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Conformational Asymmetry and Polymer–Polymer Thermodynamics

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The thermodynamics of mixing for high molecular weight amorphous polymers and low molecular weight liquids have much in common and several important differences. Flory[1] and Huggins[2] were among the first individuals to present statistical mechanical theories that dealt with the random-walk nature of polymer solutions and melts. However, the resulting expressions for the free energy of mixing bear a striking resemblance to classical regular solution theory, where the ideal combinatorial entropy of mixing for simple fluids is normalized by the degree of polymerization, N. All excess free energy contributions are included in the well-known χ parameter,

$$\chi = \chi_0 + \chi_\alpha + \chi_\beta + \ldots + \chi_\epsilon \qquad (1)$$

including the heat of mixing,

$$\chi_0 = \frac{z}{k_B T}[\epsilon_{AB} - 1/2(\epsilon_{AA} + \epsilon_{BB})] \qquad (2)$$

where ϵ_{ij} is determined by the strength of the interactions between the type i and j segments, z is an effective coordination number, and k_B is the Boltzmann constant. Excess entropies, arising from specific interactions such as hydrogen bonding and segment packing constraints, are accounted for by χ_α, χ_β, etc. In general, contributions to the excess entropy of mixing have been associated with *local* (i.e., monomer length scale) effects, with little attention paid to the *nonlocal* (i.e., length scales greater than the persistence, or Kuhn, length) excess entropy of mixing, denoted in eq 1 by χ_ϵ. Clearly, this issue is irrelevant to simple low molecular weight mixtures, where $N \sim 1$, since all interactions are short-ranged. However, in polymer–polymer systems, where $N \gg 1$, the constraint of maintaining a relatively uniform density is at odds with the traditional notion of random mixing between components that are conformationally different, leading to a long-ranged excess entropy of mixing.

Only recently has the importance of such "conformational asymmetry" become apparent.[3–8] In this paper we attempt to clarify the origins of this interesting effect and identify a parameter for quantifying conformational asymmetry that is independent of how monomers (i.e., statistical segments) are defined. We should note that, although this topic is of much current interest,[3–8] the seeds of this concept were sown many years ago in a classic series of papers by Helfand describing the consequences of Kuhn length asymmetry on interfacial composition profiles in polymer blends.[9,10] Because the interfacial profiles in the regime considered by Helfand ($N^{-1} \ll \chi \ll 1$) have thicknesses that are intermediate between the Kuhn length scale and the radius of gyration scale, the conformational asymmetry effect observed there is properly deemed a *nonlocal* effect. We shall see that it is precisely this same range of length scales that gives the dominant contribution to χ_ϵ in the case of bulk polymer mixtures. Besides providing an explicit expression for χ_ϵ, an important objective of the present paper is to clearly differentiate between *local* and *nonlocal* contributions to χ and thereby clear up confusion that exists in the polymer community about the origins of the conformational asymmetry effect.

We begin by considering a mixture of two equal molecular weight monodisperse polyolefins. Our choice of simple saturated hydrocarbons tends to minimize heat of mixing contributions to χ (i.e., χ_0 will be relatively small) and avoids *local* entropy effects due to specific interactions. As a pedagogical example we examine an amorphous polyethylene (PE) and poly(ethylethylene) (PEE) blend; this system has been fully characterized as described in a previous publication.[3] The *local* structures of PE and PEE are depicted in Figure 1, where we have chosen four-carbon repeat units in each case. For conceptual purposes we can ignore the small density difference between these chemical isomers, although this will be properly accounted for in what follows. Each component must satisfy two long-range space-filling conditions that are key to understanding the origin of χ_ϵ. First, a single polymer molecule occupies a certain volume V. Since the densities are nearly equal and the molecular weights are the same, $V_{PE} \cong V_{PEE}$. Second, owing to the random-walk nature of amorphous polymers, each macromolecule will extend over a conformational volume that is proportional to R_g^3, where $R_g = b(N/6)^{1/2}$ is the unperturbed radius of gyration of a chain in a melt of similar chains. Clearly, R_g will be quite different for PE versus PEE, since half the atoms in PEE lie pendant to the molecular backbone. Because we have specified equal molecular weights, i.e., $N_{PE} = N_{PEE}$, this difference will be reflected in the statistical segment length b. It is important to emphasize that, although b has dimensions similar in magnitude to a repeat unit length, it is truly a *nonlocal* parameter since its value depends on the complicated screening[11] of excluded-volume interactions that occurs over scales intermediate between b and R_g. Experimentally, $b_{PE} \cong 8.2$ Å and $b_{PEE} \cong 5.1$ Å at 150 °C based on the four-carbon repeat units depicted in Figure 1.[3] (A simple estimate based on the total number of backbone carbon atoms and Gaussian statistics, i.e., ignoring differences in rotational isomeric states and the screening effects mentioned above, leads to $b_{PE} = 2^{1/2}b_{PEE}$.) Thus, viewed at the magnification of Figure 1, PE appears as a long, thin molecule, while PEE looks somewhat shorter and thicker. The *nonlocal* effects that we will be concerned with in the present paper are *defined* to be associated with lengths that fall between the b scale, $\sim(b_{PE}b_{PEE})^{1/2}$, and the R_g scale, $\sim(R_{PE}R_{PEE})^{1/2}$, i.e., lengths where Gaussian statistics are approximately obeyed. Sketches depicting these *nonlocal* conformational features for equal molecular weight (i.e., equal V's) PE and PEE are illustrated in Figure 1.

The classical Flory–Huggins free energy of mixing contains one *nonlocal* contribution, the ideal combinatorial entropy. Unperturbed polymer coils are modeled as mixing randomly without changes in their respective conformational characteristics. Obviously, this is simply not possible with PE and PEE. If the overall density remains constant (note that there is a very severe free energy penalty associated with density fluctuations), then unperturbed PE and PEE molecules cannot be randomly interchanged. Insertion of a PE molecule into the volume left vacant by removing a PEE molecule from a pure melt causes frustration, because the delicate balance of forces that produces excluded-volume screening on length scales

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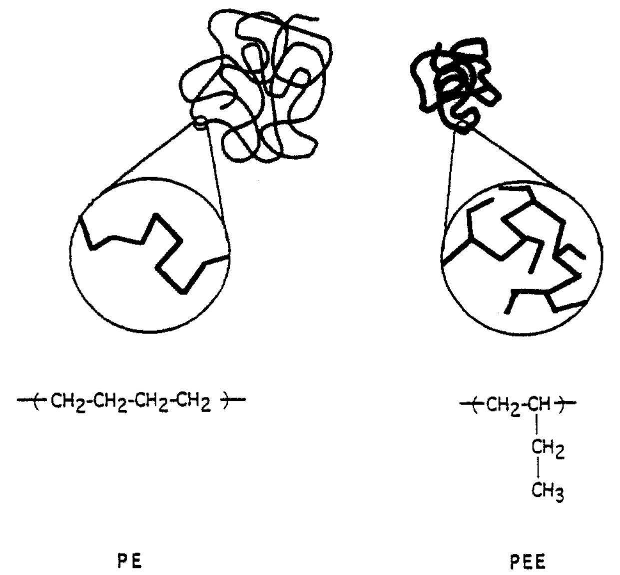

Figure 1. Illustrative example of a conformationally asymmetric pair of polymers, polyethylene (PE) and poly(ethylethylene) (PEE). These Gaussian coil projections have been constructed based on chains with equal molecular volumes, V. Because half of the carbon atoms lie pendant to the backbone in PEE, this chain appears to be shorter and thicker than PE, leading to a smaller R_g and $\beta_{\mathrm{PEE}} < \beta_{\mathrm{PE}}$. Local and nonlocal contributions to the overall mixing free energy can be crudely associated with length scales smaller and larger, respectively, than the magnified sections.

between b_{PEE} and R_{PEE} is disrupted. We anticipate a *positive* excess free energy of mixing associated with this entropic frustration. This point is graphically illustrated by attempts to exchange the two coils sketched in Figure 1. If we vary the N's in order to match the R_g's, then the V's will be mismatched, and visa versa. Nonrandom mixing, or conformational rearrangements that facilitate mixing, will thus be manifested as a *nonlocal* excess entropy term, χ_ϵ, in the Flory–Huggins formalism.

Next, we show that the above heuristic arguments can be given a basis in statistical mechanics. Toward this end, we have analyzed a simple model of a binary polymer melt, with pure components obeying Gaussian statistics and having statistical segment lengths b_A and b_B and segment volumes v_A and v_B. The degrees of polymerization are respectively N_A and N_B. As an idealized model of segment–segment interactions in the melt, we assume an interaction Hamiltonian that is a local quadratic form (energy units of k_BT):[10,12]

$$\rho_0 \sum_{ij} w_{ij} \int \mathrm{d}\mathbf{r}\, \hat{\phi}_i(\mathbf{r})\, \hat{\phi}_j(\mathbf{r}) \tag{3}$$

where $\rho_0 = (v_A v_B)^{-1/2}$ is a mean segment density, $\hat{\phi}_i(\mathbf{r})$ is the microscopic volume fraction of type i (A or B) segments near $\mathbf{r}$, and the interaction matrix w_{ij} is of the form

$$\mathbf{w} = \begin{pmatrix} \kappa & \kappa + \chi_0/2 \\ \kappa + \chi_0/2 & \kappa \end{pmatrix} \tag{4}$$

In this simple model, *total* density fluctuations are penalized by κ (inversely proportional to the compressibility) and χ_0 is the familiar heat of mixing parameter of eq 2. The incompressible limit is approached by taking $\kappa \to \infty$.

For the above model it is possible to analytically calculate the excess free energy of mixing, provided that the conformational asymmetry is small (see below) and $\chi_0(N_A N_B)^{1/2} \ll 1$; i.e., the mixture is deep in the one-phase region or χ_0 makes a negligible contribution to the total χ (nearly athermal blends). In such cases, the density fluctuations are sufficiently weak that the random-phase approximation[11] can be applied. Specifically, we have followed the approach of Barrat et al.,[12] where the quadratic interactions of eq 3 are decoupled via an Edwards transformation. In the incompressible limit ($\kappa \to \infty$) and for $\chi_0(N_A N_B)^{1/2} \ll 1$ the resulting expression for the excess free energy density is particularly compact:

$$F_\epsilon = \frac{1}{2(2\pi)^3} \int \mathrm{d}\mathbf{k}\, \ln[N_A v_A \phi g(x_A) + N_B v_B (1-\phi) g(x_B)] \tag{5}$$

where $x_i = k^2 R_i^2$ and $R_i^2 = N_i b_i^2/6$ is the unperturbed (pure-component) radius of gyration of a type i chain. In addition, ϕ is the mean volume fraction of type A chains and $g(x) = 2x^{-2}[x + \exp(-x) - 1]$ is the familiar Debye function. Physically, the integral in eq 5 sums the contribution to the free energy at each wavevector $\mathbf{k}$ made by chemical potential fluctuations on the length scale $2\pi/k$ that are compatible with the constraint of constant total density.

By noting that the usual Flory–Huggins heat of mixing per unit volume is of the form $\rho_0 \chi_0 \phi(1-\phi)$, the excess contribution to $\tilde{\chi} \equiv -(2\rho_0)^{-1} \partial^2 F/\partial\phi^2$ (this is the quantity obtained from small-angle scattering measurements) is easily calculated as

$$\tilde{\chi}_\epsilon = -\frac{1}{2\rho_0} \frac{\partial^2 F_\epsilon}{\partial \phi^2} = \frac{1}{8\pi^2 \rho_0} \int_0^{\Lambda_b} \mathrm{d}k\, k^2 \left[\frac{N_A v_A g(x_A) - N_B v_B g(x_B)}{N_A v_A \phi g(x_A) + N_B v_B (1-\phi) g(x_B)} \right]^2 \tag{6}$$

where we have introduced an ultraviolet cutoff at $\Lambda_b \sim (b_A b_B)^{-1/2}$ to ensure convergence of the integral. Physically, this cutoff is required because the contributions of very high wavevector chemical potential fluctuations, $k > \Lambda_b$, are governed by the *local* liquid structure and are not properly treated by our coarse-grained polymer model. A proper treatment of such modes would require atomistic simulations or liquid-state methods such as RISM.[13,14]

Equation 6 is a general formula for the excess contribution to $\tilde{\chi}$ of a binary polymer blend, subject only to the weak restrictions given above. (Similar expressions can be derived for copolymer melts or blends of copolymers with arbitrary architectures, sequence distributions, and compositions.[15]) In cases where the radii of gyration of the two components are not too different, the integral on the right-hand side of eq 6 can be approximately evaluated by breaking the domain of integration into two intervals, $(0, \Lambda_R)$ and (Λ_R, Λ_b), where $\Lambda_R \sim (R_A R_B)^{-1/2}$. (When this condition is not met, more than two intervals are required.) Over the interval $(0, \Lambda_R)$, corresponding to modes with wavelengths exceeding the R_g scale, we can approximate the factors of $g(x)$ in the integrand by unity. Correspondingly, for the interval (Λ_R, Λ_b), our *nonlocal* regime of scales between b and R_g, we can make the approximate replacement $g(x) \approx 2/x$. It follows that the contribution from the former interval is $\Lambda_R^3/\Lambda_b^3 \sim (N_A N_B)^{-3/4}$ smaller than the second and can be neglected. Our final result is thus

$$\tilde{\chi}_\epsilon = \frac{\Lambda_b^3}{24\pi^2 \rho_0} \left[\frac{1 - (\beta_A/\beta_B)^2}{\phi + (1-\phi)(\beta_A/\beta_B)^2} \right]^2 \tag{7}$$

where

$$\beta_i^2 \equiv b_i^2/6v_i \tag{8}$$

are the invariant (independent of segment definition) parameters introduced by Helfand and Sapse.[10]

Equation 7 is a very illuminating and useful expression for the contribution to $\tilde{\chi}$ arising from conformational asymmetry. When the β's of the two components are precisely matched, $\tilde{\chi}_\epsilon$ vanishes because then there is no disruption of the liquid structure on scales between $1/\Lambda_b$ and $1/\Lambda_R$ when chains of the two species are mixed. As the ratio of the β's departs from unity, $\tilde{\chi}_\epsilon$ grows roughly as the square of the difference between β_A and β_B. We note that an expression similar to eq 7 was derived previously,[5] although the model employed there was quite different and the results less straightforward to interpret. Also of interest is the composition dependence of $\tilde{\chi}_\epsilon$ predicted by eq 7. For β_A/β_B of order unity, the dependence on ϕ is smooth, the quantity in square brackets varying between $(\beta_B/\beta_A)^2 - 1$ for $\phi = 0$ and $1 - (\beta_A/\beta_B)^2$ for $\phi = 1$. However, for β_A/β_B small or large compared with unity (but the R_i still nearly matched), $\tilde{\chi}_\epsilon$ has a more singular variation with composition, $\tilde{\chi}_\epsilon \sim \phi^{-2}$ or $\tilde{\chi}_\epsilon \sim (1 - \phi)^{-2}$, respectively. Finally, we note that while the O(1) prefactor in eq 7 is nonuniversal due to the presence of the cutoff (depending on *local* liquid structure and chemical details of the monomers), the quantity in square brackets is *universal* for all binary polymer mixtures with the same values of ϕ and β_A/β_B and requires only *pure-component properties* for evaluation.

It is important to emphasize the fact that β_i is truly a *nonlocal* parameter, in spite of its dependence on the segment-scale parameters, b_i and v_i. As our derivation of eq 7 clearly highlights, β_i is the invariant combination of variables that dictates the conformational flexibility of species i under melt conditions and for length scales intermediate between b_i and R_i. In prior discussions[3-7] we have presented this conformational parameter in a different, although equivalent, manner. There N_i and b_i were normalized for each polymer component based on a single reference volume leading to a_i, denoted "the statistical segment length at constant segment volume". While this approach has certain advantages (e.g., it is consistent with the spirit of lattice theory and is easily applied to scattering theory), it tends to obscure the *nonlocal* nature of β_i. Nevertheless, the two approaches are obviously related by $\beta_i \sim a_i$. Finally, the above suggests defining a variable ϵ as a particularly convenient measure of conformational asymmetry in polymer–polymer mixtures: so that $\epsilon = 1$ signifies conformational symmetry and $\epsilon \neq 1$ conformational asymmetry. For PE and PEE, $\epsilon = 3.1$ at 150 °C. It is important to note, however, that certain locally asymmetric segments, such as PEE and poly(vinylcyclohexane) (PVCH), can exhibit nonlocal symmetry, $\epsilon = 1.1$.[16]

The effects of conformational asymmetry have only recently become evident as polymer–polymer systems that contain small *local* excess free-energy contributions have been investigated. Saturated, and some unsaturated, polyolefins are especially susceptible to conformational asymmetry effects. In polymer–polymer mixtures the influence of conformational asymmetry is manifested in the bulk compatibility, and at surfaces, where differences in the β's can produce preferential surface segregation.[7,8] Block copolymer melts can exhibit even more dramatic effects due to constraints on microphase spacing, in addition to the constant density restriction. Recently, Vavasour and Whitmore[17] pointed out that $\epsilon \neq 1$ will influence the mean-field phase diagram for diblock copolymers, and for simplicity, we have retained their notation in the present work. Experimentally, one of us has shown that even the types of phases that occur for $f < 1/2$ can be different than for $f > 1/2$ when ϵ becomes sufficiently large.[18] In addition, when placed in contact with a symmetry-breaking surface, there is a demonstrated tendency for the smaller β block to segregate to the interface.[6] While these anecdotal examples firmly establish the importance of conformational asymmetry, our current understanding of this issue is rather primitive, and further experimental and theoretical work is necessary. In particular, we must stress that the quantitative results summarized here apply to linear homopolymer mixtures. More complex molecular architectures, microphase separation, and symmetry-breaking surfaces will introduce additional complexities.[15]

In summary, we have briefly reviewed the origins of conformational asymmetry effects in polymer–polymer thermodynamics and have provided a new expression for quantitative assessment of these effects in linear homopolymer mixtures. Differences in conformational (R_g) and volume-filling (V) characteristics can lead to a *nonlocal* excess entropy of mixing that is readily parametrized in terms of $\epsilon = (\beta_A/\beta_B)^2$, where $\beta^2 = R_g^2/V$. When the *local* excess free energy of mixing becomes small, this *nonlocal* effect can produce significant and unanticipated modifications to the thermodynamic properties of polymer mixtures and block copolymers.

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