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Periodic spinodal decomposition in a binary fluid under shear

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Résumé. — On étudie par diffusion de la lumière le changement de phase d'un mélange critique de nitrobenzène et n-hexane soumis à un cisaillement hydrodynamique. Celui-ci empêche le processus de décomposition de se développer. Lorsque l'on stoppe brutalement le cisaillement, le système est alors soumis à l'équivalent d'une trempe, et des anneaux anisotropes de décomposition spinodale apparaissent. Si l'on applique un cisaillement périodique (fréquence Ω), on observe alors des anneaux anisotropes permanents. Le rayon de l'anneau, en unité de longueur de corrélation, obéit à une loi d'échelle par rapport à Ω^{-1} ou au temps t après la trempe, si Ω^{-1} ou t sont exprimés en unités de temps de vie des fluctuations. Les théories de champ moyen semblent bien décrire les résultats.

Abstract. — Light scattering techniques have been used to study the phase separation of a sheared binary fluid of nitrobenzene and n-hexane at critical composition. Shear was seen to prevent the development of decomposition. The system is quenched when the shear is removed, allowing anisotropic spinodal decomposition rings to appear. When a periodic (frequency Ω) shear was applied, a permanent anisotropic ring pattern was formed. The radius of the ring, in units of the correlation length, exhibits a scaled behaviour *versus* Ω^{-1} or the time t after the quench, if Ω^{-1} or t are expressed in units of the fluctuation lifetime. Mean-field theory seems to be relevant.

Binary fluids near their liquid-liquid phase separation temperature $T = T_c$ exhibit the same universal behaviour as pure fluids or Ising systems near their critical point [1]. The order parameter is the relative concentration $M = c - c_c$, where c_c is the critical concentration. Mean-field theories do not apply to this universality class in the usual physical space since the upper critical dimensionality $d_c = 4$. However, when a binary fluid is put out of equilibrium by a shear flow, d_c is lowered to 2.4 and mean-field theory becomes relevant [2, 3]. It is the aim of this work to report an experimental investigation by light scattering techniques of the phase separation process in such sheared fluids. For this purpose 2 distinct-but related-experiments were done in the 2-phases region, at constant temperature $T < T_c$: (i) We imposed a periodic shear $S = \frac{S_0}{2}(1 + \cos 2\,\pi\Omega t)$ where t is time, Ω is the frequency and S_0 is the shear amplitude. This is what we call the *periodic* (P) mode. (ii) Once a steady state was obtained in the P-mode, the shear is removed. This is called the *quench* (Q) mode.

Let us first review what is known about critical fluids under shear in the homogeneous phase. We will denote the quantities out of equilibrium by the same symbols as at equilibrium, but with the superscript (*). The influence of shear will be effective only in the « strong shear » region where $S\tau(T, M) > 1$. The typical time τ of the order parameter fluctuation which size is ξ (the correlation length) is simply the diffusion time on scale ξ, i.e. $\tau \simeq \frac{16\,\eta}{k_B\,T}\,\xi^3$. Here η is the shear viscosity and k_B is the Boltzmann constant. One can also define a typical wavevector k_c such that $k_c = \xi^{-1}(S\tau = 1) = (16\,\eta S/k_B\,T)^{1/3}$, and the strong shear regime holds when $k_c\,\xi > 1$. In this regime, c_c remains unchanged, but T_c is lowered by $T_c^* - T_c = -\,vT_c(k_c\,\xi_0)^{1/\nu}$. The parameter ξ_0 is the amplitude of $\xi = \xi_0\,\varepsilon^{-\nu}$, $\nu \simeq 0.63$ is the universal exponent and $\varepsilon = (T/T_c) - 1$. From the Onuki-Kawasaki (O.-K.) expectations [2] $v = 0.083\,2$, whereas experimentally the value $v \simeq 0.02$ is found [3c]. The concentration fluctuations become anisotropic and look elongated in the flow direction. Especially, the correlation length perpendicular to the flow varies as $\xi^* = \xi_0^*\,\varepsilon^{*-1/2}$, where $\xi_0^* = k_c^{-1}(k_c\,\xi_0)^{1/2\nu}$.

The *dynamical properties*, contrary to the static properties, have not yet been experimentally investigated. The O.-K. predictions [2c] concerning the linewidth Γ_q^* measured perpendicular to the flow, at the transfer wavevector q, is : $\Gamma_q^* \simeq Sk_c^{-4}(\xi^{*-2} + q^2)\,q^2$. We infer the typical lifetime τ^*, defined as above : $\tau^* = S^{-1}\,k_c^4\,\xi^{*4}$, where the mean-field value of the dynamical exponent is used. Some experimental information exists concerning the time τ_q^e that the system takes to recover its equilibrium when shear has been stopped. This time τ_q^e has been found to be much larger than the corresponding values Γ_q^{*-1} or Γ_q^{-1} [3b-c]. This will have an influence when interpretating the Q-mode data.

1. Experiment.

We used the nitrobenzene-n hexane (N-H) mixture because this system has been already studied at various concentrations and for different shear rates [3c]. It was prepared at the critical N-mass fraction ($\simeq 0.526$). The concentration was checked in the sample by turbidity measurements and was found to be close to criticality (0.530 ± 0.001). The shear flow is a Poiseuille flow produced in a tilted (near horizontal) rectangular quartz pipe (C). At each of the extremities cylindrical containers are connected by an extra pyrex tube of the same diameter (15 mm). After filling the cell, it was pumped to ensure that the sample pressure was the vapour pressure of the components. The cell was sealed by a teflon screwtap. C was set on a vertical rotary mount (M) which axis nearly coincided with the symmetry axis (0) of C. We define the X, Y, Z axes with respect to the flow : X along the flow, Y perpendicular to the flow in the vertical plane and Z perpendicular to the flow and along the rotation axis of M. The inner dimensions of C are $L_x = 150$ mm, $L_y = 5$ mm, $L_z = 2$ mm.

A simple mechanism makes M oscillate with frequency $\Omega/2$ and angular amplitude α. This leads to corresponding oscillations of the fluid level in the cell, with amplitude variation ΔH and frequency Ω. The amplitude ΔH could be varied between 0 and 3.2 cm, and Ω between 0.317 and 0.033 3 s^{-1}. The amplitude of the velocity profile, and therefore the shear rate in the observation region, is proportional to ΔH. We recorded ΔH *versus* time t for each value of α and found a variation close to $\Delta H = \frac{\Delta H_0}{2}(1 + \cos 2\,\pi\Omega t)$. The amplitude ΔH_0 is proportional to α, but a small Ω-dependence was detected. We have determined the mean shear S_0 in the observation region, using a Poiseuille flow distribution as checked in reference [3], for each value of the couple (α, Ω).

In our case, the temperature increase due to shear is negligible. Indeed, it is certainly lower than the temperature variation estimated for a permanent Poiseuille flow, where a classical calculation [4] yields a maximum value of 1 mK.

The light scattering study was performed using a slightly focused laser beam directed parallel to the Z-axis and incident near 0. This beam could be moved in the Y direction so that the illuminated volume could be submitted to a shear with direction Z (beam strictly in the middle of the sample), or with direction Y (beam close to a side wall). The scattered light was detected in an observation plane perpendicular to Z. Visual observation could be made. We performed also recordings with a professional video system.

The sample and its rotary mount were immersed in a water bath with thermal regulation $\pm$ 0.1 mK.

2. Observations.

Each set of measurements was done at constant α-values, i.e. at nearly constant shear S_0 with ε and Ω (P-mode) or t (Q-mode) varying. We have first verified that the observed phenomena were nearly insensitive to the direction of shear (Z or Y), showing that the flow direction (X) was a symmetry axis. We will therefore report here only measurements performed in the centre of the sample (shear direction Z), where we varied the mean shear rate from 200 to 900 s^{-1}. Concerning the Q-mode, we have always performed the observations, unless specified, from the highest frequency $\Omega_0 = 0.317\ s^{-1}$. With respect to temperature, always below T_c, 3 main regions could be distinguished.

I. $-1\ mK < \varepsilon T_c < 0$. — No difference from the 1-phase region behaviour could be evidenced *in the P-mode* when $S_0 \gtrsim 200\ s^{-1}$ and $\Omega > 0.03\ s^{-1}$. Beyond this limit the usual phase decomposition progressively occurred. At the highest frequency ($\sim$ 0.3 s^{-1}), we observed an isotropic ring with little contrast at the moment where S went to zero. *In the Q-mode*, decomposition progressively took place.

II. $-7\ mK \lesssim \varepsilon T_c \lesssim -1\ mK$. — *In the P-mode*, anisotropic rings of spinodal decomposition (S-D) appeared each time that $S = 0$ (Fig. 1*a*). Let $q_m = q_y$ be the ring wavevector in the Y direction, and $q_m/\Delta = q_x$ in the X direction. $\Delta = q_y/q_x$ is greater than one and measures the ring anisotropy. At a given ε, q_m varied as Ω. At a given Ω, q_m increased when $|\varepsilon|$ decreased. Δ was chiefly a function of shear. When $S \neq 0$, an extra highly anisotropic scattering perpendicular to the flow was observed, whose intensity became more important when $|\varepsilon|$ increased at Ω fixed or when Ω decreased at fixed $|\varepsilon|$; moreover a structure was seen which looked like a very anisotropic ring (Fig. 1*b*). Note that these phenomena were reproducible and did not exhibit any hysteresis *versus* ε, Ω or S_0. However sometime was necessary to obtain a permanent state when Ω or S_0 was changed.

In the Q-mode, an anisotropic ring (q_m, Δ) also appeared. q_m decreased with time, whereas Δ kept nearly constant at constant S_0 (Fig. 1*c*, *d*). When compared to a thermal quench with the same final temperature, the dynamics of the Q-mode is *much faster* (see Fig. 2). The diameter of the ring was smaller, and its dynamic faster, if we started from $\Omega < \Omega_0$. For the smallest frequencies, no more rings were observable.

III. $-1\ K \lesssim \varepsilon T_c \lesssim -7\ mK$. — No S-D rings could be observed, neither in the P-nor the Q-modes. *In the P-mode*, a very intense anisotropic scattering was seen, which split into a large and highly anisotropic ring when S went to zero. For large values of $|\varepsilon|$, the shear was not high enough to homogeneize the fluid, the meniscus remaining visible during the flow. *In the Q-mode*, the same kind of ring as in the P-mode appeared, then it vanished after a few seconds and the usual phase decomposition occurred.

3. Discussion.

It seems clear from the observations that shear prevents the phase separation process from developing. Setting S to zero is analogous to quenching the system, and rings of S-D naturally appear. The system is still out of equilibrium, rings are anisotropic and mean-field should be relevant in describing the S-D process.

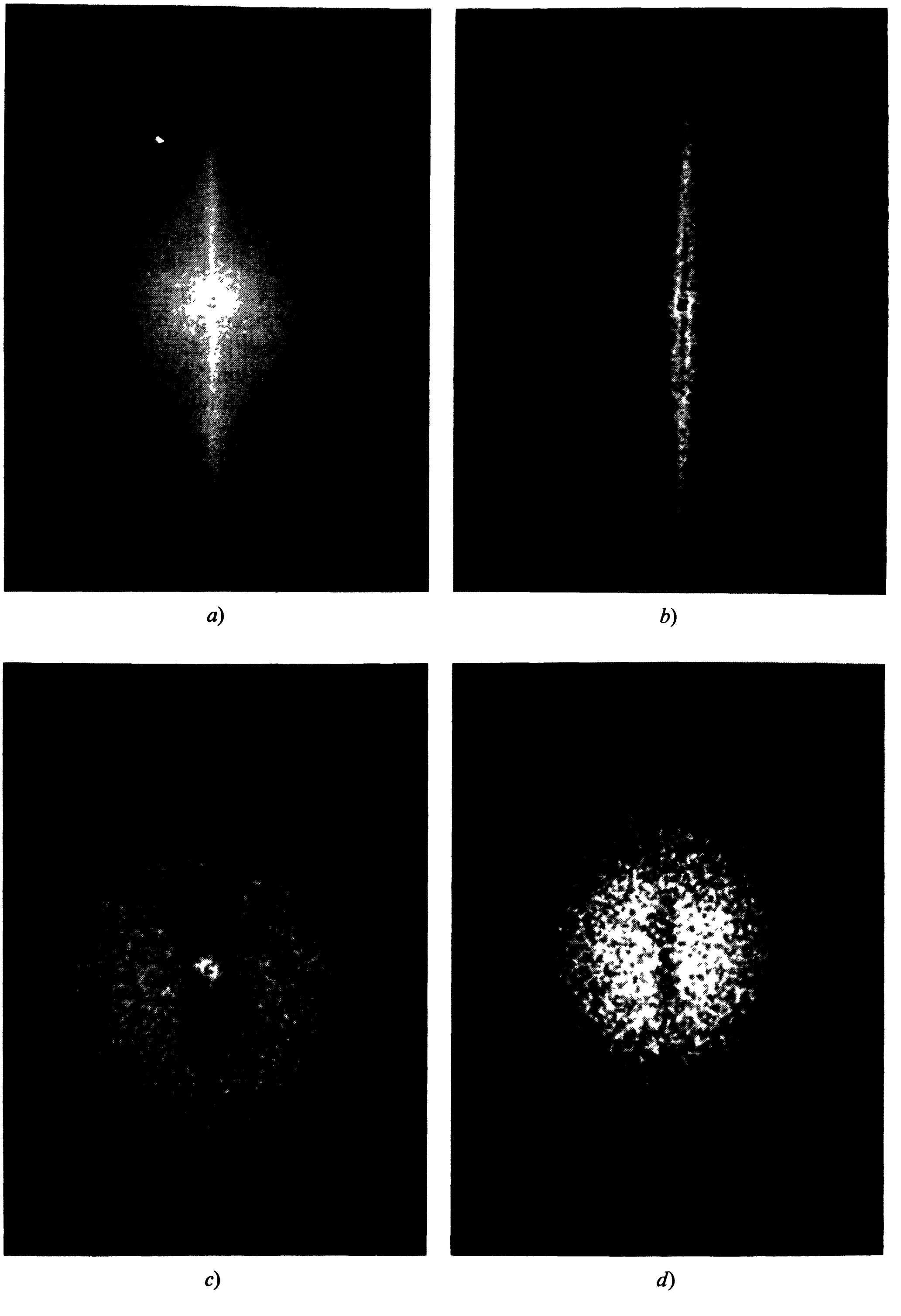

Fig. 1. — Photos of S-D under shear ($T - T_c \sim -3$ mK, $\Omega = 0.317\ s^{-1}$). Flow is horizontal and shear is in the observation direction. *a*) P-mode, $S = 0$. Superposition of a permanent ring, a vertical highly anisotropic scattering and of some horizontal stray light. *b*) P-mode, $S \neq 0$. *c*) Q-mode, close to the initial state. *d*) Q-mode, close to the final state.

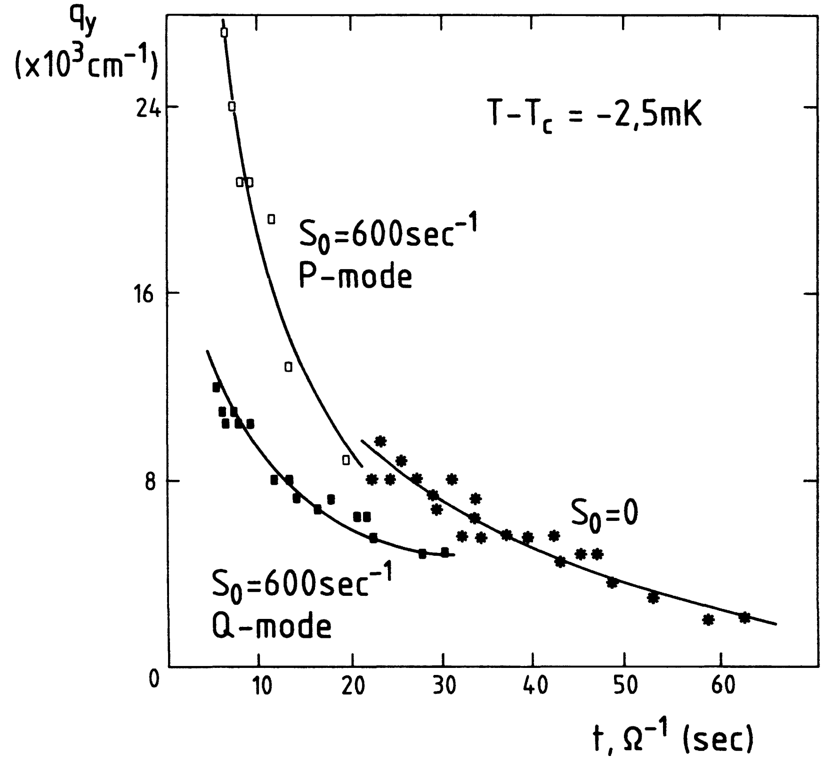

Fig. 2. — Radius $q_m = q_y$ of the S-D ring *versus* Ω^{-1} (P-mode) or time t (Q-mode). Temperature is constant and equal to $T_c - 2.5$ mK. The case $S_0 = 0$ corresponds to a thermal quench from an initial temperature $T_c + 0.5$ mK to a final temperature $T_c - 2.5$ mK.

On the other hand, the use of a periodic shear means that most of the Onuki predictions [5] concerning periodic quenches of system at equilibrium should apply, provided that the quantities ξ and τ are changed to the corresponding quantities (ξ^*, τ^*) out of equilibrium. The basic idea of Onuki is that a periodic quench (Ω) allows only the fluctuations of typical time $\tau^* \sim \Omega^{-1}$ to grow. The time τ^* is connected to the maximum quench depth, i.e. here to the highest shear S_0. It is therefore given by $\tau^* = S_0^{-1}[k_c(S_0).\xi^*(S_0)]^4$.

In domain I, the shear range investigated corresponds to a T_c-lowering of [0.3-0.7] mK when using the data of reference 3*c*. In this domain the system is therefore either in the 2-phases region when $S = 0$, or in the 1-phase region when both S is $\neq 0$ and large enough to compensate the temperature lowering. The fact that the shear variation cannot be used as a quench is presumably due to its time variation, which is not fast enough, or its depth, which is not large enough.

In domain II, the system should remain in the 2-phases region. S-D occurs *in the P-mode* for $(\Omega\tau^*)^{-1} \gtrsim 2$ (Fig. 3), which compares favourably with the Onuki expectations $(\Omega\tau)^{-1} \gtrsim 1$. The permanent state of the decomposition is well supported by the remaining ring during the flow. The intense scattering with no structure can be attributed to the increasing concentration of droplets which have reached their final stage and which are easily elongated by the flow, owing to the weak interfacial tension. As for thermal quenches [6], q in units of ξ^{*-1} would exhibit a scaled behaviour *versus* Ω^{-1} in units of τ^*. Here Ω^{-1} plays the rôle of the time t after the quench. The product $q_m\,\xi^*$, where q_m is the ring radius in the Y direction when $S = 0$, is plotted in figure 3 *versus* $(\Omega\tau^*)^{-1}$. The large range of values for S_0, ε, Ω and the relatively small scattering of data for this kind of experiment (see e.g. Ref. 6) is in support of scaling. Note that the early stage of S-D can be reached, and our data behave according to the usual Binder-Stauffer [7] behaviour in $t^{-1/3}$, i.e. $q_m \xi^* \sim (\Omega\tau^*)^{1/3}$. *The anisotropy* Δ *versus* $(\Omega\tau^*)$ remains nearly constant and roughly equal to 1.8. This is not surprising since the S_0-dependence of the variable $(\Omega\tau^*)^{-1}$ is very low $\sim S_0^{(2/3\nu)-1}$.

In the Q-mode, the evolution of the ring compares well to the P-mode if we take $t \sim \Omega^{-1}$ (see Fig. 3). However the system is neither at real equilibrium nor under shear. In the q_m and ε-ranges investigated, the time τ_q^e for recovering equilibrium is much larger than the duration of the ring (see [3*b*, *c*]), and the fluctuations can be considered as being still anisotropic but without flow convection. Then the typical fluctuation time τ^* should be replaced by the time τ^{**} that

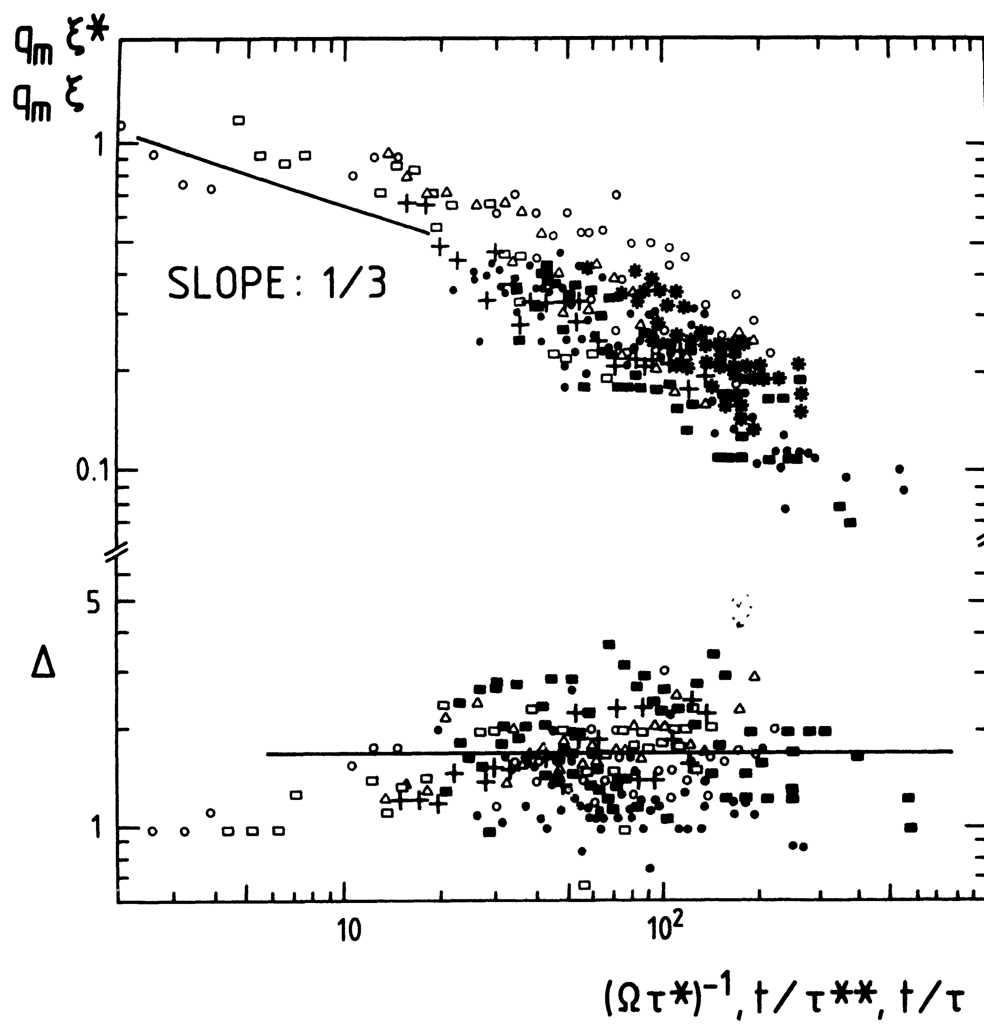

Fig. 3. — Radius q_m of the S-D ring in units of ξ^{*-1} and ring anisotropy Δ as function of the reduced times $(\Omega\tau^*)^{-1}$ [P-mode], (t/τ^{**}) [Q-mode], or (t/τ) [thermal quench]. P-mode : $S_0 = 900\ \mathrm{s}^{-1}$ (○), $600\ \mathrm{s}^{-1}$ (□, △), $300\ \mathrm{s}^{-1}$ (+). Q-mode : $S_0 = 900\ \mathrm{s}^{-1}$ (●), $600\ \mathrm{s}^{-1}$ (■). The data (*) correspond to a thermal quench, where $q_m \xi$ is reported *versus* t/τ. We used the numerical values $T_c = 293$ K, $\xi_0 = 2.65$ Å, $\eta = 7.8 \times 10^{-3}\ P_0$ [Ref. 3*c*].

a droplet of size ξ^* takes to vanish in a fluid at rest, i.e. $\tau^{**} \simeq \frac{16\ \eta}{k_B\ T}\ \xi^{*3}$. Figure 3 shows $q_m\ \xi^*$ as a function of t/τ^{**}, and the scaled behaviour is not very different from above in the P-mode. We have also reported a typical thermal quench in the same units ($q_m\ \xi$, t/τ), which compares favourably with the other data. It is worth noticing that replacing the quantities τ^* by τ^{**} or τ, or ξ^* by ξ, substantially modifies the results in figure 3, which exhibit a greater scatter of data. This is why we estimate that the mean-field theory, as expressed above, seems to be relevant.

In domain III, $(\Omega\tau^*)^{-1} \gg 1$ and the system decomposes without any visible S-D, the coefficient of mass diffusion becoming too large. The droplet concentration is high and constant in time because the shear destroys the meniscus which would have formed in the fluid at rest. These droplets are elongated in the flow, causing a very anisotropic diffusion pattern. This phenomenon was observed a long time ago with polymers [8]. The « ring » which appears when $S = 0$ corresponds to the growing of the droplets which tend to recover a spherical shape, the interfacial tension increasing with ε as $|\ \varepsilon\ |^{1.25}$. The lower limit of this temperature region can be interpretated as being the point where an instability of the Kelvin-Helmholtz type occurs under a periodic shear. The periodic flow ensures a permanent mixing of the fluid, enforced by the influence of the walls of the pipe. Unfortunately, the stability of such periodic flows has been little studied [9].

4. Conclusion.

In the 2-phase region close to T_c, shear was seen to prevent the unstable fluctuations from growing. Stopping the shear is therefore analogous to performing a quench, and S-D occurs. When using a periodic shear, permanent S-D rings have been seen, in agreement with the Onuki expectations. This S-D occurs under shear, so the mean-field approach we have followed for ξ^* and τ^* should remain valid. S-D preliminary states can be obtained, and our results agree qualitatively with the Binder-Stauffer theory. Further away from T_c, hydrodynamic instabilities connected to the interfacial tension occur, which seems to be a phenomenon of interest. On the other hand, S-D under shear is seen to be a means of studying the non equilibrium dynamics of critical fluids. Note that we have observed this phenomenon in other critical mixtures. Further experiments with Couette flow where shear is well defined are envisaged.

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