Light-Scattering Observations of Long-Range Correlations in a Nonequilibrium Liquid

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We have performed small-angle Rayleigh-scattering measurements in toluene subject to a stationary temperature gradient. The experiments demonstrate the existence of long-range equal-time correlations through a strong enhancement of the thermal fluctuations and they also reveal a negative contribution at short time scales from the viscous fluctuations in agreement with the theoretical predictions. The experiments confirm that both effects vary with $(\nabla T)^2/q^4$, where ∇T is the temperature gradient and q the wave number of the fluctuations.

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There has been a considerable amount of theoretical interest in liquids far removed from equilibrium by a large temperature gradient.¹⁻⁴ In the presence of a temperature gradient long-range correlations appear in the liquid because of mode-coupling effects which can be investigated experimentally by the performance of lightscattering experiments. The induced long-range correlations parallel to the temperature gradient produce an asymmetry in the Brillouin components of the lightscattering spectrum. Brillouin-scattering measurements from a liquid in the presence of a temperature gradient have been reported by two groups of investigators,^{5,6} but the interpretation of such experiments is complicated by the possible presence of effects from adjacent sound-absorbing and -reflecting walls.^{7,8} Long-range correlations perpendicular to the gradient enchance and modify the Rayleigh line: The heat-mode fluctuations observed in equilibrium are enhanced and a new central component due to viscous fluctuations should appear.^{1,2} Both effects are predicted to be proportional to $(\nabla T)^2/q^4$, where ∇T is the temperature gradient and q the wave number of the observed fluctuations. In spite of a suggestion made by Wegdam, Keulen and Michielsen,⁹ the nonpropagating modes responsible for the Rayleigh line should not be affected by wall effects² and Rayleigh scattering in the presence of a temperature gradient should give direct experimental information about the long-range correlations in the nonequilibrium fluid itself.

We have obtained small-angle Rayleigh-scattering data from toluene in the presence of a temperature gradient. Our experimental time-dependent correlation functions differ qualitatively from those previously reported in Physical Review Letters, ¹⁰ but the structure of our correlation functions conforms precisely to the structure originally predicted by Kirkpatrick, Cohen, and Dorfman¹ and subsequently by Ronis and Procaccia:² a strongly enhanced heat-mode component and a negative contribution from the fast viscous mode. Moreover, our experiments confirm that both effects are proportional to $(\nabla T)^2/q^4$.

A quantitative study of the Rayleigh line of a fluid in the presence of a temperature gradient poses considerable experimental problems. To resolve the heat mode and the viscous mode in the Rayleigh spectrum it is necessary to perform the measurements at small scattering angles θ less than about 0.75° (because of the q^{-4} dependence). At such small scattering angles there is strong static scattering from all optical surfaces in the line of sight of the detector. For liquids in thermal equilibrium, Hendrix et al.¹¹ have measured thermal diffusivities from light scattered at angles between 3° and 5° with accuracies of the order of 1%. In order to reduce the scattering angles further and to accommodate the temperature gradient we have adopted the modified scattering arrangement shown in Fig. 1. The incident argon-ion laser beam with an incident power of 0.2 W propagates *parallel* to the temperature gradient. This configuration enables us to avoid problems with beam bending and defocusing encountered in all previous nonequilibrium light-scattering experiments where the incident beam was perpendicular to the temperature gradient.^{5,6,10} We chose a thin cell (2 mm) so that large temperature gradients could be produced by applying small temperature differences, thus limiting the variation of the liquid properties over the height of the cell. The intense static scattering from optical surfaces is reduced to manageable levels with the aid of a number of techniques. First the sample cell is sandwiched between two 0.5-in.-thick index-matching windows so that the airglass surface has been removed from the line of sight. The outer surfaces of the windows are antireflection coated to reduce surface scattering. A gentle stream of nitrogen gas is continuously directed at the window surfaces to remove dust particles. Finally, the composite cell system, window-sample-window, is reimaged on a 200- μ m pinhole (P2) with the aid of two lenses (L1 and L2). With this geometry the signal-to-background levels lie in the range from 0.1% and 3%. Indium O rings provide good thermal contact between the windows and the copper hot and cold plates. The time dependence of the



FIG. 1. Schematic representation of the experimental arrangement. W, window; P1, P2, and P3, pinholes; L1 and L2, lenses; BS, beam splitter; g, direction of gravity.

scattered light is detected by heterodyning with the residual scattering from the optical surfaces (local oscillator). The scattered light is detected by two photomultipliers whose signals are cross correlated in order to reduce the effects of afterpulsing.¹¹⁻¹³ Reagent-grade toluene, which had been filtered through a 0.22- μ m filter, was used as the liquid sample because information on its thermophysical properties is readily available.¹⁴⁻¹⁷

We have measured the time-dependent correlation function C(t) at three different scattering angles θ between 0.5° and 0.75° with temperature gradients up to about 140 K/cm. The sample time was, in general, chosen such that the 144-channel correlator covered three diffusion decay times. The normalized nonequilibrium correlation function $C(t)/C_B$, where C_B is the background scattering, observed with $\theta=0.75^\circ$ and $\nabla T=138$ K/cm is shown in Fig. 2(a) together with the corresponding equilibrium correlation function with $\nabla T=0$: The strong enhancement in intensity of the thermal fluctuations is readily apparent. In Fig. 2(b) we show an experimental correlation function under the



FIG. 2. Normalized experimental correlation function $C(t)/C_B$ obtained with a scattering angle $\theta = 0.75^{\circ}$. (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.

same nonequilibrium conditions but at a shorter time scale: The change in slope at shorter times reveals a *suppression* of the scattering due to the appearance of the viscous mode. This phenomenon differs qualitatively from the anomalous *enhancement* at shorter times reported by Wegdam, Keulen, and Michielsen.¹⁰ It is difficult to assess the cause of the enhancement observed by Wegdam, Keulen, and Michielsen, but subsequent experiments have indicated that the effect is spurious.⁹

Kirkpatrick and co-workers¹ and Ronis and Procaccia² have derived an explicit expression for the effects of the temperature gradient on the structure factor S as a function of wave number and frequency. In the time domain these theories predict for the heterodyne correlation function C(t) an expression of the form

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

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Here C_B is the background static scattering from the associated optical surfaces in the vicinity of the sample scattering volume, C_e the signal-to-background ratio in equilibrium ($\nabla T = 0$), D_T the thermal diffusivity, v the kinematic viscosity, and $P = v/D_T$ the Prandtl number of the liquid. The amplitude A in (1) is given by

$$A = (B | \nabla T | ^2/q^4) \hat{\mathbf{q}}_{\perp}^2, \qquad (2)$$

where $\hat{\mathbf{q}}_{\perp}$ is the unit scattering vector perpendicular to the temperature gradient and where $B = c_p/T(P^2 - 1)D_T^2$ is a parameter characteristic of the liquid, c_p being the isobaric specific heat. Note that the last term in (1) has a minus sign indicating the negative effect of the viscous fluctuations seen at short times in our experiments. For a quantitative analysis of the experiment we define an equilibrium diffusive amplitude $a_D(e) = C_e$, a nonequilibrium diffusive amplitude $a_D(n) = C_eAP$, and a nonequi-

librium viscous amplitude
$$a_v(n) = -C_e A$$
 so that

$$a_D(n)/a_D(e) = BP |\nabla T|^2/q^4,$$
 (3)

$$a_{\nu}(n)/a_{D}(e) = -B |\nabla T|^{2}/q^{4}.$$
 (4)

In order to interpret the experimental correlation functions, the wave number q needs to be known very accurately. We have determined q from a comparison of the decay rate of the experimental correlation function in the absence of a temperature gradient with the known thermal diffusivity of toluene¹⁴⁻¹⁶; this procedure yields q to better than 2%.

For small-angle light scattering one must take account of the finite spread in q values due to focusing of the beam in the sample and due to the finite collection angle ($\approx 0.1^{\circ}$). We have therefore numerically convoluted the ideal correlation function (1) with a Gaussian beam profile:¹⁸

$$\overline{C}(t) = \frac{1}{(2\pi)^{1/2} \sigma \Phi(\frac{3}{2}\sqrt{2})} \int_{q-3\sigma}^{q+3\sigma} C(t,q') \exp\left(-\frac{(q-q')^2}{2\sigma^2}\right) dq',$$
(5)

where q is now the average wave number, while σ is a measure of the width of the distribution of experimental wave numbers, and $\Phi(x)$ is the error function. As a consistency check of this procedure we have confirmed that all experimental correlation functions are fitted with a single value of $\sigma = 190 \pm 5$ cm⁻¹ independent of both q and ∇T . This value is reasonably close to the value of 220 cm⁻¹ deduced from the estimated collection angle. A nonlinear least-squares program, which incorporates a procedure for the integration of Eq. (5), has been used to fit the nonequilibrium light-scattering data with the decay rate vq^2 fixed from the known value for the viscosity¹⁷ of toluene and with $D_T q^2$ and C_e deduced from the experimental correlation function in the absence of a temperature gradient, thus leaving the amplitudes C_B , AP, and A as adjustable parameters. This procedure yielded χ^2 values of order unity for all experimental nonequilibrium correlation functions, thus confirming that their structure is in excellent agreement with the shape (1) predicted theoretically for the Rayleigh line.

The experimental values obtained for the diffusive amplitude ratio, defined by (3), and for the viscous amplitude ratio, defined by (4), are plotted in Fig. 3 as functions of $(\nabla T)^2/q^4$. All experimental amplitudes have been corrected so that they correspond to the same average temperature. The error bars represent the 1-standard-deviation spread in experimental amplitude ratios. Our experiments confirm the theoretical prediction that both amplitude ratios should vary linearly with $(\nabla T)^2/q^4$. The slopes of the lines in Figs. 3(a) and 3(b) yield respectively $BP = (5.8 \pm 0.4) \times 10^9$ K⁻² cm⁻² and $B = (0.81 \pm 0.08) \times 10^9$ K⁻² cm⁻². The ratio $P = 7.2 \pm 1.2$ is in excellent agreement with the known value 7.12 for the Prandtl number of toluene.

The only aspect of the theory not yet confirmed by our

experiments is the magnitude of the amplitude *B*. From the known thermophysical properties of toluene we calculate $B = 1.5 \times 10^9$ K⁻² cm⁻² which is larger than our



FIG. 3. Amplitude ratios for the (a) thermal and (b) viscous modifications to the Rayleigh line. Crosses, q = 2360 cm⁻¹; solid squares, q = 1960 cm⁻¹; open squares, q = 1470 cm⁻¹. The horizontal error bars indicate the $\pm 8\%$ error in q^4 . Solid line is the best fit to the data.

experimental value of 0.8×10^9 K⁻² cm⁻². We suspect that the discrepancy is due to inhomogeneities in the temperature gradient between the hot and cold plates which turned out to be larger than originally expected. The temperature distribution, which could only be accurately measured at the hot and cold plates, was modeled to estimate ∇T at the location of the scattering volume; however, any discontinuities in the temperature profile at boundaries could not be modeled. As a consequence we have insufficient information on the absolute magnitude of the temperature gradient and can only assert the proportionality with $(\nabla T)^2$. We plan to pursue this issue by developing an improved cell design for which the temperature distribution can be measured more accurately.

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