

Supporting information to the manuscript, Spinodal Decomposition of a Polymer and Ionic Liquid Mixture: Effects of Electrostatic Interactions and Hydrogen Bonds on Phase Instability

Issei Nakamura*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China

E-mail: nakamura@ciac.ac.cn

1 Derivation of the free-energy functional for a homopolymer and ionic liquid mixture

We first introduce the coarse-grained number density field $c_s(\vec{r})$ for species s using the identity

$$1 = \int \mathcal{D}c_s \delta[c_s(\vec{r}) - \hat{c}_s(\vec{r})] = \int \mathcal{D}c_s \mathcal{D}\omega_s \times \exp\left\{i \int d\vec{r} \omega_s(\vec{r}) [c_s(\vec{r}) - \hat{c}_s(\vec{r})]\right\}, \quad (\text{S1})$$

where the right-hand side of the equation results from the Fourier representation of the δ function with $\omega_s(\vec{r})$ being the Fourier conjugate field to $c_s(\vec{r})$. A similar procedure is performed for the total charge density $\hat{\rho}(\vec{r})$ with the charge density field $\rho(\vec{r})$, which introduces the conjugate field $\psi(\vec{r})$.

Using the identity operator in Eq. (S1), we replace the instantaneous particle density $\hat{c}_s(\vec{r})$ with the coarse-grained (average) density $c_s(\vec{r})$. The partition function Z in Eq. (4) can then be cast into

a functional integral as follows:

$$\begin{aligned} Z &= \int \prod_{s=p,\pm} \mathcal{D}c_s \mathcal{D}\omega_s \mathcal{D}\rho \mathcal{D}\psi \\ &\times \exp\left\{-\frac{1}{2} \int d\vec{r} d\vec{r}' \rho(\vec{r}) v(\vec{r} - \vec{r}') \rho(\vec{r}') \right. \\ &+ i \int d\vec{r} \rho(\vec{r}) \psi(\vec{r}) + i \sum_{s=p,\pm} \int d\vec{r} c_s(\vec{r}) \omega_s(\vec{r}) \\ &- \int d\vec{r} \chi c_p(\vec{r}) \phi_{\text{IL}}(\vec{r}) \left. \prod_{s=p,\pm} \sum_{n_s} \frac{\lambda_s^{n_s}}{n_s!} \int \prod_{i=1}^{n_p} \right. \\ &\quad \mathcal{D}\vec{R}_i(t) \prod_{j=1}^{n_0} d\vec{r}_j^{(+)} d\vec{r}_j^{(-)} \delta[v_p \hat{c}_p(\vec{r}) + v_0 \hat{c}_+(\vec{r}) \\ &\quad + v_0 \hat{c}_-(\vec{r}) - 1] \exp\left\{-\sum_{i=1}^{n_p} \int_0^N dt \frac{3}{2b_p^2} \right. \\ &\quad \times \left[\frac{d\vec{R}_i(t)}{dt}\right]^2 - i \sum_{i=1}^{n_p} \int_0^N dt \omega_p[\vec{R}_i(t)] \\ &\quad \left. \left. - i \sum_{s=\pm} \left[\sum_{i=1}^{n_0} \omega[\vec{r}_i^{(s)}] + \sum_{i=1}^{n_0} q_s \psi[\vec{r}_i^{(s)}]\right] \right\} \right\} \\ &= \int \prod_{s=p,\pm} \mathcal{D}c_s \mathcal{D}\omega_s \mathcal{D}\rho \mathcal{D}\psi \exp(-F) \\ &\times \delta[v_p \hat{c}_p(\vec{r}) + v_0 \hat{c}_+(\vec{r}) + v_0 \hat{c}_-(\vec{r}) - 1], \quad (\text{S2}) \end{aligned}$$

*To whom correspondence should be addressed

where

$$\begin{aligned}
\frac{F}{k_B T} &= \frac{1}{2} \int d\vec{r} d\vec{r}' \rho(\vec{r}) v(\vec{r} - \vec{r}') \rho(\vec{r}') \\
&- i \sum_{s=p,\pm} \int d\vec{r} c_s(\vec{r}) \omega_s(\vec{r}) \\
&- i \int d\vec{r} \rho(\vec{r}) \psi(\vec{r}) - \lambda_p V Q_p \\
&- \sum_{s=\pm} \lambda_s V Q_s + \int d\vec{r} \chi c_p(\vec{r}) \phi_{\text{IL}}(\vec{r}).
\end{aligned} \tag{S3}$$

Here, we have performed the following calculation:

$$\begin{aligned}
\int d\vec{r} \hat{c}_p(\vec{r}) \hat{\omega}_p(\vec{r}) &= \int d\vec{r} \sum_{i=1}^{n_p} \int_0^N dt \delta[\vec{r} - \vec{R}_i(t)] \\
&\times \omega_p(\vec{r}) \\
&= \sum_{i=1}^{n_p} \int_0^N dt \omega_p[\vec{R}_i(t)], \tag{S4}
\end{aligned}$$

and the summation over the particle number using the identity $\sum_{N=0}^{\infty} (x^N / N!) = e^x$.

Extremizing the free energy functional in Eq. (S3) yields coupled mean-field equations. To rationalize the field variables in terms of observable quantities, we must replace $i\psi(\vec{r})$ and $i\omega_p(\vec{r})$ by $\psi(\vec{r})$ and $\omega_p(\vec{r})$ because the original fields $\psi(\vec{r})$ and $\omega_p(\vec{r})$ are purely imaginary at the saddle point. For charge neutrality, the bulk charge density becomes $\bar{\rho} = 0$. Without loss of generality, we set the electrostatic potential around the homogeneous phase as $\bar{\psi} = 0$. Interested readers are referred to the detail of these field-theoretical methods in, for example, Refs. 1 and 2. The thermodynamically consequential free energy density for the homogeneous phase is then given by $\frac{v_p F_{\text{FH}}}{k_B T V} = \frac{\phi_p}{N} \ln \phi_p - \frac{\phi_p}{N} + \sum_{s=\pm} [\frac{v_p \phi_s}{v_0} \ln \frac{v_p \phi_s}{v_0} - \frac{v_p \phi_s}{v_0}] + \chi \phi_p (1 - \phi_p)$.

2 Gaussian integral for the fluctuation

To perform the Gaussian functional integral in $Z \approx \exp[-\frac{F_{\text{FH}}}{k_B T}] \int \mathcal{D}\Omega \delta[v_p \delta c_p(\vec{r}) + v_0 \delta c_+(\vec{r}) + v_0 \delta c_-(\vec{r})] \exp[-\frac{\Delta F^{(2)}}{k_B T}]$ over the field variables, we use the identity $\int_{-\infty}^{+\infty} dx \exp(-\frac{ax^2}{2} + iJx) =$

$\sqrt{\frac{2\pi}{a}} \exp(\frac{-J^2}{2a})$. For convenience, a is simply given by the second derivative of $-\frac{ax^2}{2} + iJx$. Because the integrals are Gaussian, the calculation for $\exp(\frac{-J^2}{2a})$ can be performed simply by extremizing the integrand with respect to the field variables. We then obtain the effective free energy $\Delta F_{\text{eff}} = -k_B T \ln Z = \Delta F_{\text{FH}} + \frac{k_B T V}{2(2\pi)^3} \int d\vec{k} \ln(\lambda_\rho \lambda_\psi \lambda_{\omega_p} \lambda_{\omega_+} \lambda_{\omega_-} \lambda_{n_-} \lambda_{n_p})$, where the values of λ_s are systematically calculated by

$$\begin{aligned}
\lambda_\rho &= \frac{\delta^2 \Delta F^{(2)}(\rho, \psi, \omega_p, \omega_+, \omega_-, n_-, n_p)}{k_B T \delta \rho^2} \\
\lambda_\psi &= \frac{\delta^2 \Delta F^{(2)}(\rho^*, \psi, \omega_p, \omega_+, \omega_-, n_-, n_p)}{k_B T \delta \psi^2} \\
\lambda_{\omega_p} &= \frac{\delta^2 \Delta F^{(2)}(\rho^*, \psi^*, \omega_p, \omega_+, \omega_-, n_-, n_p)}{k_B T \delta \omega_p^2} \\
\lambda_{\omega_+} &= \frac{\delta^2 \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+, \omega_-, n_-, n_p)}{k_B T \delta \omega_+^2} \\
\lambda_{\omega_-} &= \frac{\delta^2 \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+^*, \omega_-, n_-, n_p)}{k_B T \delta \omega_-^2} \\
\lambda_{n_-} &= \frac{\delta^2 \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+^*, \omega_-^*, n_-, n_p)}{k_B T \delta n_-^2} \\
\lambda_{n_p} &= \frac{\delta^2 \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+^*, \omega_-^*, n_-^*, n_p)}{k_B T \delta n_p^2}.
\end{aligned} \tag{S5}$$

Here, ρ^* , ψ^* , ω_p^* , ω_+^* , ω_-^* , and n_-^* are the solutions of

$$\begin{aligned}
\frac{\delta \Delta F^{(2)}(\rho, \psi, \omega_p, \omega_+, \omega_-, n_-, n_p)}{\delta \rho} &= 0 \\
\frac{\delta \Delta F^{(2)}(\rho^*, \psi, \omega_p, \omega_+, \omega_-, n_-, n_p)}{\delta \psi} &= 0 \\
\frac{\delta \Delta F^{(2)}(\rho^*, \psi^*, \omega_p, \omega_+, \omega_-, n_-, n_p)}{\delta \omega_p} &= 0 \\
\frac{\delta \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+, \omega_-, n_-, n_p)}{\delta \omega_+} &= 0 \\
\frac{\delta \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+^*, \omega_-, n_-, n_p)}{\delta \omega_-} &= 0 \\
\frac{\delta \Delta F^{(2)}(\rho^*, \psi^*, \omega_p^*, \omega_+^*, \omega_-^*, n_-, n_p)}{\delta n_-} &= 0.
\end{aligned} \tag{S6}$$

Eqs. (S5) and (S6) then lead to

$$\begin{aligned}
\lambda_p &= \frac{4\pi l_0}{\epsilon_r k^2}, \lambda_\psi = \frac{\epsilon_r k^2}{4\pi l_0} + 2q_0^2 c_0, \\
\lambda_{\omega_p} &= N^2 c_p g_p(R_g^2 k^2) \\
\lambda_{\omega_+} &= \frac{c_0(4c_0 q_0^2 \pi l_0 + \epsilon_r k^2)}{[k^2 \epsilon_r + 8\pi l_0 q_0^2 c_0]}, \\
\lambda_{\omega_-} &= \frac{c_0 \epsilon_r k^2}{(4\pi l_0 q_0^2 c_0 + \epsilon_r k^2)}, \lambda_{n_-} = \frac{2}{c_0} + \frac{16\pi l_0 q_0^2}{\epsilon_r k^2}, \\
\lambda_{n_p} &= [2g_p(R_g^2 k^2) c_p c_0 v_0^2 N^2]^{-1} [N^2 c_p v_d^2 g_p(R_g^2 k^2) \\
&\quad + 2c_0 v_0^2 - 4c_0 \chi v_p v_0^2 N^2 c_p g_p(R_g^2 k^2)], \quad (S7)
\end{aligned}$$

where we have set $q_+ = -q_- = q_0$ for charge neutrality. We then obtain

$$\begin{aligned}
F_{\text{eff}} &= F_{\text{FH}} + \frac{k_B T V}{2(2\pi)^3} \int d\vec{k} [\ln G_{\text{chain}}(k) \\
&\quad + \ln G_{\text{el}}(k)] \\
G_{\text{chain}}(k) &= \left[\frac{N^2 c_p v_p^2 g_p(R_g^2 k^2)}{v_0} + 2c_0 v_0 \right. \\
&\quad \left. - 4\chi v_p c_p v_0 c_0 N^2 g_p(R_g^2 k^2) \right] \\
G_{\text{el}}(k) &= 1 + \frac{8\pi l_0 q_0^2 c_0}{\epsilon_r k^2}. \quad (S8)
\end{aligned}$$

Incidentally, the effective free energy resulted from $G_{\text{chain}}(k)$ is consistent with those for charge-neutral polymer blends in Refs. 3 and 4, with one of the components being a non-polymeric solvent, and that in Ref. 5, with $\chi = 0$ set in our theory. In addition, $G_{\text{el}}(k)$ is an analog of the self-energy of ions in Ref. 6.

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