q Divergence of Nonequilibrium Fluctuations and Its Gravity-Induced Frustration in a Temperature Stressed Liquid Mixture

Alberto Vailati and Marzio Giglio

Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Milano, via Celoria 16, Milano 20133, Italy

(Received 29 December 1995; revised manuscript received 31 May 1996)

We present the first direct measurements of the scattered intensity from a nonequilibrium, temperature stressed liquid mixture (heating from above). The data have been obtained with an unconventional very low angle light scattering instrument. While at larger q the intensity diverges with a q^{-4} power law, we show for the first time that at smaller q the divergence is frustrated by gravity-induced effects. In spite of this, a staggering increase of more than 5 orders of magnitude above equilibrium scattering is reported. [S0031-9007(96)00848-4]

PACS numbers: 47.20.Bp, 05.40.+j, 05.70.Ln, 78.35.+c

Equilibrium fluctuations of thermodynamic quantities have been investigated for more than a century, the most classical tools to determine both their rms amplitude and the excitation spectrum being scattering methods, and light scattering in particular.

Spontaneous nonequilibrium (NE) fluctuations have been investigated experimentally only much more recently. The reason for such a delay is the weakness of the NE contributions, unless one moves to hardly accessible, unusually small scattering angles, since the theory predicts that the scattered intensity from NE fluctuation should exhibit an impressive q^{-4} divergence [1,2]. The first accurate and very meticulous data on spontaneous NE fluctuations in temperature stressed pure liquids and binary liquid mixtures were obtained by the Sengers group [3–7]. The technique used was dynamic (heterodyning) light scattering, and from these data the NE contribution to the scattered intensity was derived. While the results of Sengers *et al.* are unambiguous, the data are over a fairly limited range of q vectors (less than a factor of 2).

In this Letter we present some extremely low angle light scattering data obtained with an unconventional scattering machine covering almost two decades in q vectors. The sample is a thin ($d = 0.98$ mm), horizontal layer of an anyline-cyclohexane mixture at the critical concentration, the temperature gradient being applied across it (heating was from above, the stable configuration where there are no convective instabilities). The temperature of both plates is above the critical temperature T_c, so the mixture is in a one phase state. Because of the wide range of scattering angles, we present for the first time the full q dependence of the NE fluctuations. At large q the impressive q^{-4} divergence is observed. The main emphasis of this Letter, however, is on the observation of the gravity-induced quench of the divergence at extremely small q, an effect predicted by the theory [8,9] and never observed before.

Loosely speaking, the anomalously large fluctuations in a NE system are brought about because, due to the order parameter gradients induced by an applied field, the velocity fluctuations are not anymore as innocuous as in thermodynamic equilibrium. They can indeed produce spatial irregularities by displacing sample parcels along the order parameter gradient. A typical example is a layer of fluid stressed by a temperature gradient. For pure fluids the situation is simpler, since the applied temperature gradient creates a density gradient. For mixtures, an additional effect arises because of the Soret effect, and a concentration gradient is also formed as a consequence of the temperature gradient. Since both density and concentration fluctuations cause refractive index fluctuations, light scattering is an ideal tool for these studies.

The layout of the low angle light scattering machine has already been described [10]. The most important component is a solid state monolithic photodiode sensor array. Each sensor is annular in shape, and the optics feeds to each sensor the light scattered at an angle proportional to the sensor average radius. The 31 sensors have radii scaled logarithmically so as to cover two decades in scattering wave vectors. The actual setup used here is a modified version that covers two decades in q vectors, but has a builtin flexibility to position this range between $q =$ 20 and $50\,000$ cm^{-1}. As we shall see the full use of the machine down to the smallest angles proved to be unnecessary.

The last portion of the instrument was rigged vertically, so as to position the thin layer scattering cell horizontally. The cell design is very critical. The temperature gradient is vertical, and the main scattering beam is also vertical. In this way the scattering wave vector is orthogonal to the gradient, and this is the case contemplated by the theory [8,9].

Sapphire has been chosen for the upper and lower windows, because of its reasonably good thermal conductivity. A crude sketch of the cell is shown in Fig. 1. The temperature of the sapphire plates is controlled via two annular peltier elements sandwiched between each plate and a temperature reservoir controlled by a circulating temperature bath. The inner diameter of the annular peltier

 0031-9007/96/77(8)/1484(4)$10.00 © 1996 The American Physical Society

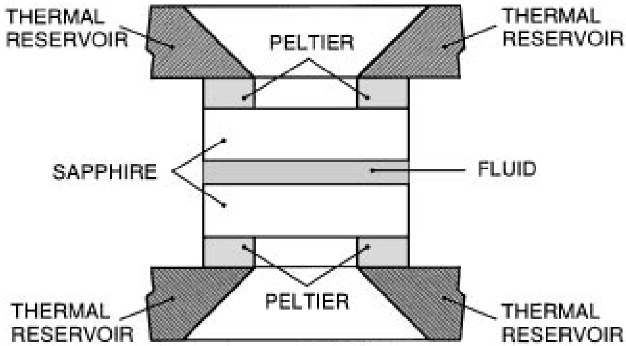

FIG. 1. Sketch of the scattering cell (side view). The main beam (not shown) is vertical. The drawing is out of scale.

elements is 27 mm, and this sets the clear aperture of the stressed sample.

The choice of the liquid mixture is also very peculiar. In order to make the NE fluctuations as large as possible, we searched for a mixture with a large Soret effect. Let us briefly recall that this off-diagonal effect produces at steady state a concentration gradient ∇c as the result of an applied temperature gradient ∇T:

$$\nabla c = -\frac{k_T}{T}\nabla T = -S_T c(c - 1)\nabla T, \qquad (1)$$

where k_T is the thermal diffusion ratio, S_T the Soret coefficient, c the mass concentration of the heavier component, and T the average sample temperature. Usually the effect is that the denser component migrates to the cold plate. It is known [11] that k_T diverges at a critical consolation point, $k_T =$ const $\times (T - T_c)^{-\varphi}$, with $\varphi = 0.73$. It should be mentioned that this divergence exactly balances the vanishing of the mass diffusion coefficient D, and therefore $k_T D =$ const. As we will show later, if one considers the expressions for the scattered intensity from NE fluctuations [see Eq. (3)] and takes into account the above indicated divergences, one easily realizes that although it is profitable to exploit the generally large Soret effect of critical fluids, there is no advantage in going very close to T_c, since necessarily $\Delta T = T_1 - T_2$ (T_1 and T_2 are the upper and lower temperatures, respectively) has to be smaller than $T - T_c$, and the benefit of a large k_T is countered by the small ∇T applicable. The best compromise was found operating at $T_{\rm ave} = (T_1 + T_2)/2$ roughly 10 K away from T_c. Attempts have been done with increasing values of ΔT, and reasonably good data could be obtained by applying a rather severe value. We settled for $\Delta T = 16$ K. Of course such a large value makes the concentration gradient nonuniform, but this is the price to pay to make the effect visible at all.

The data have been collected according to the following procedure. The cell was brought under isothermal conditions at $T_{\rm ave} - T_c \sim 10$ K, and then blank stray light contributions were measured. The gradient was then applied, and we waited for the system to reach stationary conditions. Blank measurements were properly subtracted from the raw data, and a typical set of data is shown in Fig. 2. No transient measurements were attempted because the time constant $\tau_{\rm th}$ that characterize the thermal time constant of the cell was fully comparable with the diffusion time constant $\tau_{\rm diff} = d^2/\pi^2 D$. The plot is on a log-log scale, and one can notice the strong q^{-4} divergence at larger q vectors and a roll-off, the data leveling at a constant value at small q. We point out that the position of the roll-off $q_{\rm ro} = 537$ cm^{-1} corresponds to excitations with a wavelength $\Lambda = 2\pi/q_{\rm ro} = 0.012$ cm, quite a macroscopic size.

We will start by comparing the position of the roll-off in the data with the theoretical predictions. The effect of gravity has been explicitly considered for the case of pure fluids [8], but the results can be easily duplicated for binary mixtures near a critical point, where the relevant variable is the concentration c. As customary, one introduces a q dependent Rayleigh number ratio $R(q)/R_c$,

$$\frac{R(q)}{R_c} = -\frac{\beta k_T \mathbf{g} \cdot \nabla T}{\nu D T q^4}, \qquad (2)$$

where R_c is the appropriate threshold value for the onset of the convective instability when heating from below [12]. Also, $\beta = \rho^{-1}(\partial\rho/\partial c)_{p,T}$, D is the diffusion coefficient, and ν is the kinematic viscosity, g being the gravity acceleration. Notice that by heating from above $R(q)/R_c$ is negative. The contribution to the scattered intensity distribution due to the nonequilibrium fluctuations is given by [7]

$$I(q) \propto \frac{A_c^*}{1 - R(q)/R_c}\frac{\nabla T^2}{q^4}, \qquad (3)$$

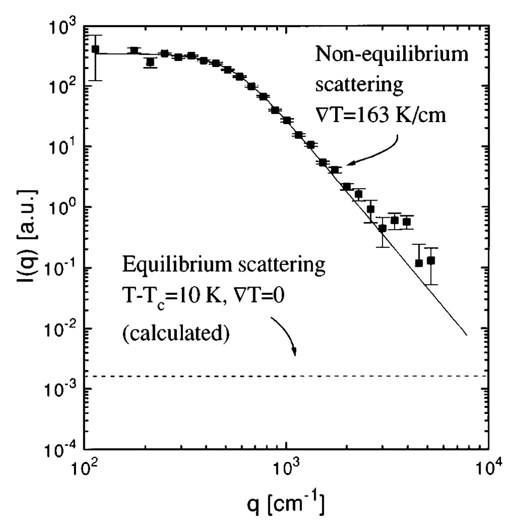

FIG. 2. Plot of the scattered intensity $I(q)$ vs scattering wave vector q. The solid line through the data is a best fit of the nonequilibrium data with Eq. (3). Roll-off position is at $q_{\rm ro} = 537$ cm^{-1}. The corresponding excitations are at $\Lambda = 2\pi/q_{\rm ro} = 0.012$ cm. The applied temperature gradient is 163 K/cm. The dashed line is the equilibrium scattered intensity calculated from reference data (see text).

where $A_c^* = (\partial\mu/\partial c)_{p,T} k_T^2/\nu D T^2$ is the sample dependent quantity that controls the amplitude of nonequilibrium scattering contributions. The term $1 - R(q)/R_c$ describing the gravity-induced quench has been introduced in analogy to the formula for pure fluids. Also, some simplifications apply close to a consolute critical point, and the expression becomes considerably simpler than for the ordinary liquid mixtures [7].

Notice that when $|R(q)/R_c| \ll 1$ Eq. (3) accounts for the classical $\nabla c^2/q^4$ dependence of NE fluctuations and for $R(q)/R_c \ll -1$, the scattered intensity becomes independent of q, and it scales with ∇c. Also, if one works out the algebra of the various divergences, one finds that there is no advantage in acquiring data close to the critical point, as discussed previously.

The roll-off occurs at $R(q_{\mathrm{ro}})/R_c = -1$, and let us compare the experimental value of q_{ro} with the theoretical predictions. All the quantities entering into Eq. (2) can be derived from the literature [11,13]. We find that the fitting of the data gives $q_{\mathrm{ro}} = 537\ \mathrm{cm}^{-1}$, while the theoretical value is $410\ \mathrm{cm}^{-1}$. The agreement is more than satisfactory, since, as discussed above, both temperature and concentration vary in the cell, and the above estimate based on Eq. (2) has been determined for the average value in the cell. It should be pointed out, however, that due to $\frac{1}{4}$ power law dependence of q_{ro} on the sample parameters and temperature gradient, the numerical estimate is very insensitive to possible variations of the thermodynamic variables. As an example, the overall variation of the parameters along the entire temperature range, and assuming for simplicity a quasicritical isochore path, would lead to a variation of q_{ro} of less than a factor of 2.

We will now compare the intensity of the nonequilibrium scattered light with the theoretical predictions.

We have to stress that the signal to noise ratio gets poor at both the extremes of the range. At large q the noise is due to the precipitous decrease of $I(q)$, while at small q it is due to the small solid angle of collection of the inner scattering channels. This is a typical difficulty with all the very low angle static light scattering schemes. As a consequence of the limitations due to stray light, we have been unable to assess the scattering from an equilibrium, isothermal sample at the average temperature. Since the comparison between the data at equilibrium and the NE data is very interesting because it permits a direct comparison of the data with the theory, we have attempted to remedy this difficulty in the following way.

The instrument has been calibrated by obtaining a light scattering curve from a reference sample. This was a cellulose filter membrane immersed in quasi-index-matching fluid [14]. The large q decay follows a strong power law, and virtually all the scattered power is collected by the sensor. The beam attenuation is of the order of 37% and could therefore be reliably determined. We are then in the position to calibrate the scattered intensity scale of the instrument, since the integrated scattered power must equal the beam power loss (the choice of the index matched filter as a sample is accidental). What one needs is the scattered intensity profile and the beam attenuation. The shape of the intensity distribution is irrelevant, provided (almost) all the scattered power gets collected by the sensor). This allows us to calculate and draw on the same plot the intensity distribution of the light scattered from an isothermal critical fluid at the average temperature $T - T_c = 10$ K and the distribution when the temperature gradient is applied.

The procedure is as follows. The scattered intensity from an equilibrium critical fluid is described by the Fisher-Burford function $I(q) = B/[1 + (q\xi)^2]$, where B is a constant and ξ is the long range correlation function [15]. We get the reference value at $T - T_c = 10$ K [16] $\xi = 1.9 \times 10^{-7}$ cm. We then adjust the constant B so that the integrated scattered intensity is consistent with the reference [16] value for the turbidity $\mu = 3.4 \times 10^{-3}\ \mathrm{cm}^{-1}$. In other words, by integrating the equilibrium scattering curve we calculated, we float B until the beam attenuation is quantitatively the one calculated from reference data. We estimate that the uncertainty in locating this curve is less than 20%, and this is more than adequate for the analysis here.

The equilibrium scattering curve is displayed in Fig. 2 with the dashed line together with the nonequilibrium data. One can immediately appreciate the staggering change in the scattering intensity levels at low wave vectors between equilibrium and nonequilibrium conditions. As it can be noticed, the equilibrium intensity distribution is constant, since $1/\xi = 5 \times 10^6\ \mathrm{cm}^{-1}$ is well outside the instrumental range.

We can compare the relative position of the two curves in Fig. 2 with the theoretical predictions. This comparison is rather difficult, since both temperature and concentration change as a function of height, and all the relevant parameters depend on these variables. For simplicity we will assume that all the parameters retain their value at the average temperature and at the critical concentration.

Again, using reference values in the expression for the constant A_c^*, we find $A_c^* = 1.5 \times 10^{11}\ \mathrm{K}^{-2}\,\mathrm{cm}^{-2}$, to be compared with the value $A_c^* = 7.2 \times 10^{11}\ \mathrm{K}^{-2}\,\mathrm{cm}^{-2}$ extracted from the data in Fig. 2. The agreement is within an order of 5, which can be considered as very satisfactory. An accurate calculation would be very difficult. We point out here that there are two opposing effects to be considered. The layers closer to T_c should exhibit a rather strong increase of the Soret driven concentration gradient and hence in the scattered intensity (most of the NE scattered light would come from the layers close to the colder plate, the nearest to the critical temperature). On the contrary, in reality, the concentration also changes away from critical, and this counteracts the changes that one would guess should be concentration be critical everywhere.

In concluding, we point out some strong ties with a germane subject, that is buoyancy driven instabilities. The roll-off in this experiment is due to the fact that by heating from above gravity actually discourages long wavelength fluctuations. When heating from below $[R(q)/R_c > 0]$ gravity actually encourages fluctuations that appear to diverge at threshold [see Eq. (2)]. In a recent beautiful experiment by Wu, Ahlers, and Cannell [17] a shadowgraph technique has been used to visualize and measure the nonequilibrium fluctuations in a thin (0.468 mm) layer of fluid heated from below. In that case pretransitional fluctuations get greatly enhanced around the wave vector of the instability platform. The data do show the divergence of the fluctuations as the threshold is approached. In the present experiment the opposite occurs and the fluctuations are quenched. It is interesting to notice that low angle light scattering has been pushed in this experiment to such long wavelength fluctuations that it can almost cover length scales that are more traditionally covered by phase sensitive techniques such as shadowgraph and schlieren.

We acknowledge early discussions on this topic with Phil Segrè and Jan Sengers. We thank M. Carpineti and L. Cipelletti for some help with the scattering machine, and L. Cipelletti again for the thermal simulation of the scattering cell. Financial support from the Italian Ministry of the University and Research (MURST) as well from the Italian Space Agency (ASI).

[1] T. R. Kirkpatrick, E. G. D. Cohen, and J. R. Dorfman, Phys. Rev. A **26**, 995 (1982).
[2] D. Ronis and I. Procaccia, Phys. Rev. A **26**, 1812 (1982).
[3] B. M. Law, R. W. Gammon, and J. V. Sengers, Phys. Rev. Lett. **60**, 1554 (1988).
[4] B. M. Law, P. N. Segrè, R. W. Gammon, and J. V. Sengers, Phys. Rev. A **41**, 816 (1990).
[5] P. N. Segrè, R. W. Gammon, J. V. Sengers, and B. M. Law, Phys. Rev. A **45**, 714 (1992).
[6] P. N. Segrè, R. W. Gammon, and J. V. Sengers, Phys. Rev. E **47**, 1026 (1993).
[7] W. B. Li, P. N. Segrè, R. W. Gammon, and J. V. Sengers, Physica (Amsterdam) **204A**, 399 (1994).
[8] P. N. Segrè, R. Schmitz, and J. V. Sengers, Physica (Amsterdam) **195A**, 31 (1993).
[9] P. N. Segrè and J. V. Sengers, Physica (Amsterdam) **198A**, 46 (1993).
[10] M. Carpineti, F. Ferri, M. Giglio, E. Paganini, and U. Perini, Phys. Rev. A **42**, 7347 (1990).
[11] M. Giglio and A. Vendramini, Phys. Rev. Lett. **34**, 561 (1975).
[12] M. G. Verlarde and R. S. Schechler, Phys. Fluids **15**, 1707 (1972).
[13] G. Arcovito, C. Faloci, M. Roberti, and L. Mistura, Phys. Rev. Lett. **22**, 1040 (1969).
[14] L. Cipelletti, M. Carpineti, and M. Giglio, Physica (Amsterdam) (to be published).
[15] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971).
[16] P. Calmettes, I. Lagues, and C. Laj, Phys. Rev. Lett. **28**, 478 (1972).
[17] M. Wu, G. Ahlers, and D. S. Cannell, Phys. Rev. Lett. **75**, 1743 (1995).