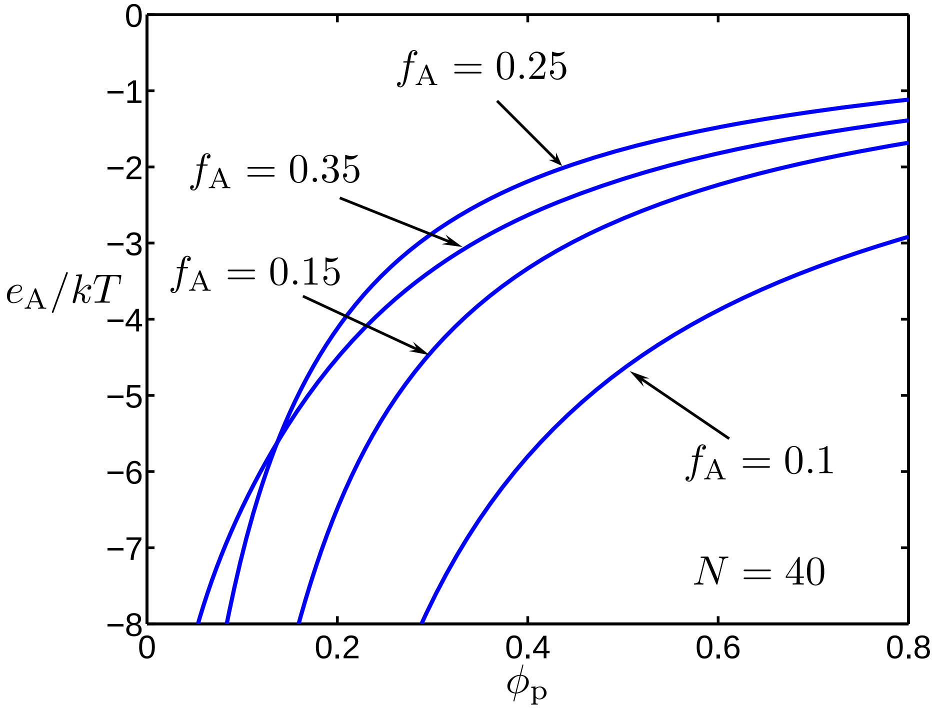

Figure 2.5: Microphase spinodal calculated using the virial-type expansion instead of strict volume incompressibility. The chain length is $N = 40$ with $c_1 = 1k_BT$ and $c_2 = 6k_BT$. Results are shown for $f_A = 0.1, 0.15, 0.25, 0.35$.

Our calculations suggest that one can start from the basic microscopic model to study the thermodynamics of gelation, without *a priori* assumptions of the gel phase. But the nature of reversible gelation, like the glass transition, is different from conventional phase transitions, and calls upon new theoretical tools. In the next chapter, which is adapted from our published paper, we analyze the possibility of glass transitions associated with this microscopic spinodal.

Appendix 2.A Self-consistent field calculation

2.A.1 Calculations of the partition functions of non-interacting polymers in external fields

In this subsection we solve the partition function $Z(iW_\alpha)$ as defined in Eq. (2.10). First we replace iW_α by W_α, it will turn out that thus defined W_α are real. From Eq. (2.12) we have

$$Z_s(iW_S) = \int \mathcal{D}[\mathbf{r}_n]_{n=1,2,\cdots n_s} \exp\left[-\int W_S(\mathbf{r})\,\hat{\phi}_S(\mathbf{r})\,\mathrm{d}\mathbf{r}\right]$$

$$= \int \mathcal{D}[\mathbf{r}_\mathrm{n}] \exp\left[-\int W_\mathrm{S}(\mathbf{r}) \sum_{n=1}^{n_\mathrm{s}} \delta(\mathbf{r}-\mathbf{r}_\mathrm{n})\,\mathrm{d}\mathbf{r}\right] = \left[\int e^{-W_\mathrm{S}(\mathbf{r})}\mathrm{d}\mathbf{r}\right]^{n_\mathrm{s}} = q_\mathrm{s}^{n_\mathrm{s}}. \tag{2.29}$$

We still need to calculate the single chain partition function q_p.

Using the Green's function for Gaussian chains (Doi and Edwards, 1986) we can express the partition function q_p as

$$q_\mathrm{p} = \int G(\mathbf{r}, \mathbf{r}'; N),$$

where $G(\mathbf{r}, \mathbf{r}'; N)$ satisfies

$$\left[\frac{\partial}{\partial N} - \frac{b^2}{6}\nabla_\mathbf{r}^2 + W(\mathbf{r})\right] G(\mathbf{r}, \mathbf{r}'; N) = \delta(\mathbf{r}-\mathbf{r}'). \tag{2.30}$$

To calculate q_p, we only need $q(\mathbf{r}, l)$, the once-integrated Green's function (propagator) (see Wood and Wang, 2002; Tzeremes et al., 2002; Drolet and Fredrickson, 1999; Fredrickson et al., 2002)

$$q(\mathbf{r}, l) = \int G(\mathbf{r}, \mathbf{r}'; l)\mathrm{d}\mathbf{r}',$$

which satisfies the same diffusion equation as $G(\mathbf{r}, \mathbf{r}')$

$$\left[\frac{\partial}{\partial l} - \frac{b^2}{6}\nabla_\mathbf{r}^2 + \sum_\alpha \delta_\alpha(l) W_\alpha(\mathbf{r})\right] q(\mathbf{r}, l) = 0, \tag{2.30$'$}$$

but with the following initial condition:

$$q(\mathbf{r}, 0) = 1.$$

$q^*(\mathbf{r}, l)$, the conjugate of q, satisfies

$$\left[\frac{\partial}{\partial l} - \frac{b^2}{6}\nabla_\mathbf{r}^2 + \sum_\alpha \delta_\alpha(N-l) W_\alpha(\mathbf{r})\right] q^*(\mathbf{r}, l) = 0 \tag{2.30$''$}$$

with the same initial condition. We can rescale l by $t = l/N$, $0 \le t \le 1$, then the equations become

$$\left[\frac{\partial}{\partial t} - \frac{Nb^2}{6}\nabla_\mathbf{r}^2 + N\sum_\alpha \delta_\alpha(t) W_\alpha(\mathbf{r})\right] q(\mathbf{r}, t) = 0$$

$\delta_\mathrm{A,B}(t)$ are defined the same as in Eq. (2.17). And

$$q_\mathrm{p} = \int q(\mathbf{r}, 1)\,\mathrm{d}\mathbf{r} = \int q^*(\mathbf{r}, 1)\mathrm{d}\mathbf{r}. \tag{2.31}$$

2.A.2 Grand canonical ensemble calculation

We have obtained the grand canonical partition function in Section 2.1.2 as

$$\begin{aligned}\Xi\left(\mu_{\mathrm{p}},\mu_{\mathrm{s}}\right) &= \sum_{n_{\mathrm{p}}=0}^{\infty}\sum_{n_{\mathrm{s}}=0}^{\infty}\frac{\exp\left(\beta\mu_{\mathrm{p}}n_{\mathrm{p}}+\beta\mu_{\mathrm{s}}n_{\mathrm{s}}\right)}{n_s!n_p!}Z(n_{\mathrm{p}},n_{\mathrm{s}}),\\ &= \frac{1}{\mathcal{N}}\int\mathcal{D}\phi_\alpha\int\mathcal{D}W_\alpha\int\mathcal{D}\Pi\\ &\quad \exp\left\{-\beta H_1[\phi_\alpha]+W_\alpha\phi_\alpha+\Pi\left(\sum_\alpha\phi_\alpha-\rho\right)+e^{\mu_{\mathrm{s}}}q_{\mathrm{s}}+e^{\mu_{\mathrm{p}}}q_{\mathrm{p}}\right\}. \qquad (2.32)\end{aligned}$$

where μ_{p} and μ_{s} are the chemical potential of the polymers and the solvents.

In the grand canonical ensemble, Eq. (2.14) is replaced by

$$\frac{\delta}{\delta W_{\mathrm{S}}\left(\mathbf{r}\right)}=0 \quad \Rightarrow \phi_{\mathrm{S}}=e^{\beta\mu_{\mathrm{s}}-W_{\mathrm{S}}}; \tag{2.33a}$$

$$\frac{\delta}{\delta W_{\mathrm{A,B}}\left(\mathbf{r}\right)}=0 \quad \Rightarrow \phi_{\mathrm{A,B}}\left(\mathbf{r}\right)=\exp\left(\beta\mu_{\mathrm{p}}\right)\int_0^1\theta_{\mathrm{A,B}}(t)q\left(\mathbf{r},t\right)q^*\left(\mathbf{r},1-t\right)\mathrm{d}t; \tag{2.33b}$$

$$\frac{\delta}{\delta\Pi(\mathbf{r})}=0 \quad \Rightarrow \sum_\alpha\phi_\alpha(\mathbf{r})=\rho; \tag{2.33c}$$

$$\frac{\delta}{\delta\phi_\alpha(\mathbf{r})}=0 \quad \Rightarrow W_\alpha(\mathbf{r})=\frac{\beta\partial H_1(\phi_\alpha)}{\partial\phi_\alpha}. \tag{2.33d}$$

If we use the virial expansion instead of strict incompressibility we have the following SCF equations ($\varepsilon_{\alpha\beta}$ and c_1, c_2 are given in unit of $k_{\mathrm{B}}T$):

$$W_{\mathrm{A}}\left(\mathbf{r}\right)=\varepsilon_{\mathrm{AA}}\phi_{\mathrm{A}}(\mathbf{r})+\varepsilon_{\mathrm{AB}}\phi_{\mathrm{B}}\left(\mathbf{r}\right)+\varepsilon_{\mathrm{AS}}\phi_{\mathrm{S}}\left(\mathbf{r}\right)+2c_1\phi_{\mathrm{p}}(\mathbf{r})+3c_2\phi_{\mathrm{p}}^2(\mathbf{r}), \tag{2.34a}$$

$$W_{\mathrm{B}}\left(\mathbf{r}\right)=\varepsilon_{\mathrm{BB}}\phi_{\mathrm{B}}(\mathbf{r})+\varepsilon_{\mathrm{AB}}\phi_{\mathrm{A}}\left(\mathbf{r}\right)+\varepsilon_{\mathrm{BS}}\phi_{\mathrm{S}}\left(\mathbf{r}\right)+2c_1\phi_{\mathrm{p}}(\mathbf{r})+3c_2\phi_{\mathrm{p}}^2(\mathbf{r}), \tag{2.34b}$$

$$W_{\mathrm{S}}\left(\mathbf{r}\right)=\varepsilon_{\mathrm{SS}}\phi_{\mathrm{S}}(\mathbf{r})+\varepsilon_{\mathrm{AS}}\phi_{\mathrm{A}}\left(\mathbf{r}\right)+\varepsilon_{\mathrm{BS}}\phi_{\mathrm{B}}(\mathbf{r}); \tag{2.34c}$$

$$\phi_{\mathrm{A}}=\exp\left(\beta\mu_{\mathrm{p}}\right)\int_0^1\theta_{\mathrm{A}}(t)q\left(\mathbf{r},t\right)q^*\left(\mathbf{r},1-t\right)\mathrm{d}t, \tag{2.34d}$$

$$\phi_{\mathrm{B}}=\exp\left(\beta\mu_{\mathrm{p}}\right)\int_0^1\theta_{\mathrm{B}}\left(t\right)q\left(\mathbf{r},t\right)q^*\left(\mathbf{r},1-t\right)\mathrm{d}t, \tag{2.34e}$$

$$\phi_{\mathrm{S}}=\exp\left(\beta\mu_{\mathrm{s}}-W_{\mathrm{S}}\right). \tag{2.34f}$$

Finally the grand potential is

$$G=-k_{\mathrm{B}}T\ln\Xi=H_1(\phi_\alpha)-e^{\beta\mu_{\mathrm{p}}}q_{\mathrm{p}}-e^{\beta\mu_{\mathrm{s}}}q_{\mathrm{s}}-W_\alpha\phi_\alpha. \tag{2.35}$$

In the grand canonical calculation we want to fix the concentration of the polymers in the reservoir instead of by their total density, therefore only one chemical potential is independent. We can take $\mu_{\mathrm{s}}=0$ for convenience and choose μ_{p} as in a uniform polymer solution with given volume fraction of polymer segments, which can be calculated from Eqs. (2.35) and (2.34).

The canonical free energy of the system is

$$F(\phi_\alpha) = H_1(\phi_\alpha) - k_\mathrm{B}T\left(W_\alpha\phi_\alpha + n_\mathrm{p}\ln q_\mathrm{p} + n_\mathrm{s}\ln q_\mathrm{s}\right). \tag{2.36}$$

2.A.3 Numerical solution of the SCF equations

To implement numerical solutions of the self-consistent equations (2.14) or (2.34), we first note that the inputting parameters are $\varepsilon_{\alpha\beta}$, c_1 and c_2, N, f_α, and μ_p in the grand canonical ensemble, and $\varepsilon_{\alpha\beta}$, c_1 and c_2, N, f_α, and the average concentrations $\bar{\phi}_\mathrm{p}$ and $\bar{\phi}_\mathrm{s}$ in the canonical ensemble. f_α are the fractions of different blocks in each chain.

We adopt the following iteration scheme (Drolet and Fredrickson, 2001; Tzeremes et al., 2002):

1. The initial density distributions $\phi_\alpha^{(0)}(\mathbf{r})$ are generated by adding a tiny fluctuation to the uniform distribution, the conjugate fields $W_\alpha^{(0)}(\mathbf{r})$ are calculated from the first 3 equations of Eqs. (2.14) or (2.34);

2. For a set of $W_\alpha^{(\mathrm{i})}(\mathbf{r})$, $\phi_\alpha^{(\mathrm{i}')}(\mathbf{r})$ are obtained using the remaining 3 equations, and $W_\alpha^{(\mathrm{i}')}(\mathbf{r})$ are calculated from $\phi_\alpha^{(\mathrm{i}')}(\mathbf{r})$ using the first 3 equations;

3. $W_\alpha^{(\mathrm{i})}$ are updated by:

$$\begin{aligned} W_\alpha^{(\mathrm{i+1})} &= W_\alpha^{(\mathrm{i})} + y_1\Delta W_\alpha^{(\mathrm{i})} + y_2\Delta\phi_\alpha^{(\mathrm{i})}, & (2.37)\\ \Delta W_\alpha^{(\mathrm{i})} &= W_\alpha^{(\mathrm{i}')} - W_\alpha^{(\mathrm{i})}, & (2.38)\\ \Delta\phi_\alpha^{(\mathrm{i})} &= \phi_\alpha^{(\mathrm{i}')} - \phi_\alpha^{(\mathrm{i})}. & (2.39)\end{aligned}$$

4. $\phi_\alpha^{(\mathrm{i+1})}$ are updated for $W_\alpha^{(\mathrm{i+1})}$ from the last 3 equations and step (ii) and step (iii) are repeated.

To calculate the Green's functions (the N factor has been adsorbed into $W(\mathbf{r})$):

$$q(\mathbf{r},0) = 1, \left(\frac{\partial}{\partial t} - \frac{Nb^2}{6}\nabla_\mathbf{r}^2 + W_\alpha(\mathbf{r})\right) q(\mathbf{r},t) = 0, \tag{2.40}$$

first we rescale $\mathbf{r}$ by $R_\mathrm{g} = \left(Nb^2/6\right)^{1/2}$, and the solution can be formally written as

$$q(\mathbf{r},t+\mathrm{d}t) = \exp\left[\left(\nabla^2 - W(\mathbf{r})\right)\mathrm{d}t\right] q(\mathbf{r},t). \tag{2.41}$$

From the Baker-Hausdorff operator identity (Tzeremes et al., 2002),

$$\exp(\hat{A})\exp(\hat{B}) = \exp\left\{\hat{A} + \hat{B} - \frac{1}{2}[\hat{A},\hat{B}] + \cdots\right\},$$

Eq. (2.41) can be written as

$$q\left(\mathbf{r},t+\mathrm{d}t\right)=\exp\left(-\frac{\mathrm{d}t}{2}W\left(\mathbf{r}\right)\right)\exp\left(\mathrm{d}t\nabla^{2}\right)\exp\left(-\frac{\mathrm{d}t}{2}W\left(\mathbf{r}\right)\right)q\left(\mathbf{r},t\right), \tag{2.42}$$

which is accurate to $\mathrm{d}t^2$. Eq. (2.42) can be numerically implemented by Fourier transform,

$$q\left(\mathbf{r},t+\mathrm{d}t\right)=\exp\left(-\frac{\mathrm{d}t}{2}W\left(\mathbf{r}\right)\right)\mathcal{F}^{-1}\left\{\exp\left(-\mathrm{d}t\mathbf{k}^{2}\right)\mathcal{F}\left[\exp\left(-\frac{\mathrm{d}t}{2}W\left(\mathbf{r}\right)\right)q\left(\mathbf{r},t\right)\right]\right\}; \tag{2.43}$$

$\mathcal{F}$ denotes the Fourier transform, which can be implemented using fast Fourier transform. The fast Fourier transform (FFT) automatically ensures the periodic boundary conditions.

In the simulation we need to specify the size and discretization of the system. If we choose the discretization lattice to be 64×64 and the size of the system to be $6.4R_g\times6.4R_g$, then we can resolve the density profile to $\sim 0.1R_g$ (R_g is the radius of gyration of the polymer). In our simulations we use square lattices and resolve the density profile to $0.1\sim0.2R_g$.

2.A.4 Analysis of the iteration scheme

Self-consistent equations for polymer systems are highly non-linear and it is notoriously difficult to obtain convergent solutions. Here we briefly analyze possible steepest descent schemes to solve the self-consistent equations.

In Section 2.1 and Section 2.2 we have obtained the mean field free energy potential $F[\phi_\alpha]$:

$$F=-\ln\int\mathcal{D}\phi_\alpha\mathcal{D}W_\alpha\exp\left(-\beta H_1[\phi_\alpha]+W_\alpha\phi_\alpha-G[W_\alpha]\right). \tag{2.44}$$

Taking the saddle point we have

$$\frac{\delta F}{\delta W_\alpha}=0,\frac{\delta F}{\delta\phi_\alpha}=0.$$

From

$$\frac{\delta F}{\delta W_\alpha}=0$$

we obtain

$$\phi_\alpha=\frac{\delta G[W_\alpha]}{\delta W_\alpha}=\Phi(W_\alpha). \tag{2.45}$$

Therefore in terms of ϕ_α, the saddle point free energy is

$$F^*[\phi_\alpha]=H_1[\phi_\alpha]-\Phi^{-1}[\phi_\alpha]\phi_\alpha+G[\Phi^{-1}(\phi_\alpha)]. \tag{2.46}$$

The gradient of F^* against ϕ_α is

$$\frac{\delta F^*[\phi_\alpha]}{\delta \phi_\alpha} = \frac{\partial H_1[\phi_\alpha]}{\partial \phi_\alpha} - \Phi^{-1}(\phi_\alpha). \tag{2.47}$$

Φ^{-1} or Φ can be expanded as an asymptotic series of ϕ_α or W_α as done in the free energy expansion in Section 2.2, but we do not have close-form expressions. Therefore it is inconvenient to implement steepest descent or Langevin type dynamics in the ϕ field.

Alternatively we can first take

$$\frac{\delta F}{\delta \phi_\alpha} = 0,$$

and we have

$$W_\alpha = \frac{\partial H_1[\phi_\alpha]}{\partial \phi_\alpha} = \mathcal{W}(\phi_\alpha). \tag{2.48}$$

Then

$$F^*[W_\alpha] = H_1[\mathcal{W}^{-1}(W_\alpha)] - \mathcal{W}^{-1}(W_\alpha)W_\alpha + G[W_\alpha], \tag{2.49}$$

and the free energy gradient is

$$\frac{\delta F^*[W_\alpha]}{\delta W_\alpha} = \Phi(W_\alpha) - \mathcal{W}^{-1}(W_\alpha). \tag{2.50}$$

In most cases we do have a close form expression for $\mathcal{W}^{-1}$ or $\mathcal{W}$ from Eq. (2.48), therefore in principle we could do a steepest ascent on W_α fields. But to ensure that the steepest descent on the free energy landscape is well-behaved, we have to input the extra constraint that

$$\frac{\delta^2 F^*[W_\alpha]}{\delta W_\alpha \delta W_\beta}$$

is negative/non-positive definite. This is generally true for the first term $\Phi(W_\alpha)$. For $\mathcal{W}^{-1}$ this imposes an extra constraint on H_1 such that

$$\frac{\delta^2 H[\phi_\alpha]}{\delta \phi_\alpha \delta \phi_\beta}$$

is positive definite. But we know that **this is not the case!** Therefore the solutions to the self-consistent equations of interest to us (for H_1 with double minima) are not the extrema in W_α fields, but saddle points. It is tempting to use the "string method" to be discussed in the Chapter 5 in Part II, which is an efficient method to locate extremum as well as saddle points on the free energy landscape, or to adapt the cell dynamics approach by Bahiana and Oono (1990).

Appendix 2.B Free Energy Expansion

2.B.1 Calculation of the connected correlation functions

From Eq. (2.20), we have

$$G^{(\mathrm{m})}_{\alpha_1\alpha_2\cdots\alpha_{\mathrm{m}}}(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_{\mathrm{m}}) = \left\langle \hat{\phi}_{\alpha_1}(\mathbf{x}_1)\hat{\phi}_{\alpha_2}(\mathbf{x}_2)\cdots\hat{\phi}_{\alpha_{\mathrm{m}}}(\mathbf{x}_{\mathrm{m}})\right\rangle_c .$$

From now on we shall adopt the short-hand label $\mathbf{m}$ for $\mathbf{x}_m$. To calculate these correlation functions, note that the system consists of n non-interacting polymer chains, therefore

$$G^{(\mathrm{m})}_{\alpha_1\alpha_2\cdots\alpha_{\mathrm{m}}}(\mathbf{1},\mathbf{2},\ldots\mathbf{m}) = n g^{(\mathrm{m})}_{\alpha_1\alpha_2\cdots\alpha_{\mathrm{m}}}(\mathbf{1},\mathbf{2},\ldots\mathbf{m}), \tag{2.51}$$

where g is the connected correlation function for a single chain, which is the joint probability distribution $P_{\alpha_1\alpha_2\cdots\alpha_{\mathrm{m}}}(\mathbf{1},\mathbf{2},\ldots\mathbf{m})$, i.e., the probability that at $\mathbf{r}_1$ there is an α_1 segment, at $\mathbf{r}_2$ there is an α_2 segment, etc.

We first study $P_{i_1i_2\cdots i_m}(\mathbf{1},\mathbf{2},\ldots\mathbf{m})$ which is the joint probability that there is the i_1th segment at $\mathbf{r}_1$, i_2th segment at $\mathbf{r}_2$, etc. Because the Gaussian chain (Brownian motion) is Markovian, we can express $P_{i_1i_2\cdots i_m}(\mathbf{1},\mathbf{2},\ldots\mathbf{m})$ using the transition probabilities (two-point propagators):

$$P_{i_1i_2\cdots i_m}(\mathbf{1},\mathbf{2},\ldots\mathbf{m}) = P_{i_1}(\mathbf{1})P_{i_1i_2}(\mathbf{1},\mathbf{2})P_{i_2i_3}(\mathbf{2},\mathbf{3})\cdots P_{i_{m-1}i_m}(\mathbf{m-1},\mathbf{m}) \tag{2.52}$$

where

$$P_{i_1}(\mathbf{1}) = \frac{1}{V}$$

is the probability that the first segment is located at position $\mathbf{r}_1$, and

$$P_{i_1i_2}(\mathbf{1},\mathbf{2}) = \left(\frac{3}{2\pi\left|i_2-i_1\right|b^2}\right)^3 \exp\left[-\frac{3\left|\mathbf{r_2}-\mathbf{r}_1\right|^2}{2\left|i_2-i_1\right|b^2}\right] \tag{2.53}$$

is the propagator of a Gaussian chain from $\mathbf{r}_1$ to $\mathbf{r_2}$ with capacity $(i_2-i_1)b^2$.

To evaluate $P_{i_1i_2\cdots i_m}$, it is convenient to use the characteristic function of $P_{i_1i_2}(\mathbf{1},\mathbf{2})$

$$P_{i_1i_2}(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}}P_{i_1i_2}(\mathbf{r})\mathrm{d}\mathbf{r} = \exp\left[\frac{-\left|i_2-i_1\right|b^2\mathbf{q}^2}{6}\right]. \tag{2.54}$$

We now go on to evaluate $g_{i_1i_2\cdots i_m}$.

$$\begin{aligned} g_{i_1i_2}(\mathbf{q}_1,\mathbf{q}_2) &= \int e^{i(\mathbf{q}_1\cdot\mathbf{r}_1+\mathbf{q}_2\cdot\mathbf{r}_2)}P_{i_1}(\mathbf{1})P_{i_1i_2}(\mathbf{r}_2-\mathbf{r}_1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ &= \frac{1}{V}\delta(\mathbf{q}_1+\mathbf{q}_2)P_{i_1i_2}(\mathbf{q}_2); \end{aligned} \tag{2.55}$$

$$\begin{aligned} g_{i_1 i_2 i_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) &= \int e^{i(\mathbf{q}_1\cdot\mathbf{r}_1+\mathbf{q}_2\cdot\mathbf{r}_2+\mathbf{q}_3\cdot\mathbf{r}_3)} P_{i_1}(\mathbf{1}) P_{i_1 i_2}(\mathbf{r}_2 - \mathbf{r}_1) P_{i_2 i_3}(\mathbf{r}_3 - \mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3 \\ &= \frac{1}{V} \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3) P_{i_1 i_2}(\mathbf{q}_1) P_{i_2 i_3}(\mathbf{q}_3); \qquad (2.56) \\ g_{i_1 i_2 i_3 i_4}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) &= \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 e^{i(\mathbf{q}_1\cdot\mathbf{r}_1+\mathbf{q}_2\cdot\mathbf{r}_2+\mathbf{q}_3\cdot\mathbf{r}_3+\mathbf{q}_4\cdot\mathbf{r}_4)} \\ &\quad P_{i_1}(\mathbf{1}) P_{i_1 i_2}(\mathbf{r}_2 - \mathbf{r}_1) P_{i_2 i_3}(\mathbf{r}_3 - \mathbf{r}_2) P_{i_3 i_4}(\mathbf{r}_4 - \mathbf{r}_3) \\ &= \frac{1}{V} \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4) P_{i_1 i_2}(\mathbf{q}_1) P_{i_2 i_3}(\mathbf{q}_1 + \mathbf{q}_2) P_{i_3 i_4}(\mathbf{q}_4). \qquad (2.57) \end{aligned}$$

The connected correlation functions $G_{\alpha_1 \alpha_2 \cdots \alpha_\mathrm{m}}(\mathbf{q}_1, \mathbf{q}_2, \ldots \mathbf{q}_\mathrm{m})$ are obtained via

$$G_{\alpha_1 \alpha_2 \cdots \alpha_\mathrm{m}}(\mathbf{q}_1, \mathbf{q}_2, \ldots \mathbf{q}_\mathrm{m}) = \int_{\alpha_1} \mathrm{d}i_1 \int_{\alpha_2} \mathrm{d}i_2 \cdots \int_{\alpha_\mathrm{m}} \mathrm{d}i_\mathrm{m} G_{i_1 i_2 i_3 \cdots i_\mathrm{m}}(\mathbf{q}_1, \mathbf{q}_2, \ldots \mathbf{q}_\mathrm{m}). \qquad (2.58)$$

The integral is over different blocks α_i.

2.B.2 Spinodal limit

We now study the system of associating A-B-A triblock copolymers in a theta solution for B but poor solution for A. The spinodal limit is defined as when the uniform phase becomes unstable. To calculate the spinodal transition lines we expand the free energy of the solution to the leading (quadratic) order.

The monomer interactions are assumed to be $\varepsilon_{\mathrm{AA}} = -e_\mathrm{A}$, $\varepsilon_{\alpha\beta} = 0$ otherwise. From Eqs. (2.24) and (2.27) the quadratic term in the free energy expansion is

$$\frac{F^{(2)}\{\varphi_\alpha + \bar{\phi}_\alpha\} - F^{(2)}\{\bar{\phi}_\alpha\}}{k_\mathrm{B}T} = \frac{1}{2} \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \varphi_\alpha(\mathbf{x}_1) G^{-1}_{\alpha\beta}(\mathbf{x_1}, \mathbf{x_2}) \varphi_\beta(\mathbf{x_2}) + H^{(2)}_1, \qquad (2.59)$$

where

$$H^{(2)}_1 = -\frac{1}{2} e_\mathrm{A} \int \varphi^2_\mathrm{A}(\mathbf{x}) \mathrm{d}\mathbf{x} + c_1 \int \left(\varphi_\mathrm{A}(\mathbf{x}) + \varphi_\mathrm{B}(\mathbf{x})\right)^2 \mathrm{d}\mathbf{x} + 3c_2 \int \left(\varphi_\mathrm{A}(\mathbf{x}) + \varphi_\mathrm{B}(\mathbf{x})\right)^2 \bar{\phi}_\mathrm{p} \mathrm{d}\mathbf{x}. \qquad (2.60)$$

$\bar{\phi}_\alpha$ is the bulk average density of component α; $\bar{\phi}_\mathrm{p} = \bar{\phi}_\mathrm{A} + \bar{\phi}_\mathrm{B}$, is the bulk average density of polymer segments.

$F^{(2)}$ can be expressed in terms of $\varphi_\alpha(\mathbf{q})$,

$$\begin{aligned} F^{(2)} &= V k_\mathrm{B} T \sum_{\mathbf{q}} \\ &\quad \left[\frac{1}{2} \varphi_\alpha(\mathbf{q}) G^{-1}_{\alpha\beta}(\mathbf{q}, -\mathbf{q}) \varphi_\beta(-\mathbf{q}) - \frac{e_\mathrm{A}}{2} \varphi_\mathrm{A}(\mathbf{q}) \varphi_\mathrm{A}(-\mathbf{q}) + c_1 \varphi_\mathrm{p}(\mathbf{q}) \varphi_\mathrm{p}(-\mathbf{q}) + 3c_2 \varphi_\mathrm{p}(\mathbf{q}) \varphi_\mathrm{p}(-\mathbf{q}) \bar{\phi}_\mathrm{p}\right], \end{aligned} \qquad (2.61)$$

where $\varphi_\mathrm{p} = \varphi_\mathrm{A} + \varphi_\mathrm{B}$.

$G_{\alpha\beta}$ can be obtained from Eqs. (2.55) and (2.58). Here we assume that each A block has N_{A} segments and the midblock has N_{B} segments. Then

$$G_{\alpha\beta} = \frac{n}{V}\begin{pmatrix} 2N_{\mathrm{A}}^2(D(x_{\mathrm{A}}) + E(x_{\mathrm{A}})) & 2N_{\mathrm{A}}N_{\mathrm{B}}H(x_{\mathrm{A}}, x_{\mathrm{B}}) \\ 2N_{\mathrm{A}}N_{\mathrm{B}}H(x_{\mathrm{A}}, x_{\mathrm{B}}) & N_{\mathrm{B}}^2 D(x_{\mathrm{B}}) \end{pmatrix} = \frac{n}{V}Q_{\alpha\beta} \tag{2.62}$$

where N_{A} is the length of the first A block, and

$$x_\alpha = \frac{N_\alpha q^2 b^2}{6},$$

$$D(x) = \frac{x - 1 + e^{-x}}{x^2},$$

$$E(x) = \frac{e^{-x}(1 - e^{-x})^2}{x^2},$$

$$H(x_{\mathrm{A}}, x_{\mathrm{B}}) = \frac{(1 - e^{-x_{\mathrm{A}}})(1 - e^{-x_{\mathrm{B}}})}{x_{\mathrm{A}} x_{\mathrm{B}}}.$$

Next we minimize $F^{(2)}$ with respect to $\varphi_{\mathrm{B}}(\mathbf{q})$ or $\varphi_{\mathrm{B}}(-\mathbf{q})$,

$$\varphi_{\mathrm{B}}(\mathbf{q}) = \frac{N\left[Q^{-1}\right]_{\mathrm{AB}} + 6c_2\bar{\phi}_{\mathrm{p}}^2 + 2c_1\bar{\phi}_{\mathrm{p}}}{-6c_2\bar{\phi}_{\mathrm{p}}^2 - 2c_1\bar{\phi}_{\mathrm{p}}} - N\left[Q^{-1}\right]_{\mathrm{BB}}\varphi_{\mathrm{A}}(\mathbf{q}). \tag{2.63}$$

$[Q]_{\alpha\beta}^{-1}$ is the inverse of $[Q]_{\alpha\beta}$

$$[Q]_{\alpha\beta}^{-1}\,[Q]_{\beta\gamma} = \delta_{\alpha\gamma}.$$

Substitute Eq. (2.63) back into Eq. (2.61), and we obtain

$$\begin{aligned} \beta F^{(2)} &= \frac{V}{2}\sum_{\mathbf{q}}\left\{\frac{N}{\bar{\phi}_{\mathrm{p}}}\left[\frac{(Q_{\mathrm{BB}} + 2Q_{\mathrm{AB}} + Q_{\mathrm{AA}})\left(2c_1\bar{\phi}_{\mathrm{p}} + 6c_2\bar{\phi}_{\mathrm{p}}^2\right) - N}{\left(6c_2\bar{\phi}_{\mathrm{p}}^2 + 2c_1\bar{\phi}_{\mathrm{p}}\right)\left(Q_{\mathrm{AA}}Q_{\mathrm{BB}} - Q_{\mathrm{AB}}^2\right) - NQ_{\mathrm{AA}}}\right] - \beta e_{\mathrm{A}}\right\}\varphi_{\mathrm{A}}(\mathbf{q})\varphi_{\mathrm{A}}(-\mathbf{q}) \qquad (2.64) \\ &= \frac{V}{2}\sum_{\mathbf{q}}\left[S^{-1}(q) - \beta e_{\mathrm{A}}\right]\varphi_{\mathrm{A}}(\mathbf{q})\varphi_{\mathrm{A}}(-\mathbf{q}). \end{aligned}$$

In the strict incompressible case, $S^{-1}(q)$ is given by

$$S^{-1}(q) = \frac{N^3 D(x) + N^2(1 - \bar{\phi}_{\mathrm{p}})/\bar{\phi}_{\mathrm{p}}}{\bar{\phi}_{\mathrm{p}}\left(Q_{\mathrm{AA}}Q_{\mathrm{BB}} - Q_{\mathrm{AB}}^2\right) + (1 - \bar{\phi}_{\mathrm{p}})NQ_{\mathrm{AA}}}.$$

Note that the Q functions are dependent on q. The term in the square bracket attains a minimum at q_{m} and at $q = 0$. Once βe_{A} exceeds this minimum, the free energy becomes unstable with respect to perturbations at q_{m}. This gives the spinodal limit. At $q = q_{\mathrm{m}}$, $e_{\mathrm{A}} \sim N^{-1}$ gives the spinodal limit of a microscopic phase transition; while at $q = 0$, $e_{\mathrm{A}} \sim N^0$ corresponds to the spinodal limit of the macroscopic phase separation.