}})\cos\Theta}\right)\right) \left(\exp\frac{d}{\lambda(E_{\text{Ga}})\cos\Theta}\right). \quad (4.10)$$

Here, $I_{\text{Bi}}/I_{\text{Ga}}$ and $I_{\text{Bi},0}/I_{\text{Ga},0}$ are the ratios of the Bi and Ga XPS peak intensities measured for the alloy and the pure elemental standards, respectively; the $\lambda(E)_i$ are the inelastic mean free paths of the photoelectrons at the respective excitation energies E_i , and $\cos\Theta$ is an instrumental constant. In (4.10), it is assumed that the film consists of pure Bi and that the bulk can be approximated by pure Ga. In the experiments reported below, the temperature accuracy determined by calibration with pure Bi and Ga is estimated to be $\pm 2\text{ K}$.

Figure 4.15 shows two thickness profiles at the surface of a $\text{Ga}_{0.989}\text{Bi}_{0.011}$ alloy as obtained from AES measurements [4.61]. The surface freezing temperature is 133°C , which is near the expected value of 130°C according to Fig. 4.13. On top of the bulk melt at 134°C , exists a Bi-rich wetting film with a thickness of 1–2 ML. The thickness of the surface freezing film at 132°C varies from 10 to 35 Å, the thicker values being near the centre of the surface. A second example demonstrates the effect of cooling rates on the film thickness; see Fig. 4.16. These results have been obtained by XPS measurements and so the thickness values represent an average over an area of $\sim 10\text{ mm}^2$ corresponding to the cross section of the X-ray beam [4.62]. The variation of film thickness is shown as a function of temperature for an alloy $\text{Ga}_{0.985}\text{Bi}_{0.015}$ with $T_{\text{sf}} \sim 130^\circ\text{C}$. At slow cooling of 5 K h^{-1} , the thickness jumps near T_{sf} from a 5 Å thick wetting film to a 20 Å thick surface freezing film. On cooling down to room temperature, this thickness remains nearly constant. During reheating, a strange reduction of the thickness appears well below T_{sf} . Surface freezing films that are an order of magnitude thicker are achieved if the same

Fig. 4.16 Effect of cooling rates and temperature on the thickness of surface freezing films in a $\text{Ga}_{0.985}\text{Bi}_{0.015}$ alloy; the thickness d has been determined by XPS. See also [4.62]

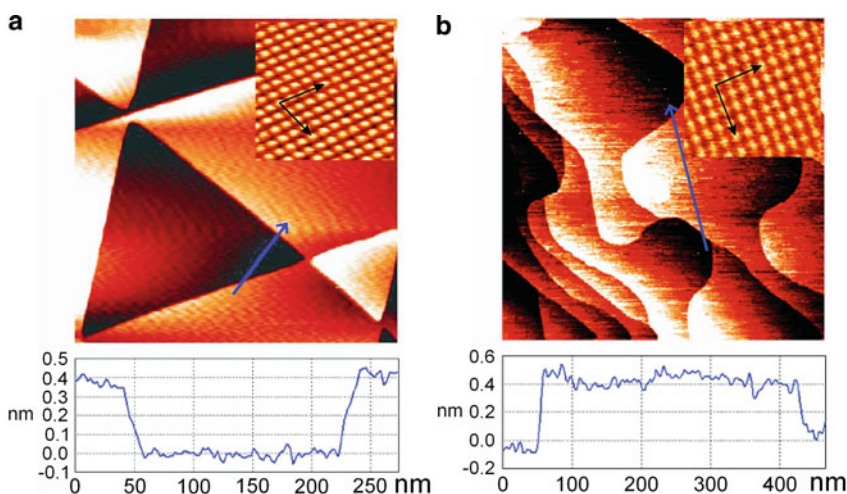
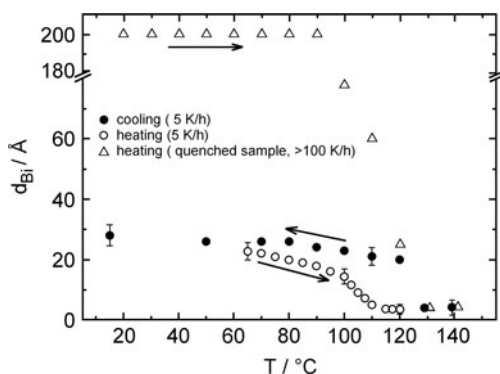
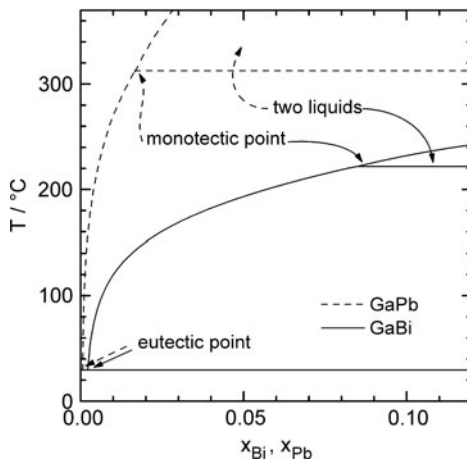


Fig. 4.17 STM images ($1,000 \times 1,000 \text{ nm}^2$, $I_t = 0.22 \text{ nA}$, $V_{\text{bias}} = 0.2 \text{ V}$) presenting atomically flat terraces of surface freezing films of Ga–Bi alloys cooled down to 25°C . The *insets* show atomically resolved pictures ($5 \times 5 \text{ nm}^2$); the *z*-profiles below the STM images are taken along the *arrows*; (a) $\text{Ga}_{0.985}\text{Bi}_{0.015}$ alloy, hexagonal structure, $d = 0.42 \pm 0.02 \text{ nm}$, terrace height = $0.4 \pm 0.04 \text{ nm}$; (b) $\text{Ga}_{0.997}\text{Bi}_{0.003}$ alloy, square lattice, $d = 0.5 \pm 0.03 \text{ nm}$, terrace thickness = $0.4 \pm 0.05 \text{ nm}$. See also [4.62]

sample is quenched using a rate of $\sim 100 \text{ K h}^{-1}$. This indicates that the evolution of the surface freezing films depends on the thermal history.

The surface structure of surface freezing films was probed in situ by UHV variable temperature scanning tunnelling microscope (STM). Typical large-scale STM images and atomically resolved pictures (see insets) measured at room temperature are given in Fig. 4.17 [4.62]. Figure 4.17a, which corresponds to a $\text{Ga}_{0.985}\text{Bi}_{0.015}$ alloy, shows the surface structure of the trigonal Bi (0 0 0 1) plane with a lattice constant of $d = 0.42 \pm 0.02 \text{ nm}$. The different structure of the second alloy, $\text{Ga}_{0.997}\text{Bi}_{0.003}$, is remarkable, and can be described by a square lattice with a lattice constant of $0.5 \pm 0.03 \text{ nm}$; see Fig. 4.17b. This unusual structure, which is not

Fig. 4.18 Comparison of the Ga-rich end of the phase diagram of Ga–Bi [4.59] with that of Ga–Pb [4.64]. See also [4.58]



consistent with crystalline bismuth, indicates that the films do not exist in a thermal equilibrium state. In both cases, extended atomically flat terraces are observed – see also the z -profiles below the STM images. Altogether, the STM results confirm that the surface films consist of pure Bi, which was assumed before on the basis of the bulk phase diagram. Furthermore, the large terraces indicate that the films exist in a well-ordered crystalline structure. Heating the films of Fig. 4.17 by 40 K above the eutectic temperature produces a relatively high density of cracks on the atomic scale, but the gross features of the surface structure such as the extension of terraces and the step edge heights remain. In particular, this behaviour shows that the surface freezing films are not affected by the bulk melting at T_E , but behave as an independent surface phase.

In the case of gallium–lead alloys, the situation is a bit more complicated. Problems may arise in relating surface freezing transitions with specific bulk phase transitions along the liquidus or the metastable binodal line. There are two main reasons for this: (1) The liquidus rises very steeply at the very Ga-rich end (see Fig. 4.18) with the eutectic being at $x_E \sim 5 \times 10^{-5}$ [4.63]; taking into account the possibility of oxide contamination, these low concentrations represent a real challenge to the experimentalist. (2) In comparison with the Ga–Bi system, the Ga-rich end of the Ga–Pb phase diagram is not as well characterized experimentally. Despite the different thermodynamic assessments in the literature, there remains a larger uncertainty in the phase diagram of Ga–Pb in comparison with that of Ga–Bi. Similar arguments apply for Ga–Tl alloys.

In a recent publication by Chatain et al., a re-assessed phase diagram of the Ga-rich end of Ga–Pb has been discussed [4.65]. On the basis of this diagram, the authors claim that most of the studies on surface freezing in Ga–Pb alloys reported in the literature do not belong to conditions in the homogeneous liquid phase, but have been conducted in undercooled states near the metastable bimodal. This may indeed be the case. But still, the surface freezing transitions observed in Ga–Pb liquid alloys exhibit the main characteristics of those in Ga–Bi alloys, which are

detailed below. Besides these uncertainties in the phase diagram, in experiments with alloys very dilute in lead, further error sources that can reduce the amount of dissolved Pb must be envisaged: (1) Intense Ar-ion sputtering, which is usually done in situ, before the actual measurements, to clean the surface; since Pb is enriched at the liquid/vapour interface, sputtering leads to a loss of this component. (2) Oxide impurities affect both the concentration scale and the phase diagram. So, it cannot be excluded that in some of the experiments reported in the literature, the real lead concentration is lower than the given nominal one.

Investigations of surface freezing in liquid Ga–Pb alloys by capillary wave spectroscopy show a behaviour very similar to that in Ga–Bi alloys. For instance, for an alloy with $x_{\text{Pb}} = 0.00063$, a discontinuous change of the surface entropy is found, followed by a first-order surface freezing transition with a surface melting temperature of 90°C [4.2]. An interesting experiment on surface freezing of a dilute Ga–Pb alloy has been reported by Rice and coworkers [4.66]. Employing X-ray reflectivity and grazing incidence X-ray diffraction, they found that the liquid/vapour interface of an alloy with a nominal composition $x_{\text{Pb}} = 0.00054$ is stratified for several atomic diameters into the bulk liquid. Up to $\sim 58^\circ\text{C}$, the outermost Pb monolayer is in an ordered hexagonal phase; at higher temperatures, it undergoes a first-order transition to a hexatic phase that remains stable up to 76°C . A hexagonal surface structure has also been observed by STM at room temperature on a surface freezing film of a $\text{Ga}_{0.996}\text{Pb}_{0.004}$ alloy [4.62]. On comparing the results of capillary wave spectroscopy with those of the X-ray reflectivity experiment, close similarities become evident. On the one hand, a discontinuity of the surface excess entropy is found, which can be interpreted by a variation of the surface from a liquid to an ordered structure. On further cooling, a first-order surface freezing transition follows, which is characterized by hysteresis behaviour. From the X-ray reflectivity and grazing incidence diffraction studies, it has been inferred that a fluid to hexatic phase transition at higher temperatures is separated from a first-order transition to a hexagonal 2D solid. So, in both cases, a two-step mechanism is suggested for surface freezing in Ga–Pb alloys. Here, an analogy becomes visible with 2D melting, although, in general, the KTHNY theory predicts continuous transitions. With respect to the hexatic phase in Ga–Pb alloys, it is interesting to note that this has also been found by molecular dynamics simulations at the liquid/vapour interface of pure Au [4.67]. At strong undercooling conditions, these calculations indicate a transition from a fluid to a hexatic surface structure.

Finally, a critical comment on the thickness of surface freezing films in Ga–Pb alloys and, more generally, in Ga-based alloys is necessary. Figure 4.19 shows results obtained by XPS and Auger measurements of a $\text{Ga}_{0.9948}\text{Pb}_{0.0052}$ alloy [4.68]. The indicated surface freezing temperature $T_{\text{sf}} = 183.5^\circ\text{C}$ at this composition stems from separate SHG measurements [4.69]. In this experiment, the sample surface area was $\sim 0.5\text{ cm}^2$, the base pressure $\sim 10^{-10}$ mbar, and in situ electron spectroscopy of the sample surface did not reveal any oxide contaminations. As can be seen in Fig. 4.19, the film thickness above T_{sf} has a constant value corresponding to 1 ML of a Pb-rich liquid prewetting film at conditions off of liquid–liquid coexistence. The occurrence of such a thin wetting film down to $\sim 184^\circ\text{C}$ is evidence

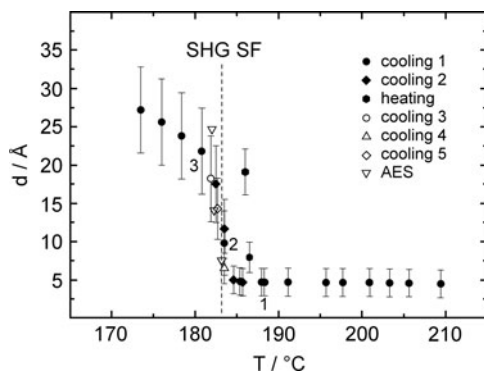


Fig. 4.19 Temperature dependence of wetting and surface freezing film thickness measured at the liquid/vapour interface of a dilute $\text{Ga}_{0.9948}\text{Pb}_{0.0052}$ alloy by XPS and AES. The indicated surface freezing temperature of 183.5°C stems from separate SHG measurements [4.69]. See also [4.68]

that T_{sf} of 183.5°C is neither near the metastable bimodal nor near the liquidus line. At T_{sf} , the thickness jumps to a value of $\sim 10 \text{ \AA}$ and on further cooling to 175°C increases to $\sim 25 \text{ \AA}$. The cooling rate in this experiment was extremely low with a time interval between neighbouring points of $\sim 3 \text{ h}$. Qualitatively, these results compare well with those of the Ga–Bi alloy at slow cooling conditions as given in Fig. 4.16. However, in independent ellipsometric investigations of surface freezing in liquid Ga–Pb and Ga–Tl alloys, a film thickness of $\sim 40 \text{ nm}$ was found for a $\text{Ga}_{0.9944}\text{Pb}_{0.0054}$ alloy at a temperature slightly below $T_{\text{sf}} = 188^\circ\text{C}$ [4.70]. So, there is a discrepancy that has not yet been solved. If oxide impurities played a role, they should have mattered more in the ellipsometric measurement as here the sample surface of $\sim 13 \text{ cm}^2$ was relatively large and the base pressure in the vacuum chamber was $\sim 10^{-9} \text{ mbar}$.

In conclusion, surface freezing at the liquid/vapour interface of Ga-based alloys takes place in two steps: first, a transition from a fluid prewetting film to an ordered, presumably hexatic phase occurs, which, on further cooling, is followed by a surface freezing transition characterized by distinct hysteresis behaviour. Both transitions are of first order. At the surface freezing temperature quasi-2D crystalline films grow with a thickness of a few monolayers. They are of the pure state of that component, which is segregated at the interface in forming the fluid wetting phase. Thus, there is a distinct link between the prewetting and the surface freezing transition.

Different mechanisms have been considered for surface or surface-induced crystallization in supercooled liquids and in liquid alloys not exhibiting a wetting transition. In a molecular dynamics simulation of undercooled liquid silicon and germanium, Li et al. show that surface-induced nucleation plays a key role in the freezing process of these systems [4.53]. The presence of the free surface may enhance the nucleation rate by several orders of magnitude with respect to that in the bulk. The authors also give a simple explanation for the nucleation mechanism by which the energy barrier for nucleation is lowered at the liquid surface. As in tetrahedral liquids, like Si or Ge, the melting curve has a negative slope, $(\partial T / \partial p)_{\text{coex}} < 0$,

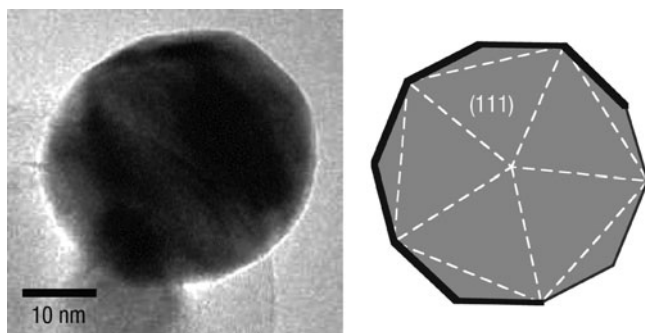


Fig. 4.20 *Left*: TEM image of a crystalline $\text{Au}_{72}\text{Ge}_{28}$ cluster that underwent extensive transient surface faceting in the liquid state; *right*: Projection of the icosahedral motif bound by (111) facets matching the facets of the cluster shown to the *left*. Reprinted with permission from Macmillan Publishers Ltd: Nature Materials, see Ref. [4.71], copyright (2010)

and the density is decreased on solidification. So, the free surface can accommodate volume more easily, owing to surface tension, and nucleation in its vicinity is preferred. The authors also point out that this nucleation mechanism is homogeneous and that they do not find any signature of surface layering.

Two experimental investigations on surface crystallization in Au–Ge and Au–Si liquid alloys have been reported recently. In the first experiment, nearly free-standing zeptolitre (10^{-21} l) liquid $\text{Au}_{27}\text{Ge}_{28}$ droplets were produced and their liquid–solid phase transformation was observed by transmission electron microscopy [4.71]. From the observed liquid-state surface faceting – see Fig. 4.20 – of the undercooled drops, it is concluded that a nucleationless surface-induced process governs crystallization instead of nucleation in the interior. In the second experiment, the liquid/vapour interface of a bulk liquid eutectic $\text{Au}_{82}\text{Si}_{18}$ alloy was probed by X-ray reflectivity and grazing incidence X-ray diffraction [4.72]. Above the eutectic temperature of 360°C , the X-ray measurements reveal a crystalline monolayer with a Au_4Si_8 structure at the surface, which is stable up to 371°C . Below this monolayer, 7–8 well-defined layers occur that are liquid in the lateral direction but ordered in the normal direction. This indicates that surface crystallization in this alloy is accompanied by a pronounced interfacial layering. However, the origin of surface crystallization in this alloy is not yet clear. An XPS analysis of the same $\text{Au}_{82}\text{Si}_{18}$ sample used in the X-ray measurement reveals an enrichment of Si at the liquid/vapour interface of $x_{\text{Si}}^{(\sigma)} \sim 0.6$ at 370°C , which is consistent with the compound composition Au_4Si_8 [4.73]. Yet another oxide peak with a surface concentration of ~ 4 at% has been found. So, it cannot be excluded that in this alloy surface, crystallization is induced and increased by oxide impurities; see also [4.74].

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Chapter 5

Electrified Ionic Liquid/Solid Interfaces

Abstract At an electrified interface the double-layer problem plays a key role. Its characteristics for ionic liquids are discussed on the basis of recent experimental and theoretical investigations and are contrasted with the classical GCS model for aqueous electrolytes. Emphasis of this chapter is on 2D and 3D electrochemical phase formation and growth at the ionic liquid/electrode interface studied by in situ scanning probe methods. The concept of underpotential (UPD) deposition is briefly introduced and for the example of Ag UPD on Au(111) the different behaviour in an ionic liquid and aqueous electrolytes is described. Phenomena of surface alloying and the underlying spinodal mechanism are treated in more detail. The characteristic spinodal structures and their evolution during surface alloying in Zn–Au(111) and Cd–Au(111) are presented. Nanoscale electrochemical phase formation and growth of metal and semiconductor clusters from ionic liquid electrolytes is the topic of the last section. Selected examples are Al electrodeposition on Si(111):H, Ni, and Fe nanocrystal growth; Co–Al bulk alloying; and AlSb and ZnSb compound semiconductor deposition. The chapter ends with an example of a thickness induced metal–nonmetal transition in ultrathin Ge films electrodeposited on Au(111) or Si(111):H.

5.1 Characteristics of Electrochemical Interfaces

The electrode/electrolyte interface is of fundamental significance in electrochemistry. At this interface, charge transfer takes place and changes in the electrical and chemical potentials occur, which drive electrochemical reactions. For aqueous electrolytes of dilute and moderate concentrations of dissolved ions, a relatively detailed description of the structure and properties of the electrified solid¹ (metal)/liquid interface exists. This is based on the double-layer (DL) model as described by the Gouy–Chapman–Stern theory; see e.g. [5.1]. It gives insight into the potential profile

¹ The solid electrode can be metal, semi-metal such as highly oriented pyrolytic graphite (HOPG), or semiconductor, but here we focus on metal electrodes.

across the interface and its differential capacitance. In the case of Coulomb liquids, molten salts, and ionic liquids, knowledge of the interfacial electrochemical characteristics is less advanced, both experimentally and theoretically. For instance, experimental results of the capacitance–potential curves for different ionic media show no coherent picture and are partly conflicting. Although experimental data for classical inorganic molten salts indicate a clear minimum at elevated temperatures [5.2], recent measurements on various room temperature ionic liquids exhibit both maxima and minima in the capacitance–potential curves [5.3, 5.4] in some cases for the same ionic liquid [5.5, 5.6]. In most of these studies, the effect of the state of the electrode material, for example, whether crystalline or not, has not been considered. On the theoretical side, progress has been made recently by different simulation studies including *ab initio* based simulations [5.7–5.11]. A mean-field lattice-gas model has been developed for the ionic liquid double layer that takes into account the finite volume occupied by the ions and makes predictions for the variation of the differential capacitance as a function of the lattice saturation [5.12]. In the following, we briefly summarize the main features of the classical double-layer model and contrast them with the recent theoretical results for the electrified metal/ionic liquid interface; see also Fig. 5.1.

In the double-layer model, the electrode/electrolyte interface is approximated by a plate condenser where one plate is the metal electrode with its surface excess charge, σ_M , and the other plate is built by the solution phase with charge density $\sigma_s = -\sigma_M$. In solution, one can distinguish two zones of ions: A Helmholtz layer formed by ions or solvated ions at close approach to the electrode and the diffuse layer constituting the remaining ions; see Fig. 5.1a. Since the charge density inside the Helmholtz layer is assumed zero, the potential ϕ decreases linearly with the distance z from the electrode according to the Poisson equation. In the diffuse layer, the distribution of ions at thermal equilibrium with respect to the electrode is determined by the Boltzmann distribution and so $\phi(z)$ is obtained from solving the Poisson–Boltzmann equation; see [5.1]. At a highly charged electrode (ϕ_M high) $\phi(z)$ decays steeply away from the electrode, whereas at lower ϕ_M -values it decays exponentially, $\phi/\phi_M = -\exp(-kz)$, with k^{-1} being the Debye length or the characteristic thickness of the diffuse layer – for example, in an aqueous 1:1 electrolyte at 300 K, $k^{-1} \sim 3 \text{ \AA}$ for 1 M and $\sim 30 \text{ \AA}$ for 10^{-2} M solutions; see Fig. 5.1a. From knowledge of $\sigma_M(\phi_M)$, the differential capacitance C_d of the diffuse layer can be calculated. It is characterized by a minimum at the potential of zero charge, E_{PZC} , and a steep rise on either side. Within the Gouy–Chapmann–Stern model, the capacitance of the solution is given by: $C_s^{-1} = C_H^{-1} + C_d^{-1}$. Since $C_H = \epsilon\epsilon_0 z_H^{-1}$ is independent of potential, the differential solution capacitance approaches C_H further away from E_{PZC} ; see Fig. 5.1a.

In contrast to aqueous electrolytes, molten salts and ionic liquids are characterized by a well-defined ordering of oppositely charged ions at the charged interface that extends over several ionic diameters into the bulk liquid; see also Figs. 2.19 and 2.20. The effect of these charge oscillations on the electrochemical charge transfer and the mean electrical potential has been studied in several simulation calculations by Madden and coworkers [5.8, 5.9]. Figure 5.1b shows a sketch of the

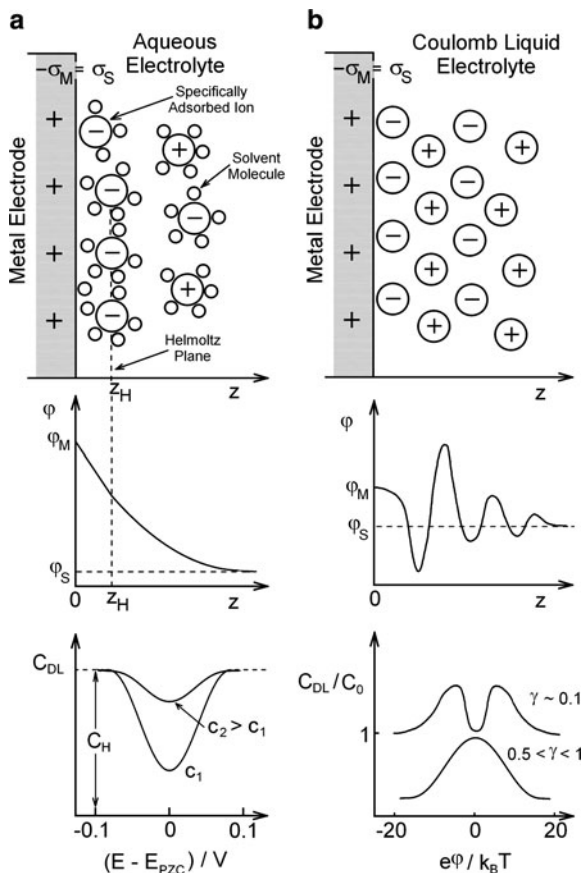


Fig. 5.1 Schematic pictures of the metal/electrolyte interface for (a) an aqueous electrolyte and (b) a molten salt or ionic liquid electrolyte. In (a), the solution phase is divided into the compact Helmholtz layer and the diffusion layer. The potential profile ϕ in the Helmholtz layer is linear and it decays exponentially in the diffuse layer provided that the metal potential ϕ_M is sufficiently low; see [5.1]. The differential capacitance C_{DL} of the solution side of the double layer (DL) is treated as a series network of Helmholtz, C_H , and diffuse layer capacitance C_d , where the latter exhibits a typical V-shape with a minimum at the potential of zero charge, E_{PZC} . At larger values of C_d , the potential-independent Helmholtz capacitance takes over. In (b), the typical charge ordering of an ionic melt near a charged metal electrode is illustrated. The corresponding potential profile is characterized by the out-of-phase oscillations of the densities of oppositely charged ions. For complete screening of the electrode potential, several layers of ions are necessary. In the last diagram, the behaviour of the differential capacitance, C_{DL}/C_0 vs $e\phi / k_B T$, is sketched as predicted by mean-field theory for ionic liquids [5.12]. The parameter $\gamma = \langle N \rangle / N$ is the ratio of the total number of ions in the bulk, $\langle N \rangle$, and the total number of available sites N .

electrostatic potential profile calculated for an Al electrode in contact with a LiCl melt [5.9]. In this ab initio based simulation, induced dipole interactions among the ions and with the electrode surface have been taken into account. As can be seen, the potential profile strongly reflects the charge oscillations of the ionic melt structure.

It takes about four interionic distances in LiCl before the potential in the bulk liquid is reached. The differential capacitance calculated for the same system shows a maximum near the potential of zero charge. In the mean-field lattice-gas model of concentrated electrolytes, the entropy of mixing is calculated from the number of combinations for the distribution of $\langle N \rangle$ cations and anions on N available lattice sites [5.12]. With this entropy the free energy of the system and the concentrations of cations and anions are determined. The latter define the charge density of the solution, $\sigma_s = e(c_+ - c_-)$, from which the potential curve $\phi(z)$ can be calculated via the Poisson equation. Schematic diagrams of the corresponding differential capacitance curves are given in Fig. 5.1b. Depending on the lattice-saturation parameter, $\gamma = \langle N \rangle / N$, both bell-shape and camel-shape curves are possible. For densely packed Coulomb liquids γ is near 1.

In the comparison so far, mainly the electrostatic screening in solution and its effect on the surface excess charge have been considered. However, in realistic systems, additional influences play an important role. For example, if ions are bound to the electrode surface – so-called specifically adsorbed ions; see Fig. 5.1 – this has an impact on σ_M and can strongly alter the potential profile in the vicinity of the interface; see also [5.1]. The corresponding potential shifts are not accounted for by the simple electrostatic double-layer model. Another important influence concerns the surface structure of the metal electrode. If single-crystal electrodes are used, the differently oriented surfaces such as Ag(111) or Ag(100) have distinct surface free energies that cause shifts in the potential and the corresponding capacitance curves. On cycling the electrode potential, the surface structure can change significantly – for instance, a reconstructed Ag(111) surface can be lifted to form the Ag(100) structure – which is accompanied by large changes in the capacitance curves [5.13]. Furthermore, adsorbed ion layers may undergo 2D phase transitions with varying potential. As an illustration, Fig. 5.2 shows the ordered structures of adsorbed PF_6^- anions at different potentials recorded by in situ electrochemical STM (see Sect. A.5) at the electrified Au(111)/[C₄mim][PF₆] interface [5.14]. At potentials positive of -0.4 V vs. Pt quasi-reference, the PF_6^- anions on Au(111) form a nearly hexagonal Moiré pattern (Fig. 5.2a), whereas below -0.4 V the structure transforms into a $\sqrt{3} \times \sqrt{3}$ phase. Very similar STM observations have been reported recently for the cation adsorption at the electrified Au(100)/[C₄mim][BF₄] interface [5.6]. It is interesting to note that in the *ab initio* calculations of the Al(solid)/LiCl (melt) interface a potential-induced phase transition is found in the first layer of adsorbed ions [5.9]. This is associated with a relatively sharp peak in the interfacial capacitance.

In the following sections, we concentrate on 2D and 3D electrochemical phase formation and phase transitions at the electrified metal/ionic liquid interface. Ionic liquids, in comparison with aqueous electrolytes, have some specific properties that are an advantage in electrodeposition experiments; see also [5.15]. Besides their low melting points and extreme low vapour pressures, they exhibit in the pure state negligible gas or hydrogen evolution, which in aqueous electrolytes can interfere with the structure formation and quality of electrodeposits. In particular, the electrochemical

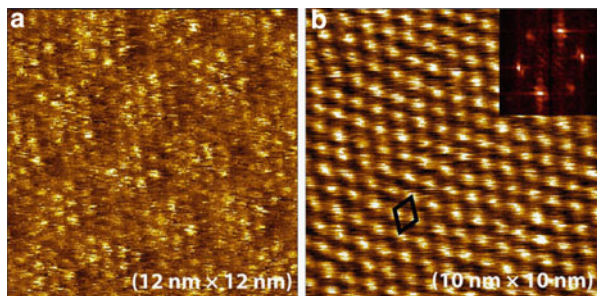


Fig. 5.2 High-resolution STM images of PF_6^- adsorbed on Au(111) at different potentials vs. Pt quasi-reference. (a) STM image at 0 V revealing the structure of the anions and their long-range packing forming a nearly hexagonal Moiré pattern with a nearest neighbour distance of ~ 2.5 nm; (b) At -0.4 V, a $\sqrt{3} \times \sqrt{3}$ structure occurs with a distance of 0.5 ± 0.02 nm, which is almost $\sqrt{3}$ times the distance of the underlying Au(111) substrate; the inset shows the Fast Fourier Transform of the structure ($V_{\text{bias}} = 0.8$ V, $I_t = 0.35$ nA). See also [5.14]

potential window, the difference between the oxidation and reduction potential limits, in ionic liquids can be as high as ~ 6 V. This enables electrodeposition of light metals such as Al or Ti and also elemental and compound semiconductors [5.16]. However, in many, nonspecifically designed ionic liquids, the solubility of metal salts is relatively low, which may cause a problem in practical applications.

5.2 Two-Dimensional Electrochemical Phase Formation and Phase Transitions

Electrocrystallization of a metal (Me) at the interface of an electronically conducting substrate (S) with an electrolyte containing metal ions (Me^{z+}) takes place in several stages:

1. Me^{z+} ions are reduced to Me adatoms that are adsorbed at energetically favourable sites of S, specific defects such as kink sites.
2. Subsequent Me adatoms are adsorbed at these sites forming 2D or 3D critical nuclei.
3. In the final stage, 2D or 3D growth leads to formation of a metal film or a bulk crystal.

For all steps, the interaction with the electrolyte plays an important role. Depending on the electrolyte, differences have to be considered not only in the deposition potentials, but also in the nucleation and growth kinetics; see also [5.17].

In cases where $S = \text{Me}$, the basic equilibrium reaction at the Me^{z+}/Me electrode is as follows:



where e is the electronic charge. At equilibrium, the electrochemical potentials of species i in the solution and at the metal electrode phase are equal, i.e. $\eta_i(\text{Me}) = \eta_i(\text{Me}^{z+})$, where $\eta_i(\alpha) = \mu_i(\alpha) + z_i F \phi(\alpha)$ and $\mu_i(\alpha)$ is the chemical potential of species i in phase α and F is the Faraday constant. From this equilibrium condition, the potential difference across the interface is given by

$$\Delta\phi = \phi(\text{Me}) - \phi(\text{Me}^{z+}) = \Delta\phi^\theta + (RT/zF) \ln a(\text{Me}^{z+}). \quad (5.2)$$

Here, $\phi(\text{Me})$ denotes the potential in the metal phase and $\phi(\text{Me}^{z+})$ that in the bulk electrolyte, $a(\text{Me}^{z+})$ is the activity of ions in solution, and the activity of bulk metal is $a(\text{Me}) = 1$ by convention. The standard Galvani potential $\Delta\phi^\theta$ corresponds to $a(\text{Me}^{z+}) = 1$. The potential difference $\Delta\phi$ cannot be measured directly since a voltmeter needs two connections. Therefore, two electrode interfaces have to be combined, thus forming an electrochemical cell. The electromotive force (EMF) or potential difference E of this cell is then given by the difference of the right-hand and left-hand electrode potentials, $E = E_r - E_l$. Taking the left-hand electrode as reference electrode and setting arbitrarily $E_l = 0$, then $E = E_r = \Delta\phi$, i.e. $\Delta\phi$ is given by the Nernst equilibrium potential E . In this derivation, it is assumed that the contact potentials between the two metal contacts of the voltmeter and the metal electrodes of the cell cancel out.

In an electrodeposition experiment, the Me^{z+}/Me electrode – also called the working electrode – is part of an electrochemical cell through which current with density j is flowing. Under these conditions, the electrode potential E is shifted to a value $E(j)$, which is related with the overpotential η by

$$\eta = E(j) - E. \quad (5.3)$$

The overpotential η is required to overcome hindrance of the overall electrode reaction by partial reactions coupled with the current flow, such as charge transfer, diffusion, chemical reactions, and the crystallization process, whereby atoms are incorporated into the crystal lattice. The slowest of these reactions is rate-determining and defines η . Bulk metal deposition occurs usually at cathodic overpotentials, $\eta < 0$, $E(j) < E$, also termed overpotential deposition (OPD). In contrast to this metal dissolution takes place at anodic overpotentials, $\eta > 0$. The same holds for bulk metal deposits on a foreign substrate S, as long as the Me^{z+}/Me electrode potential is defined by (5.2). In cases where the metal–substrate interaction is stronger than that between metal atoms in deposited metal, 2D or quasi-2D metal films can be deposited on S at potentials positive of the Nernst potential E , i.e. $E(j) > E$. This is called underpotential deposition (UPD) of Me on S.

A relatively simple, but useful, tool to obtain information about electrode reactions is cyclic voltammetry (CV). With this technique, the electrode potential $E(t)$ is swept linearly at a constant scan rate v in a given potential range starting at $E(t_0)$, so that at time t the potential is $E(t) = E(t_0) - v(t - t_0)$. If, for example, the potential is swept in the cathodic direction and passes the Me deposition potential at $E(j)$, the answer of the system is a peak in the electric current density.

Similarly, on reversing the sweep direction, a current peak occurs at the anodic oxidation or Me dissolution reaction. Thus, a cyclic voltammogram represents the current–potential dependence of the electrode reactions. For reversible reactions, the peak potential is independent of the scan rate and the peak current varies proportional to $v^{1/2}$ for diffusion-controlled reactions and proportional to v for a reversible adsorption–desorption reaction.

In the following, the focus is on Me UPD processes at the electrified ionic liquid/Au(111) interface. For the example of Ag UPD, comparative investigations of 2D phase formation in aqueous and ionic liquid electrolytes are discussed. Next, the phenomenon of surface alloying (e.g. Zn or Cd UPD on Au(111)) is described in detail.

The cyclic voltammograms of Ag UPD on a single crystal Au(111) surface obtained in an aqueous electrolyte (1 mM Ag_2SO_4 + 0.1 M H_2SO_4) and an ionic liquid (2 mM AgCl in AlCl_3 – $[\text{C}_4\text{mim}][\text{Cl}]$ (58:42) melt) at scan rates of 30 and 50 mVs^{-1} , respectively, are compared in the two upper panels of Fig. 5.3. Included in this figure are the corresponding desorption isotherms, the charge–potential curves $Q(E)$. They have been determined by linear sweep voltammetry using the so-called loop technique [5.17]. The electrochemical measurements yield the following main results [5.18]. In the aqueous electrolyte, two distinct interfacial processes occur indicated by two sharp reduction or deposition peaks at 520 and 25 mV and the corresponding oxidation or stripping peaks at 528 and 50 mV. These observations are in good agreement with the literature data [5.19, 5.20]. A detailed analysis of the anodic peak at 528 mV shows that it can be decomposed into two components at 528 and 539 mV, respectively [5.21]. At the respective UPD processes, the desorption isotherms exhibit distinct steps of $55 \pm 10 \mu\text{C cm}^{-2}$ (UPDI) and $190 \pm 30 \mu\text{C cm}^{-2}$ (UPDII) – see Fig. 5.3c – where the main error contribution is due to the double-layer charging correction. Careful inspection of the charge increase at UPDI shows that this is not a discontinuous step function as expected for a first-order phase transition below the critical temperature. This can have different reasons: Either co-adsorption of sulphate ions still exists at this potential, or the adsorbate–adsorbate interaction in the deposited Ag layer is weak resulting in a low critical temperature. Taking into account that for a pseudomorphic dense Ag monolayer the theoretical charge density is $222 \mu\text{C cm}^{-2}$, a more open adlayer with a coverage of 0.25 ML is expected at the UPDI process.

Continuing with the measurements in the ionic liquid, the CV scans have a clearly different appearance (Fig. 5.3b). In the potential range between 600 and 500 mV, a weak, broad cathodic wave (C_2) is indicated, which unambiguously can be assigned to AlCl_4^- anion adsorption as shown by the in situ STM images below; see Fig. 5.5. CV measurements of the pure ionic liquid suggest that this anion adsorption extends over a wider range of potentials from ~ 300 to ~ 600 mV [5.18, 5.21]. The first Ag UPD arises at the reduction wave C_3 with a peak potential of 410 mV. Linear sweep voltammograms of C_3 and C_4 are proportional to the sweep rate, which indicates that these reactions are adsorption controlled [5.21]. A second UPD process sets in at 120 mV where again the peak currents depend linearly on the sweep rate. From the desorption isotherm, it is found that the charge

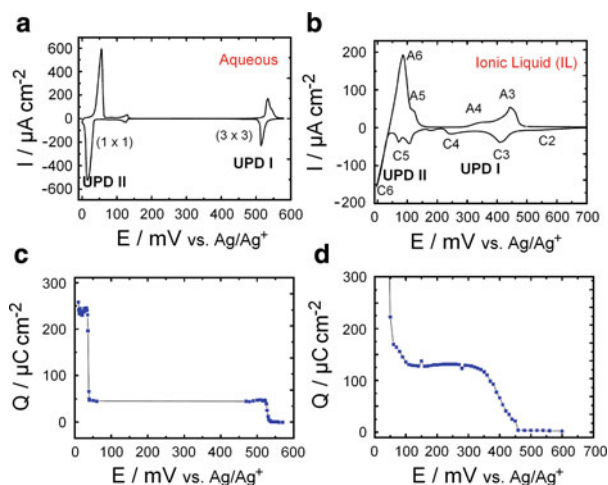


Fig. 5.3 Cyclic voltammograms (a, b) and charge–potential desorption isotherms $Q(E)$ (c, d) of Ag UPD on a single crystal Au(111) substrate; (a) and (c) correspond to aqueous electrolytes of 1 mM Ag_2SO_4 in 0.1 M H_2SO_4 with CV sweep rate of 30 mV s^{-1} ; (b) and (d) were measured with an ionic liquid of 2 mM AgCl in $\text{AlCl}_3 - [\text{C}_4\text{mim}][\text{Cl}]$ (58:42) with CV sweep rate of 50 mV s^{-1} . Temperature in all cases was 298 K. See also [5.21]

increases continuously to $131 \pm 25 \mu\text{C cm}^{-2}$ during the first UPD process and reaches a value of $220 \pm 42 \mu\text{C cm}^{-2}$ near 50 mV. On approaching the Nernst potential, $Q(E)$ increases steeply, indicating incipient 3D deposition.

In conclusion, cyclic voltammetry and desorption measurements exhibit differences between the 2D electrochemical phase formation of Ag on Au(111) in an ionic liquid and an aqueous electrolyte. The final stage, in both cases, is the formation of a densely packed Ag monolayer that occurs at low underpotential. The interesting question is now which structural changes belong to the different UPD processes. This has been studied by in situ electrochemical scanning tunnelling microscopy (EC-STM; see Sect. A.5), which is presented next, beginning with results of aqueous electrolytes. Figure 5.4 shows in situ STM images of Ag deposited at 500 mV at the Au(111)/aqueous electrolyte interface [5.18]. The large-scale picture reveals a compact Ag adlayer containing a small number of monoatomically deep holes and a few islands. The atomically resolved image in Fig. 5.4b shows an ordered Ag adlayer with a surface structure of $a = 8.3 \pm 0.5 \text{ \AA}$, $b = 8.7 \pm 0.2 \text{ \AA}$, and an angle $\Gamma = 110 \pm 10^\circ$, which is consistent with a (3×3) structure of Ag on Au(111). A schematic representation of this structure is given in Fig. 5.4c, with Ag atoms taking both atop and twofold bridged sites. Alternating higher and lower rows of Ag atoms reflect exactly the pattern of the STM image in Fig. 5.4b. The structure reported here is in agreement with that of Gewirth et al. for Ag deposition at 420 mV [5.22], but is different from that reported by Itaya [5.19] and by Kolb et al. [5.20], whereby the latter group finds coexistence of a (3×3) and a $(\sqrt{3} \times \sqrt{3}) \text{ R}30^\circ$ structure at 500 mV. The (3×3) structure corresponds to a surface coverage of 0.44 ML (see

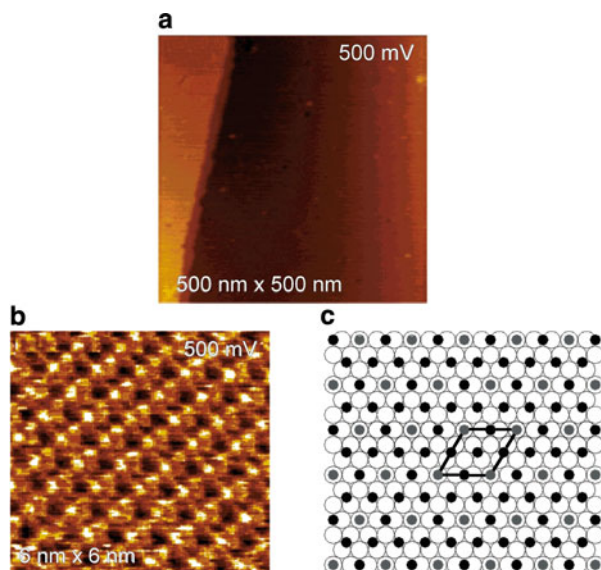


Fig. 5.4 In situ STM images of Ag underpotential deposition on Au(111) in an aqueous electrolyte (Fig. 5.3) at 500 mV and 298 K; (a) large-scale image of a compact Ag adlayer ($V_{\text{bias}} = -0.3$ V, I_t 0.5 nA); (b) atomically resolved detail of a; (c) schematic representation of the (3×3) structure of Ag on Au(111) with Ag adatoms on atop (grey) and bridging (black) sites. See also [5.21]

Fig. 5.4c), which differs from the value 0.25 ML derived from desorption isotherms. This discrepancy possibly results from surface alloying of Ag on Au(111), which is indicated by monoatomically deep pits in the Au(111) surface after dissolution of Ag at 600 mV over a longer period [5.21] – see also the corresponding STM images below for the dissolution in an ionic liquid. Obviously, this effect is underestimated in the charge-derived coverage where the anodic sweep rate was 1 mVs^{-1} [5.21].

On comparing the cyclic voltammograms in Fig. 5.3, it is apparent that Ag UPD on Au(111) in the ionic liquid is more complicated. Partly, this puzzle could be resolved by in situ STM investigations at potentials of the single UPD processes. Figure 5.5 shows a larger scale and an atomically resolved STM image of the ionic liquid/Au(111) interface at a potential where anion adsorption is indicated in the CV marked by process C₂. Obviously, the Au(111) electrode is covered by a well-ordered layer of adsorbed AlCl_4^- anions consistent with the positive polarisation of the electrode. The structure of this adlayer has lattice constants of $a = 8.3 \pm 0.5 \text{ \AA}$ and $b = 9.8 \pm 0.5 \text{ \AA}$ and is incommensurate with the underlying Au(111) surface [5.18].

In the first Ag UPD range from 400 to 200 mV (see Fig. 5.3b), silver deposition is characterized by the coexistence of different 2D Ag phase: There are both homogeneous patches of an ordered structure and regions of a disordered phase. This is demonstrated by the STM image in Fig. 5.6, where the enlarged picture of a patch

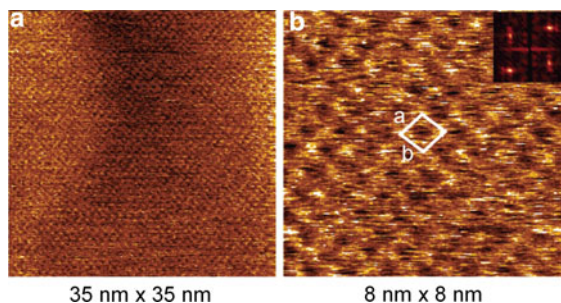


Fig. 5.5 In situ STM images of an adsorbed AlCl_4^- adlayer on Au(111) at 500 mV in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ melt at 298 K ($V_{\text{bias}} = 0.1$ V, $I_t = 1$ nA); (a) 35×35 nm², (b) 8×8 nm². *Inset* in (b) shows the Fourier transform of the structure with lattice constants of $a = 8.3 \pm 0.5$ Å and $b = 9.8 \pm 0.5$ Å. Reprinted from [5.21]

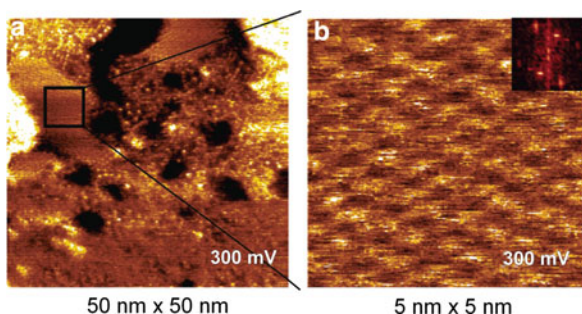


Fig. 5.6 In situ STM images of Ag UPD on Au(111) in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ at 300 mV and 298 K; (a) 50×50 nm² size; (b) (5×5) nm² size, detail from (a) as indicated; *inset* gives the Fourier transform of the STM image ($V_{\text{bias}} = 0.1$ V, $I_t = 1$ nA). See also [5.21]

of the ordered phase corresponds to a close-packed $\sqrt{3} \times \sqrt{3}$ R30° structure with $a = 4.4 \pm 0.6$ Å, $b = 5.5 \pm 0.5$ Å, and $\Gamma = 58 \pm 3^\circ$ (Fig. 5.6b). On decreasing the potential towards 200 mV, the fraction of the ordered phase increases continuously. So it seems that the first Ag UPD process in the ionic liquid is governed by a potential-induced order–disorder transition. On approaching the second UPD process below 120 mV, a second layer starts to form on top of a homogeneously covered surface; see Fig. 5.7. This is in line with the strong rise in the $Q(E)$ curve in Fig. 5.3d.

An interesting observation has been made during dissolution of the inhomogeneous Ag adlayers deposited in the UPDI process. This is illustrated by the STM images in Fig. 5.8. Starting from a deposit at 200 mV and stepping the potential gradually back to 500 mV, the following characteristic changes occur at the interface: At 250 mV, inhomogeneously spread small pits appear on the surface (Fig. 5.8a), they transform into a worm-like structure on further dissolution at 400 mV (Fig. 5.8b), and finally, at 500 mV, a distribution of monoatomically deep holes with diameters between 5 and 20 nm is seen all over the Au terraces (Fig. 5.8c).

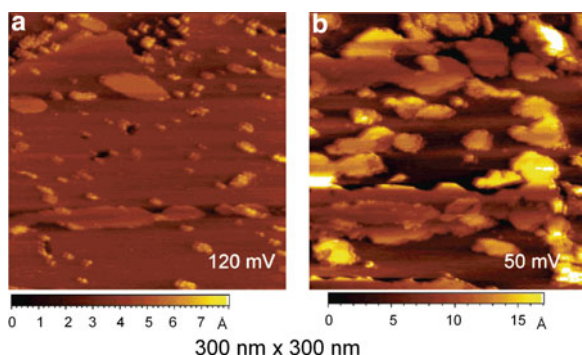


Fig. 5.7 In situ STM images ($300 \text{ nm} \times 300 \text{ nm}$) of the second UPD process of Ag on Au(111) in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ at 298 K ($V_{\text{bias}} = 0.1 \text{ V}$, $I_t = 1 \text{ nA}$); (a) incipient island formation at 120 mV; (b) progressive formation of a second Ag layer at 50 mV, about 6 min after a). See also [5.21]

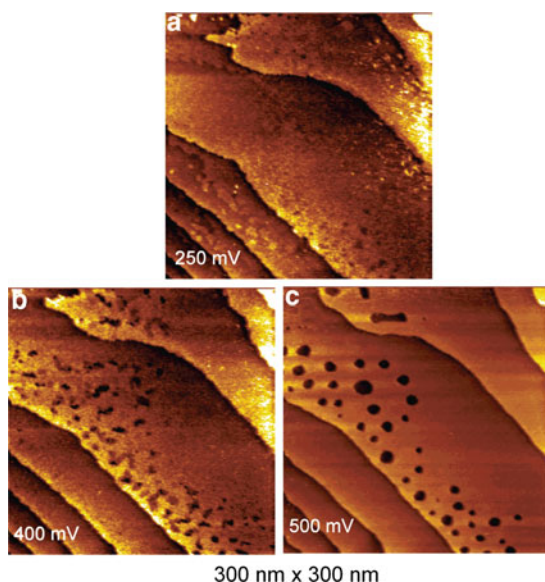


Fig. 5.8 In situ STM images ($300 \times 300 \text{ nm}$) of the anodic dissolution process of Ag UPD on Au(111) (deposition at 200 mV) in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ at 298 K ($V_{\text{bias}} = 0.05 \text{ V}$, $I_t = 1 \text{ nA}$). (a) Dissolution at 250 mV, (b) at 400 mV, and (c) at 500 mV. See also [5.21]

The whole dissolution process in this example took about 30 min. This phenomenon is not typical for a regular anodic dissolution of an adlayer, but indicates a stronger interaction between adatoms and atoms in the first layer of the substrate, which mutually exchange positions during deposition and thus form a surface alloy. This can explain the worm-like structures and monoatomically deep holes seen on dissolution. After dissolution of the $\text{Au}_x\text{Ag}_{1-x}$ surface alloy, rapid surface diffusion of

Au adatoms left on the surface leads to filling of the holes in a relatively short time of ~ 20 min. This could be documented by a series of additional STM images [5.18].

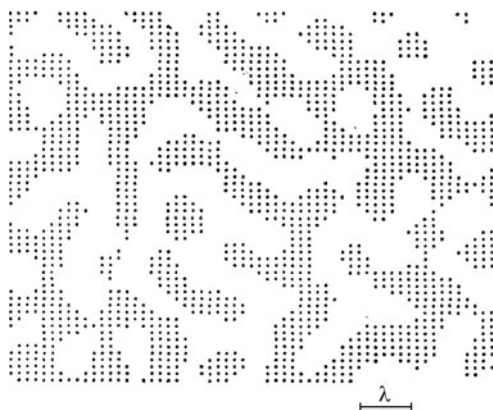
UPD of Ag on Au(111) in different electrolytes, aqueous vs. ionic liquid, takes place by distinct mechanisms. In an aqueous electrolyte, ordered Ag adlayers with different structures are formed at a high and low underpotential. In the employed chloroaluminate ionic liquid, homogeneous and ordered anion adsorption occurs, which is stable over a relatively wide potential range. It interferes with 2D electrochemical phase formation of Ag on Au(111) at intermediate potentials where ordered and disordered deposits coexist and partial destruction of the Au(111) surface becomes visible; see Fig. 5.6 and also [5.6]. Only at low underpotentials of ~ 100 mV, an ordered and coherent surface structure develops and a second Ag adlayer forms approaching the Nernst potential. Anodic dissolution of the coherent films strongly indicates that $\text{Au}_x\text{Ag}_{1-x}$ surface alloying plays an important role during Ag electrodeposition at the ionic liquid/Au(111) interface. This process, presumably, is favoured by a strong interaction between adsorbed anions – or, more generally, the ionic liquid – and surface atoms of the substrate, thus leading to weakening of bonding in the uppermost Au(111) layer. Further characteristics of the surface alloying phenomenon are described and discussed in the following for the example of Zn and Cd UPD on Au(111). Before we continue with electrochemical phase formation in these systems, a brief excursion to spinodal reactions and decomposition is required.

Usually, 2D and 3D phase formation takes place by nucleation and growth mechanisms, whereby metastable states are passed through [5.17]. In these cases, mass transport is governed by normal diffusion, i.e. down the concentration gradient. However, there are other situations where phase formation is driven by spinodal reactions; a 3D example is the Zn–Al alloy [5.23]. In order to illustrate this mechanism further, we first consider a dense fluid that is rapidly quenched below its critical temperature and estimate the time taken by the fluid to decompose into the liquid and vapour phases. Estimating the time constant τ_D of decomposition with the Einstein–Smoluchowski relation, $\tau_D = d^2/D$, and taking for the diffusional jump distance d and the diffusion coefficient D typical liquid values, this yields $\tau_D \leq 10^{-8}$ s, clearly less than microseconds. Only if the fluid could be quenched faster than 10^{-8} s, there might be a chance to suppress the spinodal reaction. In solids, spinodal decomposition can be a slow process that can be resolved by conventional techniques. Cahn and Hilliard could show that transport in the spinodal regime occurs by diffusion modified by thermodynamic requirements [5.24, 5.25]. Under these conditions, concentration fluctuations lead to an effective flux in the direction up the concentration gradient. The solutions of the Cahn–Hilliard diffusion equation have the following general form:

$$c(t) - c(t_0) = \exp(R(q)t) \cos(qr) \quad (5.4)$$

where $c(t)$ is the time evolution of the spinodal concentration profile and the amplification factor $R(q)$ is negative in the metastable region and positive in the spinodal regime for small wave numbers $q < q_c$. Equation (5.4) describes the two-phase spinodal structures that are characterized by a well-defined connectivity. They are

Fig. 5.9 Section of a two-phase spinodal structure computed with 100 random sine waves. Reprinted with permission from [5.25]; copyright permission(2010) by American Institute of Physics



expected to arise when the volume fraction of the minor phase exceeds about 15% [5.25]. By calculating the concentration profiles according to (5.4), it is sufficient to consider those Fourier components for which $R(q)$ is a maximum. In this way, a characteristic length scale or wavelength $\lambda = 2\pi/q_m$ is defined for the spinodal structure. Figure 5.9 presents for the isotropic case a computed section through a two-phase spinodal structure (50:50 volume fraction), which has been obtained by summing up 100 random sine waves with wavelength λ [5.25]. If the concentration is below a given c_0 , the area is left blank; if it exceeds c_0 , dark dots are printed. Thus, the blanks and dots describe points in what will become one phase or the other during spinodal decomposition. Because of the appearance of the concentration distribution in Fig. 5.9, spinodal structures are also called worm-like or labyrinth structures exhibiting a characteristic wave length λ . Summing up, it is worthwhile to contrast again the essential differences of the spinodal mechanism with that of nucleation and growth. In the latter, the structure at any time is clearly two phase and the compositions are those of either one phase or the other. In the spinodal mechanism, the composition changes gradually from the average, and with time, the spread in composition increases. The growth is not in extent – as in the nucleation and growth mechanism – but in the concentration amplitude.

In recent years, a few examples of 2D spinodal structures have been reported. During vapour deposition of Ag on Ag(100) and Cu on Cu(100), Pai et al. observed the formation of typical worm-like structures [5.26]. The adlayer coverage in these studies was typically 0.6 ML. Evidence of nanocrystal self-assembly by fluid spinodal decomposition at a fluid/wall interface has been published by Ge and Brus [5.27]. By drying thin wet films of an organic solvent containing monodisperse CdSe nanocrystals on a smooth HOPG substrate, the authors observed labyrinth patterns with varying coverage. This is explained by increased van der Waals interaction between the nanocrystals in air as compared with solution. Two investigations of spinodal decomposition at electrified interfaces have been reported in the literature [5.28, 5.29]. Schuster et al. have studied the electrochemical dissolution of Au(111) surfaces by applying microsecond voltage pulses and monitoring

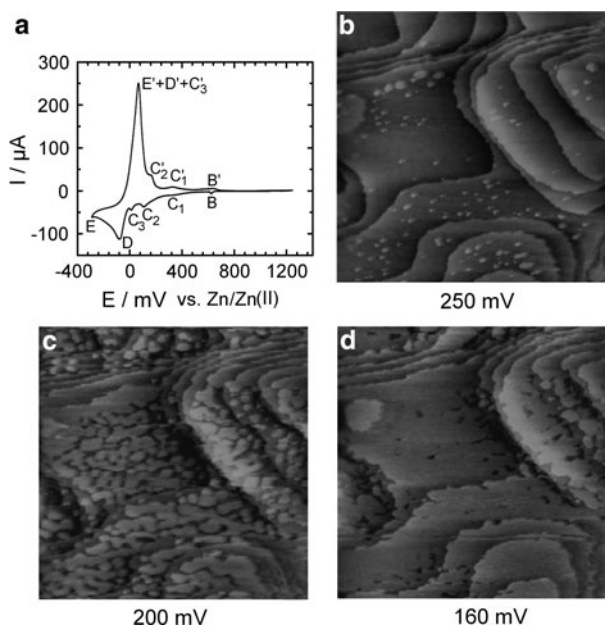


Fig. 5.10 (a) Cyclic voltammogram of UPD and OPD of Zn on Au(111) in AlCl_3 – $[\text{C}_4\text{mim}][\text{Cl}]$ (58 : 42) + 1 mM Zn(II) recorded at a scan rate of 5 mVs^{-1} at 298 K. (b)–(d) In situ STM images ($110 \times 110\text{ nm}^2$) belonging to Zn UPD (C_2) at different potentials and 298 K: (b) 250 mV, (c) 200 mV, (d) 160 mV taken at time intervals of $\sim 5\text{ min}$ ($V_{\text{bias}} = 100\text{ mV}$, $I_t = 5\text{ nA}$). See also [5.30]

the surface structure by in situ STM imaging. At Au coverages between 0.4 and 0.9 ML, they found typical labyrinth patterns with a characteristic length scale of $\sim 4\text{ nm}$ [5.28]. Similar observations were made by Erlebacher et al. at a Ag–Au alloy surface after selective dissolution of Ag by electrochemical etching. Typical length scales of the spinodal structures in these experiments lie in the range 5–10 nm [5.29].

The first detailed investigations of spinodal reactions during surface alloying at underpotential conditions were performed by in situ STM measurements for the systems Zn–Au and Cd–Au [5.30, 5.31]. These results are described in detail now. Figure 5.10 shows the cyclic voltammogram of the UPD and OPD processes of Zn on Au(111) in the ionic liquid AlCl_3 – $[\text{C}_4\text{mim}][\text{Cl}]$ (58:42) containing 1 mM Zn(II). Also given are selected STM images representing different stages of the UPD process C_2 . According to the CV, there are different reduction processes in the UPD range. The weak redox couple B, B' can be assigned to gold step edge oxidation as was shown in previous STM studies [5.32]. In the Zn UPD range, three reduction waves are indicated at $\sim 300\text{ mV}(\text{C}_1)$, $\sim 150\text{ mV}(\text{C}_2)$, and $\sim 10\text{ mV}(\text{C}_3)$. A similar multitude of reduction steps was reported by Pittner and Hussey in their Zn UPD study on polycrystalline Au in the ionic liquid AlCl_3 – $[\text{C}_2\text{mim}][\text{Cl}]$ [5.33]. In the OPD range, Zn bulk deposition occurs around $-80\text{ mV}(\text{D})$, which is followed by Al–Zn codeposition at potentials negative of -300 mV .

Focusing on the Zn UPD process around C_2 , the STM images give the following insight into the structural changes at the ionic liquid/Au(111) interface. At a potential of 250 mV, the Au(111) terraces are covered by a small fraction of monoatomically high islands with an extension of several nanometres. On reducing the potential to 200 mV, the surface structure changes significantly. A dense labyrinth structure is apparent, the signature of a spinodal reaction. We interpret this by an exchange reaction of Zn and Au atoms at the interface resulting in the formation of a Zn–Au surface alloy. At 160 mV, surface alloying is completed and the Au(111) terraces are covered by a dense alloy adlayer with a small concentration of defects. STM measurements of the height profile of the structures in Fig. 5.10c, d yielded a thickness of the alloy adlayer of $2.2 \pm 0.2 \text{ \AA}$ in comparison with the Au(111) step edge height of $2.3 \text{ \AA}$ taken for calibration [5.30]. Further STM investigations of the Zn UPD processes C_i indicate a layer-by-layer growth of Zn adlayers on top of the 2D surface alloy phase. Their thicknesses were found to be $2.4 \pm 0.2 \text{ \AA}$. The layer-by-layer growth mechanism continues in the OPD region of bulk Zn deposition [5.30].

Very similar structural changes at the ionic liquid/Au(111) interface have been observed during Cd–Au surface alloying, which is demonstrated by a few representative STM images in Fig. 5.11 [5.31]. In this system, the UPD process of surface alloying occurs in the potential range 0.5–0.45 V vs. Al^{3+}/Al quasi-reference. In the beginning of the Cd UPD process at 0.5 V, again Cd islands are spread over

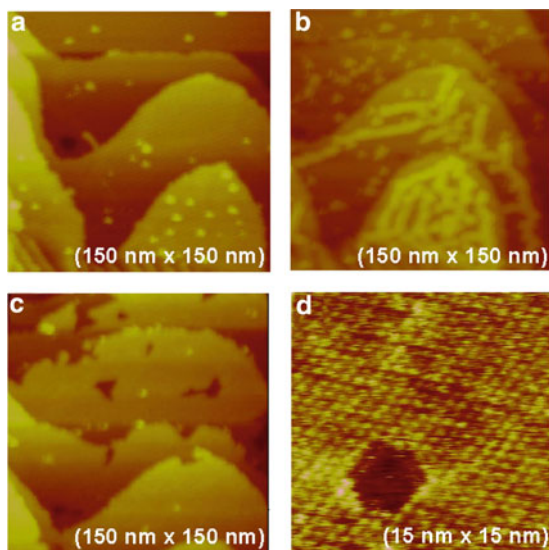


Fig. 5.11 STM images of Cd–Au surface alloy formation on Au(111) in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}] + 5 \text{ mM CdCl}_2$; (a) Cd island formation on Au(111) at $E = 0.5 \text{ V}$; (b) spinodal structure at $E = 0.45 \text{ V}$; (c) complete surface alloy layer, half an hour after (b) ($V_{\text{bias}} = 100 \text{ mV}$, $I_t = 1 \text{ nA}$, all potentials vs. Al^{3+}/Al quasi-reference). (d) High-resolution STM image, section of (c) ($V_{\text{bias}} = 0.2 \text{ V}$, $I_t = 1.2 \text{ nA}$); all measurements at 298 K. See also [5.31]

the Au(111) terraces. On reducing the potential to 0.45 V, spinodal structures form all over the surface. After a longer polarization time at this potential (~ 30 min), they transform to a densely packed homogeneous surface alloy with a few larger defects; see Fig. 5.11c. The structure of the Cd–Au surface alloy as determined from a high-resolution STM image is consistent with a $\sqrt{3} \times \sqrt{3}$ structure with a nearest neighbour distance of 5 ± 1 Å [5.31]. On reducing the potential further to 0.2 V, a second Cd UPD process is indicated in the CV. Here, a second layer grows in the same way as described above, so that two Cd–Au alloy layers are formed in the Cd UPD range in the ionic liquid. It is interesting to point out that for Cd UPD on Ag(111) in an aqueous electrolyte, a somewhat different mechanism has been reported [5.34]. Accordingly, a condensed close-packed Cd monolayer is formed first, which then undergoes a slow transformation involving place exchange between Cd atoms and Ag surface atoms. Spinodal structures have not been reported.

Characteristic features of surface alloying become evident during its dissolution by anodic stripping. This is illustrated by the STM images in Fig. 5.12, which are typical for the dissolution process of the Cd–Au surface alloy phase. Starting from a homogeneous Cd–Au layer obtained after extended polarization at the deposition potential of 0.45, the potential is stepped anodically to 0.85 V (Fig. 5.12a). This results in a substantial Cd dissolution and a corresponding reverse spinodal reaction as evidenced by the structural patterns in Fig. 5.12a, b. Keeping the potential constant, the spinodal structures can be imaged over a longer period depending on the stripping potential. This reflects a relatively slow kinetics of the spinodal reaction (see also below). Accelerating the dissolution by increasing the anodic stripping potential leads to a disappearance of the labyrinth structures, and the original substrate is recovered with a larger number of holes and islands that are of monoatomic depth and height, respectively (Fig. 5.12c). At the potential of 0.95 V, it takes about 1 h until all the holes are healed by surface diffusing Au atoms that are left after dissolution of Cd. It should be mentioned that very similar characteristics have been observed for the anodic stripping of Zn–Au surface alloy phases [5.30].

We come back to the characteristic length scale λ and the kinetics of the spinodal structures governing surface alloying. As was shown by Budevski and coworkers [5.35], the kinetics can be described by a simple reversible reaction between atoms adsorbed on the substrate, n_{ad} , and those which have reacted with it, n_{re} , forming the surface alloy:



Here, k_{F} is rate constant of the forward reaction and k_{B} that of the back reaction. At any time t , the number of deposited atoms is $n_{\text{o}} = n_{\text{ad}} + n_{\text{re}}$. Changing from the n_i to the corresponding coverage, Θ_i , where $\Theta_i = n_i/N$ with N being the total number of sites at complete coverage of the substrate, the rate law is

$$d\Theta_{\text{re}}/dt = k_{\text{F}}(\Theta_{\text{o}} - \Theta_{\text{re}}) - k_{\text{B}}\Theta_{\text{re}}. \quad (5.6)$$

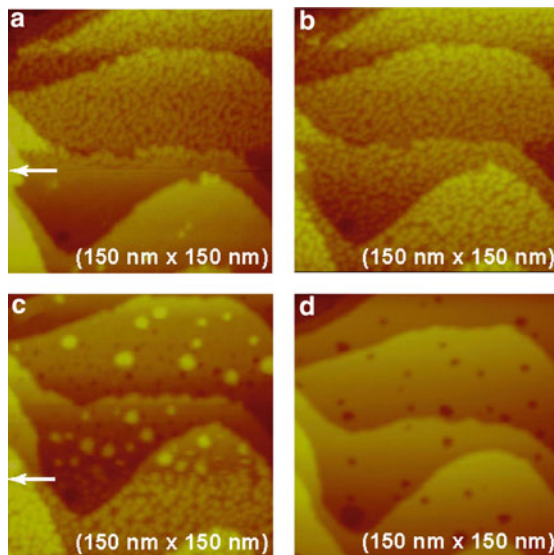


Fig. 5.12 In situ STM images illustrating anodic dissolution of a Cd–Au surface alloy layer on Au(111) in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ (58 : 42) + 5 mM CdCl_2 : (a) potential step from 0.45 to 0.85 V (see arrow); (b) $E = 0.85$ V; (c) potential step from 0.85 to 0.95 V (see arrow); (d) 0.5 h after (c) ($V_{\text{bias}} = 0.1$ V, $I_t = 1$ nA). The white arrows indicate the positions where the potential has been changed; all potentials vs. Al^{3+}/Al quasi-reference; temperature was 298 K. See also [5.31]

Integration yields:

$$\Theta(t) = \Theta_{\text{re}} / \Theta_0 = \frac{k_F}{k_F + k_B} (1 - \exp(-(k_F + k_B)t)) \quad (5.7)$$

During electrodeposition at a constant potential clearly below the anodic stripping potential, the inequality $k_F \gg k_B$ holds. Thus, k_F is directly accessible by $\Theta(t)$ -measurements. Assuming that the spinodal structure represents the amount of surface alloy at time t , $\Theta(t)$ has been determined from the integrated area of this structure relative to the total area of the STM image; see also Figs. 5.10 and 5.11. Results of this evaluation are shown in Fig. 5.13 for the Zn–Au surface alloy deposited at 200 mV for two different temperatures [5.36]. The rate constants are $k_F = (1.6 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ (298 K) and $k_F = (2.3 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ (323 K), indicating a slow reaction. In retrospect, this slow kinetics explains why spinodal surface alloying reactions can be visualized on the time scale of an STM scan.

The evolution of the spinodal structures in time and area has been investigated both with the aid of STM images and by calculations using a 2D hydrodynamic continuum model [5.36]. From the STM images, the power spectral density has been determined, which presents the dominant Fourier components and may be considered as a surface structure factor S_q . For this evaluation, smaller sections of the STM images have been scanned at different time intervals. The results for Zn–Au

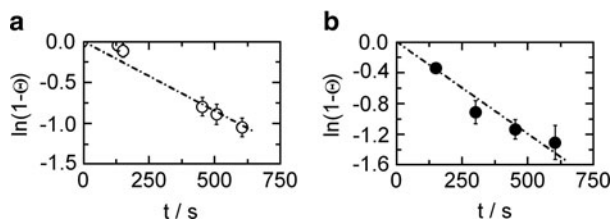


Fig. 5.13 Logarithmic plot of coverage Θ vs. time t of Zn–Au surface alloying on Au(111) during electrodeposition at 200 mV in the ionic liquid $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}] + 1 \text{ mM Zn(II)}$ at 298 K (a) and 323 K (b). See also [5.36]

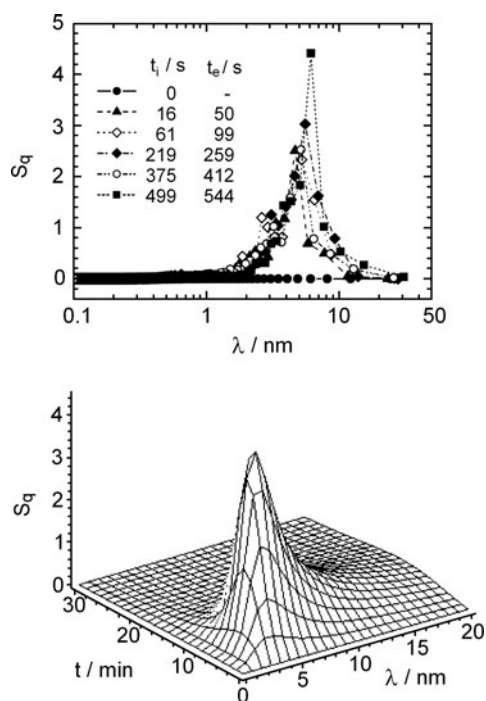


Fig. 5.14 Evolution of the power spectral density S_q with wavelength λ and time t of Zn–Au labyrinth structures deposited on Au(111) at 200 mV in $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}] + 1 \text{ mM Zn(II)}$: (a) determined from STM image sections at time intervals $t_1 \leq t \leq t_0$ at 323 K; (b) model calculations. See also [5.36]

surface alloys deposited at 200 mV are presented in Fig. 5.14. As can be seen, the agreement between experiment and model calculation is rather satisfactory. Most interestingly, the surface structure exhibits a peak at a characteristic wavelength of $\lambda = 5 \text{ nm}$ – typical of surface spinodal reactions – and at a time of $\sim 10 \text{ min}$ after beginning of deposition. At longer times $> 20 \text{ min}$, phase separation is completed and the extended Zn–Au surface phase is formed.

5.3 Nanoscale Electrodeposition of Metals and Semiconductors

Nanoscale electrodeposition presupposes in situ observation of nucleation and growth phenomena with nanometre or, if possible, atomic resolution and under electrochemical control of the deposition potential η . Such measurements became possible by the development of EC-SPM in the 1980s and 1990s, first successfully employed in investigations of electrified aqueous electrolyte/electrode interfaces [5.37–5.41] and later extended to electrodeposition studies with ionic liquids in our laboratory [5.42, 5.43]. This method enables insight into the surface topography in real time and space. An essential prerequisite is that the deposition potential and the tunnelling tip potential can be varied independently by using a bipotentiostat [5.1]. Details of this technique and its adaptation to ionic liquid studies are described in Sect. A.5. Here, we briefly summarize the principle information that can be obtained with the EC-SPM method, with emphasis on the scanning tunnelling spectroscopy mode (STS). The basic equation for the tunnelling current I_t is given by [5.44]:

$$I_t \propto \int_0^{eV} n(E)_T n(E - eV)_S \exp(-\alpha \cdot s (\tilde{\phi} + eV - E)^{1/2}) dE. \quad (5.8)$$

Here, $n(E)_T$ and $n(E - eV)_S$ are the electronic density of states of tunnelling tip and sample (working electrode), respectively, and the exponential function describes the tunnelling transmission probability; furthermore, $\alpha = 2(2m_e \hbar^{-2})^{1/2} = 1.025 \text{Å}^{-1} \text{eV}^{-1/2}$, s is the distance between sample and tip (typically $\sim 1 \text{ nm}$), $\tilde{\phi}$ is the effective tunnelling barrier height reflecting the work function of sample and tip, and $V \equiv V_{\text{bias}}$ is the bias voltage applied between sample and tip. According to (5.8), the tunnelling probability and thus I_t is largest for electrons at the Fermi level, i.e. for negative sample bias ($eV < 0$) electrons from occupied sample states near E_F tunnel into unoccupied tip states, and vice versa for $eV > 0$. It is also seen from (5.8) that any STM image is a convolution of the sample electronic density of states with that of the tip. However, in favourable cases $n(E)_T$ can be approximated by a nearly uniform density of states of s-waves and, for low bias voltages, contributes by $n(E_F)_T$ to the tunnelling current. Under these conditions, an STM image – in particular for metals – reflects a contour of the density of states of the sample at E_F , which can be interpreted by a surface charge density contour or a surface topography. Valuable information on the electronic structure of surface states is obtained by STS. In this mode the STM scan is interrupted for a few hundred microseconds at a fixed sample–tip separation and the bias voltage is ramped to record $I_t - V$ curves. By acquiring the $I_t - V$ curve rapidly compared to the scan speed of the tip, both the sample topography and the spatially resolved $I_t - V$ characteristics can be measured [5.44]. During ramping of V , both occupied and unoccupied energy states are probed, which enables direct distinction between metallic or semiconducting properties and allows the determination of e.g. semiconducting gap energies. STS measurements also yield information on the effective tunnelling barrier $\tilde{\phi}$, which can be obtained from measured $I_t - V$ curves by fitting with (5.8). In this way,

relative changes of the electronic structure during metal alloying can be followed; see below.

In this chapter, we consider a few representative examples of 3D metal and semiconductor electrocrystallizations from ionic liquids and discuss the characteristic properties on the nanometre scale. Beginning with pure aluminium, this is an element that cannot be deposited from an aqueous electrolyte due to its reduced electrochemical window. From a nanotechnology point of view, nanoscale Al deposition on a semiconductor substrate such as Si is of particular interest. This was achieved for the first time from a chloroaluminate melt ($\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$) on hydrogen terminated $\text{Si}(111):\text{H}$ and was characterized by in situ SPM measurements [5.45]. Figure 5.15a shows a typical STM image of the topography of an $n\text{-Si}(111):\text{H}$ surface in contact with $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ taken at an open circuit potential (OCP) of +100 mV. As can be seen, the surface is characterized by atomically flat, regularly spaced terraces with a lateral width of $\sim 65\text{ nm}$ and steps of $\sim 3\text{ \AA}$ height as expected for Si bilayers [5.46]. The tunnelling spectrum in Fig. 5.15b was recorded prior to Al deposition on the bare $\text{Si}(111):\text{H}/\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ interface. It exhibits semi-conducting behaviour with a band gap of $\sim 1.1\text{ eV}$ – see also the derivative spectrum in the inset – which is in accord with the well-known gap energy of bulk Si.

Electrocrystallization of Al on $n\text{-Si}(111):\text{H}$ is documented by CV and SPM results in Fig. 5.16. The cyclic voltammogram in Fig. 5.16a is a classical example of a nucleation loop associated with electrodeposition of a metal on a foreign substrate and subsequent anodic stripping. In the forward sweep, stable Al nuclei are formed on the Si surface, which requires a nucleation overpotential. It is more negative than the potential needed to reduce Al^{3+} cations. Negative of the nucleation potential bulk deposition commences. According to Fig. 5.16a, the nucleation overpotential

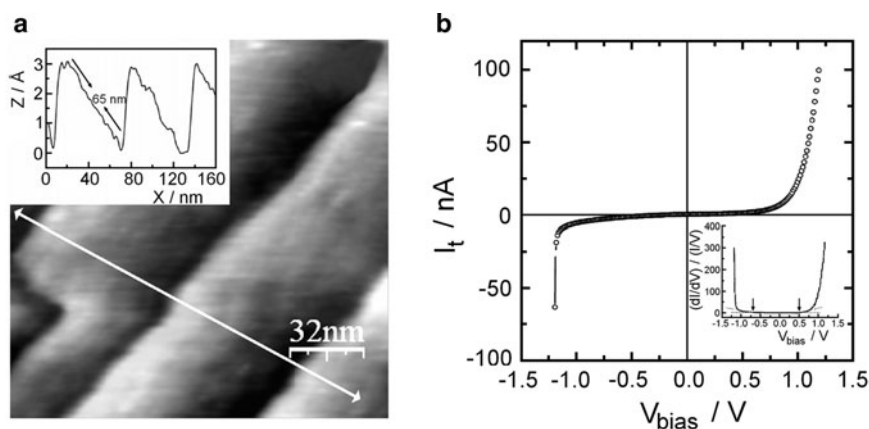


Fig. 5.15 (a) STM image ($160 \times 160\text{ nm}^2$) showing the surface topography of an $n\text{-Si}(111):\text{H}$ substrate in contact with $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}]$ (58:42) at 100 mV (OCP) and 298 K; the *inset* gives the height profile of the atomically flat, bilayer high Si(111) terraces ($V_{\text{bias}} = 1.5\text{ V}$, $I_t = 0.5\text{ nA}$). (b) $I_t - V$ curve of the interface in (a), indicating a gap energy of $\sim 1.1\text{ eV}$; see also the derivative spectrum in the *inset*. See also [5.45]

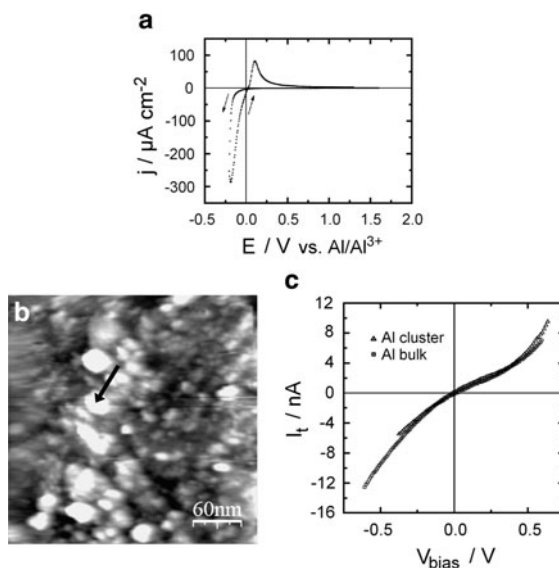


Fig. 5.16 (a) Cyclic voltammogram of Al electrodeposition on n -Si(111):H from AlCl_3 -[C₄mim][Cl] (58:42) measured in the dark at a scan rate of 100 mV s^{-1} and at 290 K; (b) STM image ($300 \times 300 \text{ nm}^2$) of bulk Al deposit recorded after 20 min polarization at $-400 \text{ mV vs. Al/Al}^{3+}$ ($V_{\text{bias}} = 1 \text{ V}$, $I_t = 0, 5 \text{ nA}$); (c) $I_t - V$ tunnelling spectra of an Al cluster ($E = -200 \text{ mV vs. Al/Al}^{3+}$) and bulk Al deposit ($E = -400 \text{ mV vs. Al/Al}^{3+}$). See also [5.45]

for Al deposition on n -Si(111):H in AlCl_3 -[C₄mim][Cl] is about -200 mV . On the reverse sweep, deposition continues on the Al surface until the Nernst potential is reached. A crossover occurs in the CV when the anodic stripping reaction starts. Figure 5.16b shows an STM image of bulk Al on Si(111):H deposited at a potential of $-400 \text{ mV vs. Al/Al}^{3+}$ and recorded after a polarization time of 20 min. The Si surface is completely covered with Al clusters with thicknesses greater than 1 nm and extensions in the range 5 – 50 nm . For the cluster indicated by an arrow $I_t - V$ curves have been recorded, which are given in Fig. 5.16c. They exhibit clearly metallic characteristics of similar quality for both Al clusters and Al bulk deposits.

Aluminium alloys have wide applications in different engineering constructions. Many of these alloys can be obtained by electrodeposition from ionic liquids at conditions near room temperature including rare materials such as Ti–Al alloys [5.47]. The electrochemical fabrication of these materials, in particular, their applications as coating materials, has the special advantage that the composition can be varied relatively easily by continuously changing the deposition overpotential η . This shall be illustrated for the example of Co–Al codeposition from an AlCl_3 -[C₄mim][Cl] melt containing 5 mM Co(II) [5.48]. Figure 5.17 shows two STM images of $\text{Co}_x\text{Al}_{1-x}$ alloys deposited at -0.43 V and $-0.7 \text{ V vs. Co/Co(II)}$ together with the corresponding $I_t - V$ spectra taken at specific positions marked by black crosses in the respective images. Also given are the tunnelling barrier heights $\tilde{\phi}$, which have been

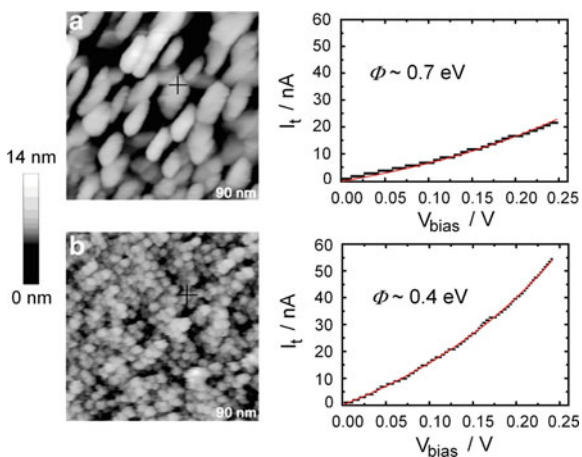


Fig. 5.17 STM images (left, $90 \times 90 \text{ nm}^2$) and corresponding $I_t - V$ curves of $\text{Co}_x\text{Al}_{1-x}$ nanostructures deposited at -0.43 V (a) and -0.7 V (b) vs. Co/Co(II) on Au(111) from $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}] + 5 \text{ mM Co(II)}$. The crosses in the STM images indicate where the STS spectra have been taken. The effective tunnelling barriers $\tilde{\phi}$ have been determined from fits of the $I_t - V$ curves by (5.9). See also [5.48]

determined from fits of the measured $I_t - V$ curves using the following simplified expression for $I_t(V)$; see also [5.44]:

$$I_t = \text{const} \int_0^{eV} \exp(-\alpha \cdot s(\tilde{\phi} - eV)^{1/2}) dV. \quad (5.9)$$

The symbols in this expression have the same meaning as those defined in (5.8). From Fig 5.17, it is apparent that the two Co–Al alloys deposited at different potentials exhibit distinct morphologies and electronic structures indicated by the different $\tilde{\phi}$ -values. With the SPM method, these differences can be probed so to say in status nascendi.

SPM measurements offer the possibility to follow in situ the variation of the alloy properties over a wide range of compositions. This is demonstrated in Fig. 5.18 for $\text{Co}_x\text{Al}_{1-x}$ alloys that have been deposited in the potential range from 0.5 to 0 V vs. Al/Al^{3+} . Included in this figure are the alloy compositions ($0.4 \leq x \leq 1$) determined by different electrochemical methods as indicated [5.49,5.50]. The comparison of the x -scale with the variation of the tunnelling barrier height $\tilde{\phi}$ shows that both quantities within experimental errors exhibit a similar potential dependence. So one may conclude that SPM measurements are a suitable tool to probe in situ relative compositional changes during alloy deposition with high spatial ($\sim 1 \text{ nm}$) and time ($\sim 1 \text{ ms}$) resolution.

A particular strength of electrochemical in situ SPM techniques is that they enable a microscopic insight into UPD and OPD processes and the corresponding nucleation and growth mechanisms. On the basis of this knowledge, proper

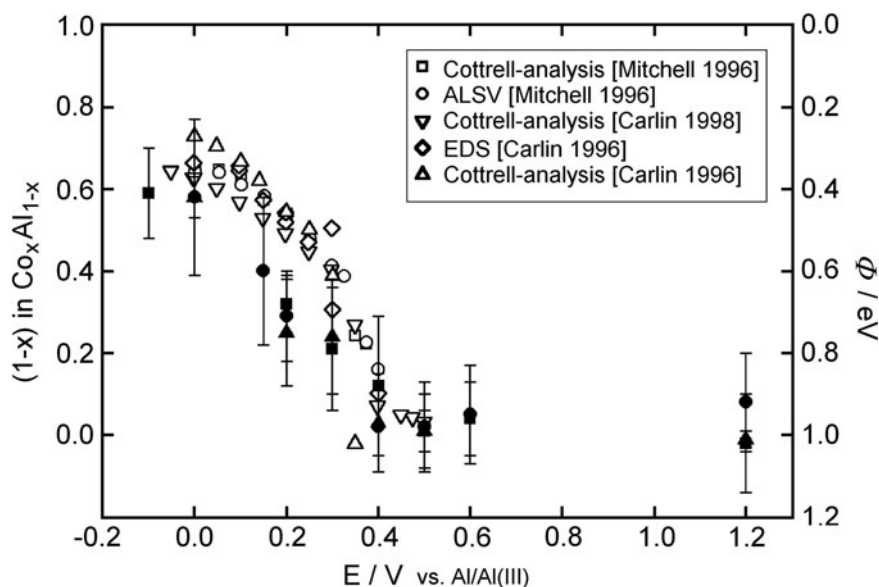


Fig. 5.18 Variation of Co_xAl_{1-x} alloy compositions in alloys that have been electrodeposited from $AlCl_3$ -[C₄mim][Cl] + 5 mM Co(II) on a Au(111) surface at 298 K; the x -scale to the left corresponds to results from different electrochemical measurements (*open symbols*); the potential dependence of the tunnelling barrier $\tilde{\phi}$ to the right has been determined from STS spectra (*full symbols*). See also [5.48]

sequences of potential steps can be chosen for specific modifications of nanostructures. This shall be demonstrated in detail for the electrocrystallization of distinct Ni nanostructures. Again an ionic liquid electrolyte has been used to avoid hydrogen evolution, which in aqueous media can occur in parallel with metal reduction and thus affects the morphology of the metal deposit. At the Au(111) interface with an $AlCl_3$ -[C₄mim][Cl] melt containing 5 mM Ni(II), two UPD processes can be distinguished [5.51]. In the potential range from the OCP at 0.6 V down to 0.15 V vs. Ni/Ni²⁺, a well-ordered adlayer of $AlCl_4^-$ anions has been observed with an incommensurate $c(p \times 2\sqrt{3})$ structure [5.51]. Below 0.15 V, a complete Ni UPD layer forms over a relatively long period of ~ 800 s. Ni and Ni-Al overpotential deposition in this melt occurs at potentials of -0.25 V and -0.45 V vs. Ni/Ni²⁺, respectively [5.51]. Depending on the potential stepping, different nucleation and growth processes take place, which lead to distinct morphologies of 3D Ni nanostructures. This is shown in Fig. 5.19. The left-hand STM image belongs to a deposition where the potential was directly jumped from the OCP to the Ni OPD at -0.25 V. In this case, nucleation of Ni clusters starts at Au(111) step edges (not shown) and with time clusters grow in size and spread all over the substrate surface after about 300 s. They have a characteristic circular shape with diameters of ~ 15 nm and a height of ~ 2 nm.

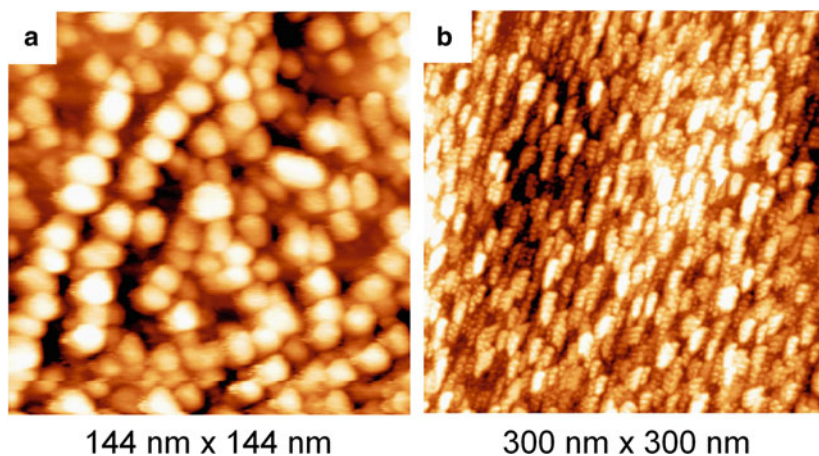


Fig. 5.19 STM images of Ni OPD on Au(111) deposited from $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}] + 5 \text{ mM Ni(II)}$ at 298 K; **(a)** ($144 \times 144 \text{ nm}^2$) clusters of circular shape obtained by jumping the potential from OCP to -0.25 V vs. Ni/Ni^{2+} ($V_{\text{bias}} = -0.3 \text{ V}$, $I_t = 1 \text{ nA}$); **(b)** ($300 \times 300 \text{ nm}^2$) rod-like clusters with aspect ratio $\sim 2\text{--}3$ obtained by the formation of a complete Ni UPD layer prior to the OPD process at -0.18 V ($V_{\text{bias}} = 0.1 \text{ V}$, $I_t = 1 \text{ nA}$). See also [5.51]

A second morphology of Ni OPD has been obtained in the following way. Instead of stepping the potential directly from OCP into the OPD range, a complete Ni UPD layer was deposited first at 0.1 V with in situ SPM control and then, after $\sim 900 \text{ s}$, the potential was jumped to -0.2 V . The resulting Ni structure is shown in Fig. 5.19b. Ni clusters of an elongated rod-like shape appear with a width of $\sim 10 \text{ nm}$ and an aspect ratio of 2 to 3. The preferred orientation of this structure that suggests magnetic interaction between neighbouring Ni nanocrystals is remarkable. Their dimensions are comparable in magnitude with the magnetic exchange length, which for ferromagnetic metals is of the order of $10\text{--}20 \text{ nm}$ [5.52]. Thus, the Ni clusters may be considered as an ordered array of single-domain ferromagnetic nanocrystals that possess a high remanence along the cylinder axes. It is worth noting that very similar observations have been made for iron deposition under similar conditions. This is illustrated by the STM image in Fig. 5.20 [5.53]. The Fe nanocrystals exhibit a similar aspect ratio as in the case of Ni, but now two preferred orientations can be distinguished. The monodisperse crystals are remarkably stable against alloying with Al, which is indicated by ex situ XPS measurements (Fig. 5.20).

The nucleation and growth mechanisms leading to the different Ni nanostructures have been further investigated by chronoamperometry or current transient measurements [5.51]. These results are presented in Fig. 5.21. The set of current transients in the upper panel corresponds to potential steps from 0.3 V vs. Ni/Ni^{2+} to different potentials in the OPD range, i.e. nucleation and growth at the Au(111)/ionic liquid interface was studied. Besides a steep current decay below 0.1 s – which is due to double-layer charging – the transients exhibit a broad maximum at short times followed by a decrease proportional to $t^{-1/2}$, which is shown for one example in the

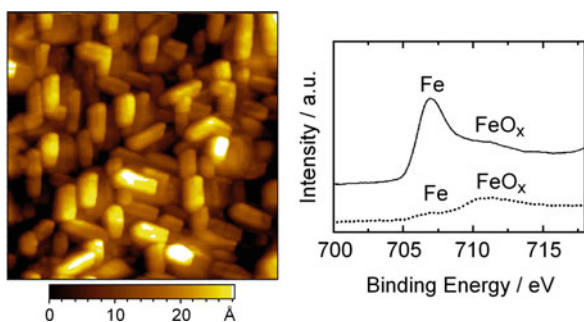


Fig. 5.20 Deposition of Fe nanocrystals on Au(111) from $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}](58 : 42) + 5 \text{ mM Fe(II)}$ at 0.4 V vs. Al/Al^{3+} at 294 K; (*left*) STM image ($160 \times 160 \text{ nm}^2$, $V_{\text{bias}} = 0.7 \text{ V}$, $I_t = 1 \text{ nA}$); (*right*) ex situ XPS spectra of the Fe nanocrystals in a) before (*dashed line*) and after sputtering (*full line*) showing the $\text{Fe } 2p_{3/2}$ excitation at 707 eV consistent with the literature value of pure Fe; no Al signal was found at this deposition potential. See also [5.53]

inset. This Cottrell behaviour indicates diffusion control at longer times [5.1]. Analysis of the current transients by a model of Scharifker et al. for 3D nucleation and hemispherical diffusion [5.54] has shown that the experimental curves are consistent with a progressive nucleation and growth mechanism [5.51]. A different time dependence of the current transients occurs if first a Ni UPD monolayer is deposited and then a potential step into the OPD range is applied; see lower panel of Fig. 5.21. In this case, the transients can be fitted by the model of 3D instantaneous nucleation on a fixed number of active sites, which is found to be $\sim 10^{10} \text{ cm}^{-2}$ [5.55]. Both model fits yield for the diffusion coefficient a value of $2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [5.51].

Similar to metal alloys, electrocrystallization of compound semiconductors has been achieved employing ionic liquids [5.56, 5.57]. For the case of the compound semiconductor AlSb, this is demonstrated in Fig. 5.22. The cyclic voltammogram of $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}](1 : 1) + 1 \text{ mM Sb(III)}$ on Au(111) shows in the OPD range a reduction peak at -0.25 V vs. Al/Al^{3+} , which is dominated by bulk Sb deposition [5.56], and a broad reduction wave with a minimum near -1.1 V , which is due to AlSb codeposition. The growth of AlSb clusters at -1.0 V as a function of time is seen in the STM images of Fig. 5.22. Over a period of $\sim 20 \text{ min}$, relatively large clusters of $\sim 50 \text{ nm}$ width and $\sim 6 \text{ nm}$ thickness are formed. For one of these clusters, an $I_t - V$ spectrum has been recorded, which is shown in Fig. 5.22. It indicates clear semiconducting characteristics with an apparent energy gap of $\sim 1 \text{ eV}$. This value is smaller than the literature value of stoichiometric crystalline AlSb, which has an indirect gap of 1.6 eV [5.58]. We explain this difference by a relatively strong deviation of the clusters deposited at -1.0 V from the stoichiometric composition AlSb, which can cause a pronounced doping. Further investigations of AlSb electrodeposition at various potentials support this interpretation [5.59].

Zinc antimonide is a compound semiconductor with an indirect gap of 0.53 eV [5.60]. Its electrocrystallization was realized with a melt of $\text{ZnCl}_2\text{--}[\text{C}_4\text{mim}][\text{Cl}](45:55)$ containing 2 mM SbCl_3 , which required measurements at elevated temperature of 50°C [5.57]. For the pure compound ZnSb that was deposited at -0.95 V vs.

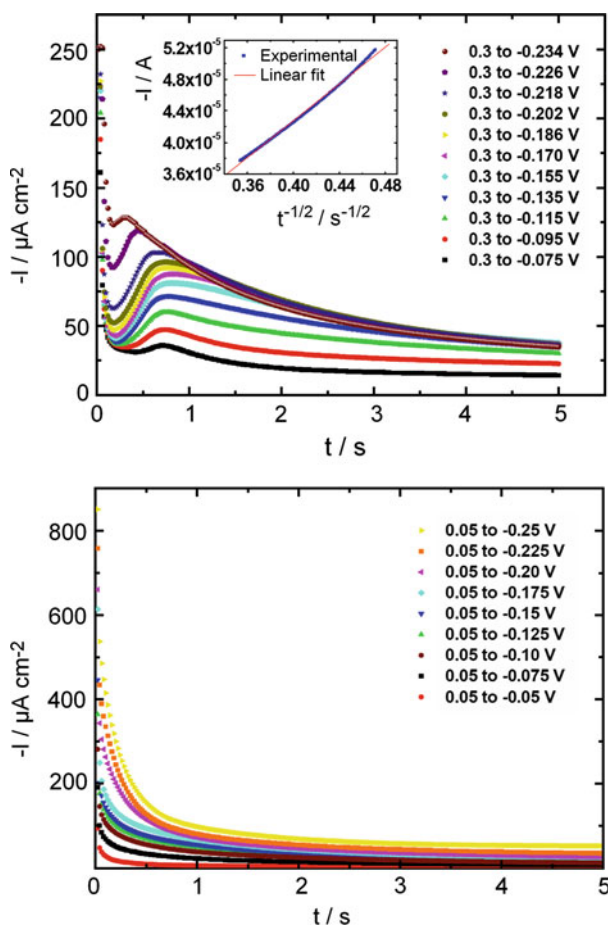


Fig. 5.21 Current transients vs. time measured at the Au(111)/ $\text{AlCl}_3\text{--}[\text{C}_4\text{mim}][\text{Cl}] + 5 \text{ mM Ni(II)}$ interface at 298 K; (*upper panel*) transients corresponding to potential jumps from 0.3 V vs. Ni/Ni^{2+} to different potentials in the OPD range; the *inset* shows a Cottrell plot of I vs. $t^{-1/2}$ for a selected current transient; (*lower panel*) current transients for potential jumps from 0.05 V to various Ni OPD potentials after formation of a complete Ni UPD monolayer on Au(111) at 0.05 V. See also [5.51]

Pt quasi-reference, a gap energy of $0.6 \pm 0.2 \text{ eV}$ was found. Deposition was also tried at potentials on both sides of -0.95 V to study the effect of doping. Preliminary results of these tests are shown in Fig. 5.23. Plotted are the normalized differential conductivity spectra that have been determined from the measured $I_t - V$ curves according to the method of Feenstra [5.61]. The spectra indicate no significant change of the band gap for excess Sb (n-doping), whereas for excess Zn (p-doping) the gap seems to be reduced to a value of $\sim 0.35 \text{ eV}$. However, further systematic studies are needed before quantitative conclusions on doping can be drawn.

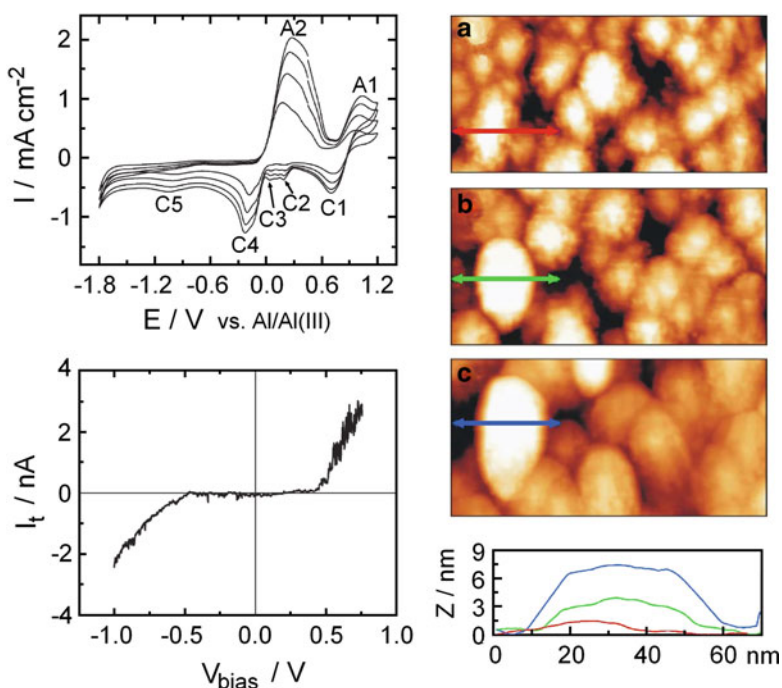


Fig. 5.22 Electrocrystallization of the compound semiconductor AlSb from AlCl_3 – $[\text{C}_4\text{mim}][\text{Cl}]$ (1 : 1) + 1 mM Sb(III) on Au(111) at 294 K. (*upper left*) Cyclic voltammograms recorded at different sweep rates from 20 to 80 mV s^{-1} ; AlSb codeposition occurs at C5 near -1.1 V vs. Al/Al^{3+} . (*lower left*) I_t – V curve corresponding to the large cluster in the STM image. (*right*) STM images ($200 \times 100 \text{ nm}^2$, $V_{\text{bias}} = -0.7 \text{ V}$, $I_t = 1 \text{ nA}$) and z -profiles of AlSb nanoclusters grown at -1.0 V vs. Al/Al^{3+} at different times of 3, 8, and 20 min, from top to bottom. See also [5.56]

The last example deals with a problem that in a way combines several of the main themes of this book and is entitled by thickness induced metal–nonmetal transition in ultrathin Ge films electrodeposited at the interface of ionic liquids with Au(111) or Si(111):H substrates. This problem is related with the more general and fundamental question how the electronic structure of ultrathin films changes with thickness and how it is affected by interactions with a substrate. In metals such as Au and Pb, quench condensed on amorphous Ge, nonmetallic behaviour was observed at thicknesses of the film below $\sim 2 \text{ nm}$ [5.62]. Investigations of vacuum-deposited Ge films on Si surfaces of different orientation have shown that their morphology and structure very much depends on the deposition rates and substrate temperature [5.63]. In general, at slow growth kinetics, a transition from 2D layered and $(2 \times n)$ reconstructed surface structures to 3D cluster growth sets in at a film thickness above $\sim 3 \text{ ML}$ [5.63]. However, at fast deposition rates and low substrate temperatures, amorphous Ge films can be produced.

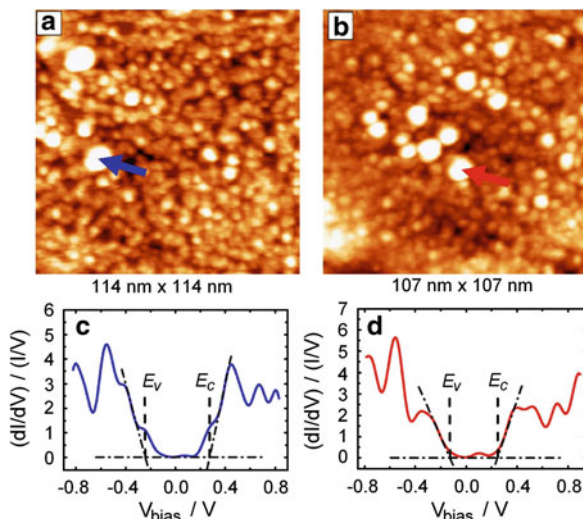


Fig. 5.23 Electrocrystallization of $\text{Zn}_x\text{Sb}_{1-x}$ compound semiconductors from ZnCl_2 – $[\text{C}_4\text{mim}][\text{Cl}](45 : 55) + 2 \text{ mM SbCl}_3$ on Au (111) at 323 K. (a) STM image corresponding to deposition at -0.8 V vs. Pt quasi-reference ($114 \times 114 \text{ nm}^2$, $V_{\text{bias}} = -0.6 \text{ V}$, $I_t = 1.6 \text{ nA}$). (b) STM image corresponding to deposition at -1.05 V vs. Pt quasi-reference ($107 \times 107 \text{ nm}^2$, $V_{\text{bias}} = -0.8 \text{ V}$, $I_t = 1.6 \text{ nA}$). The normalized differential conductivity spectra in (c) and (d) have been obtained for the clusters marked by arrows in (a) and (b), respectively. See also [5.57]

In the electrodeposition of thin Ge films with thicknesses in the range from 0.5 to 100 nm, the ionic liquid $[\text{C}_4\text{mim}][\text{PF}_6]$ saturated with GeCl_4 ($\sim 35 \text{ mM}$) has been used [5.64]. The film thickness and topography have been probed in situ by scanning tunnelling microscopy, and the electronic structure was analyzed by $I_t - V$ spectroscopy. Figure 5.24 shows the apparent band gap energy as a function of the Ge film thickness for depositions on both Au(111) and Si(111):H. Striking is a metal–semiconductor transition that sets in at a thickness above $\sim 1 \text{ nm}$. At low coverage (0.3 ML), a very rough surface structure was observed by STM, indicating a high density of defects; at higher coverages, smooth and elongated Ge clusters were regularly stacked along the substrate terraces. According to Fig. 5.24, the bulk gap energy of pure Ge of 0.7 eV is only reached for a film thickness above $\sim 5 \text{ nm}$. At lower coverages, the STS measurements indicate clearly metallic characteristics that were reproduced in several independent experiments on both Si(111):H and Au(111) substrates. We think that this behaviour is caused by a high concentration of defects or dangling bonds so that semiconducting bond saturation is only achieved at higher coverages where clusters of a larger extension and thickness grow.

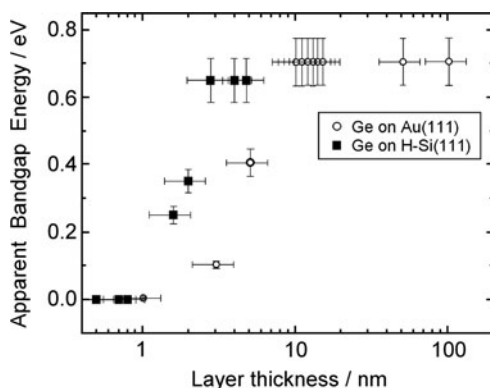


Fig. 5.24 Variation of the apparent band gap with thickness of electrodeposited Ge films on Si(111):H and on Au(111) at 298 K. See also [5.64]

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Appendix A

A.1 Structure Factor $S(q)$ ¹ and High-Temperature/High-Pressure Neutron Diffraction

We consider a one-component fluid of monatomic particles interacting via centrosymmetric forces. The scattering law is formulated for coherently scattered neutrons with scattering length b , but very analogous expressions apply for X-ray and electron scattering. The following assumptions are made: (1) Multiple scattering shall be neglected. (2) The time a neutron needs to traverse a typical diffusion length in the fluid is short in comparison with the characteristic diffusion time of particles (static scattering approximation). (3) Scattering is elastic, i.e. the incoming and scattered neutrons have the same energy, $\hbar\omega_i = \hbar\omega_s$ or $\hbar k_i = \hbar k_s$, where $\underline{k}$ is the wave vector. So, only the direction of the wave vector can be changed by elastic scattering by $\underline{q}$ with $\underline{q} = \underline{k}_i - \underline{k}_s$ and $q = 4\pi/\lambda \sin \Theta$, where λ is the wavelength and 2Θ is the scattering angle; see also Fig A.1 for the scattering geometry.

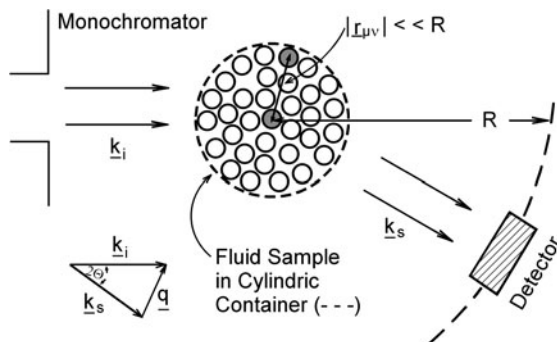


Fig. A.1 Sketch of scattering experiment and scattering geometry

¹ In the literature, both $\underline{Q}$ and $\underline{q}$ are used to describe the wave vector change.

The amplitude of radiation scattered through the angle 2Θ by particles with position vectors $\underline{r}_i$ is given by

$$A(\underline{q}) = b/R \sum_i^N \exp(-i\underline{q}\underline{r}_i), \quad (\text{A.1})$$

where b is the scattering length, R is the distance of sample centre from detector, and $\underline{q}\underline{r}_i$ is the phase shift due to scattering. The intensity of scattered radiation then is as follows:

$$I(\underline{q}) = \langle |A(\underline{q})|^2 \rangle = b^2/R^2 N \left\langle 1 + N^{-1} \sum_{i \neq j}^N \sum_{j=1}^N \exp(-i\underline{q}\underline{r}_{ij}) \right\rangle, \quad (\text{A.2})$$

with $\underline{r}_{ij} = \underline{r}_i - \underline{r}_j$. The expression in the brackets $\langle \rangle$ is the structure factor $S(\underline{q})$, where the brackets indicate that a thermal or ensemble average has to be taken. This is calculated with the aid of the pair distribution function $g(\underline{r}_{ij})$, which for centrosymmetric interactions depends only on the magnitude of $\underline{r}_{ij} = r$. Thus, one obtains for $S(\underline{q})$:

$$\begin{aligned} S(\underline{q}) &= \left(1 + N^{-1} \sum_{i \neq j}^N \sum_{j=1}^N V^{-2} \iint g(\underline{r}_{ij}) \exp(-i\underline{q}\underline{r}_{ij}) d\underline{r}_i d\underline{r}_j \right) \\ &= \left(1 + \frac{N}{V} \left(\int (g(\underline{r}) - 1) \exp(-i\underline{q}\underline{r}) d\underline{r} + \int \exp(-i\underline{q}\underline{r}) d\underline{r} \right) \right) \end{aligned} \quad (\text{A.3})$$

where the following relation has been used:

$$\iint \dots d\underline{r}_i d\underline{r}_j = V \int \dots d\underline{r}. \quad (\text{A.4})$$

In the second equation of (A.3), the last term is zero for $\underline{q} \neq 0$. So it makes no contribution to the radiation scattered by the atoms of the fluid. Finally, for centrosymmetric interactions $S(\underline{q})$ depends only on the magnitude q and with $\underline{q}\underline{r} = q r \cos \Theta$ and $|d\underline{r}| = \sin \Theta d\Theta d\phi r^2 dr$, $S(\underline{q})$ in (A.3) becomes

$$S(q) = 1 + 4\pi \frac{N}{V} \int_0^\infty \sin(qr)/(qr) (g(r) - 1) r^2 dr. \quad (\text{A.5})$$

Taking the Fourier transform, the corresponding expression for $g(r)$ is as follows:

$$g(r) = 1 + (2\pi^2)^{-1} \frac{V}{N} \int_0^\infty \sin(qr)/(qr) (S(q) - 1) q^2 dq. \quad (\text{A.6})$$

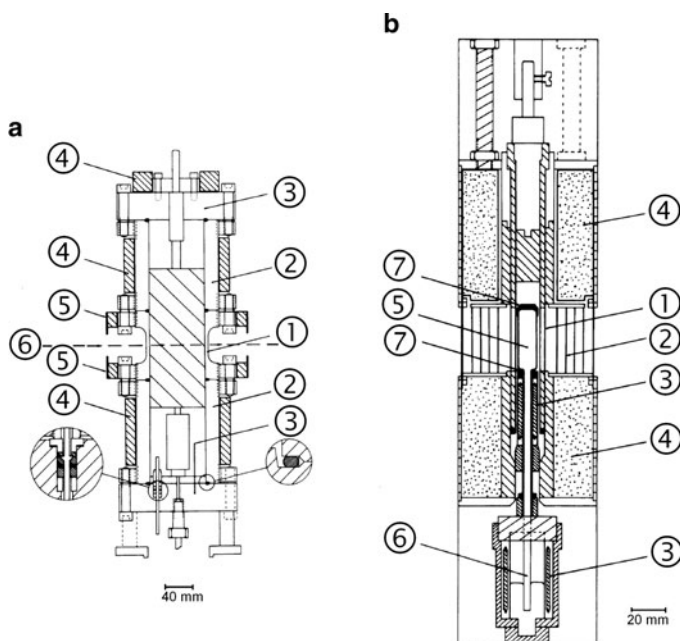


Fig. A.2 (a) High-pressure neutron diffraction autoclave: (1) Ti_{0.67}Zr_{0.33} zero alloy neutron window, (2) stainless steel cylinders, (3) high-pressure flanges, (4) water cooling, (5) Cd shields, (6) incoming neutron beam; (b) sample cell, heaters, and thermal insulation inside the autoclave: (1) W heater, (2) V heat shields, (3) additional Mo resistance heater, (4) ZrO₂ thermal insulation, (5) measurement compartment of sample cell, (6) cell capillary dipping into liquid reservoir, and (7) thermocouples. See also [A.1]

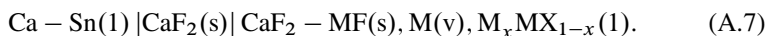
High-temperature–high-pressure neutron scattering measurements of fluids require special constructions of the sample cell and its surroundings. An arrangement, with which for the first time temperatures up to 2,000 K and pressures up to 300 bar have been achieved [A.1], is shown in Fig A.2. The central part of the high-pressure vessel consists of a cylinder with a thin wall of 5 mm thickness made from a Ti_{0.67}Zr_{0.33} alloy. This material is a purely incoherent neutron scatterer. The neutron window can withstand a maximum internal pressure of 400 bar when properly cooled. On both sides of this window, high-pressure stainless steel cylinders are connected by appropriate seals and are closed at both ends by high-pressure flanges. These contain several electrical feedthroughs for thermocouples and resistance heaters and a connection for a high-pressure Ar gas pipe. The sample cell together with the heating elements and thermal insulations as mounted inside the high-pressure vessel is shown in Fig A.2b. The upper end of the sample cell – a thin wall Mo or a single crystal sapphire tubing closed at the top end – is surrounded by a cylindrical resistance heater made from a 50 μm W foil. The temperature profile along the sample volume is controlled by additional heating elements wound directly on the capillary underneath of the measurement compartment. The advantage of the sapphire cell is that it can be oriented in the neutron beam in such a way that the sapphire Bragg

reflections lie outside the scattering plane of the sample. In the height of the neutron beam, thin foil vanadium heat shields reduce heat loss due to radiation and convection. So, in the case of the sapphire cell, only scattering of the thin wall W foil interferes with scattering of the fluid sample. At the bottom end, the cell capillary dips into a liquid reservoir. In this way, the background scattering and absorption of the empty cell plus surroundings can be measured first and then – without changing the alignment in the beam – the cell can be filled with the liquid sample by applying a small argon pressure inside the autoclave and a sample scattering run can be started.

A.2 Optical and ESR Spectroscopy with In Situ Coulometric Titration

In some spectroscopic investigations, small sample volumes of a few cubic millimeters have to be handled, for instance in optical studies of ultrathin films or in ESR spectroscopy. If, in addition, in situ variation of composition at high temperature is required, this is not an easy task. A solution of this problem is the use of an electrochemical method for the in situ concentration variation and to combine the respective sample cell with an electrochemical cell. However, at high temperatures of the order of 1,000 K, which are necessary for the doping of molten salts or liquid alloys, the choice of suitable electrochemical cells is rather limited. Here, we describe an EMF cell that has been successfully tested in optical, conductivity, and ESR studies up to 1,000 K and which enabled in situ variation of metal mole fraction in molten salts in a range $10^{-5} \leq x \leq 10^{-1}$. The technique applied is based on the Coulometric titration method [A.2, A.3].

The EMF cell is composed of a $\text{Ca}_{0.1}\text{Sn}_{0.9}$ reference and counter electrode, a single crystal CaF_2 solid electrolyte, and a working electrode consisting of a solid double salt $\text{CaF}_2\text{--MF}$ (e.g. $\text{M} = \text{Na}, \text{K}, \text{or Cs}$) and the MX melt in a separate compartment of the optical or ESR cell. In order to ensure the stability of the reference electrode, the amount of the liquid $\text{Ca}_{0.1}\text{Sn}_{0.9}$ alloy should be relatively large so that the Ca activity of 10^{-7} at 1,000 K does not change during titration. Calcium fluoride above ~ 870 K undergoes a phase transition and becomes a fast F^- ion conductor; at the same time, the high-temperature phase becomes relatively soft so that metal cups can be sealed against a CaF_2 crystal plate by simple mechanical compression. Altogether the EMF cell can be written as follows:



If, at negative polarization of the working electrode, a current is passed through the cell, metal M is formed in the double salt and F^- ions flow through the solid electrolyte and react with Ca of the Ca–Sn alloy. Excess metal dissolved in the double salt equilibrates with metal in the vapour phase and thus, via the vapour phase, the molten salt MX in a separate compartment can be doped with excess metal. Measuring the charge passed through the cell, the amount of M in molten MX is obtained from the difference of the total charge and that part which corresponds

to M dissolved in $\text{CaF}_2\text{--MF(s)}$. The latter can be determined in a calibration measurement without MX(l) . On the other hand, if the relation between metal activity and metal mole fraction, $a_M(x_M)$, is known from thermodynamic data, then x_M can be determined directly from metal activity measurements according to the Nernst equation:

$$a_M = \frac{\exp(F(E - E_0))}{RT}, \quad (\text{A.8})$$

where F = Faraday constant and E_0 = EMF at metal saturation. The E_0 values for the above EMF cell for different alkali metals are $E_0 = -133$ mV at 1,073 K for Na–NaF [A.4, A.5], $E_0 = -233$ mV at 1,073 K for K–KF– CaF_2 [A.6], and $E_0 = -230$ mV at 973 K for Cs–CsF– CaF_2 [A.6].

The realization of a combined EMF–optical cell for high-temperature measurements is presented in Fig. A.3 [3.82]. The optical cell consists of two polished sapphire discs (20 mm diameter and 5 and 10 mm thickness, respectively), which are sealed by squeezing a Ta ring (25, 50, or 100 μm Ta wire thickness, annealed under UHV) inside a stainless steel–molybdenum frame. In this way, the optical film thickness can be varied from ~ 6 to ~ 50 μm . The thicker sapphire contains a boring which connects the optical film with a spherically shaped and polished depression on its circumference. At this depression, the optical cell is sealed and connected via an iron capillary with a molybdenum plate that contains the working electrode compartment. The capillary is made from high purity iron, which is soft enough for this sealing technique using another molybdenum frame. The high vacuum tightness of these seals has been checked with a He-leak detector. The EMF cell is mounted on top of the bottom Mo plate, whereby a CaF_2 single crystal (22 mm diameter and

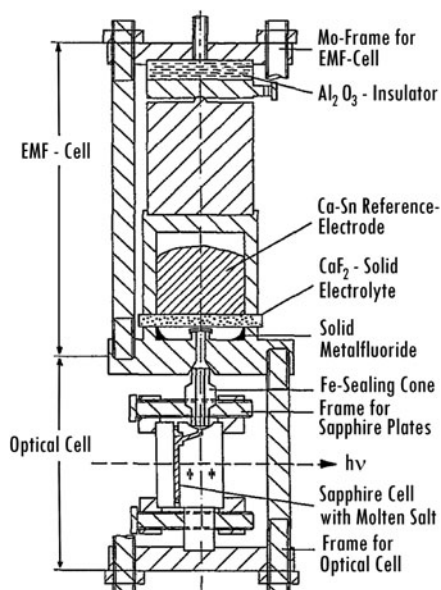


Fig. A.3 Side view of the construction of a combined EMF–optical cell for high-temperature absorption spectroscopy with in situ Coulometric titration. See also [A.6]

3 mm thickness) is pressed against the polished ends of the two Mo cups in a frame with Mo screws. On top of the reference electrode Mo cup is a stainless steel rod that ensures that on heating the pressure on the CaF_2 crystal is increased due to the larger thermal expansion of steel relative to that of the Mo screws. With this technique, tight EMF cells have been achieved working up to 10^3 K. The finally assembled combined EMF–optical cell was aligned inside a high vacuum furnace that fitted into a Cary 17H spectrometer.

A similar construction of a combined ESR–EMF cell is shown in Fig A.4 [3.84]. The EMF part of this cell is essentially the same as that described above.

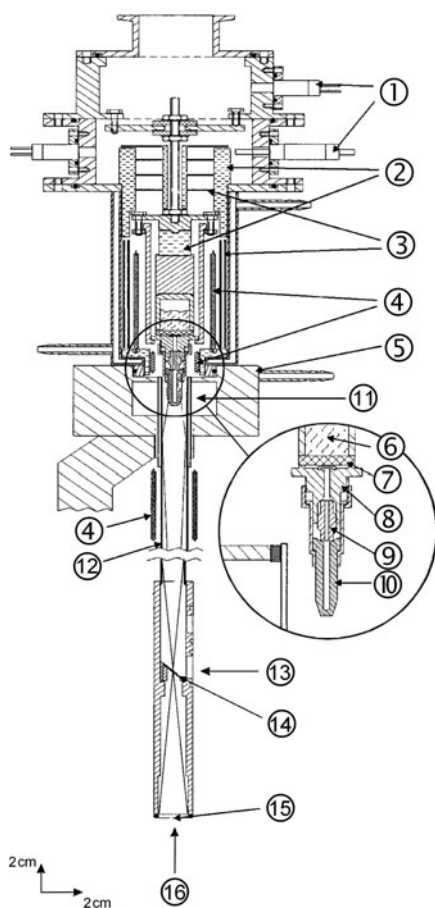


Fig. A.4 Schematic drawing of a high-temperature ESR cavity including a combined EMF–ESR sapphire cell heated by a CO_2 -laser from below; the different parts are (1) electrical feedthroughs of the vacuum jacket, (2) thermal Al_2O_3 insulation, (3) Mo heat shields, (4) Mo resistance heaters, (5) TE_{011} cavity, (6) Ca–Sn reference electrode, (7) CaF_2 single crystal disc, (8) working electrode compartment containing MF– CaF_2 double salt, (9) Ta sealing cylinder, (10) sapphire capillary, (12) sealed quartz tubing, (13) pyrometer window, (14) bored and polished Mo mirror, (15) ZnSe lens, and (16) CO_2 -laser beam. See also [3.84] and [A.7]

It is mounted on top of the ESR cavity and is surrounded by molybdenum resistance heaters and heat shields. At the lower end of the EMF cell, a sapphire capillary closed one end is sealed to the molybdenum flange. This capillary with a boring of 1 mm diameter is located in the centre of a TE₀₁₁ cavity and contains about 2–3 mg of the MX salt. It is heated from below the cavity by a CO₂ laser. For further details, see [3.84].

A.3 Capillary Wave Spectroscopy at Elevated Temperatures

On an atomic scale, the surface of a liquid is not plane and smooth, but rough. This is due to thermal motion of the molecules vertical to the interface. The vertical displacement, $\langle z^2 \rangle^{1/2}$, increases with temperature and with reducing the restoring force, the surface tension σ , i.e. $\langle z^2 \rangle^{1/2} \propto T/\sigma$. The surface displacement profiles in space and time, $z(\underline{r}, t)$, can be written as a sum of Fourier components that define the surface modes or capillary waves. These have a characteristic frequency, ω_q , and a wave vector, $\underline{q}$. Depending on the bulk viscosity η , capillary waves either propagate as a damped oscillator or are completely damped. Their frequency is determined by the bulk and interfacial properties and is obtained from solving the linearized hydrodynamic equations with proper boundary conditions – see the review by Langevin [A.8]. In the case of a free liquid/vapour interface and for low viscosities of the liquid, the solution is as follows:

$$\omega_q = \left(\frac{\sigma q^3}{\rho} \right)^{1/2} \quad \text{and} \quad \tau_q^{-1} = \Delta\omega_q = \left(\frac{2\eta q^2}{\rho} \right), \quad (\text{A.9})$$

where ρ is the bulk density, τ_q is the lifetime of the capillary wave, and $\Delta\omega_q$ is the half width of the Lorentzian component of the spectrum of scattered light. For more complex interfaces such as those of liquid crystals or with an adsorbed film, modifications of (A.9) must be considered; see [A.8].

In surface light scattering or capillary wave spectroscopy, the propagating surface modes act as a moving diffraction grating, where the scattered light is Doppler shifted by $\pm\omega_q$. In general, only the intensities of the regularly reflected light (ω_0 , k_0) and of the first order diffracted beam ($\omega_0 \pm \omega_q$, k_{1d}) are of interest and those of higher orders are weaker. The wave vector $\underline{q}$ is given by the difference of the projections of $\underline{k}_0$ and $\underline{k}_{1d}$ in the surface plane, $\underline{q} = \underline{k}_{0,s} - \underline{k}_{1d,s}$. Typically, the scattering angle $\Delta\Theta$ of first-order scattering is of the order of a degree, so that $q = k_0 \Delta\Theta$ lies in the range $100 \leq q/\text{cm}^{-1} \leq 1,000$ for He–Ne laser light with $k_0 \sim 10^5 \text{ cm}^{-1}$. The corresponding frequency for $q = 500 \text{ cm}^{-1}$, $\rho = 1 \text{ g cm}^{-3}$, and $\sigma = 10^2 \text{ mJ m}^{-2}$ is $\omega_q \sim 10^5 \text{ Hz}$.

Capillary wave spectroscopy is a contactless method to measure the surface free energy and the viscoelastic properties not only of liquid/vapour, but also of liquid/liquid – in transparent fluids – and liquid/thin film interfaces. Especially, for these last applications it is a unique method. An experimental set-up developed for

measurements at elevated temperatures is schematically drawn in Fig A.5 see also [4.5]. In brief, laser light (10 mW He–Ne laser, TEM₀₀ mode, and $\lambda = 632.8$ nm) passes a lens and pinhole arrangement, is diffracted by a holographically etched grating, and is focused by a biconvex lens and prism on the liquid surface. Light scattered at small angles by capillary waves is optically mixed at the photomultiplier with a coherent reference beam of specific order generated by the diffraction grating (optical heterodyne detection). The amplified signal at specific q is recorded in the frequency domain with a Fast Fourier Transform spectrum analyzer. All components including the vacuum chamber ($\leq 10^{-8}$ mbar) are mounted on a vibration damped table. The surface of the liquid sample can be cleaned in situ under vacuum by Ar ion sputtering or with a heated W wire brush. The spectrum of scattered light is the power spectrum of capillary waves that for large $Y \geq 10^3$ ($Y = \sigma/(4\nu^2 \rho q)$, ν = kinematic viscosity) can be approximated by a Lorentzian [A.8]. So, the power spectra can be fitted by a convolution of a Lorentzian and a Gaussian – the latter representing instrumental line broadening – and from these fits the peak frequency ω_q can be obtained with a typical precision of $\leq 1\%$. For determination of the scattering angle $\Delta\Theta$, the scattered and diffracted beams are imaged at two different positions of known distance (A and B in Fig A.5). In this way, q can be measured with an accuracy of $\sim 1\%$.

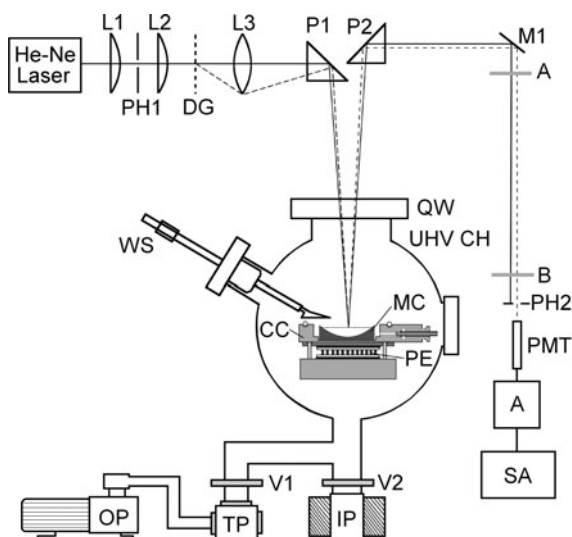


Fig. A.5 Experimental set-up for surface light scattering at fluid interfaces under UHV conditions and elevated temperatures. The different components are (L1, L2) plane convex lenses, (PH1) 80 μm pinhole, (DG) diffraction grating, (L3) biconvex lens, (P1, P2) prisms, (M1) Al mirror, (QW) quartz window, (PH2) pinhole with 0.9 mm diameter, (PMT) photomultiplier, Hamamatsu, (A) amplifier, (SA) FFT spectrum analyzer, Stanford, (UHV CH) ultra high vacuum chamber, (WS) wobble stick and Ar ion sputter gun, (MC) molybdenum crucible, (PE) Peltier element and Mo resistance heater, (V1, V2) vacuum valves, (OP, TP, IP) oil, turbo, and ion pump. See also [A.5]

A.4 High-Temperature Ellipsometry

In ellipsometry, the change of the state of polarization of polarized light interacting with an interface is recorded. It is generally assumed that this interaction is linear and energy conserving. If light is transmitted through the interface and the continuous change of polarization inside a medium is measured, this is called transmission ellipsometry. In reflection ellipsometry – for short-called ellipsometry in the following – the abrupt change of the state of polarization at the interface between two optically dissimilar media is recorded. This mode of ellipsometry is suitable to determine the complex optical constants – $N = n + ik$ or $\varepsilon = \varepsilon_1 + i\varepsilon_2$ with n being the refractive index, k the absorption coefficient, and ε the dielectric function – of highly absorbing media like metal alloys or metal–molten salt solutions; see Sect. 3.5. It can also be used to characterize thin interfacial films, their thickness, and optical properties; see Chap. 4.

The basic quantities in ellipsometry – for a comprehensive introduction, see the book by Azzam and Bashara [A.9] – are the Fresnel complex amplitude reflection coefficients that describe the change of state of polarization on reflection:

$$r_p \equiv (E_{rp}/E_{ip}) = |r_p| \exp(i\delta_{rp}) \text{ and } r_s \equiv (E_{rs}/E_{is}) = |r_s| \exp(i\delta_{rs}). \quad (\text{A.10})$$

Here, $|r_p|$ is the ratio of the amplitudes of the electric vectors of reflected (r) to incident (i) waves with the latter being polarized parallel (p) to the plane of incidence; δ_{rp} is the corresponding phase shift on reflection. The quantities $|r_s|$ and δ_{rs} have analogous meanings but now for incident waves polarized perpendicular (s, senkrecht) to the plane of incidence. The ellipsometric angles Ψ and Δ – these are the central quantities determined experimentally – are defined by the ratio ρ of the complex Fresnel reflection coefficients:

$$\rho = r_p / r_s = \tan \Psi \exp(i\Delta), \quad (\text{A.11})$$

with

$$\tan \Psi = |r_p / r_s| \text{ and } \Delta = \delta_{rp} - \delta_{rs}. \quad (\text{A.12})$$

For the determination of the corresponding optical characteristics of the interface, a model is needed. If the interface is solely defined by the contact of two isotropic and homogeneous phases with optical constants N_0 and N_1 , respectively, then the so-called two-phase model can be applied. Here, the ratio N_1/N_0 is given by an analytical expression that contains ρ and the angle of incidence Φ ; see [A.9]. In the case of a more complicated interface – e.g. a thin isotropic film of thickness d and optical constant N_2 between two bulk phases with N_0 and N_1 (three-phase or Drude slab model) – an analytical solution is not possible. Instead, the interesting parameters N_i and d must be determined from a numerical fit of the general expression for $\rho = \rho(N_i, d, \Phi)$; see also [A.10, A.11]. In this case, further experimental information is needed, which can be obtained, for instance, from measurements at different angles of incidence, $\rho(\Phi)$, or at variable frequency of the incident light, $\rho(\omega)$ (spectroscopic ellipsometry).

The principal arrangement of the optical components of a $\text{PSA}_{\text{rot}}\text{A}$ ellipsometer is shown in Fig A.6 [3.87]. Collimated light passes a polarizer (P), which defines the state of polarization of the incident light, and is reflected at an angle Φ at the sample (S). The reflected light, which in general is elliptically polarized, passes an analyser rotating at a frequency $\omega(A_{\text{rot}})$ and an analyser with fixed angle (A) and is recorded at a suitable detector (D). In this configuration, the detector signal $I(t)$ is given by a truncated Fourier series:

$$I(t) = a_0 + a_2 \cos(2\omega t) + b_2 \sin(2\omega t) + a_4 \cos(4\omega t) + b_4 \sin(4\omega t), \quad (\text{A.13})$$

where the Fourier coefficients a_i and b_i are functions of Δ and Ψ . These coefficients can be determined from the Fourier transform of the digitalized detector signal [3.87].

In the experiments on wetting films of K–KCl melts (Sect. 4.3), an ellipsometer with $\text{PSA}_{\text{rot}}\text{A}$ configuration has been employed. The ellipsometric angles Ψ and Δ have been determined at $\Phi = 70^\circ$ and, in addition, the reflectivity at $\Phi = 90^\circ$ has been measured [A.11]. Because of the elevated vapour pressure of the dissolved alkali metal, the fluid sample had to be sealed in an optical sapphire cell; see Fig A.7.

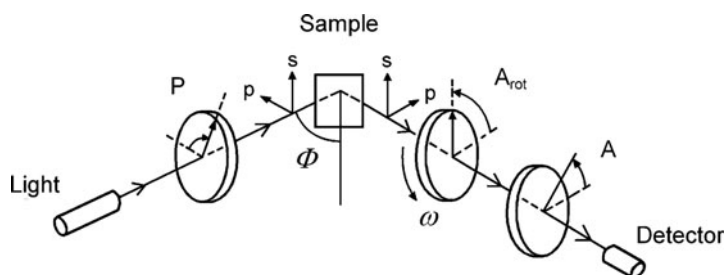


Fig. A.6 Schematic drawing of a $\text{PSA}_{\text{rot}}\text{A}$ ellipsometer: P = polarizer, S = sample, A_{rot} = rotating analyzer, A = analyser; the polarizations p and s denote light polarized parallel and perpendicular to the plane of incidence. See also [3.87]

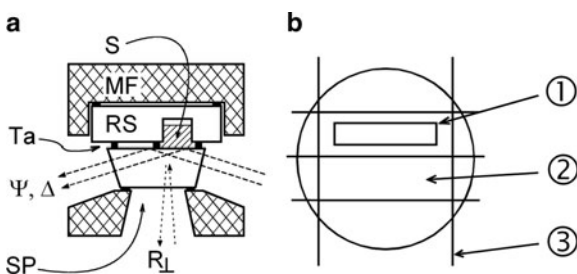


Fig. A.7 (a) Optical sapphire cell for ellipsometric measurement at high temperatures: (S) sample, (RS) reservoir sapphire, (SP) sapphire prism, (Ta) Ta sealing wire, (MF) metal frame, (*incoming upper beam*) beam for ellipsometric measurement at $\Phi = 70^\circ$, (*incoming lower beam*) beam for birefringence correction, and (R_L) reflectance measurement at $\Phi = 90^\circ$; (b) Arrangement of Ta sealing wires (3) between prismatic and reservoir sapphire in (a) defining sample (1) and reference compartment for birefringence corrections (2). See also [A.11]

This causes complications due to birefringence and stress birefringence of sapphire. The latter results from the sealing technique applied, whereby Ta sealing wires are compressed between the two sapphire discs. These contributions can be corrected by in situ measurements at the sapphire/sample and sapphire/vacuum interfaces at the same temperature and compression; see the two beams in Fig A.7.

A.5 Electrochemical Scanning Tunnelling Microscopy

The basic quantum mechanical equation and its consequences for tunnelling microscopy and spectroscopy have been introduced in Sect. 5.3. Here, this description is completed by the energy level diagram involved in electron tunnelling and, on the basis of this, the difference between tunnelling in vacuum and electrolytes shall be illustrated. Finally, the schematic set-up of an electrochemical scanning tunnelling microscopy (EC-STM) experiment is briefly described.

Figure A.8a shows the energy diagrams of two solid metals, a tunnelling tip (T) and a substrate (S), which are separated by a vacuum gap of width $d \leq 1$ nm. For simplicity, conduction band s-states that have the well-known $n(E) \propto E^{1/2}$ energy dependence of the density of states and are filled up to the Fermi energy E_F are considered. The electron wave functions of both metals decay exponentially across the gap, but for short enough values of $d \leq 1$ nm they have a small but finite probability density at the respective opposite solid. The potential barrier the electrons have to tunnel through is essentially determined by the work functions Φ_T and Φ_S , respectively; in simplest approximation, the effective barrier height is given by the average $\bar{\Phi} = (\Phi_T + \Phi_S)/2$. However, in realistic systems, image forces at the surfaces lead to a rounding of the barrier as indicated by the parabolic curve in Fig A.8; see also [5.44]. A modification of the potential barrier can be induced by applying

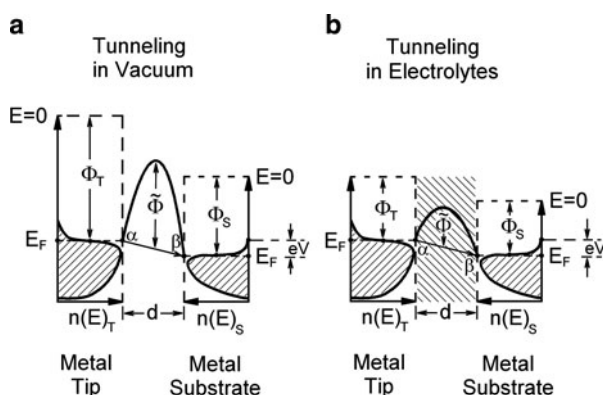


Fig. A.8 Schematic drawing of the energy diagram for tunnelling in vacuum (a) and in electrolytes (b). For details see text

a bias voltage V . At thermal equilibrium of both solids – which can be established e.g. by radiation – their respective Fermi energies are equal. However, if a bias voltage V is applied to the substrate – the tip being grounded – the Fermi level, being an electrochemical potential, is lowered by $eV > 0$. Now, tunnelling of an electron from an occupied state (α) of the tip into an empty state (β) of the substrate can take place; see Fig A.8. The reverse process requires a negative bias voltage. These considerations illustrate how by varying the bias voltage different local density of states at the substrate surface can be probed, which leads to modifications in the STM images.

Considering tunnelling through an electrolyte film in the gap, the main qualitative characteristics of vacuum tunnelling remain. The essential differences are the following. The tunnelling barrier, in general, is strongly reduced. This is caused by dipolar adsorbate–substrate interactions of ions and solvent molecules adsorbed at the tip/electrolyte and substrate/electrolyte interfaces. In the case of ionic liquids, measurements of the effective tunnelling barrier heights by tunnelling spectroscopy indicate a reduction of Φ of Au, Ni, and Co by ~ 4 eV [A.12]. Very similar results have been reported for aqueous electrolytes [A.13]. In the scheme depicted in Fig A.8b, this decrease in Φ has been taken into account. A second, not finally solved problem concerns the tunnelling process itself in electrolytes. This, indeed, is a demanding problem if one takes into account the complex configuration of overlapping double layers of tip and substrate in the gap. Different models have been suggested; see e.g. [A.14]. In MD calculations, the tunnelling process has been treated as scattering of electrons at the potential energy surface of the electrolyte. Another explanation considers resonant tunnelling where an intermediate state of a solvated electron is assumed. However, the lifetime of these states is relatively long ($\sim 10^{-12}$ s; see Sect. 3.5) in comparison with a typical tunnelling time across the gap (10^{-15} s), so that this mechanism is not very likely. A probable solution to the problem seems to be tunnelling through conduction band states of the electrolyte, which was suggested by Schmickler and Henderson [A.15].

A sketch of the principle components of an EC-STM experiment suitable for measurements with ionic liquids is depicted in Fig A.9. The electrochemical cell consists of a Teflon or glass cylinder, which is sealed by a silicon O-ring to the substrate or working electrode disc (WE). At the working electrode/ionic liquid (IL) interface, the atomic structure and a step edge at the surface are indicated by circles. For in situ EMF measurements, counter (CE) and reference (RE) electrodes are needed. For STM measurements, an STM tip (T) from Pt–Ir or W, which is connected with a piezo tubing (PT), is approached to the working electrode at a distance of ≤ 1 nm. Tungsten can be used in contact with ionic liquids as the inherent WO_x oxides can be dissolved by applying a potential; this is not the case in aqueous electrolytes. For EC-STM experiments, it is necessary that that part of the tip, which dips into the electrolyte, is electrically insulated with exception of a tiny spot of $\sim 100 \text{ nm}^2$ at the tip end. In this way, Faraday currents, which are orders of magnitude higher than the tunnelling currents, can be suppressed. To achieve such

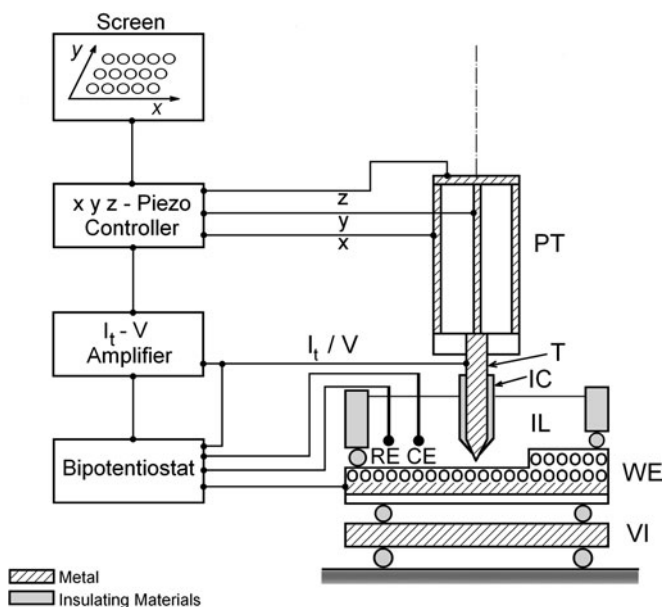


Fig. A.9 Schematic drawing of electrochemical cell with periphery of an EC-STM experiment. For further description see text

a coating (IC), the tip is covered with an insulating film and then is heated upside down in a specially programmed furnace. In experiments near room temperature, epoxid coatings have proven effective; at elevated temperatures, the combination of W tip and borsilicate glass coating with matched expansion coefficient is successful [A.16]. To achieve atomic resolution, good vibration (VI) and also acoustic insulation are important. In experiments using ionic liquid electrolytes, it is recommendable to house the electrochemical cell in a vacuum tight chamber that prevents adsorption of moisture and at the same time offers acoustic insulation. Otherwise HCl or HF may form which not only attacks the electronics of the scanner. The finally assembled electrochemical cell – with ionic liquids, filling and assembling should be done in a glove box with low water content – is connected with a piezo controller and a bipotentiostat. The latter ensures independent control of the tip bias voltage V and the cell EMF. The piezo controller with suitable feedback enables the tip movement in the x -, y -, z -directions across the substrate/ionic liquid interface. With measurements in a constant tunnelling current (I_t) mode, the z -movement of the tip is recorded during an x -, y -scan, which can be visualized on a screen. This information represents the local density of state profile of the substrate surface. A construction of an EC-STM cell for measurements at elevated temperatures is described in [A.16]. It has been tested with a W(111) single crystal electrode in an AlCl_3 – NaCl melt at temperatures up to 500 K.

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