A simple model for baroplastic behavior in block copolymer melts

A.-V. G. Ruzette,[a] P. Banerjee, and A. M. Mayes[b]
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

T. P. Russell
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

A simple model for the free energy of mixing of compressible polymer blends is derived, based on the regular solution model. Its ability to predict phase behavior for weakly interacting polymer pairs using only the pure component properties of mass density, solubility parameter, and thermal expansion coefficient is illustrated for mixtures of polystyrene and poly(n-alkyl methacrylates) with $n \leq 12$. The model yields a clear explanation for the strong pressure effects observed in some of these systems, including the first reported baroplastic elastomer. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1361072]

In dramatic contrast to the classical miscibility gap or upper critical solution transition (UCST) observed upon cooling in most organic or inorganic small molecule mixtures and alloys, polymer blends and solutions are known to also undergo, in some instances, phase separation upon heating through a lower critical solution transition (LCST).[1,2] The observation of this inverted coexistence curve is a direct consequence of the reduced combinatorial entropy of mixing in macromolecular systems compared to their small molecule analogs. Indeed, under these circumstances, additional entropic factors otherwise negligible and arising from differences in the pure component $P-V-T$ properties govern the free energy of mixing at elevated temperature and destabilize the mixture. This has been demonstrated by several authors using equation-of-state (EOS) theories such as the Prigogine cell model,[3] the Flory–Orwoll–Vrij theory,[4,5] the Sanchez–Lacombe lattice fluid model,[6,7] the lattice cluster theory[8] and the more recent EOS of Hino and Prausnitz.[9]

Similar to polymer blends, diblock copolymers, wherein the two chemically distinct polymer chains are covalently bonded together, can also undergo a disorder–order transition (local phase separation) either upon cooling (UDOT)[10] or upon heating (LDOT), or both,[11] accompanied by a rheological transition from liquidlike to solidlike properties.

The observation of LDOT-type behavior in block copolymers has important implications from an applications standpoint. Indeed, empirically, phase separation upon heating through a LCST/LDOT is always accompanied by a positive change in volume, leading to the strong pressure effects reported for this transition.[12,13] For example, by applying hydrostatic pressure, the LDOT reported for polystyrene-*block*-poly n-butyl methacrylate (PS-*b*-PBMA) is raised by as much as 150 °C/kbar, an unprecedented observation of pressure effects in polymers.[12] Pressure has an equally profound effect on the rheological properties of this

material, inducing Newtonian flow by disordering the copolymer. While it has been recognized that such ''*baroplastic*'' behavior could be highly advantageous for processing, in practice, its exploitation has been impeded by a lack of simple predictive tools for designing new baroplastic polymers of commercial relevance. In this paper, we describe a simple free energy model for compressible polymer blends, extendable to block copolymers, that can serve as a predictive tool for the design of miscibility and baroplastic behavior into weakly interacting polymer mixtures. Employing this model, the explanation behind the systematic change in phase behavior recently reported for a homologous series of styrene/n-alkyl methacrylate copolymers is made transparent.[14]

To proceed, we consider a compressible blend comprising n_A chains of polymer A, each containing N_A segments of hard core (0 K, zero pressure) volume v_A, and n_B chains of polymer B, each containing N_B segments of hard core volume v_B. The total volume occupied by each polymer component in the pure state, denoted V_i, is assumed to be a function of both temperature and pressure, thereby allowing for thermal expansion and compressibility. The total volume V occupied by the phase-mixed blend differs from the sum of the pure component volumes $V_A + V_B$ by the quantity ΔV_{mix}, the change in volume on mixing.

As pointed out by Hildebrand and Flory,[15] the change in combinatorial entropy upon mixing for a compressible two-component polymer solution or mixture should scale logarithmically with the ratios of the unoccupied or ''free'' volume available in the mixture, $V_{f,m}$, to that in the pure components, $V_{f,A}$ and $V_{f,B}$:

$$\Delta S_{\mathrm{mix}}/k = n_A \ln\left(\frac{V_{f,m}}{V_{f,A}}\right) + n_B \ln\left(\frac{V_{f,m}}{V_{f,B}}\right). \qquad (1)$$

The free volume of component i, $V_{f,i}$, is defined here as the difference between the total volume V_i at temperature T and pressure P and the occupied or hard core volume: $V_{f,i}(T,P) = V_i(T,P) - n_i N_i v_i$; similarly $V_{f,m} = V(T,P) - (n_A N_A v_A + n_B N_B v_B)$. Following the formalism typically

adopted in EOS theories,[16] $V_{f,i}$ and $V_{f,m}$ can be expressed in terms of the reduced densities $\tilde{\rho}_i = \rho_i/\rho_i^*$, where ρ_i is the mass density at T and P and $\rho_i^* = M_{u,i}/(N_0 v_i)$ is the hard core density for a monomer of molecular weight $M_{u,i}$(g/mol) (N_0 is Avogadro's number):

$$V_{f,i}(T,P) = (1 - \tilde{\rho}_i)V_i(T,P). \tag{2}$$

Using this definition, Eq. (1) can be rewritten as

$$\Delta S_{\text{mix}}/k = -[n_A \ln \phi_A + n_B \ln \phi_B]$$
$$+ \left[n_A \ln\left(\frac{1-\tilde{\rho}}{1-\tilde{\rho}_A}\right) + n_B \ln\left(\frac{1-\tilde{\rho}}{1-\tilde{\rho}_B}\right) \right], \tag{3}$$

where ϕ_i is the pure component volume fraction, defined as $V_i/(V_A + V_B)$. In Eq. (3), we have made use of the approximation $\phi_i \approx V_i/V$, since ΔV_{mix} is typically $\sim o(10^{-4})V$ for macromolecular mixtures. Equation (3) consists of two terms: the ideal (incompressible) entropy of mixing, and a second term that arises from compressibility and is related to the difference in free volume between the mixture and the pure components.

In keeping with the spirit of the well-known Flory–Huggins theory and assuming random mixing (mean field approximation), a simple expression for the change in interaction energy can also be derived. In the phase separated (pure) state, the total interaction energy can be obtained by counting the number of pairwise $A-A$ and $B-B$ interactions. Herein, this is done in terms of hardcore cohesive energy densities $\delta_{i,0}^2 = -\frac{1}{2}z\varepsilon_{ii}/v_i$ (energy/vol):

$$E_{\text{pure}} = n_A N_A v_A \times \left(\frac{1}{2} \frac{z\varepsilon_{AA}}{v_A} \right) \times \frac{n_A N_A v_A}{V_A}$$
$$+ n_B N_B v_B \times \left(\frac{1}{2} \frac{z\varepsilon_{BB}}{v_B} \right) \times \frac{n_B N_B v_B}{V_B}$$
$$= -n_A N_A v_A \delta_{A,0}^2 \tilde{\rho}_A - n_B N_B v_B \delta_{B,0}^2 \tilde{\rho}_B, \tag{4}$$

where ε_{ii} is the attractive (negative) segmental interaction energy of the $i-i$ pair and z is the number of nearest neighbor monomers in the pure melts. (An alternate ''off-lattice'' derivation for ΔE_{mix} is provided in Appendix A.[17]) The *dilution factors* $\tilde{\rho}_i$ multiplying the self-interaction energy terms reflect the reduced probability of segmental interactions in the pure compressible melts compared to the hardcore state (incompressible limit). The interaction energy in the mixed state can be calculated in a similar fashion, making use of the classical regular solution model approximation[18] for the cross-interaction energy density $\delta_{AB,0}^2$:

$$\delta_{AB,0}^2 = \frac{1}{2} \frac{z\sqrt{\varepsilon_{AA}\varepsilon_{BB}}}{\sqrt{v_A v_B}} = \delta_{A,0}\delta_{B,0}, \tag{5}$$

yielding

$$E_{\text{mixed}} = -n_A N_A v_A \delta_{A,0}^2 \phi_A \tilde{\rho}_A - n_B N_B v_B \delta_{B,0}^2 \phi_B \tilde{\rho}_B$$
$$- 2 n_A N_A v_A \delta_{A,0}\delta_{B,0}\phi_B\tilde{\rho}_B. \tag{6}$$

Again, the dilution factor $\phi_i\tilde{\rho}_i = n_i N_i v_i/V$ represents the reduced probability of interacting with a segment of type i in the compressible mixed state compared to the hardcore state.

From Eqs. (4) and (6), a very simple perfect square is obtained for the change in interaction energy per unit volume, $\Delta E_{\text{mix}}/V$:

$$\frac{\Delta E_{\text{mix}}}{V} = \phi_A\phi_B\tilde{\rho}_A^2\delta_{A,0}^2 + \phi_A\phi_B\tilde{\rho}_B^2\delta_{B,0}^2 - 2\phi_A\phi_B\tilde{\rho}_A\tilde{\rho}_B\delta_{A,0}\delta_{B,0}$$
$$= \phi_A\phi_B(\tilde{\rho}_A\delta_{A,0} - \tilde{\rho}_B\delta_{B,0})^2. \tag{7}$$

Note that, alternatively, Eq. (7) can be rewritten in a form that more transparently separates the compressible and incompressible contributions to the change in interaction energy. Adding and subtracting the sum $\phi_A\phi_B\tilde{\rho}_A\tilde{\rho}_B(\delta_{A,0}^2 - \delta_{B,0}^2)$ to (7) and defining the T- and P-dependent cohesive energy density as $\delta_i^2 = \tilde{\rho}_i\delta_{i,0}^2$, one obtains

$$\frac{\Delta E_{\text{mix}}}{V} = \phi_A\phi_B\tilde{\rho}_A\tilde{\rho}_B(\delta_{A,0} - \delta_{B,0})^2$$
$$+ \phi_A\phi_B(\tilde{\rho}_A - \tilde{\rho}_B)(\delta_A^2 - \delta_B^2). \tag{7a}$$

In (7a), the first term is the classical exchange interaction energy, diluted by the factors $\tilde{\rho}_i$. It can be related back to the Flory–Huggins' interaction energy via the approximation:

$$\chi_{AB} \approx \sqrt{v_A v_B} \frac{(\delta_{A,0} - \delta_{B,0})^2}{kT}. \tag{8}$$

The second term in (7a), which can either be positive or negative, arises from the dilution or concentration of self-interactions (ε_{ii}) upon mixing. Hence, if component B is characterized at the same time by a larger free volume ($\tilde{\rho}_A > \tilde{\rho}_B$) as well as stronger self-interactions ($\delta_B^2 > \delta_A^2$) than component A, the contraction this component will undergo upon mixing is energetically favorable.

Combining Eqs. (3) and (7a), the total change in free energy per unit volume, Δg_{mix}, at atmospheric pressure ($P\Delta V_{\text{mix}}$ term ignored) is given by

$$\Delta g_{\text{mix}} = kT\left[\frac{\phi_A\tilde{\rho}_A}{N_A v_A}\ln\phi_A + \frac{\phi_B\tilde{\rho}_B}{N_B v_B}\ln\phi_B \right] + \phi_A\phi_B\tilde{\rho}_A\tilde{\rho}_B$$
$$\times (\delta_{A,0} - \delta_{B,0})^2 + \phi_A\phi_B(\tilde{\rho}_A - \tilde{\rho}_B)(\delta_A^2 - \delta_B^2). \tag{9}$$

In this expression, the second term of Eq. (3) was neglected, since it is in fact orders of magnitude smaller than the leading terms. This yields a simplified expression for Δg_{mix}, which depends *only on the pure component properties* of reduced density and cohesive energy density or solubility parameter. As shown in Appendix B, the stability criterion for the mixed state at atmospheric pressure is then readily obtained from the second derivative of the intensive free energy with respect to composition:

$$\left.\frac{\partial^2 g}{\partial\phi_A^2}\right|_{T,P} \approx \left.\frac{\partial^2 g}{\partial\phi_A^2}\right|_{T,P,\tilde{\rho}}$$
$$= kT\left[\frac{\tilde{\rho}_A}{\phi_A N_A v_A} + \frac{\tilde{\rho}_B}{\phi_B N_B v_B} \right]$$
$$- 2\tilde{\rho}_A\tilde{\rho}_B(\delta_{A,0} - \delta_{B,0})^2$$
$$- 2(\tilde{\rho}_A - \tilde{\rho}_B)(\delta_A^2 - \delta_B^2) > 0 \tag{10}$$
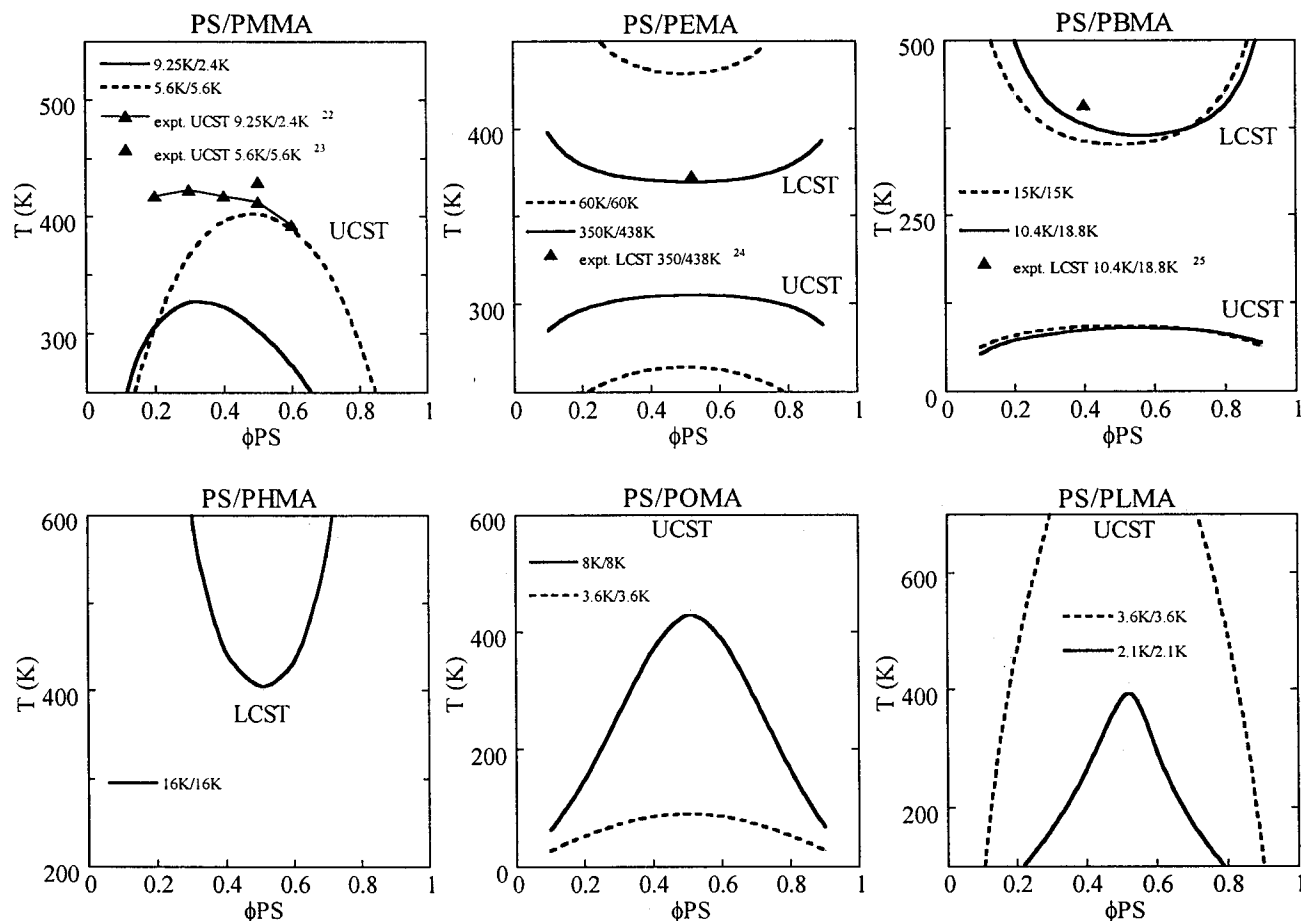
FIG. 1. Predicted phase diagrams and experimental cloud points for PS/P(n-alkyl methacrylate) blends. Homopolymer molecular weights are indicated for each spinodal or cloud point curve as follows: XX K=XX 000 g/mol.

while at the spinodal temperature, the same expression equals zero.

In the remainder of this paper, we employ the free energy model derived above to predict phase diagrams at atmospheric pressure for a series of styrene/n-alkyl methacrylate systems, the phase behavior of which was investigated experimentally and reported elsewhere.[14] To this end, the pure component properties $\tilde{\rho}_i(T)$ and $\delta_i(T)$ were determined from experimental PVT data[16] and group contribution (GC) calculations.[19] The reduced densities were obtained by simple extrapolation of Tait equation fits of mass density data to 0 K at zero pressure assuming a constant thermal expansion coefficient α_i (the melt state value) as a first approximation. This procedure yields the hardcore density ρ_i^* and, hence, $\tilde{\rho}_i(T)$ and $\delta_i^2(T) = \delta_i^2(298)(\tilde{\rho}_i(T)/\tilde{\rho}_i(298))$, where $\delta_i^2(298)$ is the room temperature cohesive energy density calculated according to van Krevelen.[19]

Previously, we reported[14] that block copolymers of PS and poly(n-alkyl methacrylates) of side chain length $2 \leq n \leq 4$, namely, poly(ethyl methacrylate), PEMA, poly(propyl methacrylate), PPMA, and PBMA, are miscible over a sizable T range, and exhibit LDOT behavior. In contrast, poly(methyl methacrylate), PMMA ($n=1$), as well as alkyl methacrylates with $n>4$, are increasingly immiscible with PS, and the corresponding block copolymers exhibit a UDOT, only observable for very low molecular weights.

Figure 1 shows the spinodals predicted from Eq. (9) for blends of PS and the six poly(n-alkyl methacrylates) for which $P-V-T$ data were available,[16,20] namely, PMMA ($n=1$), PEMA ($n=2$), PBMA ($n=4$), PHMA ($n=6$), POMA ($n=8$), and PLMA ($n=12$). Experimental coexistence (cloud point) curves for blends of these systems, only available for PS/PMMA,[21,22] PS/PEMA,[23] and PS/PBMA,[24] are also shown for comparison. As can be seen, Eq. (9) correctly captures the qualitative phase behavior of most of these systems. Hence, PS/PEMA and PS/PBMA are predicted to exhibit both a low UCST and a high LCST separated by a mixed-state window. In contrast, for PMMA, POMA, and PLMA, increasingly high UCST's are predicted, only observable in an experimentally accessible T range for very low molecular weights. Moreover, the reasonable quantitative agreement with experimental cloud points near the critical point is encouraging, considering that no adjustable parameters were used for the predictions. The only deviation from our observations is found for PS/PHMA. For this blend, a LCST is predicted, though block copolymers of these components display the UDOT.[14] Otherwise, the qualitative agreement between the model predictions and the experiments is excellent, implying that the model proposed herein can be used in a predictive capacity, at least for weakly interacting systems.

More generally, the model offers a simple molecular ex-

planation for the LCST/LDOT and the ''baroplastic'' behavior observed for PS-*b*-PBMA. Indeed, it can be readily shown that, independent of the choice of reference (hard-core) state, PS has a higher $\tilde{\rho}$ (i.e., less free volume) than the alkyl methacrylates. On the other hand, δ at 25 °C is lower for PS than for alkyl methacrylates with $n < 6$ carbon atoms. Hence, at low temperatures, the third term of Eq. (9) is negative for these systems, favoring mixing. However, as temperature increases, the values of $\tilde{\rho}$ and δ decrease due to thermal expansion. The magnitude of these changes is dictated by the value of α. Since α_{PS} is much lower than α_{PnAMA} except for PMMA,[16] the cohesive properties of most alkyl methacrylates weaken with increasing T more rapidly than those of PS. This implies that there will inevitably be a temperature at which the third term of Eq. (9) becomes positive, ultimately overcoming the combinatorial entropy of mixing and driving phase separation.

While these considerations relate to the variation of phase behavior with temperature only, an analogous discussion can be held to explain the large pressure effects observed for LCST/LDOT-type systems. Of the three terms in Eq. (9), the third term is by far the most pressure sensitive, scaling with the difference in pure component cohesive properties and, more importantly, its variation with T and P. While temperature enhances these differences in δ and $\tilde{\rho}$, pressure acts in the opposite direction, suppressing the driving force for phase separation. However, a necessary but not sufficient condition for the observation of these effects is that the exchange interaction energy $(\delta_{A,0} - \delta_{B,0})^2$ be sufficiently small, i.e., of comparable magnitude to the third term of Eq. (9), which describes precisely the case for PS and poly(alkyl methacrylates) with $2 \le n \le 4$.[14] In contrast, when $(\delta_{A,0} - \delta_{B,0})^2$ is large, this classical interaction term dominates the free energy and the system displays a UCST/UDOT, observable only for very low molecular weights and accompanied by minor pressure effects. This is seen for the PS/PMMA system and for PS blended with methacrylates having long alkyl side chains ($n > 6$).

Based on this discussion and the predicted LCST for PS/PHMA ($n = 6$), strong pressure effects were expected for this system, despite the experimentally observed UDOT. In fact, such behavior was recorded in *in situ* small-angle neutron scattering (SANS) studies under hydrostatic pressure (performed at the NIST Center for Neutron Research) on a 34 300 g/mol (34.3 K) PS-*b*-PHMA copolymer containing 49 wt % PS. The copolymer was synthesized anionically,[14] and pressure studies were performed following the approach described in Ref. 12. Figure 2 shows the circularly averaged SANS intensity profile at 140 °C and indicated pressures. At $P \le 0.2$ kbar, a sharp first-order reflection ($\Delta q/q = 0.2$) is observed, indicative of the ordered state. However, between 0.17 and 0.33 kbar, the discontinuous drop in peak intensity and broadening of the reflection ($\Delta q/q = 0.3$) signify a pressure-driven order–disorder transition. From similar data obtained at consecutive temperatures, an unexpectedly large pressure coefficient of -60 °C/kbar was determined, demonstrating ''baroplastic'' behavior for this system. This observation indicates that, despite its UDOT-type behavior, compressibility plays a dominant role in the free energy of this
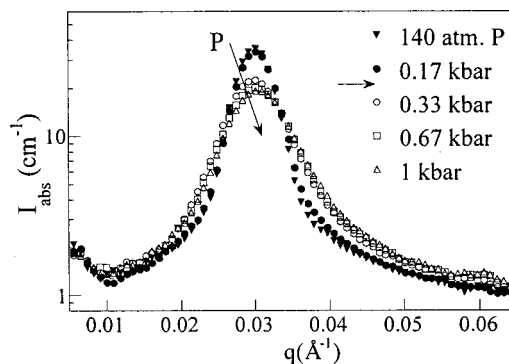

FIG. 2. SANS profile for 34.3 K PS-*b*-PHMA at 140 °C and indicated *P*.

system, as suggested by the phase diagram predicted from Eq. (9). This is in contrast to most observations of pressure effects on UDOT-type block copolymers, typically displaying much smaller and positive pressure coefficients of only $\pm 5 - 20$ °C/kbar. Given its large negative pressure coefficient and the disparate glass transitions of its two components, $T_{g,PS} = 100$ °C and $T_{g,PHMA} = -5$ °C, PS-*b*-PHMA is the first of a class of new ''baroplastic elastomers.'' This material should indeed exhibit melt-state formability at modest temperatures under the pressures characteristic of common processing methods, such as compression or injection molding.

In conclusion, a simple model for the free energy of mixing of polymer blends is proposed which qualitatively predicts the phase behavior of weakly interacting polymer pairs. This is illustrated here for a series of styrene/*n*-alkyl methacrylate blends, and in a following paper for 24 other polymer pairs, including various polyolefin mixtures, polycarbonate/PMMA, styrene-acrylonitrile/PMMA, PMMA/polyethylene oxide, PS with polybutadiene, polyisoprene, poly(vinyl methyl ether), poly(cyclohexyl methacrylate), poly(α-methyl styrene), poly(phenylene oxide), etc.[25] In its essence, the model extends the classical regular solution model for binary mixtures to account for thermal expansion. Its success in capturing the thermodynamic trends of macromolecular mixtures hints at a wider applicability to other systems, including polymer solutions, organic solutions, and possibly other small molecule mixtures or alloys.

APPENDIX A

In Eq. (7), ΔE_{mix} may be alternately derived without reference to a lattice by assuming a van der Waal's interaction potential $w_{ij}(r)$ between monomers i and j separated by a distance r to take the form $w_{ij}(r) = -C_{ij}/r^6$, where C_{ij} is the van der Waals energy coefficient, having units of energy$\times$volume.[2] The total interaction energy E_{ij} for $n_i N_i$ monomers of i interacting with $n_j N_j$ monomers of j in a volume V is given by[17]

$$
\begin{aligned}
E_{ij} &= \sum_{i,j} \frac{n_i N_i}{2} \int_{\sigma_{ij}}^{\infty} w_{ij}(r)\rho_j'(r)4\pi r^2\,dr \\
&= \sum_{i,j} \frac{n_i N_i}{2} \int_{\sigma_{ij}}^{\infty} \frac{-C_{ij}}{r^6}\rho_j'(r)4\pi r^2\,dr,
\end{aligned} \tag{A1}
$$

where $\rho_j'(r)$ is the local *number* density of j segments, σ_{ij} is an averaged segment hardcore diameter, and the system is assumed to be isotropic. Invoking the mean-field approximation $\rho_j'(r) = n_i N_i / V$, and further assuming that $C_{ij} = (C_{ii}C_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{1/2}$, the integral in (A1) yields

$$
E_{ij} = -\sum_{i,j} n_i N_i \frac{2\pi(C_{ii}C_{jj})^{1/2}}{3(\sigma_{ii}\sigma_{jj})^{3/2}}\left(\frac{n_j N_j}{V}\right). \tag{A2}
$$

The total interaction energy for the pure state is therefore

$$
\begin{aligned}
E_{\text{pure}} = E_{\text{pure},A} + E_{\text{pure},B} &= -n_A N_A \frac{2\pi C_{AA}}{3\sigma_A^3}\left(\frac{n_A N_A}{V_A}\right) \\
&\quad - n_B N_B \frac{2\pi C_{BB}}{3\sigma_B^3}\left(\frac{n_B N_B}{V_B}\right).
\end{aligned} \tag{A3}
$$

Noting that $\tilde{\rho}_i = n_i N_i v_i / V_i$, and identifying the 0 K cohesive energy density of each component as

$$
\delta_{i,0}^2 = \frac{2\pi C_{ii}}{3\sigma_{ii}^3 v_i^2} \tag{A4}
$$

we can rewrite (A3) as

$$
E_{\text{pure}} = -n_A N_A v_A \delta_{A,0}^2 \tilde{\rho}_A - n_B N_B v_B \delta_{B,0}^2 \tilde{\rho}_B \tag{A5}
$$

which is identical to Eq. (4). Similarly, the mixed state energy is given by

$$
\begin{aligned}
E_{\text{mixed}} &= -n_A N_A \frac{2\pi C_{AA}}{\sigma_A^3}\left(\frac{n_A N_A}{V}\right) - n_B N_B \frac{2\pi C_{BB}}{\sigma_B^3}\left(\frac{n_B N_B}{V}\right) \\
&\quad - n_A N_A \frac{2\pi(C_{AA}C_{BB})^{1/2}}{3(\sigma_A\sigma_B)^{3/2}}\left(\frac{n_B N_B}{V}\right) \\
&\quad - n_B N_B \frac{2\pi(C_{AA}C_{BB})^{1/2}}{3(\sigma_B\sigma_A)^{3/2}}\left(\frac{n_A N_A}{V}\right).
\end{aligned} \tag{A6}
$$

Setting $\phi_i \tilde{\rho}_i = n_i N_i v_i / V$ and $\delta_{AB,0}^2 = \delta_{A,0}\delta_{B,0}$ we obtain

$$
\begin{aligned}
E_{\text{mixed}} &= -n_A N_A v_A \delta_{A,0}^2 \phi_A \tilde{\rho}_A - n_B N_B v_B \delta_{B,0}^2 \phi_B \tilde{\rho}_B \\
&\quad - 2n_A N_A v_A \delta_{A,0}\delta_{B,0}\phi_B\tilde{\rho}_B
\end{aligned} \tag{A7}
$$

which is equivalent to Eq. (6). The change in interaction energy upon mixing is then calculated as $\Delta E_{\text{mix}} = E_{\text{mixed}} - E_{\text{pure}}$.

APPENDIX B

For a compressible binary mixture, phase stability requires that the system be stable with respect to both composition and volume fluctuations.[4,5,26,27] When the Gibbs free energy is used, this translates into the following mathematical expression for the stability condition:[26,27]

$$
\left.\frac{\partial^2 g}{\partial \phi_A^2}\right|_{T,P} = \left.\frac{\partial^2 g}{\partial \phi_A^2}\right|_{T,P,\tilde{\rho}} - \tilde{\rho}\beta\left(\left.\frac{\partial^2 g}{\partial\tilde{\rho}\partial\phi_A}\right|_{T,P}\right)^2 = 0. \tag{B1}
$$

However, since the simplified free energy expression given by Eq. (8) only depends on pure component variables and not on $\tilde{\rho}$, the second term of Eq. (B1) is equal to zero. At atmospheric pressure, spinodal temperatures can thus be readily calculated using the stability criterion given by Eq. (9).

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