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Hydrodynamic interactions and the shear-induced shift of the critical point in polymer solutions

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The shift of the critical point of dilute polymer solutions under shear was studied explicitly, by starting from the Rouse–Zimm model and from a thermodynamic model based on a non-equilibrium Gibbs free energy which includes non-equilibrium corrections. The thermodynamic criterion for the spinodal line is compatible with the dynamic analyses when the normal pressure effects along the velocity gradient may be neglected and when the fluctuations vary only along the velocity gradient direction. Our main result is that the hydrodynamic interactions between macromolecules reduce the shift in the spinodal line.

(Keywords: polymer under shear; critical point; hydrodynamic interactions)

INTRODUCTION

The analysis of fluids under steady shear flows provides an interesting benchmark for non-equilibrium thermodynamics. On one hand, there is a very active interest on this topic both from a purely experimental point of view and from a molecular dynamic perspective[1–5], aiming especially to describe phase transitions under shear flow. On the other hand, there is considerable interest in building thermodynamic theories for non-equilibrium steady states going beyond the local-equilibrium thermodynamics[6–11]. In the latter theories, the equations of state in non-equilibrium steady states are not identical to the equilibrium equations of state, but they exhibit in general some non-equilibrium corrections dependent, for instance, on the shear rate or on the shear viscous pressure. Thus, the idea that the non-equilibrium equations of state could be used to describe the phase diagram of systems under shear arises in a rather natural way[1,2,12–15]. However, a pure extension of equilibrium criteria to non-equilibrium steady states would be too naive, and therefore it cannot be accepted without a sound dynamic justification. Thus, several authors[3,4,16,17] have stressed the need for a dynamic analysis. We have shown[18] that when the velocity fluctuations are assumed to be in the main flow direction and to vary in the velocity gradient direction, the condition for the spinodal line arising from the thermodynamic point of view is fully supported by the dynamic point of view, whereas otherwise other corrections due to the normal pressure in the velocity gradient direction must be taken into account, corrections which may be important in the analysis of some special phenomena. Therefore, though not completely general, the use of the non-equilibrium equations of state is certainly useful in the situations mentioned above and it may provide, in other circumstances, an approximation to the more complex real situation. Thermodynamic methods are appealing both for their simplicity and for the conceptual interest of generalizing equilibrium thermodynamics ideas to non-equilibrium states, with the appropriate cautions. Of course, the thermodynamic method, besides being more restricted than the dynamic one, is less powerful, because it can predict neither the dynamics nor the structure of the phase separation.

The aim of this paper is to study in a theoretical way the shift of the critical point of polymer solutions under shear in the framework of thermodynamic analysis by starting from the well known models of Rouse and Zimm[19–22] and from an explicit expression for the Gibbs free energy in non-equilibrium steady states[1,2,5,6,13–15]. This approach is valid as far as the system may be described by the Maxwell upper convected derivative model, where the normal stress along the direction of the flow is non-zero but the normal stresses in the other two directions are zero, thus satisfying the conditions where the thermodynamic method is supported by the dynamic one. In particular, we have three aims. First, we want to consider the role of hydrodynamic interactions on the effects of the shear on the shift of the critical point. This aspect, to our knowledge, has not been considered in the

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previous literature. Second, we want to compare the phase diagram at constant shear viscous pressure and at constant shear rate to emphasize the role of the different constraints on the shift of the critical point. Third, the use of the well known models of Rouse and Zimm allows an analysis which is not so dependent on the details of the several models that one must use in studying more realistic situations with high polymer concentration, high shear rates and non-Newtonian behaviour[1,15,23,24]. The price paid for this is a restriction to relatively low values of the shear rate: rather than a handicap, this restriction may be of interest, because previous analyses have focused their interest on relatively high shear rates.

THERMODYNAMICS UNDER SHEAR

In non-equilibrium steady states, the thermodynamic potentials do not have the same expression as in equilibrium, but they may include explicit non-equilibrium corrections due to the non-vanishing value of the fluxes or of the forces. In particular, for a system submitted to a shear viscous pressure P^v_{12}, the Gibbs free energy takes the form[1,2,5,6,13–15,25]

$$g(u, v, \mathbf{P}^v) = g_{\mathrm{eq}}(u, v) + vJ(P^v_{12})^2 \tag{1}$$

where g_{eq} is the Gibbs free energy of the system in equilibrium and the term P^v_{12} is the non-equilibrium correction due to the presence of the shear. Several authors independently introduced non-equilibrium corrections to describe the shift in the critical point[1,2]. The inclusion of non-equilibrium terms may be justified in polymer solutions by taking into account the stretching and orientation of the polymers due to the shear flow[25]. Furthermore, it may also be justified from a more general point of view along the lines of new thermodynamic formalisms, such as the so-called extended irreversible thermodynamics[5–7,13–15], which include the dissipative fluxes, such as heat flux, viscous pressure tensor, electric flux and so on, as independent variables in non-equilibrium systems in a wide perspective ranging from ideal gases to complicated macromolecules. In equation (1) u is the internal energy per unit mass, v is the specific volume of the system (volume per unit mass) and J is the steady-state compliance.

Starting from equation (1) one may obtain a non-equilibrium chemical potential and use it to analyse the phase diagram under shear. To do this explicitly it is necessary to have expressions both for the equilibrium Gibbs free energy g_{eq} and for the steady-state compliance J. These two points will be discussed here.

Equilibrium information

The expression most widely used for g_{eq} is that given by the classical Flory–Huggins theory[26,27], which leads to the following expression for the chemical potential of the solvent temperature T:

$$\frac{\mu_1^{(0)}}{RT} = \ln(1-\phi) + \left(1 - \frac{1}{m}\right)\phi + \chi\phi^2 \tag{2}$$

where ϕ stands for the volume fraction of polymer in the solution, m the ratio between the molar volumes of the polymer and the solvent, and the parameter χ is defined as

$$\chi = \frac{1}{2} + \psi\left(\frac{\theta}{T} - 1\right) \tag{3}$$

in which θ is the theta temperature and ψ a parameter that does not depend on T. This equation of Flory–Huggins has been used by Rangel–Nafaile *et al.*[1] to analyse phase separation in solutions of polystyrene (PS) in dioctylphthalate (DOP). However, other authors[2,23,24] have used a different model proposed later by Flory[28,29] in which the parameter χ is a function of the concentration. This point of view has been used by Wolf[2] to study the system transdecalin/polystyrene (TD/PS) starting from the measurements of osmotic pressure and of the cloud-point carried out by Nakata *et al.*[30]. Here, we will restrict our attention to the simplest model, in which χ does not depend on the concentration, and we will compare our theoretical findings with the experimental behaviour observed by Rangel–Nafaile *et al.*

According to the experimental results of Nakata *et al.*[30] it is possible to know the critical temperature of the system TD/PS without shear and to obtain the value of the corresponding parameters θ and ψ in the original Flory–Huggins model. For a solution of PS in TD one gets $\psi = 0.50$ and $\theta = 294.4\,\mathrm{K}$. Furthermore, starting from the values for the molar volumes given in ref. 2, namely, $V_1 = 1.586 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}}$ and $V_2 = 0.486\,\mathrm{m^3\,mol^{-1}}$ when the PS mass is $520\,\mathrm{kg\,mol^{-1}}$, one obtains $m = 3064$. This value agrees rather well with that obtained by interpolating the values calculated from the data for ϕ_c proposed by Nakata *et al.* for several solute molecular masses in the system TD/PS. When one uses these values of ψ, θ and m, one obtains (according to Flory–Huggins theory) $T_c = 284.1\,\mathrm{K}$ for the equilibrium critical temperature.

Non-equilibrium contribution

In the context of the cell model of the Flory theory, the non-equilibrium correction in equation (1) for n moles of the mixture takes the form

$$\Delta G^{(s)} = V_1 N J (P^v_{12})^2 \tag{4}$$

where $\Delta G^{(s)}$ describes the contribution of the shear to the Gibbs free energy. Here, V_1 is the molar volume of the solvent and N is defined as $N = n_1 + mn_2$, where n_i is the number of moles of component i. To use the previous expression $\Delta G^{(s)}$ to predict the changes in the phase diagram it is necessary to know how the steady-state compliance J depends on the composition of the mixture. The theoretical prediction of this dependence may be easily obtained if one assumes that the system behaves as a generalized Maxwell model in the context of linear viscoelasticity[5,19,20]. This allows us to write

$$J = \int_0^\infty sG(s)\,\mathrm{d}s\left[\int_0^\infty G(s)\mathrm{d}s\right]^{-2} = \sum_j \eta_j\tau_j\left[\sum_j \eta_j\right]^{-2} \tag{5}$$

where the sum in the denominator must include the solvent viscosity η_s besides the viscosities related to the different normal modes of the polymer.

Furthermore, according to the Rouse–Zimm model[19–22], the relaxation times τ_j are given in terms of the intrinsic viscosity $[\eta]$ and the polymer molecular mass M_2 as

$$\tau_j = \frac{6[\eta]M_2\eta_s}{\pi^2 RT} j^{-2} \tag{6}$$

in such a way that equation (5) finally becomes[31–33]

$$J = \frac{CM_2}{cRT}\left[1 - \frac{\eta_s}{\eta}\right]^2 \tag{7}$$

where c is the polymer concentration expressed in terms of mass per unit volume, η is the viscosity of the solution and C is a parameter whose value will be discussed below.

Concerning the explicit expression for J, it is convenient to analyse its dependence on concentration. The simplest scaling law would yield $J \sim c^{-1}$. However, it is important to take into account that η also depends on the concentration. The latter dependence is crucial in the analysis of the shift of the critical point, but it is not taken into account in the simple arguments against the use of a thermodynamic formalism in the non-equilibrium steady state: this is the main reason that the thermodynamic predictions based on the simplistic hypothesis that $J \sim c^{-1}$ yield unsatisfactory results.

It is necessary to know how η depends on the concentration of the mixture; the Martin equation is often used for that purpose. However, since on the present occasion we want to analyse the thermodynamic model generically, we have preferred not to use a specific functional for $\eta(c)$ but have simply taken the expansion

$$\frac{\eta}{\eta_s} = 1 + [\eta]c + k[\eta]^2 c^2 \tag{8}$$

where k is the so-called Huggins constant.

For the system TD/PS with a polymer molecular mass of 520 kg mol^{-1}, the value 1.40, an intrinsic viscosity of 0.043 m^3 kg^{-1} and a solvent viscosity $\eta_s = 0.0023$ Pa s are proposed in ref. 2. According to these values, equation (8) predicts a viscosity which is very close to that given by the Martin equation in a concentration range for which the product $c[\eta] < 1$. Since the critical density of the system is found in this range, this limitation is not very important in the analysis of the shift of the critical point.

INFLUENCE OF HYDRODYNAMIC INTERACTIONS

Though the expression for J is the same in the models of Rouse and of Zimm, the value of the parameter C differs in the two cases. When the hydrodynamic interactions are ignored, as in the Rouse model[21], the parameter C takes the value 0.4, whereas when one takes into account the hydrodynamic interactions, as in the Zimm model[22], the value of C is 0.206. In the Tshoegl model[34] an intermediate value is obtained. A comparison with experimental data shows[31–33] that Zimm's theory may be used for low concentrations, whereas when the concentration increases the system tends to the behaviour predicted by Rouse. Therefore, there is a slow shift from the Zimm model to the Rouse model with increasing polymer concentration, analogous to the shift which is observed with respect to the frequency dependence of the dynamic viscoelastic properties[34–37].

The transition from the behaviour described by Zimm to that described by Rouse with increasing polymer concentration is monotonous and reflects the fact that with increasing concentration the hydrodynamic effects become less relevant[31,32]; according to Holmes and Ferry[32] the decrease of these effects is seen not only in the change of the value of C with concentration, but also with the change of the frequency dependence mentioned previously.

In a formulation of the Rouse–Zimm model in terms of the parameter of hydrodynamic interaction, h, introduced by Zimm[22], it is possible to write, if one takes into account equation (5) and the details which are explicitly explained in chapter 15 of ref. 19

$$C = \left[\sum_j j^{-2(2+\sigma)}\right]\left[\sum_j j^{-2(2+\sigma)}\right]^{-2} \tag{9}$$

Following refs 38 and 39 it is possible to relate σ to h through

$$\sigma = -1.40[h(M-1)^{1/2}]^{0.78} \tag{10}$$

where M is the number of segments in the polymeric chain.

As a consequence, the parameter C allows us to describe in a quantitative way the intensity of the hydrodynamic interaction, but, since the latter depends on the composition of the system, we will assume that C is a function of the composition. Furthermore, the value of the parameter h is related to the degree of overlapping of the polymer coils, which is given by the reduced concentration $\tilde{c} = [\eta]c$. Since we do not have any theoretical argument to predict the functional dependence $C = C(\tilde{c})$ we propose the following form to describe the gradual transition from Zimm to Rouse behaviour:

$$C(\tilde{c}) = 0.206 + \frac{0.194\alpha\tilde{c}}{1 + \alpha\tilde{c}} \tag{11}$$

where α is a parameter that describes the steepness of the transition.

We may summarize our hypotheses in the expression

$$\frac{\Delta G^{(s)}}{RT} = BC\frac{(P^v_{12})^2}{T^2}NF(\tilde{c}) \tag{12}$$

where C is the Rouse–Zimm parameter and B is a constant defined as $B = V_1 M_2[\eta]/R^2$ and $F(\tilde{c})$ is a function of the concentration defined as

$$F(\tilde{c}) = \tilde{c}\left[\frac{1 + k\tilde{c}}{1 + \tilde{c} + k\tilde{c}^2}\right]^2 \tag{13}$$

where $\tilde{c}$ is the reduced concentration introduced earlier.

Even in the case where the phase separation in a polymer solution may be studied through a purely thermodynamic formalism starting from the generalization of the chemical potential, to carry out the explicit analysis it is also necessary to take into account the non-Newtonian character of the fluid under consideration[2,23,24], which implies a knowledge of how the viscosity of the solution depends on the value of the shear rate $\dot{\gamma}$. This introduces empirical equations for $\eta(\dot{\gamma})\dot{\gamma}$ and, therefore, new parametrizations in the theory are needed. In order to avoid these parametrizations and to keep only the essential ingredients we will consider only the case of Newtonian behaviour. In fact, it is in this regime where the Rouse–Zimm model is valid.

Since in equation (12) the viscoelastic effects are present through the intrinsic viscosity, we must investigate for which range of values of the shear rate the behaviour is Newtonian and $[\eta]$ is independent of the shear rate $\dot{\gamma}$. The early theoretical studies on solutions of linear flexible macromolecules[22,40–42] predicted a Newtonian behaviour for this kind of system as a consequence of the linear character of the viscoelastic models taken into account, and because it was necessary to include in Rouse's model such modifications as, for instance, the imperfect flexibility of chains[43,44] or a refined model of hydrodynamic interactions[45–47] to predict non-Newtonian behaviour. In contrast, the experimental analysis by Kotaka *et al.*[48] for solutions of polystyrene of different molecular masses in several solvents (1-chlorobutane, cycloexane and *trans*-decalin) made evident that, when one represents $[\eta]/[\eta]_0$ (where the subscript zero means that the intrinsic viscosity has been measured in the limit of low shear rate) in terms of the logarithm of the dimensionless parameter β defined as

$$\beta = \frac{[\eta]_0 M_2 \eta_s}{RT}\dot{\gamma} \tag{14}$$

One obtains a constant value which is equal to 1 for values of log β of the order of -1. For the system TD/PS the behaviour is no longer Newtonian for values of log $\beta > -0.75$.

Finally, we investigate the role of keeping constant the shear rate or the shear viscous pressure. As pointed out in a previous paper[13], these different physical conditions may lead to different non-equilibrium phase diagrams. Therefore, both situations will be considered here, by keeping constant either $\dot{\gamma}$ or P^{v}_{12} during the differentiation leading to the chemical potential. Therefore, we will take into account both the chemical potential $\mu_1^{(P)}$ at constant shear viscous pressure and the chemical potential $\mu_1^{(\dot{\gamma})}$ at constant shear rate, defined respectively as

$$\mu_1^{(P)} = \left(\frac{\partial \Delta G^{(s)}}{\partial n_1}\right)_{P_{12}} \qquad \mu_1^{(\dot{\gamma})} = \left(\frac{\partial \Delta G^{(s)}}{\partial n_1}\right)_{\dot{\gamma}} \tag{15}$$

At constant P^{v}_{12} the explicit expression for the chemical potential is

$$\frac{\mu_1^{(P)}}{RT} = -\frac{2B(P^{v}_{12})^2}{T^2} C \frac{P_5(\tilde{c})}{P_6(\tilde{c})} - \frac{B(P^{v}_{12})^2}{T^2} C \tag{16}$$

where C' stands for the derivative of the Rouse–Zimm parameter with respect to $\tilde{c}$ and with the introduction of the auxiliary functions

$$P_5(\tilde{c}) = (k-1)\tilde{c}^2 + (k^2 - 3k)\tilde{c}^3 - 3k^2\tilde{c}^4 - k^3\tilde{c}^5 \tag{17}$$

$$P_6(\tilde{c}) = (1 + \tilde{c} + k\tilde{c}^2)^3 \tag{18}$$

At constant shear rate $\dot{\gamma}$, the explicit expression for the chemical potential is

$$\frac{\mu_1^{(\dot{\gamma})}}{RT} = \frac{\mu_1^{(P)}}{RT} - \frac{2B\eta_s^2\dot{\gamma}^2}{T^2} C\Omega(\tilde{c}) \tag{19}$$

where Ω is a function of the composition defined as

$$\Omega(\tilde{c}) = \tilde{c}(1 + \tilde{c} + k\tilde{c}^2)(1 + 2k\tilde{c})F(\tilde{c}) \tag{20}$$

It is easy to show that the expression for the chemical potential at constant $\dot{\gamma}$ is less than the chemical potential at constant P^{v}_{12}.

The thermodynamic criterion for the stability limit $(\partial\mu/\partial c) = 0$ yields the following expression for the spinodal line

$$\frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1}{RT}\right) = \frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1^{(0)}}{RT}\right) + \frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1^{(s)}}{RT}\right) = 0$$

$$(s = P^{v}_{12}, \dot{\gamma}) \tag{21}$$

where the explicit expressions of the corresponding derivatives are given by

$$\frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1^{(0)}}{RT}\right) = -\frac{v}{1 - v\tilde{c}} + \left(1 - \frac{1}{m}\right)v + 2\chi v^2 \tilde{c} \tag{22}$$

with v a constant defined as $v = V_2/M_2[\eta]$. For $\mu_1^{(P)}$ and $\mu_1^{(\dot{\gamma})}$ one obtains, respectively,

$$\frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1^{(P)}}{RT}\right) = -\frac{2B(P^{v}_{12})^2}{T^2}$$

$$\left[C\frac{P_6P_5' - P_5P_6'}{P_6^2} + C'\left(\frac{P_5}{P_6} + F\right) + C''\tilde{c}F\right] \tag{23}$$

$$\frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1^{(\dot{\gamma})}}{RT}\right) = \frac{\partial}{\partial \tilde{c}}\left(\frac{\mu_1^{(P)}}{RT}\right) - \frac{2B\eta_s^2\dot{\gamma}^2}{T^2}$$

$$\left[C\frac{\Omega_2(1 + \tilde{c} + k\tilde{c}^2) - \Omega_1(1 + 2k\tilde{c})}{(1 + \tilde{c} + k\tilde{c}^2)^2} + C'\Omega\right] \tag{24}$$

In the latter expressions P_n' stand for the derivatives of P_n with respect to $\tilde{c}$ and C' and C'' are the first two derivatives of the Rouse–Zimm parameter C with respect to $\tilde{c}$. Furthermore, we have introduced the auxiliary functions

$$\Omega_1(\tilde{c}) = \tilde{c}^2 + 4k\tilde{c}^3 + 5k^2\tilde{c}^4 + 2k^3\tilde{c}^5 \tag{25}$$

$$\Omega_2(\tilde{c}) = 2\tilde{c} + 12k\tilde{c}^2 + 20k^2\tilde{c}^3 + 10k^3\tilde{c}^4 \tag{26}$$

RESULTS

To obtain explicit results we consider a solution of polystyrene of molecular mass 520 kg mol^{-1} in *trans*-decalin. The results by Kotaka *et al.*[48] allow us to conclude that it is reasonable to assume Newtonian behaviour for log $\beta < -0.75$, which implies that the non-Newtonian effects will appear for values of the shear rate $\dot{\gamma}$ higher than 8100 s^{-1}. Therefore, if the system is submitted to a constant shear rate of 1500 s^{-1} the behaviour will be Newtonian and we may apply equations (21)–(24) to obtain the spinodal curve. The corresponding equilibrium and non-equilibrium spinodal lines are shown in *Figure 1*, where it is seen that at constant $\dot{\gamma}$ the presence of the shear yields a lowering of the critical temperature. This is in agreement with experimental results[2] which indicate that, at constant $\dot{\gamma}$, non-Newtonian effects are necessary to yield an increase in the critical temperature, whereas one observes a

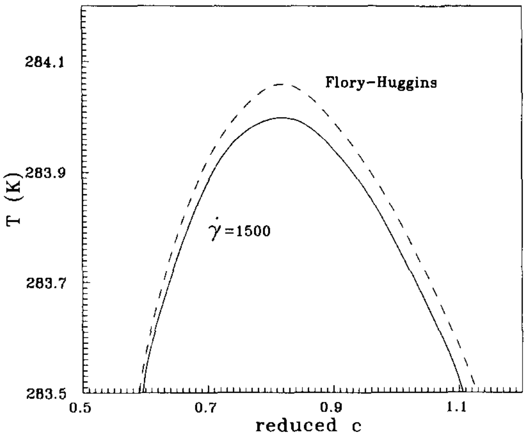

Figure 1 Spinodal curve of the binary solution at equilibrium (dashed line) and in a non-equilibrium steady state at constant shear rate $\dot{\gamma} = 1500\,\mathrm{s}^{-1}$ (continuous line)

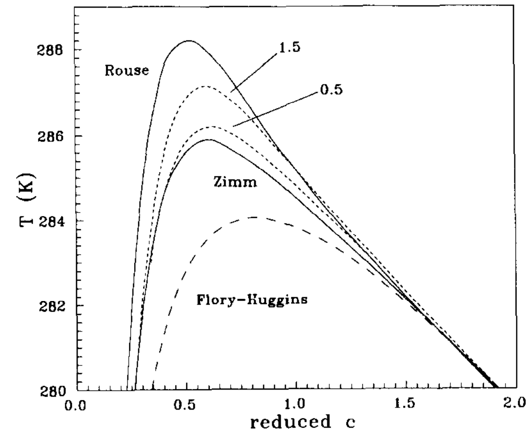

Figure 2 Spinodal curve of the binary solution at equilibrium (Flory–Huggins) and in a non-equilibrium steady state at constant shear viscous pressure $P_{12}^{v} = 150\,\mathrm{N\,m}^{-1}$. In the figure are shown the lines corresponding to the Rouse model (without hydrodynamic interactions), the Zimm model (which takes into account hydrodynamic interactions) and two intermediate models corresponding to the values $\alpha = 0.5$ and $\alpha = 1.5$ for the parameter α defined in equation (11), which describes the transition from the Rouse model to the Zimm model for increasing values of the concentration. It is seen that the higher the hydrodynamic interactions, the lower is the shift in the critical temperature

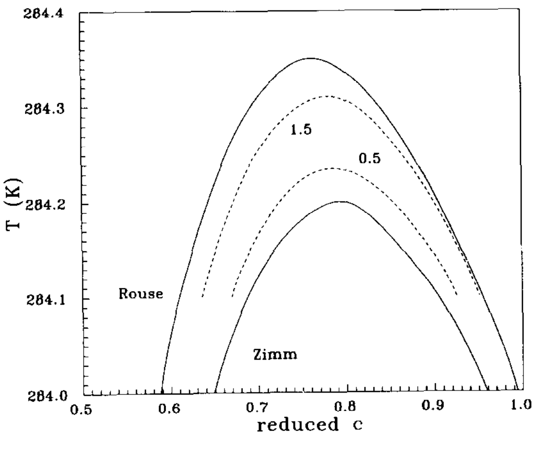

Figure 3 Spinodal lines for the binary solution in a non-equilibrium steady state at $P_{12}^{v} = 50\,\mathrm{N\,m}^{-2}$. The spinodal line corresponding to the equilibrium situation does not appear here, since it remains below the horizontal axis ($T = 284.0\,\mathrm{K}$). The lines correspond to the Rouse model, the Zimm model and two intermediate models corresponding to $\alpha = 0.5$ and $\alpha = 1.5$ for the parameter α defined in equation (11). The higher the hydrodynamic interactions, the lower is the increase in the critical temperature

lowering of the critical temperature for Newtonian fluids.

However, if one takes the same system submitted to constant P_{12}^{v}, the conclusion obtained from equations (21)–(24) is that there will be an increase in the critical temperature even in the Newtonian regime, as is seen in *Figures 2* and *3* corresponding to different values of the shear viscous pressure.

Another interesting point in *Figures 2* and *3* is the role of hydrodynamic effects in the shift of the critical point. It is seen that when these effects are neglected, as in the Rouse model, the shift in the critical point is maximal, and it is at a minimum in the Zimm model, where hydrodynamic interactions play a relevant role. Furthermore, it is seen that the parameter α in equation (11), which indicates how steep the transition is from Zimm to Rouse behaviour, also plays an important role in the shift of the critical point. The values considered here for P_{12}^{v} correspond to values of the shear rate which are less than the value of $8100\,\mathrm{s}^{-1}$ where non-Newtonian effects begin to be important. It is easy to see that for the values of P_{12}^{v} taken into account, the corresponding values of $\dot{\gamma}$ are in the range of $8600\,\mathrm{s}^{-1}$ for $\tilde{c} = 0.75$ and $2500\,\mathrm{s}^{-1}$ for $\tilde{c} = 2.0$. Though for higher values of P_{12}^{v} it is no longer consistent to assume Newtonian behaviour, the extrapolation of our model shows that the role of hydrodynamic interactions is more relevant in the shift (increase) of the critical temperature T_c than in the shift (decrease) of the critical concentration.

CONCLUSIONS

1. We have used as a starting point for the modelling of the non-equilibrium contribution to the free energy the usual Rouse and Zimm models, instead of the more complicated parametrizations which are often found in the literature. Though this implies a limit on the range of values of concentrations and shear rates it has the advantage of introducing a minimum of *ad hoc* assumptions in the analysis, so that it displays more clearly the essential effects.
2. We have shown that the hydrodynamic interactions amongst the macromolecules tend to minimize the shift in the critical point. We have studied how the steepness of the transition from the regime where the hydrodynamic interactions are relevant to the domain where they are irrelevant may influence the shift in the critical point. The steeper the transition, the higher the shift in the critical point.
3. The use of simple scaling laws for the steady-state compliance may be misleading in the prediction of the shift of the critical point, because there are dimensionless functions whose dependence on the concentration of the system plays a relevant role in the expression for the shift. Indeed, the condition $(\partial\mu_1/\partial c) = 0$ for the spinodal line yields, when equations (1), (2) and (4) are considered

$$\Delta\chi = \frac{V_1 P_{12}^2}{2RT}\frac{\partial^2 J}{\partial c^2} \tag{27}$$

with χ given by equation (3). Condition (27) is compatible with the dynamic results in equation (20) of ref. 3 when the fluctuations of concentration and velocity vary only along the y axis. If instead of equation (7) one takes the simple scaling law $J = CM_2(cRT)^{-1}$, it follows that $\partial^2 J/\partial c^2 > 0$, i.e. a shift towards lower temperatures is predicted, in contrast with the observed behaviour. It is seen in this paper that if equation (7) is used instead of the simple scaling law for J, and when the dependence of the viscosity on the concentration is taken into account, one is able to predict a temperature shift in the observed direction. Therefore, one may conclude that it is the use of simple scaling laws rather than the use of thermodynamic ideas that is invalid in the results obtained by combining equation (27) and the scaling laws.

4 We have shown that the phase diagram at constant shear rate may be rather different from the phase diagram at constant shear viscous pressure: in the first case the shear produces a decrease in the critical temperature whereas in the second case the shear $\dot{\gamma}$ yields a shift towards higher values of the critical temperature. In fact, the most realistic situation is to keep constant the shear stress, because this quantity is continuous across interfaces between droplets and fluids; however, some authors[2] have used constant shear rates, and have argued that this is a good approach when the droplets are very small. Thus, we have decided to compare the results obtained at constant shear stress with those obtained at constant shear rate. It turns out that, at least in the present system, the former results are consistent with the observed trends, whereas the latter ones predict a temperature shift in the opposite direction.

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