Effects of Shear Flow on Long-Ranged Correlations, Spinodal Demixing Kinetics, and the Location of the Critical Point and Cloud Point[1]

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A derivation of an expression for the shear rate-dependent Ornstein Zernike structure factor is discussed, together with the resulting anomalous behavior of the turbidity. The predicted scaling behavior of the turbidity, comprising the effect of both temperature and shear rate, is in good agreement with experiments on binary fluids. Then initial spinodal decomposition is discussed, and an explicit expression for the time- and shear rate-dependent effective diffusion coefficient is derived, which shows all the typical characteristics of anisotropic light scattering patterns that are observed experimentally for binary fluids. Next it is shown that the spinodal is shifted linearly with the (bare) Peclet number for not too large Peclet numbers, whereas the cloud point is singularly displaced into the unstable region due to a shear flow. This is in agreement with an experiment on a two-polymer/solvent mixture and binary fluid mixtures. It is argued that light scattering is useless to determine the location of the spinodal of a sheared system.

1. INTRODUCTION

Theoretical predictions concerning the effect of shear flow on (i) long-ranged critical correlations, (ii) initial spinodal decomposition kinetics, and (iii) the location of the spinodal and cloud-point curve are discussed and compared to experiments. The formal derivation of these predictions are not given here in full extent; I discuss only briefly the lines along which

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these formal derivations proceed. The starting point of these calculations is the Smoluchowski equation, which is an equation of motion for the probability density function $P_N(\mathbf{r}_1, \mathbf{r}_2.., \mathbf{r}_N; t)$ of the position coordinates $\{\mathbf{r}_1,..., \mathbf{r}_N\}$ of the N Brownian particles [1]. Only spherically symmetrical Brownian particles are considered, for which orientational degrees of freedom need not be considered, so that position coordinates is the relevant set of microscopic variables. Although this approach is intended to describe phenomena in colloidal systems, a number of critical phenomena may be generic, and we compare most of the theoretical predictions with results on molecular systems. In most cases, experimental data on colloidal systems are not available yet. Without shear flow, the critical behavior of colloidal and atomic/molecular systems is identical, since for both kinds of systems the equilibrium probability density function for the phase space coordinates is identical, being equal to the Boltzmann exponent of the Hamiltonian. Diffusion processes, which determine the effect of shear flow, may also share similar properties for both systems, in which case the conclusions given in the present paper also apply to atomic/molecular systems. How far relevant dynamical features of colloidal and atomic/molecular systems compare is difficult to assess.

Being an equation of motion for the probability density function of phase space coordinates, the Smoluchowski equation plays the same role in the statistical mechanics of colloidal systems as the Liouville equation for atomic/molecular systems. The present approach may thus be considered as a "Liouville equation approach" for colloidal systems.

With the neglect of hydrodynamic interactions between the Brownian particles, the Smoluchowski equation reads

$$\frac{\partial P_N}{\partial t} = \sum_{j=1}^{N} \nabla_j \cdot [D_0\{\nabla_j P_N + \beta(P_N \nabla_j \Phi)\} - P_N \Gamma \cdot \mathbf{r}_j] \tag{1}$$

Here Φ is the total potential energy of the assembly of Brownian particles and Γ is the velocity gradient tensor. The shear flow considered here is a flow in the x direction, with the gradient in the y direction. The velocity gradient tensor for this flow is

$$\Gamma = \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

with $\dot{\gamma}$ the shear-rate.

My intention here is to describe how to go about obtaining explicit results for the effect of shear flow on

(i)   critical correlations,

(ii) initial spinodal decomposition kinetics, and

(iii) the location of the spinodal and cloud-point curve.

2. LONG-RANGED CRITICAL CORRELATIONS [2]

The Smoluchowski equation can be integrated over all except two position coordinates to obtain an equation of motion for the pair-correlation function $g(\mathbf{R}; t \mid \dot{\gamma})$, with $\mathbf{R}$ the distance between two particles,

$$\frac{\partial g}{\partial t} = 2D_0 \nabla \cdot [\nabla g + \beta g (\nabla V - F_{ind})] - \nabla \cdot (g \mathbf{\Gamma} \cdot \mathbf{R}) \qquad (2)$$

where V is the pair-interaction potential, assumed to be pairwise additive. Furthermore, F_{ind} is the indirect force between two particles mediated via the other particles, which force is an integral containing the triplet correlation function. The equation of motion is closed, by means of an improved version of the superposition approximation for the triplet-correlation function. The point here is that the usual superposition approximation does not yield a diverging correlation length at the critical point. A natural improvement of the superposition approximation resolves this inconsistency [2, 3]. The asymptotic solution of the stationary nonlinear equation of motion for large distance is obtained by linearization with respect to g around $g \equiv 1$, since g becomes equal to 1 at infinity. The linearization limits the further discussion to the mean-field region [2]. The resulting linear equation can be solved with Fourier transformation. Scaling the wave-vector $\mathbf{k}$ with respect to the correlation length ξ (at the particular temperature and density under consideration for the system without shear flow),

$$\mathbf{K} \equiv \mathbf{k} \xi \qquad (3)$$

yields the following expression for the relative structure-factor distortion [$\dot{\gamma}$ is the shear rate, $S(\mathbf{K} \mid \dot{\gamma})$ is the structure factor, and $S^{eq}(K)$ is the equilibrium structure factor],

$$\frac{S(\mathbf{K} \mid \dot{\gamma}) - S^{eq}(K)}{S^{eq}(K) - 1}$$

$$= \frac{1}{\lambda K_1} \int_{K_2}^{\pm \infty} dX (K^2 - K_3^2 + X^2)(K_3^2 - X^2) \exp\left\{ - \frac{F(\mathbf{K} \mid X)}{\lambda K_1} \right\} \qquad (4)$$

where K_j is the jth component of $\mathbf{K}$, and,

$$F(\mathbf{K} \mid X) \equiv (X - K_2)(K^2 - K_2^2)(1 + K^2 - K_2^2)$$
$$+ \tfrac{1}{3}(X^3 - K_2^3)(1 + 2K^2 - 2K_2^2) + \tfrac{1}{5}(X^5 - K_2^5) \qquad (5)$$

The $+(-)$ sign in the upper integration limit in Eq. (4) is to be used for $\lambda K_1 > 0 \ (<0)$. The parameter λ is a dimensionless group that describes the effect of both temperature (via the correlation length) and shear rate on the distortion,

$$\lambda \equiv \frac{Pe^0(\dot{\gamma})}{(\xi^{-1} R_V)^4 (\beta \Sigma / R_V^2)} \qquad (6)$$

where $Pe^0 \equiv \dot{\gamma} R_V^2 / 2D_0$ is the Peclet number, D_0 is the Stokes–Einstein diffusion coefficient, $\beta = 1/k_B T$ (k_B is Boltzmann's constant and T is the temperature), R_V is the range of the pair-interaction potential, and Σ is a well-behaved function of the density and temperature which is related to the Cahn–Hilliard free-energy square-gradient coefficient. Note that $\lambda \propto \dot{\gamma}\xi^4$, so that, close to the critical point, where the correlation length ξ is large, a small shear rate $\dot{\gamma}$ is sufficient to have a significant effect. Actually, in the derivation of the above result it is assumed that $Pe^0 \ll 1$, but since ξ is so large, there is still a large effect of the shear flow for these small Peclet numbers. The transition from weak to strong shear flow occurs at $\lambda \approx 1$.

Since for $\lambda = 0$ we have, $S(\mathbf{K} \mid \dot{\gamma}) = S^{eq}(K)$, and λ occurs as a product with K_1, it follows that

$$S(\mathbf{K} \mid \dot{\gamma}) = S^{eq}(K), \qquad \text{for} \quad K_1 = 0 \qquad (7)$$

There is no effect of the shear flow on density correlations in those directions where $K_1 = 0$. In fact, numerical results obtained from the above
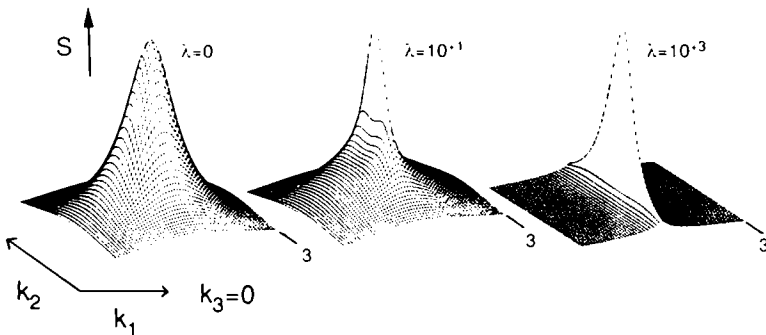

Fig. 1. The structure factor as a function of K_1 and K_2 for $K_3 = 0$, for $\lambda = 0$, 10, and 1000.
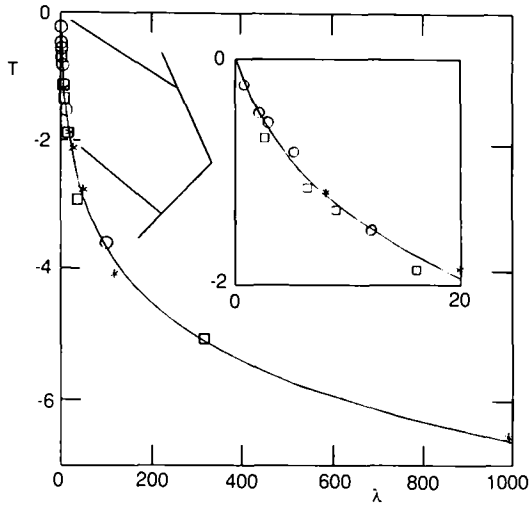
Fig. 2. The theoretical turbidity scaling function (solid curve) with data points for a mixture of aniline and cyclohexane taken from Ref. 4 and 5. The inset shows a blowup for $\lambda < 20$. Data points are for $\dot{\gamma} = 92 \, s^{-1}$ ( ), $288 \, s^{-1}$ ($\sqcap$) and $903 \, s^{-1}$ (*).

results show that correlations are already severely disrupted in all other directions for very small shear rates (that is, small Pe^0). This is illustrated in Fig. 1, where $S(\mathbf{K} \mid \dot{\gamma})$ is plotted as a function of K_1 and K_2, with $K_3 = 0$, for three values of the parameter λ ($\lambda = 0$ corresponds to the equilibrium structure factor). Clearly, in directions perpendicular to the flow, that is, in directions where $K_1 \neq 0$, the disruption of correlations is almost complete, whereas in the flow direction the structure is unaffected. Actually, the correlation length along the flow direction can be shown to depend on the shear rate through the Peclet number Pe^0 in a regular fashion, being related to the pair-correlation function for distances smaller than the range R_V of the pair-interaction potential V [2]. These distortion characteristics are in accordance with experimental findings for binary fluids [4].

The structure-factor distortion is observed experimentally in an integrated form through measurements of the turbidity (and, for example, dichroism and viscosity). On the basis of Eq. (4) it can be shown [2] that the turbidity τ is only a function of λ, which dimensionless number describes then the effect of *both* temperature (through the correlation length) and shear rate,

$$\tau \propto T(\lambda) \tag{8}$$

The "scaling" or "master" function T is an integral over the structure-factor distortion and is plotted in Fig. 2, together with experimental data on a binary fluid mixture [4, 5]. Three sets of data points are shown, referring to measurements as a function of temperature for three different shear rates. There are two unknown proportionality constants between the measured quantities, on the one hand, and the scaling function and its argument λ, on the other hand. These two proportionality constants are determined by fitting the set of data taken at the shear rate of $903\,s^{-1}$ to the theoretical scaling function. Data taken at other shear rates are then rescaled with the same proportionality constants and plotted in the scaling form without any further adjustable parameter. As can be seen, the predicted $\lambda \propto \dot{\gamma}\xi^4$ scaling is an accordance with these experiments.

3. INITIAL SPINODAL DECOMPOSITION KINETICS [6]

To describe the decomposition kinetics, an equation of motion for the macroscopic density $\rho(\mathbf{r}; t \mid \dot{\gamma})$ is required. Such an equation of motion is obtained from the Smoluchowski equation by integration over all except one position coordinate. This equation reads,

$$\frac{\partial \rho}{\partial t} = D_0 \nabla \cdot \left[\nabla \rho + \beta \rho \int d\mathbf{r}' [\nabla V(|\mathbf{r}-\mathbf{r}'|)] \, \rho(\mathbf{r}'; t \mid \dot{\gamma}) \, g(\mathbf{r}, \mathbf{r}'; t \mid \dot{\gamma}) \right] - \nabla \cdot (\rho \boldsymbol{\Gamma} \mathbf{r}) \tag{9}$$

The pair-correlation function g must be expressed in terms of the density to obtain a closed equation of motion. To describe the initial decomposition kinetics, we can write the density as

$$\rho(\mathbf{r}; t \mid \dot{\gamma}) = \bar{\rho} + \delta\rho(\mathbf{r}; t \mid \dot{\gamma}) \tag{10}$$

where $\bar{\rho} = N/V$ is the mean density, and $\delta\rho(\mathbf{r}; t \mid \dot{\gamma})$ is the change in the density, which is assumed to be small in comparison to $\bar{\rho}$. Assuming, again, very small Peclet numbers, the distortion of g for $|\mathbf{r} - \mathbf{r}'| \leqslant R_V$ (with R_V the range of the pair-interaction potential V) in Eq. (9) is negligible and g may be replaced by the equilibrium pair-correlation function $g^{eq}(|\mathbf{r} - \mathbf{r}'|)$. The effect of the shear flow is large, even for the small Peclet numbers Pe^0, since very large wave-vector density variations are unstable [6]. The change of the equilibrium pair-correlation function is linear in the change in the density in the initial stages. Assuming that this change is sinusoidal for

low-amplitude and long-wavelength sinusoidal density variations, the following closure relation is obtained:

$$\delta g(\mathbf{r}, \mathbf{r}'; t \mid \dot{\gamma}) \equiv g(\mathbf{r}, \mathbf{r}'; t \mid \dot{\gamma}) - g^{\mathrm{eq}}(|\mathbf{r} - \mathbf{r}'|)$$

$$= \frac{dq^{\mathrm{eq}}(|\mathbf{r} - \mathbf{r}'|)}{d\bar{\rho}} \, \delta\rho(\bar{\mathbf{r}}; t \mid \dot{\gamma}) \qquad \text{for} \quad |\mathbf{r} - \mathbf{r}'| \leqslant R_{\mathrm{V}} \quad (11)$$

where $\bar{\mathbf{r}} = \frac{1}{2}(\mathbf{r} + \mathbf{r}')$, and $g^{\mathrm{eq}}(|\mathbf{r} - \mathbf{r}'|)$ (with $|\mathbf{r} - \mathbf{r}'| \leqslant R_{\mathrm{V}}$), is the pair-correlation function right after the temperature quench into the unstable region of the phase diagram, before phase separation is initiated.

The above closure relation, linearization, and Fourier transformation yields the following equation of motion for the Fourier transform of the change of the density $\delta\rho(\mathbf{k}, t \mid \dot{\gamma})$

$$\left(\frac{\partial}{\partial t} - \dot{\gamma} k_1 \frac{\partial}{\partial k_2} \right) \delta\rho(\mathbf{k}; t \mid \dot{\gamma}) = -D(k) k^2 \, \delta\rho(\mathbf{k}; t \mid \dot{\gamma}) \qquad (12)$$

with the "effective diffusion coefficient" given by

$$D(k) \equiv D_0 \left[\beta \frac{d}{d\bar{\rho}} \Pi(\bar{\rho}) + \beta k^2 \Sigma(\bar{\rho}) + O((kR_{\mathrm{V}})^4) \right] \qquad (13)$$

where Π is the osmotic pressure and Σ is the same well-behaved function that appears in the dimensionless number λ, Eq. (6). When Pe^0 is not a small number, the effective diffusion coefficient becomes shear rate dependent. For zero shear this equation of motion is nothing but the (linearized) Cahn–Hilliard equation of motion, which is thus rederived from microscopic considerations. In case no shear flow is applied, the effective diffusion coefficient is zero for zero wave-vector k on the spinodal curve and is negative for a certain finite k-range around $k = 0$ below the spinodal. The equation of motion (12) is valid only in the unstable region.

The solution of Eq. (12) is

$$\delta\rho(\mathbf{k}; t \mid \dot{\gamma}) \propto \exp\{ -D^{\mathrm{eff}}(\mathbf{k}; t \mid \dot{\gamma}) k^2 t \} \qquad (14)$$

where we introduced a time- and shear rate-dependent effective diffusion coefficient, which is related to the zero-shear effective diffusion coeficient as

$$D^{\mathrm{eff}}(\mathbf{k}; t \mid \dot{\gamma}) = \frac{1}{\dot{\gamma} k_1 t} \int_{k_2}^{k_2 + \dot{\gamma} k_1 t} dx \, D(\sqrt{k_1^2 + x^2 + k_3^2}) \frac{k_1^2 + x^2 + k_3^2}{k^2} \qquad (15)$$

Note that

$$D^{\mathrm{eff}}(\mathbf{k}; t \mid \dot{\gamma}) = D(k) \qquad \text{for} \quad k_1 = 0 \qquad (16)$$

so that no effect of the shear flow on the decomposition kinetics is pre-
dicted in directions where $k_1 = 0$. Furthermore, the effective diffusion coef-
ficient depends on the shear rate and time only through their product $\dot{\gamma}t$.
Both these observations have been made experimentally for binary fluid
mixture [7]. Numerical results for the effective diffusion coefficient can be
obtained with a third virial approximation for the (short ranged) behavior
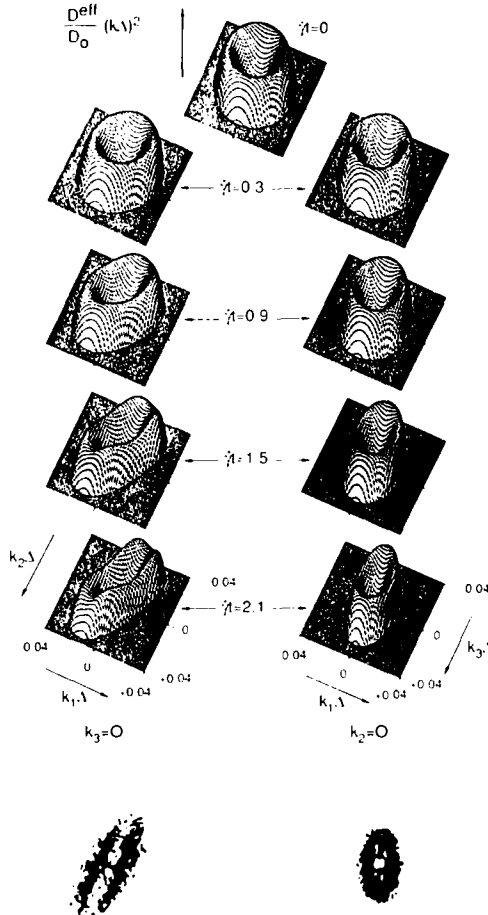
Fig. 3. Minus the effective diffusion coefficient $\times (k\Delta)^2$
as a function of (k_1, k_2) on the left and (k_1, k_3) on the
right. The pair-correlation function is a third virial
approximation for a square well with a width Δ, super-
imposed on a hard-core repulsion. Bottom: Experi-
mental scattering patterns for a demixing binary fluid
mixture, taken from Ref. 7.

of the equilibrium pair-correlation function, to calculate both Π and Σ. The pair-interaction potential is chosen as an attractive square well, super-imposed on a hard-core repulsion. The typical predicted anisotropy of (*minus*) the effective diffusion coefficient multiplied with k^2 is given in Fig. 3. In the (k_1, k_2) plane there is an ellipsoidal-like distortion with the long axis of the ellipsoid rotated, whereas in the (k_1, k_3) plane no such rotation is predicted. This is precisely what is observed experimentally for binary fluids, including the diminishing of the effective diffusion coefficient (c.q. the scattered intensity) along the long axis of the ellipsoid in the (k_1, k_2) plane (the coordinate system used in Ref. 7 must be transformed to the one we used here). The experimentally observed scattering patterns are given in Fig. 3 (bottom). These patterns are to be compared with the theoretical patterns in the two columns above.

Imaeda et al. [8] derive an equation of motion similar to Eq. (12) for binary fluids, using an expression for the free energy [the thermodynamic potential Φ in their Eq. (2.6)] which is unaffected by the shear flow. This is equivalent to our neglect of the shear rate dependence of the pair-correlation function in the closure relation (11) (as it turns out in the following section, it is just that shear rate dependence that describes the shift of the spinodal as a function of the shear rate). Due to the presence of an inhomogeneous term in their equation of motion, the solution differs from our solution (14) and contains a time integral. The quantity which is denoted $f(\mathbf{k}, t)$ in Ref. 8 is precisely our effective diffusion coefficient in Eq. (15), apart from a trivial prefactor. Although different in details, the predictions given here for colloidal systems are in overall agreement with those made for binary fluids in Ref. 8.

4. DISPLACEMENT OF THE SPINODAL AND THE CLOUD POINT [6]

In the previous sections we have made the restriction that $Pe^0 \ll 1$. This is done so that the pair-correlation function $g(\mathbf{r}\,|\,\dot{\gamma})$ in the expression,

$$D(\mathbf{k}\,|\,\dot{\gamma}) = D_0 \left[1 - \frac{1}{2}\beta\bar{\rho} \int d\mathbf{r}\, r\, \frac{dV(r)}{dr} (\hat{\mathbf{k}}\cdot\hat{\mathbf{r}})^2 \right.$$
$$\left. \times \left(2g^{\mathrm{eq}}(\mathbf{r}\,|\,\dot{\gamma}) \frac{\sin\{\mathbf{k}\cdot\mathbf{r}\}}{\mathbf{k}\cdot\mathbf{r}} + \bar{\rho}\, \frac{dg^{\mathrm{eq}}(\mathbf{r}\,|\,\dot{\gamma})}{d\bar{\rho}} \frac{\sin\{\frac{1}{2}\mathbf{k}\cdot\mathbf{r}\}}{\frac{1}{2}\mathbf{k}\cdot\mathbf{r}} \right) \right] \quad (17)$$

can be set equal to the equilibrium pair-correlation function $g^{\mathrm{eq}}(r)$:

$$Pe^0 \ll 1 \Rightarrow g(\mathbf{r}\,|\,\dot{\gamma}) \approx g^{\mathrm{eq}}(r) \qquad \text{for} \quad r \lesssim R_{\mathrm{V}}$$

with $V(r)$ the pair potential. The shear rate-dependent effective diffusion coefficient (17) then reduces to the shear rate-independent effective diffusion coefficient (13). For the calculation of the displacement, however, the shear-rate dependence in (17) is essential, as the location of the spinodal is given by

$$D^{\text{eff}}(\mathbf{k} = \mathbf{0} \mid \dot{\gamma}) = 0 \tag{18}$$

This implicit relation for the temperature and the density bounds the unstable region. Actually, this condition is a stability criterion for concentration variations of an infinitesimally low amplitude. In a real system there are always finite-amplitude fluctuations, so that the system demixes as if it were unstable before the true spinodal is reached. Without shear flow, the criterion given by Eq. (18) is the usual thermodynamic definition of the spinodal.

For $r \leqslant R_V$, the distortion of the pair-correlation function is regular in Pe^0, that is,

$$g(\mathbf{r} \mid \dot{\gamma}) = g^{\text{eq}}(r) + g^{(1)}(\mathbf{r}) \, Pe^0 + O((Pe^0)^2) \qquad \text{for} \quad r \leqslant R_V \tag{19}$$

where $g^{(1)}(\mathbf{r})$ is an $O(1)$ function. It follows then from Eq. (18) that the effective diffusion coefficient is a regular function of Pe^0, and in particular,

$$D^{\text{eff}}(\mathbf{k} = \mathbf{0} \mid \dot{\gamma}) = D^{\text{eff}}(k = 0) + D^{(1)} Pe^0 + O((Pe^0)^2) \tag{20}$$

The implicit relation between density and temperature is thus regular in Pe^0, so that the conclusion is that the spinodal shifts linearly with the Peclet number for not too large values of Pe^0.

The cloud-point curve is defined as the set of temperatures and densities that bounds the region where the turbidity diverges. This divergence is due to the long-ranged character of the pair-correlation function. In equilibrium, that is, without shear flow, the critical point is a cloud point. Being related to the long-ranged behavior of the pair-correlation function, the cloud points are shifted in a singular fashion with Pe^0. In Section 2, for example, we found that the turbidity depends on the dimensionless number λ, which is infinite, no matter how small the shear rate is, when the correlation length (in the homogeneous thermalized system before phase separation occurred, at the particular temperature and density) is infinite. The singular behavior of the pair-correlation function can also be read off the equation of motion, given by Eq. (2), for the pair-correlation function, without the need to solve that equation [2, 6]. The conclusion is that the cloud-point curve is shifted over a much larger temperature interval than the critical point, where the system becomes unstable.
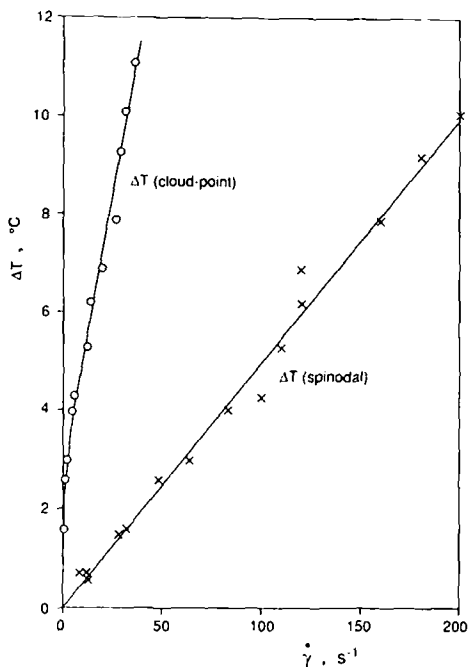
Fig. 4. The temperature shift $\Delta T(\dot{\gamma}) \equiv T(\dot{\gamma} = 0) - T(\dot{\gamma})$ of the critical point, ΔT (spinodal), and of the cloud point, ΔT (cloud point), as a function of the shear rate. The system is a mixture of ethylcellulose and polystyrene in benzene. Data are taken from Ref. 9.

This prediction is in accord with experiments on a two-polymer solvent mixture [9]. Figure 4 shows the temperature shift,

$$\Delta T(\dot{\gamma}) \equiv T(\dot{\gamma} = 0) - T(\dot{\gamma}) \tag{1}$$

of the spinodal and the cloud point at the critical composition for that mixture. These data clearly show the predicted regular shift of the spinodal and the singular shift of the cloud point. A sheared system becomes unstable on lowering the temperature in the present case and phase separates before it turns very turbid. In the homogeneous state, before phase separation occurred, the turbidity becomes infinite for the first time on lowering the temperature far into the unstable region. The conclusion is that *light scattering is useless to detect the location of the spinodal in a sheared system*. What is measured is the cloud point, which has a different location in the sheared system than the spinodal.

Similar singular displacements of the cloud point are found for binary fluids by Beysens et al. [10] and, more recently, Fukuhara et al. [11]. Although the temperatures at which the turbidity diverges are sometimes referred to as critical temperatures, they are cloud-point temperatures, which do not coincide with the spinodal where the density becomes unstable. The initial shear-rate dependence of the shift of the cloud-point temperature is found in Refs. 10 and 11 to be described, to within experimental error, by $\sim \sqrt{\dot{\gamma}}$. This could be connected to the width of the mathematical boundary layer of the singularly perturbed (Fourier-transformed) Smoluchowski equation, which varies with the shear rate as $\sqrt{\dot{\gamma}}$. Such a connection requires further study.

It is not obvious wether in a sheared system the spinodal or the cloud point should be called a critical point in the sense that, for example, the susceptibility shows anomalous behavior. It may very well be that anomalous behavior of different quantities occurs at different temperatures, depending on their sensitivity to infinitely ranged correlations in one, two, or all three directions.

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