DYNAMICS OF DENSE LIQUIDS –A SHORT COURSE ON MODE COUPLING THEORY AND ESSENTIAL PRE-REQUISITE

- *MOTIVATION*:
- In dense liquids at low temperatures, several interesting things happen. Stokes-Einstein relation does not work, relaxation becomes non-exponential and temperature dependence becomes non-Arrhenius.

Motivation (continued)

- Understanding all these phenomenon requires a fairly sophisticated theoretical approach.
- Central to such an approach is a consistent treatment of the coupling between single particle (self-diffusion) and collective (viscosity) variables.

Motivation (continued)

- Break down of hydrodynamics in a significant manner was first found near the gas-liquid critical point where the line width of the Rayleigh-Brillouin spectrum shows a marked decrease. This well-known as the "Criticial slowing down".
- This led to the formulation of the mode coupling theory of dynamics at long wavelength.

MCT of Liquids – Historical development

- * Single particle and collective motions in dense liquids --- hydrodynamic (Navier-Stokes) equations – hydrodynamic density and temperature fluctuations -- Rayleigh-Brillouin scattering – propagation of sound waves.
- * Density fluctuation at intermediate wavenumbers – de Gennes' narrowing of scattered lineshape.

**Hydrodynamics extended to intermediate wavenumbers – de Schepper-Cohen formalism.

MCT (continued)

Molecular Hydrodynamics – viscoelastic approximation – Zwanzig-Mori continued fraction representation of dynamic structure factor.

Projection operator formalism – derivation of relaxation equations.

Need for coupling between different hydrodynamic modes --- example from gas-liquid critical phenomenon.

** Mode coupling theory for diffusion and velocity correlation function, dynamic structure factor, OKE tcf, glass transition, variant of MCT for dynamics of freezing.

MCT is a result of combination of two formidable theoretical framework – renormalized kinetic theory and extended hydrodynamics. The additional feature is the self-consistency or boot-strapping.

Books & References

- Boon and Yip --- Molecular Hydrodynamics (Dover)
- Hansen and McDonald (199 6)
- Balucani and Zoppi – “Dynamics of Liquids”
- Zwanzig – Nonequilibrium Thermodynamics
- Landau-Lifshitz -- Hydrodynamics

Single particle diffusion

Note that Fick's Law is phenomenological --- D is obtained by Green -Kubo relation.

Exponential decay of wave-Number dependent density fluctuation

8.2 SPACE-DEPENDENT SELF MOTION

As an illustration of the general procedure described above, we first consider the relatively simple problem of the diffusion of tagged particles. If the tagged particles are identical to the other particles in the fluid, and if their concentration is sufficiently low that their mutual interactions can be ignored, the problem is equivalent to that of single-particle motion as described by the self part of the van Hove correlation function (see Section 7.4) The macroscopic density $\rho^{(s)}(\mathbf{r}, t)$ and current $\mathbf{j}^{(s)}(\mathbf{r}, t)$ of tagged particles satisfy a continuity equation of the form

$$\dot{\rho}^{(s)}(\mathbf{r}, t) + \nabla \cdot \mathbf{j}^{(s)}(\mathbf{r}, t) = 0 \tag{8.2.1}$$

and the corresponding constitutive relation is provided by Fick's law:

$$\mathbf{j}^{(s)}(\mathbf{r}, t) = -D\nabla\rho^{(s)}(\mathbf{r}, t) \tag{8.2.2}$$

where D is the self-diffusion constant. Combination of (8.2.1) and (8.2.2) yields the *diffusion equation*, i.e.

$$\dot{\rho}^{(s)}(\mathbf{r}, t) = D\nabla^2\rho^{(s)}(\mathbf{r}, t) \tag{8.2.3}$$

or, in reciprocal space:

$$\dot{\rho}_{\mathbf{k}}^{(s)}(t) = -Dk^2\rho_{\mathbf{k}}^{(s)}(t) \tag{8.2.4}$$

Equation (8.2.4) can be integrated immediately to give

$$\rho_{\mathbf{k}}^{(s)}(t) = \rho_{\mathbf{k}}^{(s)} \exp(-Dk^2 t) \tag{8.2.5}$$

where $\rho_{\mathbf{k}}^{(s)}$ is a Fourier component of the tagged-particle density at $t = 0$. If we multiply both sides of Eqn (8.2.5) by $\rho_{-\mathbf{k}}^{(s)}$ and average over initial conditions, we find that the normalized correlation function is

$$\frac{1}{n}\langle\rho_{\mathbf{k}}^{(s)}(t)\rho_{-\mathbf{k}}^{(s)}\rangle = \frac{1}{n}\langle\rho_{\mathbf{k}}^{(s)}\rho_{-\mathbf{k}}^{(s)}\rangle \exp(-Dk^2 t)$$

$$= \exp(-Dk^2 t) \tag{8.2.6}$$

$$S_s(k,\omega)$$

IS THE INCOHERENT DYNAMIC STRUCTURE FACTOR MEASURED BY NEUTRON SCATTERING EXPERIMENTS.

Coupling between Single particle and collective variables *missing* in hydrodynamic description.

The long-wavelength, low-frequency limit of the van Hove self correlation function is the Fourier transform of (8.2.7):

$$G_s(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp(-r^2/4Dt) \tag{8.2.8}$$

In the same limit, the self dynamical structure factor is

$$S_s(k,\omega) = \frac{1}{\pi} \frac{Dk^2}{\omega^2 + (Dk^2)^2} \tag{8.2.9}$$

Equation (8.2.9) represents a single lorentzian curve centred at $\omega = 0$ and having a width at half-height equal to $2Dk^2$. A spectrum of this type is typical of a diffusive process described by an equation similar to (8.2.3). Alternatively, the structure of the Laplace transform of (8.2.8), i.e.

$$\tilde{F}_s(k,z) = \frac{1}{-iz + Dk^2} \tag{8.2.10}$$

shows that a diffusive process is characterized by a purely imaginary pole at $z = -iDk^2$. We emphasize again that the simple result expresssed by Eqn (8.2.9) is valid only for $kl \ll 1$, $\omega\tau \ll 1$. In particular, the hydrodynamic result is invalid at high frequencies; this is reflected in the fact that the even frequency moments (beyond zeroth order) of (8.2.9) are all divergent. Note also that the transport coefficient D is related to the behaviour of $S_s(k,\omega)$ in the limit $k, \omega \to 0$. From Eqn (8.2.9) we see that

$$D = \lim_{\omega \to 0} \lim_{k \to 0} \frac{\omega^2}{k^2} \pi S_s(k,\omega) \tag{8.2.11}$$

where it is crucial that the limits are taken in the correct order, i.e. $k \to 0$ before $\omega \to 0$. In principle, Eqn (8.2.11) provides a means of determining D from the results of inelastic neutron scattering experiments.

Equations (7.5.27) and (8.2.8) show that the van Hove self correlation function is a gaussian function of distance both for $t \to 0$ (free-particle behaviour) and $t \to \infty$ (the hydrodynamic limit); it is therefore tempting to suppose that $G_s(r,t)$ is gaussian at all times. To study this point in more detail, we write $G_s(r,t)$ as a generalized gaussian function of r in the form

$$G_s(r,t) = \left(\frac{\alpha(t)}{\pi}\right)^{3/2} \exp[-\alpha(t) r^2] \tag{8.2.12}$$

where $\alpha(t)$ is a function of t but not of r; the hydrodynamic limit corresponds to taking $\alpha(t) = 1/4Dt$ and the ideal gas model to $\alpha(t) = \beta m/2t^2$. We now introduce the even moments of $G_s(r,t)$, defined as

$$\langle r^{2n}(t)\rangle \equiv \langle |\mathbf{r}(t) - \mathbf{r}(0)|^{2n}\rangle$$

Collective dynamics

Variables are the conserved Quantities : density, Momentum and energy
--- but these are coupled
To each other.

The simplest description
Of coupled equations is
Given by Navier-Stokes Hydrodynamic

Linearization of Hydrodynamic equations

conservation laws for the local densities are of the form

$$\dot{\rho}(\mathbf{r}, t) + \frac{1}{m}\nabla \cdot \mathbf{p}(\mathbf{r}, t) = 0 \tag{8.3.2}$$

$$\dot{\mathbf{p}}(\mathbf{r}, t) + \nabla \cdot \boldsymbol{\sigma}(\mathbf{r}, t) = 0 \tag{8.3.3}$$

$$\dot{e}(\mathbf{r}, t) + \nabla \cdot \mathbf{J}^e(\mathbf{r}, t) = 0 \tag{8.3.4}$$

where $\boldsymbol{\sigma}$ is the momentum current, or *stress tensor*, and $\mathbf{J}^e$ is the energy current. These equations are supplemented by two constitutive relations in which $\boldsymbol{\sigma}$ and $\mathbf{J}^e$ are expressed in terms of the dissipative processes in the fluid. The stress tensor is given macroscopically (Landau and Lifshitz, 1963) by

$$\sigma^{\alpha\beta}(\mathbf{r}, t) = \delta_{\alpha\beta}P(\mathbf{r}, t) - \eta\left(\frac{\partial u_\alpha(\mathbf{r}, t)}{\partial r_\beta} + \frac{\partial u_\beta(\mathbf{r}, t)}{\partial r_\alpha}\right) + \delta_{\alpha\beta}(\tfrac{2}{3}\eta - \zeta)\nabla \cdot \mathbf{u}(\mathbf{r}, t) \tag{8.3.5}$$

Note that stress-stress tcf gives viscosity

where $P(\mathbf{r}, t)$ is the local pressure, η is the shear viscosity and ζ is the bulk viscosity. We now choose a frame of reference in which the mean velocity of the fluid is zero, and assume that the local deviations of the hydrodynamic variables from their average values are small. The equations above may then be linearized with respect to the deviations. In particular, the momentum density may be expressed as

$$\begin{aligned}\mathbf{p}(\mathbf{r}, t) &= m[\rho + \delta\rho(\mathbf{r}, t)]\mathbf{u}(\mathbf{r}, t) \\ &\simeq m\rho\mathbf{u}(\mathbf{r}, t)\end{aligned} \tag{8.3.6}$$

Substitution of (8.3.5) and (8.3.6) in Eqn (8.3.3) gives the Navier-Stokes equation in its linearized form:

$$\rho m\dot{\mathbf{u}}(\mathbf{r}, t) + \nabla P(\mathbf{r}, t) - \eta\nabla^2\mathbf{u}(\mathbf{r}, t) - (\tfrac{1}{3}\eta + \zeta)\nabla\nabla \cdot \mathbf{u}(\mathbf{r}, t) = 0 \tag{8.3.7}$$

The second constitutive relation (Landau and Lifshitz, 1963) defines the macroscopic energy current as

$$\mathbf{J}^e(\mathbf{r}, t) = h\mathbf{u}(\mathbf{r}, t) - \lambda\nabla T(\mathbf{r}, t) \tag{8.3.8}$$

where $h = (e + P)$ is the equilibrium enthalpy density, $T(\mathbf{r}, t)$ is the local temperature and λ is the thermal conductivity; terms corresponding to viscous heating have been omitted, since these are quadratic in the local

Assumption of local equilibrium

Choice of independent fluctuating variables.

$$\dot{Q}(\mathbf{r}, t) - \lambda \nabla^2 T(\mathbf{r}, t) = 0 \tag{8.3.10}$$

where

$$Q(\mathbf{r}, t) = e(\mathbf{r}, t) - \frac{e+P}{\rho}\rho(\mathbf{r}, t) \tag{8.3.11}$$

The quantity $Q(\mathbf{r}, t)$ can be interpreted as a density of heat energy. This identification follows from a simple thermodynamic argument. If the number of particles is held constant, we see that

$$\begin{aligned} T\,\mathrm{d}S &= \mathrm{d}U + P\,\mathrm{d}V \\ &= \mathrm{d}(eV) + P\,\mathrm{d}V \\ &= V\,\mathrm{d}e - eV\frac{\mathrm{d}\rho}{\rho} - PV\frac{\mathrm{d}\rho}{\rho} \end{aligned} \tag{8.3.12}$$

Thus

$$\begin{aligned} \frac{T}{V}\mathrm{d}S &= \mathrm{d}e - \frac{e+P}{\rho}\mathrm{d}\rho \\ &= \mathrm{d}Q \end{aligned} \tag{8.3.13}$$

and a change in $Q(\mathbf{r}, t)$ is therefore equal to T multiplied by the change in entropy density.

If we invoke the hypothesis of local thermodynamic equilibrium, the deviations of the local thermodynamic variables from their average values can be expressed in terms of a set of statistically independent quantities. We choose as independent variables the density and temperature (cf. Eqn (2.7.5)), and expand $P(\mathbf{r}, t)$ and $Q(\mathbf{r}, t)$ to first order in the deviations $\delta\rho(\mathbf{r}, t) = \rho(\mathbf{r}, t) - \rho$ and $\delta T(\mathbf{r}, t) = T(\mathbf{r}, t) - T$. Then

$$\delta P(\mathbf{r}, t) = \left(\frac{\partial P}{\partial \rho}\right)_T \delta\rho(\mathbf{r}, t) + \left(\frac{\partial P}{\partial T}\right)_\rho \delta T(\mathbf{r}, t) \tag{8.3.14}$$

$$\begin{aligned} \delta Q(\mathbf{r}, t) &= \frac{T}{V}\left(\frac{\partial S}{\partial \rho}\right)_T \delta\rho(\mathbf{r}, t) + \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_\rho \delta T(\mathbf{r}, t) \\ &= \rho T\left(\frac{\partial (S/N)}{\partial \rho}\right)_T \delta\rho(\mathbf{r}, t) + \rho c_V \delta T(\mathbf{r}, t) \end{aligned} \tag{8.3.15}$$

where c_V is the specific heat per particle at constant volume. By making use of the thermodynamic relation

The set of linearized Hydrodynamic equations

Laplace-Fourier Transformation—use of isotropy

$\mathbf{j}(\mathbf{r}, t) = \rho \mathbf{u}(\mathbf{r}, t)$ of the form

$$\frac{\partial}{\partial t}\delta\rho(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \tag{8.3.17}$$

$$\left(\frac{\partial}{\partial t} - a\nabla^2\right)\delta T(\mathbf{r}, t) - \frac{T}{\rho^2 c_V}\left(\frac{\partial P}{\partial T}\right)_\rho \frac{\partial}{\partial t}\delta\rho(\mathbf{r}, t) = 0 \tag{8.3.18}$$

$$\left(\frac{\partial}{\partial t} - \frac{\eta}{\rho m}\nabla^2 - \frac{\frac{1}{3}\eta + \zeta}{\rho m}\nabla\nabla \cdot \right)\mathbf{j}(\mathbf{r}, t) + \left(\frac{\partial P}{\partial \rho}\right)_T \nabla\delta\rho(\mathbf{r}, t) + \left(\frac{\partial P}{\partial T}\right)_\rho \nabla\delta T(\mathbf{r}, T) = 0 \tag{8.3.19}$$

where

$$a = \frac{\lambda}{\rho c_V} \tag{8.3.20}$$

Equations (8.3.17) to (8.3.19) are readily solved by taking the double transforms with respect to space (Fourier) and time (Laplace) to give

$$-iz\tilde{\rho}_{\mathbf{k}}(z) + i\mathbf{k} \cdot \tilde{\mathbf{j}}_{\mathbf{k}}(z) = \rho_{\mathbf{k}} \tag{8.3.21}$$

$$(-iz + ak^2)\tilde{T}_{\mathbf{k}}(z) + \frac{iT}{\rho^2 c_V}\left(\frac{\partial P}{\partial T}\right)_\rho \mathbf{k} \cdot \tilde{\mathbf{j}}_{\mathbf{k}}(z) = T_{\mathbf{k}} \tag{8.3.22}$$

$$\left(-iz + \frac{\eta}{\rho m}k^2 + \frac{\frac{1}{3}\eta + \zeta}{\rho m}\mathbf{k}\mathbf{k} \cdot \right)\tilde{\mathbf{j}}_{\mathbf{k}}(z) + \frac{i\mathbf{k}}{m}\left(\frac{\partial P}{\partial \rho}\right)_T \tilde{\rho}_{\mathbf{k}}(z) + \frac{i\mathbf{k}}{m}\left(\frac{\partial P}{\partial T}\right)_\rho \tilde{T}_{\mathbf{k}}(z) = \mathbf{j}_{\mathbf{k}} \tag{8.3.23}$$

where, for example:

$$\tilde{\rho}_{\mathbf{k}}(z) = \int_0^\infty \mathrm{d}t \exp(izt) \int \delta\rho(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r})\, \mathrm{d}\mathbf{r} \tag{8.3.24}$$

and $\rho_{\mathbf{k}}$, $T_{\mathbf{k}}$ and $\mathbf{j}_{\mathbf{k}}$ are the spatial Fourier components at $t = 0$. We now separate the components of the current $\mathbf{j}_{\mathbf{k}}$ into their longitudinal and tranverse parts. Choosing $\mathbf{k}$ along the z-axis, we rewrite Eqn (8.3.23) as

$$(-iz + bk^2)\tilde{j}^z_{\mathbf{k}}(z) + \frac{ik}{m}\left(\frac{\partial P}{\partial T}\right)_\rho \tilde{T}_{\mathbf{k}}(z) + \frac{ik}{m}\left(\frac{\partial P}{\partial \rho}\right)_T \tilde{\rho}_{\mathbf{k}}(z) = j^z_{\mathbf{k}} \tag{8.3.25a}$$

The hydrodynamic matrix
-- note the decoupling between the transverse and the longitudinal current modes
--the determinant (which determines poles and hence the time constants of relaxation)
Becomes a prodcut of two.

$$b = \frac{\frac{4}{3}\eta + \zeta}{\rho m} \tag{8.3.26}$$

is the kinematic longitudinal viscosity and

$$\nu = \frac{\eta}{\rho m} \tag{8.3.27}$$

is the kinematic shear viscosity. Equations (8.3.21), (8.3.22) and (8.3.25) are conveniently summarized in matrix form as

$$\begin{pmatrix} -iz & 0 & ik & 0 & 0 \\ 0 & -iz + ak^2 & \frac{ikT}{\rho^2 c_V}\left(\frac{\partial P}{\partial T}\right)_\rho & 0 & 0 \\ \frac{ik}{m}\left(\frac{\partial P}{\partial \rho}\right)_T & \frac{ik}{m}\left(\frac{\partial P}{\partial T}\right)_\rho & -iz + bk^2 & 0 & 0 \\ 0 & 0 & 0 & -iz + \nu k^2 & 0 \\ 0 & 0 & 0 & 0 & -iz + \nu k^2 \end{pmatrix} \begin{pmatrix} \tilde{\rho}_{\mathbf{k}}(z) \\ \tilde{T}_{\mathbf{k}}(z) \\ \tilde{j}^z_{\mathbf{k}}(z) \\ \tilde{j}^x_{\mathbf{k}}(z) \\ \tilde{j}^y_{\mathbf{k}}(z) \end{pmatrix} = \begin{pmatrix} \rho_{\mathbf{k}} \\ T_{\mathbf{k}} \\ j^z_{\mathbf{k}} \\ j^x_{\mathbf{k}} \\ j^y_{\mathbf{k}} \end{pmatrix} \tag{8.3.28}$$

The matrix of coefficients in (8.3.28) is called the *hydrodynamic matrix*. Its block-diagonal structure shows that the transverse-current fluctuations are completely decoupled from the fluctuations in the other (longitudinal) variables. The determinant of the hydrodynamic matrix therefore factorizes into the product of purely longitudinal (l) and purely transverse (t) parts, i.e.

$$D(k, z) = D_l(k, z) D_t(k, z) \tag{8.3.29}$$

with

$$D_l(k, z) = -iz(-iz + ak^2)(-iz + bk^2) + (-iz + ak^2)\frac{k^2}{m}\left(\frac{\partial P}{\partial \rho}\right)_T - iz\frac{k^2 T}{\rho^2 m c_V}\left[\left(\frac{\partial P}{\partial T}\right)_\rho\right]^2 \tag{8.3.30}$$

and

$$D_t(k, z) = (-iz + \nu k^2)^2 \tag{8.3.31}$$

The frequency/wavenumber or *dispersion* relation for the collective modes is given by the poles of the inverse of the hydrodynamic matrix and hence by the complex roots of the equation

The factorization in (8.3.29) shows that Eqn (8.3.32) has a double root associated with transverse modes, namely

$$z = -i\nu k^2 \tag{8.3.33}$$

while the complex frequencies corresponding to longitudinal modes are obtained as the solution to the cubic equation

$$iz^3 - z^2(a+b)k^2 - iz(abk^2 + c_s^2)k^2 + (a/\gamma)c_s^2 k^4 = 0 \tag{8.3.34}$$

where $\gamma = c_P/c_V$, c_s is the adiabatic speed of sound, given by

$$c_s^2 = \frac{\gamma}{m}\left(\frac{\partial P}{\partial \rho}\right)_T \tag{8.3.35}$$

and use has been made of the thermodynamic relation

$$\left[\left(\frac{\partial P}{\partial T}\right)_\rho\right]^2 = \frac{\rho^2}{T}(c_P - c_V)\left(\frac{\partial P}{\partial \rho}\right)_T \tag{8.3.36}$$

Since the hydrodynamic calculation is valid only in the long-wavelength limit, it is sufficient to calculate the complex frequencies to order k^2. The algebra is simplified by introducing the reduced variable $s = z/c_s k$; it is then straightforward to show (Mountain, 1966) that the approximate solution to Eqn (8.3.34) is of the form

$$z_0 = -iD_T k^2 \tag{8.3.37a}$$

$$z_\pm = \pm c_s k - i\Gamma k^2 \tag{8.3.37b}$$

where

$$D_T = \frac{a}{\gamma} = \frac{\lambda}{\rho c_P} \tag{8.3.38}$$

is the thermal diffusivity and

$$\Gamma = \tfrac{1}{2}[a(\gamma - 1)/\gamma + b] \tag{8.3.39}$$

is the sound-attenuation coefficient. The purely imaginary roots in (8.3.33) and (8.3.37a) represent diffusive processes of the type already discussed in the preceding section, and the pair of complex roots in (8.3.37b) correspond to propagating sound waves, as we shall discuss in Section 8.5.

therefore more complicated than in the case of the transverse-current fluctuations discussed in the preceding section. There are three longitudinal modes, corresponding to the roots z_0, z_+ and z_- displayed in Eqns (8.3.37). The significance of the different roots is most easily grasped by solving the system of coupled longitudinal equations contained in (8.3.28) to obtain the hydrodynamic limiting form of the dynamic structure factor $S(k, \omega)$ (Mountain, 1966). The solution for $\tilde{\rho}_{\mathbf{k}}(z)$ involves terms proportional, respectively, to the initial values $\rho_{\mathbf{k}}$, $T_{\mathbf{k}}$ and $j^z_{\mathbf{k}}$. We omit the term proportional to $j^z_{\mathbf{k}}$, because $\mathbf{k}$ can always be chosen to make $\mathbf{u}_{\mathbf{k}}$ (the Fourier transform of the initial velocity field $\mathbf{u}(\mathbf{r}, 0)$) perpendicular to $\mathbf{k}$, thereby ensuring that $j^z_{\mathbf{k}} = 0$. We also ignore the term proportional to $T_{\mathbf{k}}$; this contributes nothing to the final expression for $S(k, \omega)$, since the fluctuations in temperature and density are instantaneously uncorrelated, i.e. $\langle T_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle = 0$ (cf. Eqn (2.7.5)). With these simplifications, the solution for $\tilde{\rho}_{\mathbf{k}}(z)$ can be written as

$$\tilde{\rho}_{\mathbf{k}}(z) = \rho_{\mathbf{k}} \frac{(-iz + ak^2)(-iz + bk^2) + (\gamma - 1)c_s^2 k^2/\gamma}{D_l(k, z)} \tag{8.5.1}$$

where all quantities are as defined in Section 8.3. Separation of the right-hand side of Eqn (8.5.1) into partial fractions shows that on the real axis $\tilde{\rho}_{\mathbf{k}}$ is given by

$$\tilde{\rho}_{\mathbf{k}}(\omega) = \rho_{\mathbf{k}} \left[\left(\frac{\gamma - 1}{\gamma} \right) \frac{1}{-i\omega + D_T k^2} + \frac{1}{2\gamma} \left(\frac{1}{-i\omega + \Gamma k^2 - ic_s k} + \frac{1}{-i\omega + \Gamma k^2 + ic_s k} \right) \right] \tag{8.5.2}$$

which, via an inverse transform, yields an expression for $\rho_{\mathbf{k}}(t)$ of the form

$$\rho_{\mathbf{k}}(t) = \rho_{\mathbf{k}} \left[\left(\frac{\gamma - 1}{\gamma} \right) \exp(-D_T k^2 t) + \frac{1}{\gamma} \exp(-\Gamma k^2 t) \cos c_s k t \right] \tag{8.5.3}$$

The dynamic structure factor is a sum of three peak Lorentzian known as Rayleigh-Brillouin spectra which can be measured by Light scattering experiments.

The central peak is due to density fluctuation and the corresponding hydrodynamic mode is called the “heat mode”.

The two branches are due to the sound modes

It is clear from the structure of Eqn (8.5.3) that the purely imaginary root in (8.3.37) corresponds to a fluctuation that decays without propagating, the lifetime of the fluctuation being determined by the thermal diffusivity D_T. By contrast, the complex roots correspond to a fluctuation that propagates through the fluid at the speed of sound, eventually decaying through the combined effects of viscosity and thermal conduction, as represented by the expression (8.3.39) for Γ; note that the thermal damping of the sound mode is small when $\gamma \simeq 1$. On multiplying through Eqn (8.5.3) by $\rho_{-\mathbf{k}}$, dividing by N and taking the thermal average, we obtain an expression for the density autocorrelation function $F(k, t)$; this is easily Fourier transformed to give

$$S(k,\omega) = \frac{1}{2\pi} S(k) \left[\left(\frac{\gamma - 1}{\gamma} \right) \frac{2 D_T k^2}{\omega^2 + (D_T k^2)^2} + \frac{1}{\gamma} \left(\frac{\Gamma k^2}{(\omega + c_s k)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega - c_s k)^2 + (\Gamma k^2)^2} \right) \right] \quad (8.5.4)$$

The spectrum of density fluctuations therefore consists of three components: the Rayleigh line, centred at $\omega = 0$, and two Brillouin lines at $\omega = \pm c_s k$; a typical spectrum is pictured in Figure 8.4. The two shifted components correspond to the propagating mode, and are analogous to the longitudinal acoustic phonons of a solid, whereas the central line represents the steadily decaying thermal mode. The total integrated intensity of the Rayleigh line is easily calculated to be

$$\mathcal{I}_R = \frac{\gamma - 1}{\gamma} S(k) \quad (8.5.5)$$

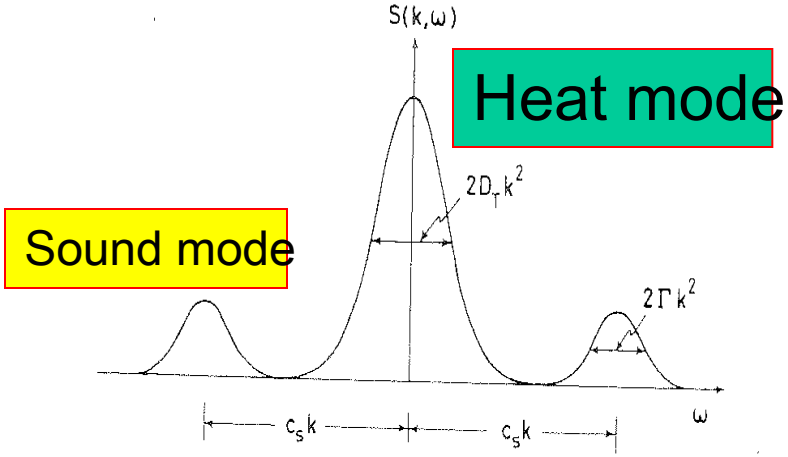


FIG. 8.4. Dynamic structure factor in the hydrodynamic limit; D_T is the thermal diffusivity, Γ is the sound-attenuation coefficient and c_s is the adiabatic speed of sound

The relation between friction and viscosity goes beyond the Stokes relation. The Navier–Stokes hydrodynamics has been generalized by Zwanzig and Bixon [23] to include the viscoelastic response of the medium. This generalization provides an elegant expression for the frequency-dependent friction which depends among other things on the frequency-dependent bulk and shear viscosities and sound velocity.

III. SLOW DYNAMICS AT LARGE WAVENUMBERS: DE GENNES NARROWING

In the previous section we have discussed the Rayleigh–Brillouin spectrum, which is observed in light scattering experiments. The wavelengths involved in these scattering experiments are typically about 5000 Å. It is thus possible to calculate the spectral distribution of scattered light from the macroscopic equations of hydrodynamics. The neutron scattering experiments, on the other hand, involves wavelengths of the order of the nearest-neighbor separation in the liquid, thus capturing completely different physics that cannot be explained from the hydrodynamic point of view.

The wavenumbers accessible in inelastic neutron scattering experiments lie typically in between 0.1 and 15 $Å^{-1}$, *which is the same range as usually studied in molecular dynamics simulations*. There has been extensive study of the density fluctuation spectra by coherent and incoherent inelastic neutron scattering experiments [24] and also by using molecular dynamics simulations [25]. As discussed earlier, the dynamic structure factor $S(q,\omega)$ at reduced wavenumbers $q\sigma \leq 1$ (where σ is the atomic diameter) has a three-peak structure where the two side peaks correspond to propagating sound waves. At shorter wavelengths, the sound waves are strongly damped and the high-frequency structure disappears when $q\sigma \geq 2$, leaving only the Lorentzian-like central peak. The width of the central peak first increases with q, but then shows a *marked decrease at wavenumbers close to* q_m, which corresponds to the wavenumber where the static structure factor has its main peak. At still larger wavenumbers the spectrum broadens again, going over finally to its free-particle limit. This decrease in the width near $q = q_m$ is called "de Gennes narrowing" and cannot be explained from the expression of dynamic structure factor obtained using the linearized hydrodynamic theory [Eq. (10)]. Many years ago, de Gennes observed that for intermediate wavenumbers (that is, for intermediate momentum transfer), correlation effects between neighboring atoms are important [26]. Often this results in a strong narrowing of the density distribution function [26]. This narrowing can also be explained by using a Smoluchowski–Vlasov-type equation to express the number density fluctuations.

De Gennes' narrowing was the first indication that dynamics at small length scales cannot be described by conventional hydrodynamics.

The microscopic derivation of de- Gennes' narrowing is simple. It uses what is known as Smoluchowski-Vlasov equation. This is an equation of motion for singlet density with a Mean-field force term.

The basic physics is that at intermediate to large wavenumbers, both momentum and energy relaxation is very fast. At such Small length scales, momentum conservation is no longer a constrain.

Instead, local environment controls density relaxation. Note that number density is conserved at all length scales.

At the wavelengths
conservation of the momentum nor the energy are relevant constra
dynamics. This is because at these wavelengths there is a rapid ex
momentum and energy between the nearest neighbors, due to bi
sions. On the other hand, *the number density must be conserved a*
scales. Thus the only slow mode relevant in this regime of wavenu
number density. Now a Smoluchowski–Vlasov-type expression ca
written down for the number density, which involves a mean-field
due to the cage effect [27, 28]:

$$\dot{\rho}(\mathbf{r},t) = D\nabla \cdot [\nabla - \beta \mathbf{F}(\mathbf{r},t)]\rho(\mathbf{r},t),$$

where $D = k_B T/m\gamma$ is the self-diffusion coefficient of the liqui
collisional frequency, and $\mathbf{F}$ is the mean field force given by

$$\mathbf{F}(\mathbf{r},t) = -\nabla V_{\text{eff}}(\mathbf{r},t).$$

Here $V_{\text{eff}}(\mathbf{r},t)$ is the effective potential energy that is determined
spherical approximation and is written in terms of the two-particle
relation function $c(\mathbf{r})$:

$$\beta V_{\text{eff}}(\mathbf{r},t) = -\int d\mathbf{r}' c(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}',t).$$

ρ_0 is the equilibrium solution of Eq. (15) and has the following

$$\rho_0(\mathbf{r}) = c' \exp\left[\int d\mathbf{r}' c(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r}')\right],$$

where c' is a constant determined from the normalization condit
From Eqs. (15)–(18), the intermediate scattering function $F($
obtained and has the following form:

$$F(q,t) = S(q)e^{-\frac{D}{S(q)}q^2 t},$$

where $S(q)$ is the static structure factor. The value of self-diffusion
is about three orders of magnitude smaller than the thermal diffu
cient. In addition, for wavenumbers near q_m, the static structure fa
ply peaked. These two combine to give rise to a marked slowi
$F(q,t)$. This slowing down in $F(q,t)$ in turn leads to a considera
ing of the zero frequency (Rayleigh) peak of the dynamic struc
which is the de Gennes narrowing. Underneath all these interpr

The density functional theory and its use as a dynamic mean-field theory

1. The basic idea is that it is possible to express the free energy as a functional of the position dependent density – that is, we consider an inhomogeneous state, for example, a liquid in an external potential giving rise to a density field. It is a straight-forward generalization of the van der Waals theory.
2. As in the vdW theory, we assign a free energy of the state characterized by average number density (ρ) and temperature (N,V,T) in the canonical ensemble.
3. One next derives a functional Taylor expansion of the free Energy with fluctuation in density as the smallness parameter.

DFT (continued….

- Therefore,
- F = F(ρ) + Terms in density fluctuation

$$\delta\rho = \rho(r) - \rho$$

- The first derivative wrt density is zero
- The 2nd derivative is the direct correlation function.

functional theory, which gives a general expression for the free energy functional of an nonhomogeneous system. The extended hydrodynamic equations for the number density and the momenta densities are [29, 35]

Molecular hydrodynamic
Equations of motion

$$\frac{\partial}{\partial t}\rho(\mathbf{X},t)+\frac{1}{m}\nabla_T\cdot\mathbf{g}_T(\mathbf{X},t)+\frac{1}{I}\nabla_\Omega\cdot\mathbf{g}_\Omega(\mathbf{X},t)=0 \tag{4.1}$$

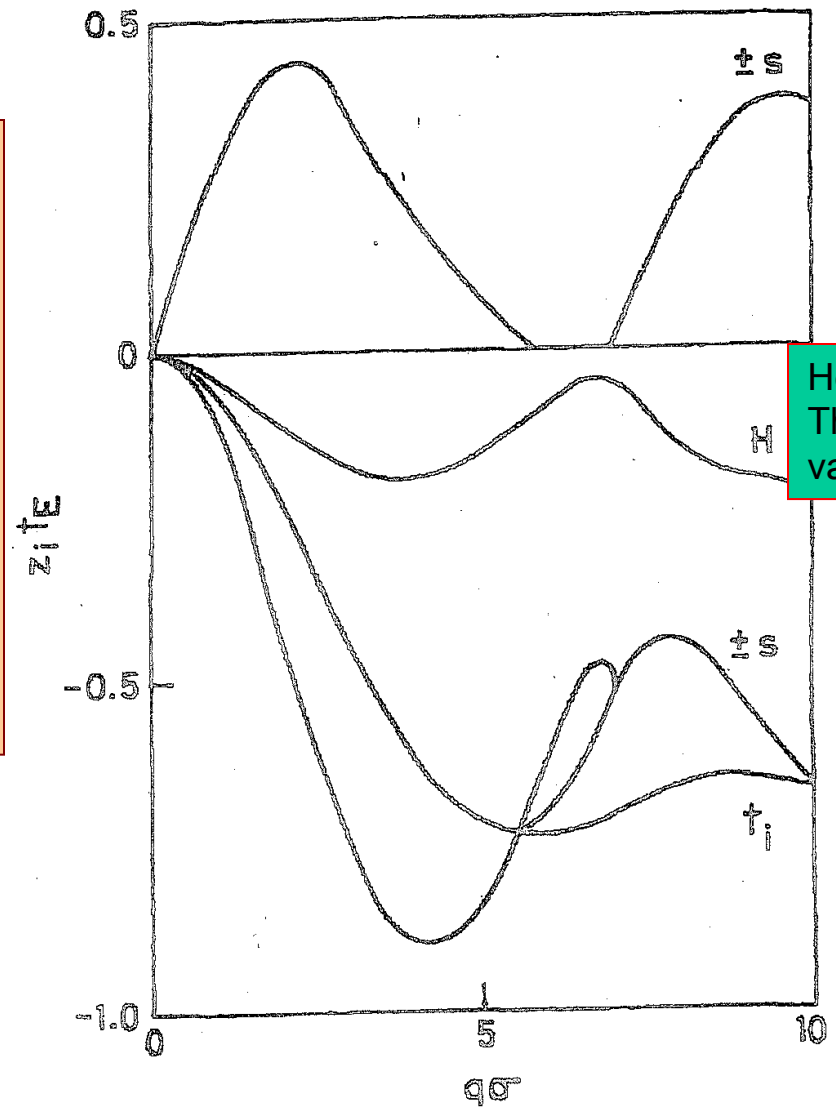
$$\begin{aligned}\frac{\partial}{\partial t}\mathbf{g}_i(\mathbf{X},t)=&-\rho(\mathbf{X},t)\nabla_i\frac{\delta F'[\rho(t)]}{\delta\rho(\mathbf{X},t)}\\&-\sum_j\int dt_1 d\mathbf{X}_1\Gamma_{ij}(\mathbf{X},\mathbf{X}_1,t-t_1;\rho(t))\frac{\delta F}{\delta\mathbf{g}_j(\mathbf{X},t)}\\&+f_i(\mathbf{X},t)\end{aligned} \tag{4.2}$$

where $\mathbf{X}=(\mathbf{r},\Omega)$, i stands for T or Ω, m and I are the mass and the moment of inertia, respectively, ∇_T and ∇_Ω are the usual spatial and angular gradient operators, $F'[\rho(t)]$ is the interaction part of the free energy for an nonhomogeneous fluid [36]. F and F' are given by the following expressions:

Density functional
Free energy

$$\begin{aligned}F'[\rho(t)]=k_BT\Big\{&\int d\mathbf{X}\rho(\mathbf{X},t)[\ln\rho(\mathbf{X},t)-1]\\&-\frac{1}{2}\int d\mathbf{X}d\mathbf{X}_1c_2(\mathbf{X},\mathbf{X}_1)\delta\rho(\mathbf{X},t)\delta\rho(\mathbf{X}_1,t)\\&-\frac{1}{6}\int d\mathbf{X}d\mathbf{X}_1d\mathbf{X}_2c_3(\mathbf{X},\mathbf{X}_1,\mathbf{X}_2)\delta\rho(\mathbf{X},t)\delta\rho(\mathbf{X}_1,t)\delta\rho(\mathbf{X}_2,t)+\cdots\end{aligned} \tag{4.3}$$

The eigen-values
Of hydrodynamic
Equations undergo
Sharp changes at
Molecular length scales
Due to the presence of
Intermolecular correlations.



Heat mode. Note
The near zero
value

$k_Q \sim 2\pi$

1. Wavenumber (q) dependence of the eigenvalues (z_i) of the extendec
ic modes. The wavenumber has been scaled by σ^{-1}, where σ is the molecula

closed set of generalized hydrodynamic equations for the time correlation functions of number density ρ, longitudinal momentum density g_l, temperature T, and transverse momentum density $t_i (i = 1, 2)$. $G_{\alpha\beta}(q, z)(\alpha, \beta = \rho, g_l, T, t_i)$ denotes the normalized time correlation functions in Fourier–Laplace (z) space. The equations of motion are the following:

$$zG_{\rho\beta}(q,z) - \frac{iq}{\sqrt{\beta m S(q)}} G_{l\beta}(q,z) = \delta_{\rho\beta}, \tag{20}$$

$$\begin{aligned} zG_{l\beta}(q,z) &- \frac{iq}{\sqrt{\beta m S(q)}} G_{\rho\beta}(q,z) - iq\left[\frac{2}{3\beta m}\right]^{1/2} \\ &\times \left[1 + 2\pi\rho\sigma^3 g(\sigma)\frac{j_1(q,\sigma)}{q\sigma}\right] G_{T\beta}(q,z) \\ &+ \frac{2}{3t_E}[1 - j_0(q\sigma) + 2j_2(q,\sigma)]G_{l\beta}(q,z) = \delta_{l\beta}, \end{aligned} \tag{21}$$

$$\begin{aligned} zG_{T\beta}(q,z) &- iq\left[\frac{2}{3\beta m}\right]^{1/2}\left[1 + 2\pi\rho\sigma^3 g(\sigma)\frac{j_1(q,\sigma)}{q\sigma}\right] G_{l\beta}(q,z) \\ &+ \frac{2}{3t_E}[1 - j_0(q\sigma)]G_{T\beta}(q,z) = \delta_{T\beta}, \end{aligned} \tag{22}$$

and $(i = 1, 2)$

$$\left[z + \frac{2}{3t_E}[1 - j_0(q\sigma) - j_2(q\sigma)]\right] G_{t_i\beta}(q,z) = \delta_{t_i\beta}. \tag{23}$$

Here $j_l(q\sigma)$ is the spherical Bessel function of order l, $g(\sigma)$ is the radial distribution function at contact, and $t_E = \sqrt{\beta m \pi}/4\pi\rho\sigma^2 g(\sigma)$ is the Enskog mean free time between collisions. The transport coefficients in the above expressions are given only by their Enskog values; that is, only collisional contributions are retained. Since it is only in dense fluids that the Enskog values represents the important contributions to transport coefficient, the above expressions are reasonable only for dense hard-sphere fluids. Earlier Alley, Alder, and Yip [32] have done molecular dynamics simulations to determine

Density Functional Theory of Freezing and Nucleation

- Since the density functional theory (DFT) allows a quantitative description of free energy cost due to the creation of a density in-homogeneity, this can be used to treat such phenomenon as freezing of a crystalline solid from homogeneous liquid, nucleation of a new phase, surface phenomena in general, wetting transition.
- Density functional theory was historically first used by van der Walls to describe gas-liquid interface. Its modern development is largely due to Yvon and to Lebowitz and Percus, Yang-Fleming-Gibbs.

DFT (continued)

- Density functional theory of freezing was developed by Ramakrishnan and Yusouff (1979,1981). This is known as RY theory. Earlier attempts (notably by Kirkwood and Monroe, 1941) failed because it was not based on proper, controlled set of approximations.
- DFT was used to develop a theory of nucleation of a crystal was used by Harowell and Oxtoby (HO).

DFT(continued)

- The essential ingredients of the density functional theory are the expansion coefficients which are the functional derivatives of free energy with respect to density
- C(r-r') = $\delta^2 F(\{\rho(r)\}) / \delta\rho(r)\delta\rho(r')$

The higher order derivatives of density with respect to The free energy gives higher order coefficients, like three Particle and four particle direct correlation functions.

We need to consider both the canonical free energy (that is, the Hemholtz free energy) and the grand canonical free energy.

Derivation of the Density functional Theory free energy Functional.

The essential step is The derivation of Local free energy Density.

(Lebowitz and Percus, ST and Buff, Yang, Fleming and Gibbs)

μ Is the chemical potential

We assume that the system is described by a classical Hamiltonian of the form

$$H = \text{K. E.} + \int d^3r\, U(\mathbf{r})\rho_M(\mathbf{r}) + \text{Pot. E}\ , \tag{A1}$$

where

$$\rho_M(\mathbf{r}) = \sum_{\alpha=1}^{N} \delta(\mathbf{r} - \mathbf{r}_\alpha)$$

is the microscopic density and $U(\mathbf{r})$ is an external potential. We have not specified the form of the interaction potential or even that the molecules interact pairwise. The only assumption that we require is that the interaction potential is short ranged.

The grand partition function for the system is given by

$$e^{W} = \mathrm{Tr}_{cl}\, e^{-\beta(H-\mu N)}\ , \tag{A2}$$

where the symbol Tr_{cl} has its usual meaning of

$$\sum_{N=0}^{\infty} \frac{1}{N!} \prod_{\alpha=1}^{N} \int \frac{d^3p_\alpha\, d^3r_\alpha}{h^6}\ .$$

h is Planck's constant and $\beta = 1/kT$, k being Boltzmann's constant. We define a dimensionless one-body potential

$$u(\mathbf{r}) = \beta\mu - \beta U(\mathbf{r})\ , \tag{A3}$$

where μ is the chemical potential. The thermodynamic

Definition
Of various
Free energy
functionals

The functional derivative of the grand partition function with respect to $u(r)$ gives

$$\frac{\delta W}{\delta u(r)} = \langle \rho_M(r) \rangle = \rho(r) \,. \tag{A4}$$

Thus W acts as a generating function, generating the local equilibrium density upon differentiation with respect to $u(r)$.

We define a dimensionless free energy by

$$F' = \int d^3r u(r)\rho(r) - W \,. \tag{A5}$$

F' is simply related to the Helmholtz free energy F by

$$\beta F = \beta(\mu N - PV) = \beta\mu N - W$$

$$= F' + \int d^3r \beta U(r)\rho(r) \,. \tag{A6}$$

The functional derivative of F' with respect to the density is

$$\frac{\delta F'}{\delta \rho(r)} = u(r) + \int d^3r' \rho(r') \frac{\delta u(r')}{\delta \rho(r)} - \int d^3r' \frac{\delta W}{\delta u(r')} \frac{\delta u(r')}{\delta \rho(r)}$$

$$= u(r) \,. \tag{A7}$$

For a system with no interaction, the density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \frac{e^{u(\mathbf{r})}}{\bar{\lambda}^3} , \tag{A8}$$

where $\bar{\lambda} = (\hbar^2/2m\pi)^{1/2}$ is the thermal wavelength. Thus, for this trivial case $u(\mathbf{r})$ is a simple functional of the density:

$$u(\mathbf{r}) = \ln\rho(\mathbf{r})\bar{\lambda}^3 . \tag{A9}$$

The free energy in the absence of interaction is

$$F' = F_0' \equiv \int d^3r\rho(\mathbf{r})\{\ln\rho(\mathbf{r})\bar{\lambda}^3 - 1\} . \tag{A10}$$

Equations (A8) and (A9) suggest that the effects of interaction may be treated in terms of an effective one-body potential. Thus we set

$$\rho(\mathbf{r}) = \frac{e^{u(\mathbf{r})+C(\mathbf{r})}}{\bar{\lambda}^3} \tag{A11}$$

or

$$u(\mathbf{r}) = \ln\rho(\mathbf{r})\bar{\lambda}^3 - C(\mathbf{r}) . \tag{A12}$$

The internal potential is seen to be a functional of the density $\rho(\mathbf{r})$. Clearly, it vanishes for zero density (for finite range of interaction), since the effects of interac

We shall derive an expression for the local free energy density by formally carrying out the functional integration. First we note that $C(\mathbf{r})$ can be derived from a potential

$$C(r) = \frac{\delta\Phi}{\delta\rho(\mathbf{r})} , \tag{A13}$$

where

$$\Phi = F_0' - F' . \tag{A14}$$

Hence all higher functional derivatives of $C(\mathbf{r})$ with respect to the density are symmetric:

$$C(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta C(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)} = \frac{\delta^2\Phi}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} = C(\mathbf{r}_2, \mathbf{r}_1) , \tag{A15a}$$

$$C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{\delta C(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)} = C(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3) , \text{ etc.}, \tag{A15b}$$

$$C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \frac{\delta C(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)\delta\rho(\mathbf{r}_4)} = C(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4) , \text{ etc.} \tag{A15c}$$

The second derivative of F' with respect to the density,

$$G^{-1}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta^2 F'}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} = \frac{\delta u(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)}$$

$$= \frac{1}{\rho(\mathbf{r}_1)}\,\delta(\mathbf{r}_1 - \mathbf{r}_2) - C(\mathbf{r}_1, \mathbf{r}_2) , \tag{A16}$$

$$C(\mathbf{r}) = \frac{\delta\Phi}{\delta\rho(\mathbf{r})} .$$

Hence we can expand the effective potential about its value for the uniform liquid C_l,

$$C(\mathbf{r}_1) = C_l + \int d\mathbf{r}_2\, C(\mathbf{r}_1, \mathbf{r}_2)[\rho(\mathbf{r}_2) - \rho_0] + \frac{1}{2}\int d\mathbf{r}_2\, d\mathbf{r}_3$$
$$\times C^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)[\rho(\mathbf{r}_2) - \rho_0][\rho(\mathbf{r}_3) - \rho_0] + \cdots , \quad \text{(II.11)}$$

where

$$C(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta^2\Phi}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} ,$$

$$C^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{\delta^3\Phi}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)} ,$$

and where ρ_0 is the density of the uniform liquid. Fo this uniform liquid $C(\mathbf{r}_1, \mathbf{r}_2)$ is rotationally invariant a therefore

$$C(\mathbf{r}_1, \mathbf{r}_2) = c(|\mathbf{r}_1 - \mathbf{r}_2|) ,$$

where $c(r)$ is the direct correlation function, usually introduced via the Ornstein–Zernike equation.

Similarly, we can expand the free energy Φ as

$$\Phi = \Phi_l + \int d\mathbf{r}_1\, C_l[\rho(\mathbf{r}_1) - \rho_0] + \frac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, C(\mathbf{r}_1, \mathbf{r}_2)$$

$$\times[\rho(\mathbf{r}_1) - \rho_0][\rho(\mathbf{r}_2) - \rho_0] + \frac{1}{6}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 C^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

$$\times[\rho(\mathbf{r}_1) - \rho_0][\rho(\mathbf{r}_2) - \rho_0][\rho(\mathbf{r}_3) - \rho_0] + \cdots . \qquad \text{(II.12)}$$

To second order in the expansion of $C(\mathbf{r}_1)$, the difference in the thermodynamic potential W for the nonuniform and uniform systems is

$$\Delta W = W - W_l$$

$$= -\int d\mathbf{r}_1 [\rho(\mathbf{r}_1) - \rho_0] + \frac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, C(\mathbf{r}_1, \mathbf{r}_2)$$

$$\times[\rho(\mathbf{r}_2) - \rho_0][\rho(\mathbf{r}_1) + \rho_0] . \qquad \text{(II.13)}$$

This is the main result of this section. For the liquid-

For Helmholtz Free energy

$$F = F_\ell + \int d\underset{\sim}{r}\; \rho(\underset{\sim}{r})\left[\ln \lambda^3 \rho(\underset{\sim}{r}) - 1\right]$$

$$- \frac{1}{2}\int d\underset{\sim}{r}\int d\underset{\sim}{r}'\; c(r-r')\,\delta\rho(r)\,\delta\rho(r')$$

$$+ \frac{1}{6}\int d\underset{\sim}{r}\int d\underset{\sim}{r}'\int d\underset{\sim}{r}'\; c(\underset{\sim}{r},\underset{\sim}{r}',\underset{\sim}{r}'')\,\delta\rho(\underset{\sim}{r})\,\delta\rho(\underset{\sim}{r}')\,\delta\rho(\underset{\sim}{r}'')$$

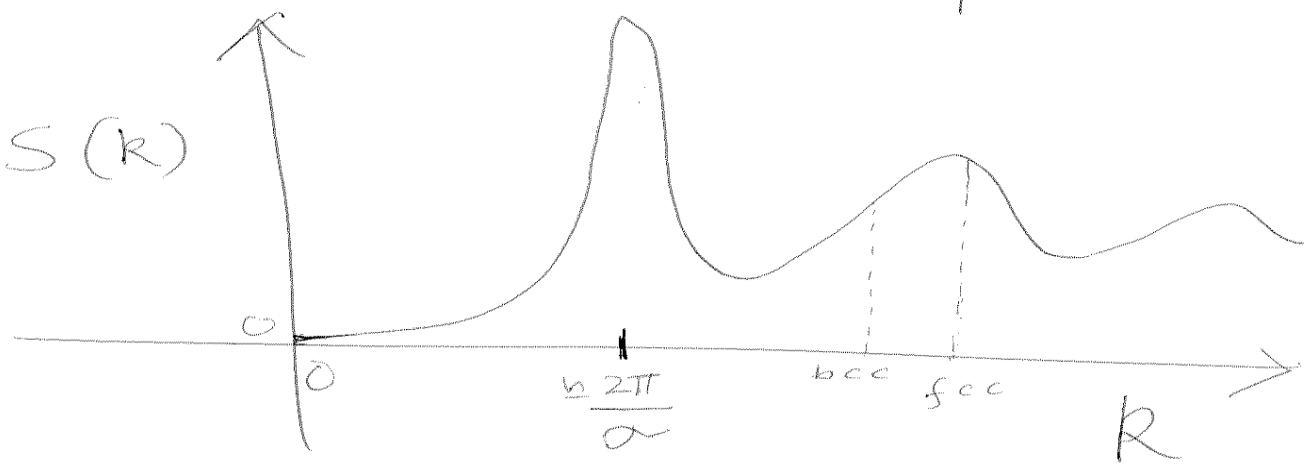
Minimization wrt to $\delta\rho(r)$ gives

$$\rho(\underset{\sim}{r}) = c\; e^{\int d\underset{\sim}{r}'\, c(r-r')\,\delta\rho(r')}$$

$$\rightarrow \boxed{\rho(\underset{\sim}{r}) = \rho_\ell\; e^{\int d\underset{\sim}{r}'\, c(r-r')\,\delta\rho(r')}}$$

Density Functional Theory of Freezing

What are the order parameters?



σ = Molecular diameter

$$\rho(\underset{\sim}{r}) = \rho_l(1+\phi_0) + \rho_l \sum_{\{\underset{\sim}{G}\}} \phi_{\underset{\sim}{G}}\, e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}$$

Order parameters of freezing

- Because liquid is isotropic, the order parameters are determined by the amplitude of the reciprocal lattice vectors. Thus, all the (+-1,+-1,+-1)$2\pi/a$, RLVs where a is the cell length, of the first set of fcc lattice vectors have the same order parameter.
- In principle, one has infinite number of RLVs – so infinite number of order parameters.
- In practice, one often finds good agreement with first two set of RLVs.

Order parameters (continued …

- The minimal model one can construct is the two order parameter model : one order parameter for density change and one parameter for the first set of RLV. In this case, we have two unknowns, ϕ_0 and ϕ_{G1}.
- The values of these parameters are zero in the liquid phase but become non-zero in the solid phase.

Expression for Order Parameter

$$1+\phi_0 = e^{c_0\phi_0}\frac{1}{\Delta}\int_{\Delta} d\underset{\sim}{r}\; e^{\sum c_G\phi_G e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}}$$

$$\phi_G = e^{c_0\phi_0}\frac{1}{\Delta}\int d\underset{\sim}{r}\, e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}\, e^{\sum c_G\phi_G e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}}$$

Let us consider G_1 of fcc

$$\underline{G_1} = (\pm 1, \pm 1, \pm 1)\, 2\pi/a$$

$$\sum e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}} = 8\cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right)$$

so,

$$1+\phi_0 = e^{c_0\phi_0}\frac{1}{a^3}\int_0^{2\pi/a}dx\int_0^{2\pi/a}dy\int_0^{2\pi/a}dz\; e^{\left(c_{G_1}\phi_{G_1}\, 8\cos\frac{2\pi}{a}x\cos\frac{2\pi}{a}y\cos\frac{2\pi}{a}z\right)}$$

$$\phi_{G_1} = e^{c_0 \phi_0} \frac{1}{\Delta} \int dx \int dy \int dz$$

$$\cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right)$$

$$e^{c_{G_1}\phi_{G_1}\, 8 \cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right)}$$

Thus, 2 order parameters, 2 unknowns.

But we need to know the density of transition.

$$\frac{\Delta W}{N} = (-1 + c_0)\phi_0 + \frac{1}{2} c_0 \phi_0^2 + \frac{1}{2} \sum c_G \phi_G^2$$

$$= 0$$

Bifurcation Analysis

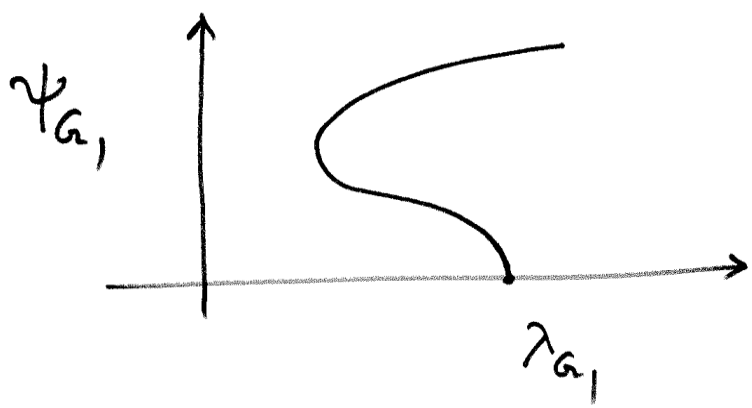
Note that if we make

$$\frac{\rho_\ell}{\rho_s}\,\phi_{G_\alpha} = \psi_{G_\alpha}$$

$$(1+\phi_0)\,c_{G_\alpha} \equiv \rho_s\, c_{G_\alpha} = \lambda_{G_\alpha}$$

we get

$$\psi_{\underset{\sim}{G}_\alpha} = \frac{\int d\underset{\sim}{r}\;\xi_{\underset{\sim}{G}_\alpha}(\underset{\sim}{r})\, e^{\sum_G \psi_G \lambda_G \xi_G(r)}}{\int d\underset{\sim}{r}\;\; e^{\sum \psi_G \lambda_G \xi_G(r)}}$$



|| Alternative description of Ordering ||

$$\Delta\rho(\underset{\sim}{r}) = \rho(\underset{\sim}{r}) - \rho_\ell$$

$$\Delta\rho(\underset{\sim}{r}) = \sum_{\{R_i\}} a_i \, e^{-\alpha_i (\underset{\sim}{r} - \underset{\sim}{R}_i)^2}$$

Sum is over the lattice site positions.

<u>Steps</u> :

Minimize free energy wrt to a_i and α_i.

Set $\Delta W = 0$

Results from the DFT theory of freezing

- The transition parameters like density and temperature are in good agreement with expts and simulation results. The temperature dependence of Debye-Waller factors of the solid are also in semi-quantitative agreement.
- The status of entropy of freezing is less clear. It seems fluctuation in order parameter values needs to be included.
- But overall it is a very satisfactory theory of freezing which can distinguish between various lattices in terms of liquid state properties.

Role of fluctuations

- It is not clear how to describe the role of fluctuations within the DFT theory. Liquid → solid transition usually occurs to defective solids.
- The study of freezing of water into ice has not been worked out in detail.

Projection Operator Formalism

Zwanzig showed how a powerful but simple technique, known as the projection operator technique, can be used to derive the relaxation equations [12]. Let us consider a vector $A(t)$, which represents an arbitrary property of the system. Since the time evolution of the system is given by the Liouville operator, the time evolution of the vector can be written as $A(\mathbf{q}, t) = e^{iLt}A(\mathbf{q})$, where A is the initial value. A projection operator P is defined such that it projects an arbitrary vector on $A(\mathbf{q})$. P can be written as

$$P \equiv (\cdots|A^*(\mathbf{q}))(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}A(\mathbf{q}), \tag{63}$$

where the brackets denote the classical scalar product, as has been defined in the derivation of viscosity. Another projection operator Q is defined in such a way that it projects an arbitrary vector on the subspace which is orthogonal to A. Thus Q can be written as

$$Q \equiv \mathbf{1} - P. \tag{64}$$

The time derivative of $A(\mathbf{q}, t)$ can be written as

$$\frac{\partial A(\mathbf{q}, t)}{\partial t} = e^{iLt}iLA(\mathbf{q}) \tag{65}$$

The identity, $P + Q = \mathbf{1}$ when inserted in the above equation, it can be rewritten as

$$\frac{\partial A(\mathbf{q}, t)}{\partial t} = e^{iLt}(P + Q)iLA(\mathbf{q}). \tag{66}$$

An important step in the derivation of relaxation equation is to apply the identity satisfied by the propagator e^{iLt}:

$$e^{iLt} = e^{iQLt} + \int_0^t d\tau e^{iL(t-\tau)} iPLe^{iQL\tau} \tag{67}$$

Using this identity, Eq. (66) can be rewritten in the following form:

$$\frac{\partial A(\mathbf{q}t)}{\partial t} = e^{iLt} PiLA(\mathbf{q}) + e^{iQLt} QiLA(\mathbf{q}) + \int_0^t d\tau e^{iL(t-\tau)} iPLe^{iQL\tau} QiLA(\mathbf{q}). \tag{68}$$

Let us now define the following quantities. The frequency $\Omega(\mathbf{q})$ is

$$\Omega(\mathbf{q}) \equiv (LA(\mathbf{q})|A^*(\mathbf{q}))(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}. \tag{69}$$

The random force $F(\mathbf{q}, \tau)$ is defined as

$$F(\mathbf{q}, \tau) = e^{iQL\tau} QiLA(\mathbf{q}) - Qe^{iQL\tau} QiLA(\mathbf{q}) = QF(\mathbf{q}, \tau). \tag{70}$$

This implies that random force remains orthogonal to $A(\mathbf{q})$ at all times.

The last integral in Eq. (68) involves the term $iPLF(\mathbf{q},\tau)$, which can be rewritten as

$$iPLF(\mathbf{q},\tau) = iPLQF(\mathbf{q},\tau) = (iLQF(\mathbf{q}\tau)|A^*(\mathbf{q}))(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}A(\mathbf{q}). \quad (71)$$

Since Q and L are both Hermitian, $iPLF(\mathbf{q},\tau)$ can be written as

$$\begin{aligned} iPLF(\mathbf{q},\tau) &= (iLQF(\mathbf{q},\tau)|A^*(\mathbf{q}))(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}A(\mathbf{q}) \\ &= -(F(\mathbf{q},\tau)|(QiLA(\mathbf{q}))^*)(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}A(\mathbf{q}) \\ &= -(F(\mathbf{q},\tau)|F^*(\mathbf{q},0))(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}A(\mathbf{q}). \end{aligned} \quad (72)$$

Now we define the memory function $\Gamma(\tau)$ as

$$\Gamma(\mathbf{q},\tau) \equiv +(F(\mathbf{q},\tau)|F^*(\mathbf{q},0))(A(\mathbf{q})|A^*(\mathbf{q}))^{-1}. \quad (73)$$

With the definition of the frequency and memory function, Eq. (68) can be rewritten as

$$\frac{\partial A(\mathbf{q},t)}{\partial t} = i\Omega(\mathbf{q})A(\mathbf{q},t) - \int_0^t d\tau\Gamma(\mathbf{q},\tau)A(\mathbf{q},t-\tau) + F(\mathbf{q},t). \tag{74}$$

Thus the equation for the time correlation function can be written as

$$\frac{\partial C(\mathbf{q},t)}{\partial t} = i\Omega(\mathbf{q})C(\mathbf{q},t) - \int_0^t d\tau\Gamma(\mathbf{q},\tau)C(\mathbf{q},t-\tau), \tag{75}$$

where $C(\mathbf{q},t) = (A(\mathbf{q},t)|A^*(\mathbf{q}))$. Equation (75) is the generalized relaxation equation and is also known as the memory function equation.

In the above discussion, only a single variable was considered. This can be extended to evaluate the time evolution of many coupled variables—for example, the five hydrodynamical variables. In that case, A is not a single variable but a column matrix and $C(\mathbf{q},t) = (A(\mathbf{q},t)|A^+(\mathbf{q}))$ is now the correlation matrix. $\Omega(\mathbf{q})$ and $\Gamma(\mathbf{q},\tau)$ are the frequency and the memory function matrices, respectively [20].

Basic ingredients of mode coupling theory

- Derivation of the Relaxation Equations for a set of dynamical variable {A} by using projection operator technique
- The resulting equation of motion for the correlation function is essentially a GLE

$$\frac{dC(q,t)}{dt} = \Omega_0(q)C(q,t) - \int_0^t d\tau M(q,t-\tau)C(q,\tau)$$

This equation is commonly written in the frequency plane
In the following form

$$C(q,z) = \frac{C(q,t=0)}{z - \Omega_0\ (q) + M(q,z)}$$

- where M(q,z) is the memory function which is defined in terms of force-force time correlation function. The force F(q,t) must be orthogonal to the dynamical variable.
- In the next step, one usually writes down a continued fraction representation (equation) for M(q,z) because one often knows the t=0 value of M(q,t=0).

Memory function from MCT

- This is done by a self-consistent calculation.
- But first an expression for memory function is obtained by projecting on the binary product of relevant modes.
- Question is : how to choose these modes?
- Learn from examples.

Velocity auto-correlation function

$$Z(t) = \left(u_{ix}, \exp(i\mathcal{L}t)u_{ix}\right)$$

Replacing full evolution operator by its projection on the subspace of product variables $\rho_{\mathbf{k}i}\mathbf{j}_{-\mathbf{k}}$:

$$\exp(i\mathcal{L}t) \approx \mathcal{P}\exp(i\mathcal{L}t)\mathcal{P}$$

Where projector is defined by

$$\mathcal{P}B = \sum_{\mathbf{k}}\sum_{\alpha}\left(\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}, B\right)\left(\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}, \rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}\right)^{-1}\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}$$

Theory of simple liquids By J. P. Hansen, I. R. McDonald

Equation of *Z(t)* becomes

$$
\begin{aligned}
Z(t) &\approx \left(u_{ix}, \mathcal{P}\exp(i\mathcal{L}t)\mathcal{P}u_{ix}\right) \\
&= \sum_{\mathbf{k},\mathbf{k}'}\sum_{\alpha}\sum_{\beta}\left(\rho_{\mathbf{k}'i}\, j^{\beta}_{-\mathbf{k}'}, u_{ix}\right)\left(\rho_{\mathbf{k}'i}\, j^{\beta}_{-\mathbf{k}'}, \rho_{\mathbf{k}'i}\, j^{\beta}_{-\mathbf{k}'}\right)^{-1} \\
&\quad \times \left(\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}, \exp(i\mathcal{L}t)\rho_{\mathbf{k}'i}\, j^{\beta}_{-\mathbf{k}'}\right) \\
&\quad \times \left(\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}, \rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}\right)^{-1}\left(u_{ix}, \rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}\right)
\end{aligned}
$$

Since

$$\langle \rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}} \rho_{-\mathbf{k}i}\, j^{\alpha}_{\mathbf{k}} \rangle = N(k_{\mathrm{B}}T/m) \text{ and } \langle u_{ix}\, \rho_{-\mathbf{k}i}\, j^{\alpha}_{\mathbf{k}} \rangle = (k_{\mathrm{B}}T/m)\delta_{\alpha x}$$

Which follows

$$\left(\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}, \rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}\right)^{-1} \left(u_{ix}, \rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}\right) = \frac{1}{N}\delta_{\alpha x}$$

Four-variable correlation functions are factorized into products of two-variable correlation functions

$$\begin{aligned}\left(\rho_{\mathbf{k}i}\, j^{\alpha}_{-\mathbf{k}}, \exp(i\mathcal{L}t)\rho_{\mathbf{k}'i}\, j^{\beta}_{-\mathbf{k}'}\right) &\approx \left(\rho_{\mathbf{k}i}, \exp(i\mathcal{L}t)\rho_{\mathbf{k}'i}\right)\left(j^{\alpha}_{-\mathbf{k}}, \exp(i\mathcal{L}t)\, j^{\beta}_{-\mathbf{k}'}\right)\delta_{\mathbf{k},\mathbf{k}'} \\ &\equiv \left\langle \rho_{\mathbf{k}i}(t)\rho_{-\mathbf{k}i}\right\rangle \left\langle j^{\beta}_{-\mathbf{k}}(t)\, j^{\alpha}_{\mathbf{k}}\right\rangle\end{aligned}$$

Therefore

$$Z(t) = \frac{1}{N^2} \sum_{\mathbf{k}} \langle \rho_{\mathbf{k}i}(t) \rho_{-\mathbf{k}i} \rangle \langle j^x_{\mathbf{k}}(t) j^x_{-\mathbf{k}} \rangle$$

The first factor is the *self intermediate scattering function $F_s(k, t)$* and the second is a *current correlation function*

Switching from a sum to an integral and replacing the current correlation function by its average over a sphere

$$Z(t) = \frac{1}{3\rho}(2\pi)^{-3} \int F_s(k,t) \frac{1}{k^2} \left[C_l(k,t) + 2C_t(k,t) \right] \mathrm{d}\mathbf{k}$$

as $t \rightarrow 0$, $Z(t)$ diverges, since $F_s(k, t = 0) = 1$ and $C_l(k, t = 0) = C_t(k, t = 0) = k^2(k_B T/m)$

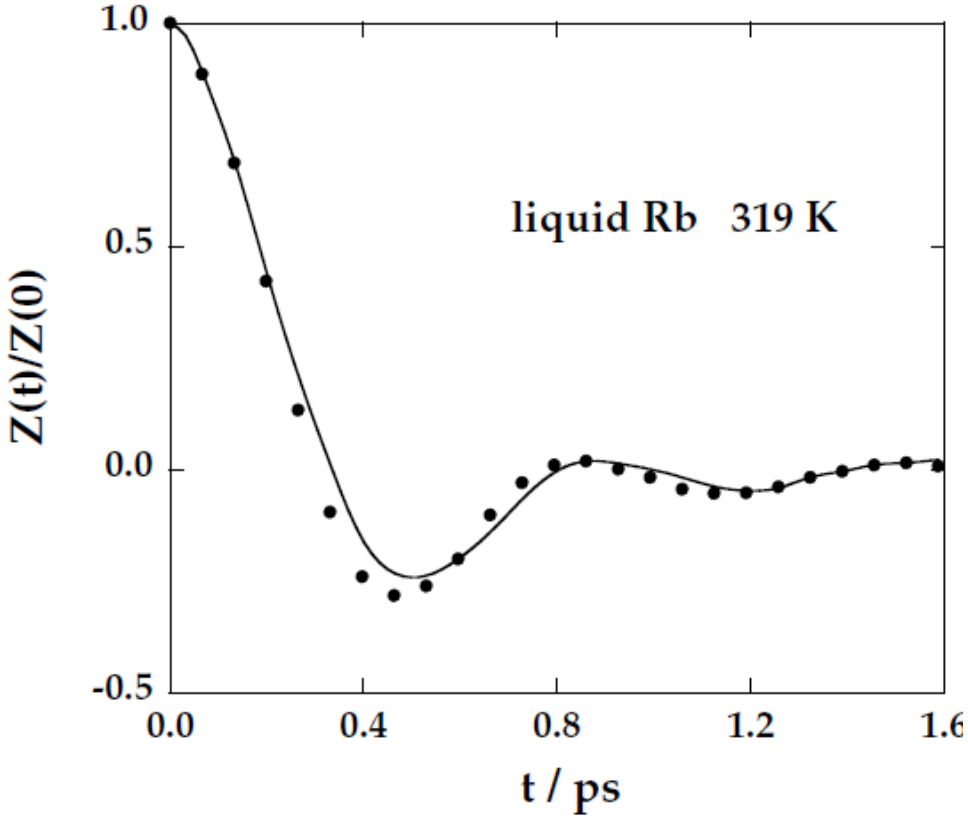
By introducing a 'form factor' $f(r)$ which ensure a cut-off at large wavenumbers this difficulty can be avoided

The expression for $Z(t)$ becomes

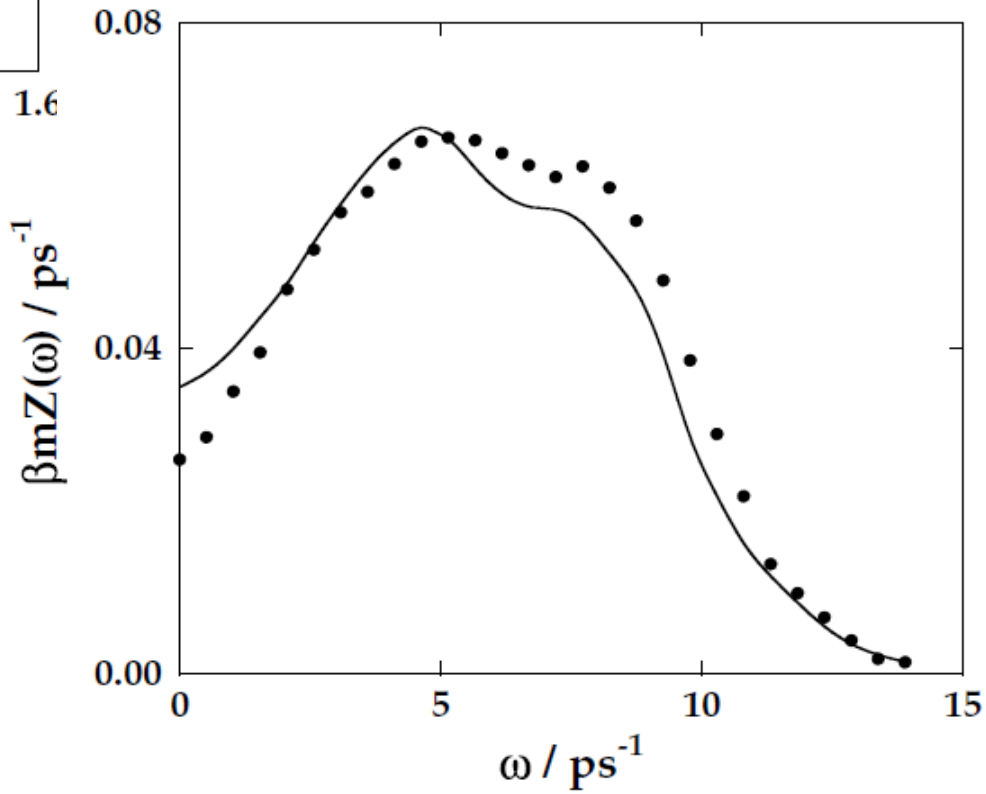
$$Z(t) = \tfrac{1}{3}(2\pi)^{-3} \int \hat{f}(k) F_s(k,t) \frac{1}{k^2} \left[C_l(k,t) + 2C_t(k,t) \right] \mathrm{d}\mathbf{k}$$

Exact frequency moments of $Z(\omega)$ can also be used to improve the short time behavior of the mode coupling approximation. Which gives

$$M_{2l,t}(t) = \frac{\Omega_0^2 m}{3\rho k_B T} (2\pi)^{-3} \int \mathcal{V}_{l,t}^2(k) F_s(k,t) \frac{1}{k^2} C_{l,t}(k,t) \, \mathrm{d}\mathbf{k}$$



Normalized velocity autocorrelation function (above) and the corresponding power spectrum (below) for a model of liquid rubidium



Dielectric friction on a slowly rotating solute

The dielectric friction is given by a time integral over the torque-torque correlation function

$$\Delta\xi_{\mathrm{DF}} = \frac{1}{2k_{\mathrm{B}}T}\int_0^\infty \mathrm{d}t\,\langle\,\delta\tau(\boldsymbol{\omega},0)\,\delta\tau(\boldsymbol{\omega},t)\,\rangle$$

The torque is

$$\tau(\boldsymbol{\omega},t) = \frac{1}{\beta}\nabla_\omega \int \mathrm{d}\boldsymbol{r}' \int \mathrm{d}\boldsymbol{\omega}'\; C_{\mathrm{s0}}(\boldsymbol{r}',\boldsymbol{\omega},\boldsymbol{\omega}')\,\delta\rho_0(\boldsymbol{r}',\boldsymbol{\omega}',t)\,.$$

G. V. Vijaydamodar, A. Chandra and B. Bagchi, Chem. Phys. Lett. **161**, 413 (1989).

Density fluctuation can be expand in spherical harmonics as

$$\delta\rho_s(\omega,t)=\sum_{lm}A_{lm}(t)Y_{lm}(\omega)$$

$$\delta\rho_0(k,\omega,t)=\sum_{lm}a_{lm}(k,t)Y_{lm}(\omega)$$

Direct correlation function can also be expand in similar way as

$$C(k,\omega,\omega')=\sum_{l_1l_2m_1}C(l_1l_2m_1;k)Y_{l_1m_1}(\omega)Y_{l_2m_1}(\omega')$$

Therefore torque-torque correlation function becomes

$$\langle \delta\tau(\boldsymbol{\omega}, t)\, \delta\tau(\boldsymbol{\omega}, 0) \rangle$$

$$= \frac{1}{(2\pi)^6 \beta^2} \left\langle \left[\int \mathrm{d}\boldsymbol{k}\, \nabla_\omega \left(\sum_{m_1=-1}^{1} (-1)^{m_1} C_{s0}(11m_1; k)\, a_{1m_1}(\boldsymbol{k}, t)\, Y_{1m_1}(\omega) \right) \right] \right.$$

$$\left. \times \left[\int \mathrm{d}\boldsymbol{k}'\, \nabla_\omega \left(\sum_{m_2=-1}^{1} (-1)^{m_2} C_{s0}(11m_2; k')\, a_{1m_2}(\boldsymbol{k}')\, Y_{1m_2}(\omega) \right) \right] \right\rangle .$$

Using the expressions for solvent-solvent correlation functions $\langle a_{lm}(-\boldsymbol{k})\, a_{lm}(\boldsymbol{k}, t)\rangle$

$$\langle a_{10}(-\boldsymbol{k})\, a_{10}(\boldsymbol{k}, t)\rangle = \langle a_{10}^2(\boldsymbol{k})\rangle \exp(-t/\tau_{\mathrm{L}}(k)) ,$$

$$\langle a_{11}(-\boldsymbol{k})\, a_{11}(\boldsymbol{k}, t)\rangle = \langle a_{11}^2(\boldsymbol{k})\rangle \exp(-t/\tau_{\mathrm{T}}(k)) ,$$

with

$$\langle a_{10}^2(\boldsymbol{k})\rangle = \frac{N}{4\pi}\left[1 + \frac{\rho_0 h(110; k)}{4\pi}\right],$$

$$\langle a_{11}^2(\boldsymbol{k})\rangle = \frac{N}{4\pi}\left[1 - \frac{\rho_0 h(111; k)}{4\pi}\right],$$

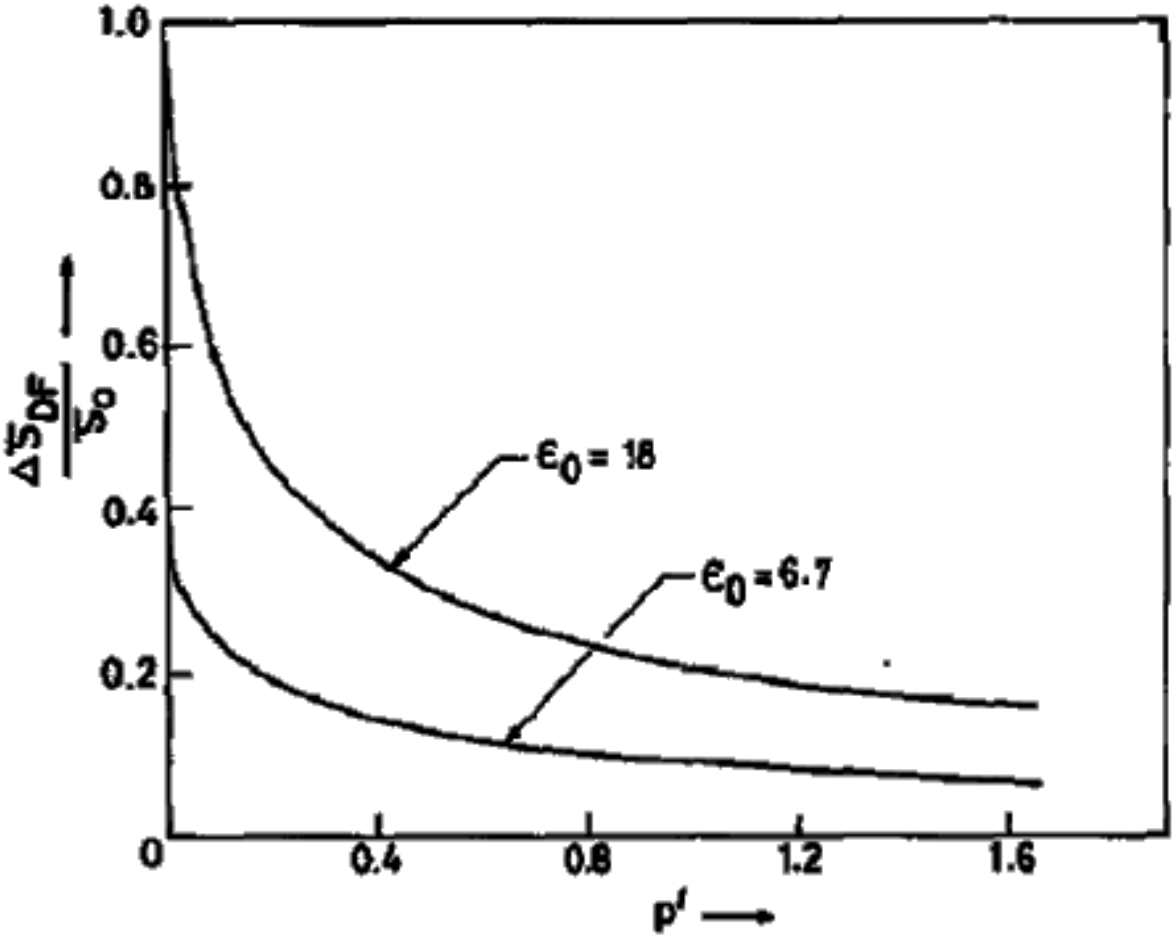
$$\tau_{\mathrm{L}}(k) = (2D_{\mathrm{R}})^{-1}\left\{[1 + p'(k\sigma)^2]\left[1 - \frac{\rho_0}{4\pi} C(110; k)\right]\right\}^{-1},$$

$$\tau_{\mathrm{T}}(k) = (2D_{\mathrm{R}})^{-1}\left\{[1 + p'(k\sigma)^2]\left[1 + \frac{\rho_0}{4\pi} C(111, k)\right]\right\}^{-1},$$

The final expression for dielectric friction is

$$\Delta\zeta_{\mathrm{DF}} = \frac{1}{2(2\pi)^4\beta}\int \mathrm{d}\boldsymbol{k}\,[C_{s0}^2(110;k)\langle a_{10}^2(\boldsymbol{k})\rangle\tau_{\mathrm{L}}(k)$$

$$+2C_{s0}^2(111;k)\langle a_{11}^2(\boldsymbol{k})\rangle\tau_{\mathrm{T}}(k)]$$



The effect of translational diffusion on the dielectric friction of a rotating dipolar hard sphere. ζ_0 is that part of the friction coefficient arising from short-range interactions and is related to $D_R^{\,0}$ by the Stokes-Einstein relation.

3rd order Raman

Classically 3rd order response is

$$R^{(3)}_{\chi\lambda\mu\nu}(t) = -\theta(t)\beta\frac{d}{dt}C_{\chi\lambda\mu\nu}(t).$$

Where

$$C_{\chi\lambda\mu\nu}(t) = \langle \Pi_{\chi\lambda}(t)\Pi_{\mu\nu}(0)\rangle.$$

$$\Pi_{\chi\lambda}(t) = N\alpha^2\delta_{\chi\lambda} + \alpha^2\sum_i \sum_{\substack{j>i \\ j}} T_{\chi\lambda}(\mathbf{r}_{ij}(t))$$

Specific tensor components of total polarizability

$$T_{\chi\lambda}(\mathbf{r}) = \frac{1}{r^3}\left(3\frac{\mathbf{r}_\chi\mathbf{r}_\lambda}{r^2} - \delta_{\chi\lambda}\right).$$

Component of the dipole interaction tensor

R. A. Denny and D. R. Reichman, J Chem Phys **116**, 1979 (2002)

The correlation function of interest

$$C_{zzzz}(t) = \langle T_{zz}(t) T_{zz}(0) \rangle,$$

Interaction induced form

$$C_{zzzz}(t) = \int d\mathbf{r} \int d\mathbf{r}' \, A(\mathbf{r}) A(\mathbf{r}') \mathcal{G}(\mathbf{r},0;\mathbf{r}',t)$$

where

$$\mathcal{G}(\mathbf{r},0;\mathbf{r}',t) = \frac{1}{N} \sum_i \sum_{\substack{j \neq i \\ j}} \sum_k \sum_{\substack{l \neq k \\ l}} \langle \delta[\mathbf{r}_{ij}(0) - \mathbf{r}] \delta[\mathbf{r}_{kl}(t) - \mathbf{r}'] \rangle$$

For a simple dense liquid, the dynamics of the variable $T_{zz}(r)$ may be decomposed into the dynamics of fluctuating pairs of density variables.

$$\sum_{i} \sum_{\substack{j \neq i \\ j}} \mathbf{T}_{zz}(\mathbf{r}_{ij}) = \sum_{\mathbf{k}} \mathbf{T}_{zz}^{\mathbf{k}} (\rho_{-\mathbf{k}} \rho_{\mathbf{k}} - N)$$

where $\mathbf{T}_{zz}^{\mathbf{k}}$ is the Fourier transform of the dipole interaction tensor, and $\rho_{\mathbf{k}} = \sum_{i=1}^{N} \exp(i\mathbf{k} \cdot \mathbf{r}_i)$ is the Fourier transform of the position dependent density.

Therefore

$$\exp(iLt) \rightarrow \wp \exp(iLt) \wp$$

Where

$$\wp(A) = \lim_{q \to 0} \frac{1}{2N^2} \sum_{\mathbf{k}} \frac{\hat{R}_{\mathbf{k},\mathbf{q}-\mathbf{k}}}{S(k)S(|q-k|)} \langle \hat{R}^{\dagger}_{\mathbf{k},\mathbf{q}-\mathbf{k}} A \rangle$$

Here $\hat{R}_{\mathbf{k},\mathbf{q}-\mathbf{k}} = \rho_{\mathbf{k}} \rho_{\mathbf{q}-\mathbf{k}}$, and *S(k)* is the static structure factor at wave vector k $[S(k) = (1/N)\langle \rho - \mathbf{k} \rho_{\mathbf{k}} \rangle]$

Projection of $\sum_i \sum_{j \neq i} \mathbf{T}_{zz}(\mathbf{r}_{ij})$ on to $\hat{R}^{\dagger}_{\mathbf{k},-\mathbf{k}}$ divided by *N* will be denoted $V_{zz}(\mathbf{k})$ and is called static vertex.

Therefore for a simple dense liquid the correlation function can be expressed as

$$\boxed{C_{zzzz}(t) = \frac{1}{4N^2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \frac{V_{zz}(\mathbf{k})}{S(k)^2} \frac{V_{zz}(\mathbf{k}')}{S(k')^2} \langle \hat{R}^{\dagger}_{\mathbf{k},-\mathbf{k}} \hat{R}_{\mathbf{k}',-\mathbf{k}'}(t) \rangle.}$$

$$\langle \hat{R}^{\dagger}_{\mathbf{k},-\mathbf{k}} \hat{R}_{\mathbf{k}',-\mathbf{k}'}(t) \rangle \approx N^2 (\delta_{\mathbf{k},\mathbf{k}'} + \delta_{\mathbf{k},-\mathbf{k}'}) F(k,t)^2$$

Where

$$F(k,t) = \frac{1}{N} \langle \rho_{-\mathbf{k}} \rho_{\mathbf{k}}(t) \rangle$$

The vertex,

$$V_{zz}(\mathbf{k}) = \frac{1}{N}\left\langle \sum_i \sum_{\substack{j>i \\ j}} \mathbf{T}_{zz}(\mathbf{r}_{ij})\hat{R}_{\mathbf{k},-\mathbf{k}} \right\rangle,$$

essentially has the rotational symmetry

$$V_{zz}(\mathbf{k}) = \left(\frac{3\cos^2(\theta_{\mathbf{k}}) - 1}{2}\right)\tilde{V}_{zz}(k),$$

Therefore

$$\boxed{C_{zzzz}(t) = \frac{N}{20\pi^2\rho}\int dk\, k^2 \left(\frac{\tilde{V}_{zz}(k)}{S(k)^2}\right)^2 F(k,t)^2.}$$

$F(k,t)$ is computed within the simple Lovesey approximation,

$$F(k,z)=\cfrac{S(k)}{z+\cfrac{\langle\omega_k^2\rangle}{z+\cfrac{\Delta_k}{z+\left(\cfrac{1}{\tau_k}\right)}}},$$

where $F(k,z)$ is the Laplace transform of $F(k,t)$, $\langle\omega_k^2\rangle=[k_BTk^2/mS(k)]$, $\Delta_k=\omega_L^2(k)-\langle\omega_k^2\rangle$,

$$\omega_L^2=\frac{3k_BTk^2}{m}+\frac{\rho}{m}\int d\mathbf{r}\frac{\partial^2\phi(r)}{\partial z^2}[1-\exp(-ikz)]g(r),$$

and $1/\tau_k=2\sqrt{\Delta_k}/\pi$.

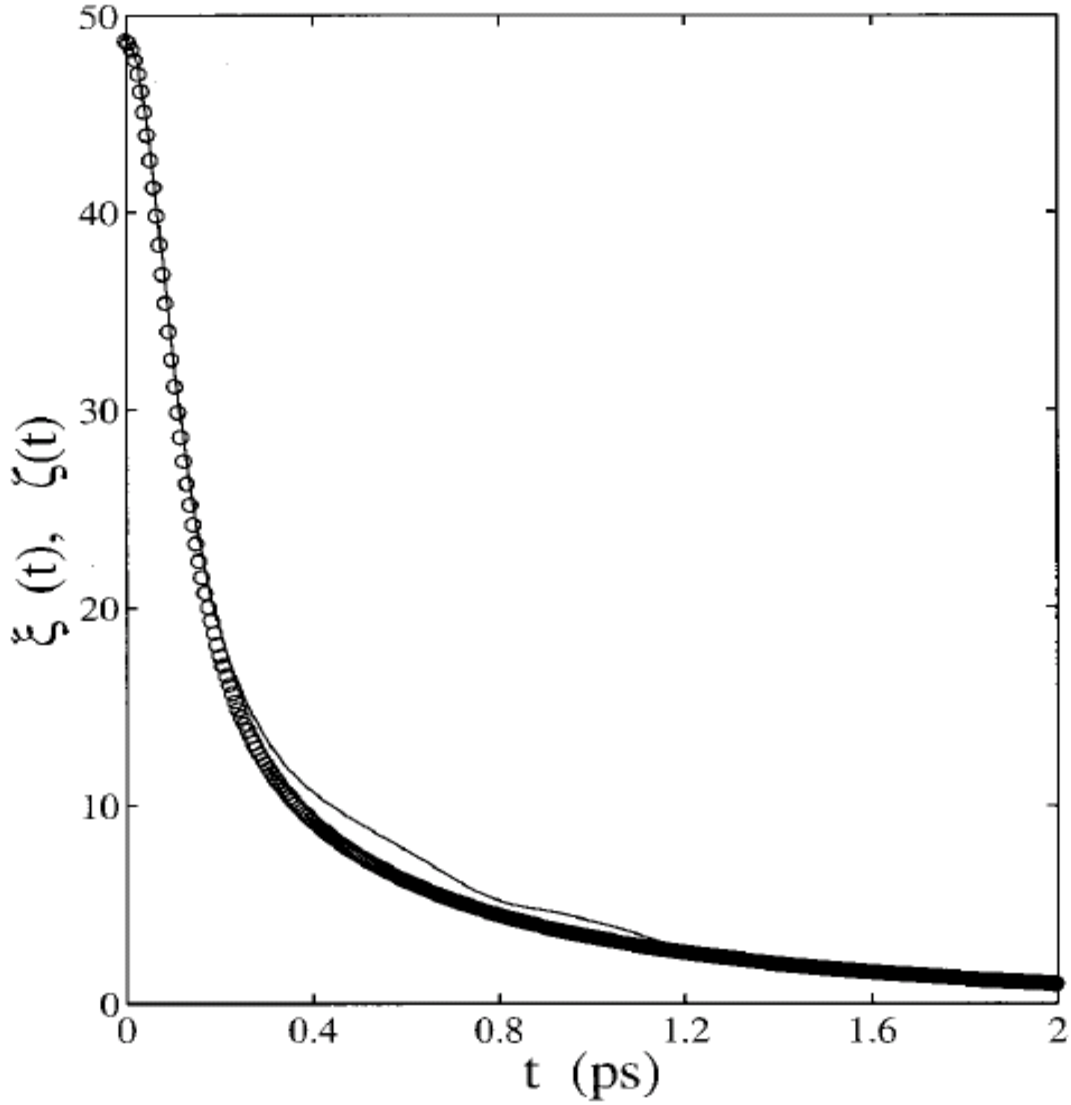


FIG. 1. Comparison of $\xi(t)$ [Eq. (4.4)] (solid line) and $\zeta(t)=\Sigma_k^{k_c}F(k,t)^2$ (open circles), shown for the state point $\rho^*=0.844$ and $T^*=0.728$ for a liquid Argon system. All input is simulated on a k-space grid with a cutoff k_c. Here k_c has a value of $31.17\sigma^{-1}$.

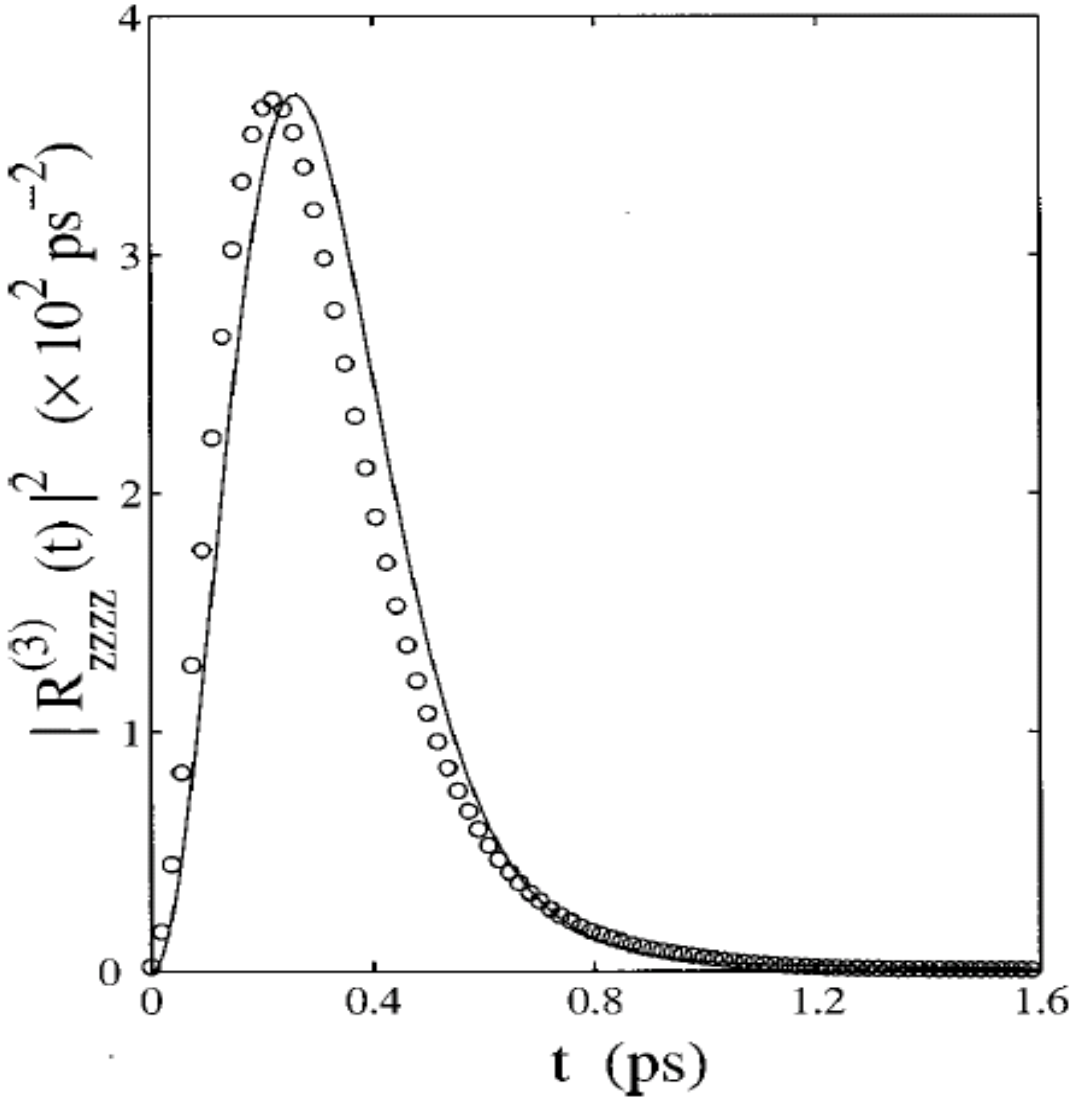


FIG. 2. Plot of $|R^{(3)}_{zzzz}(t)|^2$ vs t liquid xenon from theory (solid line) and simulation (open circles). The wave vector cutoff, $q_c = 9.05\sigma^{-1}$, $\rho^* = 0.7$, and $T^* = 1.0$.

- The calculation of the memory function for M(q,z) is often done by the mode coupling theory. The modes are usually the binary product of slow variables which are chosen to be orthogonal to the dynamical variable. In the language of projection operator technique, one projects the force term on the sub-space of binary product of slow variables.
- **In the theory of glass transition, the primary dynamical variable in question is the wavevector dependent density. M(q,z) is then the longitudinal current tcf and the memory function of longitudinal current is longitudinal viscosity (vide hydrodynamics).

EXACT EXPRESSION

$$\phi(z) = \frac{1}{z + \dfrac{<\omega_q^{\,2}>}{z + D_l(q,z)}} \qquad (1)$$

Write the continued fraction representation

$$\ddot{\phi}(q,t) + <\omega_q^{\,2}>\phi(q,t) + \int_0^t d\tau D_l(q,t-\tau)\dot{\phi}(q,\tau) = 0 \qquad (2)$$

Replace the expression of the memory function

$$\ddot{\phi}(t) + \gamma\dot{\phi}(t) + <\omega_q^{\,2}>\phi(t) + 4\lambda <\omega_q^{\,2}> \int_0^t d\tau \phi^2(\tau)\dot{\phi}(t-\tau) = 0 \qquad (3a)$$

Rewriting the longitudinal viscosity as

$$D_l(z) = \gamma + 4\lambda < \omega_q{}^2 > \mathrm{L}\left\{\phi^2(t)\right\} \qquad (3b)$$

In zeroth order, the longitudinal viscosity is

$$D_l(z) = \gamma$$

Use of this approximation in the continued fraction gives two poles in the DSF

$$\phi(z) = \frac{a_1}{z + i\nu_1} + \frac{a_2}{z + i\nu_2}$$

Use Of this DSF gives, to the first order,

$$D_l(z) = \gamma + \cfrac{4\lambda}{z + \cfrac{2}{z + \gamma + \cfrac{2}{z + 2\gamma}}}$$

The zero frequency value of the longitudinal viscosity is

$$D_l(z=0)=\gamma+2\lambda(\gamma+1/\gamma)$$

This value is greater than the zeroth order value by $\gamma+1/\gamma$

Each iteration increases the value of the viscosity, leading to a divergence, leading to an elastic peak in the. Dynamic structure factor. This is the famous feed-back mechanism(Geszti, 1983). Therefore, we make the ansatz

$$\phi(z)=\frac{f}{z}+(1-f)\phi_v(z) \qquad (4)$$

Use of this expression gives the following expression for the viscosity

$$D_l(z)=-4\lambda f^2/z+D_v(z) \qquad (5)$$

With the following value of the vibrational contributing part of the of the viscosity

$$D_v(z) = \gamma + 8\lambda f(1-f)\phi_v(z) + 4\lambda(1-f)^2 L \left\{\phi_v^2(t)\right\}$$

Use of the above expression in Eq.3a gives, after comparison With Eq.4 gives the following expression for strength f

$$f = \left(1 + \sqrt{1 - 1/\lambda}\right)/2 \qquad (6)$$

The remaining part of the dynamic structure factor is given by

$$\Phi_v(z) = \frac{1}{z + \dfrac{\Omega^2}{z + D_v(z)}} \qquad (7)$$

Where

$$\Omega^2 = 1 + 4\lambda f^2$$

Eq.6 shows that the ansatz gives acceptable solution <u>Above</u> the crtitical value λ=1 . This means the dynamic structure factor does not decay to zero for λ>=1. Instead, they decay only to f. Thus, the spectrum of density fluctuation Will show a delta function peak at ω=0. The value of f is wave-number dependent and is called the order parameter of the Transition.

The transition is purely dynamic in nature.

The vibrational part of the longitudinal viscosity follows the following relation

$$\frac{z[z+D_v(z)]D_v(z)+2z-D_v(z)(\Omega^2-2)}{z[z+D_v(z)]-\Omega^2}=\Sigma(z)$$

where

$$\Sigma(z)=\gamma+4\lambda(1-f)^2 L(\Phi_v{}^2(t))$$

Therefore, theory of dynamics in the glass phase can be formulated fully in terms of the vibrational component Of the dynamic structure factor.

The Critical region: Power Law Decay

The small frequency behaviour near the critical point can be studied analytically. At small frequencies, $z/D_v(z) \ll 1$. At the glass transition point, one gets

$$D_v(z) = [\Sigma(z) + \{\Sigma^2(z) + 8\Sigma(z)/z\}^{1/2}]/2,$$

$$\Sigma(z) = \gamma + L[\Phi_v{}^2(t)$$

At small z, $D_v(z)$ exhibits a square root singularity which means a power law decay for the dynamics structure factor,

$$D_v(z) \propto z^{\alpha-1}$$

$$\Sigma(z) \propto z^{2\alpha-1}$$

α is a solution of $\Gamma(1-2\alpha)=2\Gamma^2(1-\alpha)$. This gives a value of α=0.395. That is, the square root dependence gets modified by a small extent by the frequency dependence of $\Sigma(z)$.

The above equations imply a power law decay of the dynamic structure factor

$$\Phi(t) \propto t^{-\alpha}$$

This power law decay describes the decay of the vibrational part to the plateau.

As the dynamic structure factor develops an elastic peak, The longitudinal viscosity diverges because the longitudinal Viscosity is time integral of the square of DSF.

The detailed analysis shows that the longitudinal viscosity Diverges as

$$D_l(z=0) \square (\lambda - 1)^{-\mu},$$

$$\mu = (\alpha + 1)/2\alpha = 1.765$$

Detailed numerical solutions have put the value of the Exponent between 1.8 and 2.

Qualitative predictions

- For $\lambda \leq 1$, the spectrum of $\Phi''(z)$ consists of two contributions. One part is a sharp quasi-elastic peak of strength f (~1/2) whose width shrinks to zero as $\lambda \rightarrow 1$. This part evolves continuously to a delta function peak in frequency.
- The second part is the vibrational part whose peak at small frequency also shrinks to zero as the transition is approached as $\omega^{-(1-\alpha)}$

- The viscosity is predicted to diverge with an exponent whose value lies between 1.8 and 2. The diffusion coefficient is predicted to go to zero with the same exponent.

Other applications of mode coupling theory

Mode coupling theory approach can be used and has been Used to derive many different expressions, some of which are detailed below.

The most well-known application is of course the derivation of the velocity time correlation function.

In such application one uses projection operator technique to project the Green-Kubo expression into the binary product of slow variables.

What is Liquid State MCT?

It is a self-consistent scheme which gets the short time behaviour (nearly) exactly correct (for two point correlation functions) because the lower order moments and satisfied.

The long time behaviour is described by a correlator which is expanded in terms of the set of hydrodynamic eigenfunctions. The resulting equations are solved self-consistently.

Thus, the long time diffusive limit is described fairly accurately.

MCT is quantitatively accurate at normal liquids – far far superior to the Brownian oscillator model (BSO). (SB+BB, AD+DR, JLS, Rabani,Egorof

Please note that BSO has no diffusive behaviour in the proper sense.

Basic MCT equations for friction

$$\varsigma(z)=\varsigma^{B}(z)+\varsigma^{R}(z)$$

$$\varsigma^{R}(z)=R_{\rho\rho}(z)-\varsigma^{B}(z)R_{\rho L}(z)-$$
$$R_{\rho L}(z)\varsigma(z)-\varsigma^{B}(z)\left[R_{LL}(z)+R_{TT}(z)\right]\varsigma(z)$$

$$\varsigma(z)=\frac{\varsigma^{B}(z)+R_{\rho\rho}(z)-\varsigma^{B}(z)R_{\rho L}(z)}{1+R_{\rho L}(z)+\varsigma^{B}(z)R_{LL}(z)+\left[\varsigma^{B}(z)+R_{\rho\rho}(z)-\varsigma^{B}(z)R_{\rho L}(Z)\right]R_{TT}(z)}$$

Self-consistent scheme

$$F^s(k,t)=\exp(-\, q^2\langle\Delta r^2(t)\rangle/6)$$

$$\langle\Delta r^2(t)\rangle = 2\int d\tau\, C_v(\tau)(t-\tau)$$

$$C_v(z) = k_B\, T \,/\, [m(z + \zeta(z))]$$

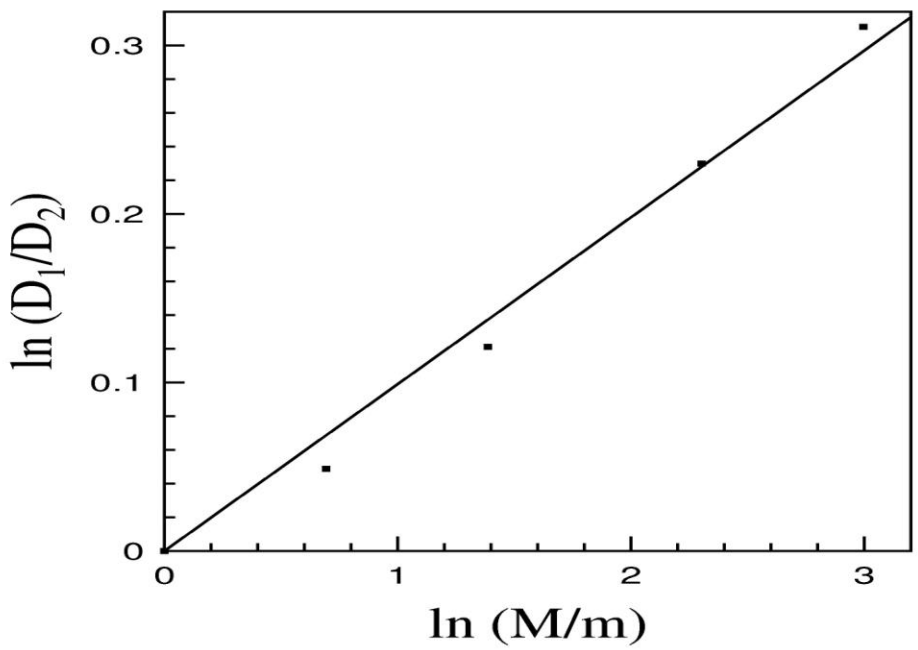
Power law and mass dependence of diffusion

D_1 and D_2 are self-diffusion coefficients of solvent and solute with masses m and M.

Straight line is the fitting

The slope of the line = 0.099.

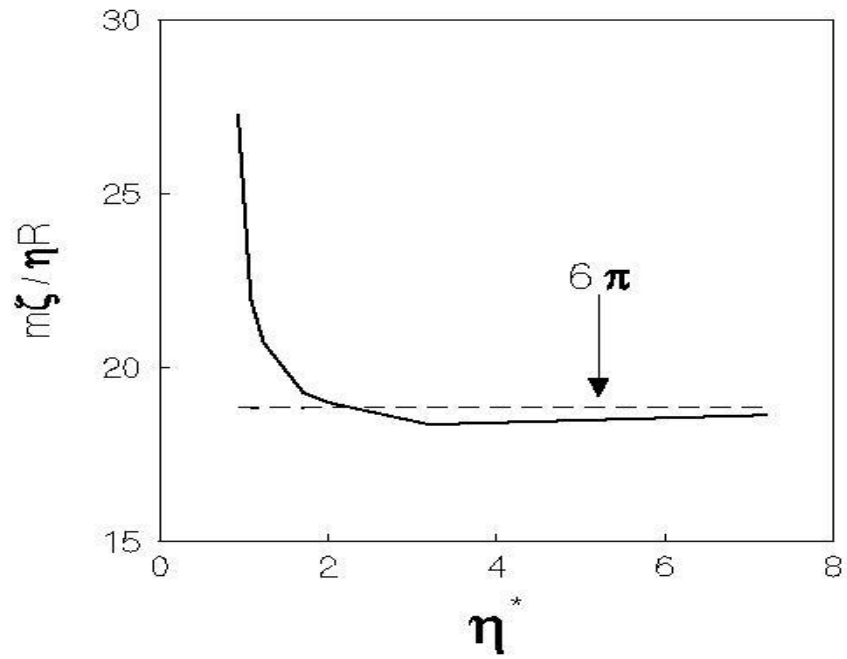
MD simulation studies predict the slope to be 0.1



S.Bhattacharyya and B. Bagchi, PRE, **61,** 3850 (2000)

Microscopic analysis of Stokes-Einstein relation

The ratio is close to 6π in the hydrodynamic Limit.



Predictions of MCT

- Divergence of viscosity as a power law with exponent ~2. This seems to fit the experimental and simulation data well at temperatures significantly above T_g.
- Theory predicts non-exponential relaxation functions. The theory also predicts power law decays at the end of beat relaxation and at the beginning of alpha relaxations which seem to be in good accord with experiments and simulations.
- The predicted critical point (T_c) is substantially above the glass transition temperature (by 30-50 K).