TRANSPORT PHENOMENA IN LIQUIDS*

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ABSTRACT

In this lecture a survey is presented of the present status of theory and experiment on transport properties in liquids, excluding the critical region and systems with long-range forces. Emphasis is placed on three topics that presently appear to be of major interest: (1) The existence of long-time tails in the time correlation functions that are employed to compute hydrodynamic transport coefficients; (2) The present application of laser light scattering to the study of the liquid state; (3) The limitations of studying molecular motions in liquids on the microscopic time scale by NMR and other spectroscopic techniques. The lecture concludes with a number of topics that are candidates for intensive work in the future.

I. INTRODUCTION

My purpose in this lecture is to provide a summary of the present status of theory and experiment on transport phenomena in liquids. This summary will hopefully help guide discussion on this important topic. In my judgement our discussions will be most interesting and profitable if attention is focused on major outstanding problems of transport in fluids. Accordingly, only brief attention will be devoted to a review of past accomplishments (such reviews are easily accessible). Primary emphasis will be placed on the discussion of items that I believe should have an important place on our research agenda. Additions or deletions of items on this research agenda would be most welcome. It seems completely appropriate for the proceedings of this conference to provide for the reader, and most especially for advanced students, one group's view of a significant research agenda for the field.

At the outset it must be admitted that our ability to describe quantitatively transport phenomena in liquids or dense fluids is not great. In a dilute gas our capability is much better primarily because a parameter of smallness has been found to exist. For a gas composed of particles that interact by a pair potential $u(1,2)$ the parameter of smallness is (ρa^d) where ρ is the number density, d, the dimensionality, and 'a' is a measure of the range of the intermolecular potential. The dimensionless parameter exists provided the potential has a hard core and $u(1,2)$ is of short-range, i.e. falls

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off with distance faster than R_{12}^{-n} with $n > d$. If these requirements are met and the dimensionless ratio (ρa^d) is much less than unity an expansion parameter is available for the analysis of the equilibrium and transport properties of the gas. A liquid, by definition, is a dense fluid where the dimensionless ratio (ρa^d) is not small and therefore this ratio cannot serve as an expansion parameter. At present a physically meaningful expansion parameter for simple liquids has not yet been found. Perhaps this is because the field of liquid theory has not yet been visited by a figure of the stature of Boltzmann or perhaps it is because such an ordering parameter simply is not present in nature. The few efforts[1] to examine the basic structure of the dynamics of classical fluid systems have not yet met with complete success.

Of course not all fluid systems are without an identifiable parameter of smallness. There are at least two cases where progress is possible. The first is the well known case of Brownian motion where one is interested in the dynamics of a single heavy particle in a bath of light particles. Here the expansion parameter is the square root of the (small) ratio of the mass of a bath particle to the mass of the Brownian particle.[2] The inverse case of a single light particle in a fluid of heavy particles [Lorentz gas] can also be studied.[3] The second case is that of a weakly interacting fluid[4] where the expansion parameter is the ratio of the strength of the short range potential to $(k_BT) = \beta^{-1}$. However, even in these two favorable instances not all aspects are sufficiently well understood. For example, in Brownian motion theory there is the celebrated problem[5] of demonstrating the equivalence between the molecular expression for the friction tensor, ζ, in terms of the equilibrium time correlation function

$$\zeta = \frac{1}{3k_BT}\int_0^\infty dt\, \langle F(0)\cdot F(t)\rangle \ , \tag{1.1}$$

and the macroscopic expression for ζ in terms of Stokes's Law:

$$\zeta = 6\pi\eta\sigma \ . \tag{1.2}$$

Here $\underset{\sim}{F}(t)$ is the force on the Brownian particle held fixed, σ is the radius of the spherical Brownian particle, and η is the solvent viscosity. While some progress has been made,[6] a definitive demonstration is not yet available.

Another class of interesting liquid problems consists of systems where the particles do not interact by short-range forces but rather by long-range forces. There are several cases where the study of the nonequilibrium behavior is of interest. Perhaps the most important are ionic solutions and dense plasmas where the charged particles interact via a Coulomb potential. A great deal of work has been done on obtaining kinetic equations for charged systems. Another case that has not received much attention, but should be of interest to the theorist, is the nonequilibrium behavior of the van der Waals system where the particles interact by weak long-range forces. There are also the important cases, largely unexplored, of polar liquids where the particles interact by the long-range, angle dependent, dipole-dipole interaction and of polymer solutions where the macromolecules interact by an effective long-range hydrodynamic interaction.

What questions do we seek to answer in studies of the liquid state? There are at least two important general questions. First, one may find empirically for a system that there are a set of observable dynamical variables $\underset{\sim}{a}(t)$ which describe pertinent aspects of the fluid's behavior on a particular spatial and/or temporal scale. The macroscopic equations may be linear

$$\frac{d\underset{\sim}{a}(t)}{dt} = i\underline{\underline{\Omega}}\cdot\underset{\sim}{a}(t) - \underline{\underline{M}}\cdot\underset{\sim}{a}(t)\ , \tag{1.3}$$

as in the case of the Bloch equations for the magnetization or they may be nonlinear

$$\frac{d\underset{\sim}{a}(t)}{dt} = -\underline{\underline{M}}[\underset{\sim}{a}(t)]\ , \tag{1.4}$$

as in the case of the Navier-Stokes equations of hydrodynamics. One also frequently encounters generalizations of the macroscopic equations that are nonlocal in time. For the linear case these equations have the form

$$\frac{d\underset{\sim}{a}(t)}{dt} = i\underline{\underline{\Omega}}\cdot\underset{\sim}{a}(t) - \int_0^t d\tau\,\underline{\underline{\phi}}(t-\tau)\cdot\underset{\sim}{a}(\tau)\ . \tag{1.5}$$

The *first question* one seeks to answer is "How are these macroscopic transport equations obtained from the exact dynamical microscopic equations of the system?"

The elements of the transport matrix $\underline{\underline{M}}$ will involve transport coefficients and other quantities characteristic of the fluid. The *second question* one seeks to answer is "How are these transport coefficients related to the microscopic properties of the fluid and how may they be computed?" For linear systems the answer to this question is provided by Linear Response theory where the nonequilibrium relaxation of $\underset{\sim}{a}(t)$ is related to equilibrium fluctuations $\langle\underset{\sim}{A}(t)\ \underset{\sim}{A}(0)\rangle$ in the set of dynamical variables $\underset{\sim}{A}$ corresponding to $\underset{\sim}{a}$. The transport coefficients are given by the Green-Kubo time correlation function expressions.

The most popular technique for the analysis of linear systems is the Projection Operator method of Mori[7] where one obtains exact equations for the evolution of the dynamical variables $\underset{\sim}{A}(t)$ in the form of a generalized Langevin equation

$$\frac{d\underset{\sim}{A}}{dt} = i\underline{\underline{\Omega}}\cdot\underset{\sim}{A}(t) - \int_0^t d\tau\phi(t-\tau)\cdot\underset{\sim}{A}(\tau) + F^+(t) , \qquad (1.6)$$

where $F^+(t)$ is the fluctuating Langevin "force" and the relaxation matrix $\underline{\underline{\phi}}(t)$ is related to $F^+(t)$ by a fluctuation-dissipation theorem. The evolution of the random force $F^+(t)$ is determined from a modified Liouville operator which involves the projection operator $\mathcal{P}$, defined by

$$\mathcal{P}\underset{\sim}{B} = \langle\underset{\sim}{B}\underset{\sim}{A}\rangle\cdot\langle\underset{\sim}{A}\underset{\sim}{A}\rangle^{-1}\cdot\underset{\sim}{A} . \qquad (1.7)$$

The difficult points in the Mori theory are (1) the absence of *a priori* criteria for selecting the set of variables $\underset{\sim}{A}$; and (2) the demonstration in particular applications of the properties of the random force $\underset{\sim}{F}^+(t)$ and hence the relaxation matrix $\underline{\underline{\phi}}(t)$.

The Mori procedure focuses attention on obtaining transport equations for the macroscopic variables. An important alternative approach focuses attention on obtaining a kinetic equation for the reduced distribution functions for the system. One may obtain an equation for the distribution function in phase space $\psi(\Gamma,t)$ so that the average value of the dynamical variables is given by

$$\underset{\sim}{a}(t) = \int A(\Gamma)\psi(\Gamma,t)d\Gamma , \qquad (1.8)$$

or one may obtain a Fokker-Planck equation for the probability density of the variables themselves $g(\underset{\sim}{A},t)$ so that $\underset{\sim}{a}(t)$ is given by

$$\underset{\sim}{a}(t) = \int \underset{\sim}{A}\, g(\underset{\sim}{A},t)d\underset{\sim}{A} . \qquad (1.9)$$

The former procedure is analogous to the derivation of the Boltzmann equation for dilute gas systems; the latter procedure is closely related to the generalized Langevin equation approach as may be appreciated by consideration of the connection between the Langevin and Fokker-Planck equations in probability theory. Zwanzig has pioneered[8] both procedures in this approach to obtaining kinetic equations for reduced distribution functions by use of a projection operator method.

I have mentioned two important general questions about transport in liquids. These are: how do transport equations arise and how are transport coefficients to be computed. With the answer to these two questions we are hopefully in a position to interpret the results of experiments in a quantitative manner. The types of experiments currently undertaken that one may wish to interpret are manifold. These include polarized and depolarized laser light scattering, neutron scattering, dielectric relaxation, nuclear and electron spin relaxation, sound absorption, and a variety of lineshape measurements including vibration-rotation, Raman and fluorescence spectroscopy. To these experiments it is important to add molecular computer dynamics which have undoubtably yielded the most interesting experimental data in recent years. It is computer experiments, not measurements on actual systems, that have caused the serious reexamination of our understanding of hydrodynamics.

It is not possible to discuss here the status of experiment and theory in all these different areas. Instead we shall select three: (1) The molecular theory of hydrodynamics; (2) Laser light scattering; (3) Nuclear magnetic relaxation. Each of these topics has been chosen for a reason. My reason for selecting hydrodynamics is that the recent discovery of long-time tails in the current correlation functions which define the transport coefficients has led to a reevaluation of theories of hydrodynamics. This reevaluation may be the most serious issue presently faced by those interested in liquid transport phenomena. The reason for selecting laser light scattering is that it presents an important new experimental technique that has the potential of wide practical applications in a variety of fields. Finally, I have chosen to discuss NMR because it is a field of spectroscopy (about which I know something) that illustrates certain limitations in experimental studies of the liquid state.

II. MOLECULAR THEORIES OF HYDRODYNAMICS

Three years ago the reasoning used to explain the form of hydrodynamic equations and the time correlation function formulas for the transport coefficients went as follows: The linearized macroscopic hydrodynamic equations have the form

$$\frac{da_{\underset{\sim}{k}}(t)}{dt} = -k^2\lambda_o \; a_{\underset{\sim}{k}}(t) \tag{2.1}$$

where $a_{\underset{\sim}{k}}(t)$ is the nonequilibrium average of the spatial Fourier transform of a conserved dynamical variable, $dA_{\underset{\sim}{k}}(t)/dt = i\underset{\sim}{k} \cdot \underset{\sim}{j}_{\underset{\sim}{k}}(t)$. (For simplicity I shall only discuss a prototype one-variable theory.) According to linear response theory[7] the nonequilibrium response of the variable $a_{\underset{\sim}{k}}(t)$ is related to the equilibrium time correlation function $\langle A_{\underset{\sim}{k}}(t) \; A_{-\underset{\sim}{k}}(0)\rangle$ by

$$a_{\underset{\sim}{k}}(t) = \langle A_{\underset{\sim}{k}}(t) \; A_{-\underset{\sim}{k}}(0)\rangle \langle A_{\underset{\sim}{k}}(0) \; A_{-\underset{\sim}{k}}(0)\rangle^{-1} \; a_{\underset{\sim}{k}}(0) \; . \tag{2.2}$$

By use of a projection operator identity the correlation function of the conserved variable may be expressed in terms of a particular current correlation function—in terms of Laplace transforms

$$\int_0^\infty dt \; e^{-zt} \langle A_{\underset{\sim}{k}}(t)A_{-\underset{\sim}{k}}(0)\rangle = [z+k^2\lambda(\underset{\sim}{k},z)]^{-1}\langle A_{\underset{\sim}{k}}(0)A_{-\underset{\sim}{k}}(0)\rangle \tag{2.3}$$

where

$$\lambda(\mathbf{k},z) = \int_0^\infty dt\; e^{-zt} \langle \mathbf{j}_{\mathbf{k}}(t)\cdot\mathbf{j}_{-\mathbf{k}}(0)\rangle^{\dagger} \;. \tag{2.4}$$

The dagger on the correlation function denotes that the time evolution is governed by the modified Liouville operator $(1-P)iL$ where P is a projection on to the conserved variables according to Eq. (1.7). If necessary the fluxes are constructed to be orthogonal to the conserved variables $\mathbf{A}_{\mathbf{k}}$,

$$\langle \mathbf{j}_{\mathbf{k}}(t)\; \mathbf{A}_{-\mathbf{k}}(0)\rangle^{\dagger} = 0 \;. \tag{2.5}$$

Use of Eqs. (2.1), (2.2) and (2.3) leads to an expression for the phenomenological transport coefficient λ in the small $\mathbf{k}$ (long wavelength), low z (long time) limit:

$$\lambda_o = \lim_{\substack{k\to o \\ z\to o}} \lambda(\mathbf{k},z) \;. \tag{2.6}$$

From Eq. (2.3) it follows that one is interested in the frequencies of order k^2. In the old days one *assumed* that the flux correlation function decayed on a time scale roughly independent of $\mathbf{k}$, i.e. much more rapidly than the conserved variables, and that $\lambda(\mathbf{k},z)$ was well behaved for small $\mathbf{k}$ and z. Arguments are available that purport to show that the $\mathbf{k}=0$ limit of $\lambda(\mathbf{k},z)$ is

$$\lambda(\mathbf{k}{=}0,z) = \frac{1}{V}\int_0^\infty dt\; e^{-zt} \langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle \quad , \tag{2.7}$$

where

$$\mathbf{J}(t) = \int_V d\mathbf{r}\; \mathbf{j}(\mathbf{r},t) \quad . \tag{2.8}$$

The essential assumption of the old reasoning was that the correlation function $\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle$ decayed rapidly on a molecular time scale, permitting one to take the limit $z \to 0$ in the expression for $\lambda(\mathbf{k}{=}0,z)$ and so incurring a negligible error for the frequencies of interest.

In the linear theory according to Eqs. (2.2) and (2.3) one has the more general transport equation

$$\hat{a}_{\mathbf{k}}(z) = [z+k^2\lambda(\mathbf{k},z)]^{-1}\; a_{\mathbf{k}}(0) \quad , \tag{2.9}$$

or in time language

$$\frac{da_{\underset{\sim}{k}}(t)}{dt} = -k^2 \int_0^t d\tau\phi(\underset{\sim}{k},t-\tau)a_{\underset{\sim}{k}}(\tau) \tag{2.10}$$

with

$$\lambda(\underset{\sim}{k},z) = \int_0^\infty dt\ e^{-zt}\ \phi(\underset{\sim}{k},t)\ . \tag{2.11}$$

In 1970, Alder and Wainwright[9] showed from their molecular dynamics data that the velocity autocorrelation function for hard spheres (three dimensions) and hard disks (two dimensions) had long time tails of the form $t^{-d/2}$ where d is the dimensionality of the system. Wainwright, Alder and Gass[10] later showed that the kinetic part of the flux for the thermal conductivity and the shear viscosity had a similar time dependence. A hydrodynamic argument was provided[9,10] to explain this observed behavior. The molecular dynamics results were catastrophic for the reasoning just described because (1) in two dimensions the t^{-1} tail meant that the conventional time correlation function did not exist and (2) the separation of time scales between the current correlation function and the conserved variable correlation function which was presumed to be present apparently was not. Furthermore the observed long time dependence of the current correlation function could be found from hydrodynamics. There immediately followed an enormous number of theories explaining the molecular dynamics results. Any remaining doubts in the community about the utility of computer molecular dynamics for producing new results also abruptly vanished.

The different theories that have been put forth to explain these long-time tails may be classified into four groups: (1) *Ad hoc* use of hydrodynamics, (2) Kinetic theory analysis of moderately dense fluids, (3) Nonlinear stochastic dynamics of collective modes, and (4) A variety of Mode-Mode coupling theories. Workers who have employed hydrodynamics to compute these long-time tails include Alder and co-workers,[9,10] Ernst, Hauge, and van Leeuwen,[11] and Pomeau.[12] The group which has approached the problem from the point of view of kinetic theory includes Pomeau[13] and Dorfman and Cohen.[14] Zwanzig has approached the problem starting from a nonlinear Langevin equation for the collective modes in the liquid.[15] Finally, the fourth group which has employed Mode-Mode coupling theory[16] includes Kawasaki,[17] Mazenko,[18] and more recently Keyes and Oppenheim.[19] The results of all these different theories are quite similar (although not identical) and strict correspondence between the approaches has not yet been demonstrated. There are, however, considerable differences, between authors, in the justification provided for the various assumptions employed. For example, Ernst, Hauge and van Leeuwen point out that in the hydrodynamic approach there is an apparent self-contradiction in assuming that transport coefficients exist in order to demonstrate that the correlation function expressions for these transport coefficients do not exist.

The essential results of the various calculations can, however, be obtained by *ad hoc* use of hydrodynamics. Here I shall present a completely phenomenological calculation[19] similar in spirit to the simple decoupled mode theory used in critical phenomena[20] that reproduces the central results. This calculation begins by assuming the possibility that the flux $\mathbf{j}_{\mathbf{k}}(t)$ may contain a slowly varying component proportional to the *square* of the conserved variable (the flux initially is constructed to be orthogonal to the conserved variable itself). In terms of spatial Fourier transforms one assumes

$$\mathbf{j}_{\mathbf{k}}(t) = \mathbf{j}^{o}_{\mathbf{k}}(t) + \sum_{\mathbf{q}} \frac{\mathbf{v}(\mathbf{k},\mathbf{q})}{x(\mathbf{k},\mathbf{q})} A_{\mathbf{k}+\mathbf{q}}(t)A_{-\mathbf{q}}(t) \ , \qquad (2.12)$$

where $\mathbf{v}$ is a coupling constant $x(\mathbf{k},q) = \langle A_{\mathbf{k}+\mathbf{q}}\ A_{-\mathbf{q}}\ A_{-\mathbf{k}-\mathbf{q}}\ A_{\mathbf{q}}\rangle$ and $\mathbf{j}^{o}_{\mathbf{k}}$ is a "microscopic flux" that has the properties previously attributed to the total flux $\mathbf{j}_{\mathbf{k}}$. Substitution of this expression for the flux into Eq. (2.4) gives

$$\lambda(\mathbf{k},z)-\lambda_o = \sum_{\mathbf{q}\mathbf{q}'} \frac{\mathbf{v}(\mathbf{k},\mathbf{q})\cdot\mathbf{v}(-\mathbf{k},-\mathbf{q}')}{x(\mathbf{k},\mathbf{q})x(-\mathbf{k},-\mathbf{q}')} \int_o^\infty dt\ e^{-zt}\ \cdot$$

$$\cdot\langle A_{\mathbf{k}+\mathbf{q}}(t)A_{-\mathbf{q}}(t)A_{-\mathbf{k}-\mathbf{q}'}(0)A_{\mathbf{q}'}(0)\rangle^{\dagger} \ . \qquad (2.13)$$

We now make the following (unjustified approximation) in order to evaluate the r.h.s. of this equation:

(1) The projected four-point correlation function may be replaced by the product of unprojected two-point correlation functions and only terms with $\mathbf{q} = \mathbf{q}'$ contribute;

$$\langle A_{k+q}(t)A_{-q}(t)A_{-k-q'}(0)A_{q'}(0)\rangle^{\dagger}$$

$$= \delta_{\mathbf{q}\mathbf{q}'}\ \langle A_{\mathbf{k}+\mathbf{q}}(t)A_{-\mathbf{k}-\mathbf{q}}(0)\rangle\ \langle A_{-\mathbf{q}}(t)A_{\mathbf{q}}(0)\rangle \ . \qquad (2.14)$$

(2) The decay of the correlation functions may be computed according to linearized hydrodynamics with the bare transport coefficient λ_o,

$$\langle A_{\mathbf{k}}(t)A_{-\mathbf{k}}(0)\rangle = \langle A_{\mathbf{k}}A_{-\mathbf{k}}\rangle\ \exp[-\lambda_o k^2 t] \ . \qquad (2.15)$$

(3) The resulting $\mathbf{k}$ and $\mathbf{q}$ dependent amplitude factor

$$\frac{v(\mathbf{k},\mathbf{q})\cdot v(-\mathbf{k},-\mathbf{q})}{x(\mathbf{k},\mathbf{q})x(-\mathbf{k},-\mathbf{q})} \langle A_{\mathbf{k}+\mathbf{q}}A_{-\mathbf{k}-\mathbf{q}}\rangle \langle A_{\mathbf{q}}A_{-\mathbf{q}}\rangle \tag{2.16}$$

in the region of interest of low $\mathbf{k}$ and $\mathbf{q}$ may be replaced by a constant α/v.

With these assumptions the expression for $\lambda(\mathbf{k},z)$ becomes

$$\lambda(\mathbf{k},z)-\lambda_o = \frac{\alpha}{(2\pi)^d}\int d\mathbf{q}\int_o^\infty dt\, \exp[-\lambda_o|\mathbf{k}+\mathbf{q}|^2]\exp[-\lambda_o q^2t]e^{-zt} , \tag{2.17}$$

where we have replaced the sum over $\mathbf{q}$ by an integral according to the usual prescription. The integral may now be evaluated in two or three dimensions. Interest focuses on the case $d = 2$ for which one obtains

$$\lambda(\mathbf{k},z)-\lambda_o = \frac{\alpha}{2\pi}\int_o^\infty dt \int_o^{k_m} dqq\, \exp[-(z+2\lambda_oq^2+k^2)t]I_o(2\lambda_oqkt) \tag{2.18}$$

where $I_o(z)$ is the modified Bessel function of zeroth order and k_m is the small wavelength cut-off. The subsequent integration over t yields

$$\lambda(\mathbf{k},z)-\lambda_o = \frac{\alpha}{2\pi}\int_o^{k_m} dqq[4\lambda_o^2q^4+4\lambda_ozq^2+(z+\lambda_ok^2)^2]^{-1/2} \tag{2.19}$$

which leads to the final result (for small $\mathbf{k}$)

$$\lambda(\mathbf{k},z) = \lambda_o + \left(\frac{\alpha}{8\pi\lambda_o}\right)\ell n\left[\frac{z+2\lambda_ok_m^2}{z+(\lambda_ok^2/2)}\right] . \qquad d = 2 \tag{2.20}$$

This result contains the qualitative features of many of the more refined theories. For example, the $\mathbf{k}\to 0$ limit yields

$$\lambda(z) = \lambda_o + (\alpha/8\pi\lambda_o)\ell n\left[\frac{z+2\lambda_ok_m^2}{z}\right] \tag{2.21}$$

which is the result obtained by Zwanzig by the nonlinear Langevin equation approach.[15] At small z, $\lambda(z)$ does not exist; the inverse Laplace transform of $\lambda(k=0,z)$ [see Eq. (2.11)] is

$$\phi(\underset{\sim}{k}=0,t) = 2\lambda_o\delta(t) + (\alpha/8\pi\lambda_o)[1-\exp(-2\lambda_o k_m^2 t)]t^{-1} \tag{2.22}$$

which displays the characteristic t^{-1} long time decay of many of the two-dimensional calculations.[9-19]

The finite $\underset{\sim}{k}$ and z expression for $\lambda(\underset{\sim}{k},t)$ Eq. (2.20) is quite similar to the form obtained by Keyes and Oppenheim[19] from their theory. The Keyes-Oppenheim theory does not assume hydrodynamics, and particular care is given to justifying approximations. The basic approach of this theory is to employ the Mori Formalism in the expanded space of linear A_k and bilinear variable $A_{\underset{\sim}{k}-\underset{\sim}{q}}A_{\underset{\sim}{q}}$ in the manner followed by Kawasaki[16] for dynamic critical phenomena. The most important difference between the expression obtained by Keyes and Oppenheim for $\lambda(\underset{\sim}{k},z)$ and Eq. (2.20) is that the "bare" transport coefficients in the argument of the logarithm is not the same as λ_o and this new coefficient does not enter into ordinary hydrodynamics. The inverse Laplace transform of $\lambda(k,t)$ is given by

$$\phi(\underset{\sim}{k},t) = 2\lambda_o\delta(t)+(\alpha/8\pi\lambda_o)[\exp(-\tfrac{1}{2}\lambda_o k^2 t)-\exp(-2\lambda_o k_m^2 t)]t^{-1}. \tag{2.23}$$

The $z \to 0$ limit of $\lambda(\underset{\sim}{k},z)$ is

$$\lambda(\underset{\sim}{k}) = \lambda_o + \left(\frac{\alpha}{4\pi\lambda_o}\right)\ln\left(\frac{2k_m}{k}\right) \tag{2.24}$$

which indicates a nonanalytic k dependence of the transport equations.[19] Finally, we note that higher-order terms can be included in the expansion of flux, Eq. (2.12) and their contribution to the flux correlation function computed in a similar phenomenological way. In the two-dimensional case the trilinear terms[11] have an asymptotic time dependence of t^{-2} so it appears that keeping all terms would not substantially affect the t^{-1} dependence found from the bilinear contribution.

A great deal of further work can be anticipated in this area. In addition to understanding the physical basis and relationships between the existing theories a number of interesting extensions are possible. These extensions are suitable topics for our discussion.

III. LIGHT SCATTERING FROM FLUID SYSTEMS

The second topic I now discuss concerns recent developments in light scattering from liquid systems. I shall not cite applications of light scattering to systems in the critical region since this topic is more appropriately included in connection with Professor Sengers's lecture. It is now widely accepted that laser light scattering has great potential for the study of dynamical processes in fluid systems. Rather than discuss any single application in detail

I would like to survey some of the applications that have recently been completed or proposed.

To obtain an expression for the light scattering spectrum in the hydrodynamic regime one may begin with the Einstein formula for the intensity of light scattered at an angle θ, $I(\underset{\sim}{k})$. This intensity is proportional to the equilibrium dielectric fluctuations of wave vector $\underset{\sim}{k}$, $\delta\hat{\varepsilon}(k)$

$$I(\underset{\sim}{k}) = \langle\delta\hat{\varepsilon}(\underset{\sim}{k})\delta\hat{\varepsilon}(-\underset{\sim}{k})\rangle \tag{3.1}$$

where

$$|\underset{\sim}{k}| = 2k_o \sin(\theta/2) \tag{3.2}$$

and $\underset{\sim}{k}_o$ is the incident wave vector (which depends on the refractive index of the medium). The total intensity is equal to the integral over all frequencies (relative to the incident frequency) ω of the spectrum $I(\underset{\sim}{k},\omega)$

$$I(\underset{\sim}{k}) = \int_{-\infty}^{+\infty} I(\underset{\sim}{k},\omega)d\omega \ . \tag{3.3}$$

An expression for $I(\underset{\sim}{k},\omega)$ is most simply obtained by formally inserting a delta function in Eq. (3.1):

$$I(\underset{\sim}{k}) = \int_{-\infty}^{+\infty} dt \ \delta(t) \ \langle\delta\hat{\varepsilon}(\underset{\sim}{k},t)\delta\hat{\varepsilon}(-k)\rangle \ , \tag{3.4}$$

$$I(k) = \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{-i\omega t} \ \langle\delta\hat{\varepsilon}(\underset{\sim}{k},t)\delta\hat{\varepsilon}(-\underset{\sim}{k})\rangle \ . \tag{3.5}$$

Identification with Eq. (3.3) leads to the following expression for the spectrum

$$I(\underset{\sim}{k},\omega) = \frac{1}{\pi} \mathrm{Re} \int_{0}^{+\infty} dt \ e^{-i\omega t} \ \langle\delta\hat{\varepsilon}(\underset{\sim}{k},t)\delta\hat{\varepsilon}(-k)\rangle \tag{3.6}$$

where use has been made of the fact that the dielectric fluctuation time correlation is even in time. A variety of alternative fluctuation-theory approaches are available[21] to derive this formula which serves as the basis for interpreting a variety of light scattering experiments.

However, this derivation based on fluctuation theory is *not* a molecular derivation for many reasons including, for example, the absence of a molecular expression for the local dielectric constant. The simplest molecular theories[22] do not take into account local field effects and the difference between the molecular polarizability and the actual density and temperature dependent effective local polarizability. These simple theories lead to an expression for the polarized spectrum from a one-component system proportional to the density-density correlation function:

$$I(\mathbf{k},\omega) \propto \mathrm{Re}\int_0^\infty dt\; e^{-i\omega t} \langle \delta\hat{\rho}(\mathbf{k},t)\,\delta\hat{\rho}(-\mathbf{k})\rangle \quad . \tag{3.7}$$

For a one-component system the difference between Eq. (3.6) and (3.7) arises from temperature fluctuations since the local dielectric constant contains both the effects of density and temperature fluctuations:

$$\delta\varepsilon(\mathbf{r},t) = \left(\frac{\partial\varepsilon}{\partial\rho}\right)_T^0 \delta\rho(\mathbf{r},t) + \left(\frac{\partial\varepsilon}{\partial T}\right)_\rho^0 \delta T(\mathbf{r},t) \quad . \tag{3.8}$$

More sophisticated molecular theories[23] that attempt to take into account so-called multiple scattering to correct for local field effects always lead to correction terms which involve higher order density correlation functions. To my knowledge there has been no satisfactory demonstration that when these effects are properly included one exactly recovers the result of macroscopic fluctuation theory. Such a demonstration would be most welcome. The difference between Eqs. (3.6) and (3.7) is not important for most polarized light scattering experiments since the equilibrium thermodynamic derivative $(\partial\varepsilon/\partial T)_\rho$ is small if the dielectric constant is evaluated at the optical frequency of the incident radiation. On the other hand, these local field effects are crucial for explaining the observed collision induced depolarized light scattering from atomic or simple spherically symmetric molecular gases and liquids.[24]

In the hydrodynamic regime the procedure employed to evaluate the spectrum is quite simple. First, one expands the dielectric constant in terms of the appropriate set of local thermodynamic variables $\{\mathbf{a}_i\} = \delta\mathbf{a}$

$$\delta\hat{\varepsilon}(\mathbf{k},t) = \mathbf{B}^T\cdot\delta\hat{\mathbf{a}}(\mathbf{k},t) \tag{3.9}$$

where $B_i = (\partial\varepsilon/\partial a_i)_{a_j}$ (some of the B_i's may be zero). One next computes the time decay of the local thermodynamic variables in terms of linearized hydrodynamic equations which may be expressed in the form of Eq. (1.3). Accordingly the spectrum $I(\mathbf{k},\omega)$, Eq. (3.6) is given by the formal expression

$$I(\underset{\sim}{k},\omega) = \frac{1}{\pi}\,\mathrm{Re}\ \underset{\sim}{B}^{T}\cdot[i\underline{\underline{I}}\omega - i\underline{\underline{\Omega}}(\underset{\sim}{k}) + \underline{\underline{M}}(\underset{\sim}{k})]^{-1}\cdot\langle\delta\hat{\underset{\sim}{a}}(\underset{\sim}{k})\delta\hat{\underset{\sim}{a}}(-\underset{\sim}{k})\rangle\cdot\underset{\sim}{B} \qquad (3.10)$$

(in general, the matrix $\underline{\underline{M}}$ could depend on frequency also). The spectrum may be displayed by expanding respectively the vectors $\underset{\sim}{B}^{T}$ and $\langle\delta\hat{\underset{\sim}{a}}(\underset{\sim}{k})\ \delta\hat{\underset{\sim}{a}}(-\underset{\sim}{k})\rangle\cdot\underset{\sim}{B}$ in terms of the left (row) and right (column) eigenvectors of the matrix $[i\underline{\underline{\Omega}} + \underline{\underline{M}}]$. (The calculation need not be accurate beyond terms linear in the transport coefficients.) Such a program is easily carried out for a number of experimentally interesting cases: (a) one-component fluids[25]; (b) two-component systems[26]; (c) systems with internal degrees of freedom,[27] i.e. frequency dependent transport coefficients or an additional internal thermodynamic variable; and (d) chemically reacting systems.[28] These conventional applications hold the promise of developing into practical techniques for determining equilibrium and transport properties of fluids.

There have been, of course, investigations into situations where this simple hydrodynamic-fluctuation theory picture of light scattering breaks down. One case deserves specific mention at this symposium. When the mean free path, ℓ, becomes large compared to the wavelength k^{-1} it is no longer appropriate to employ hydrodynamics to compute density fluctuations or the light scattering spectrum—one must employ the Boltzmann equation[29] or generalized hydrodynamics.[30] Experimental light scattering results on this transition from the kinetic to hydrodynamic regime are available for one[31] and two-component[32] systems and these results are in excellent agreement with theory. A second interesting case where the normal hydrodynamic-fluctuation theory breaks down is when the scattering volume contains only a small number of particles and the amplitude of the scattered field can no longer be considered a Gaussian random process.[33] In these circumstances the conventional experiments must be interpreted quite differently.

So far my discussion has been limited to polarized light scattering. Depolarized light scattering from liquids composed of anisotropic molecules has been an unusually active field in recent years. The depolarized VH spectrum consists of a broad background on which a sharp Rayleigh peak is superimposed. There is a $\underset{\sim}{k}$ dependent dip in the center of this Rayleigh component which gives rise to a closely spaced doublet.[34] A considerable number of theories have been put forward to explain the structure of the spectrum.[35] A particularly useful account of the differences and similarities between these theories has been given by Keyes and Kivelson.[36] The central problem is the evaluation of the lineshape expression

$$I_{if}(k,\omega) = \mathrm{Re}\int_{0}^{\infty} dt\ e^{-i\omega t}\langle[\underset{\sim}{n}_{f}\cdot\hat{\underline{\underline{\alpha}}}(\underset{\sim}{k},t)\cdot\underset{\sim}{n}_{i}][\underset{\sim}{n}_{f}\cdot\underline{\underline{\alpha}}(-\underset{\sim}{k})\cdot\underset{\sim}{n}_{i}]\rangle \qquad (3.11)$$

where $\underset{\sim}{n}_{i}$ and $\underset{\sim}{n}_{f}$ are the polarization vectors of the incident and

and outgoing fields. In order to accomplish this evaluation one must arrive at a pertinent set of slow variables that are coupled to the polarizability density $\underline{\underline{\alpha}}(\underset{\sim}{k},t)$ and determine an appropriate set of hydrodynamic equations for the description of the time dependence. The theories which have been proposed[35] differ in the selection of primary variables that have been chosen to be coupled to the polarizability density and in the hydrodynamic equations that describe their time dependence.

Many other light scattering applications have been proposed, some of them most novel and interesting. These include light scattering from fluid surfaces,[37] from turbulent fluids,[38] from bacterial suspensions[39] (in order to measure bacterial mobility and chemotactic response), and from conformational changes in biological macromolecules.[40] Finally, our group at MIT[41] has considered light scattering from chemically reactive systems in a spatially homogeneous steady state far from equilibrium. For this case at constant T and p the concentrations of the chemical species obey the nonlinear equation

$$\frac{\partial \underset{\sim}{a}(\underset{\sim}{r},t)}{\partial t} = \underline{\underline{D}}\cdot\nabla^2\underset{\sim}{a}(\underset{\sim}{r},t) + \underset{\sim}{F}[\underset{\sim}{a}(\underset{\sim}{r},t)] \tag{3.12}$$

where $\underline{\underline{D}}$ is the matrix of diffusion coefficients and $\underset{\sim}{F}$ a source term due to chemical reaction. Linearization of Eq. (3.12) about a spatially homogeneous steady state $\underset{\sim}{a}^{o}$ yields the equations

$$\frac{\partial \delta\underset{\sim}{a}(\underset{\sim}{r},t)}{\partial t} = \underline{\underline{D}}\cdot\nabla^2\delta\underset{\sim}{a}(\underset{\sim}{r},t) + \underline{\underline{\Omega}}\cdot\delta\underset{\sim}{a}(\underset{\sim}{r},t) \tag{3.13}$$

where

$$\underline{\underline{\Omega}} = (\partial\underset{\sim}{F}/\partial\underset{\sim}{a})_{\underset{\sim}{a}^{o}} \ . \tag{3.14}$$

In contrast to the equilibrium case, the decay of the linear perturbation about this steady state will occur with oscillations. If these linearized equations are used to describe the equilibrium fluctuations in this nonlinear system, one finds splittings in the central Rayleigh peak proportional to a combination of chemical rate coefficients that appear in the reaction mechanism $\underset{\sim}{F}$. Such chemically reacting systems may have points of marginal stability where the real part of one of the eigenvalues of the matrix of fluctuations approaches zero. This approach to a point of marginal stability will be manifest in the light scattering spectrum by the appearance of sharp and intense lines—a feature which may serve as a practical diagnostic for marginal stability with respect to spatially homogeneous or inhomogeneous perturbations.

Finally, an important and active area of research (both theoretical and experimental) has been concerned with light scattering from polymer solutions. In the simplest case[42] of spherical macromolecules in an optically inert solvent when $kR \ll 1$ [R is the characteristic mean end-to-end distance of a polymer molecule] the light scattering spectrum is given by Eq. (3.7) where $\delta\hat{\rho}(\underset{\sim}{k},t)$ is the density of polymer molecules

$$\hat{\rho}(\underset{\sim}{k},t) = \sum_{n} \exp[i\underset{\sim}{k}\cdot\underset{\sim}{r}_n(t)] \ . \tag{3.15}$$

The spectrum is computed on the basis of the diffusion equation

$$\frac{\partial\hat{\rho}(\underset{\sim}{k},t)}{\partial t} = -D_o k^2 \hat{\rho}(\underset{\sim}{k},t) \tag{3.16}$$

where D_o is the translational diffusion constant for a single particle at infinite dilution and one obtains a Lorentzian line of width $D_o k^2$. One might be concerned that at finite concentrations Eq. (3.16) is inappropriate since there will be the manifestation in the diffusion equation of the long-range hydrodynamic interactions between the polymer molecules. In fact, one may show[43] that the spectrum predicted by the correct N-particle diffusion equation[44]

$$\frac{\partial P(\underset{\sim}{r}^N,t)}{\partial t} = \sum_{n,m} \nabla_{\underset{\sim}{r}_n}\cdot\underline{\underline{D}}_{nm}\cdot\nabla_{\underset{\sim}{r}_m} P(\underset{\sim}{r}^N,t) \tag{3.17}$$

is identical with the spectrum predicted on the basis of Eq. (3.16) so that one need not be concerned with concentration effects arising from hydrodynamic interactions. In Eq. (3.17) the diffusion tensor is

$$\underline{\underline{D}}_{ij} = D_o\delta_{ij} + (1-\delta_{ij})(k_BT)\underline{\underline{T}}_{ij} \tag{3.18}$$

where $\underline{\underline{T}}_{ij}$ is Oseen's tensor.

$$\underline{\underline{T}}_{ij} = \frac{1}{8\pi\eta|\underset{\sim}{r}_{ij}|}\left[\underline{\underline{I}} + \left(\frac{\underset{\sim}{r}_{ij}\underset{\sim}{r}_{ij}}{|\underset{\sim}{r}_{ij}|^2}\right)\right] \ . \tag{3.19}$$

Perhaps the more interesting application of light scattering to the study of polymers arises in the case $kR \gg 1$ when the wavelength of light is small compared to the polymer length. In this case one has the possibility of using light scattering to study the internal dynamics of a polymer—an important subject about which not much is known and where little progress has been made since the late fifties. The basic theory for this case of large macromolecules was worked out by Dubois-Violette and de Gennes,[45] who consider an infinitely dilute system. The spectrum is given by Eq. (3.7) with

$\delta\hat{\rho}(\underset{\sim}{k},t)$ in the form of Eq. (3.15) with the sum over the monomer units of the polymer. Each monomer unit is assumed to be an independent isotropic scatterer. The result for the width of the spectrum is of the form[46]

$$\Delta\omega = (\text{constant})\ k^{\nu+2} \tag{3.20}$$

where ν is a parameter that characterizes the variance of the assumed Gaussian distribution of the relative position of two monomer units

$$\langle(\underset{\sim}{r}_n - \underset{\sim}{r}_{n+p})^2\rangle = b^2|p|^\nu\ . \tag{3.21}$$

The result is valid for $0 < \nu < 2$; with $0 < \nu < 1$ corresponding to negative excluded volume, $\nu = 1$ corresponding to a random coil, and $\nu = 2$ to a rigid rod. The important case of $\nu = 6/5$ leads to an angle dependence of the width proportional to $k^{16/5}$.

IV. MAGNETIC RELAXATION

I wish briefly to discuss magnetic relaxation in order to illustrate a limitation I perceive on spectroscopic line shape studies of the liquid state. It is well known that a variety of radiation absorption measurements can be employed to study molecular motion in dense fluids. A particularly lucid survey has been presented by Gordon.[47] In the linear regime the line shape $I(\omega)$ is proportional to an equilibrium time correlation function of an appropriate dynamical variable of the system. In the case of nuclear magnetic or electron spin resonance the correlation function expression for the line shape is given by

$$I(\omega) = \text{Re}\int_0^\infty dt\ e^{-i\omega t}\ \langle S_+(t)S_-(0)\rangle\ , \tag{4.1}$$

where in the simple case of intramolecular relaxation $S_\pm$ are the raising and lowering operators for the spin on a representative molecule. In many cases the nonequilibrium magnetization satisfies the Bloch equation

$$\frac{d\overline{S_+(t)}}{dt} = i\omega_o\ \overline{S_+(t)} - \frac{1}{T_2}\ \overline{S_+(t)} \tag{4.2}$$

where ω_o is the Larmor frequency and T_2 is the transverse spin relaxation time. This nonequilibrium equation may be employed to obtain an expression for $I(\omega)$

$$I(\omega) = \frac{T_2^{-1}}{(\omega-\omega_o)^2+(T_2^{-1})^2} \tag{4.3}$$

which is a Lorentzian with a width given by T_2^{-1}. The molecular expression for the relaxation time may be found by standard techniques including the projection operator method[48] discussed briefly in Section I. The expression for T_2^{-1} is

$$T_2^{-1} = \langle S_+S_-\rangle^{-1}\ \mathrm{Re}\int_o^\infty dt\ \exp[i\omega_o t]\langle h_+(t)h_-(0)\rangle\ , \tag{4.4}$$

where $\underset{\sim}{h}(t)$ is the local "random" magnetic field acting on the spin. The total Hamiltonian of this system is taken to be the sum of a zeroth order Hamiltonian H_o which includes the lattice motion and the Zeeman interaction and a spin-lattice coupling term V. In Eq. (4.4) the "random" magnetic field is given by

$$\underset{\sim}{h}(0) = (i/h)[V,\underset{\sim}{S}] \tag{4.5}$$

and the time dependence is computed by using the unperturbed Hamiltonian since the spin-lattice coupling is assumed to be weak, i.e. $T_2 \gg \tau$ where τ is a characteristic time of the lattice motion.

The spin-lattice coupling is usually of the form

$$V = \sum_q S_q F_q\ , \tag{4.6}$$

where F_q are irreducible tensor components of lattice variables appropriate to the mechanism under consideration. Substitution of Eq. (4.5) into Eq. (4.4) shows that the measured relaxation time is proportional to the Fourier transform of lattice correlation functions of the type

$$\langle F_q(t)F_{-q}(0)\rangle\ . \tag{4.7}$$

The hypothesis of those interested in using magnetic relaxation to study the liquid state is that measurements of these lattice correlation functions (obtained through relaxation or lineshape experiments) may be used effectively to distinguish between relevant models of molecular motion in liquids. I would like to argue that in fact the information obtained is quite limited and that the actual discrimination between possible models of molecular motion is not great. A simple example of this absence of discrimination is provided by the recent work of Cukier and Lakatos-Lindenberg.[49] In many cases the lattice correlation function of interest involves the spherical harmonic $Y_{\ell m}$ of the solid angle Ω that the axis of the molecule makes with the external magnetic field direction:

$$C_\ell(t) = \langle Y_{\ell m}(t) Y^*_{\ell m}(0) \rangle \ . \tag{4.8}$$

These authors show that if one adopts a generalized Debye rotational diffusion equation of the form

$$\frac{\partial P(\Omega,t)}{\partial t} = \int d\Omega' A(\Omega,\Omega') P(\Omega',t) \ , \tag{4.9}$$

there is a large class of transition kernels A that lead to single exponential behavior of the correlation function $C_\ell(t)$. Thus, even under the favorable circumstances when a single exponential behavior of a correlation function is observed it is not possible to distinguish between different models. Of course, there is a much larger class of transition kernels that do not lead to single exponential relaxation for $C_\ell(t)$. In this case the problems are even more severe. First, there are many functions $C_\ell(t)$ that, over the frequency range effectively probed in the experiment, will give rise to similar Fourier transforms. Second, there will be many transition kernels that give rise to the same $C_\ell(t)$ for a particular value of ℓ.

It is not true that in all interesting cases the relaxation of the spin occurs by a single relaxation time T_2. There may be several relaxation times involved as in the case[50] of quadrupolar relaxation for a spin with $S \geq 3/2$. Furthermore, in the general case the lattice motion and the spin relaxation occur on the same time scale, and it is then important to compute the line shape $I(\omega)$ over the entire motional range from slow tumbling to rapid motional narrowing. A particularly pertinent case, because of its practical application, arises in ESR when a spin $S = 1/2$ is fixed to a large molecule that undergoes isotropic rotational diffusion. The prototype Hamiltonian for the system (in the interaction representation) is

$$H(t) = \omega_0 S_z + a S_z P_2[\cos\theta(t)] \ , \tag{4.9}$$

where nonsecular terms have not been included. The time dependence of the orientation between the molecular fixed axis θ and the external field is assumed to be given by the Debye rotational diffusion equation

$$\frac{\partial P}{\partial t} = D\nabla^2_\Omega P(\Omega,t) \ . \tag{4.10}$$

One may compute $I(\omega)$ for this and similar, more general, cases by a variety of techniques including stochastic lineshape theory, cumulant expansions and projection operator methods.[51] Reliable results may be obtained for $I(\omega)$ over the entire range from the rigid lattice limit of slow diffusional motion $(a/D) \gg 1$ to the fast diffusional limit of $(a/D) \ll 1$ where $I(\omega)$ has the form of Eq. (4.3) with $T_2^{-1} \propto (a^2/D)$. In fact, the simple rotational diffusion model gives quite remarkable agreement with experiment over the entire range (a/D). The substantial derivations one expects from the rotational diffusion model at high frequencies (short times) or for small molecules do not appear prominently in the measured spectrum. Presumably this is due to the fact that correlation functions of the type of Eq. (4.8) are simply not sufficiently sensitive to the details of the rotational motion which go beyond the simple ideas behind the rotational diffusion equation. Perhaps even more remarkable is the fact that the Stokes-Einstein expression for the rotational diffusion constant,

$$D = (k_B T/8\pi\eta a) \quad , \qquad (4.11)$$

seems to work quite well even for small molecules although extensions of this relationship have been developed.

V. SOME OUTSTANDING PROBLEMS

In the preceding review of selected topics of transport in liquids I have attempted to stress the status of present developments and those points where our understanding is unsatisfactory. In this section I would like to mention several other topics which I believe deserve substantial attention in the future.

(1) Fluctuations in nonlinear systems. The problem of treating fluctuations in nonlinear systems arises at least in three important areas: critical phenomena, long-time tails of hydrodynamic correlation functions, and unstable chemical reactions. At present, the usual treatments begin from a phenomenological nonlinear Langevin equation. But this approach is open to objection[52] and a more fundamental, molecular justification is required.

(2) Our attention has been very strongly directed toward obtaining molecular derivations of hydrodynamic equations for fluids. Solutions of these macroscopic equations are, of course, determined by the accompanying boundary conditions. However, essentially no work[53] has been done on developing a molecular theory for theseboundary conditions. This is particularly unfortunate since the subject of boundary layers is of practical importance and undoubtably involves new physics.

(3) The field of turbulence is extremely important and active but we do not have available any molecular theories for the justification of the starting equations and stochastic assumptions that are employed in the conventional developments.[54]

(4) For the physical chemist, the ultimate prize might well be considered to be the development of a molecular theory for rate coefficients in solution. Unfortunately, we do not have an understanding of why classical transition rate theory works so well. The formal time correlation function expressions for the rate coefficient[55] have not proven useful for practical application. It is my own belief that molecular dynamics has substantial promise in this area if a

clever way can be found to put together trajectory calculations on potential surfaces and liquid state simulation computations.

(5) There has been very little progress in the field of polymer dynamics in recent years;[56] particularly absent are new insights into the underlying physics of entangled polymer motions. In my judgement this is a most fascinating and important area where advances should be possible.

In conclusion, I should like to reiterate my hope that our discussions will center on important problems for future research. This discussion need not be limited to the topics I have raised although I would be most pleased to have any comments on the views I have expressed.

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DISCUSSION. Tuesday a.m.

The discussion first centered on the question as to the theoretical and experimental consequences of the long time-tails in the correlation functions. In response to a question by B. J. Alder, I. Oppenheim said that he and T. Keyes have studied the wave number and frequency-dependent self-diffusion coefficient, D(k,s). He quoted the result at zero wave number D(k=0,s):

$$D(k=0,s) = D_o + \frac{k_B T}{3\pi^2 \rho \eta_o} \left(k_c - \frac{\pi}{2} \sqrt{\frac{s}{\eta_o}} \right) ,$$

where D_o and η_o are the "bare" coefficients of self-diffusion and of shear viscosity, k_c is a wavelength cutoff, and ρ is the density. R. Zwanzig pointed out that since the complete expression for the transport coefficients should not contain a wavelength cutoff, this cutoff must appear in the expressions for the bare coefficients. Therefore a precise definition of the "bare" part is needed. As regards this cutoff, G. F. Mazenko mentioned that within the framework of his kinetic theory calculations, the bare transport coefficients are just the Enskog values, and that the cutoff is determined by the dimensionless parameter kr_o, where r_o is a hard sphere diameter. The cutoff can be removed by using the properties of the spherical Bessel functions which appear in his work. He also thought it was interesting that all of the various approaches to the long-time tails give the same results, at least at low density.

W. W. Wood asked if there were any explicit formulas for the k and ω dependent transport coefficients in terms of correlation functions that might be studied on the computer. Oppenheim replied that his work with Keyes might be of some interest in this connection since it relates such transport coefficients to four-point correlation functions. Alder pointed out that according to the mode coupling theories, the Burnett coefficients are expected to diverge. If so, he wondered if any experiments could be done on real (laboratory) systems which would exhibit the effects predicted by these theories. For example, what are the predictions on the absorption and dispersion of sound for a dense gas? According to J. R. Dorfman, he and M. H. Ernst[1] and also Y. Pomeau[2] have obtained $k^{5/2}$ terms in the (k,ω) dispersion relation for sound propagation as a consequence of the same mechanism that produces these tails. However, the contribution of these terms is too small to be detected at the present time.

In reply to a question by G. E. Uhlenbeck as to whether sound *dispersion* has been measured in liquids, J. S. Rowlinson mentioned that this is precisely what is measured if one studies the displacement of the Brillouin lines from the Rayleigh line in light scattering experiments. No dispersion of sound has been detected in simple, dense fluids.

R. G. Gordon discussed some work that was done by him and independently by B. J. Berne[3] on molecular rotations in liquids. One expects that a rotating molecule will set up a "vortex-like" pattern which should slow down the Debye relaxation of the rotation. By considering a hydrodynamic model where the molecule is pictured as a rotating cylinder, Gordon found that the relevant correlation functions behave like $t^{-5/2}$ for long times, and a similar result was found by Berne for a rotating sphere. However, in this case also, the effects are too small to be detected.

J. M. Deutch commented that there were really two questions that must be answered: (a) What is the proper form of the transport coefficients? and (b) Given a set of transport coefficients, what is the result of solving the hydrodynamic equations? In his opinion Gordon's work as well as the CIDNP work discussed on Monday answered the second question, but that one is really looking for ways to answer the first question. He also took the opportunity to mention the work of R. Rubin on the behavior of a heavy particle in a lattice which suggests that hydrodynamics is anomalous in two, but not in one and three dimensions. Mazenko said that the same type of theory that gives the long-time tail is used to obtain transport coefficients near the critical point. Consequently the verification of the mode coupling formulae near a critical point provides some justification for the use of the formulae under other circumstances.

N. Corngold described some work that he and J. J. Duderstadt had done on correlation functions similar to those discussed by Deutch.[4] They noted that in order to describe the action of the propagators which project vectors out of the hydrodynamic subspace, one must construct eigenvectors in the orthogonal subspace. As many others have pointed out also, one can take direct products of vectors from the hydrodynamic subspace. The procedure leads directly to a power law, rather than an exponential decay, of the correlation function.

S. Yip mentioned some work of Verlet and co-workers[5] on molecular dynamics calculations of correlation functions and density fluctuations near the triple point of a liquid system whose molecules interact according to a Lennard-Jones potential. Their results indicated that the decay of the correlations could be described by two exponentials, one with very short relaxation time and another about five times larger. However, their work did not extend to the region where one might expect to see the long-time tail.

Uhlenbeck opened a long and very interesting discussion on turbulence. He mentioned that some preliminary light scattering experiments have been made on a fluid near a hydrodynamic instability to see if the instability point behaves like a critical point. Further studies of the onset of instabilities in, say, Poiseuille flow would be especially interesting for clarifying what goes on during the onset of turbulence. According to the picture described in Landau and Lifshitz,[6] the essential ingredients for the onset of turbulence are the Navier-Stokes equations plus successive instabilities or bifurcations. There are, in fact, successive instabilities which seem to cause a kind of randomizing in the fluid. In particular, the velocity distribution functions in the fluid appear to be precisely Gaussian, and this must be produced by the random processes which are associated with successive instabilities.

J. Kestin remarked that the picture of turbulence described by Uhlenbeck is consistent with now generally accepted views. These are the result of the work of Heisenberg and, in particular, of the Tollmien-Schlichting stability theory of transition. Often, the view is expressed that turbulence arises as a result of microscopic, molecular fluctuations. However, he said that there are some difficulties with this view. No one, to the best of his knowledge, has ever observed the onset of turbulence as a result of thermal fluctuations alone. Instead, turbulence always starts in regions of high shear, and even in a turbulent fluid, the flow in a sufficiently small, though macroscopic, region obeys the full Navier-Stokes equations. The measurement of fluctuating velocity components with the aid of a hot wire anemometer would otherwise be impossible. Furthermore, there does not seem to be a critical Reynolds number for the onset of turbulence; for example, in a pipe, this onset can be delayed up to Reynolds numbers of the order of 10^4 by controlling the initial disturbances in the flow.

Zwanzig described some work which was originated by S. F. Edwards. One adds a fluctuating force to the nonlinear Navier-Stokes equation and obtains an equation of the form

$$\frac{\partial \vec{v}}{\partial t} = \nu \nabla^2 \vec{v} - (\vec{v}\cdot\nabla)\vec{v} + \vec{F} \; .$$

Here $\vec{F}$ is a random force. Zwanzig[7] has examined the case where $\vec{F}$ is thermal noise and is connected to ν by the usual fluctuation-dissipation theorem. If one treats the nonlinear term $\{(\vec{v}\cdot\nabla)\vec{v}\}$ as a perturbation, one gets a nonlinear Langevin theory which leads to the long-time tails. On the other hand, if $\vec{F}$ describes "driven" noise, one may get turbulence from an equation of this sort. It is interesting to note that both the long-time tails and turbulence appear to come from the same equations, but for different random terms. Deutch remarked that this was what he had in mind as a molecular theory of turbulence. That is, one would like to know if a molecular theory can justify the adoption of certain assumptions about $\vec{F}$, as well as about the k and ω dependent transport coefficients that might be required to explain turbulence. He also took the opportunity to add nonlinear phenomena to the list of outstanding problems given in his talk.

In reply to Zwanzig, Uhlenbeck said that the addition of noise to the Navier-Stokes equations can only be strictly justified, if one neglects the nonlinear terms. This was first discussed by Landau and Lifshitz.[6] If, however, one adds the noise to the nonlinear equation, one can discuss what happens near a hydrodynamic instability. In particular one can show that the velocity fluctuations get enhanced. Furthermore one should distinguish between "driven" turbulence produced by a grid, and "spontaneous" turbulence which occurs in the flow in a pipe. K. M. Case and S. C. Chiu[8] have considered spontaneous turbulence for the Burgers-Hopf model and have completely confirmed the picture of Landau. They clearly demonstrated the onset of successive instabilities. One would like very much to perform a similar calculation for plane Poiseuille flow. Driven turbulence, however, may be quite different.

Kestin responded by saying that even for flow in a pipe there *is* a grid provided by the walls and by the upstream condition of the flow. He repeated that turbulence is produced in a region of high shear and that transition does not necessarily coincide with the Reynolds number of the first instability.

Uhlenbeck replied that one must be very careful of the entrance flow. The onset of turbulence may be delayed by the production of a metastable flow. Nevertheless, one expects that there is a critical Reynolds number which governs the onset of spontaneous turbulence for flow in a pipe.

R. Kobayashi reported some results of Angus at Case Western Reserve on the subject of boundary conditions that obtain during turbulent flow. The essence of these findings is that zero velocity at the wall cannot be assumed in the turbulent region for bulk flow in, say, a circular pipe. Measurements show that mass transfer rates from the wall to the fluid are greater than would be expected if the velocity at the wall were zero. This indicates that turbulence does exist at the wall and that zero velocity at the wall is not a legitimate boundary condition.

J. Ross mentioned that J. B. Lastovka is conducting light scattering studies at the onset of the Bénard instability at Bell Laboratories. He also mentioned that Deutch, S. Hudson, P. J. Ortoleva and he had performed some work on chemical instabilities.[9]

A major task of the theory, emphasized by Kestin, is to support and describe the actual experimental observations. To the list of outstanding problems in liquid state theory, mentioned earlier, he would, therefore, add (a) A molecular derivation of the Navier-Stokes equations [Such a derivation only exists on the basis of the Boltzmann equation for dilute gases, but has not been given for the conditions pertaining to the liquid state.]; (b) A description of the transport properties as a function of density and temperature of liquids. Alder remarked that molecular dynamics calculations can give reasonable values for the transport properties of a fluid of molecules with a given intermolecular potential, but acknowledged that this procedure amounts to replacing one experiment by another, though a more controlled one. The emphasis of current theoretical activity on the long-time behavior of the correlation functions is due to the conceptual problems associated with this behavior; its experimental significance may be minor except possibly for the resulting enhancement of the diffusion coefficient over the Enskog value as discussed on Monday. The question was raised how firmly this enhancement of the diffusion coefficient due to the long-time tail has been established. Alder explained that about half of the effect is obtained by integrating the autocorrelation function over the time interval studied with the computer; the other half of the effect is then obtained if one extrapolates the asymptotic $t^{-3/2}$ behavior to infinite times.

C. J. Pings reported experimental values of binary diffusion coefficients as a function of concentration for some binary mixtures (nitromethane-benzene and methanol-benzene) and of the thermal diffusivity for nine pure liquids and two binary liquids. These new values were obtained by measuring the central component in the spectrum of scattered light and they agree with available values obtained by more conventional techniques. In order to interpret the scattered light, one needs to separate the contributions from various effects such as mass diffusion, thermal diffusion, thermal diffusivity and relaxation of internal degrees of freedom. The work of Pings and his co-workers illustrates the feasibility of this method for measuring transport properties in liquids. The method offers distinct advantages over the conventional techniques for measuring some of these properties.

Corngold raised the practical question of how one predicts transport properties of dense fluids if one does not have the facilities for conducting molecular dynamics experiments. H. J. M. Hanley discussed a recent review article[10] in which he investigated the predictive capability of current theories of transport properties. It was concluded that a modified Enskog theory (MET) is still to be preferred over many other approaches. Using the MET he was also able to predict the viscosity of liquid fluorine at the saturation boundary which turned out to be in excellent agreement with subsequent experiments. J. V. Sengers remarked that one should distinguish between a systematic theory with well-defined approximations that tries to relate the transport properties to molecular properties and a semiempirical approach in which one follows an *ad hoc* prescription which has turned out to be useful in representing available data. Therefore, as emphasized by Rowlinson, it may not be fair procedure to judge these two different approaches on the basis of the same criteria.

Sengers said that engineers would like to predict dynamical properties, such as transport coefficients, from equilibrium properties, such as the equation of state. The modified Enskog theory is an example of such a procedure. Of course, as pointed out by Alder, such a procedure neglects correlations in the velocities of the molecules.

Kobayashi remarked that the use of corresponding states has also been successful in predicting transport properties.

Pings noted that our current ability to predict the transport properties of dense multi-component systems is limited by a severe lack of knowledge of the mixing rules.

Gordon agreed with Deutch that magnetic resonance methods provide disappointingly little help in distinguishing between different models of molecular rotation in liquids. One basic weakness of these results lies in the fact that only a single number (T_1) is measured, and this generally gives only the *area* under the rotational correlation function. More complete information about the time dependence of rotational correlation functions is available by Fourier transformation of infrared and Raman spectra.[11] This experimental information on rotation of molecules in simple liquids, such as N_2, CO and CH_2, is extremely helpful in checking the validity of molecular dynamics simulation of molecular liquids.

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