The atomic dynamics of liquids with competing interactions

von der der Fakultät für Naturwissenschaften der Technischen
Universität Chemnitz genehmigte Dissertation zur Erlangung des
akademischen Grades

doctor rerum naturalium

(Dr. rer. nat.)

vorgelegt von **Dipl.-Phys. Sandro Jahn**

geboren am 23. September 1972 in Pößneck

eingereicht am 03.01.2003

Gutachter: Prof. Dr. Jens-Boie Suck
Prof. Dr. Walter Hoyer
PD Dr. Wolf-Christian Pilgrim

Tag der Verteidigung: 08.05.2003
<http://archiv.tu-chemnitz.de/pub/2003/0054>

Bibliographische Beschreibung

Thema

Sandro Jahn: The atomic dynamics of liquids with competing interactions.
Chemnitz: Technische Universität Chemnitz, Fakultät für Naturwissenschaften,
Dissertation 2003; 110 S.; 50 Abb.; 109 Literaturquellen.

Kurzfassung

Im Mittelpunkt der vorliegenden Arbeit steht die Frage, welchen Einfluss die Art der zwischenatomaren Wechselwirkung auf die atomare Dynamik in Flüssigkeiten hat. Dafür wurden geeignete binäre Systeme ausgewählt und deren Dichtefluktuationen bei verschiedenen Konzentrationen mittels unelastischer Neutronenstreuung gemessen.

Neben den teilweise bereits bekannten strukturellen Veränderungen, die beim Übergang von rein metallischen zu ionischen und teilweise kovalenten Bindungen auftreten, konnten in dieser Arbeit vor allem die Auswirkungen wechselnder Bindungsverhältnisse auf eine Reihe dynamischer Eigenschaften nachgewiesen werden. Besonders hervorzuheben sind dabei der Nachweis eines Hochfrequenzbandes im Frequenzspektrum des flüssigen RbSb, das in Computersimulationen des benachbarten Systems KSb vorhergesagt wurde und Schwingungen zwischen kovalent gebundenen Sb^- -Anionen beschreibt, sowie in den flüssigen Na-Sn-Legierungen die Aufspaltung der aus der longitudinalen Strom-Stromkorrelationsfunktion abgeleiteten Dispersionsrelation $\omega_m(Q)$ in zwei Bänder, die die verschiedenartige Dynamik der unterschiedlich schweren Komponenten widerspiegeln.

Die optimale Nutzung einer Neutronenquelle erfordert sowohl die Weiter- als auch die Neuentwicklung von Spektrometern. Für einen im Bau befindlichen neuen Spektrometertyp, ein thermisches Neutronen-Brillouin-Spektrometer, wurden umfangreiche Monte-Carlo Simulationen durchgeführt. Die hier präsentierten Resultate dieser Rechnungen umfassen sowohl die Bestimmung der Auflösungsfunktion und des Neutronenflusses am Probenort als auch eine Abschätzung der Strahlenbelastung außerhalb der Primärabschirmung.

Schlagworte

atomare Dynamik, binäre Flüssigkeit, unelastische Neutronenstreuung, Dichtefluktuation, dynamischer Strukturfaktor, Monte-Carlo-Simulation, kollektive Anregung, Zintl-Ion, Prepeak, Gedächtnisfunktion, Einteilchendynamik, Neutronen-Brillouin-Streuung

Contents

1	Introduction	5
2	Theoretical Background	7
2.1	Dynamic Correlation Functions	7
2.1.1	Partial Dynamic Structure Factors	7
2.1.2	Frequency Moments	9
2.1.3	Longitudinal Currents and VACF	11
2.2	Inelastic Neutron Scattering	12
2.2.1	Scattering Cross-Sections	12
2.2.2	Quantum Effects	13
2.2.3	Classical Two-Component Fluid	14
2.2.4	Kinematic Region	15
2.3	The Memory Function Approach	15
2.3.1	Generalised Langevin Equation	16
2.3.2	Continued Fraction	18
2.4	Dynamic Structure Models	18
2.4.1	Hydrodynamic Limit: $Q \rightarrow 0$	18
2.4.2	Free Particle Limit: $Q \rightarrow \infty$	20
2.4.3	Intermediate Q -Region	20
3	Liquid Alkali-Metal – Post- Transition-Group-Element Alloys	25
3.1	Solid Phases and Cluster Formation	25
3.2	Physical Properties of the Liquid	27
3.3	Liquid Structure	28
3.4	Volume Contraction	31
4	INS Experiments	33
4.1	BRISP – A New Type of INS Spectrometer	34
4.1.1	Flux and Shielding Simulation using MCNP	35
4.1.2	Ray-Tracing Simulation	38
4.2	Sample Preparation	42
4.2.1	Alloying and Synthesising	42
4.2.2	Sample Container	44

4.3	Measurements	44
4.3.1	Time-of-Flight Spectrometer: IN6	45
4.3.2	Triple-Axis Spectrometer: IN1	47
5	Data Treatment	49
5.1	Cross-sections and Densities	49
5.2	Transformation from (θ, t) to (Q, ω)	51
5.3	Container and Background Scattering	52
5.4	Detector and Monitor Efficiency	52
5.5	Normalisation of the Spectra	54
5.6	Absorption and Self-shielding	55
5.7	Multiple Scattering	55
5.8	Resolution Function of the Spectrometer	60
6	Results and Discussion	63
6.1	The Binary Liquid $\text{Na}_x\text{Sn}_{1-x}$	64
6.1.1	Scattering Law	64
6.1.2	Frequency Moments	67
6.1.3	Longitudinal Currents	69
6.1.4	Frequency Spectrum	73
6.1.5	Intermediate Scattering Function	77
6.2	The Binary Liquid $\text{Rb}_x\text{Sb}_{1-x}$	79
6.2.1	Scattering Law	79
6.2.2	Frequency Moments	80
6.2.3	Collective Dynamics	82
6.2.4	Frequency Spectrum	89
6.3	The Binary Liquid $\text{Rb}_x(\text{RbBr})_{1-x}$	90
6.3.1	Scattering Law and $S(Q)$	90
6.3.2	Collective Dynamics	92
6.3.3	Frequency Spectrum	92
7	Summary	95
	Bibliography	97
	List of Figures and Tables	103
	Symbols and Abbreviations	105
	Danksagung	107
	Lebenslauf	109
	Selbständigkeitserklärung	110

Chapter 1

Introduction

Structural and dynamic properties of condensed matter can be described on the atomic scale by (in general space- and time-dependent) correlation functions of microscopic variables. These correlation functions have been studied intensively in the last fifty years, after *van Hove*'s pioneering publication in 1954 [1], for a large variety of systems using experimental and theoretical methods as well as computer simulation techniques. The microscopic approach is motivated by the endeavour to obtain a basic understanding of the physical and chemical properties of matter, that goes beyond the phenomenological theories of macroscopic properties.

The different states of matter are characterised by the relative contributions of kinetic and potential energy to the total energy. While in dilute gases (near the ideal gas state) the potential energy is negligible, it plays the dominant role in ideal crystals, where the atoms are only allowed to vibrate around their equilibrium positions. The liquid state, which will be in the centre of interest here, takes an intermediate position between these two ideal cases and both kinetic and potential energies are of similar importance. While the former breaks up the long-range atomic order and allows the particles to move, the latter preserves the strong interatomic forces typical for condensed systems and hence a particle density close to that of the solid state.

The interatomic forces, which are represented by the potential, determine the structural arrangement of the atoms as well as their dynamic behaviour. From this point of view it appears plausible that molecular liquids have very different properties than, for instance, metallic or ionic fluids. On the other hand, the knowledge of dynamic properties allows to get information about the atomic interactions.

Inelastic neutron scattering (INS) is a very favourable experimental technique for studies of the atomic dynamics in condensed matter. The specific properties of the neutron allow the measurement of the dynamic correlation function of the density fluctuations in a sample. Up to now many INS experiments have been made in the field of liquids to study simple monatomic systems, like liquid

alkali metals or liquid noble gases, molecular or ionic liquids [2]. Recently, a complementary method, inelastic X-ray scattering (IXS), became available and allowed to extend the investigations to systems that can not easily be studied with neutrons (due to kinematic restrictions, which will be discussed later).

Experimental results show that collective phonon-like excitations also exist in the liquid, but they are strongly damped towards larger momentum transfers Q . While these excitations are quite pronounced in liquid metals and visible up to momentum transfers $Q \sim 0.8Q_p$, where Q_p is the position of the principle peak in the static structure factor $S(Q)$, they have not yet been observed in ionic systems.

Since the dynamic properties obviously depend on the type of atomic interaction it is very interesting to study the effect of a continuously changing potential on the atomic dynamics. In well chosen binary liquid alloys this is achieved by varying the composition. The systems that will be studied here have attracted interest due to their unusual electronic, thermodynamic and structural properties [3]. The alloys consist of an alkali metal and a post-transition-group element. Depending on the concentration of the two elements the dominant type of interaction is changed from a metallic to an ionic and even to a partly covalent bonding regime. While such a systematic investigation of macroscopic or structural properties as a function of composition has been made for many different systems, it is, to our knowledge, the first time that the microscopic dynamics is studied in this respect.

In the next chapter the dynamic variables and correlation functions will be introduced. Then the relation to INS will be established and some theoretical models of the atomic dynamics in liquids will be discussed. In chapter 3, the structural, electronic and thermodynamic properties of the class of binary systems are examined, which give the motivation of the present study of the dynamics. In the first part of chapter 4 results of computer simulations for a new INS spectrometer, that is currently under construction, will be presented. This is followed by a description of the sample preparation and the INS experiments made at two different spectrometers. In chapter 5 the involved data treatment is presented in detail. The experimental results for the three liquid binary alloy systems investigated here are shown and discussed in chapter 6. Finally, in chapter 7 the results will be summarised.

Chapter 2

Theoretical Background

The theoretical description of the dynamic properties of liquids is still a challenging subject. Only in two limiting cases it is established in a satisfactory manner. Ordinary hydrodynamics is applied when the liquid can be treated as a continuum, i.e. for length and time scales much longer than the atomic separations and the average interaction time of the particles, respectively. On the other hand, for very short times and distances the liquid appears as a Maxwellian system of free, non-interacting particles. For the intermediate region a number of models have been proposed and tested against inelastic neutron and X-ray scattering experiments and computer simulations. For some simple systems, like liquid alkali metals or liquid noble gases, the results are quite promising. However, the agreement is still far from being perfect.

In this chapter the basic dynamic variables and correlation functions will be introduced on a classical basis that is justified for liquids of not too light particles at high temperature. Then the relation to inelastic neutron scattering will be established and some theoretical models of liquid dynamics will be discussed.

2.1 Dynamic Correlation Functions

2.1.1 Partial Dynamic Structure Factors

The dynamic behaviour of many-body systems is best described by time-dependent correlation functions of appropriate physical variables. In multicomponent systems one has to label the particles according to their species and to define partial dynamic variables. Thus, element specific dynamic properties, that reflect the different atomic masses or chemical environments, can be studied more effectively. The definition of partial correlation functions has also an experimental motivation since they are observable due to the different scattering properties of elements and isotopes. The simplest and experimentally most relevant dynamic

variables are the single particle densities

$$n_s^{(i)}(\mathbf{r}, t) = \delta(\mathbf{r} - \mathbf{r}_1^{(i)}(t)) \quad (2.1)$$

and the partial number densities

$$n^{(i)}(\mathbf{r}, t) = \sum_{k=1}^{N^{(i)}} \delta(\mathbf{r} - \mathbf{r}_k^{(i)}(t)) \quad (2.2)$$

where the $N^{(i)}$ is the number of atoms of species i in the liquid. In the binary case the total number of atoms is given by $N = N^{(1)} + N^{(2)}$. $\mathbf{r}_j^{(i)}(t)$ is the position of the j -th atom of species i at a time t . The average values are given by $\langle n^{(i)}(\mathbf{r}, t) \rangle = N^{(i)}/V = n^{(i)}$ and $\langle n_s^{(i)}(\mathbf{r}, t) \rangle = 1/V$ with V the integrated volume.

For the correlation functions one considers the density fluctuations

$$\delta n^{(i)}(\mathbf{r}, t) = n^{(i)}(\mathbf{r}, t) - \langle n^{(i)}(\mathbf{r}, t) \rangle = n^{(i)}(\mathbf{r}, t) - n^{(i)} \quad (2.3)$$

Its space Fourier transform reads

$$\delta n^{(i)}(\mathbf{Q}, t) = \sum_{k=1}^{N^{(i)}} \exp(i\mathbf{Q}\mathbf{r}_k^{(i)}(t)) - (2\pi)^3 n^{(i)} \delta(\mathbf{Q}) \quad (2.4)$$

The time-dependent partial density correlation functions, also known as *van Hove correlation functions*, are defined as [1]

$$\begin{aligned} G^{(ij)}(|\mathbf{r} - \mathbf{r}'|, t) &= \frac{1}{\sqrt{n^{(i)}n^{(j)}}} \langle \delta n^{(i)}(\mathbf{r}', 0) \delta n^{(j)}(\mathbf{r}, t) \rangle \\ &= \frac{1}{\sqrt{n^{(i)}n^{(j)}}} \sum_{k=1}^{N^{(i)}} \sum_{l=1}^{N^{(j)}} \langle \delta(\mathbf{r}' - \mathbf{r}_k^{(i)}(0)) \delta(\mathbf{r} - \mathbf{r}_l^{(j)}(t)) \rangle \\ &\quad - \sqrt{n^{(i)}n^{(j)}} \end{aligned} \quad (2.5)$$

For $i=j$ the summation over l can be split into a self-part, where $l=k$, and a distinct part with $l \neq k$. The former defines the *van Hove self-correlation function* [1]

$$G_s^{(i)}(|\mathbf{r} - \mathbf{r}'|, t) = \langle \delta(\mathbf{r}' - \mathbf{r}_1^{(i)}(0)) \delta(\mathbf{r} - \mathbf{r}_1^{(i)}(t)) \rangle - \frac{1}{V} \quad (2.6)$$

where $1/V$ vanishes for $V \rightarrow \infty$. Spatial Fourier transform of equation 2.5 leads to the partial intermediate scattering functions

$$\begin{aligned} F^{(ij)}(\mathbf{Q}, t) &= \frac{1}{\sqrt{N^{(i)}N^{(j)}}} \langle \delta n^{(i)*}(\mathbf{Q}, 0) \delta n^{(j)}(\mathbf{Q}, t) \rangle \\ &= \frac{1}{\sqrt{N^{(i)}N^{(j)}}} \sum_{k=1}^{N^{(i)}} \sum_{l=1}^{N^{(j)}} \langle \exp(i\mathbf{Q}(\mathbf{r}_l^{(j)}(t) - \mathbf{r}_k^{(i)}(0))) \rangle \\ &\quad - (2\pi)^3 \sqrt{n^{(i)}n^{(j)}} \delta(\mathbf{Q}) \end{aligned} \quad (2.7)$$

The last term containing the delta function in equation 2.7 that corresponds to forward-scattering ($Q=0$) has no practical relevance here and will be omitted. The analogue Fourier transformation of $G_s^{(i)}(|\mathbf{r} - \mathbf{r}'|, t)$ (omitting the $1/V$ term) leads to

$$F_s^{(i)}(Q, t) = \langle \exp(i\mathbf{Q}(\mathbf{r}_1^{(i)}(t) - \mathbf{r}_1^{(i)}(0))) \rangle \quad (2.8)$$

The Fourier transformations from time to frequency yield the partial dynamic structure factors

$$S^{(ij)}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\omega t) F^{(ij)}(Q, t) \quad (2.9)$$

representing the collective dynamics of the system and their self parts

$$S_s^{(i)}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\omega t) F_s^{(i)}(Q, t) \quad (2.10)$$

that give information about the single particle dynamics.

2.1.2 Frequency Moments

The Taylor expansion of the intermediate scattering function at small t reads

$$F^{(ij)}(Q, t) = \sum_{n=0}^{\infty} \frac{d^n F^{(ij)}(Q, t)}{dt^n} \bigg|_{t=0} \frac{t^n}{n!} \quad (2.11)$$

On the other hand, using the inverse Fourier transformation of equation 2.9 and expanding the exponential function leads to

$$\begin{aligned} F^{(ij)}(Q, t) &= \int_{-\infty}^{\infty} d\omega \exp(i\omega t) S^{(ij)}(Q, \omega) \\ &= \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} d\omega \frac{(i\omega t)^n}{n!} S^{(ij)}(Q, \omega) \\ &= \sum_{n=0}^{\infty} \langle \omega^n \rangle^{(ij)} \frac{(it)^n}{n!} \end{aligned} \quad (2.12)$$

Analogue expressions may be derived for $F_s^{(i)}(Q, t)$. The coefficients of the short-time expansion of $F^{(ij)}(Q, t)$ and $F_s^{(i)}(Q, t)$ are the frequency moments [4] of $S^{(ij)}(Q, \omega)$

$$\langle \omega^n \rangle^{(ij)} = (-i)^n \frac{d^n F^{(ij)}(Q, t)}{dt^n} \bigg|_{t=0} = \int_{-\infty}^{\infty} d\omega \omega^n S^{(ij)}(Q, \omega) \quad (2.13)$$

and of $S_s^{(i)}(Q, \omega)$

$$\langle \omega^n \rangle_s^{(i)} = \int_{-\infty}^{\infty} d\omega \omega^n S_s^{(i)}(Q, \omega) \quad (2.14)$$

In the classical limit considered here the correlation functions are real and even in time and frequency. Therefore all odd frequency moments vanish. For a multicomponent system, the lowest order moments are [4, 5]

$$\langle \omega^0 \rangle^{(ij)} = F^{(ij)}(Q, 0) = S^{(ij)}(Q) \quad (2.15)$$

$$\langle \omega^0 \rangle_s^{(i)} = F_s^{(i)}(Q, 0) = S_s^{(i)}(Q) = 1 \quad (2.16)$$

$$\langle \omega^2 \rangle^{(ij)} = Q^2 k_B T \delta_{ij} / M^{(i)} \quad (2.17)$$

$$\langle \omega^2 \rangle_s^{(i)} = Q^2 k_B T / M^{(i)} \quad (2.18)$$

$$\begin{aligned} \langle \omega^4 \rangle^{(ij)} = \frac{Q^2 k_B T}{M^{(i)} M^{(j)}} & \left[\delta_{ij} \left(3Q^2 k_B T + \sum_l n^{(l)} \int d\mathbf{r} g^{(il)}(r) \frac{\partial^2 \Phi^{(il)}(r)}{\partial z^2} \right) \right. \\ & \left. - \sqrt{n^{(i)} n^{(j)}} \int d\mathbf{r} g^{(ij)}(r) \cos(Qz) \frac{\partial^2 \Phi^{(ij)}(r)}{\partial z^2} \right] \end{aligned} \quad (2.19)$$

$$\langle \omega^4 \rangle_s^{(i)} = \frac{Q^2 k_B T}{M^{(i)^2}} \left(3Q^2 k_B T + \sum_l n^{(l)} \int d\mathbf{r} g^{(il)}(r) \frac{\partial^2 \Phi^{(il)}(r)}{\partial z^2} \right) \quad (2.20)$$

The $S^{(ij)}(Q)$ are the partial static structure factors. They yield information about the number of neighbours and the average distribution of atomic separations in the liquid. The second moments appear as the mean energy transfer in the system at temperature T . k_B is the Boltzmann constant and $M^{(i)}$ the atomic mass of species i . Only the fourth and higher moments contain the interatomic potentials $\Phi(r)$ used here in pair potential approximation as $\Phi^{(ij)}(r)$. The pair correlation functions $g^{(ij)}(r)$ can be obtained by a Fourier transformation of $S^{(ij)}(Q)$. Analytical expressions for the sixth moments [6] involve higher order correlation functions and higher order derivatives of the pair potential. Due to their complicated structure strong approximations have to be made for any practical use.

For large Q , i.e. on a length scale much smaller than the interatomic distances, the frequency moments of the collective and the single particle correlation functions tend to approach each other, i.e. $S^{(ij)}(Q) \rightarrow \delta_{ij}$ and $\langle \omega^4 \rangle^{(ij)} = \langle \omega^4 \rangle_s^{(i)} = 3 \left(\langle \omega^2 \rangle^{(ij)} \right)^2 \delta_{ij}$. On the contrary, at smaller Q they behave differently. While the $S_s^{(i)}(Q)$ are constant, the collective counterparts exhibit oscillations often with a principle extremum (maximum for $i=j$, minimum for $i \neq j$) at Q_p that corresponds approximately to the inverse of the next neighbour distance multiplied by 2π . For very small Q the fourth moments vanish like $\propto Q^2$ in the single particle and for $i \neq j$ in the collective case, and like $\propto Q^4$ for $i=j$ in the latter [7].

2.1.3 Longitudinal Currents and VACF

The time derivatives of the partial number densities (equation 2.4) lead to the vectorial variables of the current $\mathbf{j}^{(i)}(\mathbf{Q}, t)$

$$\begin{aligned} \frac{dn^{(i)}(\mathbf{Q}, t)}{dt} &= i\mathbf{Q} \cdot \sum_{k=1}^{N^{(i)}} \mathbf{v}_k^{(i)}(t) \exp(i\mathbf{Q}\mathbf{r}_k^{(i)}(t)) \\ &= i\mathbf{Q} \cdot \mathbf{j}^{(i)}(\mathbf{Q}, t) \end{aligned} \quad (2.21)$$

with $\mathbf{v}_k^{(i)}(t) = d\mathbf{r}_k^{(i)}(t)/dt$ the time-dependent velocity of the particle k of species i .

The autocorrelation functions of the currents can be split into two parts, one considering the components parallel to $\mathbf{Q}$ (longitudinal currents), the other perpendicular to $\mathbf{Q}$ (transverse currents). The former is related to the partial dynamic structure factors by [6]

$$J_l^{(ij)}(Q, \omega) = \frac{\omega^2}{Q^2} S^{(ij)}(Q, \omega) \quad (2.22)$$

As all frequency moments of $S^{(ij)}(Q, \omega)$ exist, i.e. the decay of $S^{(ij)}(Q, \omega)$ is faster than any power of ω , $J_l^{(ij)}(Q, \omega)$ has at least one maximum at $\omega > 0$ for any constant Q . Therefore it is sometimes easier to discuss and interpret the current correlation function than the dynamic structure factor, which might be a weakly structured or even a monotonically decreasing function in ω with a single maximum at $\omega = 0$.

The single particle density shows a time dependence

$$\frac{dn_s^{(i)}(\mathbf{Q}, t)}{dt} = i\mathbf{Q} \cdot \mathbf{v}_1^{(i)}(t) n_s^{(i)}(\mathbf{Q}, t) \quad (2.23)$$

The single particle velocities $\mathbf{v}_1^{(i)}(t)$ are used to define the normalised velocity autocorrelation function (VACF)

$$\begin{aligned} \Psi^{(i)}(t) &= \frac{\langle \mathbf{v}_1^{(i)}(0) \mathbf{v}_1^{(i)}(t) \rangle}{\langle \mathbf{v}_1^{(i)}(0) \mathbf{v}_1^{(i)}(0) \rangle} \\ &= \frac{M^{(i)}}{3k_B T} \langle \mathbf{v}_1^{(i)}(0) \mathbf{v}_1^{(i)}(t) \rangle \end{aligned} \quad (2.24)$$

where the normalisation factor $\langle \mathbf{v}_1^{(i)}(0) \mathbf{v}_1^{(i)}(0) \rangle$ is given by the square of the thermal velocity $(v_0^{(i)})^2 = 2/M^{(i)} \times 3k_B T/2$ of the particle i . The Fourier transform of $\Psi^{(i)}(t)$

$$\tilde{z}^{(i)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \frac{1}{3} \langle \mathbf{v}_1^{(i)}(0) \mathbf{v}_1^{(i)}(t) \rangle \exp(-i\omega t) \quad (2.25)$$

defines a power spectrum that corresponds in harmonic approximation to the vibrational density of states for one-phonon processes. It is related to the self-part of the partial dynamic structure factors by [8]

$$\tilde{z}^{(i)}(\omega) = \lim_{Q \rightarrow 0} \frac{\omega^2}{Q^2} S_s^{(i)}(Q, \omega) \quad (2.26)$$

In the limit $\omega \rightarrow 0$ this function yields the respective diffusion constants $D^{(i)}$

$$\tilde{z}^{(i)}(0) = D^{(i)} / \pi \quad (2.27)$$

2.2 Inelastic Neutron Scattering

Inelastic neutron scattering (INS) is a very favourable technique for the experimental investigation of dynamic properties of condensed matter on a microscopic scale. The neutron has a mass $m = 1.67 \times 10^{-27} \text{ kg}$ and is characterised by a wavevector $\mathbf{k}$ and a corresponding energy of $E = (\hbar k)^2 / 2m$. Considering a typical neutron energy for scattering experiments between 1 and 100 meV the *de Broglie* wavelength $\lambda = 2\pi/k$ of the neutron is found to be in the order of a few 10^{-10} m , the same length scale as typical interatomic distances, which allows to observe interference effects from the scattered waves. Moreover, the neutron energies cover the same range as vibrational excitation frequencies in matter.

2.2.1 Scattering Cross-Sections

Figure 2.1: Scattering problem

The basic principle of the scattering experiment is sketched in figure 2.1. An incident neutron with wavevector $\mathbf{k}_i$ and energy E_i is scattered by the sample into a solid angle element $d\Omega$. The scattering angle is denoted by θ and the final state of the neutron after the scattering is characterised by $\mathbf{k}_f$ and E_f . The two important variables from the scattering process are the neutron energy transfer

$$\hbar\omega = \frac{\hbar^2}{2m} (k_i^2 - k_f^2) \quad (2.28)$$

and the neutron momentum transfer

$$\hbar \mathbf{Q} = \hbar(\mathbf{k}_i - \mathbf{k}_f) \quad (2.29)$$

For an isotropic system only the magnitude of $\mathbf{Q}$ is relevant

$$\hbar Q = \hbar \sqrt{k_i^2 + k_f^2 - 2k_i k_f \cos \theta} \quad (2.30)$$

The probability that the neutron is scattered by the sample into a solid angle increment $d\Omega$ from its initial state $|i\rangle$ to the final state $|f\rangle$ is given by the double differential cross-section for single scattering

$$\frac{d^2\sigma}{d\Omega dE_f}(\mathbf{k}_i \rightarrow \mathbf{k}_f) \quad (2.31)$$

In the quantum mechanical treatment of this expression neutron scattering is assumed to be a weak process, i.e. the disturbance induced by the neutron on the target is small, and therefore it is possible to use first order perturbation theory in the Born approximation. This is true if the interaction length between the neutron and a nucleus of the sample is much shorter than the interatomic distances. In this case the total scattering amplitude of the sample can be expressed by the sum of those for the individual atoms.

Van Hove[1] showed that in the Born approximation the double differential cross-section can be separated into a contribution describing the coupling of the neutron to the sample and another part containing the dynamics of the sample. The latter is obtained via the fluctuation-dissipation theorem [9] that relates the fluctuating properties of the sample in equilibrium to the response of the system to external perturbations, in the present case the scattering event. The double differential cross-section can then be written as

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} \frac{\sigma_B}{4\pi} \mathcal{S}(Q, \omega) \quad (2.32)$$

with σ_B the total bound atom neutron scattering cross-section and $\mathcal{S}(Q, \omega)$ the total scattering law of the sample. Before analysing the right hand side of equation 2.32 some comments on quantum effects will be made.

2.2.2 Quantum Effects

In a rigorous quantum-mechanical treatment (see e.g. [10]) the commutator of the time dependent density operators does not vanish, i.e. the correlation functions are not even in t and hence in ω . A simple physical explanation is that due to the temperature dependent occupation of initial states in the sample the neutron has a different probability to loose or to gain energy. The resulting condition of detailed balance is given by

$$\mathcal{S}(Q, \omega) = \exp\left(\frac{\hbar\omega}{k_B T}\right) \mathcal{S}(Q, -\omega) \quad (2.33)$$

The quantum effects are most pronounced at low temperatures and in systems with light particles where the recoil energy of the atoms comes into play. For the liquids considered here these effects are rather small though they cannot be neglected. A symmetric scattering function that is even in ω can be defined by

$$\tilde{\mathcal{S}}(Q, \omega) = \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \mathcal{S}(Q, \omega) \quad (2.34)$$

In many cases this function has been used for a comparison with the corresponding classical correlation function $\mathcal{S}^{cl}(Q, \omega)$. For the ideal Boltzmann fluid of non-interacting particles the deviation between $\mathcal{S}^{cl}(Q, \omega)$ and the exact $\tilde{\mathcal{S}}(Q, \omega)$ is of the order $\hbar^2$. A different approximation frequently used leads also to agreement up to first order in $\hbar$. In this case the $\mathcal{S}^{cl}(Q, \omega)$ is identified with the relaxation function in linear response theory after switching off the external perturbation. This leads to [10]

$$\mathcal{S}(Q, \omega) \simeq \frac{\hbar\omega/k_B T}{1 - e^{-\hbar\omega/k_B T}} \mathcal{S}^{cl}(Q, \omega) \quad (2.35)$$

In the following the symmetric scattering function $\tilde{\mathcal{S}}(Q, \omega)$ will be used to represent experimental data. Further it is assumed that $\tilde{\mathcal{S}}(Q, \omega) = \mathcal{S}^{cl}(Q, \omega)$. The superscript *cl* and the tilde will be omitted. Hence $\mathcal{S}(Q, \omega)$ will denote the total scattering law of a classical system.

2.2.3 Classical Two-Component Fluid

The neutron scattering length $b^{(i)}$, which characterises the neutron-nucleus scattering process, depends not only on the atomic species, but differs also between isotopes. In addition, it is in general spin dependent. However, after statistical averaging assuming random nuclear spin orientations and random isotope distributions within one species the right term in equation 2.32 can be split into two parts

$$\frac{\sigma_B}{4\pi} \mathcal{S}(Q, \omega) = \frac{\sigma_{coh}}{4\pi} S(Q, \omega) + \frac{\sigma_{inc}}{4\pi} S_s(Q, \omega) \quad (2.36)$$

The first part describes the purely coherent response, which arises when the scattered elementary waves interfere. The corresponding dynamic structure factor $S(Q, \omega)$ is weighted with the total coherent scattering cross-section σ_{coh} . The second part yields the incoherent scattering (without interference, i.e. isotropic) contribution, which is a measure of the single particle motion.

In a binary system the incoherent part of the total scattering law is just the sum of the $S_s^{(i)}(Q, \omega)$ of the two components weighted by the respective cross-sections $\sigma_{inc}^{(i)} = 4\pi \left(\langle b^{(i)2} \rangle - \langle b^{(i)} \rangle^2 \right)$ and concentrations $c^{(i)}$

$$\frac{\sigma_{inc}}{4\pi} S_s(Q, \omega) = c^{(1)} \frac{\sigma_{inc}^{(1)}}{4\pi} S_s^{(1)}(Q, \omega) + c^{(2)} \frac{\sigma_{inc}^{(2)}}{4\pi} S_s^{(2)}(Q, \omega) \quad (2.37)$$

The coherent scattering law, on the other hand, is expressed as a weighted sum of the partial dynamic structure factors $S^{(ij)}(Q, \omega)$ [11]

$$\frac{\sigma_{coh}}{4\pi} S(Q, \omega) = \sum_{i=1}^2 \sum_{j=1}^2 \sqrt{c^{(i)} c^{(j)}} b_{coh}^{(i)} b_{coh}^{(j)} S^{(ij)}(Q, \omega) \quad (2.38)$$

with $b_{coh}^{(i)} = \langle b^{(i)} \rangle$ the coherent scattering lengths. The weighting factors determine how much the corresponding correlation functions contribute to the total measured $S(Q, \omega)$. For a given composition the only way of changing these weights is via a change of the coherent scattering cross-section. This is possible either by the use of different isotopes of an element or by the use of other probes, e.g. X-rays.

In a different approach the coherent response is represented in terms of concentration and density fluctuations using the dynamic variables $c(\mathbf{r}, t) = c^{(2)}n^{(1)}(\mathbf{r}, t) - c^{(1)}n^{(2)}(\mathbf{r}, t)$ and $n(\mathbf{r}, t) = n^{(1)}(\mathbf{r}, t) + n^{(2)}(\mathbf{r}, t)$. The equation of the respective partials is given by [12]

$$\frac{\sigma_{coh}}{4\pi} S(Q, \omega) = \langle b \rangle^2 S_{nn}(Q, \omega) + 2(b_{coh}^{(1)} - b_{coh}^{(2)}) \langle b \rangle S_{nc}(Q, \omega) + (b_{coh}^{(1)} - b_{coh}^{(2)})^2 S_{cc}(Q, \omega) \quad (2.39)$$

with $\langle b \rangle = c^{(1)}b_{coh}^{(1)} + c^{(2)}b_{coh}^{(2)}$ the mean scattering length of the sample. Depending on the weighting factors and the type of binary system one or the other representation is more appropriate.

2.2.4 Kinematic Region

The compliance of the conservation laws for energy and momentum does not allow to access every point in the Q - ω -plane. For neutrons the restriction is especially a problem in the region of Brillouin scattering, i.e. small Q and relatively large ω . This may be demonstrated by combining equations 2.28 and 2.30 and plotting the area in the Q - ω plane that is accessible by a given range of scattering angles θ . Two examples are shown in figure 2.2. The dark grey area is the available kinematic region for an incident neutron energy of 4.75 meV, varying final neutron energy and an angular range between $\theta = 10^\circ$ and 115° . With increasing incident neutron energy the kinematic range can be extended (light grey area for 35 meV and $\theta > 1^\circ$), which is desired in many cases but unfortunately accompanied with some experimental drawbacks (see below in chapter 4).

2.3 The Memory Function Approach

Existing models of liquid state dynamics, both single particle and collective, can in most cases be cast into or were originally derived from the framework of projection operators and memory functions introduced by Zwanzig[13] and

Figure 2.2: Kinematic range of the thermal neutron TAS instrument IN1 ($E_f=35$ meV) and the cold neutron TOF instrument IN6 ($E_i=4.75$ meV).

Mori[14]. The basic ideas of this approach and the approximations made in different models will therefore be discussed here. For a more detailed presentation of the memory function approach the reader is referred to the literature (e.g. [6, 7]).

Within this theory the dynamics of a many-body system with N particles is described by the time evolution of a finite number n ($n < N$) of relevant and independent dynamic variables $A_\nu(t)$ ($\nu=1, \dots, n$) and their correlation functions $C_{\nu\lambda}(t)$. The A_ν and the $C_{\nu\lambda}$ are combined to a n -dimensional column vector of dynamic variables $\mathbf{A}(t)$ and a dynamic correlation matrix $\mathbf{C}(t)$. $\mathbf{A}(t)$ obeys the equation of motion

$$\frac{d\mathbf{A}(t)}{dt} = iL\mathbf{A}(t) \quad (2.40)$$

where iL is the Liouville operator. The formal solution of this equation $\mathbf{A}(t) = \exp(iLt)\mathbf{A}$, where the components of $\mathbf{A}$ are $A_\nu = A_\nu(t=0)$, can in practice be used only in some simple cases. For dense liquids, it is necessary to rephrase equation 2.40. This leads to a generalisation of the Langevin equation of Brownian motion.

2.3.1 Generalised Langevin Equation

The basic idea of the derivation of the generalised Langevin equation is to linearise equation 2.40 and to separate off contributions non-linear in $\mathbf{A}(t)$ and from other degrees of freedom. Technically this is done by introduction of a projec-

tion operator $\mathcal{P}$ that projects an arbitrary dynamic variable $\mathbf{G}$ on the subspace spanned by the set $[A_\nu]$

$$\mathcal{P}\mathbf{G} = \langle \mathbf{A}^* \mathbf{G} \rangle \langle |\mathbf{A}|^2 \rangle^{-1} \mathbf{A} \quad (2.41)$$

where $\mathbf{A}^*$ denotes the complex conjugate of $\mathbf{A}$. The projection operator is introduced into equation 2.40

$$\begin{aligned} \frac{d\mathbf{A}(t)}{dt} &= \exp(iLt)[\mathcal{P} + (1 - \mathcal{P})]iL\mathbf{A} \\ &= i\boldsymbol{\Omega} \cdot \mathbf{A}(t) + \exp(iLt)(1 - \mathcal{P})iL\mathbf{A} \end{aligned} \quad (2.42)$$

The time-independent term $i\boldsymbol{\Omega} = \langle \mathbf{A}^* \dot{\mathbf{A}} \rangle \langle |\mathbf{A}|^2 \rangle^{-1}$ is called the proper frequency matrix and describes the correlations between the equilibrium statistical averages of the dynamical variables. As the diagonal elements of this matrix are zero, the proper frequency matrix for a single dynamical variable vanishes. The second term on the r.h.s. of equation 2.42 is rewritten as a sum of a fluctuating force $\mathbf{f}(t)$ that is perpendicular to $\mathbf{A}$ at all times, i.e. $\langle \mathbf{A}^* \mathbf{f}(t) \rangle = 0$, and another term containing the normalised correlation function of the fluctuating forces, the so called memory matrix $\mathbf{M}(t) = \langle \mathbf{f}^* \mathbf{f}(t) \rangle \langle |\mathbf{A}|^2 \rangle^{-1}$. The resulting equation of motion reads

$$\frac{d\mathbf{A}(t)}{dt} = i\boldsymbol{\Omega} \cdot \mathbf{A}(t) - \int_0^t \mathbf{M}(t - \tau) \cdot \mathbf{A}(\tau) d\tau + \mathbf{f}(t) \quad (2.43)$$

Before discussing possible approximations for $\mathbf{M}(t)$ the exact form of the generalised Langevin equation will be presented. It describes the time evolution of the correlation matrix $\mathbf{C}(t) = \langle \mathbf{A}^* \mathbf{A}(t) \rangle$

$$\frac{d\mathbf{C}(t)}{dt} = i\boldsymbol{\Omega} \cdot \mathbf{C}(t) - \int_0^t d\tau \mathbf{M}(t - \tau) \cdot \mathbf{C}(\tau) \quad (2.44)$$

For the further treatment it is favourable to perform a Laplace transformation

$$\tilde{\mathbf{C}}(z) = \int_0^\infty dt \exp(-zt) \mathbf{C}(t) \quad (2.45)$$

In Laplace space the generalised Langevin equation reads

$$\tilde{\mathbf{C}}(z) = [z\mathbf{I} - i\boldsymbol{\Omega} + \tilde{\mathbf{M}}(z)]^{-1} \cdot \mathbf{C}(0) \quad (2.46)$$

with $\mathbf{I}$ the unity matrix. In the classical case where $\mathbf{C}(t)$ is real and even in time a simple relation between the Laplace and the Fourier transformations exists

$$\pi \mathbf{C}(\omega) = \text{Re} \left\{ \tilde{\mathbf{C}}(z = i\omega) \right\} \quad (2.47)$$

2.3.2 Continued Fraction

As $\mathbf{M}(t)$ is again a correlation matrix it can be expressed in the same formalism using a higher order memory matrix $\mathbf{M}_1(t)$ and the respective frequency matrix $\boldsymbol{\Omega}_1$ [15]

$$\frac{d\mathbf{M}(t)}{dt} = i\boldsymbol{\Omega}_1 \cdot \mathbf{M}(t) - \int_0^t d\tau \mathbf{M}_1(t - \tau) \cdot \mathbf{M}(\tau) \quad (2.48)$$

and in Laplace space

$$\tilde{\mathbf{M}}(z) = [z\mathbf{I} - i\boldsymbol{\Omega}_1 + \tilde{\mathbf{M}}_1(z)]^{-1} \cdot \mathbf{M}(0) \quad (2.49)$$

This procedure can be repeated with $\mathbf{M}_1(t)$ and so on leading to a continued fraction representation of the memory matrix. The frequency matrices ($i\boldsymbol{\Omega}$, $i\boldsymbol{\Omega}_1$, ...) and the correlation matrices at $t=0$ ($\mathbf{C}(0)$, $\mathbf{M}(0)$, $\mathbf{M}_1(0)$, ...) are related to the frequency moments of $\mathbf{C}(\omega)$.

2.4 Dynamic Structure Models

The dynamic variables of primary experimental interest here are the particle densities defined in eqns. 2.1 and 2.2. The corresponding time-correlation functions are the intermediate scattering functions $\mathbf{F}(Q, t)$ and $\mathbf{F}_s(Q, t)$. The dynamic structure factor is expressed as $\pi\mathbf{S}(Q, \omega) = \text{Re} \left\{ \tilde{\mathbf{F}}(Q, z = i\omega) \right\}$ and its self-part as $\pi\mathbf{S}_s(Q, \omega) = \text{Re} \left\{ \tilde{\mathbf{F}}_s(Q, z = i\omega) \right\}$. As most of the models were derived for monatomic liquids in the following the matrix notation shall be skipped and replaced by scalar functions. Extensions to the binary case have been made in some cases. The implications of the different atoms on the model functions will be described at the appropriate places. Although, due to the increasing number of parameters, the binary models will not be very useful for a quantitative fit of experimental data they may at least be used for a qualitative interpretation and discussion.

2.4.1 Hydrodynamic Limit: $Q \rightarrow 0$

If the dynamics of the system is probed on (quasi-)macroscopic time and length scales the correlation functions yield an average over a large number of microscopic events. The macroscopic regime that is entered in the long-wavelength limit ($Q \rightarrow 0$) can be described by both the ordinary hydrodynamics in its linearised form and the microscopic memory function approach.

Simple Diffusion

As the memory function decays on a microscopic timescale even in the hydrodynamic region it may be approximated by a δ -function in time if the decay of

the density correlation function is much slower. A typical example for a so called Markoff process where the memory effects is neglected is the diffusion of a single particle caused by uncorrelated binary collisions. With the Markoffian ansatz for the memory function

$$M_s(Q, t) = 2\Gamma_s(Q)\delta(t) \quad (2.50)$$

which corresponds to an exponential decay of the time correlation function $F_s(Q, t)$, where $\Gamma_s(Q)$ is the decay rate, the spectral self-correlation function is characterised by a Lorentzian lineshape

$$S_s(Q, \omega) = \frac{1}{\pi} \frac{\Gamma_s(Q)}{\omega^2 + \Gamma_s(Q)^2} \quad (2.51)$$

This model is valid if the collision time, i.e. the time of strong interatomic interaction, is assumed to be much smaller than the time between subsequent collisions. The short-time dynamics is not considered and therefore only the zeroth frequency moment is fulfilled. In the hydrodynamic limit $\Gamma_s(Q) = DQ^2$ is related to the diffusion constant D . A Lorentzian is sometimes used to describe other diffusional processes, as well.

Navier-Stokes Hydrodynamics

For the description of the collective dynamics in the long-wavelength limit the Navier-Stokes hydrodynamics can be employed using the linearised equations for the conservation of mass, energy and momentum [16]. In this macroscopic approach, the fluctuations of the dynamic variables around their equilibrium values are considered to be small to allow a perturbative treatment. Further, the thermodynamic quantities and transport coefficients are assumed to be constant.

The same result can be derived using the microscopic formalism of memory functions. Using a three-dimensional vector $\mathbf{A}(t)$ of the conserved dynamic variables the frequency matrix $i\Omega$ now has non-vanishing elements. The resulting hydrodynamic density correlation function reads [7]

$$\tilde{F}(Q, z)_{hyd} = F(Q, t=0)_{hyd} \left[z + \frac{(c_0 Q)^2}{z + \frac{\eta_L}{nM} Q^2 + \frac{(\gamma - 1)(c_0 Q)^2}{z + (\kappa/nC_V) Q^2}} \right]^{-1} \quad (2.52)$$

where $c_0 = \sqrt{k_B T / MS(0)}$ is the isothermal sound velocity, $\gamma = C_p / C_V$ the ratio between the specific heats at constant pressure and at constant volume, κ the thermal conductivity and η_L the longitudinal viscosity coefficient.

Equation 2.52 yields basically three modes, two of them propagating with velocity c_0 and representing coupled density–pressure fluctuations (Stokes and anti-Stokes lines). The third mode stems from entropy fluctuations, is centred

at $\omega = 0$ (Rayleigh line) and non-propagating. Often these three modes can be approximated by a sum of three Lorentzians.

For a binary system concentration fluctuations have to be considered additionally. They lead to another non-propagating mode and a complicated central component. In certain simplified cases temperature and concentration modes can be represented by two independent Lorentzians. In general, the dynamic structure factor for a binary system is a complicated function, even in the hydrodynamic limit.

2.4.2 Free Particle Limit: $Q \rightarrow \infty$

For very large momentum transfers the correlation between particles gets lost. As a consequence the single particle and the collective dynamics approach each other with increasing Q and the system appears as an ideal Boltzmann fluid. For a classical liquid the scattering law is given by a Gaussian [17]

$$S(Q, \omega) = \sqrt{\frac{M}{2\pi\hbar^2 Q^2 k_B T}} \exp\left(-\frac{M\omega^2}{2k_B T Q^2}\right) \quad (2.53)$$

In a rigorous quantum-mechanical treatment $S(Q, \omega)$ is given by the same function with the centre shifted due to the recoil energy [18].

2.4.3 Intermediate Q-Region

While the two cases above give formally correct results they do not reveal the physical origin of the dynamic behaviour in the liquid system. In the hydrodynamic description the thermodynamic and transport properties are obtained phenomenologically and the free particle treatment simply ignores interatomic potentials. The intermediate Q region that is accessible to neutron scattering and covers lengths scales of interatomic distances is therefore especially interesting though much more complicated than the limiting cases. A microscopic theory should provide a dynamic picture over a large Q range including the hydrodynamic and the free particle regimes.

The memory function approach has proven as a well suited theoretical apparatus to separate relevant dynamic properties from those that can (and have to) be treated in an approximate manner. Starting from the hydrodynamic description that can also be treated in the formalism of memory functions, the correlation functions may be generalised to the intermediate Q region by introducing Q - and time-dependent properties on a physical basis.

Some of the models for the collective dynamics will be discussed in the following. Starting point is the hydrodynamic result (eq. 2.52). The extension of this model to larger Q is subject of the generalised hydrodynamic theory where the short-time behaviour (frequency moments) is combined with the hydrodynamic effects which take place on a much longer timescale. The thermodynamic

and transport coefficients then become Q -dependent. $F(Q, t = 0)_{hyd}$ can be generalised to $S(Q)$ to fulfil the zeroth frequency moment. The generalised sound velocity $c_0(Q)$ is linked to the moments via $c_0^2(Q)Q^2 = \omega_0^2(Q) = \langle \omega^2 \rangle / \langle \omega^0 \rangle$, which comes from $\omega_0^2(Q) = M(Q, t = 0)$, the initial value of the memory function. The next order memory function $M_1(Q, t)$ of equation 2.52 consists of two components, one representing the decay of the longitudinal density modes and the other of the thermal fluctuations

$$M_1(Q \rightarrow 0, t) = 2(\eta_L/nM)Q^2\delta(t) + (\gamma - 1)\omega_0^2 \exp(-(\kappa/nC_V)Q^2t) \quad (2.54)$$

Damped Harmonic Oscillator

If the thermal fluctuations are ignored, i.e. they may be small if $\gamma \approx 1$, the generalisation of $M_1(Q, t)$ may be written as (see discussion of the Markoffian ansatz in equation 2.50)

$$M_1(Q, t) = 2\Gamma(Q)\delta(t) \quad (2.55)$$

This is equivalent to an exponential decay of the memory function $M(Q, t)$. With $\Gamma(Q) = 1/\tau(Q)$ the correlation function is given by

$$\tilde{F}(Q, z) = S(Q) \left[z + \frac{\omega_0^2(Q)}{z + 1/\tau(Q)} \right]^{-1} \quad (2.56)$$

The dynamic structure factor then has the shape of a normalised damped harmonic oscillator (DHO) with the decay time $\tau(Q)$

$$S(Q, \omega) = \frac{S(Q)}{\pi} \frac{\omega_0^2(Q)/\tau(Q)}{(\omega^2 - \omega_0^2(Q))^2 + (\omega/\tau(Q))^2} \quad (2.57)$$

The DHO is frequently used for the description of phonon modes in crystals. In principle it could also be applied for collective excitations in liquids. However, it does not account for any diffusive mode, e.g. from temperature fluctuations. In a very simple picture it could be assumed that the propagating collective modes are decoupled from the temperature fluctuations. For this case, a combination of a DHO with a Lorentz function for the relaxing mode was proposed and used, e.g. for liquid Rb[19]. One could even imagine a second Lorentzian in the binary case that accounts for the concentration fluctuations. From the physical point of view it is more satisfying to avoid this rather empirical approach and improve the model by inclusion of the fourth moment.

Viscoelastic Model

The viscoelastic models, of which a frequently used one was proposed by Lovesey for both the collective [20] and the single particle case [21], exhibit a three-pole lineshape after terminating the continued-fraction representation after the second order memory function with an exponential decay

$$M_1(Q, t) = \Delta^2(Q) \exp(-t/\tau(Q)) \quad (2.58)$$

where $\tau(Q)$ is again a relaxation time and $\Delta^2(Q) = \omega_l^2(Q) - \omega_0^2(Q)$ with $\omega_0^2(Q)$ as defined above and $\omega_l^2(Q) = \langle \omega^4 \rangle / \langle \omega^2 \rangle$ the ratio of the fourth to the second moment. $\omega_l(Q)$ represents the frequency of the instantaneous collective response and is related to the generalised infinite frequency sound speed $c_\infty(Q) = \omega_l(Q)/Q$. The respective correlation functions in Laplace and frequency space are then given by

$$\tilde{F}(Q, z) = S(Q) \left[z + \frac{\omega_0^2(Q)}{z + \frac{\omega_l^2(Q) - \omega_0^2(Q)}{z + 1/\tau(Q)}} \right]^{-1} \quad (2.59)$$

and

$$S(Q, \omega) = \frac{S(Q)}{\pi} \frac{\omega_0^2(Q)\tau(Q)(\omega_l^2(Q) - \omega_0^2(Q))}{\{\omega\tau(Q)(\omega^2 - \omega_l^2(Q))\}^2 + (\omega^2 - \omega_0^2(Q))^2} \quad (2.60)$$

The viscoelastic model allows for two different decay mechanisms. If a perturbation is slow enough to allow the system to attain local equilibrium, i.e. the timescale of the perturbation $t \gg \tau$, the response will be viscous with a lower sound speed $c_0(Q)$ and damped oscillations. For very fast perturbations ($t \ll \tau$) the response of the system will be instantaneous (elastic-like) with a larger sound speed $c_\infty(Q)$ and undamped harmonic excitations [22].

The advantage of the viscoelastic model is its analytical simplicity that allows a compact representation of $S(Q, \omega)$. However, the thermal fluctuations and other decay mechanisms arising at larger Q are still not included. The viscoelastic model has been generalised to the binary case in [23] using the matrix notation in Laplace space. The partial dynamic structure factors in Q - ω space then become complicated functions.

Generalised hydrodynamic theory

If γ is not close to unity the thermal fluctuations have to be considered as well. The generalised form of eq. 2.52 using the same exponential decay for the viscoelastic term as above can be written as

$$\tilde{F}(Q, z) = S(Q) \left[z + \frac{\omega_0^2(Q)}{z + \frac{\omega_l^2(Q) - \gamma(Q)\omega_0^2(Q)}{z + 1/\tau(Q)} + \frac{(\gamma(Q) - 1)\omega_0^2(Q)}{z + a(Q)Q^2}} \right]^{-1} \quad (2.61)$$

where $a(Q)$ is a generalisation of the thermal diffusivity $D_T = \kappa/nC_v$. Adiabatic instead of isothermal behaviour is found in the hydrodynamic region ($Q \rightarrow 0$)

where the decay through the thermal channel is not possible since $\omega \gg a(Q)Q^2$. The corresponding adiabatic sound speed is given by $c_s = \sqrt{\gamma}c_0$.

The application of this model to simulations [24] and experiments [22] showed discrepancies that were explained by the insufficiency of allowing for only one relaxation channel for density fluctuations. In a rather empirical way a second relaxation time was therefore proposed to account for both a fast relaxation process due to binary collisions (' μ -process') and a slow structural relaxation process that contributes considerably especially at small Q (' α -process'). The resulting memory function is given by

$$M_1(Q, t) = \Delta_\mu^2(Q) \exp\left(-\frac{t}{\tau_\mu(Q)}\right) + \Delta_\alpha^2(Q) \exp\left(-\frac{t}{\tau_\alpha(Q)}\right) + \Delta_{th}^2(Q) \exp(-a(Q)Q^2 t) \quad (2.62)$$

where the parameters Δ_x^2 are chosen such that the frequency moments up to the fourth order are respected, i.e. $\Delta_\mu^2 + \Delta_\alpha^2 + \Delta_{th}^2 = \omega_l^2 - \omega_0^2$ at $t=0$. The respective correlation function reads

$$\tilde{F}(Q, z) = S(Q) \left[z + \frac{\omega_0^2(Q)}{z + \frac{\Delta_\mu^2(Q)}{z + 1/\tau_\mu(Q)} + \frac{\Delta_\alpha^2(Q)}{z + 1/\tau_\alpha(Q)} + \frac{\Delta_{th}^2(Q)}{z + a(Q)Q^2}} \right]^{-1} \quad (2.63)$$

It has been successfully employed to describe inelastic X-ray scattering results of liquid Li [22], Al [25] or Na [26]. The existence of a slow and a fast relaxation process is also known from supercooled liquids. More complicated theories, e.g. including coupling between different modes, exist but will not be discussed here.

It is even difficult to generalise or use one of the models described here for the binary case. Formally there is no problem but since the partial structure factors are not known the number of free parameters would be too large for a possible fit of experimental data. An additional problem arises from the fact that $S(Q)$ in the present model enters also into ω_0^2 and even worse contains still the different scattering lengths of the components.

Generalised Collective Modes Model

Another approach to generalise the hydrodynamic results to larger Q shall be mentioned briefly. The basic idea is to include short-time kinetic variables into the hydrodynamic description that only considers the slowest processes, i.e. the quasi-conserved variables mass, momentum and energy. In the generalised collective modes model the vector of dynamic variables $\mathbf{A}(t)$ is extended to include besides the three hydrodynamic elements also their lowest time-derivatives representing short-time processes in the liquid. For ν elements in $\mathbf{A}(t)$ this leads to a

$\nu \times \nu$ frequency matrix $i\mathbf{\Omega}$ with ν eigenvalues. The memory matrices are treated in Markoffian approximation. The resulting $S(Q, \omega)$ consists of ν Lorentzians of which some represent propagating, others relaxing modes depending on whether the eigenvalues are complex or real numbers.

This model was proposed in [27] and developed later to a larger number of dynamic variables in a parameter-free form [28] has proven especially useful to interpret dynamic properties obtained from computer simulation results, both in monatomic (e.g. [29]) and binary fluids (e.g. [30]).

Chapter 3

Liquid Alkali-Metal – Post-Transition-Group-Element Alloys

The liquid binary alloys studied here have attracted interest due to their very interesting thermodynamic, electronic and structural properties. They all have in common that one component is an alkali metal with typical metallic properties as a pure element. These properties change substantially if a post-transition group element, which could be a metal or a nonmetal, is added. By changing the concentration a transition from metallic behaviour to the ionic or partly covalent bonding regime is observed.

A classical example system is the mixture of the alkali metal with a molten salt, more precisely the respective alkali halide. In this case the chemical bonds change from pure metallic governed by electronic screening to pure ionic characterised by long-ranged Coulomb forces. In binary alloys of alkali metals with other post-transition group elements, i.e. group 13, 14, 15 or 16 elements, partly covalent bonds lead to the formation of clusters or dynamic networks persisting in the liquid. In the following some characteristic properties of these binary systems will be briefly described. Extensive reviews on these alloys can be found in the literature [3, 31, 32].

3.1 Solid Phases and Cluster Formation

Although liquid alkali metals and post-transition group elements are simple sp elements their mixtures form a variety of complicated structures. To understand the properties of the liquid better it is useful to consider first the solid state. In a simple picture the large difference in electronegativity of the components leads to electron transfer from the alkali to the post-transition group element. At the octet composition where both components have filled valence shells the bonding can be considered as purely ionic. In the simplest case this would be an alkali halide, like $RbBr$. If a carbon group element was involved the atomic ratio would

have to be four to one, e.g. in Li_4Pb .

A different situation arises at equiatomic composition. If again a complete charge transfer is assumed the post-transition-group element appears electronically as the neighbouring element in the periodic table. It may then form structures characteristic for the latter including covalent bonds. The alkali cations are placed on interstitial positions and ensure chemical stability.

These structures were first observed in NaTl and LiAl by Zintl and co-workers [33]. Tl is a group 13 element with three electrons in the outer shell. After accepting an additional electron from the Na it has a carbon group electronic structure with sp^3 hybridised orbitals which allows to form a diamond lattice. The alkali atoms occupy the empty places and form themselves a diamond-like sublattice. In a similar way, compounds of group 14 elements form tetrahedra, e.g. $(\text{Pb}_4)^{4-}$, $(\text{Sn}_4)^{4-}$ etc., group 15 elements infinite chains, e.g. $[\text{Sb}^-]_\infty$, and group 16 elements dimers, like $(\text{Te}_2)^{2-}$. Although only the tetrahedra and the dimers are real clustered polyanions, all these structures are known as *Zintl ions*.

The extreme case of the alkali halide where the halide anions have reached the noble gas electronic configuration at equiatomic composition is conventionally not included in this nomenclature. Alkali halides do not form clusters (or polyanions) as the other systems do but they can be regarded as a limiting situation of the charge transfer systems.

In reality the simple picture cannot always be employed. The stability of Zintl ions depends e.g. on the size of the atoms [34]. Polyanionic clustering occurs only if the alkali atom is sufficiently large to screen interactions between different clusters. Further, in many cases the charge transfer is not complete. Therefore a variety of other structures including different cluster architectures can be found at compositions deviating from the ideal case described above. First the size effect might destabilise the structures and second, for other compositions, the different electronic environment leads to different phases.

The richness of structures is best demonstrated in the phase diagram. As an example the one of Na-Sn is shown in figure 3.1. Not surprisingly, the highest melting temperature is found at the equiatomic composition where Sn tetrahedra are most stable. This compound is also characterised by a rather poor electrical conductivity, i.e. it is a semiconductor [37], by a high heat of formation and a large brittleness. On the contrary, a crystalline phase cannot be found at the expected octet composition (20 at-% Sn) but slightly shifted as $\text{Na}_{15}\text{Sn}_4$. In the phase diagram of Rb-Sb [38] two congruently melting compounds can be found at the octet and the equiatomic composition. In the third system considered here, Rb-Br, there is only one stoichiometric phase, the ionic one at equiatomic composition.

Figure 3.1: Phase diagram of Na-Sn measured by Hume-Rothery [35] (from [36]).

3.2 Physical Properties of the Liquid

The compounds found in the liquid are less well defined than in the solid. Van der Lugt proposed to define 'stoichiometric compositions' in the liquid by extrema in the physical properties plotted as a function of concentration [3]. At the compound composition, the number of free electrons should be at the minimal value. Thus, the electrical resistivity should have a maximum and the electronic density of states could show a minimum or even a (pseudo)gap. This gap can be either an ionic or a covalent gap. Measurements confirm this picture but they show differences between neighbouring systems.

The binary systems with the smallest alkali atoms, Li, do not support cluster formation. This leads, for instance in Li-Pb, to a single peak at about 20% Pb, which corresponds to the ionic composition Li_4Pb . On the contrary, for Cs-Pb the only extremum can be found around the equiatomic composition. For Na-Sn, an intermediate state is observed leading to a double peak in the electrical resistivity (fig. 3.2)[39, 40]. The positions are slightly shifted with respect to those one would expect from the ideal Zintl picture, i.e. from 20% to 23% for the ionic and from 50% to 43% for the clustered (partly covalent) compound. The latter composition with 43% Sn corresponds to the high temperature solid compound Na_4Sn_3 .

Figure 3.2: Electrical resistivity of liquid Na-Sn, 10 K (solid line) and 70 K (dashed line) above the liquidus temperatures (from [39]).

The temperature dependence of the resistivity $d\rho/dT$ shows pronounced minima at the same concentrations [39]. These observations are confirmed by measurements of other properties, like the Knight shift [41], the magnetic susceptibility [42], or thermodynamic properties [40, 43, 44].

Similar observations could be made for liquid alkali-pnictide alloys. The electrical conductivity measurements on liquid Na-Sb and Cs-Sb alloys [45] show a deep minimum at the ionic composition M_3Sb ($M=Na, Cs$). For Cs-Sb with the larger alkali atom a second shallow minimum appears at equiatomic composition. The formation of a pseudogap at the onset of the metal–non-metal transition from the alkali-rich side of Cs-Sb near 24% of Sb was found by Dupree et al [46].

3.3 Liquid Structure

The structural arrangement of atoms in a liquid can be studied experimentally by diffraction of neutrons, X-rays or electrons. The resulting one-dimensional function (after subtraction of the constant incoherent scattering contribution) is the static structure factor $S(Q)$. In chapter 2 $S(Q)$ was shown to be the zeroth frequency moment of the dynamic structure factor $S(Q, \omega)$. $S(Q)$ describes the ensemble average of the density fluctuations at a given time.

For simple liquids like liquid alkali metals the $S(Q)$ are well known and obey scaling laws. Experimental results agree very well with simulations and theoretical models. In binary systems, the different scattering lengths and the concen-

trations of the components have to be considered. They determine the weighting factors for the partial structure factors $S^{(ij)}(Q)$. The total measured $S(Q)$ is then a weighted sum of these correlation functions. Different coherent scattering lengths of the two components lead, in the case of ideal disorder, to a Q independent contribution to $S(Q)$, the so called Laue monotonic scattering. For presentations of diffraction results this plateau is often removed from $S(Q)$ to make comparisons between spectra of samples with different scattering properties easier.

The partial structure factors $S^{(ij)}(Q)$ can be obtained by combining different experiments with a variation of the scattering cross-section. This can either be done by isotope substitution in neutron diffraction, by the use of absorption edges in anomalous X-ray scattering or, in general, by a combination of scattering probes with different cross-sections for the same element. For molten salts, for instance, these methods have been employed successfully. However, the experimental difficulties and the availability and costs of isotopes restrict this approach to certain elements. Therefore, in systematic experimental studies of structural changes with concentration or temperature therefore in many cases only the total coherent structure factor can be presented and discussed.

In the $S(Q)$ of the compound-forming liquids, a prepeak appears at a Q value smaller than the principle peak position Q_p . This indicates the existence of a strong chemical short-range order on a lengthscale longer than interatomic distances. The size of the prepeak varies from one system to the other and it seems most pronounced in systems conforming best to the Zintl picture, like K-Pb or Cs-Pb [47]. Nevertheless, prepeaks could be found in a considerable concentration range in liquid Na-Sn alloys [48] (fig. 3.3) and in liquid RbSb [49]. They persist in the liquid even at high temperatures [50, 51].

In the transition region between the pure metal and the octet ionic composition some systems, e.g. Cs-Sb [52] or the metal–molten salt mixtures Rb-RbBr or K-KCl [53] show an increase of scattered intensity in $S(Q)$ towards small Q . This effect was interpreted as a tendency of phase separation or segregation as a result of competing metallic and ionic interaction.

The one-dimensional information obtained from diffraction experiments is not sufficient to understand where the positions of the atoms are. That is why computer simulation techniques have been developed to support the interpretation of the experimental results.

The reverse Monte-Carlo technique (see review [54]) can help to get an idea about possible three-dimensional atomic arrangements that conform to the measured $S(Q)$. It is used to extract partial information from measurements of $S(Q)$ or to perform a better transformation into real space. In many cases it has proved a powerful tool. In liquid KPb, for example, small Pb clusters with partially tetrahedral arrangement but also a loose structural network of Pb atoms could be found in the liquid [55, 56]. The prepeak was interpreted as a result of correlation between the Pb clusters. However, the random configurations cannot reveal

Figure 3.3: Structure factor of $\text{Na}_x\text{Sn}_{1-x}$ (from [48]).

the physical origin of the short-range order or give any dynamical information.

A different problem arises in classical molecular dynamics simulations. If simple pair potentials are used atoms will not form clusters by themselves. In first attempts simulations of liquid Zintl systems were performed using rigid polyanions, i.e. ideal tetrahedra in alkali-Pb alloys [57]. The result agreed reasonably with experimental structure data but the question of whether these polyanions really exist in the liquid could not be solved.

Therefore simulations from first principles have to be employed. So called *ab initio* simulations became possible for liquids after the pioneering work of Car and Parrinello [58] who combined molecular dynamics with density functional theory. The biggest problem with this technique is the huge computing power required and hence the restriction to a small system size. Nevertheless, very valuable information about structural, electronic and dynamic properties of the systems studied here could already be gained.

The structural arrangement in liquid NaSn was studied extensively in the groups of Seifert [59, 60, 61] and Hafner [62, 63]. They both found dynamic networks of Sn atoms rather than tetrahedral units (see figure 3.4). Simulations of other systems like liquid Li-Sn, K-Sn [63] or K-Sb [64] confirmed the dependence of the degree of polyanionic clustering on the size of the alkali atoms. It was further shown that the prepeak is a consequence of chemical short-range order

and has its main contribution from the Sn-Sn or Sb-Sb correlation functions.

Figure 3.4: Snapshot of the structural arrangement in liquid NaSn. The small spheres show the entangled network of Sn atoms, the large spheres are the Na atoms (from [63]).

However, the occurrence of a prepeak does not necessarily require more or less perfect polyanions. It was shown in the simulations that even the presense of three-dimensional dynamic networks instead of isolated polyanions can lead to the measured structural, electronic or thermodynamic characteristics. For instance in liquid K-Sb the prepeak is already present at the octet composition (25 at-% Sb) where the next neighbours of Sb atoms were found to be mostly K atoms. At equiatomic composition, short Sb-Sb chains were observed instead although the measured prepeak is only slightly larger in the latter case. The effect of the change in interatomic forces on the dynamics of the liquid system that was also studied in these simulations and is of course strongly related to the structural properties will be discussed in chapter 6.

3.4 Volume Contraction

A common property of all binary systems considered here is the anomalous behaviour of the density in the solid and the liquid state. The molar volume of the

alloy is smaller than the concentration weighted sum of the molar volumes of the two elements.

For solid Na-Sn alloys this volume contraction was measured a long time ago by Biltz and Holverscheit [65]. They found an increasing effect with larger Na concentration up to 18% for Na_4Sn . For very small Sn concentrations a volume contraction was also observed in the liquid [66]. Density measurements over the whole concentration range were performed in a liquid of the same class of binary alloys, K-Pb [67] where the volume contraction is largest near the equiatomic composition with about 26%. Further density estimations for liquid [68, 63] and amorphous [69] Na-Sn alloys can be found in the literature.

As no density measurements for liquid Rb-Sb alloys were found the behaviour of other alkali-pnictide systems will be discussed instead. A considerable volume contraction was found in solid K-Sb [38]. It seems that an ideal mixing exists between K and the ionic compound K_3Sb and between K_3Sb and Sb. A similar behaviour was observed in liquid Cs-Sb [45].

The assumption that the molar volume varies linear with concentration in a mixture of an alkali metal and the corresponding alkali-halide was used in [70].

While many of the unusual properties of these liquid binary alloys have been studied in quite some detail, the atomic dynamics is still relatively unknown. Thereby it would be very interesting to see how the change in the interatomic forces show up in the dynamic properties. Recent *ab initio* simulations show remarkable dynamic features and our experimental results will underline that these studies are really worth doing. The dynamic structure of three different systems with competing interactions, $\text{Na}_x\text{Sn}_{1-x}$ and $\text{Rb}_x\text{Sb}_{1-x}$ as representatives of compound-forming liquids and the liquid metal – molten salt mixture $\text{Rb}_x\text{RbBr}_{1-x}$, will be studied and discussed in the following. The technique of our choice is inelastic neutron scattering, which proves to be well suited for dynamic investigations on the atomic scale.

Chapter 4

INS Experiments

Before a neutron scattering experiment can be performed not only the sample has to be prepared but also the appropriate spectrometer type has to be selected. For inelastic measurements the experimentalist has the choice between triple-axis spectrometers (TAS), time-of-flight (TOF), backscattering (BS) or neutron spin-echo (NSE) instruments, between the use of cold, thermal or hot neutrons. Each of the instruments has a characteristic kinematic range, which allows to study dynamic phenomena on different time and length scales.

For the investigation of the collective and single particle dynamics in the liquids considered here the use of TOF spectrometers is preferred because they are best suited for studies of dynamic processes in isotropic systems developing on timescales of 10^{-13} to 10^{-12} s. BS and NSE spectrometers are more appropriate for studies of slower dynamic processes. TAS instruments have the disadvantage that only one single point in the kinematic plane can be measured at a time. This can be of advantage for crystalline materials where e.g. for the measurement of phonons only a small part of the dynamic plane needs to be scanned. In liquids, however, all dynamic features are rather broad and the simultaneous measurement of an extended region in $Q - \omega$ as provided by the TOF technique is clearly advantageous.

Another criterion for selecting an instrument is the kinematic range which is defined by the neutron energy and momentum. While the region around Q_p can best be studied with cold neutrons, i.e. neutrons with an energy of a few meV, the use of thermal neutrons ($E_i \sim 20$ to 100 meV) allows the access of a much larger area in the $Q-\omega$ plane (see section 2.2.4). The reasons for choosing cold neutrons despite the smaller dynamic range are the better energy resolution, which is typically a few percent of the incident neutron energy and therefore much better on the absolute scale for slower neutrons, and in the present case also the high flux of the IN6 spectrometer.

While existing cold neutron TOF instruments cover almost the full range of possible scattering angles, the TAS technique must currently be used if the small angle region is to be studied with thermal neutrons. However, it would be highly

desirable to have a TOF spectrometer also in this low Q range, which would allow neutron Brillouin scattering (NBS) experiments in a new and more effective way. Concerning the collective dynamics in liquids the motivation comes from the fact that especially in liquids in-phase vibrations are strongly damped with increasing Q due to the absence of long-range order. Therefore collective excitations show up most distinctly in the NBS region.

Such a new type of spectrometer is presently under construction at the High Flux Reactor of the Institut Laue-Langevin in Grenoble, France. Not only from the scientific but also from the economic point of view it is absolutely necessary to optimise new instruments in advance and if possible also existing instruments during operation. Computer simulations have proven most useful in all stages of the designing phase. The first part of this chapter will therefore be dedicated to present results of two different simulations, one of them concerned with the neutron flux from the reactor and the radiological shielding, the other aimed to optimise the possible performance of the instrument.

The second part deals with the sample preparation and the choice of the sample container. In the last section the INS measurements performed at two different spectrometers of the Institut Laue-Langevin, the cold neutron TOF spectrometer IN6 and the thermal neutron instrument IN1 TAS, will be described.

4.1 BRISP – A New Type of INS Spectrometer

The thermal neutron Brillouin scattering spectrometer BRISP is a new type of inelastic neutron scattering instrument and currently under construction. It will use the time-of-flight technique and is aimed for inelastic scattering experiments at small angles, i.e. in the Brillouin scattering regime. BRISP will fill a gap in currently available TOF instruments where the small angle option is only realised for cold neutrons [71]. With BRISP it will be possible to measure excitations on linearly increasing dispersions with sound velocities between 1000 and 3000 m/s.

The spectrometer (see figure 4.1) will be placed on a platform using neutrons from the inclined beam tube IH3. The incident neutron energy can be chosen via different monochromator crystal options, Cu(111), Cu(200), Cu(220), PG(002) and some higher order reflections. Each monochromator type consists of 24 single mosaic crystals. Due to the inclined beam and the horizontal alignment of the spectrometer the scattering plane is vertical and the Bragg angle is fixed to $\theta_B = 17.5^\circ$. The Fermi chopper provides short neutron pulses whereas higher order reflections are suppressed in combination with the background chopper. The collimator system together with the doubly focusing monochromator ensure the required good energy and momentum transfer resolution. A large two-dimensional position sensitive detector is used for the acquisition of the scattered signal. It can be moved on rails such that the distance between sample and detector varies between 150 and 600 cm. In order to get a sufficient angular

Figure 4.1: Schematic view of the thermal neutron Brillouin spectrometer BRISP, currently under construction (from [72]).

resolution the focusing point of the converging beam will be on the detector.

Already the engineering part like the construction of the platform or the single elements of the spectrometer is supported by a number of computer simulations to ensure that legal safety requirements are fulfilled. This comprises the mechanical load on the floor of the reactor hall, the seismic resistance of the construction, the mechanical stability of the elements under working conditions (e.g. the choppers at high speed) etc. From the radiological point of view it is necessary to respect the maximum equivalence doses in working areas. For the design of the radiological shielding again computer simulations are the necessary guides.

4.1.1 Flux and Shielding Simulation using MCNP

MCNP is a general **M**onte-**C**arlo **N**-**P**article transport code [73]. It can be used for neutron, photon and electron transport problems in an arbitrary three-dimensional geometry consisting of a number of cells filled with specified materials. The cross-sections of various processes, like particle interactions, thermal particle scattering, neutron-induced photon production or activation reactions are stored in nuclear and atomic data libraries for all elements and a large number of isotopes. Besides the geometry and the materials it is necessary to define a particle source and a number of tallies for the specific problem.

Particles are then sampled from the source distribution and transported in a random way through the problem geometry. In each step the possible contribution to a tally is checked. Variance reduction and cut-off methods can be employed to achieve a faster convergence of the results. A number of statistical checks are performed by the program to show the quality of the tally results.

In the present case MCNP was used for the simulation of the neutron trans-

port from the fuel element through the moderator and the beam tube to the monochromator. Further the radiation dose outside the first part of the radiological shielding around the beam tube exit and the monochromator chamber could be estimated.

First the beam tube IH3 was modelled from existing technical drawings and incorporated into a model of the HFR [74]. Special attention was paid to the exact internal dimensions of the beam tube and the material compositions. In the next step the geometrical modelling was extended to the shielding part close to the reactor and around the monochromator. Thereby, for seismic reasons, the shielding fixed to the platform has to be decoupled from the shielding part hanging on the reactor wall, for which a gap between the two parts is needed. A cut through the beam axis showing the exit of the beam tube and the shielding part modelled for the simulations is shown in figure 4.2.

Figure 4.2: Model of the monochromator shielding.

Two instrument components are already included in the model, the first collimator and the monochromator. The shielding around the direct beam consists

mainly of three components. A thin layer of boron rich material ($\sim 1\text{cm}$ of B_4C rich elastomer) is put just around the beam to absorb thermal neutrons, i.e. in radiological terms neutrons with energies of less than 625 meV . Next to it follows a thick Pb shielding to reduce the γ radiation that is produced in the reactor and, as a secondary product, during the neutron absorption. Finally a thick shielding of moderating material is required to stop fast neutrons. For reasons of weight reduction a light material like boronated wax was preferred to heavy concrete. As the reflection of the beam from the monochromator crystals cannot be simulated using MCNP the transport simulation was truncated at the beam stop position.

Figure 4.3: Neutron energy spectrum at the bottom of the beam tube IH3.

Because of the very long distances between the reactor core and the monochromator the simulation was divided into two parts. First the characteristics of the neutron (and γ) transport at the bottom of the beam tube was studied. Thus the energy spectrum, the angular distribution and the neutron flux could be determined. The calculated neutron energy spectrum is in good agreement with a theoretical Maxwellian distribution for thermal neutrons and a spectrum from the ILL HFR Security Report, which was calculated for a different beam tube and scaled to the present case (fig. 4.3). The same is true for the total neutron flux, which is about $1.0\text{E}15$ neutrons/ cm^2s into the full solid angle.

Having characterised the beam tube bottom the transport through the beam

tube and the shielding can be calculated. The thermal flux at the beam tube exit ($1.8\text{E}10 \text{ n/cm}^2\text{s}$) which is now directed along the tube axis could again be compared to measurements at the similar beam tube IH4 ($1.6\text{E}10 \text{ n/cm}^2\text{s}$). The agreement is again very good and inspires confidence in the simulation results. Finally the radiation dose around the shielding was calculated. As expected, the highest doses were found close to the reactor wall where the main contributions stem from fast neutrons and secondary γ -rays. Further away, where working areas are planned, the dose decreases and is expected to be below the allowed limit of $10 \mu\text{Sv/h}$.

A more detailed presentation of the MCNP simulations can be found in [75, 76]. As such a detailed modelling of the shielding has not yet been performed, at least at the ILL, further benchmarking will be necessary to be able to judge the reliability and quality of the model and the approximations made. Therefore dose measurements for BRISP under working conditions would be most welcome.

4.1.2 Ray-Tracing Simulation

The experimentalist is not primarily interested in the total neutron flux and the full energy spectrum of the source. More important for him appears the knowledge of the beam characteristics at the sample position. The comprehension of the interplay between different parameters, like flux, beam size and divergence, signal-to-noise ratio etc., allows not only to supply this information but also to optimise the instrumental setup. Although analytical approaches (e.g. in [77, 78] for TOF spectrometers) exist and can offer some guideline they are limited to rather simple problems.

In more complicated situations computer simulations have proven to be a powerful tool. The Monte-Carlo ray-tracing codes like McStas [79] or Vitess [80] have become standard programs for many types of neutron scattering instruments. For neutron Brillouin spectrometers a dedicated ray-tracing code had already been developed and used in earlier simulations [72, 81]. This program has been improved and adopted to the present design of BRISP [82]. Some results of the new simulations will be presented in the following.

In the ray-tracing technique source particles with a well defined energy and momentum are traced through different elements of the instrument modelled in a modular way. Thereby it is checked whether the particle enters and leaves each single element in a way that it is able to continue its way through the spectrometer. If this is the case the next module is called, if not the particle is declared as lost and the next source particle is started. The rules for the modules can be purely geometrical, like at the entrance and the exit of the beam tube or the collimator, or defined by probability functions as it is the case for the reflection from the monochromator crystals. Counters between different modules provide information about the beam characteristics at these points.

The virtual neutron source is defined at the bottom of the beam tube using

the flux from the MCNP simulations and a part of a Maxwellian energy distribution broad enough to cover the acceptance region of the monochromator. Neutrons hitting a sheet of the Soller collimator were assumed to be absorbed. For the reflection from the mosaic crystals of the monochromator absorption and secondary extinction was taken into account [83, 84]. The mosaic distribution of the crystals was modelled by Gaussian functions, which can have different widths within and perpendicular to the scattering plane. The elements are oriented such that the reflected beam is focused on the centre of the detector.

The converging second collimator is used to improve the Q resolution. By splitting the beam into several well collimated partial beams the angular divergence can be substantially decreased. For isotropic samples it is desirable to have an equally good collimation in all directions. Therefore a special type collimator has to be designed. By replacing the pinhole collimator [85] used in [72] by a new Cd type with a honey-comb cross-section [86] the transmission could be increased almost by a factor of three. As before there will be four options for the secondary collimator, three for different focusing lengths to account for a variation of the detector distance and a simple hole without splitting the beam.

Spatial images of the neutron intensity at different elements of the spectrometer are shown in figure 4.4. The pictures illustrate the overlap of the beam reflected from different monochromator elements, the cross-section of the honey-comb collimator and the effect of the detector distance on the angular resolution. While for the longest distance from the sample a scattering angle of 0.8° can still be resolved, the smallest θ for a sample-detector distance of 1.5 m is about 2° . On the other hand, in the latter case the intensity expected in a single detector bin and the covered solid angle are much larger. To provide a realistic picture the predicted spatial resolution of the position-sensitive detector foreseen for BRISP was used to set the counter bins in the simulation.

The uncertainty of the scattering angle is only one contribution to the Q resolution. Looking at equations 2.28 and 2.30 it becomes clear that also the wavevectors have to be considered. With $k_i = 2\pi/\lambda_i$, Bragg's law $\lambda_i = 2d \sin \theta_B$ and the Bragg angle fixed to $\theta_B = 17.5^\circ$, the wavevector resolution from the monochromator is given by

$$\left| \frac{\Delta k_i}{k_i} \right| = \left| \frac{\Delta \lambda_i}{\lambda_i} \right| = \cot \theta_B \Delta \theta_B = 3.17 \Delta \theta_B \quad (4.1)$$

A good resolution can therefore only be obtained with a tight collimation before and after the monochromator, which explains the introduction of the first collimator (with about $25'$ collimation angle). In TOF instruments the resolution of the final wavevector k_f depends on Δk_i but also on the neutron pulse width in time at the sample and the time of flight, *tof*, between sample and detector. An example of the resolution in time at the detector for elastic scattering is shown in figure 4.5.

Figure 4.4: Spatial distribution of the neutron beam at the entrance of the background chopper (upper left), having entered the honey-comb collimator (upper right). The lower pictures show the angular resolution at the detector position for two distances from the sample, 6 m (left) and 1.5 m (right). The direct and two scattered beams were considered, i.e. $\theta = 0^\circ, 0.8^\circ$ and 2° .

Figure 4.5: Time-of-flight resolution for different sample-detector distances, Cu(111) monochromator, $\omega = 0$.

For the Fermi chopper a rotation frequency of 300 s^{-1} and a collimating angle of 1.5° were assumed leading to an initial pulse width of $\Delta t_0 = 14 \mu\text{s}$ FWHM. For long distances between sample and detector and slow neutrons the major contribution stems from $\Delta k_i/k_i$ while $\Delta t_0/\text{tof}$ becomes more important for shorter distances and higher neutron energies. For a setup with $\Delta k_i/k_i = 1.2\%$ the energy resolution at the elastic line is between 2.6% ($E_i=50 \text{ meV}$, 6 m detector distance) and 6% ($E_i=140 \text{ meV}$, 1.5 m detector distance).

An even better resolution would result in a further decrease in flux. The present setup was chosen as a reasonable compromise between these two factors. The estimation of the neutron flux at the sample (table 4.1) shows again a big difference between the various monochromator options and detector distances. While in the latter case the intensity on the sample is almost constant the illuminated sample area and hence the flux on this area changes considerably.

distance sample detector [cm]	beam size [cm ²]	Cu(111) 52meV $\left[\frac{n}{s}\right]$	Cu(220) 139meV $\left[\frac{n}{s}\right]$
150	2x2	3×10^5	3×10^4
400	3.6x3.6	5×10^5	5×10^4
600	4x4	5×10^5	6×10^4

Table 4.1: Neutron intensity at the sample position.

Besides the fact that the ideal sample would have a cross-section as large as the respective beam size there are two other criteria for choosing the detector distance. The maximum count rate on the detector is expected at the shortest detector distance where the accepted solid angle is largest. On the other hand, if one aims for the best momentum transfer and energy resolution the option with the detector positioned at 6 m from the sample will be chosen.

In conclusion of this section it shall be stressed again that by means of computer simulations neutron scattering instruments can be better understood and optimised. The motivation for simulations is not restricted to instrument builders but they can also help the experimentalist in the planning of the experiment. Further the knowledge of the resolution function is essential for the interpretation of the measured spectra (see section 5.8) and it is very difficult to obtain this function experimentally for energy transfers in the inelastic region. Already today but certainly in the future instrument simulations will help to build better instruments and to perform better experiments.

In the following the sample preparation and the experiments performed at two existing INS spectrometers will be described.

4.2 Sample Preparation

4.2.1 Alloying and Synthesising

The $\text{Na}_x\text{Sn}_{1-x}$ and $\text{Rb}_x\text{Sb}_{1-x}$ samples were prepared in Chemnitz from the pure elements, Sb and Sn with 99.999% purity purchased from Spurenmateriale Freiberg, Rb with 99.9% and Na with 99.95% purity from Strem Chemicals.

Depending on the different containers a volume between 7 and 9 cm³ had to be prepared for each sample. As the alkali metals, especially Rb, and still most of the alloys are highly corrosive any contact with air had to be prevented. Therefore the elements were cut, weighted and mixed in a high purity clove box under argon atmosphere and with oxygen and water content of less than 1 ppm.

When the two components chemically react to form the equilibrium phases (see phase diagrams in figures 3.1 and 4.6) a large heat of formation is set free. To avoid a heavy reaction while heating the sample during the INS experiment the samples were synthesised during the preparation process. For this purpose it is necessary to heat them above the melting temperature of the highest melting binary compound in the phase diagram.

Due to the low melting temperature of Rb (39°C) it was possible to add the small Sb shots to a Rb melt heated by an infrared lamp. A heavy chemical reaction took place immediately and thus a considerable amount of heat of formation could already be released in a controlled manner. For the Na-Sn alloys this procedure could not be used. The Sn shots and small portions of Na were just mixed at room temperature.

Figure 4.6: Phase diagram of Rb-Sb measured by Dorn and Klemm [38] (reproduced from [36]).

For the heat treatment of the samples a conventional oven outside the glove box was used. To prevent contact with air the samples were enclosed in sealed quartz ampullae. First tests with the Rb-Sb alloys, especially the Rb rich sample with 85 at-%, showed a strong chemical reaction of the sample with the quartz ampulla. Therefore the sample with 85 at-% Rb was directly filled into the Nb container. For the other alloys (75, 65 and 50 at-% Rb), the ampulla damage was much smaller and thus these samples could be synthesised. The useful mass of the samples after the treatment was more than 90% of the initial mass. The synthesised alloys could be ground more or less easily before the powder was filled into the Nb container.

For the Na-Sn alloys (90, 77, 57, 50 and 33 at-% Na) the synthesising procedure was improved by using a corundum container for the sample inside the quartz ampulla. Thus, the reaction of the sample with the containers could be reduced to a negligible amount.

4.2.2 Sample Container

Once the samples are synthesised they have to be filled into a container suitable to resist the chemical reactive nature of the samples, for the temperatures to be used in the measurements and for the specific requirement of inelastic neutron scattering experiments. The container material chosen is Nb, which is chemically resistant, possesses a high melting point (2468°C) and has favourable scattering properties for neutrons, i.e. an almost pure coherent scattering and a small absorption cross-section (see table 5.1).

The Nb containers should be dimensioned such that the scattering from the sample is about 10%. This is a compromise between a strong scattering signal and an acceptable multiple scattering contribution (see section 5.7). The inner diameters of the Nb cylinders were therefore chosen to be 13 mm for the Rb-Sb alloys and 11.3 mm for Na-Sn. The container wall thickness could be made as small as 0.2 mm, which is very important to minimise the container scattering during the experiment.

The fill height of the sample in the container should be slightly larger than the neutron beam height which is about 5 cm on IN6. Considering the uncertainty in the mass density of the liquid (see section 5.1), the volume expansion of the liquid with temperature and the relatively low packing density of the sample powder the containers were chosen to be 100 mm long ensuring enough sample in the beam and letting sufficient free volume above the liquid for thermal expansion during the experiment.

A very important requirement is the tightness of the container under high vacuum. High vacuum is needed first to protect the container and the furnace containing Nb shields because Nb oxidises at high temperatures and second to supply a good heat isolation. Therefore the container was tightened by electron beam welding at the *Institut für Kernenergetik und Energiesysteme* in Stuttgart, Germany.

4.3 Measurements

Inelastic neutron scattering experiments were performed at two spectrometers, the cold neutron time-focusing TOF spectrometer IN6 and the TAS instrument IN1, which supplied thermal neutrons because the hot source was removed at the time of the experiment. The following measurements are necessary in both cases to be able to obtain the normalised scattering laws:

- scattering from the sample enclosed in a container at temperatures well above the melting point.
- scattering from the empty container to be subtracted from the sample run, to be measured at the same temperatures as the corresponding sample runs.

- scattering from a vanadium spiral with the same geometry as the sample used as reference sample with well known scattering properties for normalisation and to obtain the resolution function at $\omega = 0$. Vanadium is especially suited for INS experiments since it is an almost pure incoherent scatterer, i.e. it has a nearly constant structure factor $S(Q)$. This measurement and the two following were made at room temperature.
- scattering from the empty furnace, to be subtracted from the V run.
- scattering from the furnace with a piece of Cd (absorbs cold and thermal neutrons from the direct beam) at the sample position to obtain contributions to the detector count rate from fast neutrons or other scattering sources, like the sample environment. This latter measurement was only used in the TAS experiment.

4.3.1 Time-of-Flight Spectrometer: IN6

The cold neutron time-focusing time-of-flight spectrometer IN6 (see figure 4.7) is a high flux INS instrument with a triple crystal monochromator on the H15 guide. The three pyrolytic graphite monochromator crystals reflect neutrons of slightly different energies. The chopper system cuts the continuous beam into pulses. It is rotated in a way that the slower neutrons pass the choppers first. Time focusing here means that all neutrons of a chosen energy transfer arrive at the detector at the same time [77]. In the vertical direction the monochromators focus spatially on the sample position.

A cooled beryllium filter is used to cut off all neutrons with a wavelength smaller than $4\text{\AA}$ including the second order reflections from the monochromators. The frame overlap that can occur at high rotation frequencies of the Fermi-chopper is suppressed by an additional chopper rotating at a lower frequency. The background is further reduced by a large evacuated sample chamber. The incident neutron flux was measured by a monitor positioned before the sample.

The final neutron energies are measured by the time of flight between the sample and the detector. The flight path is assumed to be the same between the sample and all detector tubes and equal to 248.3 cm. The detector bank covers scattering angles between 10° and 115° and consists of 337 elliptic ^3He tubes with a gas pressure of 3 bar.

For the experiments an incident neutron energy of about 4.75 meV ($\lambda=4.1\text{\AA}$) was chosen. The chopper frequency was adjusted to focus on the elastic line ($\hbar\omega = 0$). The time window (for one neutron pulse) at the detector consists of 512 time channels each of them $11.75\text{ }\mu\text{s}$ wide with a duty cycle, i.e. the time between two pulses at the sample position, of $6070\text{ }\mu\text{s}$.

The samples were heated up in the standard furnace of the instrument. As both the heat screens and the sample container are made of Nb a high vacuum

Figure 4.7: The cold neutron TOF instrument IN6 (from [87]).

(better than 10^{-4} mbar) was needed before starting to heat. About 3 hours were spent for pumping and heating up the sample and another 3 hours for cooling. A single measurement took about 12 to 15 hours at a constant temperature. For the corresponding empty container about 2/3 of this time was spent. The vanadium spiral and the empty furnace were measured for 150 and 90 minutes, respectively.

Each beam time was used to study two different samples. The Na-Sn alloys were measured at two temperatures and for $\text{Na}_{0.77}\text{Sn}_{0.23}$ it was possible to gather data at four different temperatures. The lowest temperature was chosen to be at least 10% above the melting temperature of the respective sample. Up to now the dynamic structure of the following compositions has been measured

- Na-Sn alloys:
 - $\text{Na}_{0.90}\text{Sn}_{0.10}$: $T = 700 \text{ K}, 800 \text{ K}$
 - $\text{Na}_{0.77}\text{Sn}_{0.23}$: $T = 820 \text{ K}, 940 \text{ K}, 1140 \text{ K}, 1360 \text{ K}$
 - $\text{Na}_{0.57}\text{Sn}_{0.43}$: $T = 820 \text{ K}, 940 \text{ K}$
 - $\text{Na}_{0.50}\text{Sn}_{0.50}$: $T = 930 \text{ K}, 1060 \text{ K}$
 - $\text{Na}_{0.33}\text{Sn}_{0.67}$: $T = 820 \text{ K}, 940 \text{ K}$
- Rb-Sb alloys:
 - $\text{Rb}_{0.95}\text{Sb}_{0.05}$: $T = 920 \text{ K}$ [88, 89]
 - $\text{Rb}_{0.85}\text{Sb}_{0.15}$: $T = 970 \text{ K}$ [81, 90]
 - $\text{Rb}_{0.75}\text{Sb}_{0.25}$: $T = 1060 \text{ K}$
 - $\text{Rb}_{0.65}\text{Sb}_{0.35}$: $T = 970 \text{ K}$
 - $\text{Rb}_{0.50}\text{Sb}_{0.50}$: $T = 970 \text{ K}$ [81, 90]

In addition, spectra from earlier IN6 experiments on liquid $\text{Rb}_{0.8}\text{RbBr}_{0.2}$ at $T = 966\text{K}$ and 1060K [91, 92] were considered. For these experiments a repetition of the data treatment became necessary to extend the multiple scattering correction to larger energy transfers (see chapter 5). With the present data two classes of systems with competing interaction can be compared, one with and the other without covalent bonds.

4.3.2 Triple-Axis Spectrometer: IN1

The basic idea behind the extension of the systematic study of the dynamics in the systems mentioned above to the range of thermal neutrons is to access the NBS region where collective excitations could be observable as structures in the inelastic part of the dynamic structure factor. As the new BRISP spectrometer is not yet available, a TAS instrument was chosen for this purpose.

Figure 4.8: The thermal neutron TAS instrument IN1 (from [87]).

The instrument IN1 on the beam tube H8 (see figure 4.8) can be used in TAS mode. At the time of the experiment it used the thermal neutron spectrum, because the hot source was not available. The incident neutron energy is chosen by the reflection from the monochromator. The scattered neutrons from the sample are analysed in direction and energy by the analyser-detector system. For both the monochromator and the analyser $\text{Cu}(200)$ crystals were chosen. To obtain a good energy and angular resolution the beam has to be well collimated. For small energy transfers ω this can be achieved most efficiently if the divergence of the beam is of the same order in all parts of the instrument [93, 94]. Therefore

a collimation of $30'$ (before and after monochromator and analyser) was chosen for all 4 collimators. A measure of the incident flux was recorded by a monitor put between the monochromator and the sample. To reduce the background a large vacuum box around the sample was used.

Up to now only one liquid sample, $\text{Rb}_{0.5}\text{Sb}_{0.5}$, was measured on IN1 (at the same temperature as on IN6 ($T=970\text{K}$)). Scans were made at constant Q and with constant $k_f=4.1\text{\AA}^{-1}$ for seven different Q between 0.2 and $1.0\text{ \AA}^{-1}$. In the sample runs each point was measured with a monitor count rate of 6×10^6 , which is about 10 minutes. Here again, the time spent on the empty container scans was about $2/3$ of that of the corresponding sample run. The elastic line of the vanadium spiral was measured at three Q values with 4×10^5 monitor counts. For the Cd runs 2×10^6 monitor counts were collected.

In the next chapter the data treatment will be described in detail.

Chapter 5

Data Treatment

The measured spectra have to be converted into a form that can be used for interpretation and comparison with theoretical models. The most appropriate function for this purpose is the scattering law $\mathcal{S}(Q, \omega)$ (see eq. 2.32) at constant Q . In the following the basic steps of the data treatment procedure are described. Some corrections depend on the type of spectrometer. As already mentioned in the previous section, the TOF experiments were performed at constant k_i and the TAS experiments at constant k_f .

5.1 Cross-sections and Densities

The bound atom cross-sections for neutron scattering σ_B and neutron absorption σ_a , the atomic masses AM and mass densities ρ used for the data treatment are listed in tables 5.1–5.3. The cross-sections for the elements were taken from [95]. The values of the absorption cross-sections are listed for a neutron energy of $E=25.3$ meV. It is assumed here that σ_a varies proportional to the inverse of the neutron velocity v , i.e. $\sigma_a \propto 1/v \propto 1/\sqrt{E}$. For the binary alloys, σ_B , σ_a and AM were determined as the concentration weighted average of the element specific values.

Unfortunately, the mass densities for the liquid alloys are not known and have to be estimated. The temperature dependence of the mass densities and the molar volumes of liquid metals can be found in [96]. In principle one could estimate the molar volume V_m of an alloy A_xB_{1-x} at a certain temperature by weighting the contributions from the elements A and B with the concentration

$$V_m(A_xB_{1-x}) = xV_m(A) + (1-x)V_m(B) \quad (5.1)$$

The corresponding mass density is then given by $\rho = AM/V_m$. However, for the alloys considered here the volume contraction has to be taken into account.

The densities of the Na-Sn and the Rb-Sb samples were calculated according to eqn. 5.1 for $A=\text{Na}, \text{Rb}$ and $B=\text{Sn}, \text{Sb}$. For Na-Sn the volume contraction was

	Na	Rb	Sb	Sn	Br	V	Nb
σ_B [barn]	3.28	6.8	3.90	4.892	5.90	5.10	6.255
σ_a [barn] **	0.530	0.38	4.91	0.626	6.9	5.08	1.15
AM [g/mol]	22.9898	85.47	121.75	118.69	79.91	50.942	92.91
ρ [g/cm ³]						6.1*	8.4

Table 5.1: Cross-sections, atomic masses and mass densities of the elements used in the experiments. * For the calibration measurements spirals of vanadium sheets with the same external dimensions as the corresponding samples were used. The effective densities of the different spirals are 2.016 g/cm³ (Na-Sn experiments), 1.294 g/cm³ (Rb-Sb) and 1.2204 g/cm³ (Rb-Br). ** σ_a corresponds to a neutron energy of 25 meV.

Na_xSn_{1-x}	x=0.9	x=0.77	x=0.57	x=0.5	x=0.33
σ_B [barn]	3.4412	3.651	3.973	4.086	4.355
σ_a [barn] *	0.5396	0.552	0.571	0.578	0.594
AM [g/mol]	32.56	45.00	64.14	70.84	86.79
ρ [g/cm ³] at T [K]	1.35 700/800	2.2 820/940	3.2 820	3.41 930/1060	4.61 820
ρ [g/cm ³] at T [K]		2.0 1140/1360	3.1 940		4.51 940

Table 5.2: The cross-sections, atomic masses and densities of liquid Na_xSn_{1-x} . * σ_a corresponds to a neutron energy of 25 meV.

chosen to be about the same as in the solid phase with a maximum value of 18 % at the octet composition [65]. For Rb-Sb, the molar volume was reduced by a factor obtained by interpolation between the known volume contractions of the neighbour systems K-Sb [38] and Cs-Sb [45] at a given concentration. For Rb concentrations between x=0.75 and x=0.5 this factor is of the order of 40 % to 45 % and about 22 % for x=0.85.

For the Rb-Br alloy the densities were calculated using eqn. 5.1 and setting A=Rb and B=RbBr assuming a linear variation of V_m between metal and salt as it was already mentioned in section 3.4. The densities for molten salts as a function of temperature were taken from [97].

Simple experimental methods for estimating the densities of the liquids were tested but the uncertainties of the results do not allow to give more precise values. However, they give a confirmation of the calculated values within about 10% of relative error. First the transmission of the sample was measured during the INS experiment with two monitors, one before and one after the sample. Knowing the scattering and absorption cross-sections and the effective thickness d of the

Rb_xSb_{1-x}	x=0.85	x=0.75	x=0.65	x=0.5	$Rb_{0.8}RbBr_{0.2}$
σ_B [barn]	6.365	6.075	5.785	5.35	6.65
σ_a [barn] *	1.060	1.513	1.966	2.645	1.47
AM [g/mol]	90.912	94.54	98.168	103.61	84.54
ρ [g/cm ³]	1.83	2.75	3.32	3.92	1.463
at T [K]	970	1060	970	970	966
ρ [g/cm ³]					1.355
at T [K]					1060

Table 5.3: The cross-sections, atomic masses and densities of liquid Rb_xSb_{1-x} and $Rb_{0.8}(RbBr)_{0.2}$. * σ_a corresponds to a neutron energy of 25 meV.

sample in the beam the density can be calculated using the equation for the transmission $T = \exp(-n(\sigma_B + \sigma_a)d)$, where n is the number density. However, a measurement much longer than the 10 minutes spent here would be required to decrease the statistical error due to fluctuations in the monitor count rates.

A second method is certainly more precise. In the hard X-ray laboratory of the ILL a 2-dimensional image of the sample was taken by measuring again the attenuation of a transmitted beam. Here the achievable spatial resolution is very good, about 1 mm, which makes it possible to scan the height of the sample in the container. Knowing the inner radius of the container and the total mass of the sample the density could be determined with a precision of about 2%.

However, up to now these measurements were performed only at room temperature with the solidified samples from the INS experiments. Shrink holes and small cavities could compensate for the higher density in the solid but the error of estimating the real densities of the liquid is still too large. A technical solution for the liquid density measurements using a furnace is still in preparation. Nevertheless the densities obtained so far agree well with the tabulated values in tables 5.2 and 5.3.

5.2 Transformation from (θ, t) to (Q, ω)

Measured TOF spectra are stored as intensities as a function of scattering angle θ and time-of-flight tof . Therefore two coordinate transformations have to be made. It is convenient to perform the first one from tof to ω at the start of the data treatment. The Jacobian for the transformation is given by

$$(dtof/dE_f) = -SFP \times m^2/\hbar^3 k_f^3 \quad (5.2)$$

with m being the neutron mass and SFP the flight path between sample and detector.

The second transformation between θ and Q is done after all corrections are made and the scattering law is normalised. At this stage the data points of $\mathcal{S}(\theta, \omega)$ at a constant ω are interpolated with a spline fit to a number of constant Q values using eqn. 2.30.

With the TAS spectrometer the scans of ω were already taken at constant Q . For each data point the scattering angle is available, too, which can be used for some of the following corrections.

5.3 Container and Background Scattering

When the container contribution is subtracted one has to take into account the difference in transmission between the empty container and the container filled with the sample. On the other hand the contribution from the Cd run is not influenced by the sample or the container. Therefore the background correction can be written as

$$I_s = \left(I_{s+c} - \frac{M_{s+c}}{M_{Cd}} I_{Cd} \right) - ECF \times \frac{M_{s+c}}{M_c} \left(I_c - \frac{M_c}{M_{Cd}} I_{Cd} \right) \quad (5.3)$$

where the subscripts s, c and Cd refer to the sample, the container and the Cd covered sample spectra, respectively. ECF, the empty container factor, is the ratio between the absorption factors of the container with and without the sample and will be described later. The M_x are the monitor count rates of the different runs. They are proportional to the number of incident neutrons.

As I_{Cd} was found to be rather small compared to the other contributions and $1.0 - ECF$ is of the order of 10% the Cd run was omitted in most experiments. In the TAS experiment the sample independent background was shown to be negligible for most scattering angles. Only close to the direct beam, i.e. at scattering angles smaller than 2° , it increased slightly. In figure 5.1 the number of counts is shown as a function of the scattering angle θ for different scans with the sample position covered with Cd. Two million counts in monitor 1 were collected in approximately three minutes, which leads to a background at larger θ of less than one count per minute.

In a similar way as for the empty container correction the empty furnace (EF) measurement was subtracted from the vanadium spectrum (V)

$$I_V = I_{V+EF} - EFF \times \frac{M_{V+EF}}{M_{EF}} \times I_{EF} \quad (5.4)$$

5.4 Detector and Monitor Efficiency

Depending on whether the incident or the final neutron energies are chosen to be constant one has to account for the variations of the counting efficiencies of the detector or the monitor with energy and scattering angle.

Figure 5.1: Sample independent background for different scans (different symbols) on IN1 TAS. The solid line is a guide to the eye emphasising the increase of background towards small θ .

In the TOF experiments the incident energy is kept constant, i.e. the monitor used for the normalisation to the incident flux has a constant efficiency. On the other hand, the detectors have to count the whole spectrum of final neutron energies. The efficiency $\epsilon(E_f)$ consists of the absorption factors (at $E_0=25.3$ meV) of the detector wall (and possible other windows in the beam) μ_{wall} and the detector gas μ_{He} (pressure dependent) and the respective thicknesses

$$\epsilon(E_f) = \exp\left(-\mu_{wall}d_{wall}\sqrt{\frac{E_0}{E_f}}\right) \times \left(1 - \exp\left(-\mu_{He}d_{He}\sqrt{\frac{E_0}{E_f}}\right)\right) \quad (5.5)$$

If more than one detector is used (e.g. 337 detectors on IN6) one has to account for the difference in counting efficiency between single detectors. Hence this correction depends also on the scattering angle (if the position of each detector corresponds to a fixed θ).

On the contrary, for the TAS spectra taken at constant k_f the analyser reflectivity is constant and the detector only counts neutrons of a constant energy, i.e. the counting efficiency should be constant. However, the monitor in the incident beam is hit by neutrons of different energies and varying flux. Therefore a correction for the monitor counting efficiency, which is assumed to vary $\propto 1/\sqrt{E_i}$, has to be made. The flux problem is simply solved by measuring at constant monitor count rate. Additionally, contributions to the monitor count rate of higher order

reflections from the monochromator have to be accounted for. If E_i is smaller or around the maximum of the Maxwellian energy distribution the relative flux of the second order reflection is considerable. The correction factors $\zeta(k_i)$ taking account of this effect were obtained in measurements on the thermal neutron TAS instrument IN8 [98].

5.5 Normalisation of the Spectra

The knowledge of the scattering and absorption properties of the vanadium reference sample allows to normalise the sample spectra to the incident neutron flux. For each scattering angle (detector) a total scattering intensity (for a given number of monitor counts) may be obtained by integration over all energy transfers. For vanadium, which is an almost entirely incoherent scatterer, this total intensity is given, in good approximation, as the integral over the elastic peak divided by the Debye-Waller factor ($DWF < 1$), where the latter accounts for the small inelastic contribution to the total scattering. To get the correct scattering cross-section one has to account also for multiple scattering (MSF) and self-shielding of the vanadium sample (VAF). Here MSF was assumed to be about 5% of the total scattering. The calculation of VAF is described below. Thus, the final integral reads

$$I_V^{int} = \int_{el, peak} \frac{I_V/DWF - MSF}{VAF} d\omega \quad (5.6)$$

The normalised scattering function of the sample is then obtained for TOF by

$$SF(\theta, \omega) = \frac{\sigma_{B,V} d_V n_V M_V}{\sigma_{B,s} d_s n_s M_s} \times \frac{k_i^4 \epsilon(k_i)}{k_f^4 \epsilon(k_f)} \times \frac{I_s}{I_V^{int}} \quad (5.7)$$

with the scattering cross-sections σ_B , the thicknesses d , the number densities n and the number of monitor counts M of the vanadium and of the sample runs, respectively. The first factor accounts for differences between the sample and the vanadium of the scattering power, the geometrical dimensions, the number of scatterers and the number of incident neutrons. For TAS the same function is given by

$$SF(Q, \omega) = \frac{\sigma_{B,V} d_V n_V M_V}{\sigma_{B,s} d_s n_s M_s} \times \frac{\zeta(k_f)}{\zeta(k_i)} \times \frac{I_s}{I_V^{int}} \quad (5.8)$$

with $\zeta(k)$ the tabulated correction factors introduced in the previous section.

The last two corrections to be made are those for multiple scattering effects (SMS) and self-shielding of the sample (SAF). They will be discussed in the next two subsections. Using the symmetrisation factor from eqn. 2.34 and the cubic spline interpolation for the TOF data to transform θ into Q the symmetrised scattering law is obtained as

$$\mathcal{S}(Q, \omega) = \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \frac{SF(\theta, \omega) - SMS(\theta, \omega)}{SAF(\theta, \omega)} \quad (5.9)$$

In this form it still contains the resolution function that will be treated in the last part of this section.

5.6 Absorption and Self-shielding

A certain fraction of the scattered neutrons does not arrive at the detector position corresponding to the scattering angle due to multiple scattering and absorption in the sample and the container. The correction factors for this effect are energy and angular dependent. The different attenuation factors of the absorption correction in the present case with a simple cylindrical geometry of the sample and the detector can be calculated analytically [99, 100].

The attenuation is determined as the average over all possible scattering points for a given scattering angle and energy transfer. For each scattering point the absorption and scattering probabilities before and after the scattering are calculated. This leads to three attenuation factors

- $ACC(\theta, \omega)$ – the attenuation of the beam scattered and absorbed in the container walls
- $ACSC(\theta, \omega)$ – the attenuation of the beam scattered in the container walls and absorbed in either the sample or the container
- $ASSC(\theta, \omega)$ – the attenuation of the beam scattered in the sample and absorbed in either the sample or the container

These factors were already used before in different situations. The ECF (EFF) factor is defined as the ratio $ACSC/ACC$ (≤ 1) corresponding to the sample (vanadium) and the empty container (empty furnace) run. $ASSC$ is equivalent to VAF (as the V-run was done without a container) and SAF. As an example, the sample absorption factor of liquid $Na_{0.77}Sn_{0.23}$ is shown in figure 5.2 for the smallest and the largest scattering angle. The dependence of SAF on θ arises from the different average flight paths through the sample. As expected the variation is rather small. On the other hand, the absorption effect is energy dependent and largest, of course, at the smallest final neutron energies.

A small temperature dependence of the absorption factors is due to the variation of the density as a function of temperature, which was also taken into account.

5.7 Multiple Scattering

In contrast to the self-shielding the correction of multiple scattering effects is much more complicated. The determination of the neutron fraction arriving at the detector after being scattered more than once requires the exact energy and

Figure 5.2: Sample absorption factor for $Na_{0.77}Sn_{0.23}$ for two extreme scattering angles as a function of the energy transfer.

momentum dependent cross-section, i.e. the scattering law, which, however, is the subject of the investigation and a priory unknown.

An analytical approach for the estimation of the multiple scattering contribution for a cylindrical sample-cell geometry can be used in the static case [101]. For inelastic spectra, however, the complexity of the formalism increases considerably. Therefore the preferred method is the Monte-Carlo simulation of the scattering experiment. Here, a dedicated simulation program for time-of-flight instruments, MSCAT [102], was used.

In this code neutrons are generated with an incident energy, a direction-of-flight and an initial time, that are either constants (ideal resolution run) or sampled from distribution functions (finite resolution run). Scattering points within the sample and/or the sample container are chosen randomly as well as the scattering angle θ and the energy transfer ω . From each scattering event the possible contribution to different tallies, here the single detectors and time channels with dimensions as in the real experiment, are calculated. As the scattering probability for cold and thermal neutrons depends on energy and scattering angle a scattering law for the sample and/or the sample container has to be supplied as a lookup table. Contributions from single scattering and multiple scattering are collected separately. The comparison of the total scattering from the simulation with the measured spectra yields a measure of the quality of the modelled scattering law. With a suitable weighting factor the multiple scattering contribution obtained for the model is then subtracted from the total measured spectra.

The most critical question is how to obtain a good model for the dynamic structure factor. For simple monatomic liquids the viscoelastic models with a single relaxation times proved to be quite useful, both the coherent [20] and the incoherent [21] scattering versions. The big advantage of these models were the analytical simplicity and the small number of parameters. Unfortunately, the discrepancies become large between the peak shapes of these models and the real dynamic structure factors for more complicated liquids.

The idea was therefore to produce a suitable model structure factor by fitting the experimental scattering law (eqn. 5.9) without multiple scattering correction with a model at constant Q values. This model should not be physically unreasonable and should fit the experimental data well. As the dynamic range in (Q, ω) needed for the simulation is much larger than the one experimentally accessible, the fit parameters have then to be extrapolated to smaller and larger Q s. In ω the fit function is parametrised and is easily accessible at any value.

The dynamic structure model is then used to run MSCAT. After the simulation the total scattering law is compared to the measured spectrum. The ratio $\mathcal{S}(\theta, \omega)^{exp.} / \mathcal{S}(\theta, \omega)^{mod.}$ should in the ideal case be constant over θ (sum over all ω) and over ω (sum over all θ). From this ratio the average weighting factor mentioned above is determined, which is multiplied with the calculated multiple scattering contribution. The result gives a first guess of the factor $SMS(\theta, \omega)$. The corrections in eqn. 5.9 are then repeated.

The model used above contained still the multiple scattering contributions which, on a relative scale, are more considerable at small angles and large ω than close to the elastic line at larger angles. Therefore the first guess might not have been good enough and the whole procedure has to be repeated in an iterative way. The experience with this procedure shows that for a good model ansatz the second iteration yield very satisfactory results.

For the fits the generalised hydrodynamic model (eq. 2.61) was used. In comparison to Lovesey's model it has only two more fit parameters due to the second decay channel assigned to the thermal fluctuations. It is not surprising that this model fits very well spectra of the samples with a large fraction of alkali atoms. For the samples around the equiatomic compositions the model does not have the power to separate the different dynamical processes very well over all wavevectors but it gives at least acceptable results for the multiple scattering correction.

In figure 5.3 an example is shown of the quality that can be achieved after the second iteration. A third iteration step would not improve the result considerably as the model approximations become the dominant error source. Figure 5.4 demonstrates that the multiple scattering contribution varies only little with Q or scattering angle. The spectral shape in ω is rather smooth with a maximum at $\omega = 0$. The relative contribution of the multiple to the total scattering is considerable over the full ω range and especially large at small scattering angles, as it is demonstrated in figure 5.5. In $\text{Na}_{0.77}\text{Sn}_{0.23}$ the incoherent scattering

Figure 5.3: Comparison between TOF spectra from experiment and MSCAT simulation for $\text{Na}_{0.23}\text{Sn}_{0.77}$ at $T=820\text{K}$. The functions $S(Q)$ and $S(\omega)$ are obtained by integration of the 3-dimensional spectra over all energy transfers and all scattering angles, respectively. The lower diagrams show the corresponding ratios, resulting in an adjustment factor of about 1.5 ($\approx \pi/2$).

Figure 5.4: Multiple scattering function for $\text{Na}_{0.23}\text{Sn}_{0.77}$ at $T=820\text{K}$.

Figure 5.5: Relative contribution of multiple scattering to the total scattering for $\text{Na}_{0.77}\text{Sn}_{0.23}$ at $T=820\text{K}$ at three different angles.

cross-section leads to a relatively large quasielastic scattering intensity around $\omega = 0$ even at small θ , which will be discussed in the following chapter. As a consequence, the relative contribution of multiple scattering is comparably low in this region. The oscillating behaviour of the curves shown in figure 5.5 is mainly caused by the representation of the scattering law at constant scattering angle since the multiple scattering correction is made before the transformation to constant Q .

5.8 Resolution Function of the Spectrometer

The experimental data after all corrections mentioned above are still convoluted with the resolution function $R(Q, \omega)$ of the spectrometer.

$$\mathcal{S}(Q, \omega)^{exp.} = \mathcal{S}(Q, \omega) \otimes R(Q, \omega) \quad (5.10)$$

In general, dependent on the experimental setup, $R(Q, \omega)$ is a multidimensional function that cannot easily be obtained. However, the width of the vanadium peak gives a measure of the resolution at $\omega = 0$ in one dimension. For the two instruments used these functions are shown in figure 5.6. From a fit with a Gaussian function the width of the elastic resolution function was determined as $\sigma = 0.069$ meV for IN6 and $\sigma = 0.48$ meV for IN1 which corresponds to FWHMs of 0.16 meV and 1.1 meV, respectively.

Figure 5.6: Measured elastic peak resolution functions of IN6 and IN1. Different symbols stem from different spectra. The full curves represent a Gaussian fit.

Because of the cylinder geometry the energy resolution is essentially constant in Q but it depends strongly on energy. Especially on IN6, due to the time focusing, the width of the resolution function for the neutron energy gain spectra increases considerably at larger energy transfers. There are analytical models for calculating the resolution functions of both TAS [93, 94, 103] and TOF [77, 78] spectrometers. In many cases they give a satisfactory estimation of the quantities needed for data treatment. If the simplifications made in these models are not sufficient anymore, computer simulations, as e.g. described above for the new BRISP instrument, may help to overcome these limitations.

For the comparison of the experimentally obtained scattering law with a theoretical model it is much more reasonable to convolute the model with the resolution function than to deconvolute $\mathcal{S}(Q, \omega)^{exp.}$. In the latter case $\mathcal{S}(Q, \omega)^{exp.}$ would have to be Fourier transformed into time space. This would cause big problems with cutoff effects as, especially at small Q , the available ω range is not large enough for $\mathcal{S}(Q, \omega)^{exp.}$ to decay towards zero. Here the elastic resolution function is considered as one-dimensional and constant over the full ω range. This assumption simplifies very much the convolution procedure and is justified by the fact that structures in $\mathcal{S}(Q, \omega)^{exp.}$ coming from the sample and having a comparable width with respect to the resolution function are only observed in the quasielastic region around $\omega = 0$.

Chapter 6

Results and Discussion

The scattering law $\mathcal{S}(Q, \omega)$ describes the total dynamic response of the system. As already mentioned in section 2.2.3, it consists of a weighted sum of partial contributions. As both the weighting factors and the partial structure factors (due to the changing interatomic forces) vary with composition the interpretation of changes in $\mathcal{S}(Q, \omega)$ has to be done with special care. While the partial structure factors are not accessible from a single experiment their weighting factors can be calculated using equations 2.36 to 2.39. They indicate which of the partials are expected to be dominant. The weights (divided by the corresponding total scattering cross-section $\sigma_B/4\pi$) of the three partial coherent and the total incoherent structure factors are shown in figures 6.1 and 6.2 for Na-Sn and Rb-Sb alloys, respectively. The incoherent contributions stem almost entirely from the corresponding alkali metal.

Figure 6.1: Weighting factors for the partial contributions to $\mathcal{S}(Q, \omega)$ of Na-Sn alloys in species specific (left) and density-concentration (right) separations. w_{inc} and w_{NaNa} are almost identical.

Figure 6.2: Weighting factors for the partial contributions to $\mathcal{S}(Q, \omega)$ of Rb-Sb alloys in species specific (left) and density-concentration (right) separations.

In Na-Sn all partial contributions play a significant role, although their weight changes with composition. On the contrary, the weighting factors for incoherent scattering and the concentration-concentration correlation are rather small in Rb-Sb over the full range of concentrations. For the third system considered here, Rb-Br, the weighting factors are similar to Rb-Sb but with even smaller w_{cc} and w_{nc} due to the very similar coherent scattering lengths of Rb and Br.

In the following, keeping these remarks in mind, the experimentally obtained $\mathcal{S}(Q, \omega)$ will be presented and compared with respect to their dependence on temperature and concentration. Related properties, like frequency moments, dispersions relations and frequency spectra, will be extracted and discussed.

6.1 The Binary Liquid $\text{Na}_x\text{Sn}_{1-x}$

6.1.1 Scattering Law

A three-dimensional representation of the scattering laws $\mathcal{S}(Q, \omega)$ (although still convoluted with the instrumental resolution function) allows already a qualitative discussion of the changes in the dynamic behaviour in terms of temperature and concentration. For example, figure 6.3 shows $\mathcal{S}(Q, \omega)$ of $\text{Na}_{0.77}\text{Sn}_{0.23}$ at two different temperatures. Zero intensity is shown in regions of the Q - ω plane that is inaccessible for kinematic reasons (cf. figure 2.2).

Due to the incoherent scattering cross-section of Na the total scattering law contains a considerable contribution from the self-part of the dynamic structure factor $S_s^{(\text{Na})}(Q, \omega)$, which yields information about the single-particle motions of the Na atoms. The spectral shape of $S_s(Q, \omega)$ at constant Q is characterised by a

Figure 6.3: $\mathcal{S}(Q, \omega)$ of liquid $\text{Na}_{0.77}\text{Sn}_{0.23}$ at two different temperatures.

monotonous decay with increasing $|\omega|$, i.e. a single maximum at $\omega = 0$. Since the zeroth frequency moment of $S_s(Q, \omega)$, namely the self-part of the static structure factor $S_s(Q)$, does essentially not depend on Q and the spectral width of $S_s(Q, \omega)$ increases roughly with Q^2 in the low Q range, the intensity at $\omega = 0$ rises towards smaller Q , as may be seen in the figure.

The origin of the oscillatory behaviour in Q (and possibly also ω) can be found in the coherent response function, i.e. the dynamic structure factor $S(Q, \omega)$. As the integral of $S(Q, \omega)$ over ω gives the static structure factor $S(Q)$ the main features of the latter can also be seen in $\mathcal{S}(Q, \omega)$. The dynamic range presented here contains both the principal peak of $S(Q)$ at $Q=Q_p$ and the prepeak, which is in this case at about $Q=Q_p/2$.

With increasing temperature the scattering function becomes much broader, especially at larger Q . This is not surprising since, with the increasing mobility of the particles at larger T , one would expect shorter correlation times and hence broader features in frequency space. The shoulder in the quasielastic region at about $1.15 \text{ \AA}^{-1}$, an indication of the prepeak and clearly visible at the lower temperature, seems to have almost disappeared at 1360K. Two cuts of the scattering law at constant Q (figure 6.4) show the temperature dependence over the full measured temperature range. While close to the elastic line the intensity always decreases with temperature, the change of the actual lineshape cannot be predicted easily, the more so as $S(Q)$ itself depends on temperature.

With increasing Sn concentration (figure 6.5) the incoherent scattering contribution decreases and the prepeak becomes more pronounced, as expected from the static structure factor measurements (see figure 3.3). Although the prepeak appears only as a rather small structure in $\mathcal{S}(Q)$ it is of dominant size around zero energy transfer in $\mathcal{S}(Q, \omega)$ for the samples around $x=0.5$. The very small

Figure 6.4: Cuts of $\mathcal{S}(Q, \omega)$ of liquid $\text{Na}_{0.77}\text{Sn}_{0.23}$ at constant Q for different temperatures.

Figure 6.5: $\mathcal{S}(Q, \omega)$ of liquid $\text{Na}_{0.57}\text{Sn}_{0.43}$ and $\text{Na}_{0.33}\text{Sn}_{0.67}$.

quasielastic line width around the prepeak is a strong signature for structures that should be particularly stable compared to the average correlation times in the liquid.

6.1.2 Frequency Moments

If the measured data are of good quality and the corrections were appropriately made the frequency moments should be fulfilled. Integration of $\mathcal{S}(Q, \omega)$ over ω yields the zeroth frequency moment, $\mathcal{S}(Q)$. After subtraction of the constant contribution from incoherent scattering one gets the static structure factor, $S(Q)$. As in the ideal case $\mathcal{S}(Q)$ should be normalised to unity for $Q \rightarrow \infty$, $S(Q)$ can be calculated by

$$S(Q) = (\sigma_B \mathcal{S}(Q) - \sigma_{inc}) / \sigma_{coh} \quad (6.1)$$

using the respective cross-sections as defined in section 2.2.3. In figure 6.6, the $S(Q)$ of the Na-Sn alloys obtained from the integration of the inelastic spectra are compared with the results from diffraction measurements [48] (cf. figure 3.3). The agreement is very good bearing in mind the partially incomplete integral over ω due to the limited dynamic range of cold neutron scattering experiments. On IN6, for example, the elastic line is dynamically accessible only at Q between 0.3 and 2.5 $\text{\AA}^{-1}$. Already at about 2 $\text{\AA}^{-1}$ the scattering law is sufficiently broad that cutoff effects from the integration over ω become important. This explains the differences the diffraction and the present data at larger Q .

With increasing concentration of Sn the principle peak at Q_p shifts to larger Q . As larger Q indicate smaller interatomic distances d ($\propto 1/Q$) and as the unbound Sn atoms (ions) are larger than the Na atoms (ions) one would expect the opposite effect if the interatomic forces were unchanged. This is already a first clear evidence that the bonds between the atoms become stronger. The shift of Q_p is concentrated in the region between pure Na to the octet composition, i.e. in the transition from the metallic to the ionic bonding regime. Around the equiatomic composition the position of Q_p is almost unchanged, which is in good agreement with the diffraction results [48].

Already at compositions with presumed dominant ionic character of the bonds, a prepeak can be found signalling a short-range order effect in the liquid. The prepeak grows in size when covalent bonds between the anions play an increasing role. It is most pronounced at 57 at-% Na, a composition where extrema in the physical properties were found and hence a *stoichiometric composition* according to the definition of van der Lugt [3]. At $x=0.33$ the prepeak has almost disappeared. In contrast to the behaviour of the principle peak the shift in position of the prepeak is to smaller Q with increasing concentration of Sn. Thus, the correlation length of the long living structures responsible for the prepeak increases, while the average bond length in the system becomes shorter.

The temperature dependence of $\mathcal{S}(Q)$ (including the incoherent part) is demon-

Figure 6.6: Static structure factors $S(Q)$ of liquid $\text{Na}_x\text{Sn}_{1-x}$ from the IN6 experiments (symbols) compared to the literature [48] (full lines).

Figure 6.7: $\mathcal{S}(Q)$ of liquid $\text{Na}_{0.77}\text{Sn}_{0.23}$ at different temperatures.

strated for $x=0.77$ in figure 6.7. The broadening of the scattering law with increasing temperature mentioned above leads to a continuous decrease of the size of the principle peak in the static structure factor. Due to the thermal expansion the maximum is found at slightly smaller Q for the higher temperatures. The behaviour of the prepeak is similar to that measured at equiatomic composition [51]. With increasing temperature the height of the prepeak decreases and it is shifted to smaller Q . All together it seems that the disorder in the liquid increases and the units causing the prepeak become less stable towards higher temperature.

The accuracy of higher order moments obtained from integration is much lower due to truncation effects from the restricted experimental ω range. At least the second moment shows a reasonable behaviour as shown in figure 6.8. As $\langle \omega^2 \rangle$ should scale with the inverse mass at a given temperature the slope should decrease towards the heavier element, which is indeed observed. The moments obtained by simple integration fit well between the two limiting theoretical curves of the pure elements. Especially in the Q region below $2\text{\AA}^{-1}$ the cutoff effects are considerable.

6.1.3 Longitudinal Currents

The correlation function of the longitudinal currents $J_l(Q, \omega)$ can easily be obtained from the dynamic structure factor $S(Q, \omega)$ (cf. section 2.1.3). However, the total scattering law $\mathcal{S}(Q, \omega)$ available here still contains $S_s(Q, \omega)$ with a non-trivial spectral shape. Therefore, a reasonable separation of $S(Q, \omega)$ and $S_s(Q, \omega)$

Figure 6.8: Second frequency moments of $\text{Na}_x\text{Sn}_{1-x}$ obtained from integration of the scattering law.

cannot be done with the current sets of data. For the present discussion it is useful to introduce a generalised current correlation function $\mathcal{J}_l(Q, \omega)$ that is related to $\mathcal{S}(Q, \omega)$ by

$$\mathcal{J}_l(Q, \omega) = \frac{\omega^2}{Q^2} \mathcal{S}(Q, \omega) \quad (6.2)$$

A dispersion relation can be obtained by plotting the position of the maxima of $\mathcal{J}_l(Q, \omega)$, ω_m , over Q . Examples of $\mathcal{J}_l(Q, \omega)$ at constant Q and the respective dispersions are shown in figures 6.9 and 6.10 for the different compositions of liquid Na-Sn. The ω_m were obtained by fitting a polynomial to the cuts of $\mathcal{J}_l(Q, \omega)$ at constant Q and obtaining the zeros of its first derivative.

The minimum of the upper dispersion branch in figure 6.10 is shifted to higher frequencies and larger momentum transfers with increasing concentration of Sn until the equiatomic composition is reached [104]. On the Sn-rich side this trend is reversed and the dispersion minimum is found again at smaller frequencies and smaller Q . Although the relative weight of the partial contributions changes with composition and therefore the $\mathcal{J}_l(Q, \omega)$ are also functions of concentration and scattering lengths of the components, this behaviour of the dispersion gives a strong indication of a considerable change in the atomic interactions in the liquid alloy with composition. If the shift was only caused by mass and concentration effects it would have been expected to be monotonous over the whole concentration range.

The examples of $\mathcal{J}_l(Q, \omega)$ at different Q in figure 6.9 show the appearance of a second maximum at smaller energy transfer for the Sn rich samples. The

Figure 6.9: $J_l(Q, \omega)$ of liquid $\text{Na}_x\text{Sn}_{1-x}$ for different concentrations and momentum transfers.

Figure 6.10: Dispersion from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$ at $T=820\text{K}$ ($T=930\text{K}$ for $x=0.5$).

dispersions of this second branch (lower curves in figure 6.10) confirm the trend towards lower Q and ω for compositions beyond the equiatomic compound. As the lower branch occurs only at the larger Sn concentrations it may be assumed that it stems from motions of the Sn atoms while the higher frequency band may be assigned to the lighter Na atoms. This allocation is endorsed by the following argument. If the interatomic forces between the Sn atoms and between the Na atoms are not too different the ratio of the vibrational frequencies should scale roughly with the inverse ratio of the square roots of the atomic mass, i.e.

$$\omega_{Na}/\omega_{Sn} \sim \sqrt{AM_{Sn}/AM_{Na}} \sim 2.3 \quad (6.3)$$

This scaling ratio is indeed almost fulfilled as shown in figure 6.10, which confirms the assignment made above.

However, there are strong indications that the covalently bound Sn atoms can be distinguished from the Na atoms not only by a pure mass effect. First, the minimum of the lower lying band is found at larger Q than that of the respective upper branch, which indicates shorter bonds between the Sn atoms. Second, the peaks that lead to the upper dispersion are sometimes very broad (see figure 6.9) and therefore their positions can only be determined with a rather large error of a few meV. If the partials could be separated and the relatively sharp low frequency contribution were subtracted from the total $\mathcal{J}_l(Q, \omega)$, the maximum would probably shift to lower frequencies. Then the frequency ratio would become

smaller and hence the Sn atoms would vibrate with a higher relative frequency, which could be interpreted as a strengthening of the bonds and an increase of the force constant (possibly due to the covalent part of the interaction). A definite statement on this issue can only be given when the partial contributions are known.

The temperature dependence of the dispersions $\omega_m(Q)$ was studied in detail for liquid alkali metals, especially for liquid Rb [105, 19, 106]. It was shown that for $Q < Q_p$ the dispersion is governed by the interatomic potential, while for $Q \gg Q_p$ the main contribution comes from the 'free particle' behaviour [106]. Only the 'free particle' term should depend on temperature with $\omega_m \propto \sqrt{T}$. However, if the density of the sample is not constant at all temperatures, which is the case here, the potential part is expected to change, as well. Due to the weaker potential at smaller density a shift of ω_m towards smaller frequencies should be observed in the small Q range.

Figure 6.11 shows the temperature dependence of $\omega_m(Q)$ for the different Na-Sn alloys. For large concentrations of Na the behaviour is similar to that of pure alkali metals. An increase of ω_m with temperature is only observed for $Q > 1.9\text{\AA}^{-1}$. At smaller Q there is little change in the accessible Q range and even a slight decrease in frequency at the smallest Q shown in the figure.

In the case of $x=0.77$ and $x=0.57$, the maximum of $\mathcal{J}_l(Q, \omega)$ for $Q < 2\text{\AA}^{-1}$ is very broad and the position obtained has a fairly large error. However, regarding the full Q range one could say that the simple shift of the dispersion as observed for $x=0.9$ does not occur anymore. A reason for that could be the increasing weight of partial contributions of the Sn-Sn and the Na-Sn correlations and hence a nontrivial interplay between the weighting factors and the temperature dependence of the partials. For $x=0.5$ there is almost no temperature dependence in the studied range. Finally, the Na dispersion branch of the Sn richest sample shows a rather unexpected behaviour, i.e. a shift to smaller frequencies at the higher temperature for $Q > Q_p$. A more detailed study of these effects would again require the separation of the partials.

6.1.4 Frequency Spectrum

In section 2.1.3 the velocity autocorrelation function was introduced as a single particle dynamic property. Its frequency spectrum is related to the self-part of the scattering law. As above for the longitudinal currents, the inability to separate $S(Q, \omega)$ and $S_s(Q, \omega)$ requires a generalised treatment of the correlation functions. Thus, in analogy to equation 2.26, a generalised frequency spectrum is defined as

$$\mathcal{Z}(\omega) = \lim_{Q \rightarrow 0} \frac{\omega^2}{Q^2} \mathcal{S}(Q, \omega) \quad (6.4)$$

This function contains both single particle and collective contributions. The latter include interference effects that cause the oscillating behaviour in Q . For

Figure 6.11: Dispersion from the maxima ω_m of $J_l(Q, \omega)$ as a function of temperature for the different concentrations.

a meaningful extrapolation to $Q=0$ these coherence effects have to be averaged out. Therefore the following procedure was used. From the three-dimensional data of $\mathcal{J}_l(Q, \omega)$ cuts are taken at constant ω over the full measured Q range. A regression line is fitted to these data and extrapolated to $Q=0$. Three extreme examples are shown in figure 6.12.

Figure 6.12: Extrapolation for three different ω ($\text{Na}_{0.9}\text{Sn}_{0.1}$, 800K).

For higher energy transfers, which here means $|\omega| > 10\text{ meV}$, the averaging can be done in a reasonable way. At smaller ω the coherence effects become much stronger, especially around the principle peak position Q_p of $S(Q)$. Consequently, the available Q range is not sufficient anymore for the extrapolation. Therefore the average diffusion constant in the limit $\omega \rightarrow 0$ (eq. 2.27) cannot be determined by this means. The frequency spectra $\mathcal{Z}(\omega)$ obtained for the different Na-Sn

Figure 6.13: Frequency spectra of liquid $\text{Na}_x\text{Sn}_{1-x}$ at $T=820\text{K}$.

samples are displayed in figure 6.13. For this comparison the integrals of $\mathcal{Z}(\omega)$ over ω between $\omega = 0$ (with an extrapolated value for $\mathcal{Z}(\omega = 0)$) and a cutoff energy of 39 meV are normalised to unity.

As already seen in the dispersions $\omega_m(Q)$ of $\mathcal{J}_l(Q, \omega)$ the shift of the frequencies to larger values can be observed in $\mathcal{Z}(\omega)$ in the transition region between the liquid metal and the first stoichiometric composition. Between $x=0.77$ and $x=0.33$ there is only little change in the position of the maximum and only a small change in shape of the frequency distribution. When the temperature is raised, the position of the maximum is not changed significantly but the spectral weight is shifted to higher energy excitations (figure 6.14). In a harmonic system multiphonons would have the same effect.

For $x=0.5$, $\mathcal{Z}(\omega)$ can be compared to simulation results [63]. In the calculations the partial frequency distribution functions $\tilde{z}^{(i)}(\omega)$ were obtained. While for the heavier Sn atom the most probable vibrational frequency is found around 5 meV, the partial spectrum of the Na atoms has a broad maximum at around 17 meV. If these partials were weighted with the total scattering cross-sections of the two elements one would expect two peaks in $\mathcal{Z}(\omega)$, the first at 5 meV and the second at about 12 meV. The latter peak is also observed in the present data. The relatively sharp first peak at 5 meV is in a frequency range where the simple extrapolation scheme is not sensitive anymore and can therefore not be resolved in the experimentally obtained $\mathcal{Z}(\omega)$. However, the dispersion branches

Figure 6.14: Frequency spectra of liquid $\text{Na}_{0.77}\text{Sn}_{0.23}$ as a function of temperature.

obtained from $\mathcal{J}_l(Q, \omega)$ (figure 6.10) give a strong indication of existence of the second vibrational mode at lower frequencies in the experimental spectra. The lower lying branch assigned to the motions of the Sn atoms is indeed found in the low energy transfer range between 4 and 6 meV, in agreement with the maximum in the simulated $\tilde{z}^{\text{Sn}}(\omega)$ at 5 meV. The dispersion at higher frequency can again be identified with motions of the Na atoms.

6.1.5 Intermediate Scattering Function

From the theoretical point of view there is no problem in studying the time dependence of the density correlation functions after a simple Fourier transformation of $\mathcal{S}(Q, \omega)$. By this means the instrumental resolution function could be elegantly eliminated by dividing the experimental total intermediate scattering function $\mathcal{F}(Q, t)$ by the Fourier transform of the resolution function. Unfortunately, the cutoff effects due to the kinematic restrictions make this Fourier transformation awkward. Only around Q_p the available frequency range is large enough to make a reasonable transformation.

Some examples of the resulting normalised $\mathcal{F}(Q, t)/\mathcal{F}(Q, 0)$ at Q around Q_p are shown in figure 6.15. In this Q region the resolution function only has a minor influence. As expected, the relaxation time has a maximum at Q_p where the dynamics on the length scale of the interatomic separations is probed and the

Figure 6.15: Normalised intermediate scattering functions $\mathcal{F}(Q,t)/\mathcal{F}(Q,0)$ for different samples at different Q obtained from the Fourier transformation of $\mathcal{S}(Q,\omega)$.

correlations between the atoms are strongest and live longest. On the other hand, in this region of Q -values collective excitations are already completely damped out, which explains the smooth drop of the intensity. There is, however, also a strong dependence on concentration. On the alkali rich side the correlation function decays much faster, which may be explained by a higher mobility of the average particle, i.e. the relative weight of the partial correlation function of the lighter Na atoms is largest there. However, the increase of the relaxation time with increasing content of Sn does not scale with concentration. This observation is again a strong indication of the influence of the interatomic potential on the dynamics of the system.

6.2 The Binary Liquid $\text{Rb}_x\text{Sb}_{1-x}$

6.2.1 Scattering Law

In the Rb-Sb alloys the weighting factors of incoherent scattering w_{inc} and scattering from concentration fluctuations w_{cc} are much smaller than in the Na-Sn system (cf. figures 6.1 and 6.2). As the scattering is now almost coherent the scattering intensity at low Q is rather small, except for $x=0.85$ where considerable small angle scattering is observed. Four of the scattering laws $\mathcal{S}(Q, \omega)$ obtained from the IN6 experiments are shown in figures 6.16 and 6.17.

Figure 6.16: Dynamic structure factors of liquid $\text{Rb}_x\text{Sb}_{1-x}$ for $x=0.95$ [88] and $x=0.85$ [81].

Because of the small w_{cc} there is only a small contribution of $S_{cc}(Q, \omega)$ to the total scattering. Thereby it is known from simulations that this partial correlation function is mainly responsible for the prepeak, which explains the relatively small

Figure 6.17: Dynamic structure factors of liquid $\text{Rb}_x\text{Sb}_{1-x}$, $x=0.75$ and $x=0.50$ [81].

size of the latter in the experimentally obtained $\mathcal{S}(Q, \omega)$. The prepeak is again observable in an extended range of concentrations, i.e. between the octet and the equiatomic compositions. A shift of the position of the principal maximum to larger Q with increasing concentration of Sb is clearly visible.

6.2.2 Frequency Moments

The static structure factors $S(Q)$ obtained by integration of $\mathcal{S}(Q, \omega)$ over ω and subtracting the incoherent contribution are shown in figure 6.18, together with the respective $S(Q)$ of pure liquid Rb [105] and Sb [107]. In contrast to Na-Sn, the different atoms are now of similar size, which makes it easier to identify the shift of Q_p with a change of the atomic interaction. The shift is again discontinuous and especially large between liquid Rb and the octet composition ($x=0.75$). From the structural point of view there is not much change between $x=0.75$ and $x=0.5$.

The small Q region of $S(Q)$ is shown enlarged on the r.h.s. of figure 6.18. As in the similar system liquid Cs-Sb [52], at $x=0.85$ an increase of $S(Q)$ towards small Q is observed. At this composition a competition between metallic and ionic bonds is expected, which might cause a segregation effect.

In agreement with computer simulations [64] on liquid K-Sb the prepeak can be found already in the ionic interaction regime, namely at $x=0.75$. It arises as a short-range order effect from correlations between isolated anions (Sb^{3-}). As their nearest neighbours are mainly cations the anion-anion correlation is dominated by the second nearest neighbour distance, which leads to the superstructure peak. Similar to Na-Sn the prepeak grows towards the composition with $x=0.5$ and it is at the same time shifted to slightly smaller momentum transfers. In the regime

Figure 6.18: Static structure factors of liquid $\text{Rb}_x\text{Sb}_{1-x}$ obtained from integration of $\mathcal{S}(Q, \omega)$. The scale of the ordinate is drawn for the lowest $S(Q)$. For a better visibility subsequent $S(Q)$ are shifted by 0.5 (left) and 0.1 (right), respectively.

Figure 6.19: Second frequency moment of $\text{Rb}_x\text{Sb}_{1-x}$ obtained from integration of the scattering law.

with partly covalent bonds (around $x=0.5$) short chains of Sb^- were found in the simulations [64] and the prepeak arises then from the correlation between these polyanionic structures.

Figure 6.19 shows the second frequency moments integrated from the scattering laws and compared to the theoretical values of the pure elements. As the mass difference between Rb and Sb is much smaller than between Na and Sn, the $\langle \omega^2 \rangle$ here vary much less with composition. Again the agreement is reasonable taking into account the truncation effects and the normalisation errors, that may arise, for instance, from the uncertainty of the mass density of the samples.

6.2.3 Collective Dynamics

The $\mathcal{S}(Q, \omega)$ of the Rb-Sb alloys stem mainly from coherent scattering and provide therefore a measure of the collective dynamics. As before for Na-Sn the IN6 experiments yield information about the behaviour in the dynamic region around the principle peak of $\mathcal{S}(Q)$. Different cuts of $\mathcal{J}_l(Q, \omega)$ at constant Q are shown in figure 6.20, the respective dispersions obtained from the maxima of these functions in figure 6.21 [108].

The position of the minimum of the dispersion curve follows again the behaviour of $\mathcal{S}(Q)$, i.e. it is shifted to larger Q with increasing concentration of Sb. The dispersion of pure Rb [19] was obtained from measurements at slightly lower temperature. As in simple liquids the minimum is shifted with increasing

Figure 6.20: $J_l(Q, \omega)$ of liquid $\text{Rb}_x\text{Sb}_{1-x}$ for different concentrations and momentum transfers.

Figure 6.21: Dispersions from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$.

temperature to lower Q and higher frequencies this might explain the slight negative shift in Q between pure Rb and the sample with $x=0.95$. Beside the Q dependence, which reflects changes in the interatomic distances, there is also a variation on the frequency scale. The observed shift to larger Q and higher ω is most likely due to the formation of stronger bonds with shorter bond length and increasing force constants.

Apart from the scattering properties there are other major differences between Na-Sn and Rb-Sb alloys. First of all the mass difference between Rb and Sb is much smaller and therefore a second peak in $\mathcal{J}_l(Q, \omega)$ as in the case of Na-Sn is not observed. Second, since the Rb atoms are much larger than the Na atoms, the interatomic distances in the pure liquid alkali metals differ as well. Indeed, the principle peak position Q_p of liquid Rb is found at $1.5\text{\AA}^{-1}$, i.e. at smaller Q . Thus, the shift in Q and ω , especially between the pure alkali metal and the octet composition, is more pronounced in Rb-Sb than in Na-Sn. This might be the reason for the stronger segregation tendency in Rb-Sb between the pure alkali metal and the octet composition at $x=0.75$, indicated by the strong small angle scattering at $x=0.85$ in figure 6.16.

The dispersions in figure 6.21 confirm the discontinuous transition from the metallic to the ionic regime already observed in $S(Q)$. While for $x=0.95$ the system still seems to be metallic [88] with a single well pronounced maximum in $\mathcal{J}_l(Q, \omega)$ at constant Q , there are at least two dynamic processes in $\mathcal{J}_l(Q, \omega)$ at $x=0.85$,

which lead to the unusual shape of the dispersion. There is still a small jump in the dispersion at the octet composition, while at $x=0.5$ the dispersion is again completely continuous. In contrast to the alkali-rich side, where the dispersion depends strongly on concentration, the frequency range covered is very similar between $x=0.25$ and $x=0.5$.

Up to now only the dynamic region around Q_p has been considered. However, as mentioned before in chapter 4, acoustic-like excitations in liquids have been observed mainly in the range of Brillouin scattering, i.e. at much smaller Q than Q_p [2]. The question of whether collective excitations are visible in systems with partly covalent bonds was the motivation to extend the current studies to a larger dynamic range using thermal neutrons. Indeed, the resulting $\mathcal{S}(Q, \omega)$ of $\text{Rb}_{0.5}\text{Sb}_{0.5}$ obtained from the INS measurements on IN1 show at least shoulders of inelastic excitations (figure 6.22).

Figure 6.22: Cuts of $\mathcal{S}(Q, \omega)$ (convoluted with the resolution function) at constant Q for liquid $\text{Rb}_{0.5}\text{Sb}_{0.5}$ together with model fits as described in the text.

The availability of experimental data in an extended Q range for $x=0.5$ provides a good opportunity to test different models of $\mathcal{S}(Q, \omega)$. Before fitting a model function to $\mathcal{S}(Q, \omega)$ at constant Q , it is convoluted with the instrumental resolution function. The fitting procedure consists of a sequence of common algorithms to minimise χ^2 taken from the CERNLIB library [109]. The simplest models used for monatomic liquids, like the viscoelastic model (eq. 2.60), the

kinetic model (3 Lorentzians) or the damped harmonic oscillator (DHO) model (eq. 2.57), are not able to describe reasonably well the measured spectra of the binary alloys. Two of the extended models discussed in section 2.4.3 were used instead. Some examples of the excellent fits are shown in figure 6.22.

First, a combination of a DHO and two Lorentzians was applied. While the DHO is intended to account for a mode of coupled pressure-density fluctuations, which might be propagating or overdamped, the two Lorentzians describe relaxation processes due to temperature and concentration fluctuations. The total number of fit parameters is seven: three for the amplitudes of the fit functions, three for their respective widths Γ , and one for $\omega_0(Q)$ of the DHO. As the IN6 data cover the quasielastic range with a better resolution, cuts of $\mathcal{S}(Q, \omega)$ at constant Q obtained from the two different experiments were fitted at the same time.

Figure 6.23: Dispersions for liquid RbSb at $T=970\text{K}$ obtained from fits with the two different models and from the maxima ω_m of $\mathcal{I}_l(Q, \omega)$.

The resulting dispersion $\omega_0(Q)$ of the DHO is shown in figure 6.23. For $Q < 0.8\text{\AA}^{-1}$ the dispersion is almost linear in Q with a corresponding sound velocity c_0 of about 2250 m/s. This value is larger than the sound velocities of the pure elements ($c_{s,Rb} = 1260$ m/s, $c_{s,Sb} = 1893$ m/s) at their melting point [96] and hence another consequence of the stiffer bonds and the increased particle density. The correlations that lead to the prepeak cause a complicated spectral shape of $\mathcal{S}(Q, \omega)$ around $Q \sim 1\text{\AA}^{-1}$. As a result, the accuracy of the fitted ω_0

decreases in this Q range. For larger momentum transfers, where the measured ω range is more extended, the short-time behaviour of the correlation function becomes more important and the memory function has to be modelled more carefully. Especially Lorentzians are not able to describe well enough anymore features of the scattering law at Q larger than $2\text{\AA}^{-1}$.

A more sophisticated model that includes the frequency moments up to the fourth order was introduced as the generalised hydrodynamic theory. Equation 2.63 provides three independent exponential decay channels of the memory function $M_1(Q, t)$. It can be interpreted as an extension of the simple viscoelastic model with only one relaxation time (eq. 2.60) that was successfully used for liquid alkali metals and also for the binary alloy $\text{Rb}_{0.95}\text{Sb}_{0.05}$ [88]. However, for compositions with $x < 0.9$ the simple model is not sufficient anymore to describe $\mathcal{S}(Q, \omega)$ quantitatively.

The number of the Q dependent parameters in equation 2.63 was reduced by one to seven since one relaxation time turned out to be so small that the exponential decay could be approximated by a δ function. To avoid a misleading interpretation the fitted parameters are not assigned to the three processes μ , α and th . Thus, the fit function reads

$$\mathcal{S}(Q, \omega) = \frac{\mathcal{S}(Q)}{\pi} \text{Re} \left\{ i\omega + \frac{\omega_0^2(Q)}{i\omega + \frac{\Delta_1^2(Q)}{i\omega + \Gamma_1(Q)} + \frac{\Delta_2^2(Q)}{i\omega + \Gamma_2(Q)} + \zeta_3^2(Q)} \right\}^{-1} \quad (6.5)$$

with $\zeta_3^2(Q) = \Delta_3^2(Q)/\Gamma_3(Q)$ and $\Gamma_i(Q) = 1/\tau_i(Q)$. The dispersion $\omega_0(Q)$ obtained from the fit of this function is also shown in figure 6.23 together with the respective $\omega_m(Q)$ from the maxima of $\mathcal{J}_l(Q, \omega)$. Similar to other disordered systems [2] the change of the dynamic variable from the density to the longitudinal current is connected with a shift of the dispersion to higher frequencies.

Surprisingly, the dispersions $\omega_0(Q)$ obtained by the fit of the two different models also show considerable differences. Although both models have the same number of fit parameters their strength can be found in different regions of Q . At small Q the accessible ω range is quite restricted and therefore the shortest-time behaviour cannot be probed sufficiently precise. In this region the DHO model and especially the tails of the Lorentzian lead to a shape of the dispersion $\omega_0(Q)$ as known from other liquids. Because the DHO does not fulfil basic sum rules (frequency moments) it is not a good fit function for the data at larger Q .

Generalised hydrodynamics provides a very powerful fit model over a large Q range. However, to resolve the different decay channels a sufficiently large ω range is required. While at least the shape of the dispersion is well established around Q_p the present results do not provide conclusive information about the influence of the prepeak on the dispersion. While in the DHO model the prepeak is mainly fitted by an independent Lorentzian and the dispersion extracted from

the DHO does not show an unusual behaviour, the interplay of the parameters in the other model suggests at least a dip in $\omega_0(Q)$ at about $1\text{\AA}$. This is presently in the focus of other investigations.

The prepeak itself is very sharp. Its line width was obtained by a fit of two Lorentzians to the quasielastic region ($\pm 3\text{meV}$), of which one is to describe the prepeak contribution alone and the other accounts for the much broader features of all the other contributions to the scattering law. The full width at half maximum (FWHM) of the former is about 0.12 meV ($\Gamma=0.06\text{meV}$), which is smaller than the resolution function. Assuming $\Gamma = DQ^2$ this is equivalent to a diffusion constant of about $0.11 \times 10^{-4}\text{cm}^2/\text{s}$. The prepeak of the respective Na-Sn composition leads to an about four times larger diffusivity ($0.4 \times 10^{-4}\text{cm}^2/\text{s}$), which may be explained by the more stable and hence less mobile polyanions in RbSb.

Figure 6.24: Dispersions $\omega_0(Q)$ of $\text{Rb}_x\text{Sb}_{1-x}$ obtained from a model fit with three decay channels.

The shift of the dispersion $\omega_0(Q)$ with composition (figure 6.24) is less pronounced than that for $\omega_m(Q)$. However, it confirms the observation that the change of the interatomic potential with concentration is much stronger on the alkali-rich side, i.e. for $x > 0.75$.

6.2.4 Frequency Spectrum

The frequency spectra $\mathcal{Z}(\omega)$ obtained with the same procedure as for Na-Sn are shown in figure 6.25. As in the other system the shift of the maximum to larger frequencies is most pronounced in the concentration region between the alkali metal and the octet composition. Again this shift confirms the behaviour of the dispersion $\omega_m(Q)$.

Figure 6.25: Frequency spectra of liquid $\text{Rb}_x\text{Sb}_{1-x}$.

While for Sb concentrations larger than 25 at-% the dispersion $\omega_m(Q)$ does not show any important changes, the frequency spectra clearly show the increasing content of covalent bonds. In *ab initio* computer simulations of liquid K-Sb [64] the occurrence of a high-frequency peak in the Sb spectrum was predicted at about 26 ps^{-1} (17 meV). The high-frequency modes are attributed to the Sb vibrations in short Sb chains stabilised by strong covalent forces. The shoulder around 17 meV, rather weak at $x=0.75$ and $x=0.65$ but clearly visible at equiatomic composition, has to be taken as an experimental prove that this predicted mode really exists in this liquid.

Since the two systems, Rb-Sb and K-Sb, are not expected to have very different dynamic properties a further comparison of the experimental data with simulation results seems very reasonable. The low-frequency peak in the computed partial Sb spectrum was found at about 5 meV, a frequency where the

extrapolation scheme for the experimental data has already large uncertainties. The main peak in the partial K spectrum at 13 meV that corresponds to vibrational motions of the alkali atoms can, of course, not be found for Rb at the same frequency due to the difference in mass. If a simple scaling with the square root of the mass is assumed the Rb peak would be expected at around 9 meV, which is in excellent agreement with the measured data.

6.3 The Binary Liquid $\text{Rb}_x(\text{RbBr})_{1-x}$

6.3.1 Scattering Law and $S(Q)$

Mixtures of liquid alkali metals with their respective alkali halides are model systems for investigations of the transition from metallic to ionic interactions without covalent effects. For the comparison with the other two systems the spectra from earlier IN6 experiments on liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$, measured at $T=966\text{K}$ and 1160K [92], were reevaluated, now with an extended correction for multiple scattering out to 40 meV.

Figure 6.26: $\mathcal{S}(Q, \omega)$ of liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$ at $T=966\text{K}$.

When the scattering law of $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$ (figure 6.26) is compared with the corresponding $\mathcal{S}(Q, \omega)$ of the systems discussed above it is most similar to that of $\text{Rb}_{0.85}\text{Sb}_{0.15}$. In both cases a relatively broad principle peak and an increase of the scattering intensity towards small Q is observed. This behaviour is not surprising as $\text{Rb}_{0.85}\text{Sb}_{0.15}$ can also be interpreted as an alkali-salt mixture, namely $\text{Rb}_{0.73}(\text{Rb}_3\text{Sb})_{0.27}$. The small angle scattering intensity indicates concentration fluctuations and hence a tendency to phase segregation due to the competing metallic and ionic interactions. The additional intensity at $\omega = 0$ in figure 6.26

Figure 6.27: Static structure factor $S(Q)$ of liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$ compared to the respective results from diffraction experiments at 941K and 1160K [53] and $S(Q)$ of liquid Rb at $T=1073\text{K}$ [105].

probably stems from some uncorrected background, which is left even after a careful subtraction of the empty container [92].

In [92] the good agreement of the static structure factors $S(Q)$ obtained from $\mathcal{S}(Q, \omega)$ and from diffraction experiments was already demonstrated. This result can be confirmed after the improved data treatment presented here (figure 6.27). For a better comparison with the earlier published results the integration of $\mathcal{S}(Q, \omega)$ over ω was restricted to the neutron energy gain part of the inelastic and quasielastic spectra. This method reduces the cutoff effects at larger Q compared to the integration over the full measured energy range. However, the discrepancies at small Q remain due to the limited dynamic range in this region. While the position of Q_p is almost unchanged with respect to pure liquid Rb the height of the principle peak of $S(Q)$ is reduced and a shoulder beyond Q_p indicates the onset of ionic short-range interactions [53].

6.3.2 Collective Dynamics

The dispersions $\omega_m(Q)$ obtained from $\mathcal{J}_l(Q, \omega)$ are shown in figure 6.28. As in simple liquids, the minimum of $\omega_m(Q)$ is shifted towards higher frequencies with increasing temperature. As the position of Q_p in $S(Q)$ does not change significantly with respect to pure liquid Rb, there is no such shift in the dispersion, either. On the contrary, for the higher temperature the minimum of the dispersion appears at even slightly lower Q in $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$. Compared to $\text{Rb}_{0.85}\text{Sb}_{0.15}$, the dispersions in this alloy are completely continuous and do not show an unusual behaviour. This may be interpreted as a consequence of the different atomic interactions in the two systems. It seems that in the metal–molten-salt mixture the change of the structure and hence also the dynamic properties is less drastic than in the *Zintl* type alloy.

Figure 6.28: Dispersion from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$.

The dispersions $\omega_0(Q)$ from the fit of the multiple relaxation time model (eq. 6.5) are in surprisingly good agreement with $\omega_m(Q)$ around Q_p (see figure 6.29). For other Q they are observed at smaller ω as it would have been expected from the results presented above for Rb-Sb alloys.

6.3.3 Frequency Spectrum

The frequency spectrum of $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$ (figure 6.30) does not show any unexpected features. Compared to the corresponding liquid alloy (with $x=0.85$) in the

Figure 6.29: Comparison of the dispersions $\omega_m(Q)$ and $\omega_0(Q)$. Both dispersions for $T=1160\text{K}$ are shifted to higher ω by 2 meV.

Figure 6.30: Frequency spectra of liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$.

Rb-Sb system the maximum of $\mathcal{Z}(\omega)$ is found at slightly smaller frequency, which is consistent with the frequency of the minimum of $\omega_m(Q)$. The temperature dependence of $\mathcal{Z}(\omega)$ is again characterised by a slight shift to higher frequencies.

Chapter 7

Summary

The microscopic description of the liquid state is still a challenging subject. Especially the atomic dynamics of non-simple liquids is not yet well understood. However, it is known from structural, electronic and thermodynamic investigations that the properties of the liquid depend strongly on the atomic interaction potential. As a systematic study of the influence of the *type* of the interatomic forces on the atomic dynamics had not been done experimentally before, this problem has been addressed here.

In certain binary systems, the dominant type of interaction can be changed continuously by varying the concentration of the components. The systems of choice here were two binary liquid alloys with a tendency to form partial covalent bonds, $\text{Rb}_x\text{Sb}_{1-x}$ and $\text{Na}_x\text{Sn}_{1-x}$, and a liquid alkali metal – molten salt mixture, $\text{Rb}_x(\text{RbBr})_{1-x}$. Thus the transition from purely metallic to ionic and (partly) covalent behaviour could be studied.

On the experimental side, inelastic scattering of neutrons or X-rays have proven to be favourable techniques. Recent achievements in instrumentation allow to make more efficient measurements today than ten years ago. Another step forward will be the new neutron Brillouin spectrometer BRISP, which is currently under construction. It is a dedicated instrument for thermal neutron Brillouin scattering, i.e. for studies of the atomic dynamics in the region of small momentum transfers, which is the most interesting dynamic region in disordered systems including liquids. The results of various Monte-Carlo computer simulations for this new spectrometer have been presented. These simulations provide necessary guidelines for the optimisation of the new instrument, which is absolutely essential from the scientific and the economic point of view. Further, the simulations can help to satisfy safety requirements.

The inelastic neutron scattering experiments were performed at the cold neutron time-focusing time-of-flight spectrometer IN6 and the triple-axis spectrometer IN1TAS (using thermal neutrons) of the Institut Laue-Langevin, Grenoble, France. The liquid samples with different compositions were measured also as a function of temperature. After the experiment the spectra had to be processed

through a number of data treatment routines, including an extensive correction procedure for multiple scattering. The resulting total scattering laws $\mathcal{S}(Q, \omega)$ yield the basis for the interpretation of the data and for the comparison with theoretical models.

As a first test for the quality of the data the zeroth and the second frequency moments of the scattering law were derived by integration over ω . The former, which are just the static structure factors, compare well with results from diffraction experiments, while the latter are in satisfactory agreement with the theoretical values considering the uncertainties in the mass density and the truncation errors. A special feature of the alloys with partly covalent bonds is the occurrence of a prepeak. Because it is very sharp in ω it shows up much more pronounced in $\mathcal{S}(Q, \omega)$ at $\omega = 0$ than in $S(Q)$.

In a next step the dispersions $\omega_m(Q)$ from the maxima of the longitudinal current correlation function $\mathcal{J}_l(Q, \omega)$ were obtained. They clearly show a discontinuous change with composition in the Rb-Sb and the Na-Sn alloy systems, which is interpreted to be the consequence of the different types of interaction and proves that a change of interaction is visible in the collective dynamics of liquids. In both cases the overlap of different modes has been found at certain compositions leading to a rather unusual shape of the dispersion curves. This is in contrast to the behaviour of simple fluids (and also liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$) where the dispersions are completely continuous. Most remarkable is the occurrence of a second dispersion branch in liquid $\text{Na}_x\text{Sn}_{1-x}$, which has been discussed with respect to computer simulation results.

For the $\text{Rb}_x\text{Sb}_{1-x}$ alloys different models were fitted to the scattering law. It turned out that the damped harmonic oscillator model gives only satisfying results at smallest Q where the accessible ω range is quite restricted. Better results were obtained using the generalised hydrodynamic model. The respective dispersion curves for $\omega_0(Q)$ were compared and discussed. It is most likely that in the region of the prepeak, which has a very sharp spectral shape and indicates the existence of long-living units in the liquid, the dispersion has a dip. For $x=0.5$ a velocity of sound was estimated, which is much larger than those of the pure elements. This is again an indication of the stronger atomic interaction.

Finally, generalised frequency spectra were obtained by an extrapolation procedure. The maxima of these functions change in frequency like the corresponding dispersions. For $\text{Rb}_{0.5}\text{Sb}_{0.5}$ a second frequency band occurs at high frequencies, in agreement with computer simulation results of a similar system. To our knowledge, this signature of covalency in the liquid was observed experimentally for the first time.

In conclusion, it seems very fruitful and timely to study these non-simple liquids. New features in the dynamic structure could be found and also partly interpreted with the help of very recent computer simulations. The increasing power of these simulations combined with new experimental facilities will certainly allow to improve our understanding of (liquid) matter in the future.

Bibliography

- [1] L. VAN HOVE, *Phys. Rev.* **95**, 249 (1954).
- [2] J.-B. SUCK, *Int. J. Mod. Phys. B* **7**, 3003 (1993).
- [3] W. VAN DER LUGT, *J. Phys.: Condens. Matter* **8**, 6115 (1996).
- [4] P. G. DE GENNES, *Physica* **25**, 825 (1959).
- [5] D. L. PRICE and J. R. D. COPLEY, *Phys. Rev. A* **11**, 2124 (1975).
- [6] J. P. BOON and S. YIP, *Molecular Hydrodynamics*, McGraw-Hill, New York, 1980.
- [7] U. BALUCANI and M. ZOPPI, *Dynamics of the liquid state*, Oxford University Press Inc., New York, 1994.
- [8] P. A. EGELSTAFF and P. SCHOFIELD, *Nucl. Sci. Eng.* **12**, 260 (1962).
- [9] R. KUBO, *Rep. Prog. Phys.* **29**, 255 (1966).
- [10] S. W. LOVESEY, *Theory of neutron scattering from condensed matter*, Oxford University Press, 1984.
- [11] N. W. ASHCROFT and D. C. LANGRETH, *Phys. Rev.* **156**, 685 (1967).
- [12] A. B. BHATIA and D. E. THORNTON, *Phys. Rev. B* **2**, 3004 (1970).
- [13] R. ZWANZIG, *Boulder Lectures in Theoretical Physics*, volume III, chapter a, p. 106, Wiley-Interscience, New York, 1961.
- [14] H. MORI, *Prog. Theor. Phys.* **33**, 423 (1965).
- [15] H. MORI, *Prog. Theor. Phys.* **34**, 399 (1965).
- [16] L. D. LANDAU and E. M. LIFSHITZ, *Fluid Mechanics*, Pergamon Press, London, 1959.
- [17] J. R. D. COPLEY and S. W. LOVESEY, *Rep. Prog. Phys.* **38**, 461 (1975).

- [18] W. MARSHALL and S. W. LOVESEY, *Theory of thermal neutron scattering*, Oxford University Press, 1971.
- [19] P. CHIEUX, J. DUPUY-PHILON, J.-F. JAL, and J.-B. SUCK, *J. Non-Cryst. Solids* **205-207**, 370 (1996).
- [20] S. W. LOVESEY, *J. Phys. C: Solid State Phys.* **4**, 3057 (1971).
- [21] S. W. LOVESEY, *J. Phys. C: Solid State Phys.* **6**, 1856 (1973).
- [22] T. SCOPIGNO, U. BALUCANI, G. RUOCCO, and F. SETTE, *J. Phys.: Condens. Matter* **12**, 8009 (2000).
- [23] Y. CHUSHAK, T. BRYK, A. BAUMKERTNER, G. KAHL, and J. HAFNER, *Phys. Chem. Liq.* **32**, 87 (1996).
- [24] D. LEVESQUE, L. VERLET, and J. KÜRKIJARVI, *Phys. Rev. A* **7**, 1690 (1973).
- [25] T. SCOPIGNO, U. BALUCANI, G. RUOCCO, and F. SETTE, *Phys. Rev. E* **63**, 011210 (2001).
- [26] T. SCOPIGNO, U. BALUCANI, G. RUOCCO, and F. SETTE, *Phys. Rev. E* **65**, 031205 (2002).
- [27] I. M. DE SCHEPPER, E. G. D. COHEN, C. BRUIN, J. C. VAN RIJS, W. MONTFROOIJ, and L. A. DE GRAAF, *Phys. Rev. A* **38**, 271 (1988).
- [28] I. M. MRYGŁOD, I. P. OMEL'YAN, and M. V. TOKARCHUK, *Mol. Phys.* **84**, 235 (1995).
- [29] T. BRYK and I. MRYGŁOD, *Phys. Rev. E* **63**, 051202 (2001).
- [30] T. BRYK and I. MRYGŁOD, *J. Phys.: Condens. Matter* **12**, 6063 (2000).
- [31] S. M. KAUZLARICH, editor, *Chemistry, structure and bonding of Zintl phases and ions*, VCH Publishers, New York, 1996.
- [32] W. VAN DER LUGT and P. VERKERK, *Plasmas & Ions* **3**, 3 (2000).
- [33] E. ZINTL and G. WOLTERS DORF, *Z. Elektrochem.* **41**, 876 (1935).
- [34] W. GEERTSMA, J. DIJKSTRA, and W. VAN DER LUGT, *J. Phys. F: Met. Phys.* **14**, 1833 (1984).
- [35] W. HUME-ROTHERY, *J. Chem. Soc.* **131**, 947 (1928).
- [36] T. B. MASSALSKI, editor, *Binary Alloys Phase Diagrams*, ASM International, 1990.

- [37] F. SPRINGELKAMP, R. A. DE GROOT, W. GEERTSMA, W. VAN DER LUGT, and F. M. MUELLER, *Phys. Rev. B* **32**, 2319 (1985).
- [38] F. W. DORN and W. KLEMM, *Z. Anorg. Allg. Chem.* **309**, 189 (1961).
- [39] C. VAN DER MAREL, A. B. VAN OOSTEN, W. GEERTSMA, and W. VAN DER LUGT, *J. Phys. F: Met. Phys.* **12**, 2349 (1982).
- [40] A. RAIS, N. E. CUSACK, and F. E. NEALE, *J. Phys. F: Met. Phys.* **12**, 1091 (1982).
- [41] C. VAN DER MAREL, P. C. STEIN, and W. VAN DER LUGT, *Phys. Lett.* **95A**, 451 (1983).
- [42] S. TAMAKI, *Z. Phys. Chem. (NF)* **156**, 537 (1988).
- [43] S. TAMAKI, T. ISHIGURO, and S. TAKEDA, *J. Phys. F: Met. Phys.* **12**, 1613 (1982).
- [44] W. GEERTSMA and M.-L. SABOUNGI, *J. Phys.: Condens. Matter* **7**, 4803 (1995).
- [45] H. REDSLOB, G. STEINLEITNER, and W. FREYLAND, *Z. Naturforsch.* **27a**, 587 (1982).
- [46] R. DUPREE, D. J. KIRBY, and W. FREYLAND, *Phil. Mag. B* **46**, 595 (1982).
- [47] H. T. J. REIJERS, M.-L. SABOUNGI, D. PRICE, J. W. RICHARDSON, K. J. VOLIN, and W. VAN DER LUGT, *Phys. Rev. B* **40**, 6018 (1989).
- [48] B. P. ALBLAS, W. VAN DER LUGT, J. DIJKSTRA, W. GEERTSMA, and C. VAN DIJK, *J. Phys. F: Met. Phys.* **13**, 2465 (1983).
- [49] U. BECK and W. FREYLAND, *J. Non-Cryst. Solids* **250-252**, 250 (1999).
- [50] M. STOLZ, O. LEICHTWEISS, R. WINTER, M.-L. SABOUNGI, J. FORTNER, and W. S. HOWELLS, *Europhys. Lett.* **27**, 221 (1994).
- [51] R. WINTER, O. LEICHTWEISS, C. BIERMANN, M.-L. SABOUNGI, R. L. MCGREEVY, and W. S. HOWELLS, *J. Non-Cryst. Solids* **205-207**, 66 (1996).
- [52] P. LAMPARTER, W. MARTIN, S. STEEB, and W. FREYLAND, *Z. Naturforsch.* **38a**, 329 (1983).
- [53] G. CHABRIER, J. F. JAL, P. CHIEUX, and J. DUPUY, *Phys. Lett.* **93A**, 47 (1982).

- [54] R. L. MCGREEVY, *J. Phys.: Condens. Matter* **13**, R877 (2001).
- [55] M. A. HOWE and R. L. MCGREEVY, *J. Phys.: Condens. Matter* **3**, 577 (1991).
- [56] M. STOLZ, R. WINTER, W. S. HOWELLS, and R. L. MCGREEVY, *J. Phys.: Condens. Matter* **7**, 5733 (1995).
- [57] H. T. J. REIJERS, W. VAN DER LUGT, and M.-L. SABOUNGI, *Phys. Rev. B* **42**, 3395 (1990).
- [58] R. CAR and M. PARRINELLO, *Phys. Rev. Lett.* **55**, 2471 (1985).
- [59] M. SCHÖNE, R. KASCHNER, and G. SEIFERT, *J. Phys.: Condens. Matter* **7**, L19 (1995).
- [60] R. KASCHNER, M. SCHÖNE, G. SEIFERT, and G. PASTORE, *J. Phys.: Condens. Matter* **8**, L653 (1996).
- [61] G. SEIFERT, R. KASCHNER, M. SCHÖNE, and G. PASTORE, *J. Phys.: Condens. Matter* **10**, 1175 (1998).
- [62] O. GENSER and J. HAFNER, *J. Phys.: Condens. Matter* **13**, 959 (2001).
- [63] O. GENSER and J. HAFNER, *J. Phys.: Condens. Matter* **13**, 981 (2001).
- [64] K. SEIFERT-LORENZ and J. HAFNER, *Phys. Rev. B* **59**, 843 (1999).
- [65] W. BILTZ and W. HOLVERSCHEIT, *Z. Anorg. Allg. Chem.* **140**, 261 (1924).
- [66] S. P. MCALISTER, *Phil. Mag.* **26**, 853 (1972).
- [67] J. SAAR and H. RUPPERSBERG, *Z. Phys. Chem. (NF)* **156**, 587 (1988).
- [68] J. HAFNER, A. PASTUREL, and P. HICTER, *J. Phys. F: Met. Phys.* **14**, 2279 (1984).
- [69] O. MADEL, *Atomare Struktur und elektrischer Widerstand amorpher $\text{Na}_x\text{Sn}_{100-x}$ Legierungen*, PhD thesis, TU Chemnitz, 1998.
- [70] G. CHABRIER and J.-P. HANSEN, *Mol. Phys.* **50**, 901 (1983).
- [71] P. A. EGELSTAFF, G. KEARLEY, J.-B. SUCK, and J. P. A. YODEN, *Europhys. Lett.* **10**, 37 (1989).
- [72] S. JAHN and J.-B. SUCK, *Nucl. Instr. Meth. A* **438**, 452 (1999).
- [73] *MCNP4C-A General Monte Carlo N-Particle Transport Code*, Los Alamos, 2000.

- [74] S. MAHLING-ENNAOUI, MCNP for HFR Grenoble, Technical report, Institut Laue-Langevin, 1999, internal report.
- [75] S. MAHLING-ENNAOUI and S. JAHN, *Proc. ILL millenium symposium*, 281 (2001).
- [76] S. MAHLING-ENNAOUI and S. JAHN, Shielding Calculations: Instrument BRISP, Technical report, Institut Laue-Langevin, 2002, Internal report.
- [77] R. SCHERM, C. CARLILE, J. DIANOUX, J.-B. SUCK, and J. WHITE, *ILL Scientific Report* **76S235S** (1976).
- [78] H. MUTKA, *Nucl. Instr. Met. A* **338**, 144 (1994).
- [79] K. LEFMANN and K. NIELSEN, *Neutron News* **10**, 20 (1999).
- [80] D. WECHSLER, G. ZSIGMOND, F. STREFFER, and F. MEZEI, *Neutron News* **11**, 25 (2000).
- [81] S. JAHN, Flüssigkeiten mit kovalentem Bindungsanteil und Neutronen Brillouin Spektroskopie, <http://archiv.tu-chemnitz.de/pub/1999/0011/index.html>, 1999, Diplom thesis (in German).
- [82] S. JAHN and J.-B. SUCK, *Appl. Phys. A* **74**, S1465 (2002).
- [83] O. W. DIETRICH and J. ALS-NIELSEN, *Acta Cryst.* **18**, 184 (1965).
- [84] V. F. SEARS, *Acta Cryst.* **A53**, 35 (1997).
- [85] G. L. GLINKA, J. M. ROWE, and J. G. LAROCK, *J. Appl. Cryst.* **19**, 427 (1986).
- [86] F. FORMISANO, E. GUARINI, F. SACCHETTI, and C. PETRILLO, *submitted for publication*.
- [87] ILL YellowBook: <http://www.ill.fr/YellowBook>.
- [88] G. PRATESI and J.-B. SUCK, *J. Phys.: Condens. Matter* **9**, 11035 (1997).
- [89] G. PRATESI and J.-B. SUCK, *J. Non-Cryst. Solids* **232-234**, 252 (1998).
- [90] S. JAHN, G. PRATESI, and J.-B. SUCK, *J. Non-Cryst. Solids* **250-252**, 263 (1999).
- [91] C. MATHIEU, J.-F. JAL, J. DUPUY, J.-B. SUCK, and P. CHIEUX, *Il Nuovo Cimento* **12D**, 673 (1990).
- [92] P. CHIEUX, J. DUPUY-PHILON, J.-F. JAL, C. MORKEL, and J.-B. SUCK, *J. Phys.: Condens. Matter* **6**, A235 (1994).

- [93] M. J. COOPER and R. NATHANS, *Acta Cryst.* **23**, 357 (1967).
- [94] B. DORNER, *Acta Cryst.* **A28**, 319 (1972).
- [95] V. F. SEARS, *Neutron News* **3**, 26 (1992).
- [96] T. IIDA and I. L. GUTHRIE, *The physical properties of liquid metals*, Clarendon Press Oxford, 1988.
- [97] G. J. JANZ, *Molten salts handbook*, Academic Press, New York, 1967.
- [98] A. HIESS, private communication.
- [99] H. PAALMAN and C. PINGS, *J. Appl. Phys.* **33**, 2635 (1962).
- [100] P. PONCET, Inelastic scattering from a liquid sample confined within a cylindrical container: subtraction and attenuation corrections, Technical report, Institut Laue-Langevin, 1977, Internal report 77P0139S.
- [101] I. A. BLECH and B. L. AVERBACH, *Phys. Rev.* **137**, A1113 (1965).
- [102] J. R. D. COPLEY, P. VERKERK, A. A. VAN WELL, and H. FREDERIKZE, *Comp. Phys. Comm.* **40**, 337 (1986).
- [103] J. KULDA, *Physica B* **213-214**, 926 (1995).
- [104] S. JAHN and J.-B. SUCK, *J. Non-Cryst. Solids* **312-314**, 134 (2002).
- [105] R. WINTER, C. PILGRIM, F. HENSEL, C. MORKEL, and W. GLÄSER, *J. Non-Cryst. Solids* **156-158**, 9 (1993).
- [106] G. PRATESI, J.-B. SUCK, and P. A. EGELSTAFF, *J. Non-Cryst. Solids* **250-252**, 91 (1999).
- [107] T. HALM, H. NEUMANN, and W. HOYER, *Z. Naturforsch.* **49a**, 530 (1994).
- [108] S. JAHN, G. PRATESI, and J.-B. SUCK, *Appl. Phys. A* **74**, S1664 (2002).
- [109] <http://cern.ch/cernlib/>.

List of Figures

2.1	Scattering problem	12
2.2	Kinematic range of IN1 and IN6.	15
3.1	Phase diagram of Na-Sn measured by Hume-Rothery.	27
3.2	Electrical resistivity of liquid Na-Sn.	28
3.3	Structure factor of Na-Sn.	30
3.4	Snapshot of the structural arrangement in liquid NaSn.	31
4.1	Schematic view of the thermal neutron Brillouin spectrometer BRISP.	35
4.2	Model of the monochromator shielding.	36
4.3	Neutron energy spectrum at the bottom of the beam tube IH3.	37
4.4	Spatial distribution of the neutron beam at the entrance of the background chopper, having entered the honey-comb collimator and at the detector position.	40
4.5	Time-of-flight resolution for different sample-detector distances, Cu(111) monochromator, $\omega = 0$	41
4.6	Phase diagram of Rb-Sb measured by Dorn and Klemm.	43
4.7	The cold neutron TOF instrument IN6.	45
4.8	The thermal neutron TAS instrument IN1.	47
5.1	Sample independent background for different scans on IN1 TAS.	53
5.2	Sample absorption factor for $Na_{0.77}Sn_{0.23}$ for two extreme scattering angles as a function of the energy transfer.	55
5.3	Comparison between TOF spectra from experiment and MSCAT simulation for $Na_{0.23}Sn_{0.77}$ at $T=820K$	57
5.4	Multiple scattering function for $Na_{0.23}Sn_{0.77}$ at $T=820K$	58
5.5	Relative contribution of multiple scattering to the total scattering for $Na_{0.77}Sn_{0.23}$ at $T=820K$ at three different angles.	58
5.6	Measured elastic peak resolution functions of IN6 and IN1.	60
6.1	Weighting factors for the partial contributions to $\mathcal{S}(Q, \omega)$ of Na-Sn alloys in species specific and density-concentration separations.	61
6.2	Weighting factors for the partial contributions to $\mathcal{S}(Q, \omega)$ of Rb-Sb alloys in species specific and density-concentration separations.	62
6.3	$\mathcal{S}(Q, \omega)$ of liquid $Na_{0.77}Sn_{0.23}$ at two different temperatures.	63
6.4	Cuts of $\mathcal{S}(Q, \omega)$ of liquid $Na_{0.77}Sn_{0.23}$ at constant Q for different temperatures.	64
6.5	$\mathcal{S}(Q, \omega)$ of liquid $Na_{0.57}Sn_{0.43}$ and $Na_{0.33}Sn_{0.67}$	64
6.6	Static structure factors $S(Q)$ of liquid Na_xSn_{1-x} from the IN6 experiments compared to literature values.	66
6.7	$\mathcal{S}(Q)$ of liquid $Na_{0.77}Sn_{0.23}$ at different temperatures.	67
6.8	Second frequency moments of Na_xSn_{1-x} obtained from integration of the scattering law.	68
6.9	$\mathcal{I}_l(Q, \omega)$ of liquid Na_xSn_{1-x} for different concentrations and momentum transfers.	69

6.10	Dispersion from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$ at T=820K.	70
6.11	Dispersion from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$ as a function of temperature for the different concentrations.	72
6.12	Extrapolation for three different ω ($\text{Na}_{0.9}\text{Sn}_{0.1}$, 800K).	73
6.13	Frequency spectra of liquid $\text{Na}_x\text{Sn}_{1-x}$ at T=820K.	74
6.14	Frequency spectra of liquid $\text{Na}_{0.77}\text{Sn}_{0.23}$ as a function of temperature.	75
6.15	Normalised intermediate scattering functions $\mathcal{F}(Q, t)/\mathcal{F}(Q, 0)$ for different samples at different Q obtained from the Fourier transformation of $\mathcal{S}(Q, \omega)$	76
6.16	Dynamic structure factors of liquid $\text{Rb}_x\text{Sb}_{1-x}$ for x=0.95 and x=0.85.	77
6.17	Dynamic structure factors of liquid $\text{Rb}_x\text{Sb}_{1-x}$, x=0.75 and x=0.50.	78
6.18	Static structure factors of liquid $\text{Rb}_x\text{Sb}_{1-x}$ obtained from integration of $\mathcal{S}(Q, \omega)$	79
6.19	Second frequency moment of $\text{Rb}_x\text{Sb}_{1-x}$ obtained from integration of the scattering law.	80
6.20	$\mathcal{J}_l(Q, \omega)$ of liquid $\text{Rb}_x\text{Sb}_{1-x}$ for different concentrations and momentum transfers.	81
6.21	Dispersions from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$	82
6.22	Cuts of $\mathcal{S}(Q, \omega)$ (convoluted with the resolution function) at constant Q for liquid $\text{Rb}_{0.5}\text{Sb}_{0.5}$ together with model fits as described in the text.	83
6.23	Dispersions for liquid RbSb at T=970K obtained from fits with the two different models and from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$	84
6.24	Dispersions $\omega_0(Q)$ of $\text{Rb}_x\text{Sb}_{1-x}$ obtained from a model fit with three decay channels.	86
6.25	Frequency spectra of liquid $\text{Rb}_x\text{Sb}_{1-x}$	87
6.26	$\mathcal{S}(Q, \omega)$ of liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$ at T=966K.	88
6.27	Static structure factor $S(Q)$ of liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$ compared to the respective results from diffraction experiments at 941K and 1160K and $S(Q)$ of liquid Rb at T=1073K.	89
6.28	Dispersion from the maxima ω_m of $\mathcal{J}_l(Q, \omega)$	90
6.29	Comparison of the dispersions $\omega_m(Q)$ and $\omega_0(Q)$. Both dispersions for T=1160K are shifted to higher ω by 2 meV.	90
6.30	Frequency spectra of liquid $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$	91

List of Tables

4.1	Neutron intensity at the sample position.	41
5.1	Cross-sections, atomic masses and mass densities of the elements used in the experiments.	50
5.2	The cross-sections, atomic masses and densities of liquid $\text{Na}_x\text{Sn}_{1-x}$	50
5.3	The cross-sections, atomic masses and densities of liquid $\text{Rb}_x\text{Sb}_{1-x}$ and $\text{Rb}_{0.8}(\text{RbBr})_{0.2}$	51

Symbols and Abbreviations

In the following the most important symbols and abbreviations are listed.

Symbols

d	lattice spacing in Bragg's law; thickness
E_f, E_i	final and incident neutron energy
$\mathcal{F}(Q, t)$	total intermediate scattering function
$F^{(ij)}(Q, t)$	partial intermediate scattering function
$F_s^{(i)}(Q, t)$	self-part of the partial intermediate scattering function
$g^{(ij)}(r)$	partial pair correlation function
$G^{(ij)}(r, t)$	partial van Hove correlation function
$G_s^{(i)}(r, t)$	partial van Hove self correlation function
$\hbar$	Planck's constant divided by 2π
$\mathcal{J}_l(Q, \omega)$	total longitudinal current-current correlation function
$J_l^{(ij)}(Q, \omega)$	partial longitudinal current-current correlation function
k_B	Boltzmann constant
$\mathbf{k}_f, \mathbf{k}_i$	final and incident wave vector of the neutron
$\mathbf{j}^{(i)}(\mathbf{Q}, t)$	partial dynamic variable of the current
m	neutron mass
$M^{(i)}$	atomic mass of species i
N	total number of atoms
$N^{(i)}$	number of atoms of species i
$n^{(i)}$	average number density of species i
$n^{(i)}(\mathbf{r}, t)$	partial number density of species i
$\delta n^{(i)}(\mathbf{r}, t)$	density fluctuation $n^{(i)}(\mathbf{r}, t) - n^{(i)}$
$n_s^{(i)}(\mathbf{r}, t)$	single particle density of species i
$\mathbf{r}, r$	vectorial and radial space variable
$\mathbf{r}_k^{(i)}(t)$	position vector of the k th particle of species i
$\mathbf{Q}, Q$	vector and magnitude of the momentum transfer
Q_p	position of the principal maximum of $S(Q)$
$S(Q)$	total coherent static structure factor
$S^{(ij)}(Q)$	partial static structure factor
$\mathcal{S}(Q, \omega)$	total scattering law
$S(Q, \omega)$	total coherent scattering law
$S^{(ij)}(Q, \omega)$	partial dynamic structure factor
$S_s(Q, \omega)$	total incoherent scattering law
$S_s^{(i)}(Q, \omega)$	self-part of the partial dynamic structure factor

t	time
T	temperature
Δt_0	FWHM of the neutron pulse created by the Fermi chopper
tof	time of flight between sample and detector
$\mathbf{v}_k^{(i)}(t)$	velocity of the k th particle of species i
$\tilde{z}^{(i)}(\omega)$	frequency spectrum (Fourier transform of $\Psi^{(i)}(t)$)
$\mathcal{Z}(\omega)$	generalised frequency spectrum
θ	scattering angle
θ_B	Bragg angle
λ_i	wavelength of the incident neutron
σ_a	total neutron absorption cross-section
σ_B	total bound atom neutron scattering cross-section
σ_{coh}	total coherent scattering cross-section
σ_{inc}	total incoherent scattering cross-section
$\Phi^{(ij)}(\mathbf{r})$	pair potential
$\Psi^{(i)}(t)$	partial velocity autocorrelation function
ω	energy transfer
$\omega_0(Q)$	isothermal dispersion
$\omega_l(Q)$	dispersion of the instantaneous collective response
$\omega_m(Q)$	dispersion obtained from the maxima of $J_l(Q, \omega)$
$\langle \omega^n \rangle^{(ij)}$	n th frequency moment of $S^{(ij)}(Q, \omega)$
$\langle \omega^n \rangle_s^{(i)}$	n th frequency moment of $S_s^{(i)}(Q, \omega)$

Abbreviations

BRISP	NBS spectrometer at the ILL (under construction)
DHO	damped harmonic oscillator
FWHM	full width at half maximum
HFR	High Flux Reactor
IH3, IH4	inclined beam tubes at the ILL
ILL	Institut Laue-Langevin, Grenoble, France
IN1	TAS spectrometer at the ILL
IN6	TOF spectrometer at the ILL
INS	inelastic neutron scattering
IXS	inelastic X-ray scattering
MCNP	Monte-Carlo N-Particle Code
MSCAT	Monte-Carlo code for the multiple scattering correction
NBS	neutron Brillouin scattering
PG	pyrolithic graphite
TAS	triple-axis spectroscopy
TOF	time-of-flight
VACF	velocity autocorrelation function

Danksagung

An dieser Stelle möchte ich mich bei all denen bedanken, ohne die diese Arbeit nicht zustande gekommen wäre. In erster Linie gilt dies für Herrn Professor Jens-Boie Suck, der mein Interesse an den Flüssigkeiten und der Neutronenstreuung erweckt und mich in den letzten Jahren hervorragend betreut hat.

Frau Heidemarie Teichmann danke ich für ihre Hilfe und Geduld bei der Probenvorbereitung, ebenso wie Herrn Dr. Mayer und Herrn Herrmann vom *Institut für Kernenergetik und Energiesysteme* in Stuttgart für die Herstellung und das Verschweißen der Probenbehälter.

Allen Mitarbeitern der Professur *Materialforschung und Flüssigkeiten* sei Dank für die angenehme Arbeitsatmosphäre und die vielen interessanten Diskussionen. Ohne die ständige Hilfsbereitschaft dieser Kollegen wären viele Probleme nicht so schnell lösbar gewesen. Hervorheben möchte ich die Herren Doktoren Thomas Hellweg, Hartmut Neumann und Max Scheffer, die mein Verständnis für die Physik der Flüssigkeiten und anderer nichtkristalliner Materialien sowie für die "*LINUX-Welt*" wesentlich erweitert haben.

Ein besonderer Dank gilt den Mitarbeitern des Instituts Laue-Langevin in Grenoble, Frankreich, für die sehr gute Betreuung bei den Neutronenstreuexperimenten und die vielen Diskussionen während meines Aufenthaltes an dieser Einrichtung. Stellvertretend für viele andere möchte ich mich bei Herrn Dr. Bruno Dörner bedanken, der mich am ILL nicht nur sehr gut betreut, sondern mir auch das Einleben in Frankreich sehr erleichtert hat. Weiterhin danke ich den Herren Doktoren Albert Dianoux, Michael Koza und Alexander Ivanov sowie den Herren Pierre Palleau und Steve Jenkins für ihre Hilfe bei den Experimenten an IN6 und IN1. Mit Herrn Dr. Franz Demmel habe ich interessante Diskussionen über unelastische Streuung an Flüssigkeiten geführt. Profitiert habe ich auch von der guten Zusammenarbeit mit Herrn Dr. Gabriele Pratesi bei den IN6-Experimenten an den flüssigen Rb-Sb Legierungen.

Herrn Dr. Günter Fieg vom *Forschungszentrum Karlsruhe* danke ich für die hervorragende Einführung in die MCNP-Strahlenschutzrechnungen. Ebenso möchte ich mich bei Frau Professor Sabine Mahling-Ennaoui von der *Fachhochschule Furtwangen* für die gute Zusammenarbeit bei den Rechnungen für die Abschirmung des BRISP-Spektrometers bedanken. Viele dieser Rechnungen wären ohne die Hilfe der Strahlenschutz- und der Konstruktionsabteilungen des ILL

nicht möglich gewesen. Nicht zuletzt habe ich viel Unterstützung von der italienischen Seite des BRISP-Projektes erfahren, besonders von Herrn Dr. Ferdinando Formisano, bei dem ich mich an dieser Stelle bedanken möchte.

Nicht vergessen möchte ich auch meinen Eltern zu danken, die mich zu meiner wissenschaftlicher Laufbahn ermutigt und während der gesamten Ausbildung unterstützt haben.

Lebenslauf

Persönliche Angaben

Name: Jahn
Vorname: Sandro
Geburtsdatum: 23. September 1972
Geburtsort: Pößneck
Eltern: Jürgen und Erdmute Jahn
Familienstand: ledig
Staatsangehörigkeit: BR Deutschland

Ausbildung und wissenschaftlicher Werdegang

1979-1989	Polytechnische Oberschule in Chemnitz (damals Karl-Marx-Stadt)
1989-1992	Berufsausbildung mit Abitur, gewerbliche Berufsschule in Chemnitz
1992	Abitur und Facharbeiterabschluß als Maschinenbauer
1992-1993	Zivildienst im sozialen Bereich
1993-1998	Diplomstudiengang Physik an der Technischen Universität Chemnitz
1996-1997	Studienaufenthalt an der <i>Loughborough University</i> in Großbritannien im Rahmen des ERASMUS-Programms
1998	Diplomarbeit zum Thema "Flüssigkeiten mit kovalentem Bindungsanteil und Neutronen Brillouin Spektroskopie"
12/1998	Abschluß als Diplomphysiker
01/1999-09/2002	wissenschaftlicher Mitarbeiter an der Professur "Materialforschung und Flüssigkeiten" an der Technischen Universität Chemnitz
01/2000-09/2002	Doktorand am <i>Institut Laue-Langevin Grenoble</i> , Frankreich
seit 10/2002	Forschungsassistent am <i>Physical and Theoretical Chemistry Laboratory</i> der <i>University of Oxford</i> , Großbritannien

Selbständigkeitserklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Literatur und Hilfsmittel angefertigt habe.

Ich erkläre, nicht bereits früher oder gleichzeitig bei anderen Hochschulen oder an dieser Universität ein Promotionsverfahren beantragt zu haben.

Sandro Jahn