and n (cf. (34)) while (50) and (51) lead to a ϕ dependence of u and n in that domain. The situation is quite similar for the polymer osmotic pressure. A good agreement is found for semidilute solutions but for concentrated ones, a log $(1 - \phi)$ behavior is expected within the lattice model, while a ϕ^2 or $\phi^{3/2}$ dependence is obtained in ref 3. A possible solution to this dilemma is that eq 19 and 22, being scaling results, are valuable for large n only, and concentrated solutions are actually characterized by rather low n values.

What is a bit more surprising is that the lattice model expression (15) for the entropy is rather different in its structure from the result (49) of field theoretic calculations. Since S_1 is the analogue of our $\mathcal{N}_n(u)$, one sees that within the lattice model (i) no isolated ϕ^2 term is found, (ii) a $(un)^{-1}(1 - u\phi)\log(1 - u\phi)$ term is found instead of $(un)^{-1}$, and (iii) a ϕ/n term is found instead of ϕ/u. The last two discrepancies are probably not crucial insofar as, due to (28) or (36b), we get a $(un)^{-1}$ term for the large range $\phi^* < \phi < \tilde{\phi}$ and, due to (29), the ϕ/n term is equivalent to ϕ/u^α. But it is hard to see how an isolated ϕ^2 term could be deduced from a lattice model.

VIII. Concluding Remarks

The double-lattice model (DLM) pictured in Figure 1 is a natural extension of the Flory–Huggins lattice; the two basic ingredients of the DLM are Flory's excluded volume and de Gennes' blobs. The entropy of mixing (35) and the polymer osmotic pressure (42) deduced from the DLM have rather simple expressions; they are most conveniently written in terms of u, the relative excluded volume per polymer (or blob).

The special case of DLM we presented here is very simplified. If hypothesis (21) is suppressed and if the maximum of $\mathcal{N}_n(u)$ is located at

$$n = Bu^\alpha$$

then the entropy of the solution becomes

$$-\frac{s}{k_\mathrm{B}} = \frac{\phi}{N}\log\frac{\phi}{N} + \frac{\phi}{N}(A - 1) - \tilde{A}\phi(1 - u^{-\alpha}) + \frac{\phi}{n}\left[1 - A + \frac{1 - u\phi}{u\phi}\log(1 - u\phi) + \tilde{A}B\log\frac{u^\alpha}{n}\right] \quad (53)$$

where

$$A = \log(Z - 1)$$

and

$$\tilde{A} = \log\tilde{Z}$$

Our simple expression (23) corresponds to $A = \tilde{A}$ (cf. (21)) and $B = 1$. The three-parameter expression (53) would perhaps better fit with experimental results, but remember that B cannot be taken as a true parameter (at variance with the lattice parameters A and $\tilde{A}$) and in the absence of any firmly established value for B, we deliberately chose to work with the one-parameter expression (23) since it is very simple and it keeps all the basic features of (53).

It is rather surprising that the DLM leads to an expression for the entropy of mixing which is rather different from that deduced with field theoretic methods. Despite this, the results concerning the osmotic pressure are quite similar, except for concentrated solutions. We have no explanation yet for these discrepancies.

If not perfectly rigorous, the DLM is undeniably simple and can prove useful for numerical simulations of polymer solutions. It now remains to find the energy of mixing along the same lines.

Acknowledgment. D.L. is indebted to J. des Cloizeaux for decisive remarks about $\mathcal{N}_n(x)$.

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Thermodynamics of Flow-Induced Phase Separation in Polymers

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ABSTRACT: The thermodynamics of a liquid–liquid phase separation as a way of explaining flow-induced structure formation in polymer solutions is presented. The effect of the flow field is taken into account by using two fundamentally different approaches: the reduced flexibility and the stored free energy approach. The basis of both models is clarified, and phase diagrams are constructed for the reduced flexibility case. The binodal curves are shown to become broader compared with the quiescent phase diagrams and can be shifted to higher temperatures depending on the values of the flexibility parameters.

Introduction

It has been recognized for some time that flow-induced liquid phase structure formation may be involved in a number of phenomena ranging from rheological characterization to oriented phase transformation. In the latter case, studies of high molecular weight polyethylene fiber growth in Poiseuille[1] and Couette[2] flow geometries have established that fiber crystallization at elevated temperatures is preceded by the formation of amorphous gel-like liquid precursor phases. A similar suggestion has been made in studies of rigid systems such as poly(ethylene terephthalate)[3] and others[4] and could be implied from the

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observations of fiber formation in poly(ethylene oxide) solutions.[5] An important implication is that the phase diagram for a crystallizable polymer solution can be changed qualitatively as well as quantitatively by an applied flow. For example, the polyethylene–xylene system exhibits a single solidus line for the equilibrium melting point under quiescent conditions. Metastable, nucleation-controlled lamellar crystallization at various supercoolings in such systems is well established. In order to accommodate precursor formation from a thermodynamic viewpoint one needs to be able to predict the formation of the flow-induced liquid binodal (or gelation) curve in the phase diagram as well as account for modifications in crystal nucleation caused by the applied stresses.[6] In one case,[7] a study of the effects of deformation was carried out on a system (polycapramide–caprolactam) which exhibits a liquid binodal in the *quiescent* phase diagram. However, modification of the liquid phase separation was not analyzed per se, except for the qualitative suggestion that temperatures of transformation should be affected as a consequence of entropy reductions upon chain elongation.

Structure formation during flow of amorphous polymer solutions has been reported over the years in a variety of circumstances, generally associated with rheological characterization studies.[8] Explanations of elastic and/or rheopectic phenomena, as well as shear-thickening effects, have most often been based on shear-induced entanglement or chain association arguments (e.g., ref 9 and 10). These are essentially kinetic arguments which have been made without reference to thermodynamic implications regarding the existence of stable phases. Recently, Rangel-Nafaile[11] and co-workers[8] have discussed in some detail a thermodynamic approach to structure formation in flowing solutions, basing their arguments on earlier studies[12] which indicated that a reversible, liquid–liquid phase transformation can be induced by flow. They presented a formalism for constructing the phase diagram under flow based on a stored free energy argument and showed results from their experiments which agreed well with their model calculations. However, as will be discussed in this paper, there appear to be inconsistencies in the stored free energy approach used in these calculations.

In a number of papers[4,13,14] a different thermodynamic approach has been taken to explain flow-induced oriented structure formation in crystallizable systems which we feel is based on a more clearly recognizable thermodynamic formalism. However, the assumption needs to be made that flexible macromolecules under an applied stress will spontaneously form an anisotropic liquid phase prior to crystallization.[13-15] Since direct observations of the polyethylene fiber precursor phase in our Poiseuille flow studies[1] clearly indicate that it is randomly oriented rather than anisotropic, a modification in the theory appears to be needed. We do not doubt that the mechanism of phase separation under flow is intimately connected with high molecular weight chain entanglements, and whether the entire phenomenon is in fact purely kinetic in nature is open to argument. The possible formation of crystalline network junctions in crystallizable polymers and the analysis of the stress field in two-phase flow makes the problem more complicated. Nevertheless, thermodynamic calculations, based on the existence of stable liquid phases in equilibrium, can be quite important for evaluating limiting conditions under which applied stress fields will initiate such phase formation in otherwise homogeneous systems. Phenomena such as fractionation during flow-induced crystallization[16,17] might also be more reasonably rationalized by such an approach.

We feel that a detailed analysis of the two above-mentioned thermodynamic approaches is warranted since, in our view, in neither case have clear derivations of the proposed equations been presented nor has there been adequate recognition of the fact that they are fundamentally different and can lead to quite different predictions for the phase diagram. Since a main goal is to clarify the basis of the two approaches in the discussion to follow, we shall assume that the conditions normally associated with Flory–Huggins theory hold[18] and that the polymer is monodisperse.

Theory

On the basis of expressions for the free energy of mixing one can write equilibrium relationships between the dilute and the concentrated phases, assuming the polymer molecules are randomly mixed in both phases. The construction of the binodal requires that the chemical potentials be equal in the two phases. Therefore

$$\mu_1 = \mu_1' \tag{1}$$

and

$$\mu_2 = \mu_2' \tag{2}$$

where μ's, the chemical potentials, are given by the partial derivatives of the free energy of mixing. Subscripts 1 and 2 refer to the solvent and polymer, and primes are used to indicate the more concentrated phase.

Under flow, frictional forces cause the macromolecules to uncoil from their random quiescent conformation to a more extended state of lower conformational entropy. The effect this will have on the chemical potential of the system can be considered in one of two ways. In the first instance, a term for the so-called "stored free energy" can be added to the Flory–Huggins expression for the free energy of mixing polymer and solvent. In the second case, one can visualize the effect of chain stretching as equivalent to introducing a degree of rigidity to the polymer coils whose thermodynamic properties then become those of a system of "semiflexible" chains. These two approaches are not at all equivalent and can produce quite different phase diagrams. We begin by considering the case of reduced flexibility.

Flexibility and the Phase Diagram

Frenkel[4] first suggested that stretching macromolecular coils should be equivalent to increasing their rigidity, thus "shifting" the binodal to higher concentrations and a higher critical temperature; however, no theoretical justification was given, nor were any thermodynamic relationships derived. Elyashevich[13] proposed that the effective flexibility parameter, f, of semiflexible macromolecules stretched by a force can be written as

$$f = \frac{(z-2)\exp\left[-\dfrac{\epsilon}{kT} - \dfrac{Fl}{kT}\right]}{1 + (z-2)\exp\left[-\dfrac{\epsilon}{kT} - \dfrac{Fl}{kT}\right]} \tag{3}$$

where F is the extending force applied to a segment of length l, and z and ϵ are respectively the lattice coordination number and intrinsic segment energy relative to the energetically favored configuration prior to the application of flow. Though this expression has been discussed in several references,[4,13,14] no rigorous derivation has been given. A rationalization for its form can be made provided one accepts the term Fl as representing the free energy increase associated with displacing a segment of the macromolecule having some characteristic length l. In such

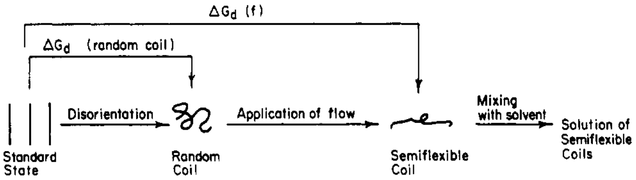

Figure 1. Schematic illustration of the free energy diagram associated with transferring a polymer molecule from the standard state to the solvated stretched coil state according to the flexibility argument.

a case the free energy of a system of semiflexible coils in solution containing n_2 polymer molecules and n_1 solvent molecules would be written as follows

$$\Delta G = kTn_2\left\{(x - 1) - \ln\left(\frac{xz}{2}\right) + (x - 2)\,[f \ln f + (1 - f) \ln (1 - f) - f \ln (z - 2)]\right\} + n_2\{f(x - 2)(\epsilon + Fl)\} + kT\{n_1 \ln v_1 + n_2 \ln v_2 + \chi x n_2 v_1\} \quad (4)$$

Minimization of eq 4 with respect to f leads directly to the expression given by eq 3 for the equilibrium effective flexibility parameter. The form of eq 3 is in fact dissatisfying in that no means are given for either evaluating the energy term Fl or easily relating this quantity to the stress-deformation rate fields associated with the macroscopic flow. On the other hand, an exact correspondence between Fl and the actual molecular deformation may not be critical, since the fundamental assumption is that the thermodynamic mixing behavior of a system of random coils under stress will be equivalent to that of a "model" system of semiflexible macromolecules in the absence of applied forces. And it is the model system for which the calculation has been carried out from a rigorous equilibrium, statistical thermodynamic basis. Consequently, a link between the model and real systems can be made by equating a measurable or calculable macroscopic property of the two, such as the mean square chain end-to-end separation. In such a case, one has for the semiflexible chain having x segments of length l[19]

$$\langle r^2 \rangle = \frac{xl^2(2 - f)}{f} \quad (5)$$

A measurement or calculation of $\langle r^2 \rangle$ for the real system under flow enables determination of f. It should be noted that the limiting form of eq 5 for complete flexibility (i.e., no flow and $\epsilon = 0$) will be given by $xzl^2/(z - 2)$. Substitution of eq 3 into eq 4 gives the familiar expression for the free energy of mixing as given by Flory[19]

$$\Delta G_M = RT\left\{n_1 \ln v_1 + n_2 \ln v_2 + \chi x n_2 v_1 - n_2\left[\ln x + \ln\left(\frac{z}{2e}\right) + (x - 2) \ln\left(\frac{1}{(1 - f)e}\right)\right]\right\} \quad (6)$$

where n_1 and n_2 now represent numbers of moles. Chemical potentials are readily calculated from eq 6 by appropriate differentiation.

Figure 1 illustrates the overall process associated with transferring a molecule from the standard state to the solvated, stretched coil state. Since the free energy changes associated with mixing either a completely random coil or partially rigid chain with solvent are the same,[19] then the former can be obtained from eq 6 by substituting $(1 - f) = (z - 1)^{-1}$. Therefore the free energy change per mole of polymer associated with the application of flow in this calculation is easily shown to be

$$\Delta G_f = RT(x - 2) \ln [(1 - f)(z - 1)] \quad (7)$$

Construction of thermodynamic diagrams requires a distinction between the cases of equal flexibility in the two phases and unequal flexibility. In addition, the interaction parameter can be taken as a function of temperature as originally defined by Flory[18]

$$\chi = \frac{1}{2} + \psi_1\left(\frac{\Theta}{T} - 1\right) \quad (8)$$

or following the suggestion by Koningsveld,[20] a temperature and concentration dependent form can be used

$$\chi = A_1 + \frac{A_2}{T} + Bv_2 \quad (9)$$

in which A_1, A_2, and B are empirical constants. Equation 9 is a more general form which encompasses eq 8 as a special case and was therefore used in what follows.

If one assumes that the polymer molecules in the two equilibrium phases have the same flexibility, i.e., that they are stretched by equal amounts after phase separation occurs, then upon equating the chemical potentials one finds that the flexibility parameter cancels. The predicted phase diagram is given by the already known expression for the binodal in the polymer solutions[18] and it is limited to low polymer volume fractions.

For the case where the flexibility in the concentrated phase, f', differs from that in the dilute phase, f, substitution of eq 9 into eq 6 followed by appropriate differentiation and substitutions into eq 1 and 2 give the following relationships for the binodal curve

$$\left[1 - \frac{v_2(A + 1)}{2}\right] \ln\left(\frac{1 - Av_2}{1 - v_2}\right) + v_2(A - 1) \times \left(1 - \frac{1}{x}\right) + \frac{v_2(A + 1)(\ln A - \alpha)}{2x} + \frac{B(A - 1)^3 v_2^{\,3}}{2} = 0 \quad (10)$$

where

$$\alpha = (x - 2) \ln\left(\frac{1 - f}{1 - f'}\right) \quad (11)$$

and

$$A_1 + \frac{A_2}{T} = \left\{1 - \frac{1}{x} + \frac{\ln A - \alpha}{xv_2(A - 1)} + 2B[1 + v_2^{\,2}(A^2 + A + 1) - 2v_2(A + 1)]\right\} \Big/ \{2 - v_2(A + 1)\} \quad (12)$$

As is shown in the Appendix, by considering the roots of eq 10, one can readily demonstrate that solutions in the range $0 < v_2 < 1$ will only exist for the case $f > f'$. This means that for the change in flexibility to have any effect on the binodal, the chains in the more concentrated phase must be less randomly coiled. This leads to a somewhat different interpretation of the phase equilibrium than that considered by Flory[19] and inherently treated in the previously mentioned references.[13,14] In those, the equilibrium is assumed to occur between a perfectly ordered nematic concentrated phase and a completely disordered dilute phase of semiflexible molecules. The argument being proposed here is somewhat different, in the sense that for perfectly flexible coils ($\epsilon \simeq 0$) the system can lower its free energy by spontaneously forming a second liquid phase in which the order is still *random* and the flexibility (due to the applied stress) is *lessened* but it not necessarily zero. Unless the inherent molecular stiffness of the macro-

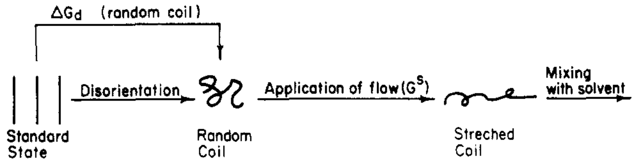

Figure 2. Schematic illustration of the free energy diagram associated with transferring a polymer molecule from the standard state to the solvated stretched coil state according to the stored free energy argument.

molecule is sufficiently large, it appears to us that the assumption of the formation of a disordered concentrated liquid phase is more reasonable than that of an ordered crystal.

Stored Free Energy and the Phase Diagram

As indicated, the fundamental assumption in this approach is that a term for the stored free energy can be added to the free energy of mixing to account for the entropic effect on the overall mixing process. Taking the standard states again to be pure ordered polymer and pure solvent and noting, as was the case with the semiflexible molecules, that the order of calculating the free energy of mixing is immaterial (i.e., one can visualize the process as first mixing the coils with solvent followed by stretching or vice versa), one then has in place of eq 6, the following expression for the free energy of mixing

$$\Delta G_{\mathrm{M}} = RT\left\{n_1 \ln v_1 + n_2 \ln v_2 + \chi x n_2 v_1 - n_2\left[\ln\frac{x}{2} + \ln\frac{z}{z-1} + (x-1)\ln\left(\frac{z-1}{e}\right)\right]\right\} + n_2 G_s \qquad (13)$$

In eq 13, G_s represents the free energy change upon stretching 1 mol of macromolecules and the first two terms represent the free energy changes for the mixing and disorientation processes, respectively. Figure 2 shows the equivalent thermodynamic diagram for this process in which it is clear that the effect of flow shows up in the (as yet unspecified) term G_s. It is important to note that this term is for the *individual* polymer molecules and is therefore independent of concentration, depending only on chain elongation (elastic free energy) and/or average orientation. In a similar sense to the rigidity model, one can calculate G_s from a rigorous equilibrium statistical thermodynamic basis (leading for example in the case of elastic free energy to the well-known rubber elasticity expressions[18]) for the model system and then compare this to predictions for a rheological model (such as the elastic dumbbell[6]). Nevertheless, the fundamental point remains unchanged, namely that one is calculating the change in energy associated with a given equilibrium conformational (or orientational) change for a given molecule independently of its surroundings. In our opinion this point has not been treated in the previously mentioned free energy approaches.

Starting from eq 13 expressions for the binodal can readily be calculated. Thus for the previously assumed temperature and concentration dependence of χ, one obtains

$$\left[1 - \frac{v_2(A+1)}{2}\right]\ln\left(\frac{1-Av_2}{1-v_2}\right) + \frac{v_2(A+1)\ln A}{2x} + \frac{Bv_2^{3}(A-1)^{3}}{2} + v_2(A-1)\left(1-\frac{1}{x}\right) + (G_s' - G_s)\frac{v_2(A+1)}{2RTx} = 0 \qquad (14)$$

and

$$A_1 + \frac{A_2}{T} = \left\{\frac{\ln A}{xv_2(A-1)} + \left(1-\frac{1}{x}\right) + 2B[1 - 2v_2(A+1) + v_2^{2}(A^2+A+1)] + \frac{G_s' - G_s}{RTxv_2(A-1)}\right\}\Big/\{2 - v_2(A+1)\} \qquad (15)$$

If $G_s' = G_s$, i.e., if the free energy change upon stretching the macromolecules is the same in both phases after phase separation occurs, then no shifting of the binodal can be predicted. This is in agreement with the case of equal flexibility in the two phases, and the constructed thermodynamic phase diagram will be limited to low polymer concentrations. If the stored free energy is independent of molecular weight, then eq 14 leads to inconsistencies at high molecular weights, since it does not predict any effect of the flow field as $x \to \infty$. As can be easily seen from eq 10, there is no such problem in the flexibility approach. A careful selection of a rheological expression for the stored free energy is therefore needed. If, on the other hand, G_s and G_s' are given by eq 7 then

$$G_s' - G_s = RT(x-2)\ln\frac{1-f'}{1-f} \qquad (16)$$

and eq 14 becomes identical with eq 10. Therefore the reduced flexibility and the stored free energy approaches become identical when G_s is interpreted as the free energy of transferring a molecule from the completely random state to the stretched, "semiflexible" coil state. Expressions for G_s used in the past[11,12] were based on solution properties and were not referred to the individual polymer molecules, as a thermodynamic analysis would require. Furthermore, no distinction between G_s and G_s' was made; this is important since shifting of the binodal can occur only if $G_s \neq G_s'$. Arbitrary addition of a "stored free energy" term to the free energy of mixing can therefore lead to inconsistencies as our derivation showed.

Discussion

The main goal of our calculations was to show the dependence of the thermodynamic phase diagram on the parameters involved in the case of the flexibility approach. As is shown in the Appendix, a solution for the shifted binodal exists only if $f > f'$. If $\langle r^2 \rangle$ and $\langle r'^2 \rangle$ are the mean square end-to-end separations of the polymer molecules in the dilute and concentrated phases respectively, then it follows from eq 5 that

$$\frac{\langle r'^2 \rangle}{\langle r^2 \rangle} = \frac{2/f' - 1}{2/f - 1} > 1 \qquad (17)$$

The parameter $(1-f)/(1-f')$ is very important. As it decreases, the ratio $\langle r'^2 \rangle / \langle r^2 \rangle$ increases and the macromolecules in the concentrated phase become "stiffer". The effect of $(1-f)/(1-f')$ on the binodal is shown in Figure 3. In this and in the following figures only part of the binodals are sketched for better comparison between the curves. The selected values for the parameters A_1, A_2, and B are typical of polymer solutions and $x = 10\,000$. The two-phase region becomes broader as the "rigidity" of the polymer molecules in the concentrated phase increases, and the binodal is shifted to higher temperatures as $(1-f)/(1-f')$ increases.

Figure 4 demonstrates the molecular weight dependence of the binodal for $x = 1000$ and $x = 10\,000$. This is the

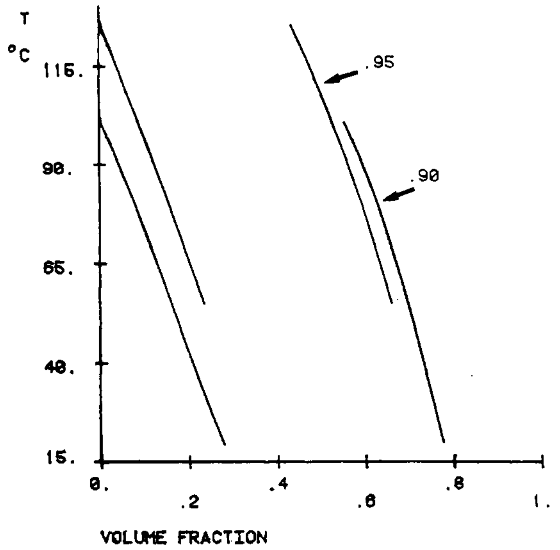

Figure 3. Dependence of the binodal curve on the ratio $(1-f)/(1-f')$. The values of the ratio are shown on the graph. $A_1 = -0.6$, $A_2 = 500$, $B = 0$, and $x = 10\,000$.

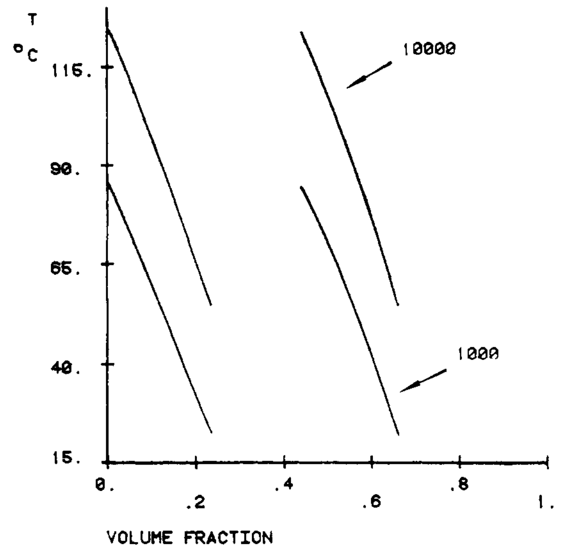

Figure 4. Molecular weight dependence of the binodal for two values of x. $(1-f)/(1-f') = 0.95$, $A_1 = -0.6$, $A_2 = 500$, and $B = 0$.

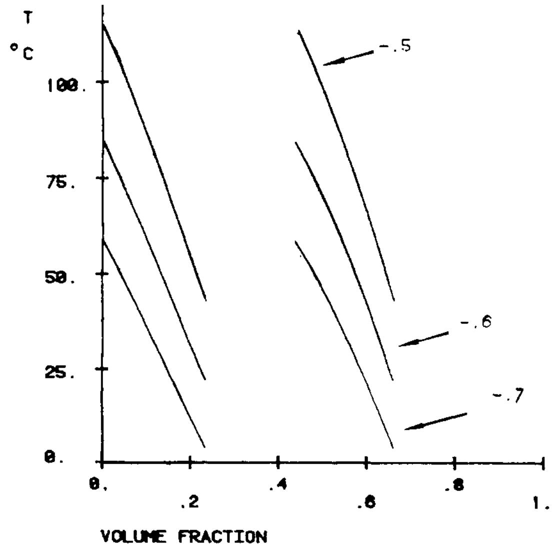

Figure 5. Dependence of the binodal on A_1. $(1-f)/(1-f') = 0.95$, $A_2 = 450$, $B = 0$, and $x = 10\,000$.

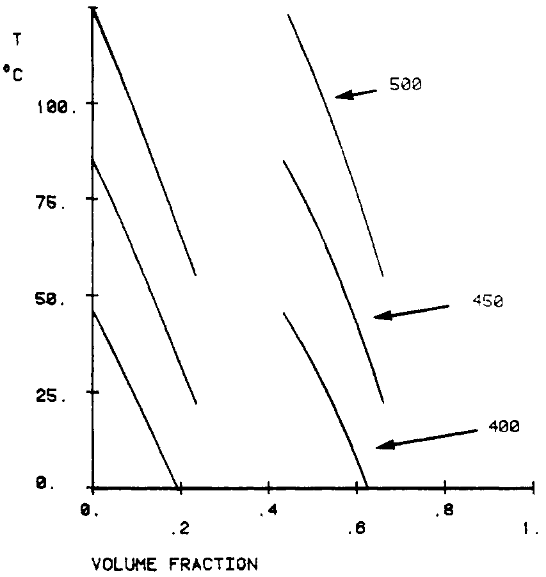

Figure 6. Dependence of the binodal on A_2. $A_1 = -0.6$, $B = 0$, $(1-f)/(1-f') = 0.95$, and $x = 10\,000$.

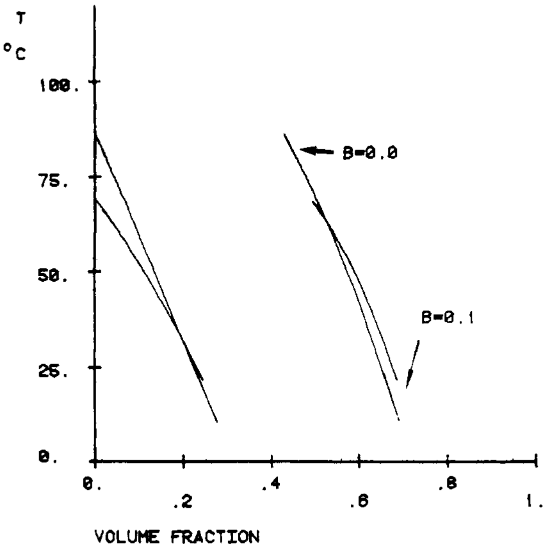

Figure 7. Dependence of the binodal on B. $A_1 = -0.6$, $A_2 = 450$, $(1-f)/(1-f') = 0.95$, and $x = 10\,000$.

usual behavior in polymeric systems.

The influence of the parameters A_1, A_2, and B is shown on Figures 5–7.

A quantitative phase diagram requires knowledge of A_1, A_2, B, and measurement or calculation of f and f' through the mean square end-to-end separation of the macromolecules. A comparison with the stored free energy approach needs in addition an expression for G_s and cannot be made at this point since there are no experimental data available.

Conclusion

The thermodynamics of the reduced flexibility and stored free energy approaches, used to describe flow-induced liquid–liquid phase separation, is analyzed, and the two approaches are shown to be fundamentally different. In the case of the reduced flexibility the binodal curves give high polymer concentrations for the equilibrium concentrated phase, and it can be shifted to high temperatures depending on the values of the flexibility parameters. The stored free energy approach requires the use of a rheological model, and it can be equivalent with

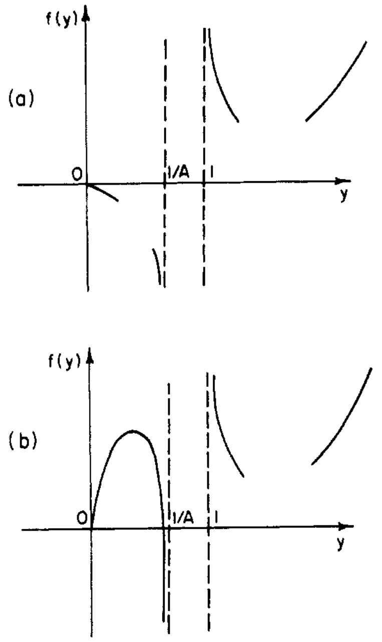

Figure 8. Behavior of the function $f(y)$ vs. y for (a) $f < f'$ and (b) $f > f'$.

the reduced flexibility approach under certain conditions. A quantitative comparison between the two cannot be made because no data are available yet.

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Appendix

Analysis of eq 10 indicates that we need values of v_2 such that $0 < v_2 < 1/A$. Substitutions of v_2 with y and of the function on the left-hand side of eq 10 with the notation $f(y)$ give

$$f(y) = P_1 y + (1 - P_3 y) \ln \left(\frac{1 - P_2 y}{1 - y} \right) + \frac{B(P_2 - 1)^3 y^3}{2}$$

where

$$P_1 = \frac{(A + 1)(\ln A - \alpha) + 2(A - 1)(x - 1)}{2x}$$

and

$$P_2 = A$$

$$P_3 = \frac{A + 1}{2}$$

$$f'(y) = P_1 - (P_3 y - 1) \left[\frac{1}{1 - y} - \frac{P_2}{1 - P_2 y} \right] - P_3 \ln \left(\frac{1 - P_2 y}{1 - y} \right) + \frac{3B(P_2 - 1)^3 y^2}{2}$$

As $y \to (1/A)^-$, $f(y) \to -\infty$ since $P_2 > 1$. At $y = 0$

$$f'(0) = \frac{(P_2 + 1)(\ln P_2 - \alpha) + 2(1 - P_2)}{2x}$$

Since $P_2 > 1$ and $|\alpha| \gg \ln P_2$, we have if $\alpha > 0$, $f'(0) < 0$, and if $\alpha < 0$, $f'(0) > 0$. Also

$$f''(y) = \frac{-(P_2 - 1)^3 y}{2(1 - y)^2 (1 - P_2 y)^2} + 3B(P_2 - 1)^3 y$$

Thus since the first term in the second derivative dominates, we have $f''(y) < 0$ for all y between 0 and $(1/A)$, for any α.

Figure 8 shows the asymptotic behavior of the function $f(y)$ vs. y depending on the relationship between the flexibility parameters f and f'. There might be solutions of $f(y)$ for values of y greater than 1 because as $y \to 1^+$, $f(y) \to +\infty$ and as $y \to +\infty$, $f(y) \to +\infty$. These have no physical meaning though, since v_2 and hence y represent volume fractions.

A	ratio of polymer volume fractions in the concentrated and dilute phases
A_1, A_2	parameters describing the temperature dependence of the interaction parameter
B	parameter describing the polymer volume fraction dependence of the interaction parameter
f, f'	flexibility parameters in the dilute and concentrated phases, respectively
$f(y)$	function used in the Appendix
F	applied force per segment
G_s	stored free energy per polymer mole
k	Boltzmann's constant
l	length of segment of a polymer molecule
n_1, n_2	number of moles (or molecules) of solvent and polymer, respectively
R	gas constant
T	absolute temperature
v_1, v_2	volume fractions of the solvent and polymer, respectively
x	number of segments in each polymer molecule
y	parameter used in the Appendix to represent v_2
z	lattice coordination number
ΔG_M	free energy of mixing
ϵ	intrinsic segment energy prior to the application of flow
Θ	theta temperature
μ_1, μ_1'	chemical potentials of the solvent in the dilute and concentrated phases, respectively
μ_2, μ_2'	chemical potentials of the polymer in the dilute and concentrated phases, respectively
χ	polymer–solvent interaction parameter
ψ_1	entropic parameter for the χ dependence on temperature

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Statistical Thermodynamics of Multicomponent Fluids. 2. Equation of State and Phase Relations

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ABSTRACT: The theory previously formulated for the equation of state (*PVT*) is now extended to the free energy change ΔG_m by including the requisite additional contributions to the free energies of components and mixtures. As an example of a compatible binary mixture with experimentally known *PVT* and chemical potentials, we consider the *n*-hexane + *n*-hexadecane pair. The former data set had previously been discussed in terms of the theory. Without introduction of additional parameters, both sets of properties are quantitatively described. The very minor corrections in the scaling pressure arise from two facts. First, this parameter is predicted by the theory without adjustment to pressure data of the mixture, and second, ΔG_m is computed as a difference between large quantities. This correction leaves the predicted equation of state practically unaltered. General procedures for the combined analysis of chemical potentials and *PVT* are outlined. As an example of a polymer solution we consider the polyethylene + *n*-hexane pair for a low (M = 8000) and high (M = 177 000) uniform molecular weight. The equation of state of both components and thus their scaling parameters are known, but sufficient information for the mixture is not available, to define the corresponding parameters. Here a relative cross-interaction parameter becomes the important quantity to be explored. Lower critical solution temperatures (T_c) and cloud point curves are computed. Small variations in the above parameters within the bounds suggested by the equation of state analysis of the C_6 + C_{16} pair have a significant effect on T_c. In view of the success of the equation of state it is of interest to examine the effect of pressure. The computed increments of T_c conform to an iso-free volume difference condition, where free volume is defined in terms of the hole fraction inherent in the theory. Similarly a reduced cloud point curve can be established.

I. Introduction

We have recently extended the particular version of statistical theory for a homogeneous melt to multicomponent systems.[1] The specific applications were to the equation of state of low[1] and high molecular weight[2] blends. The essential consequence of this extension is the view of the mixture as a homogeneous system with explicitly composition-dependent parameters. The dependence of the scaling parameters of pressure, volume, and temperature in particular involves self- and cross-segmental attractive and repulsive interactions. A particular result is the prediction of the scaling pressure without further recourse in principle to pressure experimentation required.

The theory has shown quantitative success for a variety of fluids and their mixtures in respect to the volume derivative of the free energy. This implies that the characteristic parameters, extracted from extensive comparisons with *PVT* experiments at low and elevated pressures, are to be regarded as true constants of the system at fixed composition. No variations with temperature or pressure are permitted to generate acceptable concordance between theory and experiment. Admittedly, this agreement is obtained at the minor price inherent in the model, of *evaluating numerically transcendental equations.*

Having gone this far, the purpose of this paper is to explore the position and *some* results of the model in respect to compositional derivatives of the free energy. Chemical potentials are to be computed under single- and two-phase conditions, arising from the existence of lower critical solution temperatures (LCST). As in the instance of the equation of state, we begin with a low molecular weight mixture. Extensive experimental information exists, albeit for free energies of mixing at atmospheric pressure only. The equation of state and thus volume changes ΔV_m have been previously analyzed in theoretical terms at atmospheric and elevated pressures. We continue with an illustration of a polymer solution at low and slightly elevated pressures. Here equation of state data for the components, but not for the mixture, are available. Hence we investigate the influence of variations in certain interaction parameters, guided for reasonable magnitudes by the results for a low molecular weight analogue. A basic question concerns the characteristic parameters. Is the set derived from equation of state data adequate for a description of compositional derivatives, or if corrections have to be introduced, what is their origin and magnitude?

Starting with the early work of Prigogine and his collaborators on chain-molecular fluids, there have been several theoretical approaches connecting equation of state and free energy of mixing. We emphasize that the purpose here is not detailed comparison of our theory with earlier theories. *Our concern in this first evaluation of extended* theory is to make a detailed comparison with experiment in one case and to illustrate quantitative reasonableness and make some comparison in another.

II. Theory

The molar Helmholtz free energy F_i of component i equals[3]

$$F_i/RT = \ln (y/s_i) + s_i y^{-1}(1 - y) \ln (1 - y) - (s_i - 1) \ln [(z - 1)/e] - 3c_i\{\ln [(M_{0i}V_i^*/N_A)^{1/3}(y\tilde{V})^{1/3}(1 - \eta)(2\pi M_{0i}kT/N_A h^2)^{1/2}] - (y/6\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 2.409]\} \quad (1)$$

with

$$\eta = 2^{-1/6}y(y\tilde{V})^{-1/3}$$