Shear Induced Displacement of the Spinodal of Brownian Systems

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The displacement of the gas-liquid spinodal of colloids on applying a shear flow is analyzed on the basis of the Smoluchowski equation. Relatively simple arguments predict that the off-critical part of the spinodal is displaced linearly with the shear rate $\dot{\gamma}$, while the shift of the critical temperature is $\sim \dot{\gamma}^{1/\gamma}$, with γ the critical exponent for the reciprocal equilibrium compressibility. This differs considerably from what is known for molecular systems. It is also argued that the cloud-point curve under shear no longer coincides with the spinodal, and is displaced far into the unstable region of the phase diagram. A sharp increase of forward scattered intensity in a sheared system does not probe the location of the spinodal. [S0031-9007(96)00310-9]

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Renormalization group theoretical expansions in 4 - d(with d the spatial dimensionality) for molecular fluids as performed by Onuki et al. [1,2] predict a shift of the critical temperature due to shearing motion $\sim \dot{\gamma}^p$, with $p \approx 0.52$, where $\dot{\gamma}$ is the shear rate. This paper presents a relatively simple calculation of the shift of the spinodal due to shear flow for Brownian systems, including the off-critical part, starting from an equation of motion for the probability density function of the phase space coordinates. It is found that the shift of the off-critical part of the spinodal is a linear function of the shear rate $\dot{\gamma}$, while the critical temperature is shifted $\sim \dot{\gamma}^{1/\gamma}$, with γ the critical exponent for the inverse compressibility. Since equilibrium critical exponents for molecular fluids are the same as for colloids, and the critical exponent γ for molecular fluids is ≈ 1.23 , this predicts that the critical temperature for colloids is shifted such as $\sim \dot{\gamma}^p$ with $p \approx 0.81$. This exponent differs considerably from that found for molecular fluids.

The displacement of the spinodal, including its offcritical part, can be described on the basis of the Smoluchowski equation. This is the equation of motion on the diffusive time scale for the probability density function (PDF) *P* of the position coordinates $\{\mathbf{r}_j\}$ of the *N* Brownian particles in the system. This "Liouville equation on the diffusive time scale" reads [3–5], with the neglect of hydrodynamic interactions,

$$\frac{\partial}{\partial t}P = \sum_{j=1}^{N} \nabla_{j} \cdot \{ D[\nabla_{j}P + \beta P \nabla_{j} \Phi] - (\Gamma \cdot \mathbf{r}_{j}P) \}, \quad (1)$$

where $\beta = 1/k_B T$ (with k_B being the Boltzmann's constant and T the temperature), Φ is the potential energy of the assembly of Brownian particles, D is the Stokes-Einstein diffusion constant, and ∇_j is the gradient operator with respect to \mathbf{r}_j . Furthermore, Γ is the velocity gradient tensor, with $\Gamma_{12} = \dot{\gamma}$, and all other entries equal to 0. This corresponds to a flow in the *x* direction with its gradient in the *y* direction. The equation of motion (1) is a conservation equation, where the velocity of phase space coordinates is driven by a Brownian force $-k_B T \nabla_j \ln\{P\}$, by a force due to direct interactions $-\nabla_j \Phi$, and where there is an additional convective contribution to the velocity ity equal to $\Gamma \cdot \mathbf{r}_j$.

The spinodal is defined as the points in the temperature T versus number density $\overline{\rho} = N/V$ diagram, where the system becomes unstable against density fluctuations of infinite wavelength and infinitesimally small amplitude. Hence, to calculate the spinodal, an equation of motion for the number density must be obtained from Eq. (1), after which a simple linear stability analysis for zero wave vectors can be performed to locate the spinodal. In the metastable region of the phase diagram things are much more complicated, and at least the leading order nonlinear term must be included in the stability analysis to calculate the binodal. The discussion here is restricted to the spinodal.

Integration of Eq. (1), assuming a pairwise additive potential energy, yields the following equation of motion for the macroscopic density $\rho(\mathbf{r}, t | \dot{\gamma})$,

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t|\dot{\gamma}) = D\left\{\nabla^{2}\rho(\mathbf{r},t|\dot{\gamma}) + \beta\nabla\cdot\rho(\mathbf{r},t|\dot{\gamma})\int d\mathbf{r}'[\nabla V(|\mathbf{r}-\mathbf{r}'|)]\rho(\mathbf{r}',t|\dot{\gamma})g(\mathbf{r},\mathbf{r}',t|\dot{\gamma})\right\} - \nabla\cdot[\Gamma\cdot\mathbf{r}\rho(\mathbf{r},t|\dot{\gamma})],$$
(2)

where V is the pair-interaction potential. The time and shear rate dependences are denoted explicitly. A closed equation of motion for the macroscopic density is obtained when a sensible closure relation for the paircorrelation function $g(\mathbf{r}, \mathbf{r}', t | \dot{\gamma})$ can be derived. Since our interest is restricted to the *displacement* of the spinodal,

we only need to derive an appropriate form for the change of the pair-correlation function on applying a shear flow. The crucial thing here is that the pair-correlation function in Eq. (2) is multiplied in the integrand by the pair force $\nabla V(|\mathbf{r} - \mathbf{r}'|)$. A closure relation is therefore needed only for distances $|\mathbf{r} - \mathbf{r}'| \leq R_V$, with R_V the range of the pair-interaction potential. This fact has important consequences. First of all, relaxation of the stable short wavelength density fluctuations is very fast compared to relaxation (or demixing) rates of long wavelength density fluctuations, the dynamics of which is severely slowed down close to the spinodal [see, in this respect also, the comment below Eq. (10)]. As a consequence, the nonequilibrium pair-correlation function relaxes for distances $|\mathbf{r} - \mathbf{r}'| \le R_V$ on a time scale that still resolves the dynamics of the long wavelengths, which render the system unstable below the spinodal. For the small distances for which the closure relation is needed, the pair-correlation function can therefore be replaced by

the stationary solution $g^{\text{stat}}(|\mathbf{r} - \mathbf{r}'| \dot{\gamma})|_{\overline{\rho} = \rho((\mathbf{r} + \mathbf{r}')/2, t|\dot{\gamma})}$ of its equation of motion, at the local density $\rho((\mathbf{r} +$ $\mathbf{r}')/2, t|\dot{\boldsymbol{\gamma}})$. Without shear flow, the stationary solution is nothing but the equilibrium pair-correlation function, and this separation in time scales between demixing unstable long wavelengths, and the relaxation of stable small wavelengths may be regarded as the statistical analog of thermodynamic local equilibrium. In fact, Eq. (2) can be used to rederive the Cahn-Hilliard equation of motion for spinodal decomposition, where the assumption of thermodynamic local equilibrium is employed. Second, the equation of motion for the pair-correlation function [which can be obtained by integration of Eq. (1)] is regularly perturbed by the shear flow for such small distances, since the perturbing term in that equation, being equal to $-\nabla \cdot [\Gamma \cdot (\mathbf{r} - \mathbf{r}')g]$, is bounded from above by a form that is linear in the shear rate provided that $|\mathbf{r} - \mathbf{r}'| \le R_V$. In fact, it is readily shown that (with $\mathbf{R}=\mathbf{r}-\mathbf{r}^{\prime}),$

$$g^{\text{stat}}(\mathbf{R}|\dot{\boldsymbol{\gamma}})|_{\overline{\rho}=\rho((\mathbf{r}+\mathbf{r}')/2,t|\dot{\boldsymbol{\gamma}})} = g^{\text{eq}}(R)|_{\overline{\rho}=\rho((\mathbf{r}+\mathbf{r}')/2,t|\dot{\boldsymbol{\gamma}})} + F(\mathbf{R})|_{\overline{\rho}=\rho((\mathbf{r}+\mathbf{r}')/2,t|\dot{\boldsymbol{\gamma}})}\text{Pe}^{0} + \mathcal{O}((\text{Pe}^{0})^{2}) \quad \text{for } R \leq R_{V}, \quad (3)$$

where

$$Pe^0 = \frac{\dot{\gamma}R_V^2}{2D} \tag{4}$$

is the bare Peclet number, which measures shear induced microstructural distortion over distances of the order R_V . The function F in Eq. (3) describes the distortion of the pair-correlation function for small distances and can, in principle, be calculated as the linear response solution of its equation in motion.

Substitution of the closure relation (3) into the equation of motion (2), linearization with respect to the deviation $\delta \rho(\mathbf{r}, t | \dot{\gamma}) = \rho(\mathbf{r}, t | \dot{\gamma}) - \overline{\rho}$ of the density relative to the average density $\overline{\rho} = N/V$, Fourier transformation and expanding up to $\mathcal{O}((kR_V)^4)$ yields

$$\left[\frac{\partial}{\partial t} - \dot{\gamma}k_1\frac{\partial}{\partial k_2}\right]\delta\rho(\mathbf{k},t|\dot{\gamma}) = -D^{\text{eff}}(\mathbf{k}|\dot{\gamma})k^2\delta\rho(\mathbf{k},t|\dot{\gamma}),$$
(5)

with k_j the *j*th component of the wave vector, and where the effective diffusion coefficient is equal to

$$D^{\text{eff}}(\mathbf{k}|\dot{\boldsymbol{\gamma}}) = D \bigg[\beta \frac{\partial p^{\text{eq}}(\overline{\rho}, T)}{\partial \overline{\rho}} + f_0(\hat{\mathbf{k}}|\overline{\rho}, T) \text{Pe}^0 + k^2 [\beta \Sigma(\overline{\rho}, T) + f_1(\hat{\mathbf{k}}|\overline{\rho}, T) \text{Pe}^0] + \mathcal{O}((\text{Pe}^0)^2, (kR_V)^4) \bigg], \qquad (6)$$

with

 $p^{\rm eq}(\overline{\rho},T) = \overline{\rho}k_BT$

$$-\frac{2\pi}{3}\overline{\rho}^2 \int_0^\infty dR R^3 \frac{dV(R)}{dR} g^{\text{eq}}(R|\overline{\rho},T) \quad (7)$$

the pressure of the unsheared, equilibrium system (the density and temperature dependence of the paircorrelation function is denoted explicitly here), and

$$\Sigma(\overline{\rho}, T) = \frac{2\pi}{15} \overline{\rho} \int_0^\infty dR \, R^5 \, \frac{dV(R)}{dR} \\ \times \left[g^{\text{eq}}(R|\overline{\rho}, T) + \frac{1}{8} \, \overline{\rho} \frac{dg^{\text{eq}}(R|\overline{\rho}, T)}{d\overline{\rho}} \right] \quad (8)$$

is directly proportional to the Cahn-Hilliard squaregradient coefficient. Furthermore,

$$f_{0}(\hat{\mathbf{k}}|\overline{\rho},T) = -\beta\overline{\rho} \int d\mathbf{R}(\hat{\mathbf{k}}\cdot\mathbf{R})^{2} \frac{1}{R} \frac{dV(R)}{dR} \times \left[F(\mathbf{R}|\overline{\rho},T) + \frac{1}{2}\overline{\rho}\frac{\partial F(\mathbf{R}|\overline{\rho},T)}{\partial\overline{\rho}}\right], \quad (9)$$

$$f_{1}(\hat{\mathbf{k}}|\overline{\rho},T) = \frac{1}{6}\beta\overline{\rho}\int d\mathbf{R}(\hat{\mathbf{k}}\cdot\mathbf{R})^{4}\frac{1}{R}\frac{d\mathbf{v}(\mathbf{R})}{dR}$$
$$\times \left[F(\mathbf{R}|\overline{\rho},T) + \frac{1}{8}\overline{\rho}\frac{\partial F(\mathbf{R}|\overline{\rho},T)}{\partial\overline{\rho}}\right], (10)$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$ is the unit wave vector. These integrals can be evaluated after the function *F* is determined as the linear response solution of the equation of motion for the pair-correlation function for small distances $R = |\mathbf{r} - \mathbf{r}'| \le R_V$.

Notice that close to the spinodal, where $\beta \partial p^{eq} / \partial \overline{\rho}$ is small, the effective diffusion coefficient (6) for small wave vectors is much smaller than *D*. Together with the factor k^2 in Eq. (5) that multiplies the diffusion coefficient, this implies the separation of time scales for long and short wavelength dynamics referred to earlier in connection with the closure relation (3).

The spinodal is defined as the set of densities and temperatures where the system becomes unstable against density fluctuations of infinite wavelength and infinitesimally small amplitude. This happens if, and only if, the effective diffusion coefficient at zero wave vector becomes equal to 0. There is a subtlety involved here related to the dependence of the function f_0 in Eq. (6) for the effective diffusion coefficient on the direction of the wave vector. Wave vectors with the particular direction where f_0 attains its minimum value become unstable first. Let

$$f_0^{(-)}(\overline{\rho}, T) \equiv \min_{\hat{\mathbf{k}}} f_0(\hat{\mathbf{k}} | \overline{\rho}, T)$$
(11)

denote the minimum value of f_0 with respect to all directions of wave vector for a given density and temperature. The implicit relation between the temperature and the density that defines the spinodal now follows from Eq. (6),

$$\beta \frac{\partial p^{\text{eq}}(\overline{\rho}, T)}{\partial \overline{\rho}} + f_0^{(-)}(\overline{\rho}, T) \text{Pe}^0 = 0$$

defines the spinodal $T \equiv T(\overline{\rho})$, (12)

where higher order contributions in Pe⁰ are omitted. For zero shear rates this reproduces the well-known thermodynamic definition of the spinodal. The above relation is a generalization of that thermodynamic definition which includes effects of shear flow.

As $f_0^{(-)}$ is related to the short-ranged shear induced distortion of the pair-correlation function, we will assume that it is well behaved on the spinodal.

Let us first consider the displacement of the spinodal away from the critical point, where $\partial^2 p^{\text{eq}}(\overline{\rho}, T_s^0) / \partial \overline{\rho}^2 \neq 0$, where the subscript *s* refers to quantities on the spinodal, and the superscript 0 refers to the quiescent, unsheared system. Let δT_s denote the shift of the spinodal temperature at a given fixed number density $\overline{\rho}$ when a shear flow is applied. Writing $T_s = T_s^0 + \delta T_s$, with T_s and T_s^0 the spinodal temperature of the sheared and unsheared system, respectively, and expanding Eq. (12) up to leading order in δT_s and Pe⁰ gives

$$\delta T_s = -\frac{f_0^{(-)}(\overline{\rho}, T_s^0)}{\beta \partial^2 p^{\text{eq}}(\overline{\rho}, T_s^0)/\partial \overline{\rho}^2} \operatorname{Pe}^0.$$
(13)

The shift of the spinodal temperature at a given density is thus seen to vary linearly with the shear rate.

The above arguments fail at the critical point since there $\partial^2 p^{\text{eq}}(\overline{\rho}, T_c^0) / \partial \overline{\rho}^2 = 0$, where the subscript *c* is used to indicate quantities at the critical point, and, as above, a superscript 0 refers to the quiescent, unsheared equilibrium system. Close to the critical point of the unsheared system, the divergence of the reciprocal equilibrium compressibility is characterized by the critical exponent γ ,

$$\beta \frac{\partial p^{\text{eq}}(\overline{\rho}, T)}{\partial \overline{\rho}} = c(T - T_c^0)^{\gamma}, \qquad (14)$$

where *c* is a constant independent of density and temperature. Substitution of this expression into Eq. (12) yields the following prediction for the shift δT_c of the critical temperature:

$$\delta T_c = \left(\frac{-f_0^{(-)}(\overline{\rho}, T_c^0)}{c}\right)^{1/\gamma} (\mathrm{Pe}^0)^{1/\gamma}.$$
 (15)

Contrary to the displacement of the spinodal temperature away from the critical point, the displacement of the critical temperature is generally proportional to a fractional power of the shear rate.

In order to determine whether the spinodal temperature is increased or decreased by applying a shear flow, the linear response solution of the equation of motion for the pair-correlation function for small distances $|\mathbf{r} - \mathbf{r}'| \leq R_V$ should be calculated. This is beyond the scope of this Letter.

The turbidity of a colloidal system measures the total amount of light that is scattered by the colloidal particles, and is formally equal to an integral over the scattered intensity. The cloud-point curve is defined as the set of temperatures and densities where the turbidity diverges. This divergence is due to the development of long-ranged structure, that is, due to the long-ranged character of the pair-correlation function. The displacement of the cloudpoint curve due to shear flow is therefore related to the effect that the shearing motion has on the long-ranged structure of the pair-correlation function. This is different for the displacement of the spinodal, which is related to the effect of shearing motion on the short-ranged behavior of the pair-correlation function, as explained in detail above. Since the shear rate dependence of the long-ranged part of the pair-correlation function is highly nonlinear, contrary to its short-ranged part [see Eq. (3)], the displacement of the cloud-point curve is expected to be much more pronounced than for the spinodal. In the quiescent dispersion the cloud-point curve coincides with the spinodal. In a sheared system, however, the two do not coincide, since for the spinodal and cloud-point curve the distortion of the short-ranged and long-ranged part of the pair-correlation function are, respectively, responsible for their displacement. The cloud-point curve in a sheared system is expected to be located below the spinodal, in the unstable part of the phase diagram.

There are a number of experiments on systems with an upper critical point where the critical temperature is found to be lowered by shear flow, such as polystyrene/cellulose/benzene [6], polystyrene/polybutadiene/dioctylphthalate [7,8], isobuteric acid/water [9–11], and polystyrene/ trans-decaline of low molecular mass [12] (polystyrene solutions in trans-decaline with high molecular mass show a decrease of the critical temperature). For deformable particles, such as high molecular weight polymers, and anisometric particles, there is an additional effect of shear, not included in the present theory due to changes of interactions on the pair level as a result of single particle deformation and alignment.

In the above-mentioned systems an exponent for the shift of the critical temperature of about 0.50 is reported, except in Ref. [6], where a linear displacement of the critical temperature is found. It should be mentioned that in some of these experiments the location of the cloud-point curve might have been probed instead of the



FIG. 1. A schematic of the displacement of the spinodal due to shear flow, where a lowering of the spinodal due to shear and $\gamma > 1$ are assumed. The off-critical part of the spinodal is shifted linearly with the shear rate, while the critical point is shifted with the reciprocal critical exponent of the inverse compressibility $\partial p^{\text{eq}}(\overline{p}, T)/\partial \overline{p}$. The cloud-point curve in the sheared system is expected to be located far below the sheared spinodal, in the unstable part of the phase diagram.

critical point. It seems the displacement of the cloud point varies with the shear rate as $\dot{\gamma}^p$, with $p \approx 0.50$. The displacement of the cloud point as reported in Ref. [6] can indeed be fitted with such a power law.

When experiments on the displacement of the critical temperature are performed either at a somewhat offcritical density or at temperatures not very close to the critical point (so that γ attains its mean-field value 1), a linear displacement of the critical temperature will be found. No experiments on colloidal systems that unambiguously probe the location of the critical point exist as yet to test the above predictions.

The above predictions are summarized in Fig. 1, where a decrease of the spinodal temperature is assumed. Away from the critical point the displacement is linear in the shear rate; at the critical point the displacement is larger, provided that $\gamma > 1$, and there is a crossover between these two scenarios on approach of the critical point, as indicated by the dashed part of the spinodal of the sheared system.

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