

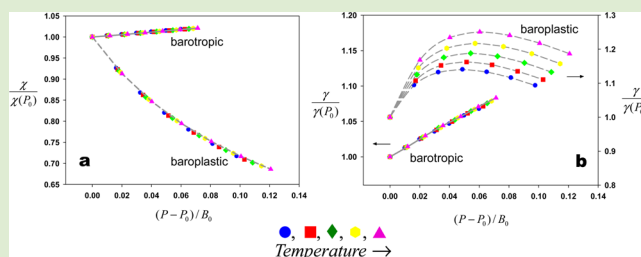
# Superposition in Flory–Huggins $\chi$ and Interfacial Tension for Compressible Polymer Blends

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## Supporting Information

**ABSTRACT:** We investigate theoretically the response of interfacial tension  $\gamma$  for compressible polymer blends to thermodynamic variables. Helfand's self-consistent field theory is first extended to be combined with an off-lattice equation-of-state model to describe compressibility. Typical incompatible blends reveal that the effects of temperature and pressure ( $T$ – $P$ ) on  $\gamma$  are superposed into a single curve by a dimensionless pressure variable through the superposition in Flory–Huggins  $\chi$  and density. In the case of polymer blends with strong compressibility difference,  $\gamma$  shows an anomaly upon pressurization with no  $T$ – $P$  superposition, even though  $\chi$  still follows the superposition.



It was found phenomenologically and theoretically that the volume or density of polymer melts and solutions satisfies a principle of temperature and pressure ( $T$ – $P$ ) superposition.<sup>1,2</sup> This principle states that the effects of temperature and pressure on the scaled volume ( $V/V(P_0)$ ) or density ( $\eta/\eta(P_0)$ ) are superposed into a universal curve, where  $P_0$  is ambient pressure. It was shown that the superposition is attributed to temperature insensitivity of the first pressure coefficient  $B_1$  of bulk modulus  $B_T$  ( $\equiv \partial P/\partial \ln \eta$ )<sub>T</sub> at  $P_0$ , which is the measure of asymmetry of free energy between dilation and compression. However, the implication and the range of applicability of this superposition still remain to be fully explored.

The interfacial behaviors of polymer mixtures are of great importance because a wide variety of polymer products are made of mixtures and then involved with phase segregation and self-assembly due to incompatibility.<sup>3</sup> The direct manifestation of interfacial behavior can be represented by interfacial tension  $\gamma$ . In most of the experimental works, the change in  $\gamma$  upon pressurization has not frequently been investigated due to the difficulty in setting up measuring devices. Here, we theoretically predict for the first time that typical incompatible blends reveal a  $T$ – $P$  superposition in  $\gamma$ , which originates in  $T$ – $P$  superposition of effective Flory–Huggins  $\chi$  and density (volume).

To analyze the interfacial behaviors, a field theory for the mixtures is often employed. In most of the polymer field theories, it is common to assume incompressibility, where the change in volume is ignored and the formulation of theories becomes simplified.<sup>4</sup> Since pressure is as equal a thermodynamic variable as temperature, there is a definite need for incorporation of finite compressibility in polymer field theories. This need has been addressed by compressible random-phase approximation (RPA) theories.<sup>5–9</sup> However, the truncation of free-energy series up to usually fourth-order limits RPA theories useful for the weak segregation regime. On the other hand,

Helfand suggested a self-consistent field theory (SCFT) based on Gaussian threads with perturbing interactions.<sup>10</sup> This approach has proved particularly useful for studying the interfacial region in the weak to intermediate segregation limit. Here, we extend Helfand's SCFT to compressible polymer blends by the incorporation of an off-lattice equation-of-state model. The formalism is quite general, so that any model can be used to make up the compressible SCFT.

The basic methodology in the present work is a general Edwards Hamiltonian or a Gaussian thread approach for polymer mixtures.<sup>10,11</sup> It is possible through the chosen approach to design desired micro- or nanostructures and predict physical properties and then to apply to structured bulk materials, thin films, and organic layers. The Edwards Hamiltonian is divided into its contribution by Gaussian chains and perturbing intermonomer interactions to describe the local association in given polymer mixtures.

Let us consider a binary polymer blend in the canonical ensemble, where there are  $n_j$  chains of  $j$ -species and each  $j$ -chain consists of  $N_j$  monomers. The Edwards Hamiltonian for the given system is given as follows

$$\beta H = \beta H_0 + \beta W\{\vec{r}_j\} = \frac{1}{2} \sum_{j=A,B} \sum_{k=1}^{n_j} \int_0^{N_j} d\tau_k \left( \frac{d\vec{r}_j(\tau_k)}{d\tau_k} \right)^2 + \beta W\{\vec{r}_j\} \quad (1)$$

Received: March 7, 2013

Accepted: May 28, 2013

Published: June 5, 2013

where the first term implies the Weiner potential energy for Gaussian chains, and  $W$  indicates the non-Gaussian potential energy for intersegmental interactions.  $\beta$  has its usual definition of  $1/kT$ . Each  $j$ -monomer on a  $k$ th chain is placed at the position vector  $\vec{r}_j(\tau_k)$  parametrized by a contour variable  $\tau_k$ . The partition function  $Z$  can be formally written as

$$Z = \prod_j \frac{V^{n_j}}{n_j!} \cdot \int \prod_j \prod_{k=1}^{n_j} \left[ \frac{1}{V} \cdot D\vec{r}_j e^{-\beta H_0(\vec{r}_j(\tau_k))} \right] \cdot e^{-\beta W} \quad (2)$$

where  $V$  is the system volume. The kinetic term represented by the thermal de Broglie wavelength  $\Lambda_j$  is not explicitly shown. If we define  $Z_0$  as the partition function of the Gaussian chains without any intersegmental interaction, then the ratio  $Q$  of  $Z$  to  $Z_0$  can be written as

$$Q = \frac{Z}{Z_0} = \frac{\int \prod_j \prod_{k=1}^{n_j} \left[ \frac{1}{V} \cdot D\vec{r}_j e^{-\beta H_0(\vec{r}_j(\tau_k))} \right] \cdot e^{-\beta W}}{\int \prod_j \prod_{k=1}^{n_j} \left[ \frac{1}{V} \cdot D\vec{r}_j e^{-\beta H_0(\vec{r}_j(\tau_k))} \right]} \quad (3)$$

An operator, which describes the local particle density of  $j$ -monomers on a polymer chain, is denoted as  $\hat{\rho}_j(\vec{r}) (= 1/V \sum_{k=1}^{n_j} \int_0^{N_j} d\tau_k \delta_{\text{Dirac}}(\vec{r} - \vec{r}_j(\tau_k)))$ . Alternatively, the local particle packing density operator  $\hat{\eta}_j(\vec{r}) (= v^* \cdot \hat{\rho}_j(\vec{r}))$  can be used instead, where  $v^*$  implies the theoretical volume of a monomer. A field variable  $\rho_j(\vec{r})$  corresponding to  $\hat{\rho}_j(\vec{r})$  describes the density of  $j$ -monomers at  $\vec{r}$  over the whole system. The  $\hat{\eta}_j(\vec{r})$  operator and the associated field variable  $\eta_j(\vec{r})$  have a similar relationship. A local concentration  $\phi_j(\vec{r})$  is defined as  $\phi_j(\vec{r}) \equiv \eta_j(\vec{r})/\eta(\vec{r})$ , where  $\eta(\vec{r})$  is the sum of  $\eta_j(\vec{r})$ 's as  $\eta(\vec{r}) = \sum_j \eta_j(\vec{r})$ . This  $\phi_j(\vec{r})$  factors out the concentration fluctuations from  $\eta(\vec{r})$ , which represents the overall density fluctuations.

The particle description of the free energy given above is now converted to the field description through the Hubbard–Stratonovich transformation.<sup>4,12</sup> The Edwards Hamiltonian  $H$  and the partition function  $Z$  can be manipulated to yield

$$Q = \left( \int \prod_j D\rho_j D\omega_j \prod_{k=1}^{n_j} \left[ \frac{1}{V} \cdot D\vec{r}_j \cdot e^{-\beta H_0(\vec{r}_j) - i \int d\vec{r} \omega_j \hat{\rho}_j} \right] \cdot e^{-\beta W + i \int d\vec{r} \omega_j \rho_j} \right) / \left( \int \prod_j \prod_{k=1}^{n_j} \left[ \frac{1}{V} \cdot D\vec{r}_j \cdot e^{-\beta H_0(\vec{r}_j)} \right] \right) \quad (4)$$

where  $\omega_j(\vec{r})$  is the hypothetical (dimensionless) external potential conjugate to  $\rho_j(\vec{r})$ , which transfers the effect of  $W$  on chain conformations to the partition function. Using the definition of  $\hat{\rho}_j(\vec{r})$ , the term inside the bracket in eq 4 can be equated to

$$\frac{\int D\vec{r}_j \cdot e^{-\beta H_0(\vec{r}_j) - i \int d\vec{r} \omega_j \hat{\rho}_j}}{\int D\vec{r}_j \cdot e^{-\beta H_0(\vec{r}_j)}} = \frac{\int d\vec{r} \cdot q_j(i\omega_j)}{V} \quad (5)$$

where  $q_j$  is the end-segment distribution function (chain propagator) of the Gaussian chains along the chain contour variable  $\tau$  or a scaled contour variable  $s$  ( $\equiv \tau/N_j$ ) spanning from 0 to 1.

Under the influence of  $i\omega_j(\vec{r})$ ,  $q_j$  should satisfy a modified diffusion equation<sup>13</sup> given below

$$\frac{1}{N_j} \frac{\partial q_j}{\partial s} = \frac{\sigma^2}{6} \nabla^2 q_j - i\omega_j \cdot q_j \quad (6)$$

with the initial condition that  $q_j(\vec{r}, 0) = 1$ . In eq 6, the symbol  $\sigma$  denotes the monomer diameter, and therefore  $v^* = \pi\sigma^3/6$ .

A conventional treatment of  $W$  is to ignore all the molecular details in a given polymeric system, and the so-called incompressibility constraint ( $\eta \rightarrow 1$ ) is assumed. A phenomenological interaction parameter  $\chi$  is taken into consideration as

$$\beta W\{\vec{r}_j\} = -\chi \int d\vec{r} \hat{\phi}_A(\vec{r}) \hat{\phi}_B(\vec{r}) \quad (7)$$

where  $\hat{\phi}_j(\vec{r})$  is the particle-based concentration conjugate to  $\phi_j(\vec{r})$ . The assumed incompressibility condition requires an additional field  $\xi(\vec{r})$  as a Lagrange multiplier. However, free space is indispensible in a continuum description of a polymeric system given here. A finite compressibility or equation of state (EOS) then naturally pervades the theoretical treatment. Previously, Hong and Noolandi adopted the lattice vacancy concept to describe compressible inhomogeneous polymeric systems.<sup>14</sup> Recently, Ginzburg et al. utilized the lattice vacancy to analyze the effects of compressibility on the thermodynamic behavior of polymer–clay nanocomposites.<sup>15</sup> These methods treat a solution of polymer systems and replace conceptually the solvent molecules with lattice vacancy. The purpose of this study is to avoid such a lattice vacancy concept by starting with an off-lattice description of free volume. Our choice of a compressible polymer mixture is an equation-of-state model for perturbed hard sphere chains suggested by the present author and Sanchez (Cho-Sanchez).<sup>2,16</sup> The free energy  $A^{\text{id}}$  of the reference system of Gaussian chains can be written as  $A^{\text{id}} = -kT \ln Z_0$  and stated mathematically as

$$\frac{\beta A^{\text{id}}}{\sum_j n_j N_j} = \sum_j \frac{\phi_j}{N_j} \ln \eta \phi_j K_j \quad (8a)$$

where  $K_j$  is a molecular constant that is irrelevant to thermodynamic properties. The perturbation contribution  $A^{\text{EV}}$  by excluded volume (EV) to EOS is described by Chiew's approach<sup>17</sup> as

$$\frac{\beta A^{\text{EV}}}{\sum_j n_j N_j} = \left\{ \frac{3}{2} \left[ \frac{1}{(1-\eta)^2} - \left( 1 - \sum_j \frac{\phi_j}{N_j} \right) \frac{1}{1-\eta} \right] - \sum_j \frac{\phi_j}{N_j} \left[ \ln(1-\eta) + \frac{3}{2} \right] \right\} \quad (8b)$$

A Bethe–Peierls-type mean-field energy  $A^{\text{nb}}$  is then added as the contribution by nonbonded interaction as<sup>18</sup>

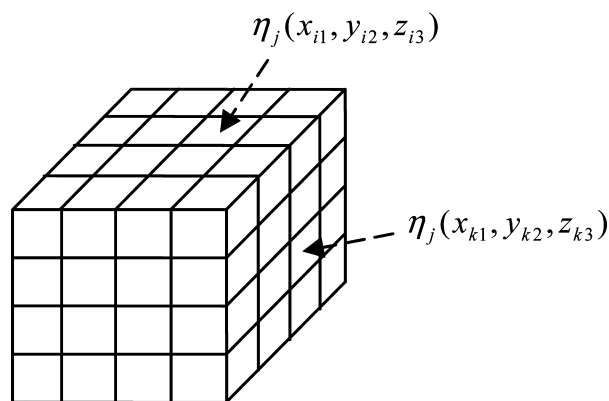
$$\frac{\beta A^{\text{nb}}}{\sum_j n_j N_j} = \frac{1}{2} \cdot \beta \bar{\epsilon} \cdot u(\eta) = \frac{1}{2} \cdot \beta \cdot \sum_{ij} \phi_i \phi_j \bar{\epsilon}_{ij} \cdot u(\eta) \quad (8c)$$

where the characteristic  $ij$ -monomer contact energy is given as  $\bar{\epsilon}_{ij}$ . The  $u(\eta)$  gives the Bethe–Peierls mean-field description of the attractive energy of locally packed nonbonded monomers for its density dependence as  $u(\eta) = f_p \cdot [(g/C)^{p/3} \eta^{p/3} - (g/C)^2 \eta^2]$ , where  $g$  and  $C$  are, respectively,  $1/\sqrt{2}$  and  $\pi/6$ . If the Lennard–Jones potential is taken as intermonomer potential here, then  $p$  and  $f_p$  become 12 and 4, respectively. The resultant free energy for the CS model is given as  $A = A^{\text{id}} + A^{\text{EV}} + A^{\text{nb}}$ , which is not only easy to use because of its analytical character but also supports the principle of  $T$ – $P$  superposition in polymeric liquids. The observed superposition states that  $\eta/$

$\eta(P_0)$  is a universal function of  $\Delta P/B_0 \equiv (P - P_0)/B_0$ , where  $B_0$  is the bulk modulus at  $P_0$ .<sup>1,2</sup> The necessary condition for the superposition is the temperature insensitivity of  $B_1 \equiv (\partial B_T/\partial P)_{P \rightarrow P_0}$ , where  $B_1$  is the measure of the asymmetry of free energy between dilation and compression. For organic polymers and their blends,  $B_1$  upon  $P_0 \rightarrow 0$  is contributed mainly by internal pressure, in particular, the exponents of  $u(\eta)$  as  $B_1 = 2 + (p/3 + 2) + \zeta$ , where  $\zeta$  is the residual contributions from internal and thermal pressures.<sup>2</sup> As  $T$  goes to zero,  $\zeta$  vanishes. In the useful temperature range,  $\zeta$  grows only slowly as  $\Delta\zeta \sim 0.02$  over 100 K. This analysis proves the insensitivity of  $B_1$ , which then gives the basis of  $T$ - $P$  superposition in  $\eta$ .

We denote the non-Gaussian parts of the free energy  $A$  as  $A^{\text{ni}} = A^{\text{EV}} + A^{\text{nb}}$ , and  $f^{\text{ni}}$  represents  $A^{\text{ni}}$  per unit volume as  $f^{\text{ni}} = A^{\text{ni}}/V$ . It is then proposed that the interaction  $W$  is given from the local version of  $f^{\text{ni}}$ . This action requires the replacement of  $\eta_j = v^* \cdot \rho_j$  with  $\hat{\eta}_j(\vec{r}) = v^* \cdot \hat{\rho}_j(\vec{r})$ , where the conceptual scheme is given in Figure 1.

$$\beta W\{\vec{r}_j\} = \int d\vec{r} \beta f^{\text{ni}}(\hat{\eta}_j(\vec{r})) = \int d\vec{r} \beta f^{\text{ni}}(\hat{\rho}_j(\vec{r})) \quad (9)$$



**Figure 1.** Implementation of the local version of free energy. Our system is discretized, and then for each cell centered at  $(x_{i1}, y_{i2}, z_{i3})$ , a locally equilibrated packing density  $\eta_j(x_{i1}, y_{i2}, z_{i3})$  is assigned. A further discretization of the box with finer meshes leads to a continuum description of the local density field  $\eta_j(\vec{r})$ . A field  $\hat{\eta}_j(\vec{r})$  is then defined as an operator that is conjugate to  $\eta_j(\vec{r})$ .

The partition function  $Z = Z_0 \cdot Q$  from eq 4 is in general evaluated by performing the Feynman path integral, which is a demanding task. The so-called self-consistent field theory (SCFT) deals only with the saddle point of the partition function  $Z^*$ , which in turn gives the mean-field free energy  $A_{\text{inh}} (\approx -kT \ln Z^*)$  of the inhomogeneous blend. The resultant self-consistent field equations are obtained by the functional differentiation of  $Z$  with respect to  $\omega_j$  and  $\eta_j$ . The  $\delta Z/\delta \eta_j(\vec{r})$  yields the following expression

$$-N_j v^* \cdot \frac{\partial \beta f^{\text{ni}}}{\partial \eta_j(\vec{r})} + N_j \cdot i\omega_j = 0 \quad (10)$$

In this situation, there is no need for a Lagrange multiplier to suppress compressibility. It is seen that  $\partial \beta f^{\text{ni}}/\partial \eta_j(\vec{r})$  is equal to the nonideal part of the chemical potential per a monomer as it should.

The  $\delta Z/\delta(i\omega_j(\vec{r}))$  gives the connection of each constituent density to  $q_j$  as

$$\eta_j(\vec{r}) = \frac{\eta_j}{\frac{1}{V} \int d\vec{r} q_j(\vec{r}, s=1)} \cdot \int_0^1 ds \cdot q_j(\vec{r}, s) q_j(\vec{r}, 1-s) \quad (11)$$

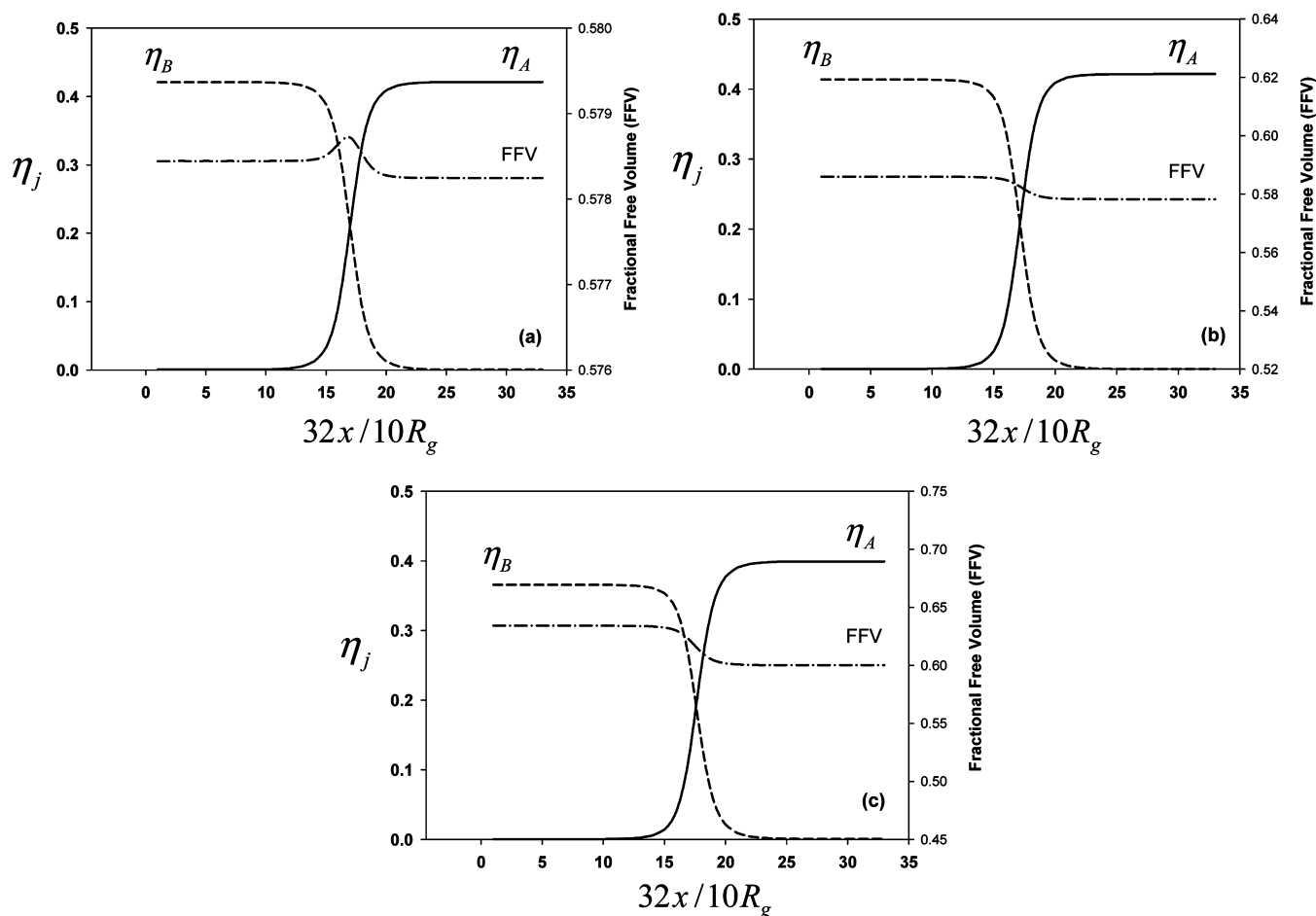
Solving eqs 6, 10, and 11 for all  $j$ -constituents completes the self-consistent field theory based on the suggested Edwards Hamiltonian for the compressible polymer mixture. It needs to be recalled that  $\omega_j(\vec{r})$  at the saddle point is pure imaginary. The present SCFT formalism is general, so that any statistical mechanical equation of state theory, which correctly possesses the ideal gas limit, can be incorporated to investigate systems with finite compressibility and thus pressure-related phenomena.

The interfacial tension  $\gamma$  is obtained as the difference between phase-segregated free energy and that in the mixed state per interfacial area  $\mathcal{A}$ , which can be stated mathematically as

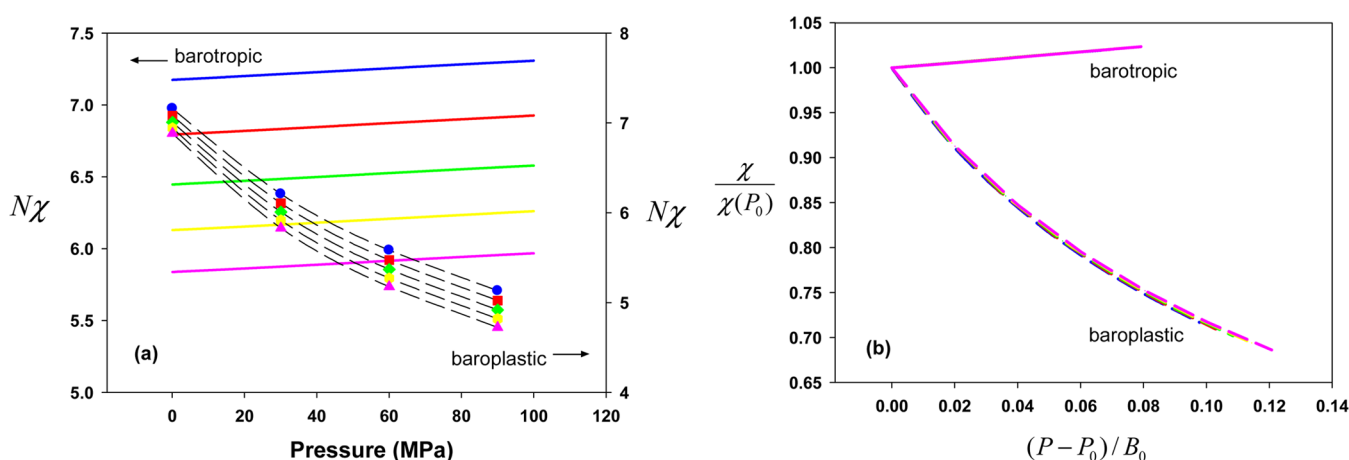
$$\begin{aligned} \gamma \cdot \mathcal{A} &= [A_{\text{inh}} + PV - \sum_j n_j \mu_j] \\ &= \frac{V}{v^*} \left[ \frac{A_{\text{inh}} \cdot \eta}{\sum_j n_j N_j} + P v^* - \sum_j \frac{\eta_j}{N_j} \cdot \mu_j \right] \end{aligned} \quad (12)$$

where  $V = \sum_j n_j N_j v^*/\eta$  is used. In eq 12,  $\mu_j$  is the chemical potential of the  $j$ -constituent from either phase in the bulk state.  $V/\mathcal{A}$  is rewritten as  $X \cdot (N_j)^{1/2} \cdot \sigma_j/\sqrt{6}$ , where  $X$  is the system size in terms of radius of gyration ( $R_{g,j} = (N_j)^{1/2} \sigma_j/\sqrt{6}$ ) of the  $j$ -constituent. Prior to the prediction of superposition in  $\gamma$ , we briefly test the validity of our approach by calculating  $\gamma$  for a widely studied incompatible blend of polystyrene (PS) and polybutadiene (PBD). The CS model requires three homopolymer parameters: the self-interaction parameter  $\bar{\epsilon}_{jj}$ ,  $\sigma_j$ , and  $N_j$ . A set of homopolymer parameters for PS (A) and PBD (B) is given as follows:  $\sigma_j = 4.04 \text{ \AA}$  (all);  $\bar{\epsilon}_{jj}/k = 4107.0$  (PS) and  $4065.9 \text{ K}$  (PBD);  $N_j \pi \sigma_j^3/6M_j = 0.41857$  (PS) and  $0.49395 \text{ cm}^3/\text{g}$  (PBD). Cross interaction between different polymers is characterized by  $\bar{\epsilon}_{AB}$ , which is an adjustable parameter and determined by fitting phase behavior of a given blend system. The ratio  $\bar{\epsilon}_{AB}/(\bar{\epsilon}_{AA}\bar{\epsilon}_{BB})^{1/2} = 0.99565$  is suggested for the PS/PBD pair to fit its binodal points.<sup>9</sup> For the blend at  $\phi_A = 0.5$  along with chain sizes  $N_A = 72$  and  $N_B = 80$ , respectively, the calculated interfacial tension  $\gamma$  at 420 K and at ambient pressure reads  $0.668 \text{ mN/m}$  along with  $\partial\gamma/\partial T = -0.008 \text{ mN/m/K}$ , which is in reasonably good agreement with the literature values.<sup>19</sup> These results demonstrate the validity of our SCFT approach.

The essence of the phase behavior of polymer blends including their pressure responses is concentrated on effective Flory–Huggins  $\chi$ . Using the compressible random-phase approximation (RPA) theory,<sup>20</sup>  $\chi$  was extracted from the second-order vertex function and shown to be subdivided into two terms as  $\chi = \chi_H + \chi_S$ . The former  $\chi_H (\sim \Delta\bar{\epsilon}/T \cdot |u(\eta)|)$  is the conventional enthalpic part. The symbol  $\Delta\bar{\epsilon} (= \bar{\epsilon}_{AA} + \bar{\epsilon}_{BB} - 2\bar{\epsilon}_{AB})$  implies the exchange energy between  $\bar{\epsilon}_j$ 's. Unlike incompressible situations,  $\chi_H$  possesses density dependence because of  $u(\eta)$ . The remaining  $\chi_S (\sim P_\phi^* v^*/T \eta B_T)$  represents the entropic parts of  $\chi$  from compressibility difference (disparity in EOS properties) between constituents, where  $P_\phi$  denotes the composition derivative of pressure. Symmetric blends yield  $P_\phi v^* \sim (\epsilon_{AA} - \epsilon_{BB}) \cdot \eta^2 du/d\eta$ . In general, a constituent with larger  $\bar{\epsilon}_{jj}$  has a smaller compressibility (and larger  $\eta_{\phi \rightarrow 1}$ ) due to stronger cohesive energy. Therefore,  $P_\phi$



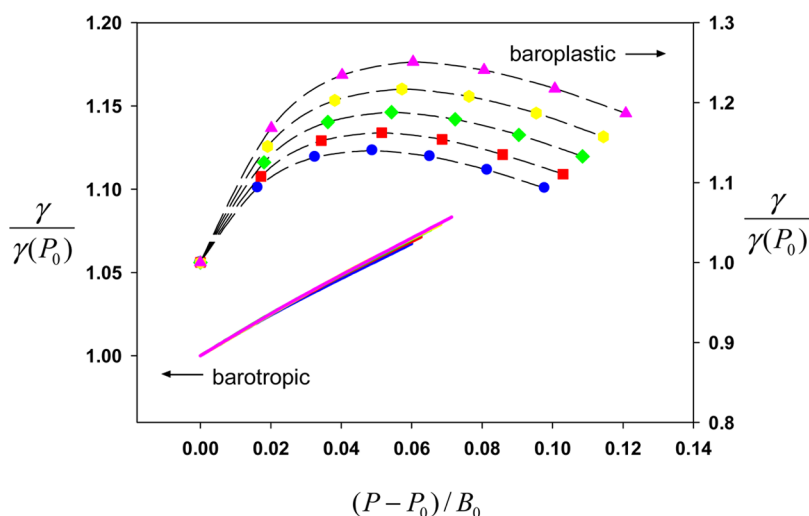
**Figure 2.** Phase-segregated local density profiles along with the local free volume fraction for three polymer blends at 0.1 MPa with  $\phi$  fixed to 0.5. The system possesses the lateral dimension of  $10 R_g$ , and the reflecting boundary condition is applied. The compressibility difference between constituents, signified by  $(\bar{\epsilon}_{AA} - \bar{\epsilon}_{BB})/\bar{\epsilon}_{AA}$ , is chosen to be 0.002 (a), 0.087 (b), and 0.270 (c). The segregation level becomes similar with  $N\chi$  of  $\sim 7$  by setting  $T = 400, 400,$  and  $520$  K, respectively. The free volume fraction (FFV) screens unfavorable AB contacts in the case of (a), while FFV is in-phase with the more compressible constituent B in cases of (b) and (c). Note that plots (a) and (b) are among barotropic blends, whereas plot (c) represents a baroplastic blend.



**Figure 3.** (a) Isotherms of  $N\chi$  at temperatures plotted against pressure for the barotropic blend in Figure 2(b) (blue line, red line, green line, yellow line, and pink line from  $T = 400$  K with  $\Delta T = 20$  K) and for the baroplastic blend in Figure 2(c) (blue circle, red square, green diamond, yellow hexagon, and pink triangle from  $T = 520$  K with  $\Delta T = 20$  K). (b) The isotherms of the scaled  $\chi/\chi(P_0)$  for the barotropic blend (solid blue line, red line, green line, yellow line, and pink line) and for the baroplastic blend (dotted blue line, red line, green line, yellow line, and pink line) plotted against the dimensionless pressure variable  $(P - P_0)/B_0$ , which, respectively, superpose into a single curve.

vanishes for the blends with the same compressibility. It is seen that the magnitude of  $\chi_S$  is determined by  $B_T$ . In response to

pressure,  $\chi_H$  and  $\chi_S$  behave in the opposite way to each other. Upon pressurization, the increased  $\eta$  augments  $\chi_H$ , whereas the



**Figure 4.** Isotherms of  $\gamma/\gamma(P_0)$  for the barotropic blend (solid blue line, red line, green line, yellow line, and pink line as in Figure 3(a)) plotted against the dimensionless pressure variable  $(P - P_0)/B_0$ , which merges into a single curve to reveal temperature–pressure superposition. In the case of the baroplastic blend (blue circle, red square, green diamond, yellow hexagon, pink triangle, and dotted lines as in Figure 3(a)), anomaly in the response of  $\gamma$  to pressure is seen with conserving no  $T$ – $P$  superposition.

increased  $B_T$  diminishes  $\chi_S$ . In the case that  $|\bar{e}_{AA} - \bar{e}_{BB}| \rightarrow 0$ ,  $\chi_S/\chi \rightarrow 0$  and  $\chi_H$  becomes a dominating contribution to  $\chi$ . Therefore, pressurization leads the system to a deeper segregation, which is the conventional behavior or barotropicity. In the case that  $|\bar{e}_{AA} - \bar{e}_{BB}|/\bar{e}_{AA}$  becomes more sizable,  $\chi_S/\chi$  gets more substantial. The applied pressure enhances  $B_T$ , which then suppresses  $\chi_S$  as well as  $\chi$ , which is called the anomalous  $\chi$  upon pressurization or baroplasticity.<sup>21,22</sup>

Now we consider three incompatible blends. It is assumed for convenience that polymer A adopts the molecular parameters of PS and polymer B differs from A only by its self-interaction as  $(\bar{e}_{AA} - \bar{e}_{BB})/\bar{e}_{AA} = 0.002, 0.087, \text{ and } 0.270$ . The cross interaction  $\bar{e}_{AB}/(\bar{e}_{AA}\bar{e}_{BB})^{1/2}$  is, respectively, set to 0.9958, 0.9950, and 1.0080. The blends are assumed to be symmetric with  $N = N_A = N_B$ , whose  $N\chi$  is to reach  $\sim 7$  at 0.1 MPa. In Figure 2, the snapshots of the phase-segregated profiles are given for these symmetric blends at  $\phi_A = 0.5$ . As  $|\bar{e}_{AA} - \bar{e}_{BB}|$  is small in the former two cases, the blends are barotropic with the similar binodal densities. The fractional free volume (FFV) to screen the unfavorable contacts at the A/B interface is of  $O(10^{-4})$ , which was visible only when  $(\bar{e}_{AA} - \bar{e}_{BB})/\bar{e}_{AA} \ll 0.010$  or  $\chi_S/\chi \ll 0.001$  as seen in plot (a). It is interesting for the system with  $(\bar{e}_{AA} - \bar{e}_{BB})/\bar{e}_{AA} = 0.087$  or  $\chi_S/\chi = 0.069$  in plot (b) that FFV is in-phase with the more compressible constituent B. Such a finite and nonvanishing  $|\bar{e}_{AA} - \bar{e}_{BB}|$  is unavoidable, so that it is more probable for free volume to behave as a weak selective solvent than as a neutral one. The plot in Figure 2(c) depicts the segregation profile of a baroplastic blend with  $|\bar{e}_{AA} - \bar{e}_{BB}|/\bar{e}_{AA} = 0.270$  or  $\chi_S \gg \chi_H$  as  $\chi_S/\chi = 0.679$ . Disparity in the binodal densities and the selectivity of free volume are clearly demonstrated.

In Figure 3(a), the isotherms of effective  $\chi$  for the blends chosen in plots 2(b) and 2(c) are calculated at selected temperatures as a function of pressure. Those values are then scaled as  $\chi/\chi(P_0)$  and plotted in Figure 3(b) against the dimensionless pressure variable  $\Delta P/B_0$  over a range of temperatures indicated. It is observed that  $\chi$ 's over the given temperature–pressure window are superposed into a single curve, which implies that the effects of temperature and pressure on  $\chi$  are interchangeable. This superposition originates

in the  $T$ – $P$  superposition of density:  $\eta/\eta(P_0) = h(\Delta P/B_0)$ . The component  $\chi_H$  ( $\sim \Delta \bar{e}/T \cdot |u(\eta)|$ ) possesses the density dependence through  $u(\eta)$ , which is fairly linear in its dependence on  $\eta$  in the useful range. Therefore,  $\chi_H$  becomes largely  $T$ – $P$  superposable. Even  $\chi_S$  ( $\sim P_0^2 v^*/T\eta B_T$ ) is  $T$ – $P$  superposable due to  $\eta$  and  $B_T$ . It can be derived from  $\eta$  that  $B_T/B_0 = \partial(\Delta P/B_0)/\partial \ln(\eta/\eta(P_0))$  also becomes the sole function of  $\Delta P/B_0$ . Therefore, the  $T$ – $P$  superposition in  $\chi$  is caused mostly by  $\chi_H$  in the former case, whereas the superposition is driven by  $\chi_S$  in the latter case.

Let us consider the interfacial tension  $\gamma$  of the same blends. Our self-consistent field theory yields  $\gamma$  over the temperature–pressure window as in Figure 3. Those  $\gamma$  values are scaled as  $\gamma/\gamma(P_0)$  and then replotted against  $\Delta P/B_0$  in Figure 4. To our surprise,  $\gamma$  in the case of the conventional barotropic blend follows the  $T$ – $P$  superposition. This prediction results from the fact that the main contributions to  $\gamma$  would be  $\eta$  and  $\chi$ . Each  $\eta$  or  $\chi$  satisfies the  $T$ – $P$  superposition. As  $\gamma$  exhibits the conventional pressure dependence, the  $T$ – $P$  superposition in  $\chi$  and  $\eta$  works constructively to yield the superposition of  $\gamma$  itself. It is notable that Helfand's prediction<sup>23</sup> of  $\gamma$  for a blend system with  $|\bar{e}_{AA} - \bar{e}_{BB}| \rightarrow 0$  at infinite  $N$  gives  $\gamma \sim kT\eta\chi^{1/2}$ , which yields the superposition as  $\gamma/\gamma(P_0) = (\eta/\eta(P_0)) \cdot (\chi/\chi(P_0))^{1/2}$ . Therefore, the  $T$ – $P$  superposition is conserved not only in the intermediate segregation but also in the strong segregation regime. The implication of this new finding is as follows. The measurements on  $\chi$  or  $\gamma$  with temperature change at ambient pressure along with its pressure scan at only one fixed temperature enable us to correctly estimate it at any other temperature and pressure prior to direct measurements, once  $B_0$ , one of the bulk properties, is known. Technically, a simple arithmetic mean of  $B_0$ 's of individual constituents is enough for  $B_0$  of the blend in the mixed state. Therefore, this finding should prove useful in designing and controlling phase and interfacial behaviors of many polymer blends. It is considered that the  $T$ – $P$  superposition in  $\gamma$  is not valid in the weak segregation limit. It was shown in the vicinity of critical point<sup>24</sup> that strong concentration fluctuations fuse the interface as  $\gamma/kT\eta \sim (\chi/\chi_C - 1)^{3/2}$  for a blend system with  $|\bar{e}_{AA} - \bar{e}_{BB}| \rightarrow 0$ .

The system should at least be far from this point to construct  $T$ – $P$  superposition.

Figure 4 also depicts  $\gamma$  in the scaled view for the baroplastic blend. It is seen from our SCFT calculations that the strongly baroplastic blend does not satisfy  $T$ – $P$  superposition.  $\gamma/\gamma(P_0)$  at each temperature shows an increase with  $\Delta P/B_0$  initially and then decreases afterward. The maxima of  $\gamma/\gamma(P_0)$  vary with temperature. The pressure response of  $\gamma$  is anomalous because  $\gamma$  does not conform with decreasing  $\chi$  for the baroplastic blend. The reason for this behavior is as follows. The main contributions to  $\gamma$  are not only  $\chi$  but also  $\eta$ . Below the threshold pressure, the increasing  $\eta$  provides the impetus to enhance the difference between free energies in the segregated and mixed states, even though segregation tendency diminishes with  $\chi$ . The suppressed segregation soon turns  $\gamma$  to yield the negative pressure coefficient ( $\partial\gamma/\partial P$ ). The threshold pressure is not fixed at different temperatures because the relative change in  $\eta$  upon pressurization is more apparent at elevated temperatures.

In summary, the effects of temperature and pressure on interfacial tension  $\gamma$  for compressible polymer blends have been studied through a self-consistent field approach. A theoretical formalism was established to incorporate an off-lattice equation-of-state model suggested by Cho and Sanchez in Helfand's self-consistent field theory. To accommodate finite compressibility, the Lagrange multiplier for the incompressibility constraint was discarded, and each constituent density freely spanned from zero to the crystal close-packing density. The theoretical calculation of  $\gamma$  for typical incompatible blends with zero to moderate disparity in their compressibilities revealed that the effects of temperature and pressure ( $T$ – $P$ ) on  $\gamma$  are superposed into a curve, which is a function of a single dimensionless pressure variable. The predicted superposition is attributed to the fact that the main contributions to  $\gamma$  are effective Flory–Huggins  $\chi$  and density  $\eta$ , where those two follow  $T$ – $P$  superposition themselves. In the case of polymer blends with strong compressibility difference,  $\gamma$  showed an anomalous behavior upon pressurization with no  $T$ – $P$  superposition, even though  $\chi$  still follows the  $T$ – $P$  superposition. The interplay between  $\chi$  and  $\eta$  yielded maxima in  $\gamma$ , when  $\gamma$  was plotted against pressure. These maxima varied according to temperature.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Supplementary SCFT calculations for compressible polymer blends at an asymmetric composition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Research Foundation of Korea through Basic Science Research Program (No. 2013030463) and also from the Center for Photofunctional Energy Materials (GRRCDankook2011-B03). We appreciate helpful discussions with Zhen-Gang Wang, Wolfgang Paul, Yongmei Wang, and Jaeup Kim.

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