Thermal Fluctuations in a Layer of Liquid CS_2 Subjected to Temperature Gradients with and without the Influence of Gravity

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We report data for nonequilibrium density fluctuations in a layer of liquid CS_2 subjected to temperature gradients on Earth and in a satellite. The structure factor $S(q)$ was measured using a calibrated shadowgraph. Upon removing gravity, $S(q)$ increased dramatically at small wave vector, until the fluctuations generated by thermal noise were limited only by the 3 mm sample thickness. The results agree with theory to within a few percent on Earth and are $\sim$14% below theory in microgravity, demonstrating that the use of equilibrium Langevin forces is appropriate in this nonequilibrium situation.

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It is well known that a fluid may undergo Rayleigh-Bénard convection, but less appreciated that thermal fluctuations can be responsible for initiating convection [1]. More generally, in the absence of other perturbations, thermal noise is responsible for driving the system away from any solution that becomes unstable as parameters are varied. In fluids and mixtures, such effects can be modeled using Langevin forces in the hydrodynamic equations. One surprising prediction [2–5] is that even a fluid layer heated from above will exhibit long-ranged fluctuations, akin to those observed near critical points. Physically, the effects result from mode coupling between velocity fluctuations and temperature, and similar effects occur in mixtures [6–9]. The main predictions (see [9] and references therein) are huge increases in spatial range and mean-squared amplitude with both range and amplitude limited by gravity, but only by sample thickness in its absence, and markedly different dynamic behavior on Earth and in microgravity. Theory relies on assuming the Langevin forces are identical to those appropriate for equilibrium, an assumption susceptible to experimental test. Accurate experiments have proved difficult however, because the main effects occur at extremely small wave vector q, where normal scattering methods fail.

Here we report data for the amplitude and q dependence of density fluctuations in a fluid layer subjected to temperature gradients on Earth and during a 12-day satellite mission. The data cover the ultralow q regime where gravity is significant, and where removing it results in fluctuations of such immense spatial range as to be limited by the thickness of the sample. The measurements, made in absolute terms, show that equilibrium Langevin forces are appropriate in this nonequilibrium situation. The data also show that removing gravity enhances the static structure factor $S(q)$ by nearly the predicted factor, and alters its q dependence and the dynamic behavior as predicted [9].

Before presenting results, we summarize the current experimental situation. Light scattering was used to measure fluctuations for fluids with stabilizing temperature gradients, but only in the high-q regime where neither gravity nor sample dimension play a role. This work [10,11] confirmed that theory predicts the amplitude and shape of the correlation function accurately in this regime. Fluctuations below the onset of convection have also been measured [12], but experimental factors limit the accuracy and/or comparison with theory. For such systems, the transition to convection is made first order by the fluctuations [13], as predicted by Swift and Hohenberg [14]. Recent measurements [15] of the dynamic structure factor $S(q, \omega)$ revealed line shapes consistent with theory, but were not made in absolute terms.

The shadowgraph instrument [16] was similar to that of de Bruyn *et al.* [17]. A 75 mm diameter CS_2 sample, at 1 atm, was confined between a sapphire window and a silicon mirror 3.00 mm apart. The window was coated with transparent conducting indium tin oxide (ITO) on the surface contacting the fluid, which was used to generate heat. Heat was removed from the mirror by 4 Peltier elements. The ITO and Peltier currents were controlled to impose gradients and hold the mean temperature at 30 °C. Light from a superluminous diode ($\lambda = 680$ nm) diverged from a monomode fiber, passed through a beam splitter and a lens. It was collimated into a diffraction-limited beam, passed through the sample and was reflected by the mirror. The beam splitter diverted 50% of the return beam to a 1024 by 1024 CCD sensor, which recorded images at an effective distance $z = 310$ cm from the sample. Dividing images, pixel by pixel, revealed the fractional intensity variation $\delta I(x, y, t)$ caused by interference between the beam and light scattered by the fluctuations. Fourier transformation of the central 512 by 512 portion of ratio images separated the fluctuations by wave vector. By taking images sufficiently rapidly [15], we could measure both $S(q)$, and $S(q, \omega)$.

The quantities we measure [$S(q)$ and $S(q, \omega)$] correspond to averages over wave vectors $\mathbf{q}$, of the same magnitude q, while the fundamental theoretical quantities are defined [9] in terms of the density fluctuations as

$$\langle \delta\rho^*(\mathbf{q}, \omega)\delta\rho(\mathbf{q}', \omega')\rangle \equiv \rho_O m_O S(\mathbf{q}, \omega)(2\pi)^4 \delta(\omega - \omega') \times \delta(\mathbf{q} - \mathbf{q}')$$

$$\text{and} \quad S(\mathbf{q}) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} S(\mathbf{q}, \omega) d\omega.$$

Here, ρ_O and m_O are the mean density and molecular weight, respectively, $S(\mathbf{q}, \omega)$ has units of time, and $S(\mathbf{q})$ is dimensionless.

To measure $S(q)$ we used independent images to determine $s_I(q) \equiv \langle |\delta I(\mathbf{q})|^2\rangle/(8A)$, where A is the digitized area (14.85 cm^2), the angular brackets denote averaging over images and over wave vectors of the same magnitude, and the factor of 8 accounts for the double-pass instrument and the use of independent image ratios. The quantity $s_I(q)$ is related to $S(q)$ via $T(q)S(q) = \rho_O \alpha^2/(4Lm_O k_0^2 (dn/dT)^2) s_I(q)$, where $\alpha = 1.25 \times 10^{-3}\ K^{-1}$ is the thermal expansion coefficient, k_0 the vacuum wave vector of the light, L the sample thickness, and $dn/dT = 7.996 \times 10^{-4}\ \mathrm{K}^{-1}$ is the temperature derivative of the refractive index [18], corrected for wavelength [19]. $T(q)$ is the shadowgraph transfer function which we measured as discussed below. To determine $S(q, \omega)$ we used frame rates from 0.5 to 30 Hz, and averaged blocks of 256 images to obtain average images, that were in turn divided pixel by pixel into the 256 images to obtain $\delta I(x, y, t)$. Spatial and temporal Fourier transformation yielded the quantity $s_I(q, \omega) \equiv \langle |\delta I(q, \omega)|^2\rangle/(2\pi A T)$, which is directly proportional to $T(q)S(q, \omega)$.

We determined $T(q)$ using 2-micron diameter polystyrene spheres suspended in isopropyl alcohol, which provided strong q-independent scattering at low q. To mix the suspension, the instrument was run with the mirror and window surfaces vertical, and a 4.5 K/cm gradient applied to cause convection. Uncorrelated images were used to compute $s_I(q)$, and $s_I(q)$ measured for pure alcohol was subtracted as a background. We characterized $s_I(q)$ for the spheres as the product of the decaying oscillatory envelope $WP(q, \varphi) = \langle [\sin^2(\mathbf{q}^2 z/(2k_0) + \varphi)P^2(\mathbf{q})] \otimes W^2(\mathbf{q})\rangle$ that results from windowing and averaging over pixels, and the square of a function $M(q)$, which decreased monotonically with q. Here $\otimes$ denotes two-dimensional convolution, $P(\mathbf{q}) = \mathrm{sinc}(q_x p/2)\mathrm{sinc}(q_y p/2)$, where p is the pixel size, and $W(\mathbf{q}) = (W/2\pi)\mathrm{sinc}(q_x W/2)\mathrm{sinc}(q_y W/2)$, where W is the side length of the digitized area. Having determined $M(q)$ by fitting the data for spheres, we deduced the transfer function $T(q) = M^2(q)WP(q, \varphi = 0)$ appropriate for fluctuations, the scattering from which has a different phase shift ($\varphi = 0$), than does that from the spheres [20]. Over the q range for which we report data, $M(q)$ decreased by about 20%.

After the flight, data were taken on Earth with stabilizing gradients from 4.5 to 101 K/cm. Images taken at 0.4 Hz were analyzed to provide $T(q)S(q)$, and the results for 17.9 K/cm are shown in Fig. 1. The solid line is the product of $T(q)$ and $S(q)$ calculated using a one-mode Galerkin approximation [21]. No parameters have been adjusted, but a small baseline equal to the average of the data at very high q was subtracted, to allow for error in background subtraction. Obviously theory does a remarkable job, being only 2% above the data for the major peaks. The Galerkin model is known [9] to yield results ~20% too small in the high-q regime where $S(q) \propto q^{-4}$, and indeed the data exceed the theory in that region, as they did for all data sets. For quantitative comparison, we fit the theory to the data, adjusting only an overall scale factor, and obtained scale factors of 1.07, 0.97, 0.98, 0.94, 0.97, 0.98, and 1.00, for gradients of 4.5, 7.9, 17.9, 34.5, 51.2, 67.9, and 101 K/cm, respectively. The predictions for $S(q)$ thus appear to be accurate to within a few percent on Earth.

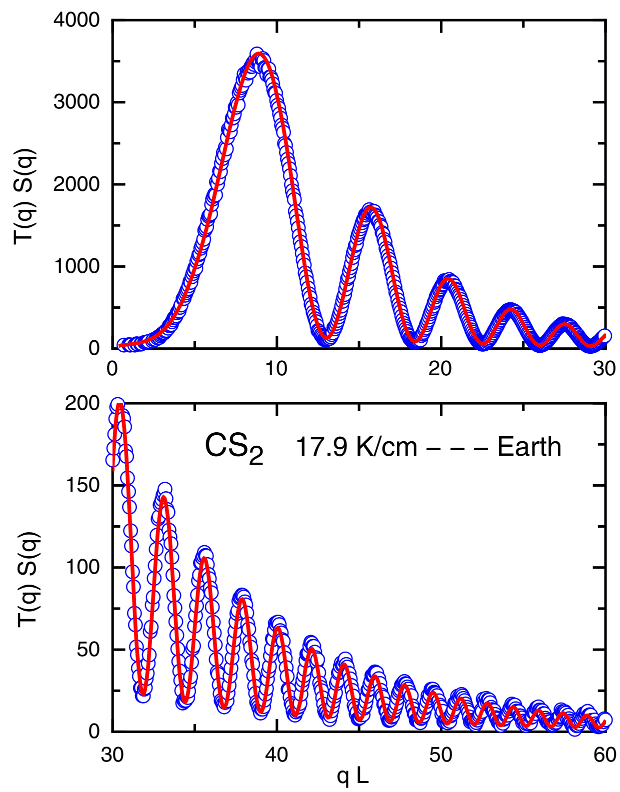

FIG. 1 (color online). Data (circles) and theory (line) for $T(q)S(q)$ in absolute (dimensionless) units for fluctuations in a 3.00 mm thick layer of CS_2, on Earth, vs the dimensionless wave vector qL, with a stabilizing gradient of 17.9 K/cm.

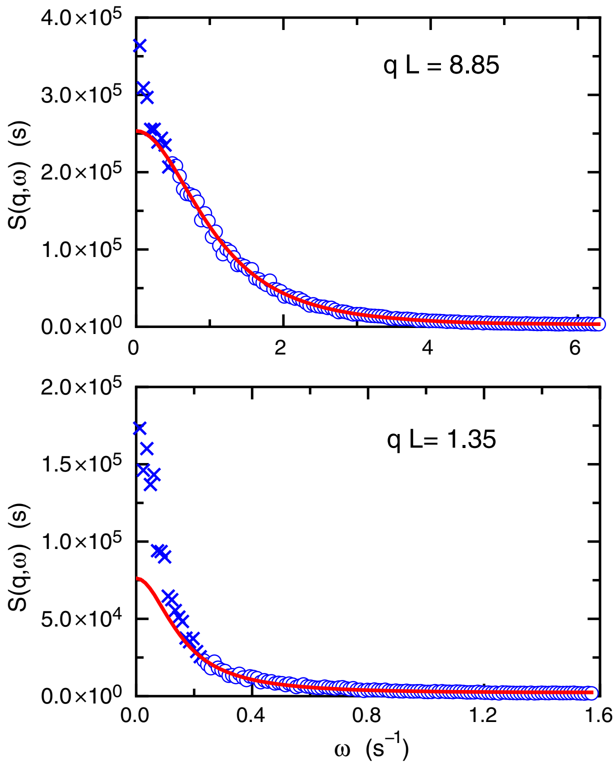

FIG. 2 (color online). Fits of theory to dynamic data taken in microgravity with a gradient of 101 K/cm. The data for the upper panel were taken at 2 Hz, while a frame rate of 0.5 Hz was used for the lower one. Points shown as crosses were excluded from the fits.

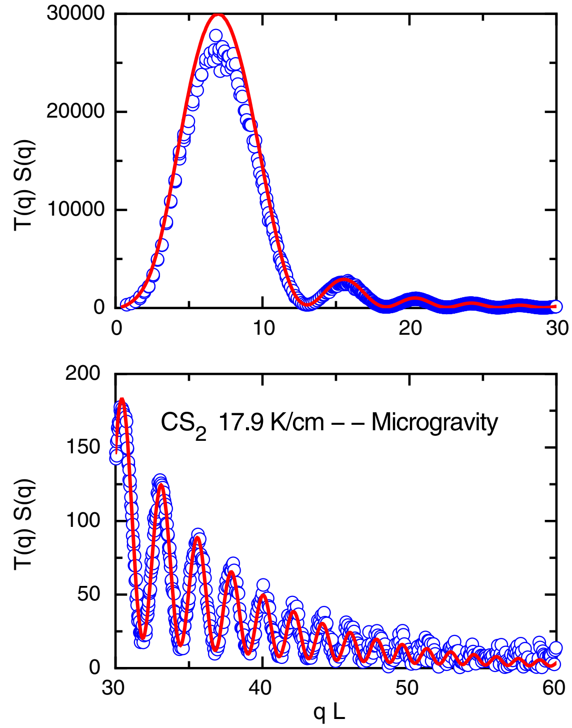

FIG. 3 (color online). Data (circles) and theory (line) for $T(q)S(q)$ in absolute terms for a 3.00 mm thick layer of CS_2, subjected to a 17.9 K/cm gradient in microgravity, vs the dimensionless wave vector qL. Comparison with Fig. 1 shows the striking effect of removing gravity.

The instrument behaved somewhat unexpectedly in flight. With a gradient, some image distortion occurred in the outer regions of the sample, and changed slightly over hours. We suspect this was due to small lateral temperature gradients. However, the data-taking region suffered distortion only at the insignificant level of $\pm 0.15\%$. We also observed several small bright spots that appeared within seconds of passing current through the ITO. These spots indicate light being focused, such as would occur if they were caused by small regions slightly colder than the surrounding fluid. Neither effect occurred on Earth before or after flight. However, in space, the results for $s_I(q)$ depended on which portion of the images we used, and on the data run. The nature of the problem became evident when we measured the temporal power spectrum, $s_I(q, \omega)$. For $q > 30\ \mathrm{cm}^{-1}$, theory described $s_I(q, \omega)$ well, however, for $q < 30\ \mathrm{cm}^{-1}$, the higher frequency portion agreed with theory, but additional power was obvious at lower frequencies, and became increasingly significant at smaller q. By fitting the higher frequency data, adjusting the amplitude of the theory and a small additive background, we separated the fluctuations from the noise. We numerically integrated the fitted spectrum to deduce $T(q)S(q)$. This treatment was not necessary for ground-based data, which showed no such noise. Typical fits of $s_I(q, \omega)$ in the range where the noise was significant are shown in Fig. 2, with the points being fitted shown as open circles, and points being excluded as crosses. Note that the theory fits the data well at higher frequencies and that the noise at lower frequencies is very evident. Judging from the fits to the portion of the data shown as circles and to all of the data for $q > 30\ \mathrm{cm}^{-1}$, the spectral shape is well described by the theory, which also does well with the more complicated line shapes observed on Earth [15]. Despite this method of analysis, the unknown noise severely limited the accuracy with which we were able to measure $S(q)$ at low q.

Results for $S(q)$ measured during flight agreed well, but not perfectly, with theory, and data and theory (with no adjusted parameters) for a gradient of 17.9 K/cm are shown in Fig. 3. Comparison with Fig. 1 shows the amplitude has increased by $\sim 8X$, and the first peak has moved to smaller q. This shift occurs because in the absence of gravity, $S(q)$ continues to diverge as $q \rightarrow 0$ until limited by sample thickness rather than being quenched by gravity. The theory is about 14% larger than the signal for the lower peaks, where the signal is most robust. Fitting the theory to the data, adjusting only an overall scale factor, resulted in scale factors of 0.85, 0.83, 0.88, 0.90, 0.90, 0.91, and 0.89 for applied temperature gradients of 4.5, 7.9, 17.9, 34.5, 51.2, 67.9, and 101 K/cm, respectively. On average, these fits indicate that the theory is about 14% larger than the

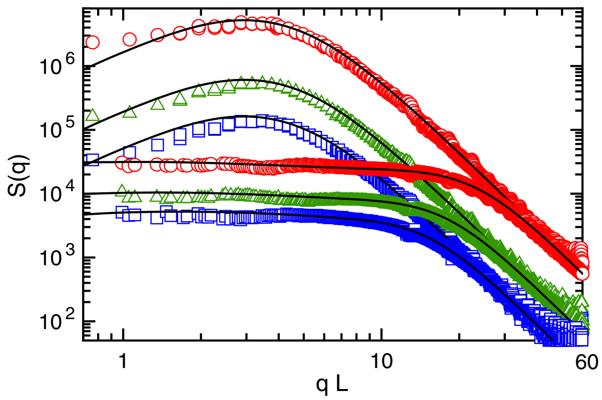

FIG. 4 (color online). Log-log plots of experimental results for $S(q)$ vs qL, with applied gradients of 17.9 (squares), 34.5 (triangles), and 101 (circles) K/cm, in microgravity (upper curves) and on Earth. The lines are the theoretical predictions.

data in the absence of gravity. Given the presence of an unknown noise source, we cannot say this is serious. The fits result in essentially perfect agreement with the data for values of qL below about 20 (where the unscaled theory is clearly high), and fall progressively below the data for larger q, as expected for the Galerkin model.

To display the overall behavior we divided the data by $T(q)$ to obtain $S(q)$ for gradients of 17.9, 34.5, and 101 K/cm, as shown in Fig. 4. The upper curves and data correspond to flight and the lower to ground-based data. The curves are the theoretical results with no adjustable parameters. The most obvious effects that result from removing gravity are the immense increase in $S(q)$ ($\sim 180X$ for the largest gradient) and the replacement of a wide plateau region by a maximum. This maximum, located very near $qL = \pi$, corresponding to fluctuations of wavelength 6 mm, is the evidence that the thermally generated density fluctuations have become sensitive to the 3 mm sample thickness, a rather extraordinary situation.

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