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Translational Hydrodynamics and Light Scattering from Molecular Fluids*

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The density fluctuations in a molecular fluid are studied by treating the fluid as a multicomponent reacting mixture. The *ordinary* hydrodynamic equations for a reacting mixture form the starting point of the present derivation. The description is then contracted to that appropriate for the one-component molecular fluid. The resulting *translational hydrodynamics* theory contains memory effects due to the internal relaxation process. The results are compared with a recent kinetic model and with two previous theories of Mountain. The dynamic structure factor $S(k, \omega)$ and the roots of the dispersion relation are computed for parahydrogen gas and studied as a function of density. The results indicate that the treatment of the thermal-diffusivity mode in the theories by Mountain breaks down in the low-density region. It is suggested that Rayleigh-Brillouin scattering experiments on dilute parahydrogen gas at room temperature and densities between 5 and 30 amagats can quantitatively verify the predictions of translational hydrodynamics.

I. INTRODUCTION

In this article we consider the calculation of density fluctuations in a single-component molecular fluid, and the interpretation of light scattering experiments which can be used to probe these fluctuations. For simple liquids, it is natural to attempt such calculations by using the linearized hydrody-

amic equations.¹ However, it is well known from ultrasonics² and light scattering experiments³ that for molecular fluids these equations do not correctly describe the frequency dependence of the sound absorption coefficient or the spectrum of the scattered light. If the molecular fluid is a dilute gas, the appropriate kinetic equations are well known and have been used to interpret the Brillouin spec-

tra.⁴ For dense gases or liquids the hydrodynamic equations can be generalized to take into account the internal relaxation processes which occur in molecular fluids. The modifications of the hydrodynamic equations have usually been carried out in two ways.

One method introduces memory into the normal hydrodynamic equations via a frequency-dependent bulk viscosity. The justification for the introduction of a relaxing bulk viscosity is based on an explicit calculation of the frequency dependence of the transport coefficients by Zwanzig.⁵ When weak coupling between the translational and internal motions is assumed, the bulk viscosity is found to consist of a translational part plus a frequency-dependent internal part. In the same weak-coupling approximation the shear viscosity is not affected by the internal relaxation process and the thermal conductivity is the sum of a translational part and a frequency-independent Eucken correction due to the diffusion of energy in the internal modes. The application of this approach to the calculation of the spectrum of the light scattered from molecular fluids has been made by Mountain.⁶ We denote this theory as the M_n theory.

The second approach is similar in spirit to the first but attempts to describe explicitly the origin of the frequency dependence in the hydrodynamic equations. The normal hydrodynamic equations are supplemented with an equation which describes the relaxation of another variable coupled to the density, temperature, and momentum fluctuations.² The light scattering spectrum which results from this description of the fluid has been calculated by Mountain⁷ (denoted as M_t theory) and compared with the results obtained using a frequency-dependent bulk viscosity. The two theories are not equivalent.

Both of these theories have been used to interpret light scattering experiments on molecular fluids. The spectra predicted by these theories are in good agreement with experiment for the liquids investigated in Refs. 3(a) and 3(b). The agreement with experiment is not quite so satisfying for molecular gases especially in the low-density regions [see Ref. 3(c)]. The region of applicability of the present calculations is in general greater than either of the above theories. The motivation behind the approach pursued in this article can be seen, in a qualitative way, through the following considerations.

The introduction of a relaxing bulk viscosity is quite general and does not require an explicit specification of the internal relaxation process. In complicated molecular fluids it is not always possible to identify the internal motions which are responsible for the deviations from classical behavior. In such circumstances the justification for the introduction of a relaxing variable in the second approach

is not an easy matter. In this work, we exclude these complicated situations from consideration. Rather, we focus on the description of fluids composed of small molecules where the choice of relaxing variables is easily made. For diatomic and small polyatomic molecules only the relaxation within a well-defined set of internal states need to be taken into account in order to describe the Brillouin spectra. The fluids investigated in Ref. 3 provide examples. In the CCl_4 and CS_2 liquids only a few vibrational states participate, while in compressed hydrogen gas only a few rotational states need to be considered. In these situations it is clear that the appropriate variables to couple to the normal hydrodynamic variables are the variables which characterize the populations of the individual internal states. This is the approach we pursue in this paper.

We take the point of view that a single-component molecular fluid can be considered as a multicomponent chemically reacting fluid. The various internal states are treated as distinct chemical species. This type of description has been used earlier by other authors.⁸ We restrict ourselves to those molecular fluids in which the polarized light scattering intensity only involves the total density fluctuations. This implies two approximations: One is the neglect of the temperature fluctuations as contributing to the dielectric tensor fluctuations and another requires that the molecules in different internal states have the same effective polarizability. Starting from the multicomponent description, we eliminate the individual internal state densities in favor of the total density to construct equations which describe the relaxation of the total density fluctuation. In this contracted description, which we label "translational hydrodynamics" (TH), the relaxation matrix has a well-defined frequency and wave-vector dependence.

Other derivations have also been carried out in terms of Mori's generalized Langevin equation. In these derivations the total density, momentum, and temperature fluctuations of normal hydrodynamics have been supplemented with either the fluxes associated with the above variables⁹ or an internal energy-density variable.¹⁰ The relation of both of these approaches to the work of Mountain has been described in these papers. We also mention a calculation of the effect of an internal relaxation process on the concentration fluctuations in a chemically reacting fluid where a similar set of density variables has been used to obtain the results.¹¹

In Sec. II we present explicit results for the relaxation matrix for a two-state molecular fluid. In the numerical calculations presented in the remaining sections of this paper we have assumed that the thermal diffusion (D_T) and l_{v1} coefficients can be neglected. In spite of the simplicity of the two-

state model, there are a number of real systems to which this model can be applied (see Ref. 3).

In Sec. III these results are used to calculate the dynamic structure factor $S(k, \omega)$ for parahydrogen gas at room temperature. A two-state model is a very good approximation for this system. A detailed numerical comparison of the present results with the theories of Mountain is made. In general, the three theories are *not* equivalent. Except for the well-justified approximation involving the neglect of the D_T and l_{v1} coefficients, our results for $S(k, \omega)$ involve no additional assumptions for the thermal relaxation of a two-state system. At high densities, greater than approximately 60 amagats, the three theories are in close agreement. In the lower-density regions the results differ by significant amounts, which are accessible to experimental verification. Experiments are currently in progress which will be able to test several aspects of the theory presented here.¹² For two values of the density (0.92 and 5.57 amagats) the results are also compared with the results of a modeled kinetic theory calculation.

A detailed analysis of the roots of the dispersion equation is made in Sec. IV. In part of this analysis, the coupling between bulk viscosity and chemical reaction is retained and an examination of the sound attenuation coefficient is made in order to justify the neglect of l_{v1} for the parahydrogen calculation considered in this paper. The dispersion equation is fourth order in the frequency even if this coupling is retained. The roots of the dispersion relation, when l_{v1} is set equal to zero, have been studied numerically as a function of density and compared with the corresponding roots in the theories of Mountain.

The detailed comparison made in Sec. III with an accurate kinetic model^{4(b)} gives us confidence in the correctness of translational hydrodynamics approach, since the kinetic model has been found to have excellent agreement with experiments where the M_n and M_t theories have failed. From the dispersion analysis made in Sec. IV we conclude that the treatment of the thermal-diffusivity mode in M_n and M_t theories is qualitatively different from that in the TH theory. It is our belief that this is where the M_n and M_t theories fail.

II. TRANSLATIONAL HYDRODYNAMICS

We consider a single-component molecular fluid and suppose that each molecule can exist in any of the different internal states. For dilute molecular gases, the appropriate kinetic equation for the description of the various scalar relaxation processes is the Wang Chang-Uhlenbeck equation (or the Waldmann-Snyder equation for more general tensorial processes). For liquids or dense gases, there is no single kinetic equation which is as

widely used; instead, one uses hydrodynamic-type approaches suitably generalized to describe a given aspect of the fluid relaxation. In this article, each internal state is treated as a distinct "chemical" species, and the resulting relaxation equations have the same structure as the linearized hydrodynamic equations for a reacting mixture where all the species have the same mass. For a two-state nonreacting fluid (i. e., a binary mixture), the appropriate hydrodynamic equations have been derived using the generalized Langevin approach.¹³ In the Appendix, we indicate how the "reaction" terms, i. e., the effect of inelastic collisions, would alter the equations. The generalization to the n -state problem is straightforward. Instead of giving this lengthy derivation, we give here the motivation behind the use of such a description, and also give the explicit results for a two-state molecular fluid.

The analysis is based on a consideration of different time scales characteristic of the system. These are (i) the translation relaxation time τ_t which describes the relaxation of dynamic variables which depend on the center-of-mass motion of the molecule, (ii) various internal relaxation times τ_i which characterize such processes as translational to internal energy transfer (isomerization) and internal to internal energy transfer, and (iii) the hydrodynamic relaxation time τ_h associated with the removal of macroscopic spatial gradients in the system. In order for our kinetic description to be valid, we require that τ_t be well separated from τ_i and τ_h , i. e., $\tau_t \ll \tau_i, \tau_h$. This inequality ensures that the starting equations of our analysis need only depend on the internal-state variables (i. e., molecular velocities do not appear explicitly in the description) and contain frequency-independent transport coefficients. This inequality also demands a special treatment for the fluctuation in the translational energy variable, which can be connected with a translational temperature fluctuation.

Although the form of the kinetic equations is identical to that of the macroscopic (hydrodynamic) equations for a reacting fluid mixture, the equations are not macroscopic for the description of the one-component molecular fluid. Typically, in order for a macroscopic description of a reacting fluid mixture to be applicable, it is usually assumed that the molecular interconversion process is sufficiently slow that the chemical species can easily be distinguished in macroscopic experiments. In the present situation we do not impose such a stringent condition on the magnitude of the internal relaxation time. On the contrary, we consider a situation where the internal relaxation process is sufficiently rapid that the most convenient description is in terms of the total density rather than the densities of the individual internal

states, but not so rapid that normal hydrodynamics with frequency-independent transport coefficients is applicable for the interpretation of certain radiation scattering experiments.

The set of equations which describes the two-level molecular fluid as a reacting mixture can be written as¹⁴

$$\frac{\partial \underline{\alpha}(\vec{k}, t)}{\partial t} = -\underline{\mathfrak{N}}(k) \underline{\alpha}(\vec{k}, t), \quad (2.1)$$

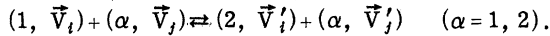
where $\underline{\mathfrak{N}}(k)$ is a matrix containing the transport coefficients and thermodynamic derivatives [the elements of this matrix are given in the Appendix; see Eqs. (A22)–(A40)], and \vec{k} is the wave vector. The vector $\underline{\alpha}(\vec{k})$ contains a collection of variables

$$\underline{\alpha}(\vec{k}) = \begin{bmatrix} \rho_1(\vec{k}) \\ \rho_2(\vec{k}) \\ \Theta(\vec{k}) \\ J(\vec{k}) \end{bmatrix}, \quad (2.2)$$

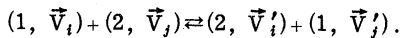
where $\rho_1(\vec{k})$ and $\rho_2(\vec{k})$ are the Fourier transforms of the mass densities of the molecules in the individual internal states, $J(\vec{k})$ is the Fourier transform of the total longitudinal momentum density, and $\Theta(\vec{k})$ is equal to that part of the Fourier transform of the energy density which is orthogonal to $\rho_1(\vec{k})$ and $\rho_2(\vec{k})$. $\Theta(\vec{k})$ does not contain the internal energy of the molecules, since this is merely a certain linear combination of the internal-state mass densities. Moreover, since the total density fluctuation $\rho(\vec{k})$ is the sum of $\rho_1(\vec{k})$ and $\rho_2(\vec{k})$, $\Theta(\vec{k})$ is also orthogonal to $\rho(\vec{k})$. Thus $\Theta(\vec{k})$ is, apart from a constant, the customary translational temperature fluctuation

$$\Theta(\vec{k}) = \rho_0 c_{vt} T(\vec{k}), \quad (2.3)$$

where c_{vt} is the translational specific heat per unit mass and ρ_0 is the equilibrium mass density. For the two-state fluid under consideration, only the translational to internal energy-transfer processes are included here. These processes correspond to a bimolecular isomerization reaction



The velocity of molecule i is \vec{v}_i before collision and \vec{v}'_i after collision. Since velocity does not appear in our description, it has been implicitly assumed that the translational energy relaxation occurs rapidly and is well separated from the above inelastic process as discussed earlier. The processes which we have ignored are of the type



These resonance processes do not change either the individual level mass density, the total internal energy density, or the total translational energy density of the fluid.

The variables $\underline{\alpha}(\vec{k})$ are used to provide a proper description of the coupling of an internal relaxation process with normal hydrodynamics. However, many (but not all) radiation scattering experiments are not sensitive to the fluctuations in the individual level densities. For analyzing such experiments, we contract the above description to the set of variables

$$\underline{\mathfrak{B}}(\vec{k}) = \begin{bmatrix} \rho(\vec{k}) \\ \Theta(\vec{k}) \\ J(\vec{k}) \end{bmatrix}. \quad (2.4)$$

If we use Eq. (2.1), assume that at $t=0$ fluctuations exist only in the variables $\rho(\vec{k})$, $\Theta(\vec{k})$, and $J(\vec{k})$ —i. e., initial correlations in $\rho_1(\vec{k})$ and $\rho_2(\vec{k})$ are not independent but $\rho_1(\vec{k}) = (\rho_{10}/\rho_0)\rho(\vec{k})$, with an analogous equation for $\rho_2(\vec{k})$ —and eliminate $\rho_1(\vec{k})$ and $\rho_2(\vec{k})$ in favor of $\rho(\vec{k})$, we obtain an equation for $\underline{\mathfrak{B}}(\vec{k})$,

$$\frac{\partial \underline{\mathfrak{B}}(\vec{k}, t)}{\partial t} = -\underline{N}(k) \underline{\mathfrak{B}}(\vec{k}, t) + \int_0^t ds \underline{K}(k, s) \underline{\mathfrak{B}}(\vec{k}, t-s). \quad (2.5)$$

The $\underline{N}(k)$ matrix has the following elements:

$$N_{11}(k) = N_{12}(k) = 0, \quad (2.6)$$

$$N_{13}(k) = -ik, \quad (2.7)$$

$$N_{21}(k) = (k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv}) \bar{v}_{12} / \rho_0 \kappa, \quad (2.8)$$

$$N_{22}(k) = \left\{ k^2 \left[\lambda^* + \frac{\rho_0 T_0}{D} \left(\frac{\partial \mu}{\partial c} \right)_{T,P} Y^2 \right] + l_{11} m^2 \Delta_{sv}^2 \right\} / \rho_0 c_{vt}, \quad (2.9)$$

$$N_{23}(k) = \frac{ik(l_{v1} m \Delta_{sv} - T_0 \alpha_T / \kappa)}{\rho_0}, \quad (2.10)$$

$$N_{31}(k) = \frac{-ik(l_{v1} m \bar{v}_{12} / T_0 + 1)}{\rho_0 \kappa}, \quad (2.11)$$

$$N_{32}(k) = \frac{ik(l_{v1} m \Delta_{sv} / T_0 - \alpha_T / \kappa)}{\rho_0 c_{vt}}, \quad (2.12)$$

$$N_{33}(k) = \frac{k^2 (\frac{4}{3} \eta_s^* + \eta_v^*)}{\rho_0}. \quad (2.13)$$

In Eqs. (2.6)–(2.13), κ is the isothermal compressibility, α_T the thermal expansion coefficient, m the molecular mass, and μ the chemical potential difference $\mu_1 - \mu_2$ per unit mass. It is the thermodynamic derivative of μ with respect to the relative concentration $c = \rho_1/\rho$ that appears in Eq. (2.9). Also we denote the partial specific volume difference $\bar{v}_1 - \bar{v}_2$ by \bar{v}_{12} and the partial specific entropy difference $\bar{s}_1 - \bar{s}_2$ by \bar{s}_{12} . The transport coefficients that enter the \underline{N} matrix are the diffusion coefficient D , pressure diffusion coefficient D_P , thermal diffusion coefficient D_T , bare thermal conductivity λ^* , bare shear viscosity η_s^* , bare bulk viscosity η_v^* , as well as the coefficients l_{11} and l_{v1} which are

related to the "reaction" or the energetically inelastic collisions. The coefficient l_{11} is the reaction-rate phenomenological coefficient and l_{v1} is the phenomenological coefficient expressing the coupling between bulk viscosity and the chemical reaction. Moreover, we use the symbols X , Y , and Δ_{sv} , which are defined as

$$X = \frac{1}{\rho_0} \left(\frac{\partial \mu}{\partial c} \right)_{T,P} + \frac{\bar{v}_{12}^2}{\kappa}, \quad (2.14)$$

$$Y = D_T + \frac{\alpha_T D_P}{\kappa}, \quad (2.15)$$

and

$$\Delta_{sv} = \bar{s}_{12} - \frac{\bar{v}_{12} \alpha_T}{\kappa}. \quad (2.16)$$

A superscript asterisk has been used to distinguish the transport coefficients λ^* , η_s^* , and η_\dagger^* which appear in the hydrodynamic matrix for a two-component reacting fluid, with the translational temperature as one of the variables, from the corresponding coefficients in a single-component molecular fluid. Hence λ^* , η_s^* , and η_\dagger^* are the transport coefficients at infinite frequency and can thus be called "bare" transport coefficients. These bare coefficients are renormalized after the contraction to the smaller set of variables is made.

For this two-level problem the memory matrix $\underline{K}(k, s)$ takes the form

$$\underline{K}(k, s) = e^{-\gamma(k)s} \underline{K}(k), \quad (2.17)$$

with $\gamma(k)$ given by

$$\gamma(k) = k^2 (D + \rho_0 \bar{v}_{12} D_P / \kappa) + \tau_R^{-1}. \quad (2.18)$$

The elements of the $\underline{K}(k)$ matrix are

$$K_{11}(k) = K_{12}(k) = K_{13}(k) = 0, \quad (2.19)$$

$$K_{21}(k) = \frac{(k^2 D_P + \bar{v}_{12} l_{11} m^2 / T_0 \rho_0) (k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv}) X}{\kappa}, \quad (2.20)$$

$$K_{22}(k) = \frac{(k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv})^2 X}{\rho_0 c_{vt} T_0}, \quad (2.21)$$

$$K_{23}(k) = \frac{-ik l_{v1} m (k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv}) X}{\rho_0 T_0}, \quad (2.22)$$

$$K_{31}(k) = \frac{-ik (k^2 D_P + \bar{v}_{12} l_{11} m^2 / T_0 \rho_0) (l_{v1} m X / T_0 + \bar{v}_{12} / \kappa)}{\kappa}, \quad (2.23)$$

$$K_{32}(k) = \frac{-ik (k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv}) (l_{v1} m X / T_0 + \bar{v}_{12} / \kappa)}{\rho_0 c_{vt} T_0}, \quad (2.24)$$

$$K_{33}(k) = \frac{-k^2 l_{v1} m (l_{v1} m X / T_0 + \bar{v}_{12} / \kappa)}{\rho_0 T_0}. \quad (2.25)$$

The relaxation time τ_R is related to the phenomenological coefficient l_{11} by

$$\tau_R^{-1} = l_{11} m^2 X / T_0. \quad (2.26)$$

In the interpretation of polarized light scattering experiments one needs the density-density correlation function $\langle \rho(\vec{k}, \epsilon) \rho(\vec{k}^*) \rangle$, where the angular brackets refer to the average over an appropriate equilibrium ensemble. These correlation functions can easily be obtained from the Laplace transform of Eq. (2.5). We obtain

$$\langle \rho(\vec{k}, \epsilon) \rho(\vec{k}^*) \rangle \langle \rho(\vec{k}) \rho(\vec{k}^*) \rangle^{-1} = \{ [\epsilon \underline{I} + \underline{M}(k, \epsilon)]^{-1} \}_{11}, \quad (2.27)$$

where

$$\underline{M}(k, \epsilon) = \underline{N}(k) - \underline{K}(k, \epsilon). \quad (2.28)$$

In the subsequent sections we will only be concerned with the special case of a thermal relaxation process. For this type of relaxation process the specific volume difference \bar{v}_{12} is approximately zero. If, in addition, we assume that the thermal diffusion coefficient D_T and the l_{v1} coefficient can be neglected, the $\underline{M}(k, \epsilon)$ matrix takes the simple form

$$\underline{M}(k, \epsilon) = \begin{bmatrix} 0 & 0 & -ik \\ 0 & k^2 \lambda^* / \rho_0 c_{vt} + (c_I / \tau_R c_{vt}) (1 - \{ \tau_R [\epsilon + \gamma(k)] \}^{-1}) & -ik T_0 \alpha_T / \rho_0 \kappa \\ -ik / \rho_0 \kappa & -ik \alpha_T / \rho_0 c_{vt} \kappa & (k^2 / \rho_0) (\frac{4}{3} \eta_s^* + \eta_\dagger^*) \end{bmatrix}. \quad (2.29)$$

In writing Eq. (2.29) we have used the relation

$$c_I = T_0 \Delta_{sv}^2 \left(\frac{\partial \mu}{\partial c} \right)_{T,P}, \quad (2.30)$$

which expresses the internal specific heat per unit mass in terms of other thermodynamic quantities which appear in the above equations. The $\underline{M}(k, \epsilon)$ matrix in Eq. (2.29) differs from that of a single-component structureless fluid only in the presence of an added term in the M_{22} element.

This provides an example of the renormalization of transport coefficients often discussed in the recent literature.¹⁵

Equation (2.29) will form the basis for many of the calculations which follow. Hence it is important to justify the approximations which led to this equation. The neglect of the thermal diffusion coefficient is certainly justified, since there is ample evidence for dilute gases that this coefficient is much smaller than the diffusion coefficient.

cient. It is more difficult to justify the neglect of the other cross coefficient l_{v1} . This aspect of the problem is discussed more fully in Sec. IV.

It is perhaps appropriate to point out here how the present relaxation equations differ from those used earlier by Mountain. One important difference, mentioned earlier, is that the translational temperature fluctuation is the quantity which naturally enters into the present formulation, while the total temperature fluctuation enters into Mountain's theories. Hence, Eq. (2.29) should not be compared with the results of Mountain's theories. If comparisons are to be made at this level, a linear transformation of the starting variables must be performed in order to convert the translational temperature fluctuation to the total temperature fluctuation. This linear transformation does not affect the calculation of $S(k, \omega)$. We have carried out such a transformation for the special case we consider in detail (i. e., a thermal

relaxation of a two-level system with neglect of D_T and l_{v1}). Microscopically, the total temperature fluctuation can be written in terms of a variable $\Theta'(\vec{k})$,

$$\Theta'(\vec{k}) = \rho_0 c_v T_{\text{tot}}(\vec{k}), \quad (2.31)$$

where c_v is the full specific heat per unit mass, $c_v = c_{vt} + c_I$, and

$$\Theta'(\vec{k}) = E(\vec{k}) - \langle E(\vec{k}) \rho(\vec{k})^* \rangle \langle \rho(\vec{k}) \rho(\vec{k})^* \rangle^{-1} \rho(\vec{k}). \quad (2.32)$$

Under the above conditions this variable is related to $\Theta(\vec{k})$ by (see the Appendix)

$$\Theta'(\vec{k}) = \Theta(\vec{k}) + \langle E(\vec{k}) \xi_1(\vec{k})^* \rangle \langle \xi_1(\vec{k}) \xi_1(\vec{k})^* \rangle^{-1} \xi_1(\vec{k}). \quad (2.33)$$

When this transformation is made and the contraction to the set $\{\rho(\vec{k}), \Theta'(\vec{k}), J(\vec{k})\}$ is performed, the resulting relaxation matrix, which we denote by $\underline{M}'(k, \epsilon)$, takes the form

$$\underline{M}'(k, \epsilon) = \begin{pmatrix} 0 & 0 & -ik \\ 0 & \frac{k^2}{\rho_0 c_{vt}} \left(\lambda^* - \frac{\lambda^* c_I / c_{vt} - \rho_0 c_I D}{\tau_R (\epsilon + k^2 D + \tau_R^{-1} c_v / c_{vt})} \right) & -ik \frac{T_0 \alpha_T}{\rho_0 \kappa} \\ \frac{-ik}{\rho_0 \kappa} & -\frac{ik \alpha_T}{\rho_0 c_{vt} \kappa} \left(1 - \frac{c_I}{\tau_R c_{vt} (\epsilon + k^2 D + \tau_R^{-1} c_v / c_{vt})} \right) & \frac{k^2}{\rho_0} \left(\frac{1}{3} \eta_s^* + \eta_{\ddot{\phi}}^* \right) \end{pmatrix}. \quad (2.34)$$

Equation (2.34) can now be compared with the corresponding equations of Mountain. Both the frequency and wave-vector dependence are different. The two important distinctions to notice are the following: (i) The bare thermal conductivity λ^* and diffusion coefficient D enter on a separate footing and (ii) Eq. (2.34) contains terms to all orders in the wave vector.

In Mountain's theories only the frequency dependence of normal hydrodynamics is generalized; the equations only contain terms up to order k^2 . In addition, the diffusion coefficient enters only via the Eucken correction in the thermal conductivity. In the M_η theory only the M'_{33} element is generalized through the introduction of a relaxing bulk viscosity with one relaxation time. The remaining elements of this matrix are identical to those of the normal hydrodynamic matrix. In the M_ξ theory the equation of motion for the relaxation variable ξ introduces frequency dependence only in the M'_{22} and M'_{23} elements of the \underline{M}' matrix. The explicit expressions are

$$M'_{22}(k, \epsilon) = \frac{\lambda k^2 (1 + \epsilon \tau_R)}{\rho_0 c_v (1 + \epsilon \tau_R c_{vt} / c_v)} \quad (2.35)$$

and

$$M'_{23}(k, \epsilon) = -i \frac{k T_0 \alpha_T}{\rho_0 \kappa} \frac{1 + \epsilon \tau_R}{1 + \epsilon \tau_R c_{vt} / c_v}, \quad (2.36)$$

where λ is the full thermal conductivity.

From Eq. (2.34) we note that

$$\lim_{k \rightarrow 0, \epsilon \rightarrow 0} \frac{M'_{22}(k, \epsilon)}{k^2} = \frac{\lambda^* + \rho_0 c_I D}{\rho_0 c_v} = \frac{\lambda}{\rho_0 c_v}. \quad (2.37)$$

The numerator has the form of the thermal conductivity for a molecular fluid in which translation and internal motion are weakly coupled⁵; λ^* is the translational contribution, while $\rho_0 c_I D$ is the Eucken correction due to diffusion of internal energy.

It is worthwhile to point out that the assumption of the time-scale separation $\tau_i \ll \tau_i, \tau_h$ which yields Eq. (2.34) is quite different from the weak coupling assumption of Zwanzig⁵ which results in the M_η theory for $S(k, \omega)$. In Zwanzig's calculation all collisions which result in energy transfer between the translational and internal degrees of freedom are assumed to be weak through an explicit assumption in the form of the Hamiltonian. In contrast, the translational hydrodynamics requires that such energetically inelastic collisions be infrequent compared to the elastic collisions; there is no restriction on the strength of the inelastic

collisions. For molecules with low mass and low moment of inertia, e.g., H_2 , HD, and D_2 , the energy difference between the ground state and the next excited state is of the order of a few hundred degrees. For these systems, the part of the interaction potential which governs the translational to internal energy transfer is strong, making Zwanzig's weak-coupling assumption invalid; however, the large energy-level spacings make inelastic collisions infrequent compared to the elastic collisions making the translational hydrodynamics appropriate.

In the following sections we apply the above results to parahydrogen gas at room temperature, for which the two-level approximation is quite adequate. For hydrogen, the numerator of Eq. (2.37) has been found to provide a fairly accurate description of the thermal conductivity.¹⁶ This observation provides further justification for the neglect of D_T for hydrogen.

III. CALCULATION OF $S(k, \omega)$

In this section, we apply the results of Sec. II to predict the Rayleigh-Brillouin spectrum for a two-level system. We present numerical calculations appropriate to parahydrogen gas at room temperature and over a density range up to about

100 amagats (~ 0.009 g/cm). Even though such a gas is quite dilute and binary collisions should be sufficient to describe its dynamics, the validity of the dilute-gas Boltzmann equation is limited up to about 30 amagats. This is due to the incorrect way in which the static correlations are treated by the Boltzmann equation. Our use of translational hydrodynamics restricts the theory of Sec. II to small \vec{k} and ω , but it is valid over the entire density range.

The intensity of the light scattering spectrum is proportional to the dynamic structure factor $S(k, \omega)$, which is

$$S(k, \omega) = 2 \operatorname{Re} \langle \rho(\vec{k}, \epsilon = +i\omega) \rho(\vec{k})^* \rangle. \quad (3.1)$$

Using Eq. (2.27), we can compute $S(k, \omega)$ if we have a well-defined $\underline{M}(k, \epsilon)$. For the two-state fluid, we use the approximations which neglect all the cross-coupling transport coefficients, viz., D_P , D_T , and l_{v1} , and thus we use $\underline{M}(k, \epsilon)$ as given in Eq. (2.29). From Eqs. (2.27) and (2.29) we find that

$$\frac{\langle \rho(\vec{k}, \epsilon) \rho(\vec{k})^* \rangle}{\langle \rho(\vec{k}) \rho(\vec{k})^* \rangle} = \frac{F(\epsilon)}{G(\epsilon)}, \quad (3.2)$$

where

$$F(\epsilon) = \epsilon^3 + \epsilon^2 \left((a + b_0 + D)k^2 + \frac{\tau_R^{-1} c_v}{c_{vt}} \right) + \epsilon \left[\left(ak^2 + \frac{\tau_R^{-1} c_I}{c_{vt}} \right) (b_0 + D)k^2 + (Dk^2 + \tau_R^{-1})b_0 k^2 + \tau_R^{-1} a k^2 + \frac{c_\infty^2 k^2 (\gamma_t - 1)}{\gamma_t} \right] \\ + \left[Dk^2 \left(ab_0 k^4 + \frac{\tau_R^{-1} b_0 k^2 c_I}{c_{vt}} + \frac{c_\infty^2 k^2 (\gamma_t - 1)}{\gamma_t} \right) + \tau_R^{-1} \left(ab_0 k^4 + \frac{c_\infty^2 k^2 (\gamma_t - 1)}{\gamma_t} \right) \right], \quad (3.2a)$$

$$G(\epsilon) = \epsilon^4 + \epsilon^3 \left((a + b_0 + D)k^2 + \frac{\tau_R^{-1} c_v}{c_{vt}} \right) + \epsilon^2 \left((Dk^2 + \tau_R^{-1})(a + b_0)k^2 + \frac{\tau_R^{-1} (b_0 + D)k^2 c_I}{c_{vt}} + ab_0 k^4 + c_\infty^2 k^2 \right) \\ + \epsilon \left((Dk^2 + \tau_R^{-1})(ab_0 k^4 + c_\infty^2 k^2) + \frac{\tau_R^{-1} (Db_0 k^4 + c_\infty^2 k^2 / \gamma_t) c_I}{c_{vt}} + \frac{a c_\infty^2 k^4}{\gamma_t} \right) + \frac{[a \tau_R^{-1} + D(ak^2 + \tau_R^{-1} c_I / c_{vt})] c_\infty^2 k^4}{\gamma_t}. \quad (3.2b)$$

In Eqs. (3.2a) and (3.2b), $a = \lambda^* / \rho_0 c_{vt}$, $b_0 = (\frac{4}{3} \eta_s^* + \eta_v^*) / \rho_0$, and $\gamma_t = c_{Pt} / c_{vt}$. Also c_∞ is the translational (infinite frequency) sound speed given by $c_\infty^2 = \gamma_t / \rho_0 \kappa$. The corresponding $F(\epsilon)$ and $G(\epsilon)$ in the M_η and M_t theories are given in Eqs. (17) and (18) of Ref. 6 and Eqs. (22) and (23) of Ref. 7, respectively. As mentioned earlier, previous comparisons between the two theories by Mountain and the light scattering experiments on certain liquids^{3(a),3(b)} have shown the theories to be satisfactory; however, a similar comparison with experiments on dilute gases^{3(c)} shows some area of disagreement.

At low densities, where the Boltzmann equation for molecular gases would be applicable, we also compare the present theory with a recent kinetic

model calculation^{4(b)} which has been found to give excellent agreement with the experiments^{3(c)} on normal hydrogen (nH_2), normal deuterium (nD_2), and hydrogen deuteride (HD). Such a comparison helps us in finding the region of validity of the hydrodynamic theories.

In order to calculate $S(k, \omega)$ using Eq. (3.2) or the two theories of Mountain, we need the following parameters: D , λ^* , η_s^* , η_v^* , c_{Pt} , c_{vt} , c_I , τ_R , and c_∞ . We assume D and τ_R to be proportional to ρ_0^{-1} , and we take the bare (or the structural part of the) bulk viscosity η_v^* to be zero. This is appropriate for dilute gases. For parahydrogen gas at 24 °C, we choose the value of D at 1 amagat to be 1.34 cm²/sec, which is deduced from the experimental value¹⁷ of 1.285 cm²/sec at 0 °C and 1 amagat.

The value of τ_R at 1 amagat, τ_{R0} , is chosen to be 1.19×10^{-8} sec. This value is calculated from the relaxing part of bulk viscosity, η_v , which is found to be 2100 μP in the kinetic calculation of Moraal and McCourt.¹⁸ The relaxing bulk viscosity can also be deduced from excess sound absorption measurements¹⁹ on parahydrogen. However, the appropriate measurements show large variations of up to 20%. The value of 2100 μP lies within the experimental range, but the true value could be somewhat larger; a selective experimental average is 2500 μP , which would correspond to $\tau_{R0} = 1.42 \times 10^{-8}$ sec. Various specific heats as well as the transport coefficients λ and η_s^* are assumed to be the same as those for normal hydrogen and are taken from Hara *et al.*,^{3(c)} with appropriate interpolation for intermediate densities. The bare thermal conductivity λ^* is then obtained using Eq. (2.37). The sound speed is obtained using the experimental equation of state²⁰ and the appropriate specific heats.

The relaxation time appearing in the two-level system is identical to that in the M_t theory and is related to the relaxation time τ_η in the M_η theory by $\tau_\eta = c_{vt}\tau_R/c_v$. Thus if we choose $\tau_{R0} = 1.19 \times 10^{-8}$ sec, then $\tau_{\eta 0} = 0.714 \times 10^{-8}$ sec.

It is known²¹ that for dilute gases $S(k, \omega)$ satisfies a certain scaling property; for a molecular gas,^{4(b)} $S(k, \omega)$ depends on k, ω, ρ_0, T , and the transport coefficients through the following dimensionless combinations: $c_t/k_B, x = \omega/kv_0, y = \rho_0 v_0/2k\eta_s, z = 3\eta_v/2\gamma_i\eta_s$, and $f = \lambda/\eta_s c_v$. γ_i is c_t/c_v .

Since $2\eta_s/\rho_0 v_0$ is a typical translational mean free path, y is the ratio of the probe wavelength to the mean free path; similarly, x/y is the ratio of the probe frequency to the typical elastic collision frequency. The dimensionless quantity z , usually referred to as internal relaxation number, is the ratio of the elastic collision frequency $\omega_c = n_0 k_B T_0/\eta_s$ to the internal relaxation frequency $\omega_r = 2\gamma_i n_0 k_B T_0/3\eta_v = \tau_{\eta 0}^{-1}$; f is the Eucken ratio relating the thermal conductivity and shear viscosity. In monatomic gases, the hydrodynamic region is determined by the conditions $y \gg 1$ and $x \ll y$. In molecular gases, we expect the same conditions to determine the validity of the present translational hydrodynamics theory. For ordinary hydrodynamics to be valid in molecular gases, we need not only $y \gg 1$ and $x \ll y$ but also $x \ll y/z$; i. e., the probe frequency has to be small compared to both the typical elastic frequency ω_c as well as the internal relaxation frequency ω_r . For parahydrogen with $\gamma_i = 0.4, \eta_v = 2100 \mu\text{P}$, and $\eta_s = 88 \mu\text{P}$, we get $z = 90$. Thus the condition $x \ll y/z$ is much more restrictive than $x \ll y$. Ordinary hydrodynamics is thus valid for a very small frequency range compared to translational hydrodynamics.

For $y > 30$ (densities greater than about 50 ama-

gats at room temperature and for typical 90° light scattering experiments^{3(c)}), we find that $S(k, \omega)$ calculated using the three generalized hydrodynamic theories— M_η, M_t , and TH—agree with one another almost in their entirety. It is only for these high y values that we find $S(k, \omega)$ to be sensitive to the choice of relaxation time. Sample calculations using translational hydrodynamics at $y \sim 180$ show that the effect of changing τ_{R0} from 1.19 to 1.42×10^{-8} sec is to (i) shift the sound peak by about $\frac{1}{2}\%$, (ii) increase the width of the sound peak by about 11%, and (iii) decrease the intensity of the sound peak by about 10%. Thus light scattering experiments for large y should be able to determine the relaxation time considerably more accurately than the ultrasonics measurements.¹⁹ In the interpretation of the experiments at lower y values ($y \lesssim 60$), however, an error of about 10% in τ_R should make no quantitative difference.

In Figs. 1 and 2 we show $S(k, \omega)$ at two rather low y values of 0.52 and 3.11, respectively. Figure 1 shows that for $y < 1$ the kinetic model calculation differs considerably from the generalized hydrodynamic theories as expected. For such y values, there is no substitute for a kinetic calculation, since even the translational motion is truly kinetic. It is interesting to note that the kinetic calculation predicts a very shallow minimum centered around zero frequency; the line shape dips by about 4% when compared to the maximum, which is located at $\omega/kc_\infty \approx 0.5$. We do not understand the origin of this behavior; in all likelihood it is dependent on the fine features of the model used rather than the kinetic equation. It is also interesting to note that, in Fig. 1, the M_η theory resembles ordinary hydrodynamics, whereas the M_t theory agrees with the present TH theory almost everywhere.

Figure 2 shows the remarkable agreement between the kinetic model and translational hydrodynamics; this is expected, since the y value is significantly greater than 1. On the other hand, neither the M_η theory nor the M_t theory agree with the kinetic model calculation. Comparison of the details of the line shape at higher y values are made in Sec. IV through the dispersion analysis of the four contributing modes. At $y = 3.11$, the individual contributions to $S(k, \omega)$ from the two propagating sound modes, the thermal-diffusivity mode, and the internal relaxation mode are shown in Fig. 3. It is clear that the latter two nonpropagating modes (both centered at $\omega = 0$) contribute nearly equally; this is in contrast to the situation in liquids, where the relaxation mode is very broad and much less intense. As a consequence the real test of the M_η and M_t theories is in dilute gases; here both experimentally^{3(c)} as well as when compared to the kinetic model calculations (see Fig. 2)

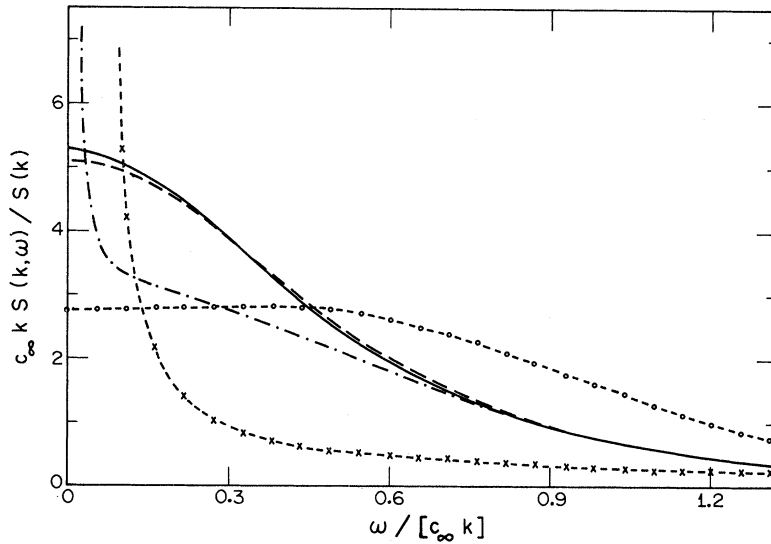


FIG. 1. Spectrum of density fluctuations from parahydrogen at 24 °C: comparison of various theories in the kinetic regime, $\rho_0 = 0.92$ amagats, $\gamma = 0.52$: Translation hydrodynamics (TH), solid line; kinetic model (BDT), $\circ-\circ-$; Mountain's thermal relaxation theory (M_η), dashed line; Mountain's relaxing bulk viscosity theory (M_ζ), $\square-\square-$; ordinary hydrodynamics, $\times-\times-$.

we find both the theories to be deficient. We therefore suggest the use of translational hydrodynamics in analyzing those light scattering experiments from molecular fluids which fall in the region $\gamma > 1$ and $x/\gamma \ll 1$. We discuss the sound mode contributions in Fig. 3 in more detail in the latter part of Sec. IV.

IV. DISPERSION ANALYSIS

Various collective modes contribute to the spectrum of the density fluctuations $S(k, \omega)$ in a fluid. The standard way to analyze these modes is to study the behavior of the poles of $S(k, \omega)$ in complex ω plane. In all the three theories, M_η , M_ζ , and TH, $S(k, \omega)$ has four poles. Two of these are

complex and correspond to the propagating sound modes, whereas the other two correspond to the purely dissipative modes of internal relaxation and thermal diffusivity. For the initial value problem at hand, the dispersion analysis involves tracing the behavior of these roots as functions of (real) wave number k . For small k , this can be done analytically using a k expansion; for arbitrary k , we study the dispersion numerically by evaluating the zeros of the denominator $G(\epsilon)$ in Eq. (3.2). In the numerical work, we have set the coupling transport coefficients D_P , D_T , and l_{v1} equal to zero. The neglect of D_P and D_T was justified in Sec. II. Here we give some plausible arguments for the neglect of l_{v1} . Partly to that end, and partly for

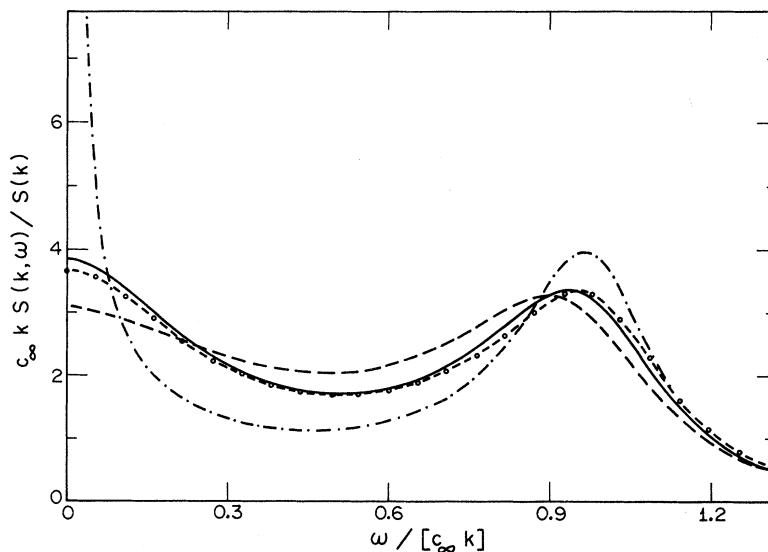


FIG. 2. Spectrum of density fluctuations from parahydrogen at 24 °C: comparison of various theories in the translationally hydrodynamic regime, $\rho_0 = 5.57$ amagats, $\gamma = 3.11$. Symbols same as Fig. 1.

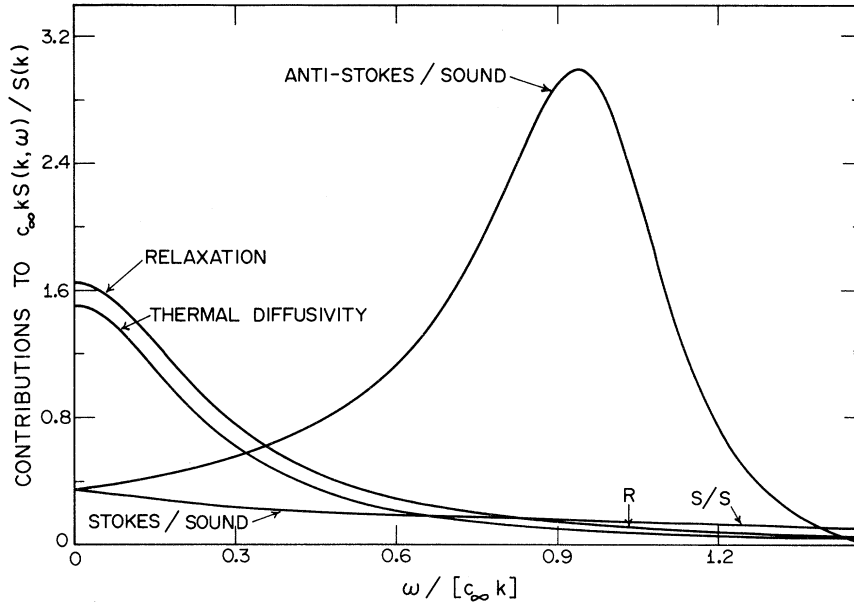


FIG. 3. Contributions from various collective modes to the spectrum of density fluctuations in the translational hydrodynamics theory: para-hydrogen at 24°C, $\rho_0 = 5.57$ amagats, and $\gamma = 3.11$

its own sake, we have considered a form for $G(\epsilon)$ more general than that in Eq. (3.2b); in this form, we do not neglect l_{v1} . By making an expansion in powers of k , we arrive at the following four roots of $G(\epsilon)$ valid to order k^2 :

thermal diffusivity:

$$\epsilon_{TD} = -k^2(\lambda^* + \rho_0 c_I D) / \rho_0 c_P; \quad (4.1)$$

internal relaxation:

$$\epsilon_R = -(\tau_R c_{vt} / c_v)^{-1} - f k^2, \quad (4.2)$$

where

$$f = \frac{\lambda^* c_I / \rho_0 c_{vt} + D c_{vt}}{c_v} - \tau_R \left[\left(\frac{c_{vt}}{c_v} (c_\infty^2 - c_0^2) \right)^{1/2} - q \right]^2 \quad (4.2a)$$

and

$$q = \frac{m l_{v1}}{\rho_0 T_0} \left(\frac{\partial \mu}{\partial c} \right)_{T,P}; \quad (4.2b)$$

sound:

$$\epsilon_s = \pm i c_0 k - \Gamma k^2, \quad (4.3)$$

where

$$\Gamma = \frac{1}{2} \left\{ \frac{(\lambda^* + \rho_0 c_I D)(1 - 1/\gamma)}{\rho_0 c_v} + \frac{\frac{1}{3} \eta_s^* + \eta_v^*}{\rho_0} + \tau_R \left[\left(\frac{c_{vt}}{c_v} (c_\infty^2 - c_0^2) \right)^{1/2} - q \right]^2 \right\} \quad (4.3a)$$

and $c_0 = (\gamma / \rho_0 \kappa)^{1/2}$ is the adiabatic sound speed. In the k^2 correction to the relaxation root and in the sound attenuation coefficient Γ , exactly the same combination of τ_R and l_{v1} appears. Thus by determining the two quantities f and Γ we cannot de-

termine the two unknowns τ_R and l_{v1} but only the combination which appears in Eqs. (4.2a) and (4.3a). When $q(l_{v1})$ is set equal to zero in Eq. (4.3a), the sound attenuation coefficient is exactly the same as that given by the M_n and M_t theories. The resulting expression is the one which is usually used to extract the relaxation time from ultrasonic experiments. Hence, if the experimental relaxation time is used in the calculation of $S(k, \omega)$, consistency demands that q should be set equal to zero. It should be stressed again that this argument in no way implies that q is actually zero; it simply means that there is insufficient experimental information to determine the value of q . However, l_{v1} reflects the coupling between chemical reaction and bulk viscosity. The corresponding diagonal coefficients are l_{11} and η_s^* . Since it is known that η_s^* is zero to a very good approximation for dilute gases, and it seems highly unlikely that the cross coefficient would be larger than the diagonal coefficient, the neglect of l_{v1} is not unreasonable.

When q is set equal to zero, the roots to order k^2 are the same as in the M_n and M_t theories except for the k^2 correction to the relaxation root. To order k^2 , τ_R does not appear in the thermal-diffusivity mode. To order k^0 , λ^* and D do not appear in the relaxation mode, but they do when the k^2 correction is made. If we set τ_R and c_I equal to zero, i. e., in absence of the "reaction" in the sense of Sec. II, the four modes reduce to (i) a pair of sound modes arising solely due to translational motion with c_∞ as sound speed and sound absorption due to bare transport coefficients λ^* , η_s^* , and η_v^* , (ii) the thermal-diffusivity mode

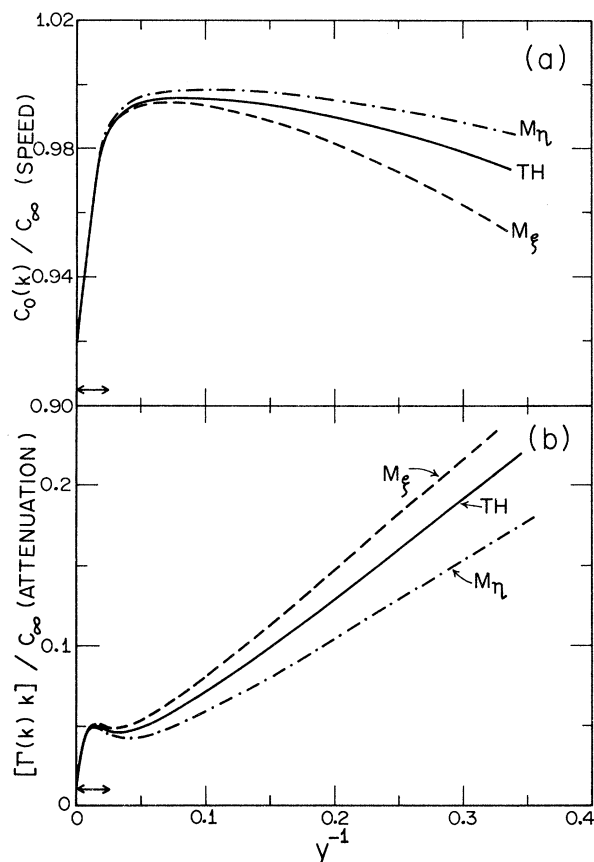


FIG. 4. Behavior of collective modes in parahydrogen at 24°C: (a) dispersion of sound speed (note that $c_0/c_\infty = 0.918$) and (b) dispersion of sound attenuation. Symbols same as Fig. 1. The arrow along the y^{-1} axis shows the usual range of light scattering experiments on liquids.

$-\lambda^*k^2/\rho_0c_P$, and (iii) the diffusion mode $-Dk^2$ as in a nonreacting binary mixture²² without the effects of the coupling transport coefficients D_P and D_T .

For not so small k , we have supplemented the above analysis by studying the dispersion numerically for the three generalized hydrodynamic theories for $y > 3$. When $y < 3$, we prefer the results of the recent kinetic model.^{4(b)} The dispersion of the four modes is shown in Figs. 4 and 5. For the sound roots and the relaxation roots all three theories show qualitatively similar and expected behavior, with TH results mostly lying between the M_η and M_ξ theories. Also for very small values of y^{-1} , all three theories become identical. For the thermal-diffusivity root, even though the three theories start in the same fashion for small y^{-1} , the results are qualitatively different for values of $y^{-1} > 0.07$ [see Fig. 5(b)]. The M_η and M_ξ theories show that the thermal-diffusivity mode reaches a maximum and then goes to zero for large values of y^{-1} . However, the TH theory shows an almost linear increase in the corresponding

behavior. This difference can be traced to the frequency and wave-number dependence of the M'_{22} element given in Eq. (2.34). In particular, the k dependence arising from the diffusion term is crucial. For dense fluids where D is of the order of 10^{-5} cm²/sec, Dk^2 is about 10^5 sec⁻¹. When compared to the typical frequency of 10^9 sec⁻¹ in the light scattering experiments and to the term with inverse relaxation time $\tau_R^{-1}c_{vt}/c_v$, which is about 10^{10} sec⁻¹, Dk^2 is negligible. It is here that the M_η and M_ξ theories have been moderately successful. In dilute gases, however, a typical value for Dk^2 is about 10^{10} sec⁻¹ and is thus quite crucial in Eq. (2.37). As y^{-1} increases (which is equivalent to increasing k), the Dk^2 term in the denominator becomes dominant and large, so that M'_{22} approaches the constant value of $\lambda^*/c_{vt}\rho_0$ for large y^{-1} . For very small values of y^{-1} , however, M'_{22} approaches $(\lambda^* + \rho_0c_T D)/\rho_0c_v$ if we put $\epsilon = 0$. The slope in Fig. 5(b) for large y^{-1} agrees with the value $\lambda^*/c_{vt}\rho_0$ as expected. (For parahydrogen gas at room temperature, λ/λ^* is about 1.36.) This

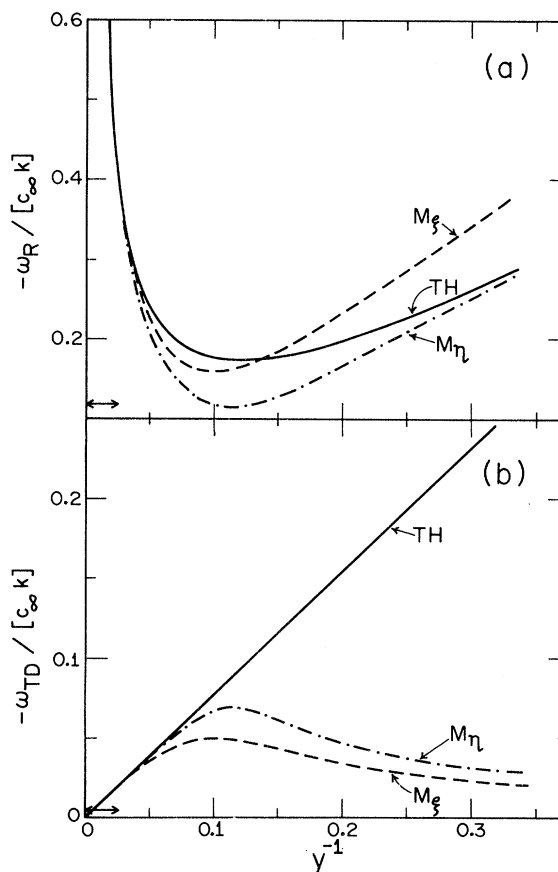


FIG. 5. Behavior of collective modes in parahydrogen at 24°C: (a) dispersion of the internal relaxation mode and (b) dispersion of the thermal-diffusivity mode. Symbols same as Fig. 1. The arrow along the y^{-1} axis shows the usual range of light scattering experiments on liquids.

also explains why the M_η and M_ξ theories have been found to be in disagreement with the dilute-gas experiments.^{3(c)} Experiments by Stoicheff and co-workers on liquids^{3(a),3(b)} have probed the region of very large y due to the larger liquid densities; the value of y^{-1} is always less than 0.02. In this region, all the theories are qualitatively identical.

The last remark concerns the sound speed and its dispersion. In Fig. 4(a), the imaginary part of complex pair of zeros of the denominator $G(\epsilon)$ in Eq. (3.2b) is shown; in Fig. 3, the contribution from these modes to $S(k, \omega)$ is shown. The peak position of the sound (Stokes) peak in Fig. 3 is in general different than the corresponding zero shown in Fig. 4(a); and both of these are different from the maximum of $S(k, \omega)$ shown in Fig. 2. The latter difference arises from the overlap of the other modes with the (Stokes) sound mode and is discussed in literature very often. For parahydrogen with $y = 3.11$, this overlap is not very significant: The peak position in the TH curve in Fig. 2 is at $\omega/c_\infty k \approx 0.935$ and that of the Stokes/sound curve in Fig. 3 is at $\omega/c_\infty k \approx 0.937$. The imaginary part of the zero of the denominator, however, occurs at $\omega/c_\infty k = 0.976$, which is quite different. The difference arises from the asymmetry in the resonancelike line shape of the sound mode.²³ In using Eqs. (3.1) and (3.2) to compute $S(k, \omega)$, we can (numerically) rationalize the polynomial ratio in Eq. (3.2) as

$$\frac{S(k, \omega)}{S(k)} (c_\infty k) = -2 \sum_{j=1}^4 \frac{B_j^R y_j^R + B_j^I (y_j^I - \omega')}{(\omega' - y_j^I)^2 + (y_j^R)^2}, \quad (4.4)$$

where $\omega' = \omega/c_\infty k$; $\epsilon_j/c_\infty k = y_j \equiv y_j^R + iy_j^I$ gives the four zeros ϵ_j of the denominator $G(\epsilon)$; and $B_j \equiv B_j^R + iB_j^I$ are the corresponding residues $F(\epsilon_j)/[G(\epsilon)/(\epsilon - \epsilon_j)]_{\epsilon=\epsilon_j}$. Since the coefficients of the polynomials F and G are real if ϵ_j is a real root, the corresponding residue B_j is real as well. But if ϵ_j is a complex root, corresponding B_j has a nonzero imaginary part B_j^I . The term $-B_j^I \omega'$ in the numerator of Eq. (4.4) causes the maximum for the j th term to be located at a value different from y_j^I . This maximum occurs at

$$\omega' = y_j^I + y_j^R (B_j^R - |B_j|) / B_j^I. \quad (4.5)$$

ACKNOWLEDGMENTS

We would like to thank C. D. Boley and A. D. May for useful discussions.

APPENDIX

In this Appendix, we give further details regarding the derivation of the hydrodynamic equations for a binary reacting mixture. This derivation uses the generalized-Langevin-equation (GLE) approach.²⁴ The derivation itself is straightforward

and closely parallels other microscopic derivations for a nonreactive binary mixture.¹³ Consequently, we will only present the microscopic definitions of the fluctuation variables and their corresponding fluxes along with some of the results for the reactive terms. For the orthogonal set of variables in the GLE, we choose the same set as in Ref. 13(a) but with microscopic definitions modified to take into account chemical reaction.

Let $\underline{Z}(\vec{k})$ denote the column vector whose elements are $\{\xi_1(\vec{k}), \xi(\vec{k}), \Theta(\vec{k}), J(\vec{k})\}$, where

$$\xi_1(\vec{k}) = \rho_{10}^{-1} \rho_1(\vec{k}) - \rho_{20}^{-1} \rho_2(\vec{k}), \quad (A1)$$

$$\xi(\vec{k}) = \bar{v}_1 \rho_1(\vec{k}) + \bar{v}_2 \rho_2(\vec{k}), \quad (A2)$$

and

$$\Theta(\vec{k}) = E(\vec{k}) - \langle E(\vec{k}) \xi_1(\vec{k})^* \rangle \langle \xi_1(\vec{k}) \xi_1(\vec{k})^* \rangle^{-1} \xi_1(\vec{k}) \\ - \langle E(\vec{k}) \xi(\vec{k})^* \rangle \langle \xi(\vec{k}) \xi(\vec{k})^* \rangle^{-1} \xi(\vec{k}). \quad (A3)$$

The mass, energy, and momentum density fluctuations are given by

$$\rho_\alpha(\vec{k}) = \sum_{i=1}^N m (e^{i\vec{k} \cdot \vec{r}_i} O_i^\alpha - \langle e^{i\vec{k} \cdot \vec{r}_i} O_i^\alpha \rangle), \quad (A4)$$

$$E(\vec{k}) = \sum_{i=1}^N (e_i e^{i\vec{k} \cdot \vec{r}_i} - \langle e_i e^{i\vec{k} \cdot \vec{r}_i} \rangle), \quad (A5)$$

with

$$e_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} V(|\vec{r}_i - \vec{r}_j|) \quad (A6)$$

and

$$J(\vec{k}) = \sum_{i=1}^N \frac{\vec{k} \cdot \vec{p}_i}{k} e^{i\vec{k} \cdot \vec{r}_i}. \quad (A7)$$

There are N particles in the system, \vec{p}_i is the momentum of the i th particle, and $V(|\vec{r}_i - \vec{r}_j|)$ is the potential energy of interaction between particles i and j . The angular brackets signify an equilibrium average in the canonical ensemble. The important modification of the corresponding equations in Ref. 13(a) is the introduction of the operators O_i^α in Eq. (A4) which determine whether the i th molecule is of type α .

The frequency matrix in the GLE is not modified by the presence of reaction and is given in Eqs. (2.11) of Ref. 13(a). The damping matrix in Mori's formalism is easily constructed from the random forces corresponding to the above variables and can be written

$$\underline{\phi}(k, \epsilon) = \langle \underline{f}(\vec{k}, \epsilon) \underline{f}(\vec{k})^\dagger \rangle \langle \underline{Z}(\vec{k}) \underline{Z}(\vec{k})^\dagger \rangle^{-1}. \quad (A8)$$

The elements of the random force vector $\underline{f}(\vec{k})$ are

$$f_{\xi_1}(\vec{k}) = (\rho_0 / \rho_{10} \rho_{20}) [ik J_d(\vec{k}) - m R(\vec{k})], \quad (A9)$$

$$f_{\xi}(\vec{k}) = \bar{v}_{12} [ik J_d(\vec{k}) - m R(\vec{k})], \quad (A10)$$

$$f_{\Theta}(\vec{k}) = ik \left[T_0 \left(\frac{\partial \mu}{\partial T} \right)_{P,c} + \frac{T_0 \alpha_T}{\kappa} \bar{v}_{12} \right] J_d(\vec{k}) + ik q(\vec{k})$$

$$+ \left(\frac{\rho_0}{\rho_{10} \rho_{20}} \frac{\langle E(\vec{k}) \xi_1(\vec{k})^* \rangle}{\langle \xi_1(\vec{k}) \xi_1(\vec{k})^* \rangle} + \bar{v}_{12} \frac{\langle E(\vec{k}) \xi(\vec{k})^* \rangle}{\langle \xi(\vec{k}) \xi(\vec{k})^* \rangle} \right) m R(\vec{k}), \quad (\text{A11})$$

and

$$f_J(\vec{k}) = ik\sigma_3(\vec{k}). \quad (\text{A12})$$

In these equations the diffusion flux $J_d(\vec{k})$ is defined by

$$J_d(\vec{k}) = [\rho_{10}^{-1} J_1(\vec{k}) - \rho_{20}^{-1} J_2(\vec{k})] \rho_{10} \rho_{20} / \rho_0, \quad (\text{A13})$$

with

$$J_\alpha(\vec{k}) = \sum_{i=1}^N \frac{\vec{k} \cdot \vec{p}_i}{k} e^{i\vec{k} \cdot \vec{r}_i} O_i^\alpha \quad (\alpha = 1, 2). \quad (\text{A14})$$

The reaction flux $R(\vec{k})$ is defined by

$$R(\vec{k}) = - \sum_{i=1}^N e^{i\vec{k} \cdot \vec{r}_i} \dot{O}_i^1 \\ = \sum_{i=1}^N e^{i\vec{k} \cdot \vec{r}_i} \dot{O}_i^2. \quad (\text{A15})$$

The quantities $q(\vec{k})$ and $\sigma_3(\vec{k})$ are the nonconserved parts of the heat flux and the longitudinal pressure tensor, respectively, and explicit expressions for these quantities are given in Eqs. (2.15a) and (2.15b) of Ref. 13(a). In writing the above expressions for the fluxes, variables describing the center-of-mass motion have been treated classically. The linear phenomenological laws for $\langle J_d(\vec{k}, t) \rangle_{ne}$ and $\langle q(\vec{k}, t) \rangle_{ne}$ remain unchanged in presence of reaction and are given in Eqs. (2.19a) and (2.19b) of Ref. 13(a). However, the longitudinal pressure tensor can couple to the chemical potential difference $\langle \mu(\vec{k}, t) \rangle_{ne}$ due to the reaction; thus Eq. (2.19c) of Ref. 13(a) changes to

$$\langle \sigma_3(t) \rangle_{ne} = ik\rho_0^{-1} (\eta_0^* + \frac{1}{3} \eta_2^*) \langle J(t) \rangle_{ne} + (l_{v1}/T_0) m \langle \mu(t) \rangle_{ne}. \quad (\text{A16})$$

Similarly, the phenomenological law for the reaction flux $\langle R(k, t) \rangle_{ne}$ is

$$\langle R(t) \rangle_{ne} = \frac{l_{1v}}{\rho_0 T_0} ik \langle J(t) \rangle_{ne} + \frac{l_{11}}{T_0} m \langle \mu(t) \rangle_{ne}. \quad (\text{A17})$$

The correlation-function expressions for the non-reactive transport coefficients are well known. Analogous expressions for the reaction-rate coefficient l_{11} and the coupling coefficient l_{v1} are

$$l_{11} = \lim_{\epsilon \rightarrow 0, k \rightarrow 0} \langle R(\vec{k}, \epsilon) R(\vec{k})^* \rangle / m^2 k_B V, \quad (\text{A18})$$

$$l_{1v} = \lim_{\epsilon \rightarrow 0, k \rightarrow 0} \langle R(\vec{k}, \epsilon) \sigma_3(\vec{k})^* \rangle / k_B V. \quad (\text{A19})$$

It should be noted that coupling coefficients l_{v1} and l_{1v} which couple the reaction and bulk viscosity have odd symmetry, i. e., $l_{v1} = -l_{1v}$. Expressions similar to Eq. (A18) have been obtained by several authors²⁵ earlier and l_{11} is easily related to the experimentally measured relaxation time τ_R [see Eq. (2.26)]. On the other hand, little information

is available concerning the coefficient l_{v1} . We know of no approximate calculations of the correlation function in Eq. (A19), even for model systems; we can only speculate that it is probably small since it is a cross effect.

Using the expressions for the random forces and the linear laws, we can write down, in a manner similar to that of Ref. 13(a), the hydrodynamic limit of the damping matrix $\underline{\phi}(k, \epsilon)$; it is frequency independent and contains terms up to order k^2 . Although the derivation outlined in this Appendix is most readily carried out using the orthogonal set of variables $\underline{Z}(\vec{k})$, the calculations described in Sec. II can be performed most conveniently using the variables $\underline{a}(\vec{k})$. If \underline{T} is the matrix which transforms the $\{\xi_1, \xi, \Theta, J\}$ basis to the $\{\rho_1, \rho_2, \Theta, J\}$ basis, the transformed damping matrix is

$$\underline{\Phi}(k) = \underline{T} \underline{\phi}(k) \underline{T}^{-1}, \quad (\text{A20})$$

and the transformed frequency matrix is

$$\underline{\Omega}(k) = \underline{T} \underline{\omega}(k) \underline{T}^{-1}. \quad (\text{A21})$$

The nonzero elements of these transformed matrices are given below. The $\underline{\mathfrak{M}}(k)$ matrix in Eq. (2.1) is the combination $\underline{\Phi}(k) - i\underline{\Omega}(k)$:

$$\Phi_{11}(k) = k^2 \left(\frac{\rho_{20}}{\rho_0} D + \frac{\rho_0 \bar{v}_1}{\kappa} D_P \right) + \frac{l_{11} m^2}{T_0} \Xi_1, \quad (\text{A22})$$

where

$$\Xi_1 = \left[\frac{\rho_{20}}{\rho_0^2} \left(\frac{\partial \mu}{\partial c} \right)_{T,P} + \frac{\bar{v}_{12} \bar{v}_1}{\kappa} \right], \quad (\text{A23})$$

$$\Phi_{12}(k) = k^2 \left(-\frac{\rho_{10}}{\rho_0} D + \frac{\rho_0 \bar{v}_2}{\kappa} D_P \right) + \frac{l_{11} m^2}{T_0} \Xi_2, \quad (\text{A24})$$

where

$$\Xi_2 = \left[-\frac{\rho_{10}}{\rho_0^2} \left(\frac{\partial \mu}{\partial c} \right)_{T,P} + \frac{\bar{v}_{12} \bar{v}_2}{\kappa} \right], \quad (\text{A25})$$

$$\Phi_{13}(k) = \frac{k^2 Y}{c_{vt}} - \frac{l_{11} m^2 \Delta_{sv}}{\rho_0 c_{vt} T_0}, \quad (\text{A26})$$

$$\Phi_{14}(k) = -\frac{ik l_{v1} m}{\rho_0 T_0}, \quad (\text{A27})$$

$$\Phi_{2\alpha}(k) = -\Phi_{1\alpha}(k) \quad (\alpha = 1, 2, 3, 4), \quad (\text{A28})$$

$$\Phi_{31}(k) = (k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv}) \Xi_1, \quad (\text{A29})$$

$$\Phi_{32}(k) = (k^2 Y \rho_0 T_0 - l_{11} m^2 \Delta_{sv}) \Xi_2, \quad (\text{A30})$$

$$\Phi_{33}(k) = \frac{k^2}{\rho_0 c_{vt}} \left[\lambda^* + \frac{\rho_0 T_0}{D} \left(\frac{\partial \mu}{\partial c} \right)_{T,P} Y^2 \right] \\ + \frac{l_{11} m^2 \Delta_{sv}^2}{\rho_0 c_{vt}}, \quad (\text{A31})$$

$$\Phi_{34}(k) = ik l_{v1} m \Delta_{sv} / \rho_0, \quad (\text{A32})$$

$$\Phi_{41}(k) = -ik l_{v1} m \Xi_1 / T_0, \quad (\text{A33})$$

$$\Phi_{42}(k) = -ik l_{v1} m \Xi_2 / T_0, \quad (\text{A34})$$

$$\Phi_{43}(k) = ik l_{v1} m \Delta_{sv} / \rho_0 T_0 c_{vt}, \quad (\text{A35})$$

$$\Phi_{44}(k) = k^2(\frac{4}{3}\eta_3^* + \eta_2^*)/\rho_0, \quad (\text{A36})$$

$$i\Omega_{\alpha 4}(k) = ik\rho_{\alpha 0}/\rho_0 \quad (\alpha = 1, 2), \quad (\text{A37})$$

$$i\Omega_{4\alpha}(k) = ik\bar{v}_\alpha/\kappa \quad (\alpha = 1, 2), \quad (\text{A38})$$

$$i\Omega_{34}(k) = ikT_0\alpha_T/\rho_0\kappa, \quad (\text{A39})$$

and

$$i\Omega_{43}(k) = ik\alpha_T/\rho_0\kappa c_{vt}. \quad (\text{A40})$$

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