

## LANGEVIN EQUATION - APPLICATION TO LIQUID STATE DYNAMICS

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### 1. Introduction

Matter can exist either as gas, liquid or solid. Sometimes one also speaks of a fourth phase i.e. a 'plasma'. The dynamics of a phase depends strongly in which state it exists. For a gas with low density the atoms move freely with binary collisions where only two atoms are involved at a time. The collision provides a mechanism for the transfer of energy and momentum which brings the system towards equilibrium. The dynamics of such a system can be formally worked out using Boltzmann transport equation.

For solids, particularly crystalline ones, there is a well known description called as Born-von-Karman theory. In this case the atoms are localized and make small excursions from the equilibrium positions. This and the translational symmetry of the system facilitates the solution of the problems in terms of the phonons.

The interaction among the phonons is normally weak below about one-third of the melting temperature and can be treated in usual fashion using the perturbation theory [1,2]. Near melting temperature and for quantum crystals above description is not applicable and the method of self-consistent approximations is to be employed [3].

The problem of atomic motion in liquids is considered more complicated and still we do not have any fully satisfactory theory. In comparison with the crystals, the regular order is lost and for the liquids [4] the atomic displacements are no longer small. This, as well as the fact that liquid densities are not low, make the problem more difficult but interesting.

The main problems of the liquid state [4,5] are the thermodynamic properties - such as equation of state, specific heat; transport properties - diffusion and heat transport; phase transition - condensation and crystallization; space-time correlation function in fluids and collective excitations.

In the set of two lectures I shall deal with only two problems, (1) motion of a tagged particle in a fluid i.e. diffusion and (2) collective excitations using the generalized Langevin equation [6,7].

### 2. Basic Definitions and Relevant Correlation Functions

We consider a fluid in which there are  $n_0$  number of tagged particles (may be a radioisotope of the host fluid). These particles will diffuse through the host fluid as the time progresses and one observes the concentration  $n_0(\vec{r}, t)$  of tagged particles which is governed by Fick's law

$$\vec{J}_o(\vec{r}, t) = -D \vec{\nabla} n_o(\vec{r}, t) \quad (2.1)$$

where  $\vec{J}_o$  is the tagged particle current density and  $D$  is the self-diffusion coefficient. The concentration of the tagged particles is given by usual continuity equation

$$\frac{\partial n_o(\vec{r}, t)}{\partial t} + \vec{\nabla} \cdot \vec{J}_o(\vec{r}, t) = 0 \quad (2.2)$$

Combining eqs. (2.1) and (2.2) one finds that the tagged particle concentration  $n_o(\vec{r}, t)$  obeys the well known diffusion equation

$$\frac{\partial n_o(\vec{r}, t)}{\partial t} = D \nabla^2 n_o(\vec{r}, t) \quad (2.3)$$

We also introduce Van Hove self-correlation function  $G_s(\vec{r}, t)$  which describes the probability of finding the tagged particle at space time point  $\vec{r}, t$  if it was initially located at  $\vec{r}=0, t=0$ . It is clear that equation (2.3) should also be obeyed by  $G_s(\vec{r}, t)$  for times larger than the collision time (i.e.  $t \gg \tau_c$ ) :

$$\frac{\partial G_s(\vec{r}, t)}{\partial t} = D \nabla^2 G_s(\vec{r}, t) \quad (2.4)$$

with the boundary condition

$$G_s(\vec{r}, t) = \delta(\vec{r}) , \quad (2.5)$$

which asserts that there was a particle at the origin at  $t=0$ . From  $G_s(\vec{r}, t)$  we also have

$$\int G_s(\vec{r}, t) d\vec{r} = 1 \quad \text{for all } t \quad (2.6)$$

Equation (2.4) can easily be solved by introducing the Fourier transform

$$F_s(\vec{k}, t) = \int d\vec{r} \exp(-i\vec{k} \cdot \vec{r}) G_s(\vec{r}, t). \quad (2.7)$$

Noting that  $F_s(\vec{k}, t=0) = 1$ , one immediately obtains from eq.(2.4) that

$$F_s(\vec{k}, t) = \exp(-k^2 D |t|) . \quad (2.8)$$

The Fourier inversion of equation (2.7) gives

$$G_s(\vec{r}, t) = (4\pi D |t|)^{-3/2} \exp\left(-\frac{r^2}{4 D |t|}\right) . \quad (2.9)$$

Using equation (2.9) one easily finds that

$$\begin{aligned} \langle r^2(t) \rangle &= \int r^2 G_s(\vec{r}, t) d\vec{r} \\ &= 6 D t \end{aligned} \quad (2.10)$$

Thus the diffusion constant is a measure of the variation with the time of the mean square displacement of the particle in the fluid.

We now proceed further to relate the diffusion coefficient in terms of  $S_s(k, \omega)$  which is the Fourier-transform of  $F_s(k, t)$  i.e.

$$S_s(k, \omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) F_s(k, t) \quad (2.11)$$

Using eq. (2.8) and (2.11) we obtain

$$S_s(k, \omega) = \frac{2Dk^2}{\omega^2 + (k^2D)^2} \quad (2.12)$$

which is valid for low frequencies and long-wavelengths. Using equation (2.12) we obtain a general expression for the diffusion coefficient as

$$D = \lim_{\omega \rightarrow 0} \frac{\omega^2}{2} \lim_{k \rightarrow 0} \frac{S_s(k, \omega)}{k^2} \quad (2.13)$$

This equation is regarded as Kubo formula for the transport coefficient. It is clear that it relates macroscopic properties of the system to microscopic motion of the atoms in the fluid.

In order to make microscopic calculation of  $S_s(k, \omega)$  we introduce the dynamical variable

$$n_o(\vec{k}, t) = e^{ikx_1(t)} \quad (2.14)$$

which is the Fourier transform of the tagged particle density. In eq.(2.14) wavevector  $\vec{k}$  is along the direction of x-axis and  $x_1(t)$  is the x-component of the position of the tagged particle. In terms of tagged particle density,  $F_s(k, t)$  is defined as

$$F_s(k, t) = \langle n_o(\vec{k}, t) n_o(-\vec{k}, 0) \rangle \quad (2.15)$$

$S_s(k, \omega)$  is then obtained by equation (2.11). Differentiating eq.(2.15) twice w.r. to  $t$  we obtain

$$\frac{\partial^2 F_s(k, t)}{\partial t^2} = -k^2 \langle v_x(t) v_x(0) e^{ik(x_1(t) - x_1(0))} \rangle \quad (2.16)$$

Introducing the velocity autocorrelation function (VAF) as

$$Z(t) = \langle v_x(t) v_x(0) \rangle \quad (2.17)$$

we obtain from (2.16)

$$Z(t) = \lim_{k \rightarrow 0} \left[ -\frac{1}{k^2} \frac{\partial^2 F_s(k, t)}{\partial t^2} \right] \quad (2.18)$$

Fourier-transform of this equation gives

$$Z(\omega) = \lim_{k \rightarrow 0} \frac{\omega^2 S_s(k, \omega)}{k^2} \quad (2.19)$$

where  $Z(\omega)$  is called the frequency spectrum of the VAF. Combining eq.(2.19) with (2.13) we obtain a relation for the diffusion coefficient in terms the VAF as

$$D = \int_0^{\infty} dt \langle v_x(t) v_x(0) \rangle = \int_0^{\infty} dt Z(t) \quad (2.20)$$

We now define the other dynamical variables of our interest such as number density, longitudinal and transverse current density fluctuations as

$$n(\vec{k}, t) = n^{-1/2} \sum_i \exp(ikx_i(t)) \quad (2.21)$$

$$J_\ell(\vec{k}, t) = n^{-1/2} \sum_i v_{ix}(t) \exp(ikx_i(t)) \quad (2.22)$$

$$J_t(\vec{k}, t) = n^{-1/2} \sum_i v_{iy}(t) \exp(ikx_i(t)) \quad (2.23)$$

respectively. Here  $x_i(t)$ ,  $v_{ix}(t)$ ,  $v_{iy}(t)$  are respectively the x-component of the position, x- and y-components of the velocity of the  $i^{\text{th}}$  particle. As noted earlier wave-vector  $k$  is taken along x-axis. We define the corresponding correlation functions as  $F(k, t)$ ,  $C_\ell(k, t)$  and  $C_t(k, t)$  similar to eq.(2.15). Their respective Fourier transforms viz.  $S(k, \omega)$ ,  $C_\ell(k, \omega)$  and  $C_t(k, \omega)$ , which give the fluctuation spectra are defined in the similar fashion to that of  $S_s(k, \omega)$  from (2.11). It is important here to give the relation between the longitudinal current correlation function  $C_\ell(k, \omega)$  with the dynamic structure function  $S(k, \omega)$  as

$$C_\ell(k, \omega) = \frac{\omega^2}{k^2} S(k, \omega) \quad (2.24)$$

which is obtained by taking the Fourier transform of the second derivative of  $F(k, t)$ . In the free particle limit the expressions for  $S(k, \omega)$  ( $C_\ell(k, \omega)$ ) and  $C_t(k, \omega)$  are quite simple and are given by

$$S^f(k, \omega) = \sqrt{\frac{2\pi m \beta}{k^2}} \exp\left(-\frac{m \beta \omega^2}{2k^2}\right) \quad (2.25)$$

$$C_t^f(k, \omega) = \sqrt{\frac{2\pi}{k^2 m \beta}} \exp\left(-\frac{m \beta \omega^2}{2k^2}\right) \quad (2.26)$$

### Sum Rules

Sum rules, commonly known as frequency moment sum rules are exactly calculable properties of the system and are defined as the short-time expansion of the time-dependent correlation function. The knowledge of these rules is very important to check the internal consistency in a theory or experiment. We describe below some low-order sum rules for the longitudinal current correlation function  $C_\ell(k, \omega)$  (hence of  $S(k, \omega)$ ) and of the transverse current correlation function  $C_t(k, \omega)$  for their use in these lectures.

We define the  $2m^{\text{th}}$  moment of  $C_\ell(k, \omega)$  as

$$\langle \omega_{\ell, t}^{2m} \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \omega^{2m} C_{\ell, t}(k, \omega) / C_{\ell, t}(k, t=0)$$

$$= (i)^{2m} \frac{d^{2m} C_{\ell,t}(k,t)}{dt^{2m}} \Big|_{t=0} / C_{\ell,t}(k,t=0) \quad (2.27)$$

In terms of these moments, the short-time expansion of the correlation functions  $C_{\ell,t}(k,t)$  are defined as

$$C_{\ell,t}(k,t) = 1 + \sum_{m=1}^{\infty} (i)^{2m} \frac{d^{2m} C_{\ell,t}(k,t)}{dt^{2m}} \Big|_{t=0} C_{\ell,t}^{-1}(k,t=0) \frac{t^{2m}}{2m!} \quad (2.28)$$

It is easy to note that  $C_{\ell,t}(k,t=0) = \frac{1}{m\beta}$ . Starting from eqs. (2.22) and (2.23), making use of eq. (2.15) for definitions of  $C_{\ell,t}(k,t)$  it is straightforward to derive the expressions for the low order moments (upto  $m=2$ ) of the spectral functions of the current correlations. These results are known [8-10] but for the sake of completeness and their extensive use in these lectures, these results are quoted here

$$\langle \omega_{\ell}^0 \rangle = \langle \omega_t^0 \rangle = \frac{k^2}{m\beta} = \omega_0^2 \quad (2.29a)$$

$$\langle \omega_{\ell}^2 \rangle = 3\omega_0^2 + \frac{n}{2m} \int d\vec{r} g(\vec{r}) (1 - \cos \vec{k} \cdot \vec{r}) [(\hat{k} \cdot \vec{\nabla})^2] \phi(r) \quad (2.29b)$$

$$\langle \omega_t^2 \rangle = \omega_0^2 + \frac{n}{m} \int d\vec{r} g(r) (1 - \cos \vec{k} \cdot \vec{r}) [\nabla^2 - (\hat{k} \cdot \nabla)^2] \phi(r) \quad (2.29c)$$

$$\begin{aligned} \langle \omega_{\ell}^4 \rangle = & 15 \omega_0^2 + \frac{n}{\beta m^2} \int d\vec{r} g(r) [15 (\vec{k} \cdot \nabla)^2 \phi(r) + \\ & 6k \sin(\vec{k} \cdot \vec{r}) (\hat{k} \cdot \nabla)^3 \phi(r) + 2\beta (1 - \cos \vec{k} \cdot \vec{r}) (\hat{k} \cdot \nabla \nabla \phi(r))^2] \\ & + \frac{n^2}{m} \iint d\vec{r} d\vec{r}' g_3(\vec{r}, \vec{r}') \{ 1 - 2 \cos \vec{k} \cdot \vec{r} + \cos[\vec{k} \cdot (\vec{r} - \vec{r}')] \} \times \\ & (\hat{k} \cdot \nabla) (\hat{k} \cdot \nabla') (\nabla \cdot \nabla') \phi(r) \phi(r') \end{aligned} \quad (2.29d)$$

$$\begin{aligned} \langle \omega_t^4 \rangle = & 3\omega_0^2 + \frac{3n}{\beta m^2} \int d\vec{r} g(r) [k^2 \nabla^2 \phi(r) - \frac{2}{3} (\vec{k} \cdot \nabla)^2 \phi(r)] \\ & + \sin(\vec{k} \cdot \vec{r}) [\nabla^2 - (\hat{k} \cdot \nabla)^2] (\hat{k} \cdot \nabla) \phi(r) \\ & + \frac{1}{3\beta} (1 - \cos \vec{k} \cdot \vec{r}) [(\nabla \nabla \phi(r))^2 - (\hat{k} \cdot \nabla \nabla \phi(r))^2] + \\ & \frac{n^2}{2m^2} \iint d\vec{r} d\vec{r}' g_3(\vec{r}, \vec{r}') \{ 1 + \cos[\vec{k} \cdot (\vec{r} - \vec{r}')] - 2 \cos \vec{k} \cdot \vec{r} \} \times \\ & \{ (\nabla \cdot \nabla')^2 - (\hat{k} \cdot \nabla) (\hat{k} \cdot \nabla') (\nabla \cdot \nabla') \} \phi(r) \phi(r') \end{aligned} \quad (2.29e)$$

In eqs.(2.29)  $g(r)$ ,  $g(\vec{r}, \vec{r}')$  are respectively the pair correlation and static triplet correlation functions and  $\phi(r)$  is the potential. Results for the moments for  $m = 3$  have been also derived by Bansal and Pathak, for these we refer the original reference [11].

Equations (2.29b) and (2.29c) are extremely simple to be evaluated for a given potential  $g(r)$ . These are plotted for liquid Ar and Rb along with their structure functions in Fig.1. The results shown in Fig.1 for liquid Ar and Rb are from molecular dynamics (MD) studies of Levesque et al and Rahman [12,13], respectively. The

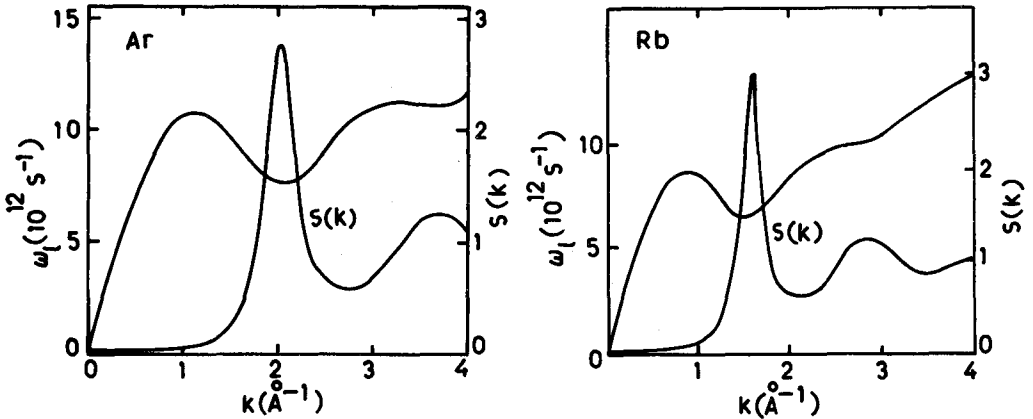


Fig. 1 The characteristic frequency  $\omega_l$ [eq.(2.29b)] vs  $k$  for liquid Ar and liquid Rb obtained from the molecular dynamics (MD) values. The structure factor  $S(k)$  is also plotted for completeness.

evaluation of eqs. (2.29d) and (2.29e) was not possible till recently due to appearance of multi-dimensional integrals. These integrals were first simplified by Bansal and Pathak [14] and evaluated using the superposition approximation (SA) for  $g_3(\vec{r}, \vec{r}')$ . Later their exact evaluation using MD method [15-16] justified the use of SA as far as the calculation of the frequency moments is concerned. These results for liquid Rb and Ar alongwith MD results are plotted in Figs. 2(a) and 2(b). Details of these are referred to original references [12,16].

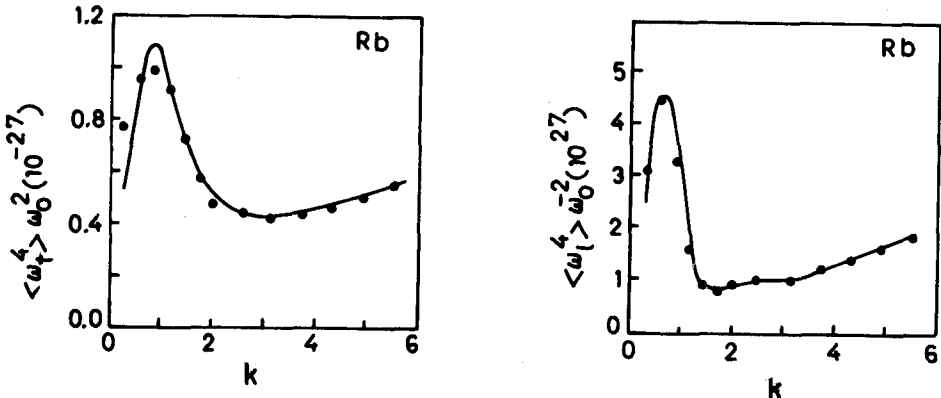
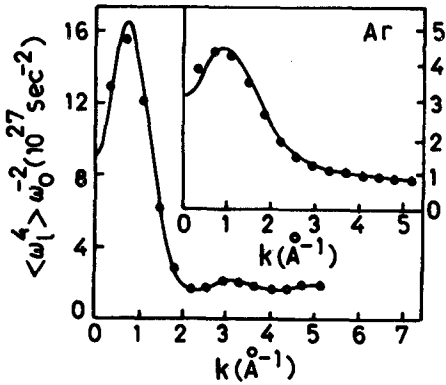


Fig. 2a The wave-number dependence of the fourth frequency moments of the longitudinal and transverse current correlation functions for liquid Rb, superposition approximation - solid curve, solid circles - MD [15].



These moments are also calculated for 3D and 2D Coulomb systems and for these and their applications to the dynamics of Coulomb system we refer to Singh et al [17] and, Agarwal and Pathak [18].

Fig. 2b Same as in 2a for liquid Ar, MD results from [16].

3. Langevin Equation

The basic ideas for the discussion of the transport processes in liquids are often taken from the theory of Brownian motion, which describes the problem of self-diffusion. It starts with a simple Langevin equation of a Brownian particle

$$m \frac{d\vec{v}(t)}{dt} + \alpha \vec{v}(t) = \vec{F}(t) \tag{3.1}$$

where  $\alpha \vec{v}(t)$  represents usual viscous drag on a particle of mass  $m$  moving with velocity  $\vec{v}(t)$ .  $\vec{F}(t)$  is the randomly fluctuating force of average value zero, representing the effect of molecular impacts on the particle. This is also responsible for the viscous drag coefficient  $\alpha$ . The random force is also uncorrelated with the initial velocity i.e.

$$\langle \vec{F}(t) \cdot \vec{v}(0) \rangle = 0 \tag{3.2}$$

The solution of eq.(3.1) has been discussed in detail by Hansen and McDonald [5], here we simply note the Einstein's relation for the diffusion coefficient in terms of the friction coefficient :

$$D = \frac{1}{\beta \alpha} \tag{3.3}$$

A direct estimate of  $\alpha$  can also be made from the Stoke's equation [5].

From eq.(3.1) we can easily obtain the expression for the VAF of the Brownian particle as

$$\begin{aligned} Z(t) &= \frac{1}{3} \langle \vec{v}(t) \cdot \vec{v}(0) \rangle \\ &= \frac{1}{m\beta} \exp \left( - \frac{\alpha t}{m} \right) \end{aligned} \tag{3.4}$$

and the frequency spectrum of the VAF is given by

$$Z(\omega) = \frac{1}{D m^2 \beta^2} \cdot \frac{2}{\omega^2 + (1/m\beta D)^2} \tag{3.5}$$

we shall see that this frequency spectrum is far from that one gets for a typical liquid. The exponential decay of the VAF is also neither applicable for short-times nor for long-times. The former can be easily ascertained from the exact knowledge of the short-time expansion of the correlation functions (2.28).

When the size of the Brownian particle becomes comparable with those of its neighbours, the Markovian approximation of the theory which sets the viscous drag force on a particle at a given time proportional to the velocity of the particle only at that time is no longer valid. Because it implies that the motion of the particle adjusts itself instantaneously to the changes in the surrounding medium. It is intuitively correct to assume that the viscous drag acting on a particle at a given time depends upon the previous history of the particle. In other words, we must associate memory effects for the motion of the particle by introducing the time-dependent frictional force as  $\alpha(t-t')$ . This leads to non-Markovian generalization of the Langevin equation written as

$$m \frac{d\vec{v}(t)}{dt} + \int_0^t \alpha(t-t') \vec{v}(t') dt' = f(t) \quad (3.6)$$

A more systematic generalization of eq.(3.6) has been given by Zwanzig and Mori using the projection operator technique. In fact their main contribution had been to provide a statistical mechanical expression for the random force. This, we briefly describe before we use them in the lectures.

In Zwanzig-Mori theory [6-7] we consider a linear vector space spanned by a set of dynamical variable  $A(\vec{k}, t)$  and define the scalar product in this space as

$$(A|B) = \beta \langle A^* B \rangle \quad (3.7)$$

The time evolution of the dynamical variable is given by the Liouville equation which has the formal solution

$$\exp(i\mathcal{L}t) A = A(t) \quad (3.8)$$

where  $\mathcal{L}$  is the Liouville operator and  $A$  is the initial value. It is convenient to define the Kubo relaxation function  $\phi_A(k, t)$  as

$$\phi_A(k, t) = \beta \langle A(\vec{k}, t) A^*(\vec{k}, 0) \rangle \quad (3.9)$$

It is also useful to define the response function associated with the dynamical variable  $A(\vec{k}, t)$  as

$$\chi(k, t) = -\theta(t) \frac{d\phi_A(k, t)}{dt} \quad (3.10)$$

Defining the Fourier-Laplace transform (FLT) of  $\phi_A(k, t)$  as

$$\tilde{\phi}_A(k, \omega) = i \int_0^{\infty} \exp(i\omega t) \phi_A(k, t) dt \quad (3.11)$$



where  $\omega$  is in the upper-half plane, one obtains

$$\chi_A(k, \omega) = \phi_A(k, t=0) + \omega \tilde{\phi}_A(k, \omega) \quad (3.12)$$

where  $\chi_A(k, \omega)$  is the Fourier transform of  $\chi_A(k, t)$ . In order to get the generalized Langevin equation it is convenient to define a projection operator [19].

$$P = |A\rangle \langle A| A^* \rangle^{-1} \langle A| \quad (3.13)$$

in the linear vector space spanned by dynamical variable  $A$ . The projection operator satisfies  $P^2 = P$  as it should. If  $Q$  denotes the projector orthogonal to  $P$  (i.e.  $P+Q=1$ ,  $PQ = QP = 0$ ,  $Q^2=Q$ ) and the resolvent is defined as  $\tilde{R}(\omega) = (\mathcal{L} - \omega)^{-1}$ , we have an identity [20]

$$[P \mathcal{L} P - \omega - P \mathcal{L} Q (Q \mathcal{L} Q - \omega)^{-1} Q \mathcal{L} P] PRP = P \quad (3.14)$$

The relaxation function defined through (3.9) can be seen to have FLT

$$\tilde{\phi}_A(k, \omega) = \beta(A(k) | (\mathcal{L} - \omega)^{-1} | A(k)) . \quad (3.15)$$

Operating the identity (3.14) on  $|A(k)\rangle$  and multiplying by  $\langle A(k)|$  from left we obtain

$$\tilde{\phi}_A(k, \omega) = \frac{\beta(A(k) | A(k))}{\Omega_A(k) - \omega - \tilde{M}_A(k, \omega)} \quad (3.16)$$

where

$$\Omega_A(k) = (A | \mathcal{L} | A) (A(k) | A(k))^{-1}$$

and

$$\tilde{M}_A(k, \omega) = - (A(k) | A(k))^{-1} (Q \mathcal{L} A(k) | (Q \mathcal{L} Q - \omega)^{-1} | Q \mathcal{L} A(k)) . \quad (3.17)$$

$\Omega_A(k)$  is zero in this case due to time reversal property of the variable  $A(k)$ . Thus we have

$$\tilde{\phi}_A(k, \omega) = - \frac{\phi(k, t=0)}{\omega + \tilde{M}_A(k, \omega)} \quad (3.18)$$

It is noted that  $\tilde{M}_A(k, \omega)$  is again a resolvent matrix element of a reduced Liouville operator  $\mathcal{L}_1 = Q \mathcal{L} Q$ . Therefore, an identity analogous to (3.15) can be used to generate the equation for  $\tilde{M}_A(k, \omega)$ . This procedure leads to Mori's continued fraction representation [7] for the relaxation kernel  $\tilde{\phi}(k, \omega)$ .

#### 4. Application to Liquid Dynamics

(a) Velocity Autocorrelation Function :

If we take the dynamical variable  $A(\vec{k}, t)$  to be tagged particle density  $n_0(\vec{k}, t)$  the relaxation kernel  $\tilde{\phi}_S(k, \omega)$ , which is related to the self-correlation function  $S_S(k, \omega)$  is obtained from eq.(3.18) as

$$\tilde{\Phi}_S(k, \omega) = - \frac{\Phi_S(k, t=0)}{\omega + \tilde{M}_S(k, \omega)} \quad (4.1)$$

here  $\Phi_S(k, t)$  is defined as (instead of eq. (3.9))

$$\Phi_S(k, t) = F_S(k, t) \quad , \quad (4.2)$$

thereby  $\Phi_S(k, t=0) = 1$ . We write eq.(4.1) for convenience as below

$$\tilde{\Phi}_S(k, \omega) = \frac{-1}{\omega + k^2 \tilde{D}(k, \omega)} \quad (4.3)$$

where

$$\begin{aligned} k^2 \tilde{D}(k, \omega) &= \tilde{M}_S(k, \omega) \\ &= - (\mathcal{Q} \mathcal{L} n_0(k) | (\mathcal{Q} \mathcal{L} \mathcal{Q} - \omega)^{-1} | \mathcal{Q} \mathcal{L} n_0(k)) \end{aligned} \quad (4.4)$$

which follows from eq.(3.17). From the definitions of  $S_S(k, \omega)$  and  $\tilde{\Phi}(k, \omega)$  [eqs. (2.11) and (3.11)] it can be seen that

$$\Phi''(k, \omega) = S_S(k, \omega)/2 \quad (4.5)$$

where  $\Phi''(k, \omega)$  is the imaginary part of  $\tilde{\Phi}(k, \omega + i0)$ . Using equation (4.5) in (2.19) it can be found that the Fourier transform of the VAF is given by

$$Z(\omega) = 2 \lim_{k \rightarrow 0} \frac{\omega^2}{k^2} \Phi''(k, \omega) \quad (4.6)$$

from which it immediately follows that the self-diffusion constant  $D$  is obtained as

$$D = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{\omega^2}{k^2} \Phi''(k, \omega) \quad (4.7)$$

From eq.(4.3) one easily calculates

$$\Phi''(k, \omega) = \frac{k^2}{\omega^2} D''(0, \omega) \quad (4.8)$$

Combining eqs.(4.6) and (4.8) we can calculate the frequency spectrum of the normalized VAF  $f(\omega)$  which is obtained as

$$f(\omega) = m \beta Z(\omega) = 2m \beta D''(0, \omega) \quad (4.9)$$

Now our job is to calculate first stage relaxation kernel given by eq.(4.4). Several phenomenological forms for the relaxation kernels have been used in the past for which we refer Copley and Ovesey [21] and latest book by Boon and Yip [22]. But we do this by calculating the relaxation kernel in microscopic mode-coupling approximation. In order to approximate the relaxation kernel given by (4.4) it is convenient to express it as

$$k^2 D(k, t) = (\mathcal{Q} \mathcal{L} n_0(k) | e^{-i\mathcal{Q} \mathcal{L} \mathcal{Q} t} | \mathcal{Q} \mathcal{L} n_0(k)). \quad (4.10)$$

It is easy to note that

$$D(k, t=0) = \frac{1}{m\beta} \quad (4.11)$$

Introducing two mode states as intermediate states in the evaluation of the matrix element of the reduced Liouville operator, using the factorization approximation and the fact that positions and velocities are classically independent, we get

$$k^2 D(k, t) = \sum_{\vec{p}} k_{\alpha} k_{\beta} F_S(p, t) C_{\alpha\beta}(\vec{k} - \vec{p}, t) \quad (4.12)$$

where  $C_{\alpha\beta}(p, t)$  is the current correlation function and is given by

$$C_{\alpha\beta}(p, t) = \frac{p_{\alpha} p_{\beta}}{p^2} C_{\ell}(p, t) + \left[ \delta_{\alpha\beta} - \frac{p_{\alpha} p_{\beta}}{p^2} \right] C_t(p, t) \quad (4.13)$$

In eq.(4.13)  $\alpha$  and  $\beta$  are cartesian coordinates.

We now substitute  $C_{\alpha\beta}(p, t)$  in eq.(4.12) and after a little bit of manipulation we get

$$D(k, t) = \frac{1}{3} \sum_p F_S(k-p, t) \left[ C_{\ell}(p, t) + 2C_t(p, t) \right] \quad (4.14)$$

which in limit  $k \rightarrow 0$  can be written as

$$D(k=0, t) = \frac{1}{3} \sum_p F_S(p, t) \left[ C_{\ell}(p, t) + 2C_t(p, t) \right] \quad (4.15)$$

The dominant contributions to the large-time behaviour of the VAF can be obtained using the asymptotic behaviour

$$F_S(p, t) \sim \exp(-p^2 D |t|)$$

and

$$C_t(p, t) \sim \frac{1}{m\beta} \exp(-p^2 m n \eta |t|)$$

and replacing the summation over  $p$  by integration, we obtain the normalized VAF  $f(t)$  as

$$f(t) = \frac{1}{3\pi^2} \int_0^{\infty} p^2 dp e^{-p^2(mn\eta+D)|t|}$$

which reduces to

$$f(t) = 1/12 \pi^{3/2} (mn\eta + D)^{3/2} |t|^{3/2} \quad (4.16)$$

Therefore, it is clear that the mode coupling theory gives the correct long-time behaviour of the VAF.

It is noted that eq.(4.15) no more gives the correct value of  $D(\vec{k}, t)$  at  $t=0$ . This is because of mode coupling approximation. In order to get the correct initial value of  $D(\vec{k}, t)$  we multiply right hand side of eq.(4.15) by  $p_{\max}^3 / 6\pi^2 n$ , where  $p_{\max}$  is some cutoff wave-number. Taking the imaginary part of FLT of  $D(\vec{k}, t)$  from eq.(4.14), we obtain the expression for  $D''(k, \omega)$  in limit  $k \rightarrow 0$  as

$$D''(\omega) = \frac{1}{4\pi p_{\max}^3} \int_0^{p_{\max}} dp p^2 \int_{-\infty}^{\infty} d\omega' s_s(p, \omega') [C_\ell(p, \omega - \omega') + 2 C_t(p, \omega - \omega')] \quad (4.17)$$

Using above expression we obtain the frequency spectrum of the normalized VAF from (4.9). For  $C_\ell(k, \omega)$  and  $C_t(k, \omega)$  mode coupling equations can also be developed and solved self-consistently [20]. However, in the present work we use models for  $C_t(k, \omega)$  and  $C_\ell(k, \omega)$  which give results closer to experimental values. For  $F_s(k, t)$  we use the gaussian approximation. More details are given by Dubey et al [23]. In these calculations a quite good agreement has been achieved as shown in Fig. (3).

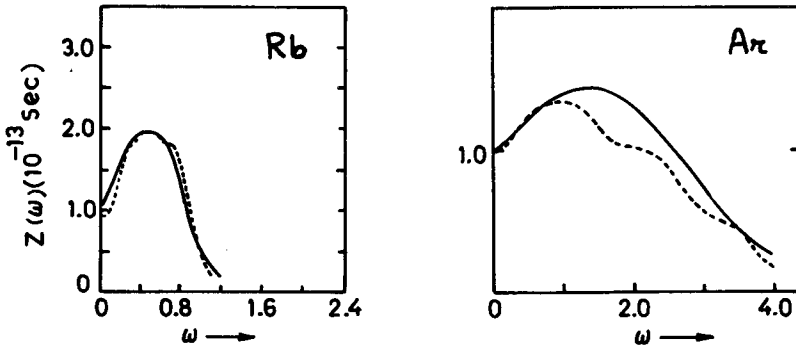


Fig. 3 Frequency spectrum  $Z(\omega)$  vs  $\omega$  for Rb and Ar, broken curves - MD results, continuous curves - mode coupling calculations [23,20].

We also present, in Fig.4, the molecular dynamics results for  $Z(t)$  for liquid Ar and Rb from [12] and [13] respectively. For details original references are suggested.

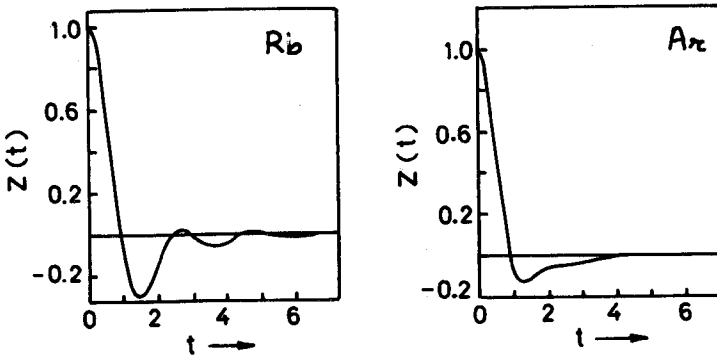


Fig. 4 MD results for Rb and Ar [13,12] for variation of the velocity autocorrelation function  $Z(t)$  with time.

In order to see more distinct features of the VAF we also present them for 3D and 2D classical Coulomb liquid in Fig. (5). The details of these calculations are given in original references [24,25] .

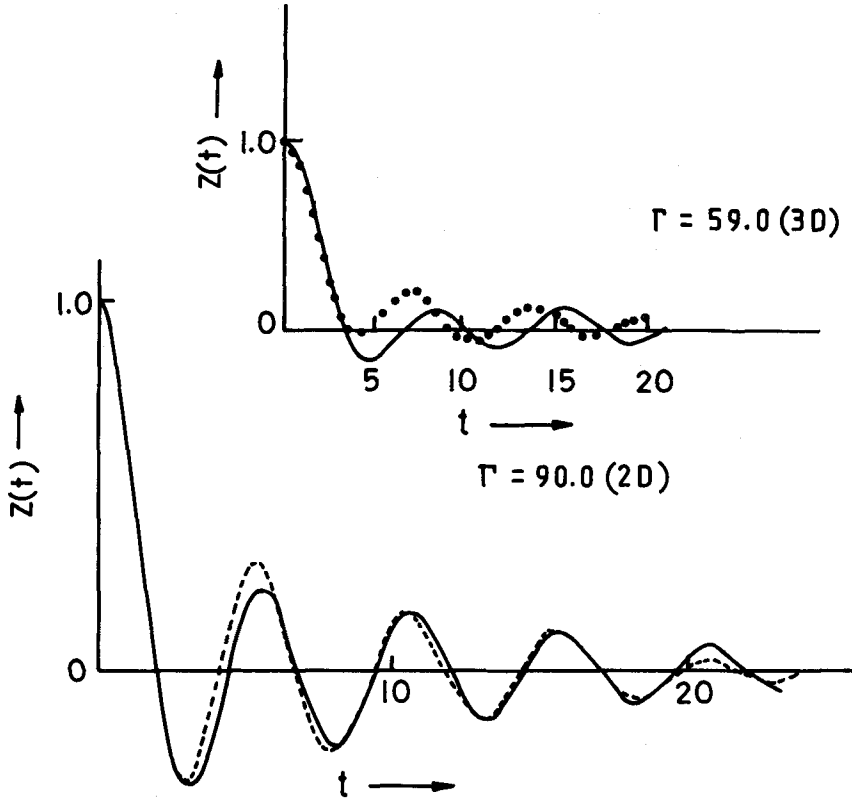


Fig. 5  $Z(t)$  for three-dimensional and two-dimensional classical Coulomb liquids, full line curves - theoretical [24,25] , dots or broken curve - MD results.

(b) Collective Excitations :

If the dynamical variable is taken as density fluctuation operator (defined by eq. (2.21)), the relaxation kernel  $\tilde{\Phi}(k, \omega)$  is obtained as

$$\tilde{\Phi}(k, \omega) = \frac{-\Phi(k, t=0)}{\omega + \tilde{M}_1(k, \omega)} \tag{4.18}$$

In above equation  $\Phi(k, t=0) = \beta F(k, t=0) = \beta S(k)$ , where  $S(k)$  is the static structure function and  $\tilde{M}_1(k, \omega)$  is the first stage memory kernel.  $\tilde{M}_1(k, \omega)$  is given as

$$\tilde{M}_1(k, \omega) = - (n(k) | n(k))^{-1} (Q \mathcal{L} n(k) | (\mathcal{L}_1 - \omega)^{-1} | Q \mathcal{L} n(k)) \tag{4.19}$$

Similar to (4.18) one write the expression for  $\tilde{M}_1(k, \omega)$  and obtains

$$\tilde{M}_1(k, \omega) = \frac{\delta_1}{\omega + \tilde{M}_2(k, \omega)} \quad (4.20)$$

and so on. In eq. (4.20)

$$\tilde{M}_2(k, \omega) = (\mathcal{Q} \mathcal{L} n(k) | \mathcal{Q} \mathcal{L} n(k))^{-1} (\mathcal{Q} \mathcal{L}^2 n(k) | (\mathcal{Q}_1 \mathcal{L} \mathcal{Q}_1 - \omega)^{-1} | \mathcal{Q} \mathcal{L}^2 n(k)) , \quad (4.21)$$

where  $\mathcal{Q}_1$  is orthogonal to  $n(k)$  and  $\mathcal{Q} \mathcal{L} n(k)$  and we have used the relations  $\mathcal{Q}_1 \mathcal{Q} \mathcal{L} \mathcal{Q} \mathcal{L} n(k) = \mathcal{Q} \mathcal{L}^2 n(k)$  and  $\mathcal{Q}_1 \mathcal{L} \mathcal{Q}_1 = \mathcal{Q}_1 \mathcal{L} \mathcal{Q}_1$ . The coefficients  $\delta_k$  are exactly calculable quantities and are obtained in terms of sum rules [eq.(2.29)]. We record first two of them here

$$\delta_1 = \frac{\omega_0^2}{S(k)} = \Omega_0^2 \quad (4.22a)$$

$$\delta_2 = \langle \omega_\ell^2 \rangle - \Omega_0^2 \quad (4.22b)$$

Combining eqs. (3.12), (4.18) and (4.20) we obtain the density response function as

$$\chi(k, \omega) = \frac{-\beta S(k) \Omega_0^2}{\omega^2 - \Omega_0^2 + \omega \tilde{M}_2(k, \omega)} \quad (4.23)$$

The dynamical structure function  $S(k, \omega)$  is obtained in terms of the imaginary part of  $\chi(k, \omega)$  using eqs. (3.11) and (3.12) and the definition of  $S(k, \omega)$ . It is given by

$$S(k, \omega) = \frac{2}{\beta \omega} \chi''(k, \omega) \quad (4.24)$$

$C_\ell(k, \omega)$  can also be calculated knowing  $S(k, \omega)$  and using the relation (2.24).

In order to proceed further one has to make approximation for the relaxation kernel  $\tilde{M}_2(k, \omega)$ . The various phenomenological approximations for  $M_2(k, t)$  i.e. exponential, gaussian and others have been made [26,27,21,22]. The parameters in these are fixed through sum rules. For the dynamics of liquid Ar essentially a single relaxation time kernel has been applied quite successfully, which is due to Pathak and Singwi [28]. In this approximation one replaces  $M(k, \omega)$  by its renormalized form as [18,29]

$$\tilde{M}_r(k, \omega) = -\omega + \frac{1}{\omega} \left[ \Omega_0^2 \text{ or } - \frac{\beta S(k) \Omega_0^2}{\tilde{\chi}_r(k, \omega)} \right] \quad (4.25)$$

where  $\tilde{\chi}_r(k, \omega)$  is the renormalized free-particle response function [18]. Numerical results for the longitudinal current excitation spectra  $C_\ell(k, \omega)$  are shown in Fig. (6a). The excitation current frequencies are shown in Fig.(6b). Similarly the current excitation frequencies in liquid sodium [30] are shown in Fig.(6c).

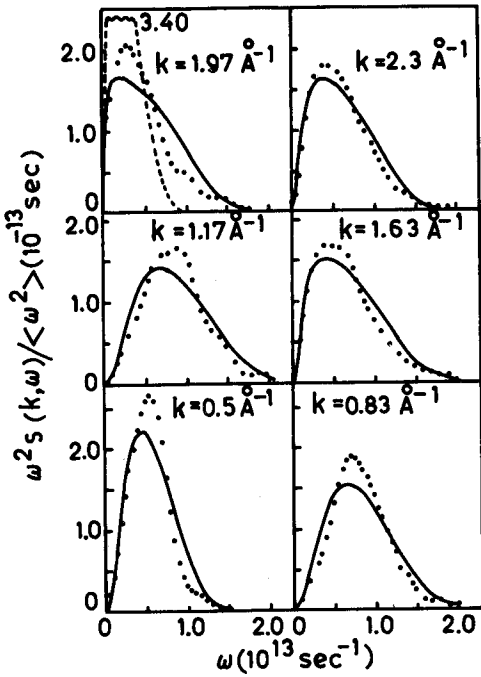


Fig.6(a) Spectral function of the longitudinal current correlations  $\omega^2 s(k, \omega) / \langle \omega^2 \rangle$  plotted as a function of the frequency. Area of each curve is normalized to  $\pi/2$  solid circles - MD calculation of Rahman.

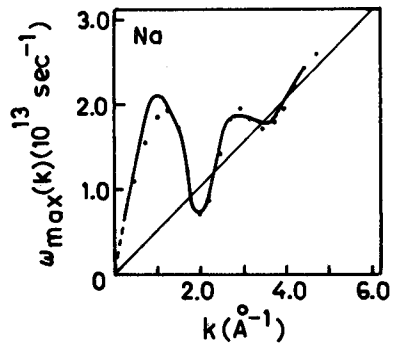
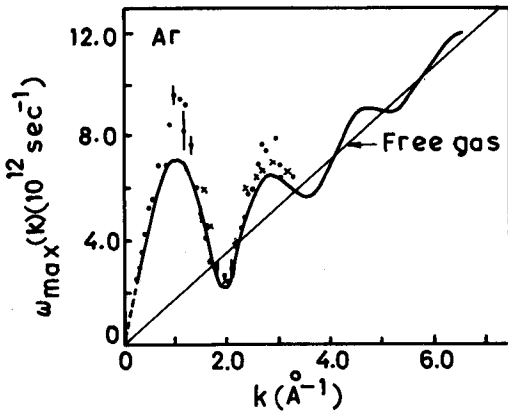


Fig. 6(b,c) Dispersion curve  $\omega_{\max}(k)$  versus  $k$  for the longitudinal current fluctuations, solid circles - MD calculation of Rahman, crosses-experimental results [37].

The experimental observations for liquid metals are more successfully explained in terms of relaxation function having two characteristic relaxation times. For example we choose for  $M(k, t)$  [36].

$$M(k,t) = A(k) e^{-t^2 / \tau_1^2(k)} + [1 - A(k)] e^{-t^2 / \tau_2^2(k)} \quad (4.26)$$

where

$$A(k) = [\langle \omega_l^2 \rangle - \gamma(k) \Omega_0^2] / [\langle \omega_l^2 \rangle - \Omega_0^2] \quad (4.27)$$

The parameters are chosen as discussed by Kahol et al [36] and the results of the calculations are shown in Figs. (7) and (8). It is evident from the Fig.7 that a good agreement with the experimental data is achieved. The results of density fluctuation spectra obtained by Jacucci and Mc Donald [17] for liquid Na and K, and their alloys are shown in Fig.9. All these curves show the existence of the collective excitations in liquid metals. The dispersion curves for the density waves are shown in Fig. 10(a) and 10(b).

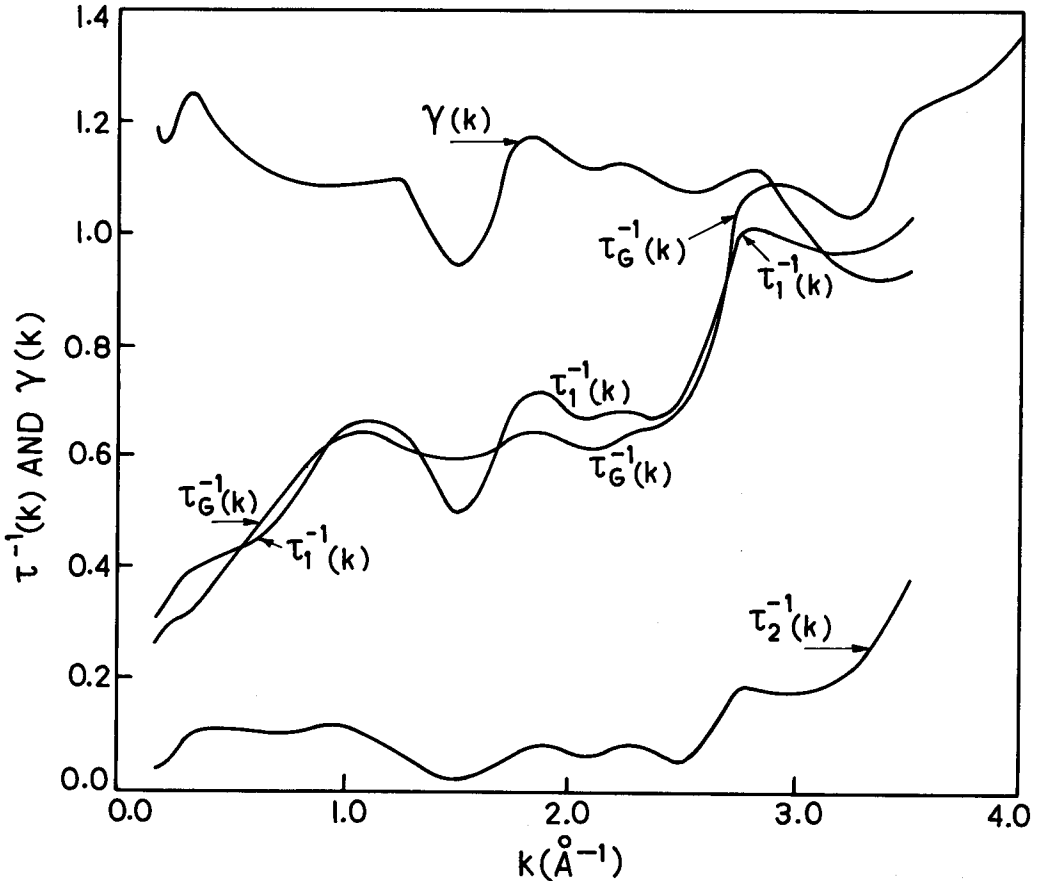


Fig. 7 Inverse relaxation times  $\tau(k)$  in units of  $10^{-13} \text{ sec}^{-1}$  versus wavenumber  $k$ .



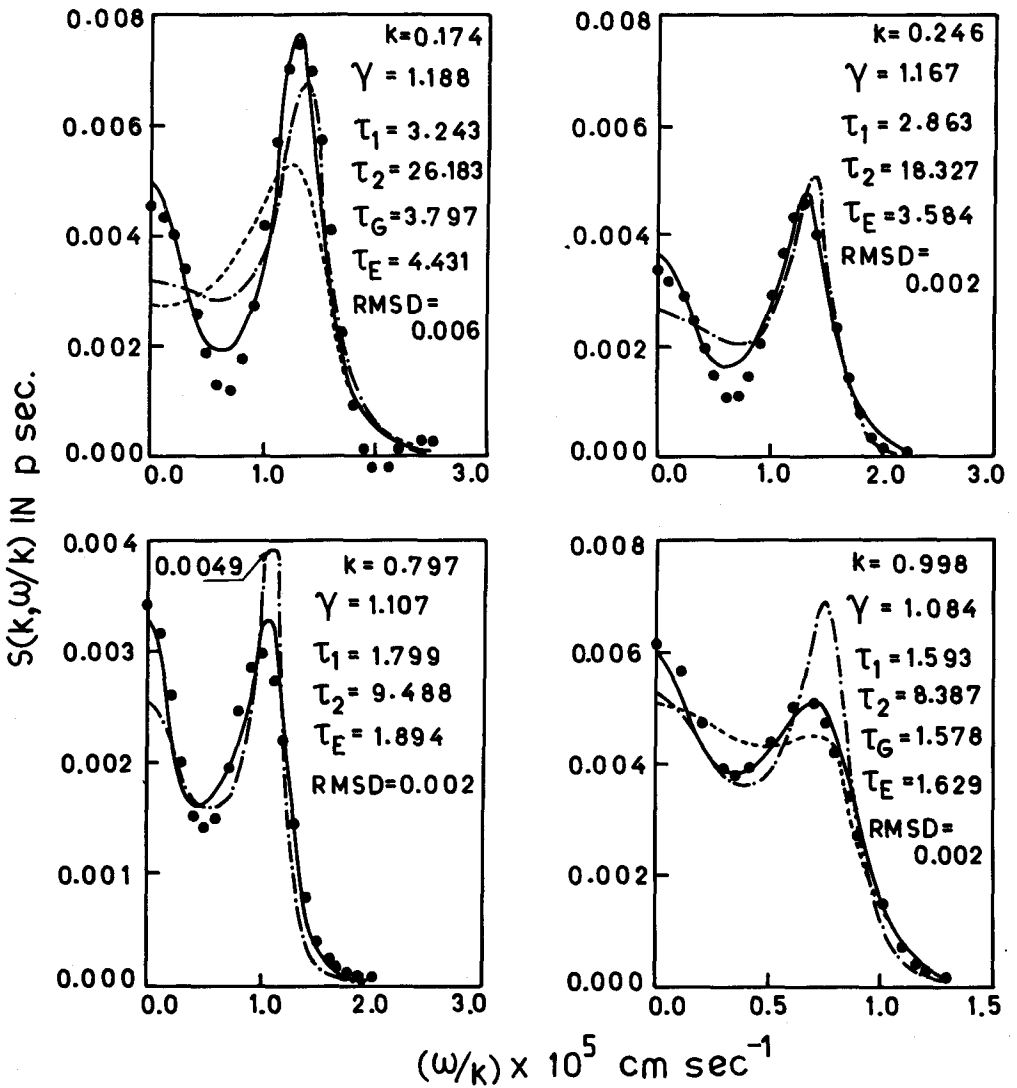


Fig. 8(a)  $S(k, \omega/k)$  as a function of velocity  $\omega/k$ , solid circles - MD calculation [13] solid and broken curves - results using single and double Gaussian memory functions respectively, dash-dot curves - results from exponential form of memory function.

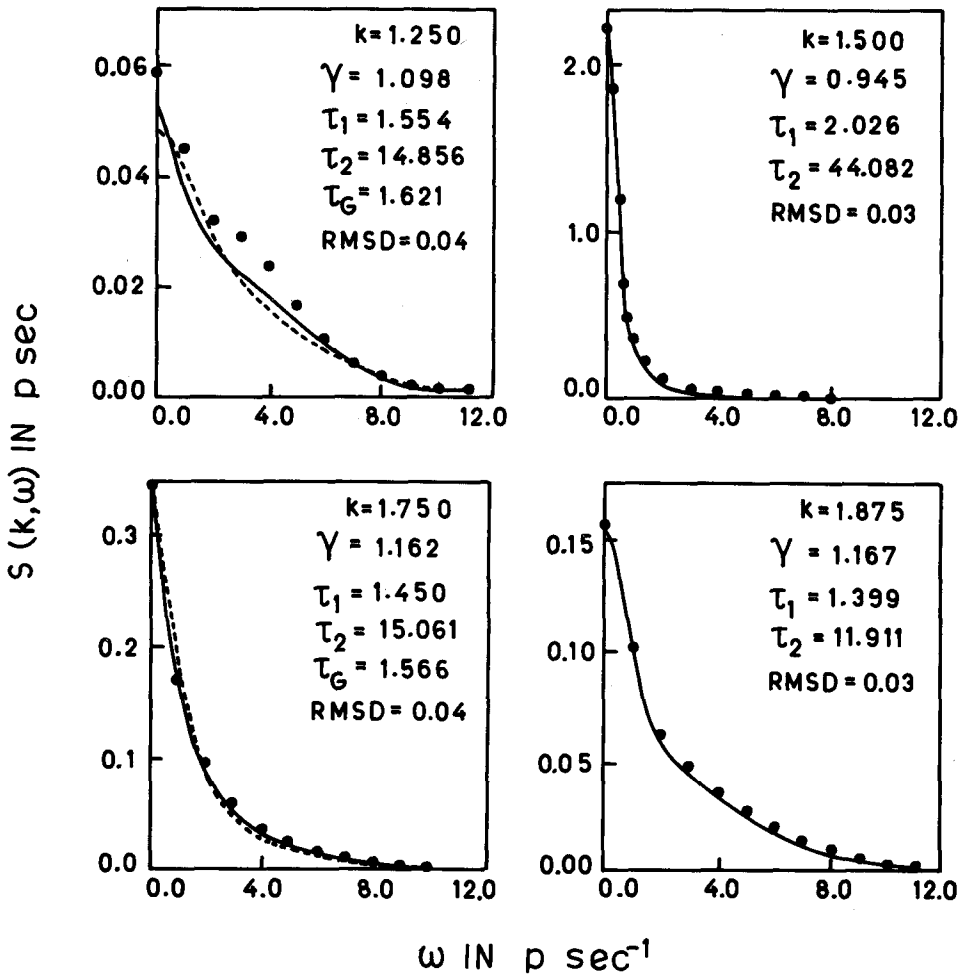


Fig. 8(b)  $S(k, \omega)$  versus  $\omega$  - solid circles - the neutron scattering experiments [38].

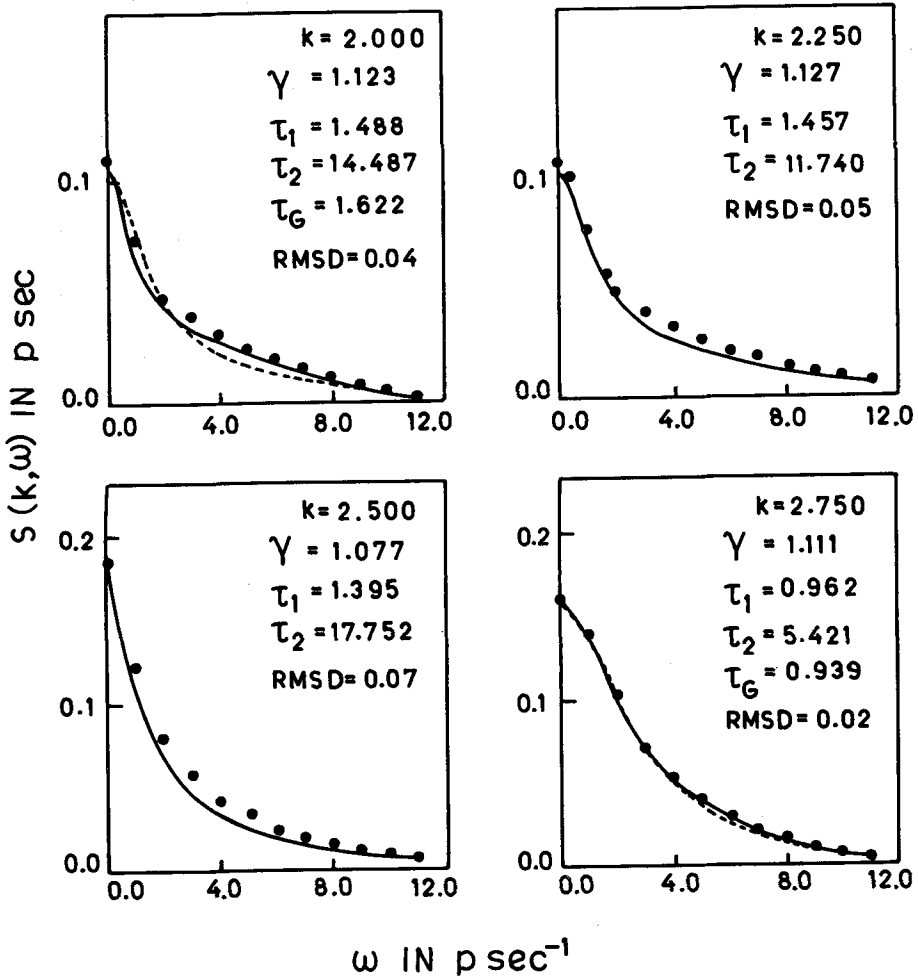


Fig. 8(c)  $S(k, \omega)$  versus  $\omega$  - solid circles - the neutron scattering experiments [38].

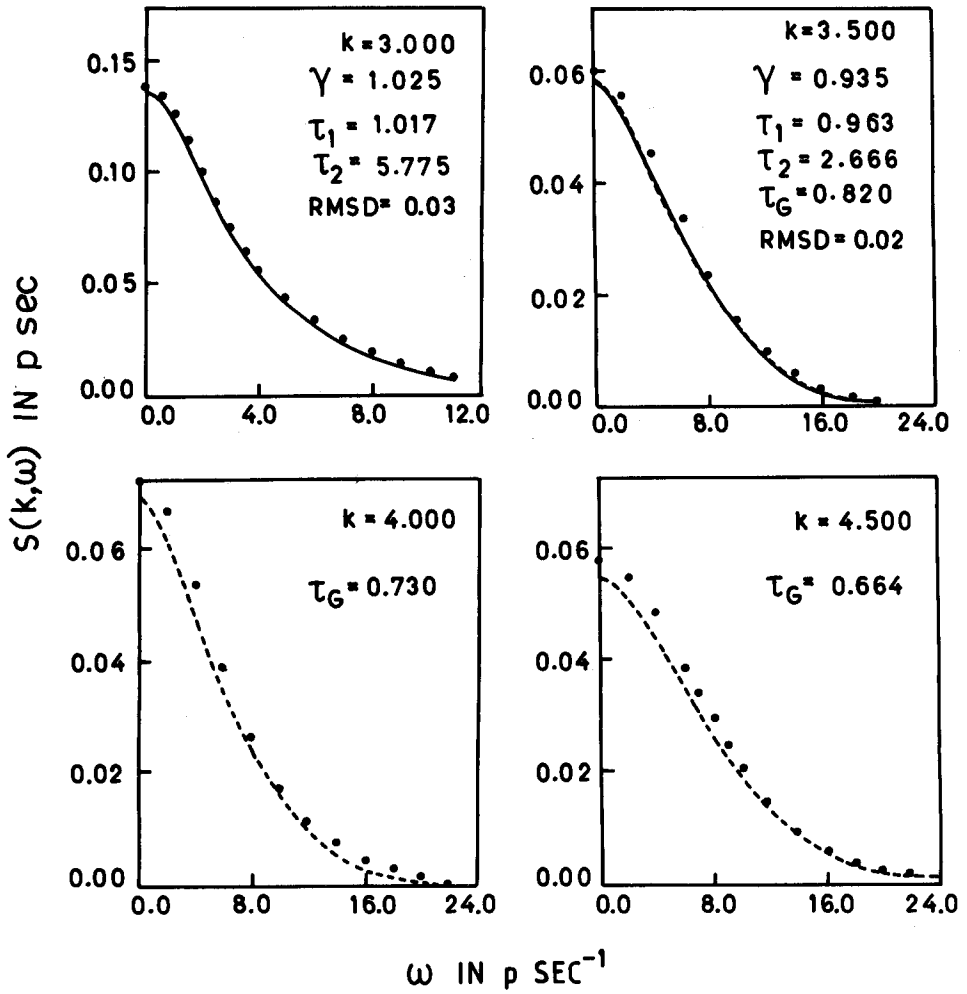


Fig. 8(d)  $S(k, \omega)$  versus  $\omega$  - solid circles - the neutron scattering experiments [38].

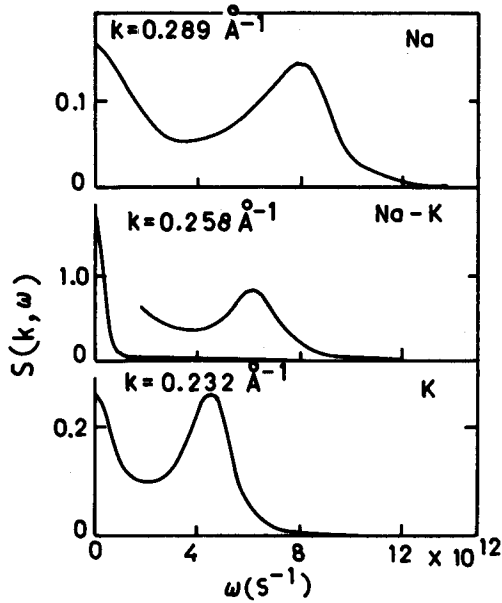


Fig. 9 The density fluctuation spectra  $S(k, \omega)$  vs  $\omega$ . High frequency region for Na-K alloys is shown on a scale amplified twenty times. The area of each curve is normalized to unity.

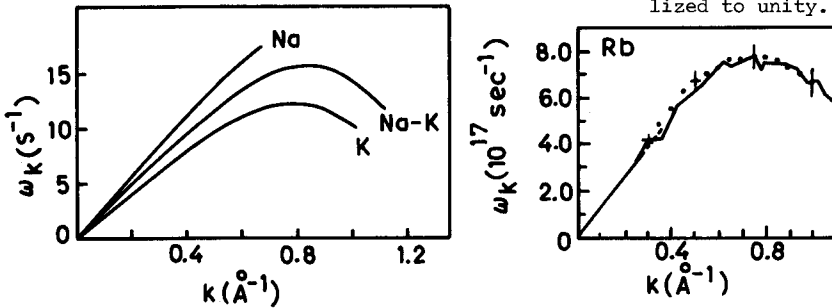


Fig. 10 Dispersion curve  $\omega_k$  vs  $k$  for Na and liquid Rb - MD studies [17,13] .

It is also found that the transverse current excitations exist in liquids for wave-number  $k$  greater than certain minimum values. These are discussed in the paper by Kahol et al [29] but more exhaustive reference for transverse current correlation function can be found in Boon and Yip [22] .

In recent years attempts have been made to develop microscopic theory for the relaxation kernel, the major effort has been made by Götze and collaborators [31-32] , and Sjölander and collaborators [33] . Götze and his collaborators have used microscopic mode coupling theory to calculate the fluctuation spectra of the various corre-

lation functions and have obtained a reasonably good agreement with the experimental data. The approximation due to Sjölander and collaborators is based on the kinetic theory and the results obtained are also in reasonably good agreement with the experimental results. More formal framework known as fully renormalized kinetic theory has been developed by Mazenko [34,35] , but it still remains to make microscopic calculations of the collision kernel.

## 5. Summary and Conclusion

In these lectures I have introduced various relevant correlation functions which are essential in the study of atomic motion of liquids. The generalized Langevin equation has been discussed and procedure to make calculations from it is outlined. A mode coupling theory for the VAF has been discussed which quite successfully explains the experimental data, as well as known long time tail. Collective excitations are discussed within the framework of phenomenological theory. It is emphasized that the liquid Argon type system can be understood in terms of essentially one relaxation time, whereas for liquid metal type systems, two distinct relaxation times are essential. Recent microscopic calculations are also pointed out. In our opinion it would be of interest to relate the two relaxation times to microscopic processes and interatomic potential. In conclusion it can be fair to say that microscopic dynamics of liquid state is still an open problem.

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