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Liquid Dynamics and Neutron Scattering.*

ALF SJÖLANDER

Chalmers Tekniska Högskola, Göteborg, Sweden

and

Argonne National Laboratory, Argonne, Illinois,
U.S.A.

INTRODUCTION

Due to the fact that this conference is meant to cover the properties of liquid metals I will in my talk on the atomic motions confine myself to those aspects which are relevant to this class of liquids. It seems, however, not very important whether the liquid is a metal or not when discussing the motion of the atoms or ions. The screening effect arising from the conduction electrons makes

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that the effective interaction between the ions is essentially short range like in non-metals. The whole subject for this conference is naturally divided into two quite different although inter-related parts, one on the motion of the electrons and the other on the motion of the ions. When discussing the electron properties, one mostly neglects the dynamical aspects of the ionic motion, taking however into account the disordered positions of the ions through the static structure factor. When considering the ionic motion one may assume the electrons to relax essentially instantaneously to an "equilibrium" distribution consistent with the positions of the ions and this makes that we can introduce an effective screened interaction between the ions. In a solid the Fermi surface is sharp and this causes the effective ion-ion interaction to have a tail of the form as $\cos(2 k_F r)/r^3$. Whether it is essentially so also in liquid metals seems to be somewhat unclear. The fact that the ions are surrounded by a screening cloud of electrons led Ziman¹ to conjecture that we can consider the ions and their clouds to form rigid neutral units which interact through an essentially short range interaction.

One would like to treat metals as two

interacting plasmas, one consisting of the conduction electrons and the other consisting of the ions.

However, we do not know how to treat properly the ionic plasma for which the interaction has both an essentially hard core part and a long Coulomb tail. Some very recent attempts² to overcome this difficulty seem very interesting and may lead to a new approach on liquid metals.

EXPERIMENTAL SITUATION

The static structure of the liquid is normally stated through the pair-correlation function $g(r)$ and it has been measured accurately both through x-ray and neutron diffraction experiments for a large number of liquids. One has tried to obtain from these data information on the effective ion-ion potential, using some approximate equation relating the pair-correlation function to the interatomic potential (Born-Green equation, Percus-Yevick equation, Hyper-netted chain approximation).³ It seems, however, difficult to obtain sufficiently accurate potentials in this way with the present accuracy of the experimental data.^{4,5} Also, we do not know very

well how accurate the theories are, on which the procedure is based.

Information on the dynamics of the atomic motion is obtained mainly from inelastic neutron scattering. The measured scattering cross section, being a function of the momentum transfer $\hbar\mathbf{q}$ and the energy transfer $\hbar\omega$ in the scattering process, is normally given through two functions $S_{\text{coh}}(\vec{q}, \omega)$ and $S_{\text{inc}}(\vec{q}, \omega)$. Depending on the nuclear properties of the sample the coherent or the incoherent part dominates. Vanadium, for instance, scatters only incoherently, whereas aluminum scatters predominantly coherently. The two scattering functions are Fourier transforms,

$$S_{\text{coh}}(\vec{q}, \omega) = \int e^{i(\vec{q} \cdot \vec{x} - \omega t)} G(\vec{x}, t) d\vec{x} dt, \quad (1)$$

$$S_{\text{inc}}(\vec{q}, \omega) = \int e^{i(\vec{q} \cdot \vec{x} - \omega t)} G_s(\vec{x}, t) d\vec{x} dt, \quad (2)$$

of the two Van Hove correlation functions $G(\vec{x}, t)$ and $G_s(\vec{x}, t)$. $G(\vec{x}, t)$ can be written as follows:

$$G(\vec{x}, t) = \langle n(\vec{x}, t) n(\infty) \rangle / n, \quad (3)$$

where $\langle \dots \rangle$ is the density auto-correlation function of the system, $n(\vec{x}, t)$ denoting the microscopic particle number density. n is the uniform mean density. From the definition in Eq. (3) it is evident that inelastic coherent scattering will give information on those collective motions which involve density fluctuations. For very small energy and momentum transfers we should expect to see certain characteristic structure is $S(\vec{q}, \omega)$, which should correspond to hydrodynamic and thermodynamic fluctuations of pressure and temperature. These motions are ordinary sound waves and heat diffusion. Due to experimental restrictions the neutron scattering technique is limited to rather large wave vectors and frequencies. One can only cover fluctuations which have wave lengths less than $10\text{-}20 \text{ \AA}$ and frequencies higher than $10^{12}\text{-}10^{13}$ per/sec. The very long wavelength fluctuations are covered in light scattering and ultrasonic measurements, and these experiments have confirmed the conclusions drawn from hydrodynamics and thermodynamics.

The function $G_s(\vec{x}, t)$, relating the incoherent scattering to the atomic motions, can be written in

the form

$$G(\vec{x}, t) = \int d\vec{x}' \langle \delta(\vec{x} + \vec{x}' - \vec{x}_i(t)) \delta(\vec{x}' - \vec{x}_i(0)) \rangle, \quad (4)$$

where $\vec{x}_i(t)$ denotes the trajectory of any atom "i". It tells us how an atom diffuses from its initial position at $t = 0$. This fact made Vineyard⁶ to conjecture that $G_s(\vec{x}, t)$ should be given approximately by the ordinary diffusion equation. Later experiments have shown that on the small time scale considered here simple diffusion theory is not very adequate.

Quite early experiments by Larsson et al.⁷ on polycrystalline and liquid aluminum gave some very striking results (Fig. 1). They found hardly any change in the scattered spectrum when melting the sample and this strongly indicated that both transverse and longitudinal modes, similar to those in solids, exist in the liquid phase. Measurements on liquid lead by Dorner et al.⁸ and by Randolph and Singwi⁹ have also indicated the existence of high frequency transverse and longitudinal modes in the liquid state. However, it seems at present to be a

somewhat controversial question whether transverse waves of the kind we have in solids really exist and propagate in these liquids. Figure 2 shows a set of scattering spectra for solid and liquid lithium obtained recently by Cocking.¹⁰ It should be noted that here both coherent and incoherent scattering contribute, the incoherent part contributing particularly to the quasi-elastic scattering.

As a general remark, I may state that the experimental data are often difficult to analyse for several reasons. Firstly, in most cases it is not possible to separate unambiguously the coherent and the incoherent parts. Secondly, the theories on which the analysis is based is not good enough for drawing any firm conclusions, at least for the coherent part.

MOLECULAR DYNAMICS

With big computers available it is nowadays possible to solve numerically Newton's equations for a system of 1000 particles or so. Rahman¹¹ has during recent years undertaken such a program and he has in great detail studied the diffusive motion of

single atoms in liquid argon. The results have been presented through the velocity auto-correlation function $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle$, which on the basis of Langevin's equation should decay strictly exponentially in time. Figure 3 shows the results obtained by Rahman. The fact that the auto-correlation function becomes negative after some time tells us that the atoms, if initially moving in one direction, will on the average reverse the direction after a short time. In fact, using for liquid sodium a potential with a weak long range tail as in solids Paskin and Rahman¹² found the velocity auto-correlation function to have several damped oscillations. Rahman has also interpreted his data in terms of a memory function $r(t)$, defined through the equation

$$\frac{d}{dt} \phi(t) + \int_0^t r(t-t') \phi(t') dt' = 0, \quad (5)$$

where

$$\phi(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle / \langle v^2 \rangle.$$

Figure 4 shows the form of $r(t)$ obtained for liquid argon. The interesting point here is that $r(t)$ shows an initial rapid decrease followed by a

weak and slowly varying tail. On the basis of Langevin's equation one should expect $\Gamma(t)$ to be essentially a $\delta(t)$ function. The long tail is responsible for some of the characteristic structure in the velocity auto-correlation function. I will later come back to a physical explanation of the characteristic features of $\Gamma(t)$.

Rahman has also investigated the possible collective motion in liquid argon. Figure 5 shows the time evolution of the space Fourier transform of the current-current correlation function $\langle \vec{j}(\vec{x}, t) \vec{j}(\infty) \rangle$, where $\vec{j}(\vec{x}, t) = \sum_i \vec{v}_i(t) \delta(\vec{x} - \vec{x}_i(t))$ is the microscopic current density. This current auto-correlation function tells us how a current, periodically varying in space, propagates. We know from hydrodynamics that for sufficiently long wavelengths the longitudinal waves propagate with a definite velocity and is damped due to frictional forces and heat diffusion. From Fig. 5 we see a clear tendency of having a damped periodic time dependence for smaller wave vectors but still far from the hydrodynamic limit. Also, we see that for wave vectors around the value for which the static structure factor has

a sharp maximum the motion is slowed down compared to the motion for neighboring wave vectors. This particular effect was first predicted from very simple theoretical arguments by De Gennes.¹³

Due to the very striking experimental results obtained especially in liquid aluminum it would be very desirable to have results from computer calculations for aluminum with a realistic interatomic potential. It seems that so far molecular dynamics has not supported the ideas of treating the atomic motions on some kind of crystalline model, which, however, seemed to be rather strongly supported by the experimental data on aluminum. Rahman intends to undertake such an investigation in order to shed some light on this question.

THEORY

As far as the collective aspects of the atomic motions are concerned, the present theoretical situation is quite unclear. One has been able to explain rather nicely many of the experimental results on the basis of quasi-crystalline models,^{14,15} introducing concepts like atomic displacements from

certain "equilibrium" positions and propagating phonons similar to those in solids. These approaches have, however, been very intuitive and have led to some conceptual difficulties which have not been removed. At present several interesting approaches are being tried, which are more closely related to first principles.^{2,16-19} A more proper discussion of self-motion is easier to pursue and for that reason the theoretical understanding of the self-motion is more complete than that of the collective motion. There is **no** time to review here the various theoretical approaches. I will confine myself to one of them, which seems promising to me and in which I have been involved myself.

Let us first consider the self-motion of the atoms and derive an equation for the velocity autocorrelation function $\phi(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle / \langle v^2 \rangle$.

Newton's equation for one of the atoms, indicated by an index zero, can be written in the form

$$\dot{\vec{v}}_0(t) = -\frac{1}{M} \int d\vec{x} \nabla V(\vec{x}_0(t) - \vec{x}) \rho(\vec{x}, t) d\vec{x}, \quad (6)$$

where $V(\vec{x})$ is the interatomic potential, M is the atomic mass and $\rho(x, t) = \sum_{i \neq 0} \delta(\vec{x} - \vec{x}_i(t))$ denotes

the microscopic density of the surrounding atoms.

We may now ask ourselves the following question.

Knowing the trajectory of the zeroth atom, how will the average density around this atom vary in time?

The following expression for the average density can be obtained from Liouville's equation:^{18,19}

$$\rho(\vec{x}, t) = n g(\vec{x} - \vec{x}_0(t)) - n \beta \int_0^t dt' \int d\vec{x}' G(\vec{x}t, \vec{x}'t' | \vec{x}_0(t)) g(\vec{x}' - \vec{x}_0(t')) \cdot \nabla V(\vec{x}' - \vec{x}_0(t')) \cdot \vec{v}_0(t') \quad (7)$$

Here $\beta = 1/k_B T$, n is the equilibrium particle density, $g(\vec{x})$ is the static pair-correlation function and $G(\vec{x}t, \vec{x}'t' | \vec{x}_0(t))$ is the density-density correlation function of the surrounding atoms with due consideration of the presence of the zeroth atom. Like the ordinary Van Hove correlation function it can be split up into a self part and a distinct part. It contains all necessary information of the transport properties of the medium surrounding the zeroth atom.

Inserting Eq. (7) into Eq. (6), multiplying with $\vec{v}(0)$ and averaging over all initial velocities we get an equation for $\phi(t)$. In an earlier version of the theory $G(\vec{x}t; \vec{x}'t' | x_0(t))$ was replaced by the self part $G_s(\vec{x}t, \vec{x}'t' | x_0(t))$ and this was furthermore approximated to have the form $\{\alpha(\vec{x} - \vec{x}_0(t)) G_s(\vec{x} - \vec{x}', t - t')\}$, $G_s(\vec{x}, t)$ being the ordinary Van Hove self correlation function. $\alpha(\vec{x} - \vec{x}_0(t))$ is a function which is zero whenever $\vec{x}$ falls inside the "hard core" radius of the zeroth atom. These approximations should have no significant effect on our conclusions. The equation to be fulfilled by $\phi(t)$ was brought in the form¹⁹

$$\frac{d}{dt} \phi(t) + \int_0^t \Gamma(t - t') \phi(t') dt' = 0, \quad (8)$$

where $\Gamma(t)$ depends explicitly on the interaction potential and the static pair-correlation function, which were assumed to be known. Figure 4 shows $\Gamma(t)$ for liquid argon (dotted curve) compared with the results obtained by Rahman from molecular dynamics (dashed curve). The rapid initial decrease in $\Gamma(t)$ arises in this treatment from the hard core

collisions between the atoms. The slowly varying tail in $\Gamma(t)$ is connected with the smooth attractive part of the potential as well as with the hard core part.

Assuming²⁰

$$G_S(x, t) = [\pi a(t)]^{-3/2} \exp[-x^2/a(t)] \quad (9)$$

with

$$a(t) = \frac{4}{M\beta} \int_0^t (t - t') \phi(t') dt', \quad (10)$$

an approximation commonly used in this context and proved to be quite good, we obtain an approximate expression for the Van Hove self-correlation function. If we had retained the full generalized Van Hove function in Eq. (7) we should have found that the equation for $G_S(\vec{x}, t)$ would also contain the distinct part $G_d(\vec{x}, t) = G(\vec{x}, t) - G_S(\vec{x}, t)$.

We may rewrite Eq. (7) in such a form that the current density of the zeroth atom, $\vec{j}_0(\vec{x}, t)$, appears explicitly. Multiplying the equation with $\vec{j}_0(0, 0)$ and averaging over all initial configurations we can

obtain an equation for how the density or the current of a surrounding atom is correlated to the current of the zeroth atom at a different time; that is the distinct part of the current-current correlation function, denoted by $C_{\alpha\beta}^{(d)}(\vec{x}, t)$. Approximations have to be made in order to proceed and in a certain approximation, for which it is no time to explain here, the following equation was obtained:²¹

$$\begin{aligned} \frac{\partial}{\partial t} C_{\alpha\beta}^{(d)}(\vec{x}, t) &= n\beta \sum_{r, \delta} \int dt' \int d\vec{x}' d\vec{x}'' C_{\alpha r}^{(d)}(\vec{x} - \vec{x}', \\ & t - t') g(\vec{x} - \vec{x}', \vec{x}'' - \vec{x}') \times \nabla V(\vec{x}' - \vec{x}'') C_{\delta\beta}^{(s)}(\vec{x}'', t') \\ & = n\beta \sum_{r, \delta} \int_0^t dt' \int d\vec{x}' d\vec{x}'' C_{\delta r}^{(s)}(\vec{x} - \vec{x}', \\ & t - t') g(\vec{x}' - \vec{x}'') \nabla_r \nabla_\delta V(\vec{x}' - \vec{x}'') C_{\delta\beta}^{(s)}(\vec{x}'', t') . \end{aligned} \quad (11)$$

Here

$g(\vec{x})$ = static pair-correlation function,

$g(\vec{x}, \vec{x}') =$ static triple-correlation function,

$V(x)$ = interatomic potential

$C_{\alpha\beta}^{(s)}(\vec{x}, t)$, $C_{\alpha\beta}^{(d)}(\vec{x}, t)$ = self and distinct parts of the current-current correlation function.

, etc. denote the Cartesian coordinates.

We see that the distinct correlation function is through Eq. (11) coupled to the self part. This work is under progress and some improvements have probably have to be made before the theory will work properly. It does however give in the present stage the correct short time behavior up to times of the order t^4 . Whether it gives the longer time behavior reasonably correct is not clear at present.

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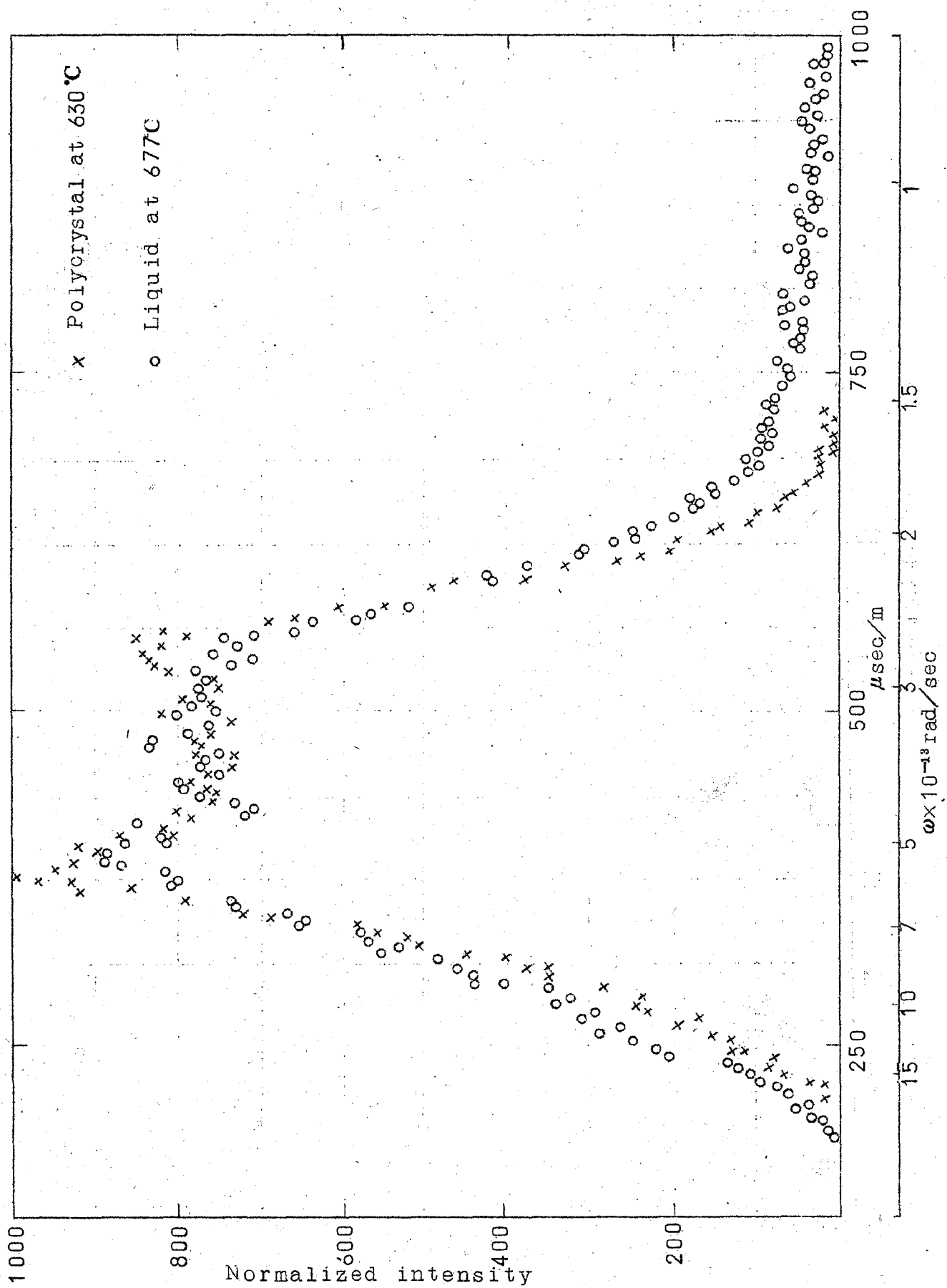
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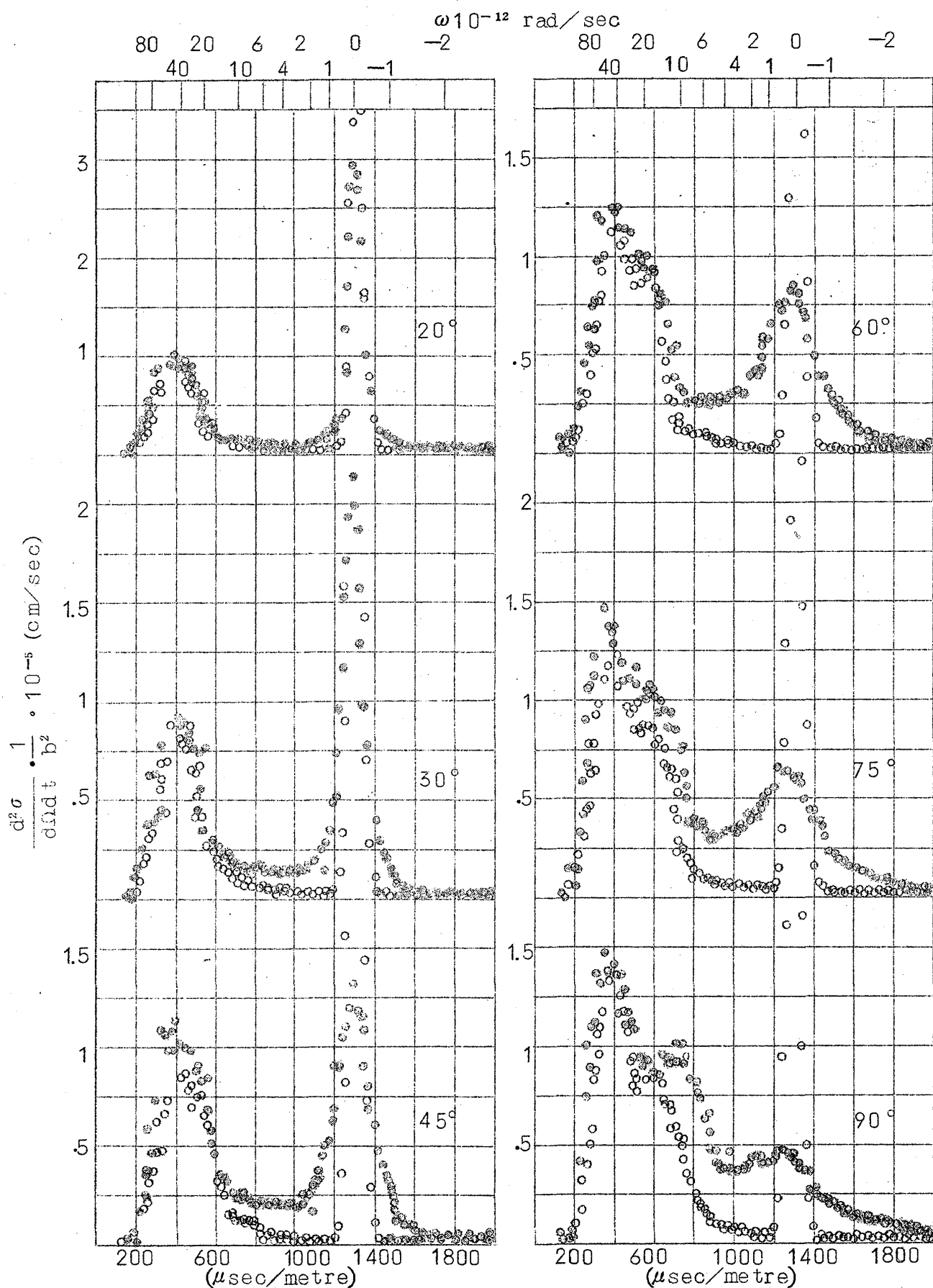
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FIGURE CAPTIONS

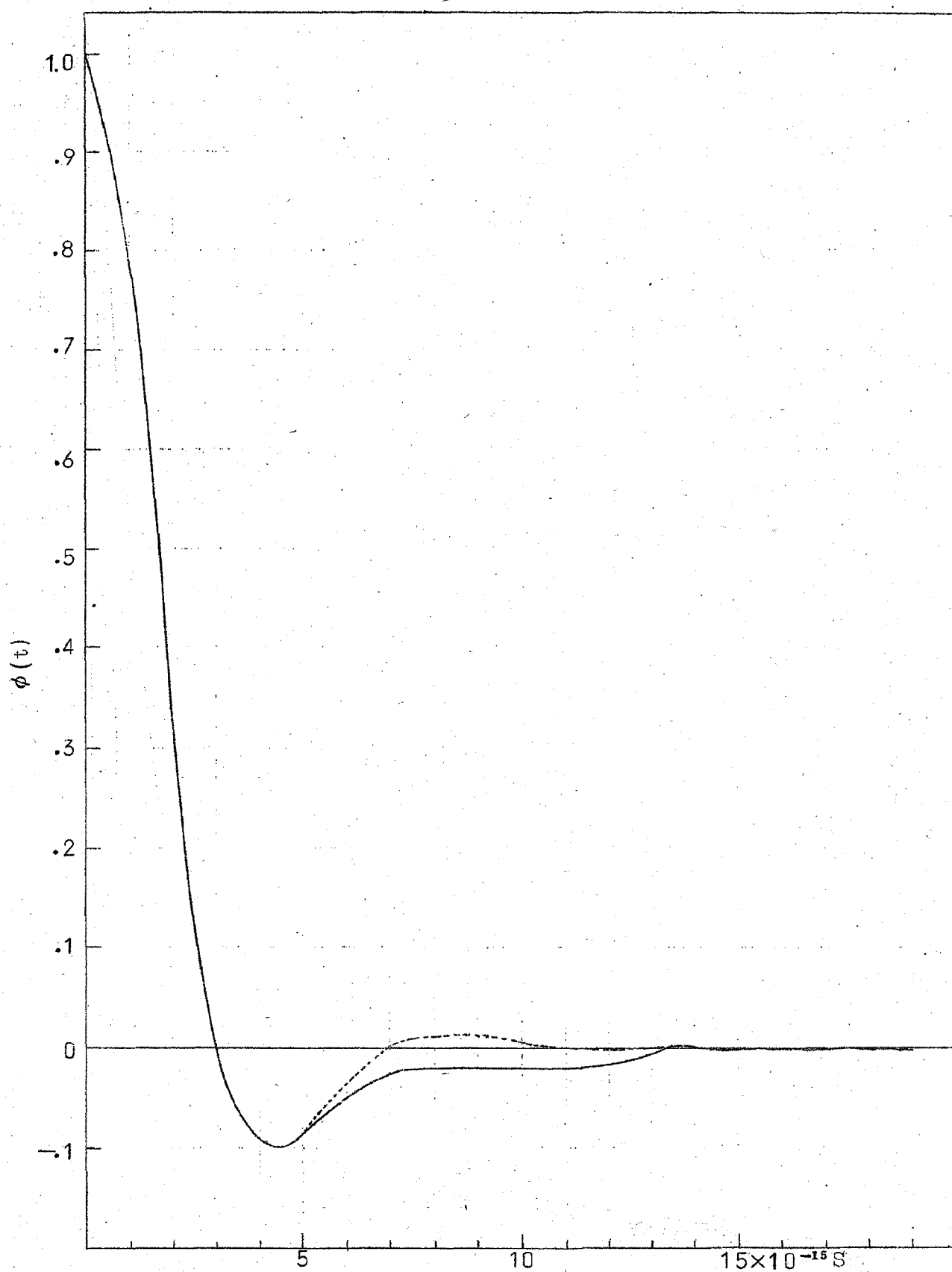
- Fig. 1. Coherently scattered neutron spectra from an aluminum polycrystal at 630°C and liquid aluminum at 677°C. The angle of observation was in both cases 60°. (After K. E. Larsson in "Thermal Neutron Scattering", Ch. 8, ed. by P. A. Egelstaff, Academic Press, New York, 1965)
- Fig. 2. Scattered neutron spectrum from solid (162°C) and liquid (205°C) lithium-7 for various scattering angles. (After S. J. Cocking, Proc. Int. Symposium on Inelastic Neutron Scattering, Copenhagen, 1968)
- Fig. 3. The velocity auto-correlation function $\phi(t)$ for liquid argon, obtained by Rahman (Ref. (10)).
- Fig. 4. The memory function $\Gamma(t)/\Gamma(0)$ for liquid argon obtained by Rahman from molecular dynamics (dashed curve) and from our theory (dotted curve). The full curve shows the results when neglecting certain relaxation effects.

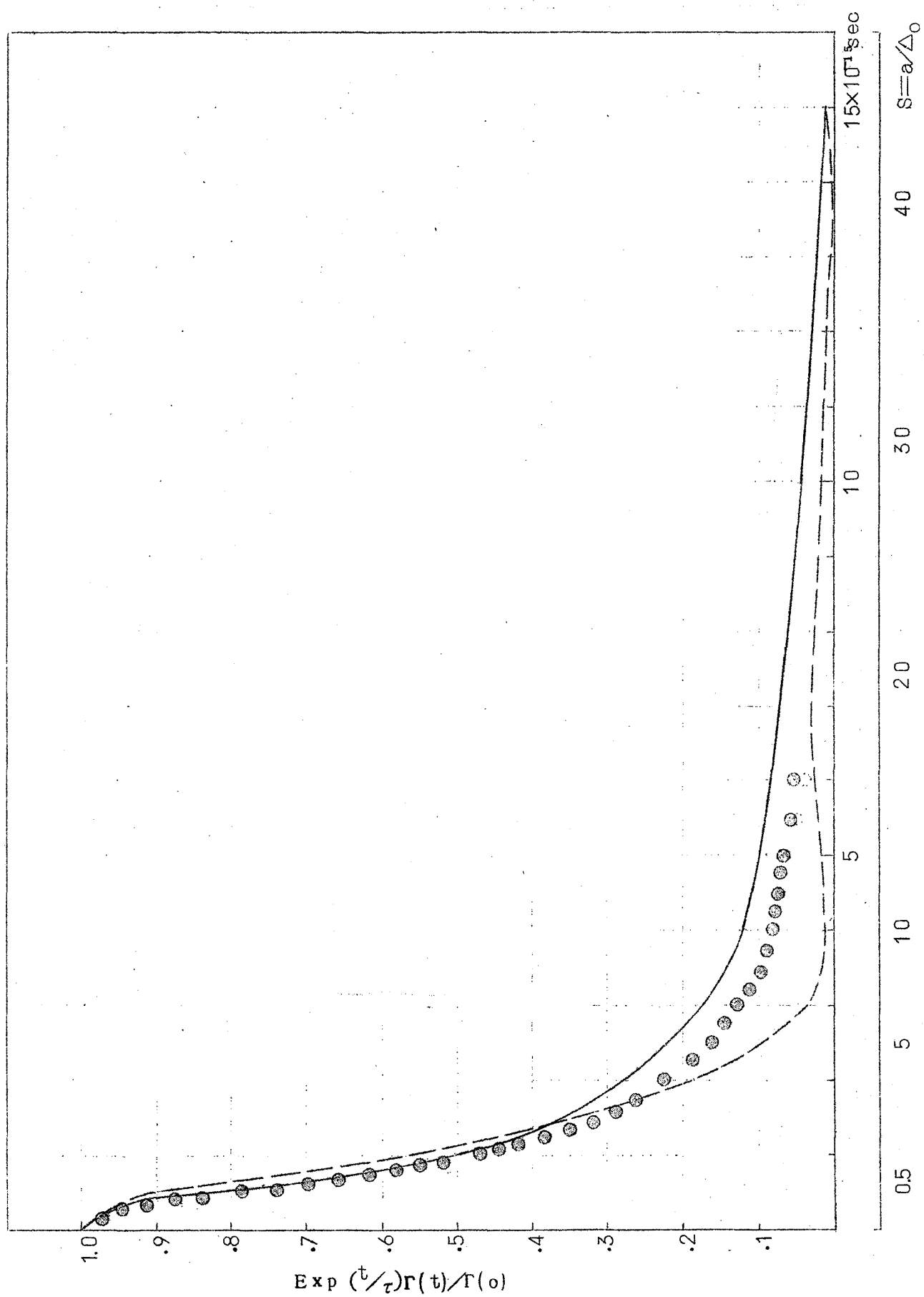
Fig. 5. Shows the time evolution of the space
Fourier-transformed longitudinal current-
current correlation function for liquid
argon for various values of the wave vector





SCATTERED NEUTRON SPECTRA FROM SOLID $\circ$ (162°C) AND
LIQUID $\circ$ (205°C) LITHIUM - 7





TIME IN 10^{-12} sec

