Supporting Information of "Phase Behaviors in Compressible Polymer Blends"

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Abstract

Supplementary derivations for the scaling behavior and data for phase behaviors are shown in this supporting information.

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1. Scaling relation of K_i

To find out the leading term in χ_c^{eff}, we just need to solve the leading order of K_1 and K_2 as a function of $\rho_A^{(0)}$ and $\rho_B^{(0)}$. By using the L' Hopital's rule, we have the expression of K_1 and K_2:

$$
\begin{aligned}
K_1 &= \frac{1}{k_B T}\left[\mu_A^{\mathrm{ex}}\left(0,\rho_B^{(0)}\right)\rho_A^{(0)} - \mu_B^{\mathrm{ex}}\left(0,\rho_B^{(0)}\right)\rho_B^{(0)} - f_{\mathrm{ex}}\left(\rho_A^{(0)},0\right) + f_{\mathrm{ex}}\left(0,\rho_B^{(0)}\right)\right] \\
K_2 &= \frac{1}{k_B T}\left[-\left(\mu_A^{\mathrm{ex}}\left(\rho_A^{(0)},0\right) + \mu_A^{\mathrm{ex}}\left(0,\rho_B^{(0)}\right)\right)\rho_A^{(0)}\right. \\
&\left. + \left(\mu_B^{\mathrm{ex}}\left(\rho_A^{(0)},0\right) + \mu_B^{\mathrm{ex}}\left(0,\rho_B^{(0)}\right)\right)\rho_B^{(0)} + 2f_{\mathrm{ex}}\left(\rho_A^{(0)},0\right) - 2f_{\mathrm{ex}}\left(0,\rho_B^{(0)}\right)\right]
\end{aligned} \tag{1}
$$

As N is large, the density $\rho_A^{(0)},\rho_B^{(0)}$ at the critical point is small, so that the leading term in equation (1) can be solved by using the Taylor expansion of $f_{\mathrm{ex}}\left(\rho_A^{(0)},\rho_B^{(0)}\right)$ nearby $(0,0)$. They are given by

$$
\begin{aligned}
K_1 &= \frac{\pi}{6}\left[\frac{1}{N_B}\sigma_A^3 + \frac{3}{2}\frac{1+N_B}{N_B}\sigma_A^2\sigma_B + \frac{3}{2}\frac{1+N_A}{N_A}\sigma_A\sigma_B^2 + \frac{1}{N_B}\sigma_B^3\right]\rho_A^{(0)}\rho_B^{(0)} \\
&- \frac{\pi}{12}\frac{5+3N_A}{N_A}\sigma_A^3\left(\rho_A^{(0)}\right)^2 - \frac{\pi}{12}\frac{5+3N_B}{N_B}\sigma_B^3\left(\rho_B^{(0)}\right)^2 + O(r^3) \\
K_2 &= O(r^3)
\end{aligned} \tag{2}
$$

with

$$
r = \sqrt{\left(\rho_A^{(0)}\right)^2 + \left(\rho_B^{(0)}\right)^2}
$$

Recalling $\rho_A^{(0)} = O(N^{-1})$ and $\rho_B^{(0)} = O(N^{-1})$, we have $r = O(N^{-1})$. Substituting it into equation (2) will give $K_1 = O(N^{-2})$ and $K_2 = O(N^{-3})$ at the point of LCP.

2. Linear approximation of χ_c^{eff}

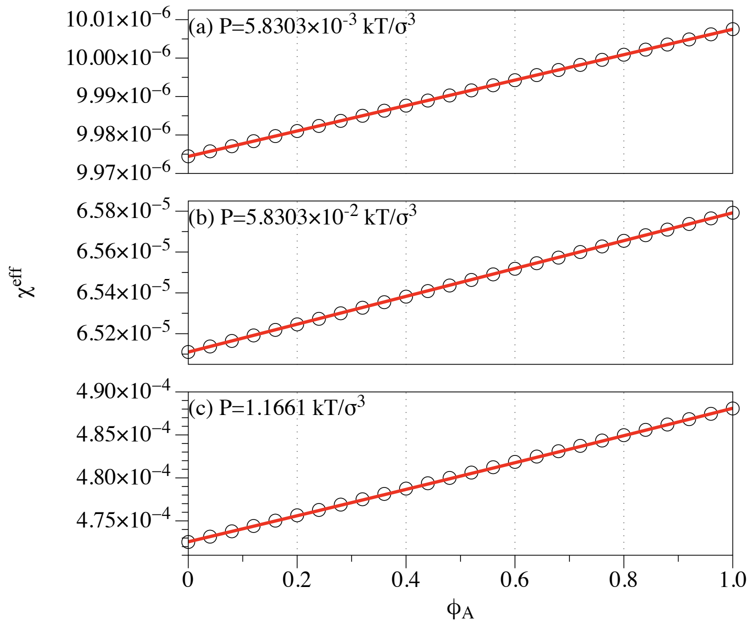

Figure S1: Effective χ parameter as a function of ϕ_A. The hollow circles are the data by equation (22) in main text, and the solid lines are the curve of equation (30).

3. Scaling relation of $\rho_i^{(0)}$

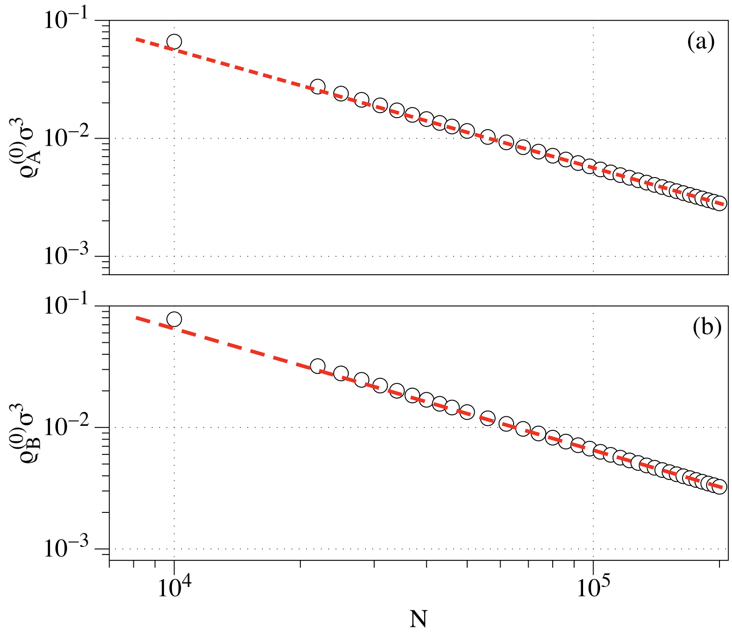

Figure S2: Scaling relation of $\rho_i^{(0)}$. The hollow circles are the raw data, and red dashed lines are the fitting curves by $O(N^{-1})$).

4. UCP-type behavior

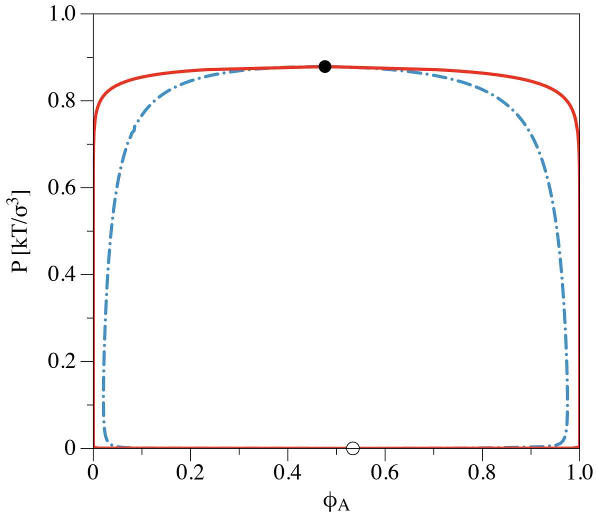

Figure S3: UCP-type behavior. The attractive strengths are $\epsilon_{AA}/k = 11K, \epsilon_{BB}/k = 10K, \epsilon_{AB} = 10.47K$. The chain length is $N = 100000$. The LCP1 is much smaller than 0.1 MPa.