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Fluctuations in Fluids out of Thermal Equilibrium

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After a brief review of dynamic correlations in equilibrium fluids, we consider the long-range correlations between the fluctuations in a fluid subjected to a large stationary temperature gradient. These long-range correlations enhance and modify the Rayleigh spectrum of the fluid. We elucidate that the modifications of the Rayleigh line are determined by the coupling of the entropy fluctuations to the transverse velocity fluctuations. Recent attempts to test the theoretical predictions with the aid of light-scattering experiments are discussed.

KEY WORDS: Fluctuations; light scattering; long-range correlations; nonequilibrium states; Rayleigh scattering.

1. INTRODUCTION

The subject of fluctuations in nonequilibrium fluids has been reviewed by several authors.(1–4) While many articles have appeared dealing with the theory of fluctuations in nonequilibrium fluids, the number of supporting experimental studies are rather limited. This article for the Festschrift in honor of E. G. D. Cohen is concerned with fluctuations in a fluid in the presence of a stationary temperature gradient, and in particular how they affect the Rayleigh spectrum as first predicted by Kirkpatrick *et al.*(5)

To illustrate the significance of the subject, we begin with two quotations from Cohen's original review(1): "In a fluid not in thermal equilibrium, long-range correlations between fluctuations exist, due to mode-coupling effects, that are absent in fluids in equilibrium. Light-scattering experiments can reveal these correlations." And: "In so far as these long-range correlations in a nonequilibrium fluid are the origin of the

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so-called long-time tail contributions to the transport coefficients, which in turn are related to the non-existence of a virial or density expansion of the transport coefficients, light-scattering experiments of fluids not in thermal equilibrium give support for the reality of the above mentioned phenomena." Stimulated by these theoretical developments we have recently, together with R. W. Gammon, initiated an attempt to perform Rayleigh scattering experiments in a liquid in a stationary temperature gradient.(6,7)

This article is organized as follows. In Section 2 we first give a brief review of dynamic correlations in equilibrium fluids alluded to in the above quotations and to which Cohen and collaborators have made some major contributions. In Section 3 we consider the theoretical prediction for the Rayleigh spectrum of a fluid in a large temperature gradient. Finally, in Section 4 we discuss to what extent we have been able to verify the theoretical predictions experimentally.

2. DYNAMIC CORRELATIONS IN EQUILIBRIUM FLUIDS

The usual transport properties, such as self-diffusion, viscosity, and thermal conductivity, govern the decay of hydrodynamic fluctuations in equilibrium fluids. They are related to time integrals over molecular correlation functions.(8) For dilute gases these properties are determined by the solution of the Boltzmann equation in which it is assumed that the molecules interact through uncorrelated binary collisions only.(9,10) A theoretical framework to extend the Boltzmann equation to dense gases was proposed by Bogoliubov.(11) The transport coefficients of moderately dense gases of molecules with short-range intermolecular forces were represented by power series in the density ρ in analogy to the virial expansion for thermodynamic properties like the compressibility factor PV/RT. Formal expressions for the coefficients of this power series involving collision sequences among successively larger number of molecules were derived by Cohen(12,13) and by Green and Piccirelli.(14) An alternative derivation of the density expansion of the transport properties was subsequently given by Zwanzig.(15) In this approach it was believed that the dynamic correlation functions would decay exponentially fast with a relaxation time of the order of the time between molecular collisions. For larger times the response of the fluid to a gradient would be determined by the local hydrodynamic variables, namely density, velocity, and energy, with time-independent transport coefficients.

The history of the discovery of the nonexistence of a virial expansion for the transport properties has been documented by Brush.(16) As far as one of the authors (J.V.S.) is concerned, it started when Dorfman at one of his visits to the National Bureau of Standards reported that he and Cohen had noticed that the phase space associated with the collision sequences among four molecules that enter into the expression for the coefficient proportional to ρ^2 diverges as $\ln \tau$, where τ represents the time between the first and last collision.(17) To evaluate the coefficients of the density expansion, one needs to consider a variety of collision sequences, some of them containing so-called noninteracting or hypothetical collisions, i.e., binary collisions that are prevented from occurring through the interference of a third particle.(18) An explicit evaluation of the triple-collision integrals for a two-dimensional gas of hard disks confirmed the nonexistence of a virial expansion for the transport properties.(19) It was argued that the maximum time τ between collisions should not be allowed to go to infinity, but should be no larger than the mean free time, which is inversely proportional to the density ρ, so that the transport coefficients should have an expansion of the form(20)

$$\mu = \mu_0 + \mu_1 \rho + \mu_2' \rho^2 \ln \rho + \mu_2 \rho^2 + \cdots \tag{1}$$

where the symbol μ represents the viscosity η, the thermal conductivity λ, or the product ρD, where D is the coefficient of self-diffusion. The presence of a $\ln \rho$ term in the density expansion was confirmed by a resummation of the most divergent terms of the original power series.(21–24) Similar results were obtained for special models, such as the Lorentz gas.(25–27)

The static molecular correlations in a fluid extend over distances of the order of the intermolecular interactions. The breakdown of a virial expansion for the transport properties is due to the fact that the dynamic molecular correlations extend over distances at least as long as the mean free path or, equivalently, over times as long as the mean free time, which diverges as $\rho \to 0$. Subsequent developments showed that the dynamic correlations in dense fluids even extend over times that are appreciably larger than the mean free time. Pomeau noticed that a resummation of the diverging density series for the transport properties does not lead to a finite result in the case of a two-dimensional gas (the two-dimensional Lorentz gas being an exception), indicating that in two dimensions linear gradient-independent transport coefficients do not exist.(28) The crucial observation was made by Alder and Wainwright, who from their molecular-dynamic studies of the velocity autocorrelation function for hard disks and hard spheres noticed a persistence of the molecular velocities associated with coherent vortexlike motions.(29) It was concluded that the velocity autocorrelation function does not decay exponentially as would be expected for short-range dynamic correlations, but instead decays as $t^{-d/2}$, where d is the dimensionality. Dorfman and Cohen were able to derive this result on the basis of the kinetic theory of gases relating the effect at the molecular level to the same "ring" collision sequences that were earlier found to be responsible for the breakdown of the virial expansion for the transport properties.(24,30) More generally, the unexpected long-time behavior of the molecular correlation functions was shown to originate from coupling among long-wavelength hydrodynamic modes,(31–33) the same mode-coupling effects that had earlier been found responsible for the anomalous behavior of the transport properties near the critical point.(34,35)

The presence of long-time effects in the dynamic correlations is now well established both from molecular-dynamic computations(29,36–41) and from theory,(30–33) although consistency between theory and computations about the magnitude of the effects has been obtained only recently.(42–44) The upshot of this development is that there exists a mesoscopic time scale larger than the mean free time during which correlations exist which find their origin in the presence of mode-coupling effects that follow from the application of generalized hydrodynamics.

The question arises as to what extent the above-mentioned phenomena have been confirmed from experiments with real fluids. Several investigators have tried to detect a term proportional to $\rho^2 \ln \rho$ in the density expansion of experimental transport coefficients.(45–51) A problem is that the coefficients μ_1 and μ_2' in the expansion (1) are only known for hard spheres(52,53) and not for a gas of molecules with realistic potentials. Moreover, the terms $\mu_2' \rho^2 \ln \rho$ and $\mu_2 \rho^2$ are strongly correlated in any least squares fit. At best, all one can conclude from the more accurate studies is that the presence of a logarithmic term in the density expansion of the transport coefficients is not inconsistent with the data.(46,48,51)

For a gas of hard spheres computer simulations have shown that the long-time tails in the velocity autocorrelation function lead to a significant enhancement of the diffusion coefficient D over the value D_E predicted by the Enskog theory, which does not incorporate the effects of correlated collision sequences.(54) Hence, attempts have been made to obtain evidence for the existence of the dynamic correlation due to mode-coupling effects by comparing the density dependence of the experimental transport properties with that predicted by the theory of Enskog.(55–58) However, since the actual molecules are not hard spheres, the need for assigning a reference hard-sphere system to specify the Enskog contribution introduces an appreciable uncertainty in the analysis.

A more interesting approach is to study the correlations directly with neutron scattering or light scattering. Evidence for the presence of mode-coupling effects on the velocity autocorrelation function has been reported from neutron-scattering experiments in molecular liquids(59–63) and in liquid sodium.(64–68) With light scattering the long-time behavior of the velocity autocorrelation function of Brownian particles has been studied.(69–74) However, with light scattering it is ordinarily not possible to observe mode-coupling effects on any of the correlation functions in molecular fluids except in the vicinity of a critical point.(75) The reason is that at the range of wave numbers accessible with light scattering the normal macroscopic hydrodynamic equations apply, leading to the well-known Rayleigh–Brillouin triplet in the light-scattering spectrum. The integrated scattering intensity is proportional to the compressibility, while the central Rayleigh line is a single Lorentzian whose linewidth is determined by the macroscopic thermal diffusivity.(76,77) As illustrated by Cohen's remarks quoted in the introduction of this article, it does become possible to observe mode-coupling effects in molecular fluids with light scattering, when the fluid is brought into a nonequilibrium steady state.(1,78) It is this approach which we discuss in the remainder of this article. Specifically, we consider light scattering in a liquid subject to a large stationary temperature gradient.

3. RAYLEIGH SPECTRUM OF A FLUID IN THE PRESENCE OF A TEMPERATURE GRADIENT

Let a fluid be confined between two horizontal plates with different, but stationary, temperatures. Here we consider the case that the fluid layer is heated from above, so as to avoid the onset of any convective fluid motions. The system thus remains in a stable stationary state far away from any convective instability. In first approximation the presence of a temperature gradient in a fluid does not affect the Rayleigh spectrum, but causes an asymmetry in the Brillouin lines, since the propagating sound modes probe regions of different temperature.(1–4,79–85) This effect, caused by long-range correlations *parallel* to the temperature gradient, is proportional to the temperature gradient ∇T. When the temperature gradient becomes large, the temperature begins to vary over distances probed by mode-coupling effects which become significantly enhanced and affect both the Brillouin lines(1,4,86,87) and the Rayleigh line.(1,4,5,88) The long-range correlations produced by these mode-coupling effects then become proportional to $(\nabla T)^2$. Brillouin-scattering measurements from a liquid in the presence of a temperature gradient have been reported by two groups of investigators.(89–91) The interpretation of such Brillouin scattering experiments is complicated by effects from adjacent sound-absorbing and sound-reflecting walls.(87,92,93) As a consequence, only the linear small-gradient effect has been observed.(91) We thus focus our attention on the effects of the temperature gradient on the Rayleigh line, which are determined by the large temperature-gradient effects directly yielding information on the long-range molecular correlations in the fluid itself.

Kirkpatrick *et al.*(5) predicted the modifications to the shape of the Rayleigh line for a pure liquid in a steady-state temperature gradient using the methods of mode coupling and kinetic theory. They found that for a system removed from equilibrium by a large temperature gradient the density–density time correlation function contains a local equilibrium heat mode contribution plus two nonequilibrium terms due to heat mode and viscous mode fluctuations; both nonequilibrium terms are proportional to $(\nabla T)^2/k^4$, where $\mathbf{k}$, the scattering vector, is in a direction *perpendicular* to the temperature gradient ∇T. These predictions were confirmed by Ronis and Procaccia(88) on the basis of fluctuating hydrodynamics. Using the method of fluctuating hydrodynamics, we give here a simple derivation of the modifications to the Rayleigh spectrum, illustrating explicitly that they are related to a coupling between the entropy fluctuations and shear fluctuations.(88)

The Onsager regression hypothesis(94) states that spontaneous fluctuations "regress" back to equilibrium according to the same relaxation equations that describe the macroscopic relaxation processes. More recently, spontaneous fluctuations have been described by supplementing the relaxation equations with Langevin random forces; the random forces represent the fast molecular processes which generate the fluctuations.(95) In thermal equilibrium the Rayleigh line is solely described by heat mode fluctuations, or, more specifically, entropy fluctuations. One might expect therefore from the Onsager regression hypothesis that the entropy fluctuations are completely described by the heat transfer equation supplemented by a random heat flux with the additional condition that pressure fluctuations can be neglected to leading order; pressure fluctuations are associated with the sound modes (Brillouin lines). For a system removed far from equilibrium by a steady-state temperature gradient we must retain the macroscopic temperature gradient term in the heat transfer equation.

The heat transfer equation,(95) linearized in terms of the entropy, pressure, and velocity fluctuations and supplemented by a random heat flux $\mathbf{g}$, is given by

$$\frac{\partial \delta s}{\partial t} - D_T \nabla^2 \delta s + \frac{c_p}{T_0}\delta\mathbf{u}\cdot\nabla T - \frac{D_T \alpha_T}{\rho_0}\nabla^2 \delta p - \frac{1}{\rho_0 T_0}\nabla\cdot\mathbf{g} = 0 \tag{2}$$

where ρ_0 is the average mass density, T_0 the average temperature, ∇T the externally imposed temperature gradient, c_p the specific heat at constant pressure, α_T the thermal expansion coefficient, D_T the thermal diffusivity $(=\lambda/\rho_0 c_p)$, and δs, δp, and $\delta\mathbf{u}$ are, respectively, the fluctuations in the specific entropy, the pressure, and the fluid velocity. The spatial variation of the transport coefficients is not considered, because this variation is negligibly small for experimentally accessible gradients and scattering vectors.(5,88) In a Fourier space and time representation this equation becomes

$$i\omega\,\delta s_{k,\omega}+k^2D_T\,\delta s_{k,\omega}+\frac{c_p}{T_0}\,\delta\mathbf{u}_{k,\omega}\cdot\nabla T+\frac{\alpha_T k^2 D_T}{\rho_0}\,\delta p_{k,\omega}+\frac{1}{\rho_0 T_0}\,i\mathbf{k}\cdot\mathbf{g}_{k,\omega}=0 \tag{3}$$

To a first approximation, the Rayleigh line in the presence of a temperature gradient is determined by the coupling of the entropy fluctuations to the transverse velocity fluctuations δu_t; that is, we can ignore pressure fluctuations and longitudinal velocity fluctuations which contribute to the Brillouin lines. This statement is justified rigorously in the Appendix. Hence, from (3),

$$\delta s_{k,\omega}=-\frac{i\mathbf{k}\cdot\mathbf{g}_{k,\omega}}{\rho_0 T_0(i\omega+k^2D_T)}-\frac{c_p\,\delta u_t}{T_0(i\omega+k^2D_T)}\left(\frac{dT}{dz}\right) \tag{4}$$

The transverse velocity fluctuation δu_t is defined as

$$\delta u_t=\delta\mathbf{u}_{k,\omega}\cdot(\mathbf{1}-\hat{k}\hat{k})\cdot\hat{z} \tag{5}$$

where $\mathbf{1}$ is the unit tensor and where $\hat{z}$ is the unit vector in the direction of the temperature gradient

$$\nabla T=\frac{dT}{dz}\hat{z}$$

From (5) it is readily seen that if the scattering vector $\mathbf{k}$ is parallel to the temperature gradient, then δu_t is zero, so that there is no effect on the Rayleigh line. For the converse case of $\mathbf{k}$ perpendicular to the temperature gradient, δu_t is a maximum. For simplicity we assume that $\mathbf{k}\perp\nabla T$. Equation (4) encapsulates all the physics of the Rayleigh line in the presence of a temperature gradient. The first term describes the equilibrium fluctuations whose decay rate depends upon the thermal diffusivity, while the second term demonstrates that the nonequilibrium enhancement is a consequence of the coupling of transverse velocity fluctuations to entropy fluctuations via the temperature gradient. The velocity fluctuations are obtained from the momentum equation(95)

$$\rho_0\frac{\partial\delta\mathbf{u}}{\partial t}=-\nabla\delta p+\eta\nabla^2\,\delta\mathbf{u}+\left(\zeta+\frac{1}{3}\eta\right)\nabla(\nabla\cdot\delta\mathbf{u})+\nabla\cdot\mathbf{S} \tag{6}$$

where η is the shear viscosity, ζ the bulk viscosity, and $\mathbf{S}$ the random stress tensor. In $\mathbf{k}$–ω space this equation takes the form

$$i\omega\,\delta\mathbf{u}_{k,\omega}=\frac{i\mathbf{k}\,\delta p_{k,\omega}}{\rho_0}-k^2\nu\,\delta\mathbf{u}_{k,\omega}-(\Gamma-\nu)\,\mathbf{k}(\mathbf{k}\cdot\delta\mathbf{u}_{k,\omega})-\frac{i\mathbf{k}\cdot\mathbf{S}_{k,\omega}}{\rho_0} \tag{7}$$

where the longitudinal kinematic viscosity is $\Gamma = (\zeta + 4\eta/3)/\rho_0$ and the transverse kinematic viscosity is $v = \eta/\rho_0$. The transverse velocity fluctuation (5) is deduced from (7) as

$$\delta u_t = -\frac{i\mathbf{k}\cdot\mathbf{S}_{k,\omega}\cdot(\mathbf{1}-\hat{k}\hat{k})\cdot\hat{z}}{\rho_0(i\omega+k^2 v)} \tag{8}$$

which when substituted into (4) yields

$$\delta s_{k,\omega} = \frac{-i\mathbf{k}\cdot\mathbf{g}_{k,\omega}}{\rho_0 T_0(i\omega+k^2 D_T)} + \frac{c_p i\mathbf{k}\cdot\mathbf{S}_{k,\omega}\cdot(\mathbf{1}-\hat{k}\hat{k})\cdot z}{\rho_0 T_0(i\omega+k^2 v)(i\omega+k^2 D_T)}\left(\frac{dT}{dz}\right) \tag{9}$$

The usual approximation made in nonequilibrium fluctuating hydrodynamics is that the random forces **g** and **S**, which represent the fast localized molecular processes, retain their local equilibrium correlations, which take the form(95)

$$\langle g^i_{k,\omega} g^{j*}_{k',\omega'}\rangle = \frac{1}{8\pi^4} k_{\mathrm{B}} T_0^2 \rho_0 c_p D_T \delta_{ij} \delta(\mathbf{k}-\mathbf{k}')\,\delta(\omega-\omega') \tag{10a}$$

$$\begin{aligned}\langle S^{ij}_{k,\omega} S^{lm*}_{k',\omega'}\rangle = \frac{k_{\mathrm{B}} T_0}{8\pi^4}\left[\eta(\delta_{il}\delta_{jm}+\delta_{im}\delta_{jl}) + \left(\zeta - \frac{2}{3}\eta\right)\delta_{ij}\delta_{lm}\right]\\ \times\,\delta(\mathbf{k}-\mathbf{k}')\,\delta(\omega-\omega')\end{aligned} \tag{10b}$$

$$\langle g^i_{k,\omega} S^{jk*}_{k',\omega'}\rangle = 0 \tag{10c}$$

From the correlations in the random forces, Eqs. (10a)–(10c), one can readily show that

$$\begin{aligned}&\langle \hat{k}\cdot\mathbf{g}_{k,\omega}\hat{k}\cdot\mathbf{g}^*_{k',\omega'}\rangle\\ &\quad = \frac{1}{8\pi^4} k_{\mathrm{B}} T_0^2 \rho_0 c_p D_T \delta(\mathbf{k}-\mathbf{k}')\,\delta(\omega-\omega')\end{aligned} \tag{11a}$$

$$\begin{aligned}&\langle \hat{k}\cdot\mathbf{S}_{k,\omega}\cdot(\mathbf{1}-\hat{k}\hat{k})\cdot\hat{z}\cdot\hat{k}'\cdot\mathbf{S}^*_{k',\omega'}\cdot(\mathbf{1}-\hat{k}'\hat{k}')\cdot\hat{z}\rangle\\ &\quad = \frac{k_{\mathrm{B}} T_0 \rho_0 v}{8\pi^4}\delta(\mathbf{k}-\mathbf{k}')\,\delta(\omega-\omega') \qquad \text{for} \quad \mathbf{k},\mathbf{k}' \perp \nabla T\end{aligned} \tag{11b}$$

Any asymmetries occur in the $\hat{z}$ direction, while in a plane perpendicular to ∇T (the scattering plane) spatial and temporal invariance holds,(88) so that $\mathbf{k} = \mathbf{k}'$ and $\omega = \omega'$. Therefore, from Eqs. (9) and (11) the entropy correlation function is given by

$$\langle \delta s_{k,\omega}\, \delta s^*_{k,\omega} \rangle = \frac{k_B c_p k^2 D_T}{8\pi^4 \rho_0 (\omega^2 + k^4 D_T^2)} \times \left[1 + \frac{c_p \nu}{T_0 D_T (\omega^2 + k^4 \nu^2)} \left(\frac{dT}{dz} \right)^2 \right] \quad \text{for} \quad \mathbf{k} \perp \nabla T \tag{12}$$

This equation agrees precisely with the form deduced by previous investigators.$^{(5,88)}$

4. EXPERIMENTAL RESULTS

The heterodyne-time correlation function, which can be determined with a photon-correlation experiment, is obtained from (12) by Fourier transforming in frequency space,

$$C(t) = C_B\{1 + C_e[(1 + AP)\exp(-D_T q^2 t) - A \exp(-\nu q^2 t)]\} \tag{13}$$

where we have included the background term C_B, which accounts for static scattering from optical surfaces in the line of sight of the detector and where C_e is the signal-to-background ratio. The amplitude A in (13) is given by

$$A = \frac{B(\nabla T)^2}{q^4} \tag{14}$$

with

$$B = \frac{c_p}{T(P^2 - 1)\, D_T^2} \tag{15}$$

$P = \nu/D_T = \eta c_p/\lambda$ is the Prandtl number. An important point to note is that the viscous mode with a decay rate of νq^2 in (13) has a negative coefficient, thus decreasing the correlations at short times. We define an equilibrium diffusive amplitude $a_D(e) = C_e$, a nonequilibrium diffusive amplitude $a_D(n) = C_e AP$, and a nonequilibrium viscous amplitude $a_\nu(n) = -C_e A$. The two ratios

$$\frac{a_D(n)}{a_D(e)} = \frac{BP\,|\nabla T|^2}{q^4} \tag{16}$$

and

$$\frac{a_\nu(n)}{a_D(e)} = -\frac{B\,|\nabla T|^2}{q^4} \tag{17}$$

are thus independent of the geometry-dependent factor C_e.

The presence of the q^{-4} term in the amplitude A implies that one must work at very small scattering angles ($\theta < 0.75°$) in order to observe the enhancements for experimentally accessible gradients ($\nabla T \simeq 100$ K/cm). The experimental technique has been described previously,$^{(6,7)}$ while the results will be reviewed here.

Typical experimental correlation functions for liquid toluene in a temperature gradient are plotted on a semilog graph in Fig. 1. Figure 1a shows the enhancement of the diffusive mode at long times for a scattering angle of $\theta = 0.75°$ and a temperature gradient of $\nabla T = 138$ K/cm. The slight difference in slopes between the equilibrium correlation function (E) and the nonequilibrium correlation function (N) is due to the finite spread in experimental q values (finite collection angle), which affects the nonequilibrium correlation function to a greater extent than the equilibrium correlation function due to the q^{-4} dependence of the former.$^{(7)}$ At shorter times (Fig. 1b) the effect of the viscous mode with negative coefficient becomes evident; it decreases the correlation function at these shorter time scales. In order to account quantitatively for the finite spread in q values,

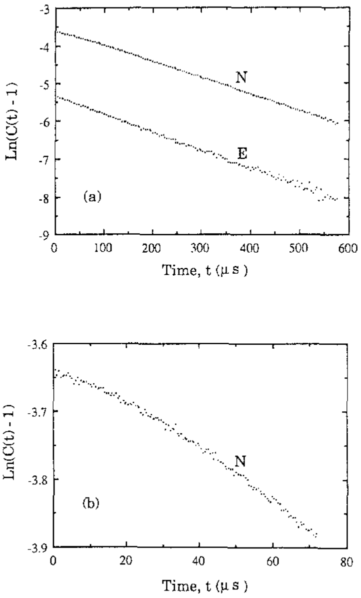

Fig. 1. Normalized experimental correlation function $[C(t) - C_B]/C_B$ obtained at a scattering angle of $\theta = 0.75°$. (a) Correlation function (N) of the nonequilibrium liquid with $\nabla T = 138$ K/cm on a time scale where the heat mode dominates; corresponding correlation function (E) for the equilibrium liquid in the absence of a temperature gradient. (b) Correlation function of the nonequilibrium liquid at shorter times, where the influence of the viscous mode is observed.

we numerically convoluted the ideal correlation function (13) with a Gaussian beam profile.(6) In Fig. 2 the results for the diffusive and the viscous amplitude ratios, as defined by (16) and (17), are presented as a function of $(\nabla T)^2/q^4$. The experiment confirms the theoretical prediction that both amplitude ratios vary linearly with $(\nabla T)^2/q^4$. The slopes of the lines in Figs. 2a and 2b yield, respectively, $BP = (5.8 \pm 0.4) \times 10^9\ \mathrm{K}^{-2}\ \mathrm{cm}^{-2}$ and $B = (0.81 \pm 0.08) \times 10^9\ \mathrm{K}^{-2}\ \mathrm{cm}^{-2}$. The ratio of the slopes determines the Prandtl number $P = 7.2 \pm 1.2$, which is in excellent agreement with the known value 7.12 for toluene at 26°C.

The one aspect of these data at variance with theory is the absolute magnitude of B. From the known thermophysical properties of toluene we calculate $B = 1.5 \times 10^9\ \mathrm{K}^{-2}\ \mathrm{cm}^{-2}$, which is larger than our experimental value of $0.8 \times 10^9\ \mathrm{K}^{-2}\ \mathrm{cm}^{-2}$. It is suspected that the discrepancy is due to inhomogeneities in the temperature gradient between the hot and cold plates, so that we have insufficient information about the magnitude of the local temperature gradient at the scattering position. Hence, our preliminary experiments only enable us to assert the proportionality with $(\nabla T)^2$.

To investigate this matter further, we have constructed a modified nonequilibrium scattering cell which will enable us to measure the tem-

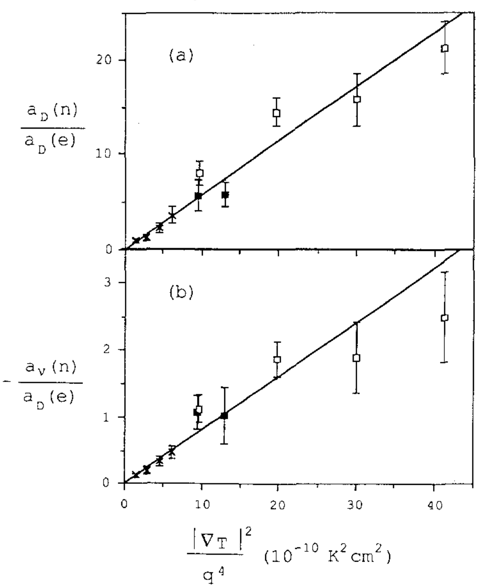

Fig. 2. Amplitude ratios for the (a) thermal and (b) viscous modifications to the Rayleigh line. Crosses, $q = 2360\ \mathrm{cm}^{-1}$; solid squares, $q = 1960\ \mathrm{cm}^{-1}$; open squares, $q = 1470\ \mathrm{cm}^{-1}$. The horizontal error bars indicate the ±8% error in q^4. Solid lines are the best fits to the data.

peratures closer to the top and bottom of the fluid layer. Initial results obtained with this improved scattering cell do appear to yield quantitative agreement between theory and experiment for the amplitudes as well. This work is still in progress and will be reported in a future publication.(96)

APPENDIX

In this Appendix we justify the statement that the Rayleigh line in the presence of a temperature gradient is determined to first order by the coupling of the entropy fluctuations to the transverse velocity fluctuations. The treatment closely follows the formulation of Schmitz and Cohen.(97) The hydrodynamic equations take the general form(95)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{A.1}$$

$$\rho T\left(\frac{\partial s}{\partial t} + \mathbf{u} \cdot \nabla s\right) = \lambda \nabla^2 T + \sigma'_{ik} \frac{\partial u_i}{\partial x_k} \tag{A.2}$$

$$\rho\left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\, \mathbf{u}\right] = -\nabla p + \eta \nabla^2 \mathbf{u} + \left(\zeta + \frac{1}{3}\eta\right) \nabla(\nabla \cdot u) \tag{A.3}$$

where σ'_{ik} are the elements of the stress tensor. If we use the thermodynamic relations

$$d\rho = \rho_0(\chi_T\, dp - \alpha_T\, dT) \qquad \text{and} \qquad ds = \frac{c_p}{T_0}\, dT - \frac{\alpha_T}{\rho_0}\, dp \tag{A.4}$$

where χ_T is the isothermal compressibility, then Eqs. (A.1)–(A.3) can be expressed solely in terms of p, s, and $\mathbf{u}$. Retaining only terms which are first order in the fluctuations, the time-dependent equations for the fluctuations δp, δs, and $\delta \mathbf{u}$ with wave vector $\mathbf{k}$ are

$$\frac{\partial \delta s}{\partial t} = -\frac{c_p}{T_0}\, \delta \mathbf{u} \cdot \nabla T_0 - k^2 D_T \delta s - \frac{\alpha_T k^2 D_T}{\rho_0}\, \delta p \tag{A.5}$$

$$\frac{\partial \delta p}{\partial t} = -\frac{(\gamma - 1)\, \rho_0 k^2 D_T}{\alpha_T}\, \delta s - (\gamma - 1)\, k^2 D_T \delta p + \rho_0 c^2 i \mathbf{k} \cdot \delta \mathbf{u} \tag{A.6}$$

$$\frac{\partial \delta \mathbf{u}}{\partial t} = \frac{i\mathbf{k}}{\rho_0}\, \delta p - k^2 \nu\, \delta \mathbf{u} - (\Gamma - \nu)\, \mathbf{k}(\mathbf{k} \cdot \delta \mathbf{u}) \tag{A.7}$$

where c is the sound velocity and $\gamma = c_p/c_v$. We express the velocity fluctuation $\delta \mathbf{u}$ in terms of the longitudinal velocity δu_l, the transverse velocity δu_t, and the vorticity δu_v, where

$$\delta \mathbf{u} = i \delta u_l \mathbf{k} - \delta u_t\, \frac{\mathbf{k} \times (\mathbf{k} \times \hat{z})}{k_\parallel^2} + i \delta u_v\, \frac{\mathbf{k} \times \hat{z}}{k_\parallel^2} \tag{A.8}$$

with $k_{\|}^2 = k_x^2 + k_y^2$, and

$$\delta u_l = -\frac{i}{k^2}\,\mathbf{k}\cdot\delta\mathbf{u} \tag{A.9}$$

$$\delta u_t = \delta\mathbf{u}\cdot(\mathbf{1} - \hat{k}\hat{k})\cdot\hat{z} \tag{A.10}$$

$$\delta u_v = i\hat{z}\cdot(\mathbf{k}\times\delta\mathbf{u}) \tag{A.11}$$

The vorticity is decoupled from the other variables,$^{(97)}$ while the coupling between δp, δs, δu_l, and δu_t is most conveniently expressed in terms of the following scaled variables:

$$\begin{aligned} \delta p' &= \left(\frac{\chi_T}{\gamma}\right)^{1/2}\delta p, \qquad & \delta s' &= \left(\frac{\rho_0 T_0}{c_p}\right)^{1/2}\delta s \\ \delta u_l' &= (\rho_0)^{1/2}\,k\,\delta u_l, \qquad & \delta u_t' &= (\rho_0)^{1/2}\,\delta u_t \end{aligned} \tag{A.12}$$

Each variable has been scaled by the square root of its local-equilibrium correlation strength in order to give the scaled variables the same dimension. Then

$$\frac{\partial}{\partial t}\begin{pmatrix}\delta x' \\ \delta y'\end{pmatrix} = -\begin{pmatrix} H_{xx} & H_{xy} \\ H_{yx} & H_{yy}\end{pmatrix}\begin{pmatrix}\delta x' \\ \delta y'\end{pmatrix} + \begin{pmatrix}\delta F_x' \\ \delta F_y'\end{pmatrix} \tag{A.13}$$

where we have added random forces $\delta F_x'$ and $\delta F_y'$ to the right-hand side and where

$$\delta x' = \begin{pmatrix}\delta s' \\ \delta u_t'\end{pmatrix}, \qquad \delta y' = \begin{pmatrix}\delta p' \\ \delta u_l'\end{pmatrix} \tag{A.14}$$

$$H_{xx} = \begin{pmatrix} k^2 D_T & \left(\dfrac{c_p}{T_0}\right)^{1/2}\dfrac{dT}{dz} \\ 0 & k^2\nu \end{pmatrix} \tag{A.15}$$

$$H_{xy} = \begin{pmatrix} (\gamma-1)^{1/2}k^2 D_T & i\left(\dfrac{c_p}{T_0}\right)^{1/2}\dfrac{dT}{dz}\dfrac{k_z}{k} \\ 0 & 0 \end{pmatrix} \tag{A.16}$$

$$H_{yx} = \begin{pmatrix} (\gamma-1)^{1/2}k^2 D_T & 0 \\ 0 & 0 \end{pmatrix} \tag{A.17}$$

and

$$H_{yy} = \begin{pmatrix} (\gamma-1)\,k^2 D_T & kc \\ -kc & k^2\Gamma \end{pmatrix} \tag{A.18}$$

If we define the dimensionless small parameters ε_1 and ε_2 as

$$\varepsilon_1 = \frac{k\Gamma'}{c} \qquad \text{with} \quad \Gamma' = D_T, \Gamma, \nu \tag{A.19}$$

and

$$\varepsilon_2 = \frac{1}{kL_\nabla} \qquad \text{with} \quad L_\nabla = \frac{c}{(c_p/T_0)^{1/2}\, dT/dz} \tag{A.20}$$

then the matrices are of order

$$H_{xx}, H_{xy}, H_{yz} = O(\varepsilon kc) \qquad \text{and} \qquad H_{yy} = O(kc) + O(\varepsilon kc)$$

with $\varepsilon \ll 1$.

For the Rayleigh line, $\omega \sim k^2 D_T = O(\varepsilon kc)$, so that from (A.13) in the frequency domain

$$i\omega\, \delta y' = -H_{xy}\, \delta x' - H_{yy}\, \delta y' + \delta F'_y \tag{A.21}$$

and to leading order $\delta y' = H_{yy}^{-1}\, \delta F'_y$. Using this value for $\delta y'$ in the equation for $\delta x'$, one finds from (A.13) that

$$i\omega\, \delta x' = -H_{xx}\, \delta x' - H_{xy} H_{yy}^{-1}\, \delta F'_y + \delta F'_x \tag{A.22}$$

where $H_{xy} H_{yy}^{-1} = O(\varepsilon)$ and $H_{xy} H'_{yy}\, \delta F'_y$ is negligible as compared to $\delta F'_x$. Thus the Rayleigh line is given to leading order by

$$i\omega\, \delta x' = -H_{xx}\, \delta x' + \delta F'_x \tag{A.23}$$

which implies that $\delta x'$ is decoupled from $\delta y'$ and the Rayleigh line is determined by the coupling of the entropy fluctuations to the transverse velocity fluctuations as specified by Eqs. (4) and (8) in the main text.

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