a good approximation for more complicated cases. In addition, the matrix elements obtained can be used to study the field dependence of other moments of the ion-distribution function.

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[1] P. P. Ong and J. B. Hasted, J. Phys. B **2**, 91 (1969).

[2] J. Heimerl, R. Johnsen, and M. A. Biondi, J. Chem. Phys. **51**, 5041 (1969).

[3] S. B. Woo and S. F. Wong, J. Chem. Phys. **55**, 3531 (1971).

[4] E. A. Mason and H. Hahn, Phys. Rev. A **5**, 438 (1972). There is an error in the expression for the energy partitioning in this paper: In Eqs. (27) and (29) the Q_j should be replaced by $\langle \nu_{rj} Q_j \rangle$.

[5] J. H. Whealton and E. A. Mason, Phys. Rev. A **6**, 1939 (1972).

[6] G. H. Wannier, Phys. Rev. **83**, 281 (1951).

[7] G. H. Wannier, Bell Syst. Tech. J. **32**, 170 (1953).

[8] T. Kihara, Rev. Mod. Phys. **25**, 844 (1953).

[9] E. A. Mason and H. W. Schamp, Ann. Phys. (N.Y.) **4**, 233 (1958).

[10] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge U.P., London, 1970), Chap. 9.

[11] G. W. Ford, Phys. Fluids **11**, 515 (1968).

[12] E. A. Mason, J. Chem. Phys. **27**, 75 (1957).

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Light-Scattering Experiments and Generalized Transport Coefficients

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We discuss the relation between the observed spectra in the Rayleigh–Brillouin light-scattering experiments for molecular fluids and the generalized transport coefficients. For a two-level molecular fluid undergoing thermal relaxation, we derive the generalized hydrodynamic equations for the conditions when translational motion is hydrodynamic. For two explicit examples of parahydrogen and sulphur hexafluoride, we numerically evaluate the wave-number- and frequency-dependent transport coefficients implied by the generalized hydrodynamic equations. We then critically examine the implication of these results for the phenomenological analysis of the polarized-light-scattering spectra, which is commonly employed by most workers in the field. We find that the most important quantity for the description of such experiments on intermediate-density fluids is a frequency- and wave-number-dependent bulk viscosity rather than a frequency-dependent thermal conductivity.

I. CORRELATIONS IN HYDRODYNAMIC VARIABLES FOR A TWO-STATE FLUID

In the past few years many investigations which utilize the laser light scattering to probe the dynamical processes occurring in liquids and gases have been reported. One aspect of this topic which has received considerable attention is the measurement and description of the polarized Rayleigh–Brillouin spectrum of molecular fluids. In this paper we will restrict our discussion to those molecular systems that can be described by an approach in which the translational motion of the molecules is hydrodynamic. This is not a great restriction, since molecular liquids and all but the lowest-density regions of gaseous systems can be described in this manner. For such systems, one usually modifies the normal hydrodynamic equations in some manner which is designed to take into account the coupling to the internal relaxation processes. Such modifications are often carried out by introducing frequency-dependent transport coefficients. The agreement between the dynamic structure factor $S(k, \omega)$ calculated from these equations and the measured value in the scattering experiment is then used to provide evidence for the existence of frequency-dependent transport coefficients. Modifications of the hydrodynamic equations which involve the introduction of a relaxing bulk viscosity have been able to adequately describe the light-scattering experiments on molecular liquids. The failure of this modification to describe the experiments on molecular gases at low density has recently been attributed to the existence of a relaxing thermal conductivity.[1] One of the goals of this paper will be to examine these interpretations in some detail.

In the analysis that follows we will only consider a particularly simple example, the thermal relaxation of a two-state system. A detailed treatment of this system has already been given elsewhere.[2] There, the starting equations have been derived and $S(k, \omega)$ has been calculated for parahydrogen gas as a function of density. Consequently, none of the details given previously need be repeated here. However, rather than focus on $S(k,\omega)$ or the roots of the dispersion equations, we will cast the starting equation into the form of generalized hydrodynamic equations and interpret the results on the basis of frequency- (ω-) and wave-number- (k-) dependent transport coefficients. In doing this, we will be able to establish clear relations between many of the previously proposed hydrodynamiclike theories and delineate their range of validity. The principal result of this investigation is that the frequency dependence of the thermal conductivity plays a minor role, and it is the introduction of wave-number dependence in the usual[3] frequency-dependent bulk viscosity that accounts for most of the observed effects for the intermediate-density fluids.

The generalized Langevin equation appropriate for the description of the thermal relaxation of the two-level system can easily be obtained by using standard methods.[4] The results can be written in the form

$$\frac{d\underline{A}(\vec{k}, t)}{dt} = -\underline{\mathfrak{M}}(k)\underline{A}(\vec{k}, t) + \underline{F}(\vec{k}, t), \tag{1.1}$$

after a Markov approximation to the damping matrix has been made.[2] The vector $\underline{A}(\vec{k})$ contains a collection of variables, $\{\rho(\vec{k}),\ T(\vec{k}),\ J(\vec{k}),\ \tilde{u}(\vec{k})\}$, and $\underline{F}(\vec{k})$ is the corresponding random force vector. Three of the variables are the normal conserved hydrodynamic variables; $\rho(\vec{k})$, $T(\vec{k})$, and $J(\vec{k})$ are the spatial Fourier transforms of the total mass-density, temperature, and longitudinal momentum-density fluctuations, respectively. For the two-level system under consideration, i.e., one in which the translational motion is hydrodynamic, little difficulty is encountered in specifying the nature of the fourth variable; it must be a variable which characterizes the relative populations of the internal states. There is still a certain degree of flexibility, since many variables of this type can be constructed [e.g., one could choose $c(\vec{k})$, the concentration fluctuation, or $u(\vec{k})$, the internal-energy-density fluctuation]. However, if one is interested in constructing extensions of hydrodynamic equations, an additional constraint must be imposed on the selection of the fourth variable (this will be described more fully in Sec. II); it must be chosen to be orthogonal to the conserved hydrodynamic variables. Hence, we define $\tilde{u}(\vec{k})$ as

$$\tilde{u}(\vec{k}) = \rho_0[u_{12}c(\vec{k}) - c_I T(\vec{k})], \tag{1.2}$$

where ρ_0 is the equilibrium mass density, c_I is the internal specific heat per unit mass, and u_{12} is the difference of the internal energies of the two states. The linearized concentration fluctuation is given by

$$c(\vec{k}) = [\rho_{20}\rho_1(\vec{k}) - \rho_{10}\rho_2(\vec{k})]/\rho_0^2, \tag{1.3}$$

where $\rho_\alpha(\vec{k})$ is the mass-density fluctuation for molecules in state α and $\rho_{\alpha 0}$ is the corresponding equilibrium quantity. Other variables proportional to $\tilde{u}(\vec{k})$ could have been selected, but $\tilde{u}(\vec{k})$ is just the orthogonalized internal-energy-density variable used in Ref. 5.

For convenience the $\underline{\mathfrak{M}}(k)$ matrix in Eq. (1.1) is given in the Appendix along with a list of the approximations made in obtaining the explicit form of $\underline{\mathfrak{M}}(k)$ used in this work.

In the remaining part of Sec. I we will be concerned with equations which describe the relaxation of the conserved variables in the presence of an internal relaxation process characterized by $\tilde{u}(\vec{k})$. We denote the collection of variables $\{\rho(\vec{k}),\ T(\vec{k}),\ J(\vec{k})\}$ by the vector $\underline{B}(\vec{k})$. Using the solution for $\tilde{u}(\vec{k}, t)$ in the remaining equations, we obtain, after Laplace transformation in time, the result

$$\underline{B}(\vec{k}, \epsilon) = [\epsilon \underline{I} + \underline{M}(k, \epsilon)]^{-1}[\underline{B}(\vec{k}) + \underline{f}(\vec{k}, \epsilon)], \tag{1.4}$$

where $\underline{M}(k, \epsilon)$ is given by

$$\underline{M}(k, \epsilon) = \begin{bmatrix} 0 & 0 & -ik \\ 0 & \dfrac{k^2\lambda(k, \epsilon)}{\rho_0 c_v} & -\dfrac{ikT_0\alpha_T}{\rho_0^2 c_v \kappa} G(k, \epsilon) \\ -\dfrac{ik}{\rho_0 \kappa} & -\dfrac{ik\alpha_T}{\kappa} G(k, \epsilon) & \dfrac{k^2}{\rho_0}[\tfrac{4}{3}\eta_s^* + \eta_v(k, \epsilon)] \end{bmatrix}. \tag{1.5}$$

The frequency- and wave-number-dependent quantities in the above equation are defined by

$$\lambda(k, \epsilon) = \lambda - \frac{k^2\rho_0 c_I c_{v\infty}(\lambda^*/\rho_0 c_{v\infty} - D)^2}{c_v[\epsilon + \delta(k)]}, \tag{1.6}$$

$$G(k, \epsilon) = 1 - \frac{k^2 c_I(\lambda^*/\rho_0 c_{v\infty} - D)}{c_v[\epsilon + \delta(k)]}, \tag{1.7}$$

and

$$\eta_v(k, \epsilon) = \eta_v^* + \frac{(c_\infty^2 - c_0^2)\rho_0}{[\epsilon + \delta(k)]}, \tag{1.8}$$

with

$$\delta(k) = \frac{k^2}{\rho_0 c_v}\left(Dc_{v\infty}\rho_0 + \frac{\lambda^* c_I}{c_{v\infty}}\right) + \frac{c_v}{c_{v\infty}\tau_R}. \tag{1.9}$$

In Eqs. (1.5)–(1.9) λ is the thermal conductivity, $\lambda = \lambda^* + \rho_0 c_I D$, where λ^* is the translational contribution, and D is the self-diffusion coefficient. $c_{v\infty}$ is the contribution to the specific heat per unit mass when internal degrees of freedom are frozen, with $c_v = c_{v\infty} + c_I$. η_s^* and η_v^* are those parts of the shear and bulk viscosities, respectively, when the internal degrees are frozen, while κ and α_T are the isothermal-compressibility and thermal-expansion coefficients, respectively. The low-frequency sound speed is c_0, and the high-frequency value is denoted by c_∞.

The vector $\underline{\mathrm{f}}(\vec{\mathrm{k}}, \epsilon)$ in Eq. (1.4) is related to the elements of $\underline{\mathrm{F}}(\vec{\mathrm{k}}, \epsilon)$ and the initial value $\tilde{u}(\vec{\mathrm{k}})$, as

$$\underline{\mathrm{f}}(\vec{\mathrm{k}}, \epsilon) = \begin{pmatrix} F_1(\vec{\mathrm{k}}, \epsilon) \\ F_2(\vec{\mathrm{k}}, \epsilon) \\ F_3(\vec{\mathrm{k}}, \epsilon) \end{pmatrix} - \begin{pmatrix} 0 \\ k^2 (D - \lambda^*/\rho_0 c_{v\infty})/(\rho_0 c_v) \\ ik\alpha_T/(\rho_0 c_v \kappa) \end{pmatrix} \times \frac{\tilde{u}(\vec{\mathrm{k}}) + F_4(\vec{\mathrm{k}}, \epsilon)}{\epsilon + \delta(k)} \; . \quad (1.10)$$

Note that if $\tilde{u}(\vec{\mathrm{k}})$ were not selected to be orthogonal to $\underline{\mathrm{B}}(\vec{\mathrm{k}})$, $\underline{\mathrm{f}}(\vec{\mathrm{k}}, \epsilon)$ would not be orthogonal to $\underline{\mathrm{B}}(k)$. However, since $\langle \underline{\mathrm{f}}(\vec{\mathrm{k}}, \epsilon) \underline{\mathrm{B}}(\vec{\mathrm{k}})^\dagger \rangle = \underline{0}$, where we have denoted the average over the equilibrium ensemble by $\langle \cdots \rangle$, the equation describing the relaxation of the matrix of conserved variables can be written in the simple form

$$\langle \underline{\mathrm{B}}(\vec{\mathrm{k}}, \epsilon) \underline{\mathrm{B}}(\vec{\mathrm{k}})^\dagger \rangle \langle \underline{\mathrm{B}}(\vec{\mathrm{k}}) \underline{\mathrm{B}}(\vec{\mathrm{k}})^\dagger \rangle^{-1} = [\epsilon \underline{\mathrm{I}} + \underline{\mathrm{M}}(k, \epsilon)]^{-1} \, . \quad (1.11)$$

In the polarized-light-scattering experiment (Rayleigh–Brillouin), one probes the fluctuations in the scalar dielectric coefficient $\delta\epsilon$. In calculating its autocorrelation function for one-component systems, one usually expresses $\delta\epsilon$ in terms of the fluctuations in two thermodynamic variables, viz., $\delta\rho$ and δT, and then makes the approximation that, owing to the smallness of the thermodynamic derivative $(\partial\epsilon/\partial T)_\rho$, the term in δT can be neglected. Then the measured line shape is proportional to the double Fourier transform of the density autocorrelation function $S(k, \omega)$. If the one-component fluid under consideration is a molecular fluid, the above identification also implies that the molecule will have the same polarizability, regardless of its internal state.

The calculation outlined earlier using the set of variables $\{\rho, T, J, \tilde{u}\}$ leads to a definite result for $S(k, \omega)$. Since the variables T, J, and $\tilde{u}$ are orthogonal to ρ, $S(k, \omega)$ does not depend on their initial values. In our previous work[2,5] we have used three other sets of variables, $\{\rho_1, \rho_2, \theta, J\}$, $\{\xi_1, \xi, \theta, J\}$, and $\{\xi_1, \rho, \theta', J\}$. All these sets are linear combinations of the set $\{\rho, T, J, \tilde{u}\}$ considered here. Moreover, the linear combinations are such that the orthogonality with respect to the total density variable ρ is maintained in the initial and the contracted descriptions. As a consequence, regardless of the initial value chosen for the remaining variables, the results for $S(k, \omega)$ using all four sets of variables are identical. The orthogonality of the density variable is an important requirement in the calculation for $S(k, \omega)$ using any extended set of variables in a generalized hydrodynamic theory.[4]

It is important to keep in mind the fact that the starting equations of the present treatment have been derived (see Appendix of Ref. 2) and are obtained by introducing certain well-defined approximations in the exact microscopic equations of motion. These starting equations are not equivalent to those assumed by Mountain in his theory which introduces a relaxing variable (M_t theory). As a consequence, $S(k, \omega)$ calculated by Mountain [Ref. 6, Eqs. (21)–(23)] is different from that obtained using any of the four sets of variables just discussed. This difference has previously been discussed by us both analytically and numerically for the case of parahydrogen gas. From Fig. 2 of Ref. 2, we note that for the two-level system, $S(k, \omega)$ implied by Eqs. (1.11) and (1.5) agrees with the result of a translationally kinetic calculation,[7] whereas that implied by the M_t theory disagrees.

II. GENERALIZED HYDRODYNAMIC EQUATIONS AND (k, ω)-DEPENDENT TRANSPORT COEFFICIENTS

Within the range of validity of the Markov approximation, Eq. (1.1) and the corresponding contracted Eq. (1.4) describe the time evolution of the microscopic fluctuating variables $\underline{\mathrm{A}}(\vec{\mathrm{k}}, t)$ and $\underline{\mathrm{B}}(\vec{\mathrm{k}}, t)$, respectively. From Eq. (1.4), we note that if the translational motion is hydrodynamic, the lag of the internal motion provides the memory in the evolution of the hydrodynamic variables as given by the nonhydrodynamic form of the elements of $\underline{\mathrm{M}}(k, \epsilon)$. Moreover, $\underline{\mathrm{f}}(\vec{\mathrm{k}}, \epsilon)$ depends not only on the random force $\underline{\mathrm{F}}(\vec{\mathrm{k}}, \epsilon)$, but also on the initial value of the internal-energy density $\tilde{u}(\vec{\mathrm{k}})$.

In order to deduce the generalized hydrodynamic equations, we have to average the microscopic equations given in Eq. (1.4) over a nonequilibrium ensemble[4] which corresponds to the usual hydrodynamic description. This implies an ensemble in which only the fluctuations of the three hydrodynamic variables are constrained to have the specified initial values $\underline{\mathrm{B}}(\vec{\mathrm{k}})$. In this ensemble, the initial values for the variables orthogonal to the hydrodynamic variables [$\tilde{u}(\vec{\mathrm{k}}, t)$ is such a variable] are not constrained and are assumed to be random. When averaged over such an ensemble, the average value of $\tilde{u}(\vec{\mathrm{k}})$ becomes zero. The random forces $\underline{\mathrm{F}}(\vec{\mathrm{k}}, \epsilon)$ are orthogonal to $\underline{\mathrm{B}}(\vec{\mathrm{k}})$, and thus they also contribute zero to the nonequilibrium ensemble average. Thus, if we denote the nonequilibrium ensemble average $\langle \cdots \rangle_{\rm ne}$, Eq. (1.4) becomes

$$\langle \underline{B}(\vec{k}, \epsilon)\rangle_{\rm ne} = [\epsilon \underline{I} + \underline{M}(k, \epsilon)]^{-1} \langle \underline{B}(\vec{k})\rangle_{\rm ne}. \qquad (2.1)$$

These are the generalized hydrodynamic equations for the macroscopic hydrodynamic variables $\langle B(\vec{k}, \epsilon)\rangle_{\rm ne}$. The relaxation matrix $\underline{M}(k, \epsilon)$ is given in Eq. (1.5); from Eq. (1.5), we can deduce the generalized transport coefficients. These are given in Eqs. (1.6)–(1.9). The important conclusion emerging from these equations is that the transport coefficients depend on wave number as well as frequency. We shall show later that (i) for the two-state model, the wave-number dependence can be quite significant in practice, and (ii) the (k, ω) dependence in the elements M_{23} and M_{32} through the Burnett-type transport coefficient G is the feature which is absent in the previous phenomenological treatments.

It should be clear from the discussion in Sec. I that it is not necessary to use the above generalized hydrodynamic equations in the interpretation of light-scattering experiments. This is due to the lack of sensitivity of these experiments to the temperature and momentum-density fluctuations. By choosing for $\underline{A}(\vec{k})$ any set of variables which is a linear transformation of the set $\{\rho, T, J, \tilde{u}\}$ and making arbitrary assumptions about the initial values of the variables orthogonal to $\rho(\vec{k})$, the same correct expression for $S(k, \omega)$ is obtained. A particular example of this procedure is described in Ref. 2, where an equation which describes the relaxation from an initially constrained state [equivalent in the present notation to setting $c(\vec{k}) = 0$] is used to calculate $S(k, \omega)$. The calculation in Ref. 2 uses a nonequilibrium ensemble that is different from the nonequilibrium hydrodynamic ensemble used in deducing Eq. (2.1). Since $c(\vec{k})$ is orthogonal to $\rho(\vec{k})$ this constraint has no effect on the calculation of the light-scattering spectrum. Hence, many relaxation equations using a variety of nonequilibrium ensembles can provide a correct description of the density fluctuations. However, only the generalized hydrodynamic matrix $\underline{M}(k, \epsilon)$ in Eq. (1.5) can be used to calculate all the elements of the correlation function matrix $\langle \underline{B}(\vec{k}, \epsilon) \underline{B}(\vec{k})^{\dagger}\rangle$. In addition it is only this matrix which will reduce to the normal hydrodynamic matrix when terms up to order k^2 are retained and ϵ is set equal to zero. Using any other set of variables, one can get a relaxation matrix with $(\vec{k}, \epsilon)$-dependent elements; however, these cannot be interpreted as generalized transport coefficients.

In recent years, it has become customary[3,8,9] to analyze the light-scattering spectrum from molecular fluids by using hydrodynamic equations with frequency-dependent transport coefficients. There are many hazards in such a phenomenological approach. For example, in the correct generalized hydrodynamic equations given in Eq. (2.1), there appear the off-diagonal elements M_{23} and M_{32} which depend on frequency and wave number. These are analogous[10,11] to the generalized Burnett transport coefficients of the dilute-gas kinetic theory and describe the coupling between the energy- and momentum-density fluctuations. In the theories where frequency-dependent transport coefficients are phenomenologically introduced in the ordinary hydrodynamic equations, there is no way to introduce these coupling effects unless one incorrectly introduces frequency dependence in equilibrium thermodynamic derivatives like specific heat. However, such coupling transport coefficients have been found to appear naturally in previously derived generalized hydrodynamic equations.[10–12]

In most of the previous studies which use frequency-dependent transport coefficients to analyze light-scattering spectra, not only are the effects due to (k, ω) dependence in the elements M_{23} and M_{32} absent, but also the wave-number dependence in the usual transport coefficients is neglected. The latter is quite crucial in calculating the correct line shape for some ranges of density and frequency.

The frequency and wave-number dependence in the transport coefficients can arise because of two different effects. One is purely due to the possibility of the translational motion being kinetic. In such a situation, a kinetic equation is usually more appropriate as compared to the generalized hydrodynamic description. In the translationally hydrodynamic region, the nonhydrodynamic nature of the internal molecular motion provides the (k, ω) dependence in the transport coefficients. In particular, for the two-state model, there are[2] two competing means available to the fluid to average out the hydrodynamic fluctuations: one which makes an excited molecule diffuse away from a given position, and another which makes it decay to the ground state at the same position. Owing to the former mechanism, the relaxation rate becomes k dependent. Equation (1.9), which gives the k-dependent relaxation rate for all the transport coefficients in the two-state model, makes the above discussion quantitative. Provided that (i) relaxation time τ_R is so small that τ_R^{-1} dominates the relaxation rate $\delta(k)$ and (ii) the scattering experiment is performed for such small k values that the terms of order k^3 and higher are negligible in various elements M_{ij} in Eq. (1.5), then Eq. (2.1) reduces to the form in which there is no wave-number dependence in the transport coefficients λ, G, and η_v, and only η_v retains the frequency dependence. This limit[5] gives the form for $S(k, \omega)$ which is identical to the weak-coupling theory used by Mountain.[3] These conditions are fulfilled in light-scattering experiments on some liquids where the

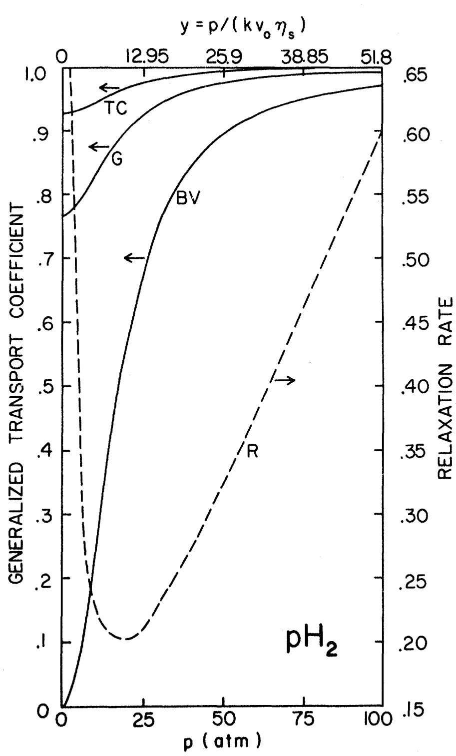

FIG. 1. Parahydrogen—generalized transport coefficients (normalized to the hydrodynamic value) as functions of pressure (lower abscissa) or y (upper abscissa), with ordinate scale on the left-hand side. The curve labeled TC shows $\lambda(k, 0)/\lambda(0, 0)$, the one labeled G shows $G(k, 0)$, and the one labeled BV shows $\eta_v(k, 0)/\eta_v(0, 0)$. Also shown is the relaxation rate $\delta(k)/kv_0$ (labeled R) as a function of pressure or y with ordinate scale on the right-hand side. See text for explanation of symbols.

phenomenological theory[3] has been found to be adequate; in this limiting case, the more general result of Eq. (2.1) would also be satisfactory. In the intermediate-fluid-density region where both k and ω dependence become important, only Eq. (2.1) coupled with Eq. (1.5) would be satisfactory.

In the remaining part of the section, we discuss the numerical results for the (k, ω) dependence in the transport coefficients λ, G, and η_v as given by Eqs. (1.6)–(1.9) for two explicit examples. One is the case of parahydrogen pH_2, where the two-state model is quite good for fairly high temperatures, and for which the calculation of $S(k, \omega)$ has been recently discussed.[2] Here we use the same set of constants for the calculation as used in Ref. 2. For the other example, we consider the vibrational relaxation in SF_6 for the same experimental conditions as those analyzed recently by Clark, Mellman, and Greytak.[9] Here we treat the system as an *effective* two-state model: c_I is the vibrational specific heat, and $c_{v\infty}$ includes the translational and rotational contribution; also λ^* includes the contribution from the translational and rotational modes to the thermal conductivity. The constants used in the computation are given in Table I. In Fig. 1 we show some of the results for pH_2 and in Fig. 2 for SF_6. In both figures we show the wave-number dependence of the three transport coefficients λ, G, and η_v at zero frequency, as well as that of the relaxation rate $\delta(k)$, through

TABLE I. Constants used in the computation.

	pH_2	SF_6
T_0 (°K)	297	296
v_0 (cm/sec)	1.56×10^5	1.83×10^4
k (cm^{-1})	1.40×10^5	1.84×10^4
$\tau_R{}^a$ (sec)	1.30×10^{-8}	7.3×10^{-7}
D^a (cm^2/sec)	1.46	3.47×10^{-2}
η (P)	8.92×10^{-5}	1.56×10^{-4}
η_v^* (P)	0	2.03×10^{-4}
λ (erg/cm sec °K)	1.81×10^4	1.43×10^3
λ^* (erg/cm sec °K)	1.31×10^4	5.23×10^2
mc_v/k_B	2.5	10.6
$mc_{v\infty}/k_B$	1.5	3

[a] Value at one atmosphere and temperature T_0.

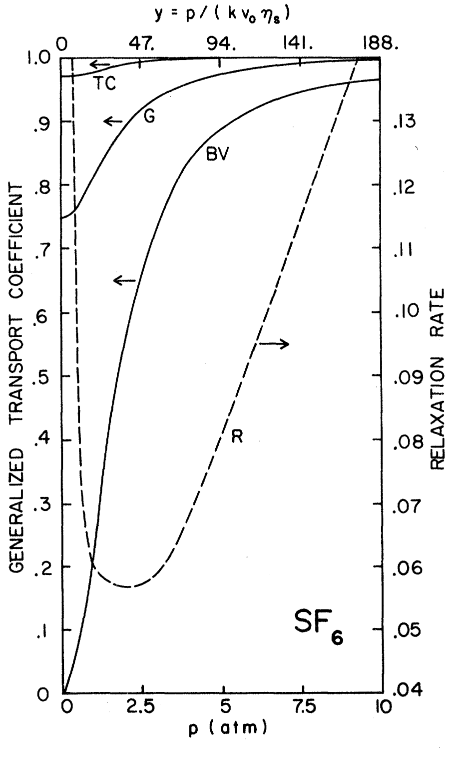

FIG. 2. SF_6—symbols same as in Fig. 1.

their variation with the dimensionless variable $y = p/(kv_0\eta_s)$, where $v_0^2 = 2k_BT/m$. Experimentally, the same variation can be seen either by changing k (scattering angle) or the pressure p. The latter variation is usually more convenient while working with low-density gases. Thus, in the figures both the y parameter and the pressure are shown as abscissas. The transport coefficients are plotted after dividing by their hydrodynamic values, and the relaxation rate is rendered dimensionless by dividing with kv_0. For comparison, the range of values that ω/kv_0 takes in a typical Rayleigh-Brillouin experiment is between 0 and 1, 5. It is assumed that in the pressure range shown, D and τ_R are inversely proportional to density. For simplicity in calculations, the ideal-gas law is also assumed to hold. But the corrections to the ideal-gas law are small for both pH_2 and SF_6 in the pressure range of interest and do not change the quantitative conclusions.

The frequency dependence of the three generalized transport coefficients (found by putting $\epsilon = -i\omega$ and taking the real part) is Lorentzian with the relaxation rate fixed by the values of k and p or y. This relaxation rate for both pH_2 and SF_6 goes through the characteristic sharp minimum, making the k dependence of the relaxation rate quite important in the description. Turning to the variation of the transport coefficients, one notes again the qualitative similarity in the results for pH_2 and SF_6. The change in the bulk viscosity is much greater than that in either the thermal conductivity or the coupling transport coefficient G. The variation in G is greater than that in λ. These conclusions are valid for the variation as a function of k, p, or y at fixed ω on the one hand, and also for the variation as a function of ω with fixed k and p. The transport coefficients λ, G, and η_v implied by all three theories of Mountain[3,6,8] would yield a straight line with constant (y-independent) value of unity in both the figures, whereas the relaxation rate would be a straight line passing through the origin and having a slope determined by τ_R alone.

The explicit numerical calculation as well as the general discussion prior to the calculation has been made to demonstrate our conviction that *ad hoc* extension[3,8,9] of ordinary hydrodynamic equations using only the frequency dependence in some or all of the hydrodynamic transport coefficients to analyze the polarized-light-scattering experiments from molecular fluids may lead to misleading results. From the present discussion, it is clear that much of the effect attributed[9] to a relaxing thermal conductivity can actually be traced to a relaxing bulk viscosity with a modified k-dependent relaxation time. We also note that the (k, ω) dependence in the higher-order Burnett-type transport coefficients cannot be obtained by a phenomenological extension of the hydrodynamic equations.

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APPENDIX

For completeness, we present the elements of the $\underline{\mathfrak{M}}(k)$ matrix which forms the starting point of the analysis presented in this paper. As mentioned in the text, this matrix is just a linear transformation of the corresponding matrix presented in the Appendix of Ref. 2, which has been derived from the microscopic generalized Langevin equation by making a Markov approximation. If we let $\overline{v}_{12} = D_T = l_{v1} = 0$ in Eqs. (A22)–(A40) of Ref. 2 (where the approximations are discussed in detail) and let $\underline{\mathfrak{U}}$ denote the matrix which transforms the set of variables $\{\rho_1(\vec{k}), \rho_2(\vec{k}), \theta(\vec{k}), J(\vec{k})\}$ to the set $\{\rho(\vec{k}), T(\vec{k}), J(\vec{k}), \tilde{u}(\vec{k})\}$ then

$$\underline{\mathfrak{M}}(k) = \underline{\mathfrak{U}}(\underline{\mathfrak{M}}(k))_{\mathrm{Ref.\,2}}\underline{\mathfrak{U}}^{-1}. \tag{A1}$$

The elements of $\underline{\mathfrak{M}}(k)$ are

$$\mathfrak{M}_{11}(k) = \mathfrak{M}_{12}(k) = \mathfrak{M}_{21}(k) = \mathfrak{M}_{41}(k) = \mathfrak{M}_{14}(k) = 0, \tag{A2}$$

$$\mathfrak{M}_{13}(k) = -ik, \tag{A3}$$

$$\mathfrak{M}_{22}(k) = k^2\lambda/\rho_0 c_V, \tag{A4}$$

$$\mathfrak{M}_{23}(k) = -ikT_0\alpha_T/\rho_0^2 c_v\kappa, \tag{A5}$$

$$\mathfrak{M}_{24}(k) = -k^2(\lambda^*/\rho_0 c_{v\infty} - D)/\rho_0 c_v, \tag{A6}$$

$$\mathfrak{M}_{31}(k) = -ik/\rho_0\kappa, \tag{A7}$$

$$\mathfrak{M}_{32}(k) = -ik\alpha_T/\kappa, \tag{A8}$$

$$\mathfrak{M}_{33}(k) = (k^2/\rho_0)(\tfrac{4}{3}\eta_s^* + \eta_v^*), \tag{A9}$$

$$\mathfrak{M}_{34}(k) = ik\alpha_T/\rho_0 c_{v\infty}\kappa, \tag{A10}$$

$$\mathfrak{M}_{42}(k) = k^2\rho_0 c_I(D - \lambda/\rho_0 c_V), \tag{A11}$$

$$\mathfrak{M}_{43}(k) = ikc_I T_0\alpha_T/c_v\rho_0\kappa, \tag{A12}$$

$$\mathfrak{M}_{44}(k) = \frac{k^2}{\rho_0 c_v}\left(Dc_{v\infty}\rho_0 + \frac{\lambda^* c_I}{c_{v\infty}}\right) + \frac{c_v}{c_{v\infty}\tau_R}. \tag{A13}$$

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[1] E. H. Hara, A. D. May, and H. F. P. Knaap, Can. J. Phys. **49**, 420 (1971).

[2] R. C. Desai and R. Kapral, Phys. Rev. A **6**, 2377 (1972).

[3] R. D. Mountain, J. Res. Natl. Bur. Stand. (U. S.) A70, 207 (1966).

[4] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).

[5] M. Weinberg and I. Oppenheim, Physica (Utr.) **61**, 1 (1972); M. Weinberg, Phys. Rev. A **6**, 320 (1972).

[6] R. D. Mountain, J. Res. Natl. Bur. Stand. (U. S.) A72, 95 (1968).

[7] C. D. Boley, R. C. Desai, and G. Tenti, Can. J. Phys. **50**, 2158 (1972).

[8] R. D. Mountain, J. Res. Natl. Bur. Stand. (U. S.) A73, 593 (1969). For the present discussion, the effects of critical-point fluctuations should be suppressed by letting the coherence length ξ be zero.

[9] N. A. Clark, G. R. Mellman, and T. J. Greytak, Phys. Rev. Lett. **29**, 150 (1972).

[10] P. A. Selwyn and I. Oppenheim, Physica (Utr.) **54**, 161 (1971); Physica (Utr.) **54**, 195 (1971).

[11] P. Gray and C. A. Cooper, Mol. Phys. **22**, 697 (1971).

[12] E. Tong and R. C. Desai, Phys. Rev. A **2**, 2129 (1970).

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Measurement of Smectic-*A*-Phase Order-Parameter Fluctuations near a Second-Order Smectic-*A*–Nematic-Phase Transition

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The anisotropic liquid-structure factor of *p*-cyanobenzylidene-amino-*p*-*n*-octyloxybenzene has been measured in the nematic phase using Cu $K\alpha$ x rays. This material exhibits a second-order phase transition to the smectic *A* phase at $T_c = 82.8\,^\circ\mathrm{C}$. The liquid-structure factor shows a non-Lorentzian peak at a wave number of $q_0 = 0.179\ \text{Å}^{-1}$ (equivalent *d* spacing 35.0 Å) of the following form: $S_q = 1 + \{3.5\epsilon^\gamma + 10\,[(q_\parallel - q_0)/q_0]^2 + 0.6(q_\perp/q_0)^\eta\}^{-1}$, where $\epsilon = (T - T_c)/T_c$, $\gamma = 1.49 \pm 0.1$, $\eta = 2.5 \pm 0.2$, and $\hbar q_\parallel$ ($\hbar q_\perp$) are the momentum transfers parallel (perpendicular) to the orienting field.

I. INTRODUCTION

The author[1] has recently published a measurement of the anisotropic-liquid-structure factor in the nematic phase of *p*-*n*-octyloxybenzylidene-*p*-toluidine (OBT), a material which has a first-order nematic-smectic-*A*-phase transition. The liquid-structure factor is peaked in field direction and at a scattering angle equal to the smectic-*A* Bragg angle. The peak shape is Lorentzian and the peak height grows as one approaches the transition to the smectic-*A* phase. This pretransition phenomenon is physically due to small regions of the nematic fluctuating into a smectic-*A*-like configuration. Mathematically one describes the phenomenon using a Landau theory of the phase transition and calculating the scattering due to order-parameter fluctuations. The Landau theory is due to the author[2] and to deGennes.[3] The theory predicts a Lorentzian peak in the liquid-structure factor with the peak height varying as $(T - T^*)^{-1}$, where T^* is a critical temperature somewhat below the first-order transition temperature. The measurements on OBT agreed well with the peak shape and temperature dependence predicted by the Landau theory. The correlation length is 84 Å, 0.3 °C above the phase transition.

In the present paper we present a measurement of the anisotropic-liquid-structure factor in the nematic phase of *p*-cyanobenzylidene-amino-*p*-*n*-octyloxybenzene (CBAOB). In this material the smectic-*A*-nematic-phase transition is second order. The peak height varies as $(T - T_c)^{-\gamma}$ with $\gamma = 1.49 \pm 0.1$ and the peak shape is no longer Lorentzian but falls off faster in the transverse direction. The longitudinal correlation length is very long, ~2500 Å, 0.2 °C above the phase transition.

The x-ray apparatus has been described previously. The present sample showed stronger scattering near the phase transition and it was, therefore, possible to work at higher resolution; collimators of 0.3×3 mm were used in addition to the 1×3-mm collimators used previously.

The sample of CBAOB obtained from Eastman (No. 923247) was relatively pure and was recrystallized once from ethanol. The transition temperatures were measured with a polarizing microscope equipped with a Mettler FP5 hot stage and the transition entropies were measured on a Perkin–Elmer DSC-1B differential scanning calorimeter; these results are reported in Table I. The smectic-*A*-nematic transition was unobservable on the calorimeter, which can detect a transition entropy of about $0.02R_0$; this transition is presumably second order.

The experimental results are presented in Sec. II and analyzed in Sec. III.

TABLE I. Transition temperatures and transition entropies of CBAOB. The smectic-*A*-nematic transition is unobservable on the scanning calorimeter.

Transition	Temperature (°C)	Entropy
Crystal → smectic *A*	73.2	$9.1R_0$
Smectic *A* → nematic	82.8	$<0.02R_0$
Nematic-isotropic	107.5	$0.26R_0$