Light-Scattering Study of a Critical Mixture with Shear Flow

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We report the first light-scattering study of a critical mixture (aniline-cyclohexane) under shear flow S which affects critical fluctuations with relaxation time τ only in the region $S\tau > 1$. All anomalies can be expressed as a function of $S\tau$ only and can be interpreted by a lowering of the critical temperature $\Delta T_0(S) = T_1 S^{1/3\nu}$, where T_1 is a constant. In addition the scattered light is found to exhibit a noticeable anisotropy with respect to the flow direction.

Critical phenomena at equilibrium have been extensively studied.[1] Close to a critical point, the fluctuations of the order parameter strongly increase, leading to the divergence of the susceptibility χ and the correlation length ξ, and the time decay τ of the fluctuations goes to zero. If T is the absolute temperature, T_c the critical temperature, and $\epsilon = (T - T_c)/T_c$, $\chi = \chi_0 \epsilon^{-\gamma}$, and $\xi = \xi_0 \epsilon^{-\nu}$, then χ_0 and ξ_0 depend on the system, and γ and ν are universal constants which depend on the spatial dimensionality d and the number n of components of the order parameter. For binary fluids, the order parameter is the difference between the concentration and its critical value $c - c_c$; the susceptibility is $\chi = (\partial c/\partial \mu)_{P,T}$ where μ is the difference between the chemical potentials $\mu = \mu_1 - \mu_2$ of the components and P is the pressure. With $d = 3$ and $n = 1$, $\gamma \simeq 1.24$ and $\nu \simeq 0.63 \simeq \frac{1}{2}\gamma$. Light-scattering techniques[2] have proved to be very useful for studying the above quantities.

Until now no studies have been reported concerning critical fluctuations out of equilibrium. We report here the first measurements concerning concentration fluctuations in a critical mixture under shear flow using light-scattering techniques.

Refer to Fig. 1(a). The binary mixture used was the cyclohexane-aniline system. Aniline was purified by distillation; cyclohexane was of spectroscopic grade. The experimental mass fraction of aniline $c = 0.4700 \pm 4\times10^{-4}$ was close to the critical composition (47% in weight).[3] The mixture was frozen in a glass cell described below, which was sealed under vacuum. The shear flow is produced in a rectangular quartz pipe c whose dimensions in Cartesian axes $Oxyz$ are $L_x = L = 15$ cm, $a_y = a = 0.3$ cm, $b_z = b = 0.5$ cm. This pipe C is set horizontal and, during the run, the liquid flowed along the x axis through C from a graduated cylindrical reservoir A (with a maximum fluid-height difference $H_0 = 7.0$ cm) into another reservoir B. At the end of the run, some liquid remained in C so that all experiments performed with or without shear could be directly compared under exactly the same geometrical and temperature conditions. The cell was fixed on a wheel which could rotate enabling the vessel A to be refilled. A mechanical locking system ensured that the capillary returned to the same position for each run. A pipe with a valve served to refill A while an extra pipe served to equalize the pressures when flow took place from A to B or from B to A.

The whole apparatus was immersed in a water bath where it could be seen through a double window. The thermal stabilization was $\pm 2\times10^{-4}$ °C over more than one hour, as verified by a quartz thermometer. A laser beam ($\lambda_0 = 6328$ Å, cross-sectional diameter $\Phi_0 = 0.35$ mm) directed parallel to the horizontal z axis enters the pipe at $x = 0$, $y = y_0 = 0.1$ cm, $z = 0.25$ cm, as verified by a cathetometer. A lens centered on the beam images the scattering volume on the photomultiplier pin hole. The lens supports an off-center pin hole, so providing a choice of scattering angle $\theta = (\vec{K}_D, \vec{K}_0)$, where $\vec{K}_0$ is the incident-light wave vector (Oz) and $\vec{K}_D$ is the scattering wave vector. When rotating the pin hole around the laser beam, θ or $|\vec{q}| = |\vec{K}_D - \vec{K}_0|$ remains constant while the azimuthal angle $\varphi = (\vec{q}, \vec{V})$ varies [see Fig. 1(a)]. Here $\vec{V}$ is the flow velocity vector, parallel to Ox. We experimentally checked that, for small scattering angles as considered, the (vertical) polarization of the laser beam does not modify the scattered intensity distribution which remains isotropic in the x-y plane.

In order to determine the velocity V, we used three methods: a calculation using a Poiseuille velocity distribution, the time variation of the liquid volume in A, and a laser Doppler velocimetry determination. All the measured and calculated

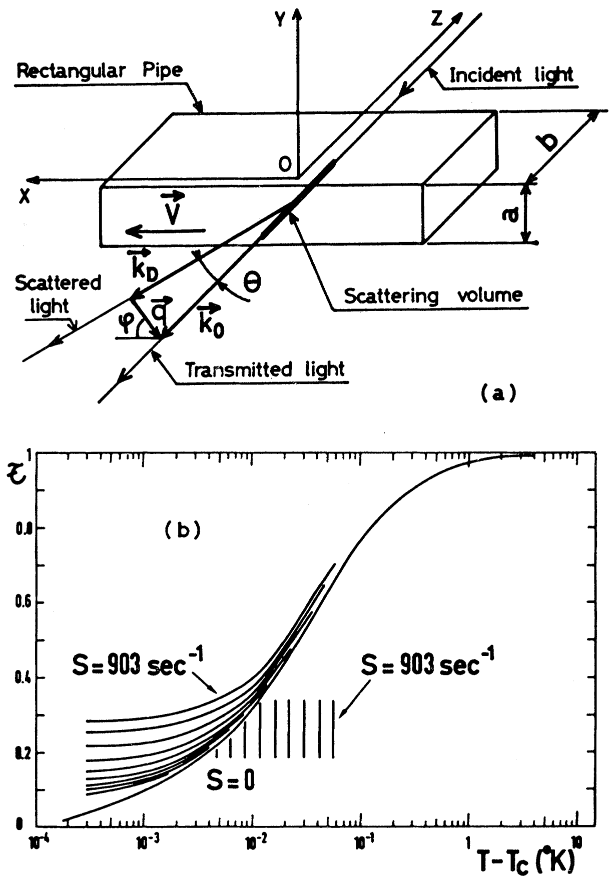

FIG. 1. (a) Scattering geometry. O is the center of symmetry of the pipe. (b) Transmitted intensity vs $T - T_c$ at decreasing shear rates S=903, 510, 288, 163, 92, 52, 29, 16, 9.5, and 0 $\sec^{-1}$. Vertical lines correspond to the crossover temperature where $S\tau = 1$.

values agree with each other, giving the following time variation: $V(t) = V_0 \exp(-t/t_0)$ with $V_0 = 93$ cm $\sec^{-1}$ and $t_0 = 13.1$ sec. We infer the Reynolds number $\mathcal{R}(t) = V(t)a/\nu_0$, where $\nu_0 = 1.93 \times 10^{-2}$ S (Ref. 4) (1 stoke = 1 cm^2/sec) is the kinematic viscosity. The maximum value $\mathcal{R}(0) = 1450$ shows that turbulence is never reached. We verified that all experiments which were started at various different values of $\mathcal{R}(0)$ (i.e., various heights in A) gave equivalent results. The length l at which the parabolic velocity distribution is obtained within 1% is $l(t) = 0.03a\mathcal{R}(t) \simeq 13 \exp(-t/t_0)$ cm. At any time $t > 5$ sec the Poiseuille distribution is therefore established in the measurement region, and the velocity at the measurement point can be written

$$V(x,y,z,t) \simeq V(y,t)$$
$$= 2V_0[1-(2y/a)]\exp(-t/t_0).$$

The influence of the velocity gradient parallel to Oz has been neglected. Indeed the corresponding gradients are smaller [ratio $(b/a)^2 \simeq 3$], and are not well defined since they are integrated over all the scattering volume. Moreover, the influence of this particular velocity gradient can be suppressed when imaging only the center of the scattering volume. The shear at $y = y_0$ can therefore be deduced:

$$S(y_0 \pm \tfrac{1}{2}\Phi_0, t) = dV(y_0 \pm \tfrac{1}{2}\Phi_0, t)/dy$$
$$= (1600 \pm 280)\exp(-t/t_0).$$

The uncertainty is mainly due to the finite diameter Φ_0 of the laser beam.

The lifetime of the concentration fluctuations in the real space, i.e., at $q\xi \sim 1$ and without shear is $\tau = A(T-T_c)^{-3\nu}$ where $A = 5\pi\eta\xi_0^3 T_c^{3\nu}/k_B T_c = 4.8 \times 10^{-6}$ cgs[5,6] using the values $\xi_0 = 2.45$ Å,[7] $T_c = 303$ K, $\eta = 1.78cP_0$,[4] and k_B is the Boltzmann constant. For experimental values $T - T_c \gtrsim 1 \times 10^{-3}$ °C, then $\tau < 2.2$ sec. In these time intervals the velocity distribution varies less than a few percent in C.

A simple calculation of the extra heating due to the shear, taking into account the experimental conditions, shows the following: (i) This heating should be proportional to S, and not S^2, since a volume element is submitted to the shear during a very short time. (ii) The maximum heating corresponding to the maximum shear (903 $\sec^{-1}$) is much lower than 10^{-4} °C, and is negligible.

The contribution of the multiple scattering is also negligible because of the dimensions of the capillary. The gravitationally induced gradients would take place only after a time much longer than the experimental measuring time.

The transmission $\mathcal{T}$ of the laser beam through C, which is related to the turbidity δ by $\delta = -(1/b)L_N \mathcal{T}$, was studied as a function of $T - T_c$ and of S. When $S = 0$ we verified that our measurements agreed with those of Ref. 7 and thus accurately determined T_c. When the mixture was submitted to the shear, Fig. 1(b) shows that $\mathcal{T}$ is an increasing function of S. So the shear reduces the fluctuations of lifetime τ only when it has enough time to distort them, i.e., when $S^{-1} < \tau$. Two regions can therefore be delimited: $S\tau < 1$ where the shear has no action on critical properties and $S\tau > 1$ where the shear affects the critical fluctuations. Moreover, two striking features can be inferred: (i) A mere change in $T - T_c$ is sufficient to normalize $\mathcal{T}$, i.e., $\mathcal{T}(T - T_c, S) = \mathcal{T}(T - T_c + \Delta T_0, 0)$ where ΔT_0 is a function only of S [Fig. 2(a)]. (ii) The ratio $\mathcal{T}(T - T_c, S)/\mathcal{T}(T - T_c, 0)$

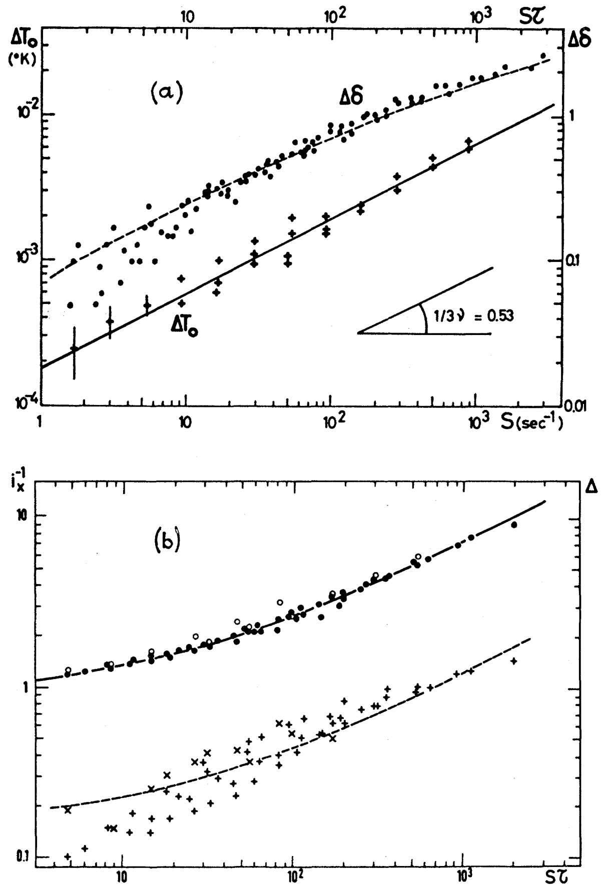

FIG. 2. (a) Lower (crosses), apparent decrease ΔT_0 of the critical temperature vs shear S, deduced from transmission measurements and compared to $T_1 S^{0.53}$. Upper (circles), turbidity change $\Delta\delta = \delta(T-T_c, 0) - \delta(T-T_c, S)$ vs the variable $S\tau$ where τ is the lifetime of fluctuations without shear. The dotted line is the calculated variation (see text). (b) Mean scattered intensity $\langle i\rangle^{-1} \simeq i_x^{-1}$ (circles) and anisotropy factor Δ (crosses) vs the reduced variable $S\tau$ at $q_1 = 1.82\times10^4$ cm^{-1} (full circles and upright crosses) and $q_2 = 2.86\times10^4$ cm^{-1} (open circles and tilted crosses). The full line represents a variation $(\xi/\xi')^2$ and the dotted line a variation $0.17(\xi/\xi')^2$ (see text).

or $\delta(T-T_c, 0) - \delta(T-T_c, S) = \Delta\delta$ shown in Fig. 2(a) is only a function of $S\tau$, as expected.[8]

In the temperature range studied $\mathcal{T} \propto (T-T_c)^{4\nu B b}$ where $B = (\pi^3/\lambda_0^4)(\partial n^2/\partial c)^2 k_B T_c \chi_0 / 2K_0 \xi_0^2$. n is the refractive index. With use of the values of Ref. 7, $B \simeq 0.62$. From (i) and (ii) we deduce that

$$\delta(T-T_c, 0) - \delta(T-T_c+\Delta T_0, 0) = 4\nu B L_N[1 + \Delta T_0/(T-T_c)]$$

is a function of $S\tau$. S and τ being independent variables, we infer $\Delta T_0(S) = T_1 S^{1/3\nu}$,[9] with T_1 a constant. Figure 2(a) shows the close agreement between this relation and the experimental data, provided that $T_1 \simeq 1.8\times10^{-4}$ cgs. $\Delta\delta$ can be evaluated from $\Delta T_0(S)$, $\Delta\delta = 1.56 L_N[1 + T_1(S\tau/A)^{1/3\nu}]$, and this formula can be compared to the data. In Fig. 2(a) the agreement is good if $T_1 \simeq 8\times10^{-5}$ cgs, which is a value of the same order of magnitude as that directly inferred from (i). We therefore have shown that the first effect of shear on critical fluctuations is to apparently change T_c by an amount $\Delta T_c = \Delta T_0 \propto S^{1/3\nu}$.

We performed most of the experiments at the light-transfer wave vector $q_1 = 1.82\times10^4$ cm^{-1} ($\theta = 7°$). Another wave vector was investigated for sake of comparison: $q_2 = 2.86\times10^4$ cm^{-1} ($\theta = 11°$). Intensity measurements $I(T, S, \varphi, \vec{q})$ were compared to the value with $S = 0$ and corrected for turbidity effects. We consider the reduced intensity

$$i(T, S, \varphi, \vec{q}) = \frac{I(T, S, \varphi, \vec{q})}{I(T, 0, \varphi, \vec{q})} \frac{\mathcal{T}(T, 0)}{\mathcal{T}(T, S)}.$$

We will write $i_{x,y}$ when $\vec{q} = q_x, q_y$. Figure 3 shows that the mean scattered intensity decreases with increasing shear as expected from the turbidity results. Moreover, a noticeable anisotropy is detected which is sharply centered at $\varphi = \pi/2$ if the finite extent of scattering angle ($\delta\varphi \simeq 10°$) is taken into account. This allows simpli-

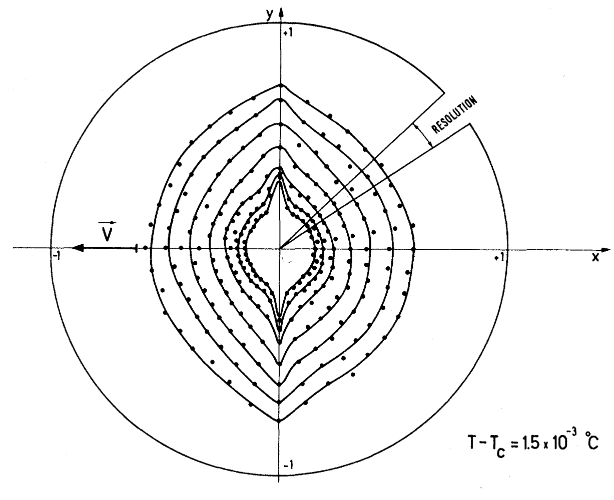

FIG. 3. Reduced intensity i (see text) in the x-y plane at constant light wave number $q_1 = 1.82\times10^4$ cm^{-1}, $T - T_c = 1.5\times10^{-3}$ °C and for decreasing shear rates $S = 903$, 510, 288, 163, 92, 52, 29, and 0 sec^{-1}. The smallest curve corresponds to $S = 903$ sec^{-1}, and the circle of radius unity to $S = 0$.

fications to be made for the mean scattered intensity at vector q: $\langle i\rangle \simeq i_x$. If we define an anisotropy factor $\Delta = i_y/i - 1$, Fig. 2(b) shows that both $\langle i\rangle$ and Δ are functions only of $S\tau$ and that they are at most weakly dependent on q. This result prevents us from comparing $\langle i\rangle$ to $(\xi'^2/\xi^2)[(1+q^2\xi^2)/(1+q^2\xi'^2)]$, where $\xi' = \xi(T')$ with $T' = T + T_1 S^{1/3\nu}$ since in the domain studied the ratio $(1+q^2\xi^2)/(1+q^2\xi'^2)$ is not a function of $S\tau$ only. So we simply tried to fit $\langle i\rangle^{-1}$ to $(\xi/\xi')^2$ and obtain

$$\langle i\rangle^{-1} \simeq i_x^{-1} \simeq \alpha^2 \frac{\xi^2}{\xi'^2} = \alpha^2\left[1+\frac{T_1}{A^{1/3\nu}}(S\tau)^{1/3\nu}\right]^{2\nu},$$

where α^2 is adjustable. The agreement is good if $\alpha^2 = 1.15$. In the same way the anisotropy factor is seen to vary roughly as $\langle i\rangle^{-1}$ so that $\Delta/\langle i\rangle \simeq \text{const} \simeq 0.17$.

The product $S\tau$ has been found to be the only relevant scale of turbidity anomalies which lie in the region $S\tau > 1$. These anomalies are well explained by a reduction of the fluctuation size corresponding to an apparent change in T_c given by $\Delta T_0 = T_1 S^{1/3\nu}$. We measured $T_1 \simeq 1.8\times10^{-4}$ cgs and $1/3\nu \simeq 0.53$ in the range $S = 2-1000$ sec^{-1}. The mean reduced scattered intensity $\langle i\rangle$ varies correspondingly with the T_c change and is almost independent of q. An anisotropy (Δ) of the scattered light was detected. Both $\langle i\rangle$ and Δ are functions of $S\tau$ only in the range $S\tau = 5-2000$.

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[9] After we have completed this study, A. Onuki and K. Kawasaki informed us that they have theoretically investigated the same problem. They reach the same general conclusions. Their estimated value $T_1 \simeq 1.3\times10^{-4}$ compares favorably with our result.

Role of Spin Fluctuations in the Superconductors Nb and V

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This paper reports investigation of the role of spin fluctuations (paramagnons) in the superconductors Nb and V. For this purpose, experimental data on specific heat and magnetic susceptibility are reanalyzed. Furthermore, the Eliashberg equations including the particle-hole t matrix are solved numerically. It is found that in Nb and V, spin fluctuations substantially reduce T_c, while their contribution to the mass enhancement m^*/m is typically of order 0.2.

In the last few years interest in a microscopic understanding of superconductivity has focused on *ab initio* calculations of the superconducting transition temperature T_c based on the Eliashberg equations.[1] The latter are believed to give accurate results for T_c within a few percent, provided reliable normal-state quantities are available. These are the electronic band structure, the lattice dynamics (phonons), and the matrix elements of the electron-phonon coupling, as well as the Coulomb repulsion between the electrons which are described in a global way by a constant μ^*.

Today, for the majority of elements one has a profound knowledge of the electronic band structure and the lattice dynamics. Nevertheless, microscopic T_c calculations for elements with these data often fail by a factor of 2 or more. In