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Hydrodynamic fluctuations, nonequilibrium equations of state, and the shift of the spinodal line in polymer solutions under flow

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In the literature, the shift of the spinodal line of polymer solutions under flow is attributed either to an actual shift of the spinodal due to a nonequilibrium modification of the equation of state for the chemical potential, or to an apparent shift due to an increase of hydrodynamic fluctuations owing to the flow. Here we see that both approaches are compatible and that both effects add up. [S1063-651X(97)00708-3]

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I. INTRODUCTION

Several authors (see [1] for a wide bibliography) have used thermodynamic models based on nonequilibrium chemical potentials including the effects of the shear to describe the shift of the spinodal line of polymer solutions submitted to a shear flow. The thermodynamic approach has been criticized from the point of view of a dynamical approach, taking into account the effects of the flow on the density fluctuations and, therefore, on the structure factor [2,3]. Indeed, most of the measurements of the effects of a shear flow on the phase diagram of polymer solutions [4,5] are based on the observation of an increase of the turbidity of the solutions in the presence of a sufficiently high value of the shear flow. This turbidity has been attributed either to a purely thermodynamic effect, i.e., to an actual shift of the spinodal line due to the shear flow [1], or to a purely dynamical effect, i.e., an enhancement of density fluctuations due to the shear [2,3]. Here, we see that both points of view are compatible and that their effects add up: i.e., the shear flow contributes to the thermodynamic equations of state and induces a shift of the spinodal line, and furthermore it also produces an enhancement of fluctuations which contribute to an increase of the turbidity, leading also to a further apparent shift of the spinodal line. The combination of both effects could explain why the available thermodynamic descriptions [1] predict a shift of the critical temperature or of the spinodal line which falls below the value corresponding to the observed increase of turbidity.

This paper is an extension both of our previous works [1], and of the works by Helfand and Fredrickson and by Onuki [2,3]. With respect to [1], where the nonequilibrium chemical potential of the so-called extended irreversible thermodynamics [6] was used to study the shift of the spinodal line, the main modification is to include the effects of the shear flow on the density fluctuations. With respect to [3] and [4], which paid special attention to the role of the flow on density fluctuations, the original aspect is to include a more detailed form of the nonequilibrium chemical potential which takes into account the flow contributions to the chemical potential and which yields a shift in the spinodal line.

In Sec. II we discuss the evolution equations for the density, the velocity, and the viscous pressure tensor and the form of the nonequilibrium free energy; Sec. III is devoted to the structure factor.

II. HYDRODYNAMICAL AND THERMODYNAMICAL EQUATIONS

The hydrodynamical equations describing the problem are the mass and momentum balance laws and the constitutive equation for the diffusion flux and the viscous pressure. The mass balance law for the solute may be written in the form

$$\frac{dc}{dt} = -\nabla\cdot\mathbf{J} \tag{1}$$

in which c is the monomer concentration related to the volume fraction ϕ by the expression $\phi = v_m c$, with v_m the molar volume of the monomer, and $\mathbf{J}$ the corresponding diffusion flux. As a constitutive equation for the diffusion flux we take

$$\mathbf{J} = -D'\nabla\mu - \beta\nabla\cdot\mathbf{P}^v, \tag{2}$$

where μ is the chemical potential, $\mathbf{P}^v$ the polymer contribution to the viscous pressure tensor, and D' and β are transport coefficients. This equation shows a coupling between viscous pressure and diffusion, and it has been used in different contexts as non-Fickian diffusion of small permeants in a polymer matrix [7] or flow-induced diffusion [8]. In particular, Helfand and Fredrickson take $D' = (\lambda/k_BT)c$ and $\beta = (\lambda/k_BT)$, with k_B the Boltzmann constant and λ a parameter which does not depend on the concentration c and which plays the role of the diffusion coefficient. For the sake of a more direct comparison with their results, we adopt here these forms.

When Eq. (2) is introduced into Eq. (1) one obtains

$$\frac{\partial c}{\partial t} + \mathbf{u}\cdot\nabla c = \frac{\lambda}{k_BT}\nabla\cdot(c\nabla\mu) + \frac{\lambda}{k_BT}\nabla\nabla{:}\mathbf{P}^v + \theta^v \tag{3}$$

except for the hydrodynamic noise θ^v, which has been included for the analysis of fluctuations.

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The balance equation for the linear momentum is the well-known equation of motion

$$\rho \frac{\partial \mathbf{u}}{\partial t} = T_{\perp} \cdot [-\rho \mathbf{u} \cdot \nabla \mathbf{u} + \eta_s \nabla^2 \mathbf{u} - \nabla \cdot \mathbf{P}^v + (\nabla c) \cdot \mu + \theta^u], \tag{4}$$

where $T_{\perp}$ is a transverse projection operator which reflects incompressibility ($\nabla \cdot \mathbf{u} = 0$), η_s is the solvent shear viscosity, and θ^u is the corresponding hydrodynamic noise.

As the evolution equation for the viscous pressure tensor we will take a generalized upper-convected Maxwell model [1]

$$\tau \left[\frac{\partial \mathbf{P}^v}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{P}^v - \mathbf{P}^v \cdot (\nabla \mathbf{u})^T - (\nabla \mathbf{u}) \cdot \mathbf{P}^v \right] = -\mathbf{P}^v - 2\eta (\nabla \mathbf{u})^s, \tag{5}$$

with τ the relaxation time and η the shear viscosity of the solution. This equation is not so general as that used by Helfand and Fredrickson [2], but the latter one reduces to Eq. (5) when the second normal stress coefficient is zero and for simple shear flows, which is the situation we are considering here.

The chemical potential may be obtained as the derivative of the free energy G. For the system constituted by n_1 moles of solvent and n_2 moles of a polymer of degree of polymerization N, we take for G the form

$$G = G_{\mathrm{eq}} + v_m (n_1 + N n_2) J (P_{12}^v)^2 + \frac{1}{2} \alpha^2 (\nabla c) \cdot (\nabla c), \tag{6}$$

where G_{eq} is the local-equilibrium free energy, which is given by the classical Flory-Huggins expression; the second term is the nonequilibrium contribution due to flow, i.e., to the presence of a nonvanishing viscous pressure tensor (since we are considering a Couette flow, we only take the xy or 12 component), where J is the steady-state compliance defined as $J = \tau / \eta$. The third term is the Ginzburg-Landau contribution of the concentration inhomogeneities with $\alpha^2 = RTv_m (2/\pi^2) R_g^2 \phi_0^{-1} N^{-1}$ a parameter related to the correlation length, R_g being the mean gyration radius of the macromolecules and ϕ_0 the mean-field value of the volume fraction. The second term was not included in the analyses in [3], whereas the third term was not included in [1].

The chemical potential of the solute at constant P_{12}^v is given by the functional derivative defined as

$$\mu = \frac{1}{V} \left(\frac{\delta G}{\delta c} \right)_{T, P_{12}^v} = \frac{1}{V} \left[\left(\frac{\partial G}{\partial c} \right)_{T, P_{12}^v} - \nabla \cdot \left(\frac{\partial G}{\partial \nabla c} \right) \right] \tag{7}$$

and accordingly it will have the form

$$\mu = \mu_{\mathrm{eq}}^{(\mathrm{FH})} + \mu^{(P)} - \alpha^2 \nabla^2 c, \tag{8}$$

where $\mu_{\mathrm{eq}}^{(\mathrm{FH})}$ is the classical Flory-Huggins contribution to the chemical potential and $\mu^{(P)}$ is the contribution of the nonvanishing viscous pressure due to the flow. The first term can be written as

$$\mu_{\mathrm{eq}}^{(\mathrm{FH})} = \mu_{\mathrm{eq}}^{(\mathrm{FH})}(\phi_0) + RTv_m [(1-\phi_0)^{-1} + (N\phi_0)^{-1} - 2\chi] \delta c, \tag{9}$$

where χ is the Flory-Huggins interaction parameter and δc is the perturbation in the concentration.

By inspection of Eq. (3) and Eqs. (6)–(8) it is seen that P_{12}^v contributes to Eq. (3) in two different ways through the first and second terms of the right-hand side. One could ask whether these two contributions include the same effects in two different ways. There are at least two arguments which show clearly that this is not so. (1) According to Eq. (6), the contribution coming from the nonclassical part of μ is of second order in P_{12}^{ν} whereas the contribution considered by Helfand and Fredickson [second term of the right-hand side of Eq. (3)] is of the first order in P_{12}^v. (2) If we consider a situation with homogeneous P_{12}^v but with an inhomogeneous concentration profile, the contribution considered by Helfand and Fredrickson vanishes (because it depends on the spatial derivatives of P_{12}^v), whereas our contribution, which in the linear aproximation has the form $(P_{12}^v)^2 (\partial J / \partial c) \nabla^2 c$, does not necessarily vanish. In fact, though this second argument points to a formal aspect which underlines the difference between the two contributions considered here, it may be more hypothetical than practical. Indeed, since the viscosity depends on the polymer concentration, in order to have a homogeneous P_{12}^v with an inhomogeneous concentration profile one should have a nonhomogeneous shear rate $\dot{\gamma}$ in such a way that $\eta \dot{\gamma}$ is constant, i.e., in such a way that the changes in the shear rate compensate the inhomogeneities in the viscosity.

Here, we use for the steady-state compliance $J = \tau / \eta$ the usual expression from the Rouse model

$$J = \frac{CM_2}{c' RT} \left[1 - \frac{\eta_s}{\eta} \right]^2, \tag{10}$$

where c' is the mass of polymer per unit volume, $C = 0.4$ is the Rouse parameter, and M_2 is the polymer molecular mass. Therefore the contribution of the shear to the free energy is

$$G^{(P)} = \frac{CM_2 v_m [\eta]}{RT} (P_{12}^v)^2 (n_1 + N n_2) F(x), \tag{11}$$

with

$$F(x) = x(1 + k_H x)^2 (1 + x + k_H x^2)^{-2}, \tag{12}$$

where k_H is the Huggins constant and $x = [\eta] M_0 c$ where $[\eta]$ is the intrinsic viscosity and M_0 is the monomer molecular mass. Therefore the nonequilibrium contribution of the flow to the chemical potential of the solute is

$$\mu^{(P)} = \frac{CM_2 v_m [\eta]}{RT} (P_{12}^v)^2 \left[\frac{F(x)}{1 - v_m c} + \frac{[\eta] M_0 F'(x)}{v_m} \right] \tag{13}$$

and can be expressed as

$$\mu^{(P)}=\mu^{(P)}(x_0)+\frac{CN[\eta]^3M_0^3}{RT}(P_{12}^v)^2\left[\frac{1}{x_0^2}F(x_0)+\frac{1}{x_0}F'(x_0)\right.$$
$$\left.+F''(x_0)\right]\delta c, \tag{14}$$

where $x_0=[\eta]M_0c_0$ and F' and F'' are the successive derivatives of F.

The values of the parameters will be taken for the system transdecalin-polystyrene [4,9], on which there are many experimental results. The molar mass of transdecalin is $M_1=0.138\ \mathrm{kg\,mol^{-1}}$, $v_1=1.586\times10^{-4}\ \mathrm{m^3\,mol^{-1}}$, and the solvent viscosity is 2.3×10^{-3} Pa s, whereas $M_0=0.104\ \mathrm{kg\,mol^{-1}}$ for the polystyrene, $N=5000$, $M_2=520\ \mathrm{kg\,mol^{-1}}$, $v_2=0.486\ \mathrm{m^3\,mol^{-1}}$, so that $v_m=v_2/N=9.7\times10^{-5}\ \mathrm{m^3\,mol^{-1}}$. The intrinsic viscosity of the solution is $[\eta]=0.043\ \mathrm{m^3\,kg^{-1}}$; the Huggins constant which describes the dependence of the viscosity as

$$\eta/\eta_s=1+[\eta]M_0c+k_H[\eta]^2M_0^2c^2 \tag{15}$$

is $k_H=1.40$; the parameters of the Flory-Huggins model are $\Theta=294.4$ K and $\Psi=0.50$ and the critical temperature foreseen for this model at equilibrium (zero shear rate) is $T_c\approx284$ K.

III. STRUCTURE FACTOR

The density fluctuations are crucial in the turbidity of the fluid. These fluctuations may increase either because one is approaching the spinodal line or because they are enhanced by the flow. We will take into account both factors in consideration. Our attention will be focused on the structure factor, defined as $S(\mathbf{k})=\langle\phi(\mathbf{k})\phi(-\mathbf{k})\rangle$ with $\mathbf{k}$ the wave vector, and which is proportional to the scattering intensity.

The flow contribution to $S(\mathbf{k})$ may be obtained by solving the equations of motion. According to Helfand and Fredrickson [2], this yields for $S(\mathbf{k})$

$$\left[2\overline{\lambda}\,\overline{\Omega}(\overline{\mathbf{k}})-\overline{\dot\gamma}\,\overline{k}_x\frac{\partial}{\partial\overline{k}_y}\right]S(\overline{\mathbf{k}})=2\overline{\lambda}\,\overline{k}^2, \tag{16}$$

where all the variables are reduced in accord with [2], i.e., $\overline{\dot\gamma}=\dot\gamma\tau$ for the shear rate ($\dot\gamma$ is the velocity gradient $\partial v_x/\partial y$), $\overline{\mathbf{k}}=\mathbf{k}R_g$ for the wave vector, and $\overline{\lambda}=\lambda T/(NR_g^2)$.

The function Ω can be written as

$$\Omega(\overline{\mathbf{k}})=\overline{k}^2[\overline{\varepsilon}+\overline{\varepsilon^{(P)}}-h(\beta)+\overline{\alpha^2}\,\overline{k}^2], \tag{17}$$

where the reduced variable $\overline{\alpha^2}=(\alpha^2N\phi_0)/(RTv_mR_g^2)$ has been introduced.

The respective contributions from the equilibrium free energy and the shear effects are taken into account in the terms

$$\overline{\varepsilon}=\phi_0N[(1-\phi_0)^{-1}+(N\phi_0)^{-1}-2\chi], \tag{18}$$

$$\overline{\varepsilon^{(P)}}=C\left(\frac{M_2[\eta]P_{12}^v}{RT}\right)^2[x_0^{-1}F(x_0)+F'(x_0)+x_0F''(x_0)]. \tag{19}$$

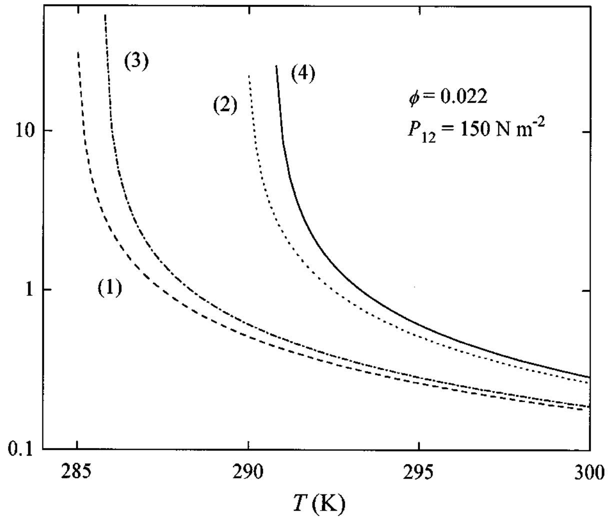

FIG. 1. Curves for $S(1)$ (i.e., for $k=1$) at an angle $\beta=36°$ [the value for which $h(\beta)$ has a maximum] in terms of T for the following situations: (1) equilibrium structure factor; (2) the nonequilibrium structure factor taking into account the flow contributions to $h(\beta)$; (3) the nonequilibrium structure factor if one considers only the flow contributions to $\overline{\varepsilon^{(P)}}$; and (4) the nonequilibrium structure factor that would follow if one considers the flow contributions (2) and (3).

It is manifested in Eq. (17) that Ω also depends on the angle β that $\mathbf{k}$ makes with the x axis (i.e., with the velocity) through the function defined as

$$h(\beta)=2l_xl_y\overline{\dot\gamma}\,\overline{\eta'}+l_x^2\overline{\dot\gamma}^2\overline{\Psi_1'}-[(l_x^2-l_y^2)\overline{\dot\gamma}\,\overline{\eta'}$$
$$-l_xl_y\overline{\dot\gamma}^2\overline{\Psi_1'}]\frac{l_x^2\overline{\dot\gamma}^2\overline{\Psi_1}}{\overline{\dot\gamma}(\overline{\eta}-\overline{\eta_s})+l_xl_y\overline{\dot\gamma}^2\overline{\Psi_1}}, \tag{20}$$

where $l_x=\cos\beta$ and $l_y=\sin\beta$.

The first normal stress coefficient is given by $\Psi_1=2\tau\eta$ in an upper-convected Maxwell fluid and the reduced quantities in Eq. (20) are defined as $\overline{\eta}=\eta Nv_m/(k_BT\tau)$ and $\overline{\Psi_1}=\Psi_1Nv_m/(k_BT\tau^2)$. This adimensionalization differs from that used by Helfand and Fredickson in a dimensionless factor $1/\phi_0$.

When $\overline{\lambda}\overline{\Omega}\gg\overline{\dot\gamma}$, S is given by

$$S(\overline{\mathbf{k}})=\frac{1}{\overline{\varepsilon}+\overline{\varepsilon^{(P)}}-h(\beta)+\overline{\alpha^2}\,\overline{k}^2}. \tag{21}$$

When $h(\beta)$ is positive, the shear flow contributes to the instability of fluctuations, which may grow to very high values.

Although the form of S is formally similar to that used by Helfand and Fredrikson, there are two interesting differences: (i) a term is incorporated to take into account nonequilibrium effects due to the flow contribution to the chemical potential; (ii) the form of $h(\beta)$ used in this paper is quantitatively different, though qualitatively similar, to that used in [3] because we have used different expressions for η and Ψ_1 than those taken in [3] and we have referred the values of the parameters to a different system, previously studied by us [10].

In Fig. 1 we plot the curves for $S(1)$ (i.e., for $k=1$), in terms of the temperature, for the following situations: (1) equilibrium structure factor according to the Flory-Huggins model (FH); (2) the nonequilibrium structure factor taking into account the flow contributions to $h(\beta)$; (3) the nonequilibrium structure factor if one considers only the flow contributions, but not those coming from $h(\beta)$; (4) the nonequilibrium structure factor that would follow if one considers the flow contributions both to $h(\beta)$ and to $\overline{\varepsilon^{(P)}}$. Curve 3 corresponds to the situation analysed in [1,10], where only the contributions of the flow were taken into account, but the role of the flow on the fluctuations was neglected; whereas curve 2 corresponds to the situation analyzed in [2], where the effects of the flow on the fluctuations were considered but not the contributions to the chemical potential. It is seen that the effects of the fluctuations on the shift of the apparent critical temperature (curve 2) are higher than those due to purely thermodynamical effects (curve 3), but the latter ones are not negligible and they should be taken into account in a detailed computation of the total shift in the critical temperature (curve 4).

IV. CONCLUDING REMARKS

The main point of this paper has been to include the effect of fluctuations into previous analyses [1] of the shear-induced shift of the spinodal line of polymer solutions under shear, as suggested by the literature which has outlined the strong effect of the flow on the fluctuations. It turns out that both effects (flow-enhanced density fluctuations and flow-induced shift of the spinodal line) are complementary, rather than incompatible. It must be mentioned that Helfand and Fredrickson's is not the only approach which takes into account the role of enhanced hydrodynamic fluctuations on the structure factor. Onuki [3] proposed also a dynamical theory for this phenomenon which, in its original form, did include in a phenomenological free energy the elastic energy of the distorted macromolecules but it ignored the coupling (2) between the shear viscous pressure and the diffusion flux. His approach was compared with that of Helfand and Fredrickson by Milner [11], who pointed out that the above-mentioned coupling is necessary. Such a coupling has been included in a more recent two-fluid model of polymer solutions under flow by Onuki [12].

When one includes both hydrodynamic and thermodynamic effects, it follows that an increase in the turbidity may appear for temperatures higher than the critical temperature. Thus, if one *a priori* identified this turbidity with the approach to the critical temperature, one would overestimate the value of the critical temperature under shear. This does not mean that the critical temperature itself is not modified by the flow. Indeed, our previous results based on the chemical potential including the effects of the flow gave for the shear-induced shift of the spinodal line lower values than those obtained from the experimental observation of turbidity. For instance we obtained [1] for a polystyrene in diotylphtalate at $P_{12}^{v}=200\ \mathrm{N\,m^{-2}}$ a shift of 3.5 K in the critical temperature under shear, whereas the observed shift according to the turbidity effects turns out to be, for this system under these conditions, of 14 K. It was argued in [1] that one possible reason of this discrepancy is that the concentration dependence of the coefficients appearing in the nonequilibrium contribution to the free energy (mainly the steady-state compliance) is not sufficiently known from the experimental point of view; and this uncertainty is amplified in its first and second derivatives with respect to the concentration. Here, we see that another possible reason of the discrepancy is the effect of the fluctuations, whose contribution to the shift in the apparent spinodal may be three or four times due to purely thermodynamic effects. However, a detailed study of the system analyzed in [1] requires the inclusion of non-Newtonian effects (i.e., the dependence of the shear viscosity on the shear rate) which is not taken into account in the model of Helfand and Fredickson. Therefore more experimental and theoretical research is necessary to completely clarify the different factors playing a role in the shift of the critical temperature under shear.

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