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with the slit function corresponding to the slit width, estimated from initial step profiles as in Figure 1a; this smearing made little significant difference to the profile half-width. Profiles thus generated are essentially identical with those published by Brochard et al.[12] and by Kramer et al.[13] for the selected R values used by these authors. This procedure was used to generate the theoretical curves appearing in Figures 2–4.

The theoretical interquartile widths $W_{1/2}$ appearing in Table II were also computed by this numerical procedure. These provide an especially useful quantitative measure of the mutual diffusion coefficient controlling the broadening, for the following reason. For an initial step-function distribution whose subsequent diffusion broadening over a time t is controlled by a *concentration-independent* diffusion coefficient $D(\phi) = D_0$, the half-width $W_{1/2}$ of the resulting complementary error function, or erfc, profile is given by

$$W_{1/2} = \beta_0(4Dt)^{1/2}$$

where $\beta_0 = 1.10$ (to 3 sf). For the case of the *concentration-dependent* diffusion coefficients $D_1(\phi)$ and $D_2(\phi)$ the interquartile width may also be written as

$$W_{1/2} = \beta_{R,i}(4D_i(1/2)t)^{1/2}$$

where $\beta_{R,i}$ ($i = 1$ or 2) is a constant depending on R and on which of the two forms of $D_i(\phi)$ is applicable, and $D_i(1/2)$ is the value of D_i (for a given R) at $\phi = {}^1/_2$. The values of $\beta_{R,i}$ all turn out to be close to β_0 (even though the *shapes* of the curves are very different from an erfc profile), and, for a given R (within the range of the present study), are within a few percent of each other, as shown in Table III. Thus the experimental $W_{1/2}$ may be used to estimate the effective mutual diffusion coefficient $D(\phi={}^1/_2)$ characterizing the broadening at the interface. This observation (that the values of β are generally close to β_0) turns out to hold also for other forms of $D(\phi)$, as long as the concentration dependence of $D(\phi)$ is not too drastic.

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Aperiodic Crystal Description of Diffusion in Concentrated Polymer–Solvent Systems

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ABSTRACT: The aperiodic crystal picture is used to predict the solvent number fraction dependence of the mutual diffusion coefficient for two dense polymer–solvent systems. This theory, which has been applied successfully to diffusion in one component glasses, gives results that are distinct from previous free volume theories. The theory provides a way to calculate the free energy surface for a dense disordered system, from which the barrier heights to diffusion can be estimated.

Introduction

The diffusion of polymers in solvents and copolymers is an important and well-studied topic.[1] The formation of polymers is strongly dependent on the diffusion of molecules both into and out of the polymer, so the ability to predict diffusion rates would be of enormous importance to polymer chemists and engineers. The rate of polymerization is dependent on how fast monomer units, initiators, and other molecules can diffuse into the growing polymers, while further processing requires the low molecular weight residues to be removed. Thus, it is evident that efficient design of polymer synthesis requires an un-

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derstanding of diffusion processes in polymers.

The diffusion of polymers can be divided into three regions: "infinitely" dilute solutions, in which the polymers interact via long range hydrodynamic interactions, semidilute solutions, in which the polymers are entangled yet can still exhibit correlated motion involving an entire chain (for instance, reptation), and concentrated solutions in which only a few segments of any polymer are moving at one time. The "infinitely" dilute region was studied by Kirkwood and Riseman,[2] who developed a theory that seems to fit experimental data at low polymer concentrations reasonably well. Semidilute solutions have seen the most attention in the past few years. Progress has been made through the use of renormalization[3] techniques. In contrast to the above, relatively little is understood about the dynamics of concentrated polymer solutions, presumably due to the complicated nature of the dynamics. Many workers have used the free volume ideas of Turnbull and Cohen[4-6] to fit diffusion data. The results have been moderately successful. The assumption made in this approach is that diffusion of solvents in concentrated polymer solutions can be thought of as diffusion in a two component glass, where the formation of a critical "free volume" is necessary before molecules can diffuse. In spite of this somewhat artificial mechanism, free volume theory has been used to treat both glasses and polymers.

Diffusion in both polymers and glasses is understood in terms of an activated process,[7] one in which the molecules must overcome a free energy barrier to move between one local free energy minimum and another. These barriers have a distribution of heights, as should be expected from the nature of an amorphous, high density glass. This distribution gives rise to the non-Arrhenius behavior that is seen, for example, in the density dependence of the diffusion constant. Thus, to predict the diffusion constant, it is necessary to describe the free energy surface.

Recently, Hall and Wolynes[8] have proposed an alternative description of diffusion in glasses, using an aperiodic crystal picture. In their formalism, an inhomogeneous density is used to describe the free energy surface for the system, from which the barriers to diffusion can be estimated. The resulting expression for the diffusion constant is distinct from the free volume expression yet fits experimental data as well or better. The ability of both functional forms to fit data is presumably due to the small range of densities (and/or temperatures) over which experimental data has been obtained. In this paper, we shall use the aperiodic crystal picture to describe the diffusion of solvents in concentrated polymeric systems. We show how an expression for the free energy barrier can be derived by a simple extension of the Hall–Wolynes description and apply the resulting functional to two cases of diffusion in polymers.

Aperiodic Crystal Picture

The aperiodic crystal picture stems from both density functional theories[9] and cell theories of liquids.[10] Our treatment will use density functional terminology, as it is the most straightforward approach. In the density functional approach, the free energy is expressed as a functional of the inhomogeneous density of the system

$$\beta F(\rho(r)) = \beta F_{\mathrm{ideal}}(\rho(r)) + \beta F_{\mathrm{int}}(\rho(r))$$

where β is $1/kT$, F_{ideal} is the ideal gas contribution to the free energy, F_{int} is the free energy due to interactions between particles, and $\rho(r)$ is the density. Given a trial density, an upper bound to the free energy can be found by minimizing the free energy with respect to the density:

$$\delta\beta F/\delta\rho(r) = 0$$

The resulting densities describe the local free energy minima.

This approach has been used successfully to describe the liquid–solid phase transition, properties of solids, and liquid–solid interfaces.[12] It is not clear that the density corresponding to the minimum free energy is necessarily periodic (cf. crystals), thus allowing for the possibility of amorphous densities representing local free energy minima. Such approaches have been used before in the treatment of glasses.[12] Hall and Wolynes[8] extended the search for minima to search for transition states between these minima (saddle points on the free energy surface). Once both minima and transition states are located, it is a simple matter to find the transition-state barriers and the diffusion constant.

The aperiodic crystal picture assumes that each atom vibrates about some aperiodic lattice site. In the simplest treatment this vibration is assumed to be harmonic, with a force constant α. The values of α are related to the Debye–Waller factors for the atoms. As the density increases, $\alpha \rightarrow \infty$ and the atoms remain fixed at their sites. As the density decreases, $\alpha \rightarrow 0$, the atoms can "vibrate" over the entire sample and the system thus approaches the liquid state. In addition, since the force constant is a measure of the difficulty of moving an atom, as $\alpha \rightarrow \infty$ the free energy barrier to diffusion increases. Hence, a simple "Marcus like" approximation to the free energy of activation can be written

$$\beta\Delta F^{\dagger} = \tfrac{1}{2}\sum_{i=1}^{N}\alpha_i\,(r_i^{\dagger} - r_i)^2$$

where $\beta\Delta F^{\dagger}$ is the activation free energy, N is the number of atoms, r_i is the lattice site for atom i at its minimum, $r_i^{\dagger}$ is the position of atom i at the transition state, and α_i is the force constant for atom i. It should be emphasized that α_i is determined from the free energy surface, rather than the potential energy surface. At the transition state, the activation energy is given approximately by

$$\beta\Delta F^{\dagger} = \tfrac{1}{2}r_0^{2}\alpha$$

where $r_0^2 = \sum_i(r_i^{\dagger} - r_i)^2 \simeq N_{\mathrm{m}}\Delta r^2$ with N_{m} the total number of atoms that move, and Δr the average distance moved by an atom. In addition, we have assumed that the α values for the moving particles are the same. This is an approximation that allows a simple analytical result to be obtained. The relaxation of this assumption is straightforward and is currently the subject of simulation studies. We expect that r_0 will have only a weak dependence on density and thus assume the bulk of the density dependence to reside in α. At high densities, it is possible to obtain the density dependence of α and hence $\beta\Delta F^{\dagger}$. For a one-component glass, Hall and Wolynes[8] showed that for the case of hard-sphere interactions

$$\alpha \propto 1/(d_{\mathrm{nn}} - \sigma)^2 \tag{1}$$

where d_{nn} is the nearest-neighbor separation and σ is the hard-sphere diameter of the molecule. The form of this result is easy to understand from simple physical considerations. Since α is the force constant for motion of a molecule, it is inversely related to the mean square displacement of the molecule from its lattice site. The mean-square displacement will be dependent on the distance that the center of the molecule can move, in this case $d_{\mathrm{nn}} - \sigma$. From dimensional analysis, then, one can see that eq 1 must be the expected result. Further, since $d_{\mathrm{nn}} \propto 1/\rho^{1/3}$ and $\sigma \propto 1/\rho_0^{1/3}$, we can easily show that

$$\alpha \propto 1/[1 - (\rho/\rho_0)^{1/3}]^2$$

Table I

	T, °C	v_1, cm^3/g	v_2, cm^3/g	χ	ln (D_0), cm^2 s^{-1}	a	b	c
ethylbenzene	115	1.282	0.9804	0.45	−10.669	0.0065	5.406	
	130	1.306	0.9887	0.45	−10.106	0.0056	5.416	
	140	1.324	0.9942	0.45	−9.77	0.0058	5.419	
toluene	110	1.282	0.9777	0.40	−11.04	0.0033	5.435	5.196
	140	1.332	0.9942	0.40	−10.49	0.0038	5.440	5.20

Thus, an expression for the density dependence of the activation free energy obtains.

This form worked quite well in describing diffusion in 1,3,5-trinapthylbenzene,[8] despite its assumption of hard-sphere interactions. The reason for this is, presumably, that at high densities the structure of the glass is determined primarily by the repulsive interactions between molecules, which can be accurately modeled with hard-sphere interactions. Hence, we shall assume the interactions that contribute to the density dependence of the activation free energy in polymers can be modeled by hard-sphere repulsions. To use this approach in a polymer–solvent system, we assume we have a two-component glass, consisting of hard spheres of diameters σ_{11} (representing the solvent) and σ_{22} (representing the polymer segments or "jumping units"). In practice, σ_{22} should probably be the diameter of a monomer. Further, we assume that the number of nearest neighbors is proportional to the number of sites per molecule, s_1 and s_2. With these assumptions, we show in the appendix that the high density limit of the solvent force constant, α_1, is given by

$$\alpha_1 = A/[x_1(\sigma_{11}/\sigma_{12}) \times (1 - \sigma_{11}(\rho/\rho_0^*)^{1/3}) + x_2 c(1 - \sigma_{12}(\rho/\rho_0^*)^{1/3})] \quad (2a)$$

where $A = 72\pi/(z\sigma_{12})^2(s_1/[s_2 c(\sigma_{12})])^2$ and

$$D_1 = D_0 \exp[-\beta\Delta F^{\dagger}] = D_0 \exp[-\alpha_1 r_0^2/2] \quad (2b)$$

Here, D_1 is the solvent self diffusion coefficient, D_0 contains an attempt frequency and any dependence on attractive interactions (which will lead to a temperature dependence of D_0), z is the number of nearest neighbors sites at a lattice site (in a one component system), x_1 and x_2 are the number fractions of solvent and polymer segment, respectively, ρ is the number density, ρ_0^* is the reduced density ($\rho_0^* = \rho_0\sigma^3$) at random close packing (usually assumed to be 1.22), σ_{12} is the solvent–polymer segment effective hard-sphere diameter, $c(\sigma_{12})$ is the direct correlation function evaluated at σ_{12} ($\simeq -4$ for the densities of interest here), and c is a constant of order unity that we set to 1 for simplicity. A similar expression exists for the polymer self-diffusion coefficient. To predict the mutual diffusion coefficient, we use the expression due to Bearman[12]

$$D_M = (\partial\mu_1/\partial \ln x_1)(D_1 x_2 + D_2 x_1)/RT$$

where μ_1 is the chemical potential of the solvent. For low-solvent mole fractions, $D_2 \simeq 0$ and, hence, D_M can be determined from a knowledge of D_1 and μ_1. For μ_1, we use the approximation of Flory[13,5] and find

$$D_M = D_1(1 - x_1)^2(1 - 2\chi x_1) \quad (3)$$

where χ is the interaction parameter that describes the free energy of mixing. In our subsequent analysis, we shall make some simplifying assumptions, but eq 2 should be regarded as the principle result of this work. For densities close to random close-packed and small number fractions of solvent, $\beta\Delta F^{\dagger}$ can be shown to be

$$\beta\Delta F^{\dagger} \propto 1/(x_1\Delta V_1 + x_2\Delta V_2)^2$$

where $\Delta V_i = V_i - V_{0i}$ and V_{0i} is the closest packed volume for species i. This should be compared to the result of Duda[5]

$$\beta\Delta F^{\dagger} \propto 1/(x_1\Delta V_1 + x_2\Delta V_2)$$

We see that, just as was found in the one-component glass case, the aperiodic crystal picture predicts a qualitatively different dependence on $V - V_0$.

Results

We apply the aperiodic crystal picture to two previously studied solvent-polymer systems:[5] ethylbenzene–polystyrene and toluene–polystyrene. In the ethylbenzene–polystyrene system, the polymer segment unit is approximately the same size as the solvent molecules (both in mass and in volume), so we make the simplifying assumption that the hard sphere radius describing the solvent–polymer and solvent–solvent interactions are the same. This reduces the number of unknown quantities yet does not seriously affect the fit. For both systems, we assume that the mass of the polymer segment unit is 104 g/mol and that the value of χ is given by Duda et al.[5] We have converted from weight fraction (the measure of composition used by Duda[5]) to segment fraction using the following relation

$$\phi_i(T) = \frac{w_i v_i(T)}{w_1 v_1(T) + w_2 v_2(T)}$$

where u_i is the weight fraction and $v_i(T)$ is the temperature-dependent specific volume (in units of cm^3/gm) of the pure components. The values of $v_i(T)$ were taken from Hocker and Flory for ethylbenzene,[14] from Timmermans[15] for toluene, and from Fox and Loshaek[16] for polystyrene. To convert to number densities (each polymer segment is considered to be an "atom"), we use

$$\rho\ (\text{Å}^{-3}) = [1/\tilde{v}_2 + \phi_1(1/\tilde{v}_1 - 1/\tilde{v}_2)]$$

where $\tilde{v}_2 = v_2 W_2/L$ is the volume per "atom" of each component, W_2 is the molecular weight, and L is Avagadro's number. Given this input, we can fit the mutual diffusion constant for a variety of temperatures. From one temperature to the next, we do not expect the parameters to change, with the exception of D_0, which will contain some energetic information not present in our hard sphere model. We fit both systems at different temperatures by using the equation

$$\ln D_M = \ln [(1 - x_1)^2(1 - 2\chi x_1)] + \ln D_0 - \frac{a}{[x_2(1 - b\rho^{1/3}) + x_1(c/b)(1 - c\rho^{1/3})]^2}$$

Table I contains the fit parameters and Figures 1–5 the best fits. As can be seen, D_0 is the only parameter with a significant temperature dependence, as was anticipated. From our work in single component glasses[8] and the work of Duda and Vrentas,[5] we have a good idea of the values of all the parameters, which will allow us to assess the fits. The range of values for ln D_0 compares favorably the values found by Vrentas and Duda, −9.29 to −10.01 for ethylbenzene and −9.14 to −9.63 for toluene. In addition, we can estimate ln D_0 from the Chapman–Enskog method.[17] For hard spheres with a mass of 100 g/mol, and diameter

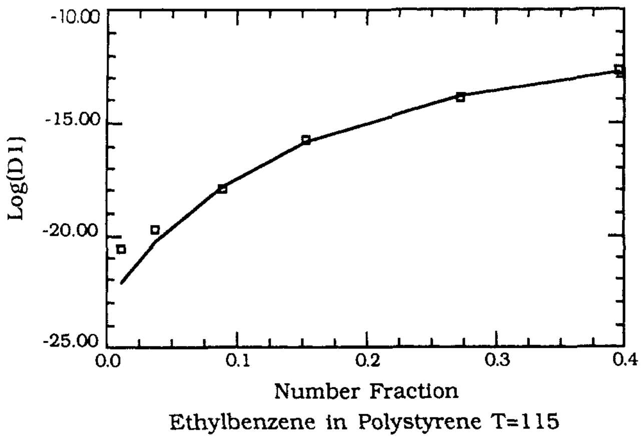

Figure 1. Plot of ln (D_1) versus x_1 (defined in text) for ethylbenzene in polystyrene at T = 115 °C. Curve, theory; squares, experimental. D_1 is obtained from D_M by subtracting the contribution from μ_1.

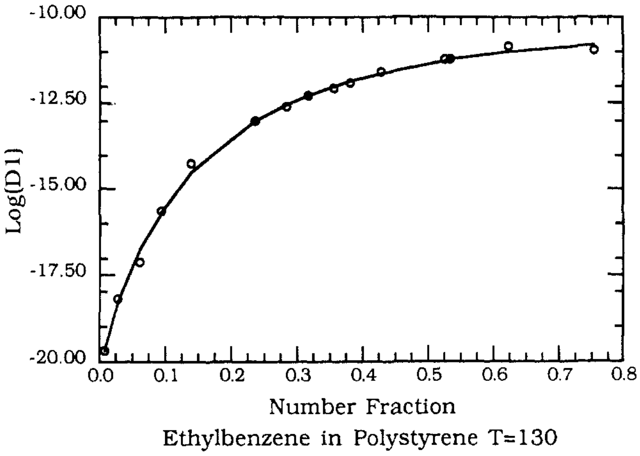

Figure 2. Same as Figure 1 except for ethylbenzene in polystyrene at T = 130 °C.

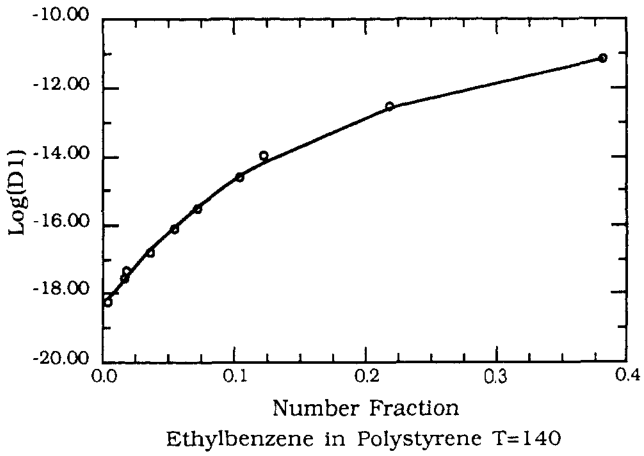

Figure 3. Same as Figure 1 except for ethylbenzene in polystyrene at T = 140 °C.

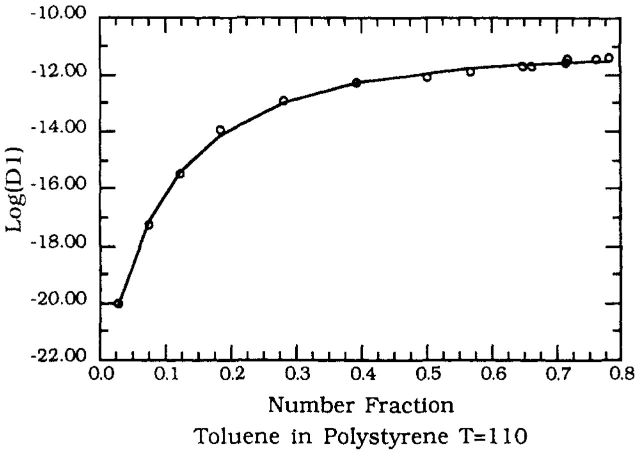

Figure 4. Same as Figure 1 except for toluene in polystyrene at T = 110 °C.

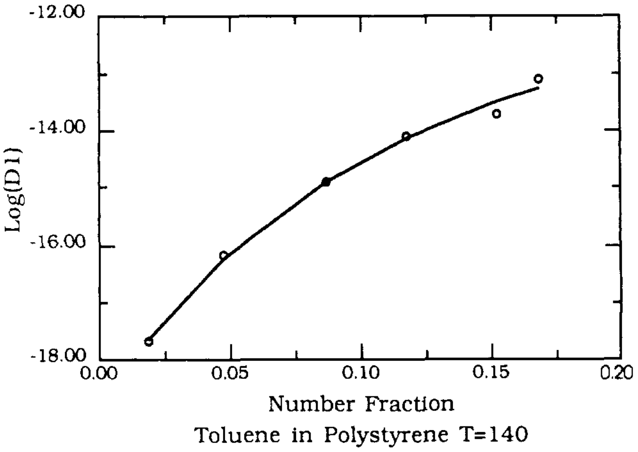

Figure 5. Same as Figure 1 except for toluene in polystyrene at T = 140 °C.

of 5.4 Å, and a number density of 0.005 Å^{-3} (a typical number for the experiments described here), we find ln D_0 to be −8.2, in reasonable agreement with our fit parameters. The value of a is

$$a = 36\pi(r_0/\sigma z c(\sigma))^2(s_2/s_1)^2N_m$$

Previous studies[18] have shown that $r_0/\sigma \simeq 0.1$ and $N_m \simeq 10$. s_2/s_1 is typically taken to be $^1/_2$ and we assume $z \simeq 12$. Thus, we should expect a value for a of approximately 0.001, which is just about the values we obtain for the fit parameters. Finally, we can compare the value of the predicted radius from the values of b and c

$$\sigma_{11} = c\rho_0{}^{*1/3}$$

$$\sigma_{12} = b\rho_0{}^{*1/3}$$

where $\rho_0{}^*$ is typically taken to be 1.22. This gives values of σ_{12} of 5.778 Å for ethylbenzene–polystyrene, 5.787 Å for toluene–polystyrene, and 5.412 Å for the toluene–toluene. These are not unreasonable values for the hard-sphere diameters. Thus, all the parameters involved are reasonable. As can be seen from the figures, the aperiodic picture successfully fits the experimental data. The success of the method encourages the use of the aperiodic crystal to describe diffusion in ternary systems, consisting of two solvents and one polymer or two polymers and one solvent. In addition, diffusion in anisotropic polymers (for instance, rigid rodlike polymers) can be discussed by using this same formalism.

Conclusions

We have shown how the aperiodic crystal picture can successfully treat diffusion in polymer–solvent systems. By treating the mixture as a two-component glass, the dependence of the mutual diffusion coefficient on composition has been predicted. The form of the function is different from the free-volume function that has been used in the past. Our treatment has ignored several potentially important features of these systems. First, we have assumed that the polymer segments do not contribute substantially to the diffusion constant. This should be true at low solvent concentrations, but not necessarily over the entire range that we have fit. Inclusion of this effect is straightforward, involving an additional set of coefficients (representing D_0 and b for the dilute polymer) which could be estimated from fits at infinite polymer dilution. Secondly, we have used the Flory-Huggins form for the chemical potential of the solvent–polymer system. It should be possible to use the density functional theory to estimate the chemical potential more accurately by taking into account the bonds between polymer segments using the free energy functional functional of Singer et al.[19] When this is differentiated with respect to the solvent concentration, an improved form for the chemical potential could be obtained. We do not feel, however, that this will make a large difference in our results since our implicit assumption is that the polymer segments are randomly distributed in the glass, an assumption similar to that used by Flory. Finally, we have assumed that only one free energy barrier exists (we have used only a single value of α) yet we know that a distribution of these barriers does exist. Work is currently in progress aimed at determining these barriers using computer simulations,[20] which should allow not only the determination of the range of α values but also the distribution of energy terms in D_0.

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Appendix

For a two-component system,[21] $\rho(r) = \rho_1(r) + \rho_2(r) = x_1\rho_1(\alpha_1,r) + x_2\rho_2(\alpha_2,r)$ with

$$\rho_i(\alpha_i,r) = \sum_i^N (\alpha_i/\pi)^{3/2} \exp(-\alpha_i(r - R_i)^2)$$

and $\{R_i\}$ is the set of N aperiodic lattice sites. The free energy is given by[9] (to lowest order in density)

$$\beta F = \int \mathrm{d}r\, \rho_1(r)[\ln(\rho_1(r)) - 1] + \int \mathrm{d}r\, \rho_2(r)[\ln(\rho_2(r)) - 1] - \tfrac{1}{2}\int \mathrm{d}r_1\, \mathrm{d}r_2\, \rho(r_1)c(r_1 - r_2)\rho(r_2) + \text{constants}$$

where $c(r)$ is the direct correlation function. At low densities, a reasonable approximation to $c(r)$ is $c(r) = c(\sigma)f(r)$, with $f(r) = \exp(-\beta V(r)) - 1$ and $V(r)$ is the pair potential (assumed to be spherically symmetric). $c(\sigma)$ is used to obtain the correct radial distribution function at contact and has a value of approximately −4 for the densities of interest in this work. For hard spheres, βF this takes the form

$$\beta F = \tfrac{3}{2}N_1 \ln(\alpha_1/\pi) + \tfrac{3}{2}N_2 \ln(\alpha_2/\pi) - \tfrac{5}{2} - c(\sigma)/2 \sum_{i,j}[x_1^2 w(R_{ij},\alpha_1,\sigma_{11}) + 2x_1x_2 w(R_{ij},2\alpha_1\alpha_2/(\alpha_1 + \alpha_2), \sigma_{12}) + x_2^2 w(R_{ij},\alpha_2,\sigma_{22})]$$

with

$$w(R,\alpha,\sigma) = 4\pi\sigma/\alpha(\alpha/2\pi)^{3/2} \exp(-\alpha r^2/2) - \Phi(\sigma\sqrt{\alpha/2}) \quad \text{if } R = 0$$

$$W(R,\alpha,\sigma) = \tfrac{1}{2}[\Phi(\sqrt{\alpha/2}(R - \sigma)) - \Phi(\sqrt{\alpha/2}(R + \sigma))] + 1/(R\sqrt{2\pi}\alpha)[\exp(-\alpha(R - \sigma)^2/2) - \exp(-\alpha(R + \sigma)^2/2)] \quad \text{if } R > 0$$

At high densities, only the nearest neighbors contribute to the interaction terms and we find (for $\alpha_2 \gg \alpha_1$)

$$\beta F = \tfrac{3}{2}N_1 \ln(\alpha_1/\pi) + \tfrac{3}{2}N_2 \ln(\alpha_2/\pi) - \tfrac{5}{2} - c(\sigma)/2[Nx_1^2 w(0,\alpha_1,\sigma_{11}) + 2Nx_1x_2 w(0,2\alpha_1,\sigma_{12}) + Nx_2^2 w(0,\alpha_2\sigma_{22})] - c(\sigma)/2\,[x_1^2 N z_{11} w(d_{\mathrm{nn}},\alpha_1,\sigma_{11}) + 2x_1x_2 N z_{12} w(d_{\mathrm{nn}},2\alpha_1,\sigma_{12}) + x_2^2 N z_{22} w(d_{\mathrm{nn}},\alpha_2,\sigma_{22})]$$

where we have assumed that the nearest-neighbor distance is independent of particle type and z_{ij} is the number of nearest neighbors if each atom of type i is surrounded by type j atoms (z_{12}/z_{11} is the ratio of the number of "contact" sites on the polymer and solvent molecules). We now minimize βF with respect to α_1. Using

$$\mathrm{d}/\mathrm{d}\alpha\,[w(0,\alpha,\sigma)] \simeq 0 \qquad \text{for } \alpha \gg 1$$

and

$$\mathrm{d}/\mathrm{d}\alpha\,[w(d,\alpha,\sigma)] = \sigma(1 - \sigma/d)/[2\sqrt{2\pi}\alpha] \exp(-\alpha(d - \sigma)^2/2)$$

we find $0 = \beta F$ gives

$$3 = \sqrt{\alpha_1}[x_1 z_{11}\sigma_{11}(1 - \sigma_{11}/d_{11})/(2\sqrt{2}) \exp(-\alpha_1/2\,(d_{11} - \sigma_{11})^2) + x_2 z_{12}\sigma_{12}(1 - \sigma_{12}/d_{12}) \exp(-\alpha_1(d_{12} - \sigma_{12})^2)]/\pi$$

which leads to eq 2 upon rearrangement, setting $d_{11} = d_{12} = d_{nn}$ and assuming that $\exp(-\alpha_1(d_{nn} - \sigma)^2)$ is a slowly varying function of α_1 (in practice, it is essentially unity).

Registry No. Ethylenebenzene, 100-41-4; polystyrene, 9003-53-6; toluene, 108-88-3.

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