Definition of Nonequilibrium Chemical Potential: Phase Separation of Polymers in Shear Flow

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Received July 9, 1990

ABSTRACT: The definition of a chemical potential in nonequilibrium situations raises a problem about the quantities to be held fixed during the differentiation of the generalized Gibbs free energy. In this paper we compare two different definitions of the nonequilibrium chemical potential of polymers under shear flow, starting from the experimental data by Rangel-Nafaile et al. concerning phase-separation experiments, under shear. The definition at fixed shear viscous pressure turns out to be more suitable than the definition at fixed conformation proposed previously in the literature by some authors.

Introduction

The analysis of phase transitions in polymer solutions under shear flow has been the subject of intense interest in recent years. This interest is motivated not only by theoretical reasons but also by possible technological implications, because shear flows of polymer solutions are frequently found in an industrial context. Some authors have reported that phase separation in polystyrene solutions with high molecular weights is enhanced under shear flow, in such a way that the spinodal temperatures become higher than in quiescent solutions, the size of the shift being in some cases of several tens of degrees.[1,2] Other authors have observed a shear-induced dissolution in mixtures of low molecular weight polymer solutions.[3,4]

From a theoretical point of view, one of the most basic and interesting open questions is whether the spinodal line under flow can be obtained by means of a thermodynamic formalism, or whether it is necessary to go to a microscopic or to a kinetic description, the latter ones being more detailed but frequently much more difficultly handled. Several authors have developed different versions of a thermodynamics under shear in order to account for these phenomena[1,2,3,5] or for other ones such as plug formation in sheared suspensions.[6] The basis of these developments is that the elastic free energy stored in the system due to chain deformation and orientation must be included into the total free energy. Such a generalized free energy is supported from kinetic theory of polymeric liquids in some simple systems[7,8] such as Rouse-Zimm polymers, but it lacks for a rigorous microscopic basis in other, more complex, situations.

Besides the problem of the kinetic foundation, these kinds of thermodynamic analyses are faced with the shortcoming of a seemingly ad hoc motivation, in such a way that they seem to be no more than very particular models tailored to very specific physical situations. In fact, however, such models and attempts could be seen from a much more general perspective provided by recent developments in nonequilibrium thermodynamics, as the so-called extended irreversible thermodynamics (EIT)[9,10] or even from previous developments in nonequilibrium thermodynamics,[11] which concentrated their attention on constitutive relations rather than on equations of state. In EIT, the dissipative fluxes as the heat flux or the viscous pressure tensor are considered as independent variables of the thermodynamic potentials, which arise in a natural way when these fluxes obey relaxational equations. Extended irreversible thermodynamics has been applied on several occasions[12,13] to the description of polymeric solutions as a particular example. Other attempts to formulate a thermodynamics under shear have been stimulated by molecular-dynamical analyses of systems of soft spheres under shear[14] or from more abstract formalisms as the one based on dissipative Poisson brackets.[15]

The subsequent thermodynamic formalism contains, in its present form, some ambiguities, which should be carefully analyzed in order to refine it and to convert it into a useful tool. In our opinion, one of the most outstanding ambiguities is the specification of the conditions under which one should derive the free energy to obtain the chemical potential: this could be done at constant shear stress, constant shear rate, or constant deformation of the macromolecules. Of course, the most suitable definition will be related to the conditions under which the experiments are performed, but several doubts have arisen concerning this point. The object of the present paper is to reexamine critically some previous analyses of the phase separation in polymer solutions under shear flow by inquiring into the results obtained under different mathematical conditions, and by comparing them with the experimental results given in ref 2 and some theoretical results in ref 16.

In the next section we examine the form of the nonequilibrium free energy, from both macroscopic and microscopic points of view. In a later section we obtain the nonequilibrium spinodal lines under several shear stresses, and finally, we present and analyze our main conclusions.

Nonequilibrium Gibbs Free Energy

The usual formalism of nonequilibrium thermodynamics is based on the local equilibrium hypothesis, which states that the form of the thermodynamic potentials in nonequilibrium states is locally the same as in equilibrium. This hypothesis is satisfactory as far as the relaxation times of the nonconserved quantities is much smaller than the characteristic macroscopic times. In other situations, supplementary variables are needed for a more suitable description. In ideal gases or in simple fluids the relaxation times of the nonconserved quantities are very short, so that the effect of the independent character of the fast variables is only perceptible at high frequencies, as in ultrasound propagation or light scattering in gases or neutron scattering in liquids. In polymers, the configurational

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0024-9297/91/2224-2834$02.50/0

relaxation times of the macromolecules are relatively long so that the molecular configuration becomes an independent variable that must be included into the free energy or any other thermodynamic potential. Since the macromolecular configuration is related to the viscous pressure tensor, it could equally be said that the thermodynamic potentials may depend on the viscous pressure tensor. We neglect for simplicity the influence of other possible dissipative fluxes, as the heat flux or the diffusion flux.

The Gibbs free energy of the system under shear flow characterized by a viscous pressure tensor $\mathbf{P}^{v}$ may be written as

$$G(T,p,\phi,\dot{\mathbf{P}}^{v}) = G_{eq}(T,p,\phi) + (V/4)\Phi(T,p,\phi,\dot{\mathbf{P}}^{v})\dot{\mathbf{P}}^{v}:\dot{\mathbf{P}}^{v} \quad (1)$$

where the : symbol stands for the double contraction of the corresponding traceless part tensors, V is the total volume, and Φ is a function whose meaning will be explained in (2) and (15) below. For low shear rates, expression 1 takes in extended thermodynamics the form[12]

$$G(T,p,\phi,\dot{\mathbf{P}}^{v}) = G_{eq}(T,p,\phi) + (V/4)\sum_{i}(\tau_i/\eta_i)\dot{\mathbf{P}}^{v}:\dot{\mathbf{P}}^{v} \quad (2)$$

The total viscous pressure tensor $\mathbf{P}^{v}$ has been assumed to decompose as a sum of several independent contributions related to different internal degrees of freedom

$$\mathbf{P}^{v} = \sum_{i}\mathbf{P}_{i}^{v} \quad (3)$$

By use of the Kramers expression for the viscous pressure tensor for bead–spring chains, the relationships between $\mathbf{P}_i^{v}$ and the normal coordinates Q_i' ($i = 1, ..., N - 1$), with N the number of monomers in the chain, in the Rouse model is given by

$$\mathbf{P}_{i}^{v} = -nH\langle Q_i'Q_i'\rangle + nkT\mathbf{U} \quad (4)$$

H being the elastic constant characterizing the intramolecular interactions, n the number of chains per unit volume, $\mathbf{U}$ the unit matrix, and the angular brackets meaning an equilibrium average over the configurations. The τ_i and η_i in (2) are the respective relaxation time and shear viscosity related to the ith normal mode, as defined in the evolution equation for $\mathbf{P}_i^{v}$, namely

$$\mathbf{P}_{i}^{v} + \tau_i(\mathbf{P}_{i}^{v})_{(1)} = -2\eta_i\mathbf{V} \quad (5)$$

with $\mathbf{V}$ the symmetric part of the velocity gradient and $(\mathbf{P}_i^{v})_{(1)}$ the contravariant convective derivative (see p 395 of ref 8).

At higher shear rates, more complicated expressions appear in the free energy. The free energy for a Rouse model in arbitrary flow field has the form[7]

$$G = G_{eq} + (^1/_2)nkT[\sum_{i}\mathrm{Tr}(\mathbf{P}_{i}'^{v}) - \sum_{i}\ln|\det(\mathbf{P}_{i}'^{v} + \mathbf{U})|] \quad (6)$$

with $\mathbf{P}_i'^{v}$ defined as $\mathbf{P}_i'^{v} = (1/nkT)\mathbf{P}_i^{v}$. Under a shear flow, the $\mathbf{P}^{v}$ have the form

$$\mathbf{P}^{v} = \begin{bmatrix} P_{11}^{v} & P_{12}^{v} & 0 \\ P_{12}^{v} & P_{22}^{v} & 0 \\ 0 & 0 & P_{33}^{v} \end{bmatrix} \quad (7)$$

The normal and tangential pressures are related to $\dot{\gamma}$, the shear rate, as[8]

$$P_{12}^{v} = -\eta(\dot{\gamma})\dot{\gamma};\quad P_{11}^{v} - P_{22}^{v} = -\psi_1(\dot{\gamma})\dot{\gamma}^2;\quad P_{22}^{v} - P_{33}^{v} = -\psi_2(\dot{\gamma})\dot{\gamma}^2 \quad (8)$$

where η is the shear viscosity and ψ_1 and ψ_2 are the first and second normal stress coefficients. For small values of the shear rate, one recovers expression 2 whereas for high values of $\dot{\gamma}^2$ the second term in brackets in (6) may be neglected and one simply has

$$G = G_{eq} + (V/2)\,\mathrm{Tr}\,\mathbf{P}^{v} \quad (9)$$

i.e., the main contribution to the free energy comes in this case from the normal components of the stress tensor. Expression 8 was proposed in ref 17 and was used in refs 2 and 3 as the basis for the analyses of experimental data. Usually it is written $\mathrm{Tr}\,\mathbf{P}^{v} = 2\mathbf{J}_e\,(P_{12}^{v})^2$ with $\mathbf{J}_e$ the steady-state shear compliance, so that even in this situation one may write the free energy as in (1).

One could also write the free energy in terms of the configurational tensor $\mathbf{W}$ related to the configuration of the macromolecule; for Rouse polymers $\mathbf{W}$ is defined as

$$\mathbf{W} = (1/N)\sum_{j}\langle Q_jQ_j\rangle - \mathbf{U} \quad (10)$$

where $Q_j = r_{j+1} - r_j$ is the relative position vector of bead $j + 1$ with respect to bead j. For more concentrated solutions $\mathbf{W}$ may be defined by considering the relative position of the successive entanglement points instead that those of the beads.[16] We do not enter here into the specific details but simply note that $\mathbf{W}$ can be supposed to obey an evolution equation[16] of the form

$$\left(\frac{\partial}{\partial t} + \upsilon\cdot\nabla\right)\mathbf{W} = 2\mathbf{V} + 2(\mathbf{V}\cdot\mathbf{W} + \mathbf{W}\cdot\mathbf{V}) - (1/\tau)\mathbf{W} \quad (11)$$

with υ the velocity field and τ the relaxation time of $\mathbf{W}$. In steady state and for not very high shear rate one has

$$\mathbf{W} = 2\tau\mathbf{V} \quad (12)$$

The tensor $\mathbf{W}$ may also be related to the viscous pressure tensor as[16]

$$\mathbf{P}^{v} = -EkT\mathbf{W} \quad (13)$$

an expression that is valid in the linear approximation, with EkT being the elastic modulus of polymers. In this case, one may assume a free energy of the form

$$G = G_{eq} + (^1/_4)(EkT)\mathbf{W}:\mathbf{W} \quad (14)$$

which may also be written in terms of $\mathbf{P}^{v}$ as

$$G = G_{eq} + (^1/_4)(1/EkT)\mathbf{P}^{v}:\mathbf{P}^{v} \quad (15)$$

Note, incidentally, that this has the form (2) predicted by EIT at low shear rates.

The behavior of the coefficient E is[16] of the form $E \sim a^{-3}\phi/N$ for low polymer concentrations ϕ and $E \sim a^{-3}\phi^3$ for high ϕ, with a the dimension of the monomers. According to these asymptotic forms, one could obtain different expressions for the chemical potential depending on the quantity kept constant on the derivation, either $\mathbf{P}^{v}$ or $\mathbf{W}$. Since the spinodal line will be given by equating to zero the second derivative of the free energy, question also arises as to what quantity must be kept fixed in the second derivative. If $\mathbf{P}^{v}$ or $\mathbf{W}$ is kept constant in the first and in the second derivatives, the form $E \sim \phi^3$ leads to a decrease in the spinodal temperatures, whereas if one quantity is kept constant in the first derivative and the other quantity is kept fixed during the second derivative ($\mathbf{W}$ and $\mathbf{P}^{v}$ or $\mathbf{P}^{v}$ and $\mathbf{W}$, respectively) an increase in the spinodal line would follow.

In his dynamical analysis of the stability of the polymer solutions under shear flow, Onuki[16] has taken the point of view that the first derivative must be taken at constant **W** and the second at constant $\mathbf{P}^{v}$ in order to be able to obtain an increase in the critical temperature in a solution under a given shear stress. Nevertheless, the analysis of Onuki is not conclusive, because his results are not directly compared with experimental data. His dynamical analysis could have also been performed by defining the chemical potential at constant $\mathbf{P}^{v}$ instead of at constant deformation **W**, and his predictions about the size and the sign of the shift in the critical temperature would have been different. His choice has been motivated to obtain a shift of the spinodal line to higher temperatures in the regime where $E \sim \phi^3$. However, the experimental data do not correspond to this regime, but to a more complicated situation regime which deserves a careful analysis. This will be done in the next section.

Nonequilibrium Spinodal Lines

In this section we obtain numerically the spinodal lines under shear at different shear rates in two different situations: (a) the chemical potential is defined at constant $\mathbf{P}^{v}$; (b) the chemical potential is defined at constant deformation **W**. The second and third derivatives of the Gibbs free energy will be taken at constant $\mathbf{P}^{v}$, since this is the condition imposed on the system. We have based our analysis on the experimental data obtained by Rangel-Nafaile et al.[2] dealing with the polystyrene dioctyl phthalate system.

In the absence of shear, one assumes that the Gibbs free energy of the solution has the well-known Flory–Huggins form

$$\Delta G_{\mathrm{FH}}/RT = n_1 \ln (1-\phi) + n_2 \ln \phi + \chi(1-\phi)N\phi \qquad (16)$$

with ϕ, the volume fraction of the polymer, defined as

$$\phi = n_2 m(n_1 + mn_2)^{-1} \qquad (17)$$

and N is given by

$$N = n_1 + mn_2 \qquad (18)$$

The parameter m is evaluated from the critical point of quiescent solution. For $M_1 = 390.6$ g/mol, $M_n = 1.38 \times 10^6$ g/mol, solvent density is 0.9 g cm^{-3}, $T_c = 285$ K, and estimating[2] the critical concentration as 0.015 g/mL, we evaluated $m = 3515.6$. The interaction parameter χ is assumed to depend on the temperature as

$$\chi = 0.5 + \Psi_1(\theta/T - 1) \qquad (19)$$

with Ψ_1 a constant and θ the θ temperature of the solution whose numerical values are[2] $\Psi_1 = 1.48$ and $\theta = 288$.

To the Flory–Huggins expression we add the nonequilibrium contribution which, following ref 2, we take as

$$\Delta G_s = (vN/2)\,\mathrm{Tr}\,\mathbf{P}^{v} = vNJ_e(P_{12}^{v})^2 \qquad (20)$$

with v the molar volume of solvent and where J_e depends on ϕ and P_{12}^{v}. Alternatively, one could write (20) in terms of the deformation W_{12} related to P_{12}^{v} as

$$W_{12} = -2vNJ_eP_{12}^{v} \qquad (21)$$

This relation has been obtained from (13) by writing the expression for EkT resulting from a comparison of (20) with (30). Using (20) and (21), we get the expression

$$\Delta G_s = ({}^1/_4)(vNJ_e)^{-1}\,W_{12}^{2} \qquad (20')$$

The values of $\mathrm{Tr}\,\mathbf{P}^{v}$ given by Rangel-Nafaile et al.[2] have been adjusted to an empirical function of volume fraction and of the shear stress of the form

$$\mathrm{Tr}\,\mathbf{P}^{v} = a\phi^{k}\exp(-b\phi^{n}) \qquad (22)$$

or according to the definition of J_e in (20)

$$J_e = \alpha\phi^{k}\exp(-b\phi^{n}) \qquad (23)$$

with $\alpha = a/2P_{12}^{2}$. Here, a, b, and n depend on P_{12} as

$$b = k/(n\phi_o^{\,n}) \qquad a = y_o\phi_o^{-k}\exp(k/n) \qquad (24)$$

where n and y_o depend on P_{12}^{v} in accordance with the empirical relations

$$n = \beta(P_{12}^{v})^{-\gamma} \qquad y_o = \delta\exp[B(P_{12}^{v})^{1/2}] \qquad (25)$$

with β, γ, δ, and B being strict constants. The meaning of y_o and ϕ_o is given in the Appendix, where the numerical values of all parameters ensuing from these empirical correlations are also given.

When the latter expressions of n and y_o are introduced into (24), one obtains

$$a = 2A\exp(\tau) \qquad (26)$$

with

$$A = ({}^1/_2)\delta\phi_o^{-k}$$

$$\tau = B(P_{12}^{v})^{1/2} + (k/\beta)(P_{12}^{v})^{\gamma} \qquad (26')$$

and one formally arrives at

$$J_e = A(P_{12}^{v})^{-2}\phi^{k}\exp(\tau - b\phi^{n}) \qquad (27)$$

which accounts for the dependence of J_e on ϕ and P_{12}^{v}.

By starting from definition 23, one may obtain the derivatives of J_e with respect to ϕ and to P_{12}^{v}, which will be of further use. One has

$$\left(\frac{\partial J_e}{\partial\phi}\right)_{P_{12}} = \phi^{-1}FJ_e \qquad (28)$$

with

$$F = k - bn\phi^{n} \qquad (29)$$

and

$$\left(\frac{\partial J_e}{\partial P_{12}^{v}}\right)_{\phi} = (P_{12}^{v})^{-1}J_e(\tilde{F} - 2) \qquad (30)$$

where

$$\tilde{F} = (B/2)(P_{12}^{v})^{1/2} + (\gamma k/\beta)(P_{12}^{v})^{\gamma} - b\gamma\phi^{n}[1 - n\ln(\phi/\phi_o)] \qquad (31)$$

We proceed now to obtain the chemical potential of the components in accordance with the usual definition

$$\mu_i = \left(\frac{\partial\,\Delta G}{\partial\,n_i}\right)_{T,p,Z} \qquad (32)$$

with Z a nonequilibrium quantity, as P_{12}^{v} or W_{12}. Since ΔG depends functionally on ϕ rather than explicitly on n_i, one has

$$\mu_i = \left(\frac{\partial\,\Delta G}{\partial\phi}\right)\left(\frac{\partial\phi}{\partial n_i}\right) \qquad (33)$$

From (17) and (18) one obtains

$$\frac{\partial\phi}{\partial n_1} = -\frac{\phi}{N} \qquad \frac{\partial\phi}{\partial n_2} = \frac{m}{N}(1-\phi) \qquad (34)$$

The equilibrium chemical potentials from the Flory–Hug-

Table I

$F' = -bn^2\phi^{n-1}$

$F'' = -bn^2(n-1)\phi^{n-2}$

$\tilde{F}' = -\gamma F' \ln(\phi/\phi_0)$

$\tilde{F}'' = -\gamma F'' \ln(\phi/\phi_0) - \gamma F'{}^{-1}\phi$

[a] Expressions for F', F'', $\tilde{F}'$, and $\tilde{F}''$ are defined in the text.

gins free energy have the form

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

$$\left(\frac{\mu_2}{RT}\right)^{\mathrm{FH}} = \ln\phi + (1-m)(1-\phi) + \chi m(1-\phi)^2 \tag{35}$$

Concerning the nonequilibrium contribution, one must take care about whether $P_{12}{}^{\mathrm{v}}$ or W_{12} is kept fixed during the derivation. At constant $P_{12}{}^{\mathrm{v}}$ the most direct procedure is to start from the definition of ΔG_{s} given by (20), so that

$$\left(\frac{\mu_i}{RT}\right)^{\mathrm{s}}_{P_{12}} = \frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2\frac{\partial}{\partial n_i}(NJ_{\mathrm{e}}) \tag{36}$$

Recalling (18) and (34) and (28), the latter expression for $i = 1$ becomes

$$\left(\frac{\mu_1}{RT}\right)^{\mathrm{s}}_{P_{12}} = -\frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2 J_{\mathrm{e}}(F-1) \tag{37}$$

When the differentiation is carried out at fixed deformation W_{12}, the calculations are now lengthy because of relation 21, which implies

$$\left(\frac{\partial P_{12}{}^{\mathrm{v}}}{\partial\phi}\right)_{W_{12}} = -\frac{P_{12}{}^{\mathrm{v}}}{N}\,\frac{\dfrac{\partial N}{\partial\phi}J_{\mathrm{e}} + N\left(\dfrac{\partial J_{\mathrm{e}}}{\partial\phi}\right)_{P_{12}{}^{\mathrm{v}}}}{J_{\mathrm{e}} + P_{12}{}^{\mathrm{v}}\left(\dfrac{\partial J_{\mathrm{e}}}{\partial P_{12}{}^{\mathrm{v}}}\right)_{\phi}} \tag{38}$$

According to (34), this derivative may be written as

$$\left(\frac{\partial P_{12}{}^{\mathrm{v}}}{\partial\phi}\right)_{W_{12}} = -(F-1)(\tilde{F}-1)^{-1}P_{12}{}^{\mathrm{v}}\phi^{-1} \tag{39}$$

The expression for μ_1 at constant W_{12} ensuing from (20′) and (39) is

$$\left(\frac{\mu_i}{RT}\right)^{\mathrm{s}}_{W_{12}} = -\frac{W_{12}{}^2}{4RTv}(NJ_{\mathrm{e}})^{-2}\left(\frac{\partial}{\partial n_i}NJ_{\mathrm{e}}\right)_{W_{12}} \tag{40}$$

where the derivative with respect to n_i must be done by taking into account the functional dependence of $P_{12}{}^{\mathrm{v}}$ with respect to ϕ at constant W_{12}, i.e.

$$NJ_{\mathrm{e}} = \Xi[P_{12}{}^{\mathrm{v}}(\phi),\phi] \tag{41}$$

After lengthy calculations, and making use of (28), (30), (34), and (39), one obtains for $i = 1$

$$\left(\frac{\mu_1}{RT}\right)^{\mathrm{s}}_{W_{12}} = \frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2 J_{\mathrm{e}}(F-1)(\tilde{F}-1)^{-1} \tag{42}$$

The spinodal line in the plane T, ϕ is given by the condition

$$\partial\mu_1/\partial\phi = 0 \tag{43}$$

and the critical temperature, corresponding to the maximum of the spinodal line, is specified by the further condition

$$\partial^2\mu_1/\partial\phi^2 = 0 \tag{44}$$

where these derivatives are calculated at constant $P_{12}{}^{\mathrm{v}}$, because the experimental data we have at hand[2] correspond to a situation in which the system is submitted to a constant shear stress.

From the Flory–Huggins expression, one immediately obtains for (43) and (44)

$$\frac{1}{RT}\left(\frac{\partial\mu_1}{\partial\phi}\right)^{\mathrm{FH}} = -(1-\phi)^{-1} + \left(1-\frac{1}{m}\right) + 2\chi\phi = 0 \tag{45}$$

and

$$\frac{1}{RT}\left(\frac{\partial^2\mu_1}{\partial\phi^2}\right)^{\mathrm{FH}} = -(1-\phi)^{-2} + 2\chi = 0 \tag{46}$$

The coordinates of the critical point for quiescent solution can be obtained from (45) and (46), where the dependence with respect to T comes from (35).

From the definition of the chemical potential at constant $P_{12}{}^{\mathrm{v}}$, the critical point will be obtained by adding to (45) and (46) the derivatives of (37) with respect to ϕ. The latter are given by

$$\frac{\partial}{\partial\phi}\left(\frac{\mu_1}{RT}\right)^{\mathrm{s}}_{P_{12}} = -\frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2 J_{\mathrm{e}}[\phi^{-1}F(F-1) + F'] \tag{47}$$

and the second derivative is seen to be

$$\frac{\partial^2}{\partial\phi^2}\left(\frac{\mu_1}{RT}\right)^{\mathrm{s}}_{P_{12}} = -\frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2 J_{\mathrm{e}}[\phi^{-2}F(F-1)^2 + \phi^{-1}(3F-1)F' + F''] \tag{48}$$

with the expression for F' and F'' given in Table I.

Let us now calculate the critical point at fixed deformation W_{12}. Our starting point will be (42), and one obtains

$$\frac{\partial}{\partial\phi}\left(\frac{\mu_i}{RT}\right)^{\mathrm{s}}_{W_{12}} = \frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2 J_{\mathrm{e}}X \tag{49}$$

with X defined as

$$X = \phi^{-1}\frac{F(F-1)}{\tilde{F}-1} + \frac{(\tilde{F}-1)F' - (F-1)\tilde{F}'}{(\tilde{F}-1)^2} \tag{50}$$

The second derivative of μ_1 with respect to ϕ at constant $P_{12}{}^{\mathrm{v}}$ is given by

$$\frac{\partial^2}{\partial\phi^2}\left(\frac{\mu_i}{RT}\right)^{\mathrm{s}}_{W_{12}} = \frac{v}{RT}(P_{12}{}^{\mathrm{v}})^2 J_{\mathrm{e}}(\phi^{-1}FX + X') \tag{51}$$

with

$$X' = -\phi^{-2}\frac{F(F-1)}{\tilde{F}-1} + \phi^{-1}(\tilde{F}-1)^{-1}\left[(2F-1)F' - \frac{F(F-1)\tilde{F}'}{\tilde{F}-1}\right] + (\tilde{F}-1)^{-1}\left[F'' - \frac{2F'\tilde{F}' + (F-1)\tilde{F}''}{\tilde{F}-1} + \frac{2(F-1)\tilde{F}'^2}{(\tilde{F}-1)^2}\right] \tag{52}$$

The expressions for $\tilde{F}'$ and $\tilde{F}''$ are given in Table I.

In Figures 1 and 2 we have represented the spinodal lines obtained from the two different definitions of the chemical potentials. It follows from our analysis that the curves ensuing from the definition of the chemical potential as the derivative at constant $P_{12}{}^{\mathrm{v}}$ are more satisfactory than those coming from the chemical potential defined at constant deformation W_{12}. It must be noted that in both cases there is an increase in the critical temperature for $P_{12}{}^{\mathrm{v}} = 200$ N m^{-2} and $P_{12}{}^{\mathrm{v}} = 400$ N m^{-2}. However, there is a critical point at $P_{12}{}^{\mathrm{v}} = 100$ N m^{-2} only for the chemical potential defined at constant $P_{12}{}^{\mathrm{v}}$.

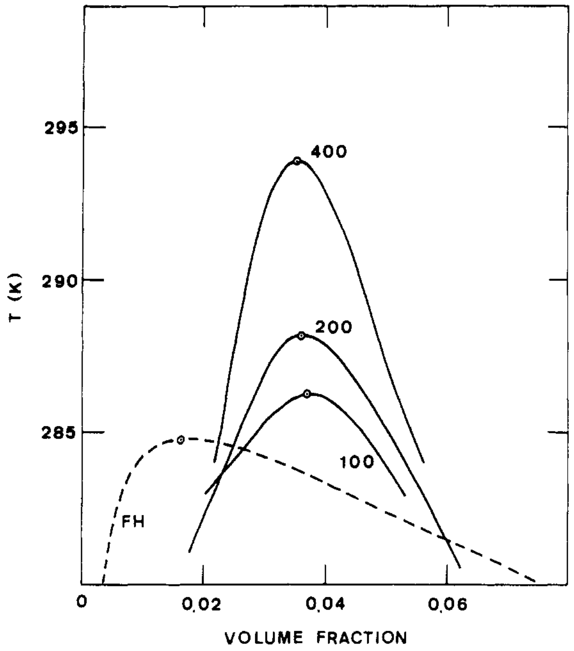

Figure 1. Spinodal lines when the chemical potential is defined as the derivative at constant P_{12}^v. Continuous lines correspond to different values of P_{12}^v; dashed line is for the Flory–Huggins model.

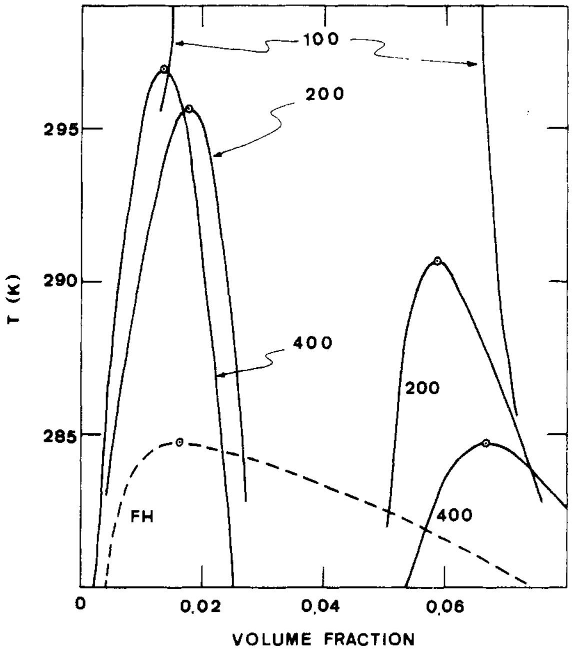

Figure 2. Spinodal lines for the chemical potential defined at constant deformation. Continuous lines correspond to different values of P_{12}^v; dashed line is for the Flory–Huggins model.

Table II
Shifts in the Critical Temperature under Shear with Respect to the Critical Temperature of the Quiescent Solution (T = 285 K)

	P_{12}^v, N m^{-2}		
	100	200	400
this work	1.6	3.5	11.2
Rangel-Nafaile et al.[2]	1.7	4.4	10.5
experimental[2]	4	14	24

The values for the critical temperature at different values of P_{12}^v are given in Table II and compared with the values obtained by Rangel-Nafaile, who used a different curve to fit the experimental data—their curve was only satisfactory near the maximum of Tr $\mathbf{P}^v$ as a function of ϕ—and a different method to obtain the values of the critical temperatures.

Conclusions

In order to clarify the ambiguities arising in the literature, in this paper we have examined the shift of the spinodal curve of polymer solutions under two different definitions of the nonequilibrium thermodynamic potential. The main conclusions of our work are the following ones:

(1) The definition of the chemical potential as the derivative of the Gibbs free energy with respect to the concentration at constant viscous pressure yields more satisfactory results than the definition based on the derivative at constant configuration. The first definition results in a steady increase of the critical temperature as a function of the applied shear stress. The second definition predicts two maxima in spinodal line for P_{12}^v = 200 N m^{-2} and P_{12}^v = 400 N m^{-2}, but it does not predict any critical point for the shear stress $P_{12}^v < 169$ N m^{-2}.

(2) Since the experiment is done at constant shear stress, it could seem natural to take the definition based on the derivative at constant viscous pressure tensor. However, this is not evident a priori. Indeed, it is usual to find in the literature[2,16] the comment that the second derivative of the free energy with respect to the density at constant P_{12}^v leads to a decrease in the critical temperature. This would be true in the domain where E in eqs 14 and 15 follows the scaling relation $E \sim \phi^{-3}$, but this does not correspond to the actual experimental situation. In this case, the concentration dependence of J_e in (20) and (21) is more complicated than the scaling relation and it is compatible with an increase of the critical temperature. Therefore, the conclusion[16] that the definition of chemical potential as the derivative at constant P_{12}^v is in contrast with the experimental results is not valid.

Other comments could be made to end our concluding remarks.

(3) The shifts in the critical temperature obtained in this work are very close to those obtained in ref 2, but they are a factor of 2–3 lower than the experimental results quoted in ref 2. In fact, since the values in the temperature shift are proportional to the second derivatives of the normal stress with respect to the concentration, they may be very sensitive to small errors in the original data.

Since we have followed the experimental data in ref 2, we have obtained the modification of the Gibbs free energy from Tr $\mathbf{P}^v$. However, one should be sure that modification coming from the entropic term $-\ln|\det(\mathbf{U} + \mathbf{P}'^v)|$ is small. This is not always the case. Indeed, we have estimated this contribution to be of the same order as the one coming from Tr $\mathbf{P}'^v$. We have taken for the factor nkT the value 100 N m^{-2}, consistent with the values of n used by Rangel-Nafaile et al.[2] The maximum value of Tr $\mathbf{P}'^v$ at P^v = 200 N m^{-2} corresponds to Tr P'^v = 1.80. The experimental information available is not enough to evaluate each of the terms $P'_{11}{}^v$, $P'_{22}{}^v$, and $P'_{33}{}^v$ appearing in the expression for det $(\mathbf{U} + \mathbf{P}'^v)$, namely

$$\det(\mathbf{U} + \mathbf{P}'^v) = (1 + P'_{33}{}^v)[(1 + P'_{11}{}^v)(1 + P'_{22}{}^v) - (P'_{12}{}^v)^2] \quad (53)$$

As an estimation, one could take $P'_{11}{}^v = 0.20$, $P'_{22}{}^v = P'_{33}{}^v = 0.80$, thus leading for this determinant to a value 3.24, of the order of Tr $\mathbf{P}'^v$. The entropic terms should be paid more careful attention than has been done up to now in the literature. Unfortunately, we do not have enough experimental information on the concentration dependence of the normal stress coefficients, so that we cannot perform here any accurate evaluation.

(4) One should not conclude from our work that the critical temperature is always raised under shear. In some situations it could be lowered, depending on the functional form of the nonequilibrium contribution to the free energy in terms of the polymer concentration. A decrease in the critical temperature has been observed by Wolf[3] in a solution of low molecular weight polystyrene solved in dioctyl phthalate. Note incidentally that his thermodynamic analysis has been performed by taking the derivatives at constant velocity gradient, rather than at constant shear stress or at constant deformation. We have not considered that case in our paper because a constant velocity gradient was not directly related to the experiments with which we are comparing our formalism.

(5) It should be pointed out that the problem of the validity of a nonequilibrium thermodynamics formalism for the description of phase separation in polymer solutions under shear is still open. Note that for some systems, such as Rouse polymers, a nonequilibrium Gibbs free energy may be obtained for arbitrary flows.[7] In other systems, such thermodynamic potentials can only be obtained from a microscopic point of view from some specific flows,[18] as in extensional flow without hydrodynamic interactions. The latter introduce a severe problem to the microscopic derivation of a nonequilibrium free energy. In extended irreversible thermodynamics, the nonequilibrium Gibbs free energy is obtained from a macroscopic argument for relatively small values of the shear stress and when the viscous pressure tensor follows relaxational evolution equations. Note, finally, that even in the case when a Gibbs free energy expression may be obtained, its properties in nonequilibrium states may be different from those in equilibrium, so that formal results of the equilibrium theory cannot be blindly extrapolated to nonequilibrium situations. A careful analysis must be done at each step of the construction of a nonequilibrium thermodynamic formalism beyond the local equilibrium hypothesis.

In summary, our paper has been able to make evident limitations of some previous work dealing with the thermodynamics of phase separation of polymer solutions under shear and to point out explicitly the differences that may arise from the use of several different definitions of the chemical potential at constant shear stress rather than at constant configuration. Further experimental work is necessary to decide about the present status of a thermodynamic formalism for phase separation of polymer solutions under shear.

Acknowledgment. The present research work was partially supported by the Direccion General de Investigación Cientifica y Técnica of the Spanish Ministry of Education under Grant PB89-0290. We express our thanks for the financial support received from the above-mentioned institution.

Appendix

In view of the experimental values (see Figure 3), we propose a functional relation of the form

$$\mathrm{Tr}\,\mathbf{P}^{\mathrm{v}} = a\phi^{k} \exp(-b\phi^{n}) \qquad (\mathrm{A.1})$$

where a, b, k, and n are adjustable but not independent parameters.

The experimental values shown in Figure 3 seem to indicate that the curves for Tr $\mathbf{P}^{\mathrm{v}}$ as a function of ϕ are the maximum for a certain value ϕ_0, which is practically independent of P_{12}^{v}. The height of the maximum, y_0, however, depends on P_{12}^{v}.

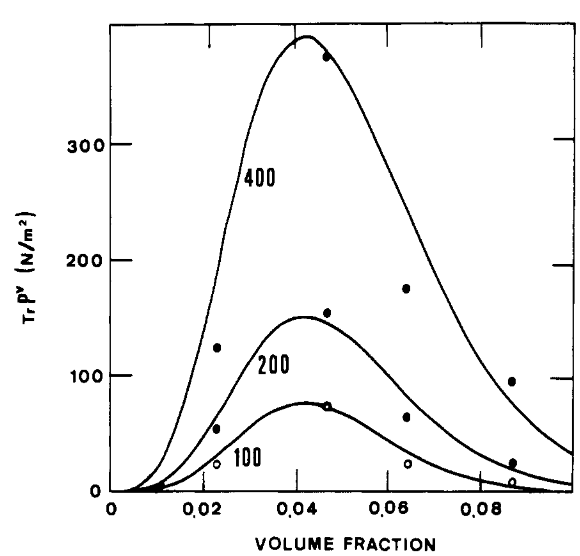

Figure 3. Experimental and fitted values of Tr $\mathbf{P}^{\mathrm{v}}$ for different P_{12}^{v}. The experimental points are taken from ref 2.

Table III

P_{12}^{v}, N m^{-2}	y_0, N m^{-2}	n	a, N m^{-2}	b
100	72	1.818	2.087×10^{8}	701.4
200	152	1.441	7.837×10^{8}	267.7
400	376	1.168	3.709×10^{9}	138.9

Accordingly to (A.1), the maximum of Tr $\mathbf{P}^{\mathrm{v}}$ corresponds to a ϕ_0 satisfying the condition

$$a\phi_0^{k-1}(k - bn\phi_0) \exp(-b\phi_0^{n}) = 0 \qquad (\mathrm{A.2})$$

i.e., it must satisfy the condition

$$b = k(n\phi_0^{n})^{-1} \qquad (\mathrm{A.3})$$

Thus, the maximum value y_0 is given by

$$y_0 = a\phi_0^{k} \exp(-b\phi_0^{n}) \qquad (\mathrm{A.4})$$

so that the parameter a may be expressed as

$$a = y_0\phi_0^{-k} \exp(b\phi_0^{n}) \qquad (\mathrm{A.5})$$

If one introduces into (A.1) the expressions A.3 and A.5 for a and b, the former expressions may be written in terms of the reduced quantities $X^* = \phi/\phi_0$ and $Y^* = (\mathrm{Tr}\,P^{\mathrm{v}})/y_0$ as

$$Y^* = X^{*k} \exp[(k/n)(1 - X^{*n})] \qquad (\mathrm{A.6})$$

Since we have only a few experimental points, a fit by minimum squares would lead to an underestimation of the zone near the maximum. Thus, we fix a priori values of ϕ_0 (for all curves $\phi_0 = 0.042$ is taken) and of y_0, and we make all curves go through those points. The remaining parameters are evaluated as follows: (1) k is assumed to be 4; (2) a and b are calculated from (A.3) and (A.5) once n is known; (3) n is obtained by a minimum squares method applied to (A.6).

In Table III are shown the results for the method just described. These numbers allow the fit of the parameters n and y_0 to the functions of P_{12}^{v} given in (25) in agreement with the numerical values $\beta = 7.85$, $\gamma = 0.319$, $\delta = 14.7$, and $B = 0.164$.

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Registry No. Polystyrene, 9003-53-6; dioctyl phthalate, 117-81-7.