Lecture Notes in Polymer Physics

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Noted by Y. X. Liu with additional derivation details

1. One mode approximation

Assume the function to be approximated can be expanded in a series

$$\phi(x) = \sum_n \phi_n(x) e^{ik_n x} \tag{1}$$

where n=0, ±1, ±2, ⋯. For one mode approximation, only the first three terms are taken, that is

$$\phi(x) = \phi_0(x) e^{ik_0 x} + \phi_{-1}(x) e^{ik_{-1} x} + \phi_1(x) e^{ik_1 x} \tag{2}$$

In two and higher dimensional space, variables, x and k, become vectors $\mathbf{x}$ and $\mathbf{k}$. To approximate high dimensional functions, one should consider the origin and its neighbors. Using two-dimensional hexagonal lattice as an example, one mode approximation retains only the origin term and the six nearest neighbors, depicted in Figure 1.

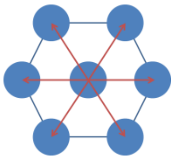


Figure 1

One mode approximation is not a good approximation for square wave. To expand square wave function according to eq. 1, ϕ_n decrease with n in an order of $1/n$, which is very slow and a large number of terms are required to approximate it well enough. This also explains that spectral method is not suitable to deal with strong segregation systems where the density profile resembles a square wave function.

2. Spinodal decomposition and nucleation (For more details, see Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p479-491)

Consider the following dynamic equation,

$$\frac{\partial \phi}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \phi} \tag{3}$$

(It is an equation that describes the evolution of conserved order parameter). In linear instability analysis, the order parameter is first re-expressed as

$$\phi = \phi_0 + \delta\phi \tag{4}$$

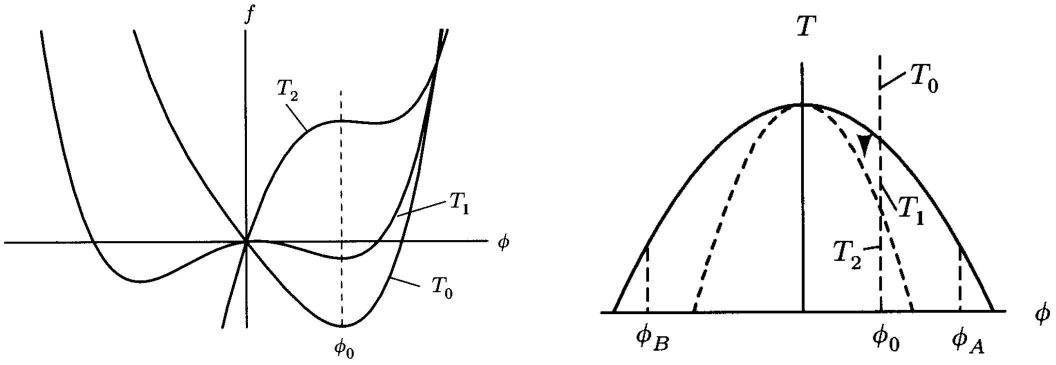
where ϕ_0 is the average order parameter, and $\delta\phi$ describes the fluctuation. Then eq. 3 finally reaches the form no matter what the exact expression of F,

$$\frac{\partial}{\partial t}\delta\phi = P(\phi)\delta\phi \tag{5}$$

If $P(\phi)>0$, fluctuation amplifies with time because

$$\delta\phi = \delta\phi_0 e^{P(\phi)t} \tag{6}$$

is an increasing function. In other words, fluctuation grows spontaneously when $P(\phi)$ is positive. This kind of evolution path is called spinodal decomposition. When $P(\phi)$ is negative, fluctuation is suppressed. To form a new phase, an energy barrier should be overcome. This kind of evolution path is called nucleation.



(a) (b)

Figure 2

The spinodal curve is, strictly speaking, a mean-field concept. In real systems, where fluctuations are important, the boundary separating nucleation from spinodal decomposition is not perfectly sharp. When the free energy barrier is close to or smaller than the thermal energy, the fluctuation is important. In this case, nucleation and spinodal decomposition behave similarly and cannot be distinguished from experiments. Therefore, it is impossible to determine spinodal curve exactly via experiments.

3. Conserved and non-conserved order parameter

Dynamic equation for non-conserved order parameter (NCOP) is

$$\frac{\partial \phi}{\partial t} = -\mu \frac{\delta F}{\delta \phi} \tag{7}$$

This is an example of dissipative equation. The degree of orientation for liquid crystal is an example for non-conserved order parameter.

An intuitive derivation of the dynamic equation for conserved order parameter (COP) is given below. Each conserved parameter is associated with a continuity equation,

$$\frac{\partial \phi}{\partial t} + \nabla \bullet \mathbf{J} = 0 \tag{8}$$

where the first term stands for the variation of the order parameter itself, and the second term represents the change of order parameter due to the in and out flux. In fluid dynamics, it can be written as

$$\frac{\partial \rho}{\partial t} + \nabla \bullet \ \nabla \rho \quad = 0 \tag{9}$$

The flux **J** is just the gradient of density. In phase separation systems, the expression for **J** is

$$\mathbf{J} = -M \nabla \mu \tag{10}$$

where M is the mobility and μ is chemical potential. Substitute eq. 10 into eq. 8, and using the definition of chemical potential

$$\mu = \frac{\delta F}{\delta \phi} \tag{11}$$

the dynamic equation can be finally written as

$$\frac{\partial \phi}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \phi} \tag{12}$$

NCOP and COP behave differently in linear stability analysis. For COP, one specific mode will be selected to grow new phase, i.e. a structure with a certain characteristic length will be formed.

4. **Ginzburg criteria** (For more details, see Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p214-216)

Ginzburg criteria are the criteria for determining whether or not the mean-field approximation breakdowns. It quantitatively measures the importance of fluctuations by considering the average over a coherence volume, $V_\xi=\xi^d$ of the deviation $\delta\phi(x)=\phi(x)-<\phi>$, of the local order parameter from its equilibrium value:

$$\delta\phi_{\text{coh}} \equiv V_\xi^{-1} \int_{V_\xi} d^d x \delta\phi(x) \tag{13}$$

Fluctuations are negligible if $<(\delta\phi_{\text{coh}})^2>$ is much less than $<\phi^2>$, otherwise, fluctuations are important and the mean-field approximation will fail.

Under what conditions will the mean-filed approximation be valid?

(1) High dimension space, $d \geq 4$.

(2) Long range interactions.

5. Scattering (For more details, see Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p29-37, p47-49)

In scattering theory, the scattering cross-section $\frac{d^2\sigma}{d\Omega}$, which is the differential cross-section per unit solid angle, is a key quantity. It represents a static cross-section obtained experimentally by integrating over all possible energy transfers to the medium. In practice, this integration is naturally accomplished by X-ray diffraction but not by neutron diffraction. In quantum mechanics, the scattering cross-section relates to the transition rate $M_{\mathbf{k},\mathbf{k}'}$ in

$$\frac{d^2\sigma}{d\Omega} \sim \frac{2\pi}{\hbar}\left|M_{\mathbf{k},\mathbf{k}'}\right|^2 \tag{14}$$

If the scattered particle interacts with the scattering medium via a potential U (and the interaction is sufficiently weak that only lowest order scattering need be considered for the entire sample), then by Fermi's golden rule, the transition rate between the incident (incoming) and final (outgoing) plane wave states of the scattered particle, |**k**> and |**k'**>, is proportional to the square of the matrix element,

$$M_{\mathbf{k},\mathbf{k}'} = \left\langle \mathbf{k}\middle|U\middle|\mathbf{k}'\right\rangle = \int d^d x e^{-i\mathbf{k}\cdot\mathbf{x}} U(\mathbf{x}) e^{-i\mathbf{k}'\cdot\mathbf{x}} \tag{15}$$

where $U(\mathbf{x})$ is the sum of terms arising from each of the individual atoms in multiparticle system:

$$U(\mathbf{x}) = \sum_\alpha U_\alpha(\mathbf{x} - \mathbf{x}_\alpha) \tag{16}$$

where $\mathbf{x}_\alpha$ is the position of the atom arbitrarily labeled α. The matrix element in the scattering cross-section then has the form

$$M_{\mathbf{k},\mathbf{k}'} = \sum_\alpha \int d^d x e^{-i\mathbf{k}\cdot\mathbf{x}} U_\alpha(\mathbf{x} - \mathbf{x}_\alpha) e^{-i\mathbf{k}'\cdot\mathbf{x}} \tag{17}$$

This can be placed in a more convenient form by taking $\mathbf{R}_\alpha = \mathbf{x} - \mathbf{x}_\alpha$:

$$
\begin{aligned}
M_{\mathbf{k},\mathbf{k}'} &= \sum_{\alpha} \int d^d R_\alpha e^{-i\mathbf{k}\cdot(\mathbf{x}_\alpha+\mathbf{R}_\alpha)} U_\alpha(\mathbf{R}_\alpha) e^{-i\mathbf{k}'\cdot(\mathbf{x}_\alpha+\mathbf{R}_\alpha)} \\
&= \sum_{\alpha} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}_\alpha} \int d^d R_\alpha e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\alpha} U_\alpha(\mathbf{R}_\alpha) \\
&= \sum_{\alpha} e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \int d^d R_\alpha U_\alpha(\mathbf{R}_\alpha) e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha} \\
&= \sum_{\alpha} U_\alpha(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha}
\end{aligned}
\tag{18}
$$

Here **q** is the scattering wave vector. The relation of **q**, **k** and **k’** is illustrated in Figure 3. $U_\alpha(\mathbf{q})$ is

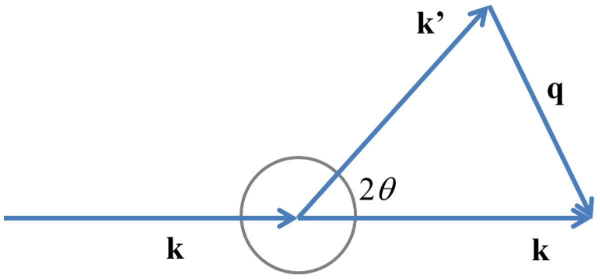


Figure 3

the atomic form factor or Fourier transform of the atomic potential. The scattering cross-section is

$$
\frac{d^2\sigma}{d\Omega} \sim \frac{2\pi}{\hbar} \sum_{\alpha,\alpha'} U_\alpha(\mathbf{q}) U^*_{\alpha'}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} e^{i\mathbf{q}\cdot\mathbf{x}_{\alpha'}}
\tag{19}
$$

Eq. 19 expresses the scattering cross-section for a particular configuration, specified by the position vector $\mathbf{x}_\alpha$, of atoms in the sample. If the positions of the atoms are rigidly fixed, as they would be in a classical system at absolute zero, then Eqs 19 and 14 correctly give the cross-section. In real materials, particles move about, probing large regions of phase space determined by the rules of statistical mechanics, and some ensemble average of the ideal cross-section is required. Assuming that time averaging and averages over all allowed configurations (ensemble averages – denotes by angular brackets < >) are equivalent (i.e. that the system is ergodic) we have the static or quasi-elastic limit. In this limit, the scattering cross-section is

$$
\frac{d^2\sigma}{d\Omega} \sim \left\langle \frac{2\pi}{\hbar} \sum_{\alpha,\alpha'} U_\alpha(\mathbf{q}) U^*_{\alpha'}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} e^{i\mathbf{q}\cdot\mathbf{x}_{\alpha'}} \right\rangle
\tag{20}
$$

If the atoms are identical, then the form factor in eq. 20 comes outside the sum and the bracket, and the scattering cross-section from a statistical system becomes

$$
\frac{d^2\sigma}{d\Omega} \sim \left|U_\alpha(\mathbf{q})\right|^2 I(\mathbf{q})
\tag{21}
$$

where the function

$$I(\mathbf{q}) = \left\langle \sum_{\alpha,\alpha'} e^{-i\mathbf{q}\cdot(\mathbf{x}_\alpha - \mathbf{x}_{\alpha'})} \right\rangle \tag{22}$$

depends only on the positions of the atoms in the scattering medium and not on the nature of the interaction between atoms and the scattering probe. $I(\mathbf{q})$ is thus called the structure function.

The structure function can be expressed in terms of density operator and correlation function as shown below. The number density operator specifying the number of particles per unit volume at position $\mathbf{x}$ in space is defined as

$$n(\mathbf{x}) \equiv \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\alpha) \tag{23}$$

where $\mathbf{x}_\alpha$ is the dynamical variable specifying the position of particle α. The ensemble average of the density operator is the average density at $\mathbf{x}$:

$$\left\langle n(\mathbf{x}) \right\rangle = \left\langle \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\alpha) \right\rangle \tag{24}$$

In homogeneous, isotropic fluids, $<n(\mathbf{x})>$ is independent of $\mathbf{x}$ and is simply the average density $n=N/V$. In crystals, $<n(\mathbf{x})>$ becomes a periodic function of $\mathbf{x}$. The Fourier transform of the density operator is

$$\begin{aligned} n(\mathbf{q}) &= \int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} n(\mathbf{x}) \\ &= \int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\alpha) \\ &= \sum_\alpha \int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} \delta(\mathbf{x} - \mathbf{x}_\alpha) \\ &= \sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \end{aligned} \tag{25}$$

Here we use the *sifting property* of the delta function which will be used over and over again throughout this note:

$$\int dx f(x) \delta(x - x_0) = f(x_0) \tag{26}$$

We can now express the structure function in terms of density operator:

$$\begin{aligned} I(\mathbf{q}) &= \left\langle \sum_{\alpha,\alpha'} e^{-i\mathbf{q}\cdot(\mathbf{x}_\alpha - \mathbf{x}_{\alpha'})} \right\rangle \\ &= \left\langle \sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \sum_{\alpha'} e^{i\mathbf{q}\cdot\mathbf{x}_{\alpha'}} \right\rangle \\ &= \left\langle \sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \sum_\alpha e^{-i(-\mathbf{q})\cdot\mathbf{x}_\alpha} \right\rangle \\ &= \left\langle n(\mathbf{q}) n(-\mathbf{q}) \right\rangle \end{aligned} \tag{27}$$

This is simply a Fourier transform of the two-point density-density correlation function, which is defined as

$$C_{nn}(\mathbf{x}_1,\mathbf{x}_2) \equiv \left\langle n(\mathbf{x}_1)n(\mathbf{x}_2)\right\rangle \tag{28}$$

It can be seen from

$$\begin{aligned}
&\int d^d x_1 d^d x_2 e^{-i\mathbf{q}\cdot(\mathbf{x}_1-\mathbf{x}_2)} C_{nn}(\mathbf{x}_1,\mathbf{x}_2)\\
&= \left\langle \int d^d x_1 d^d x_2 e^{-i\mathbf{q}\cdot(\mathbf{x}_1-\mathbf{x}_2)} n(\mathbf{x}_1)n(\mathbf{x}_2)\right\rangle\\
&= \left\langle \int d^d x_1 e^{-i\mathbf{q}\cdot\mathbf{x}_1} n(\mathbf{x}_1)\int d^d x_2 e^{i\mathbf{q}\cdot\mathbf{x}_2} n(\mathbf{x}_2)\right\rangle\\
&= \left\langle \int d^d x_1 e^{-i\mathbf{q}\cdot\mathbf{x}_1} n(\mathbf{x}_1)\int d^d x_2 e^{i\mathbf{q}\cdot\mathbf{x}_2} \sum_\alpha \delta(\mathbf{x}_2-\mathbf{x}_\alpha)\right\rangle\\
&= \left\langle \int d^d x_1 e^{-i\mathbf{q}\cdot\mathbf{x}_1} n(\mathbf{x}_1)\sum_\alpha \int d^d x_2 e^{i\mathbf{q}\cdot\mathbf{x}_2} \delta(\mathbf{x}_2-\mathbf{x}_\alpha)\right\rangle\\
&= \left\langle \int d^d x_1 e^{-i\mathbf{q}\cdot\mathbf{x}_1} n(\mathbf{x}_1)\sum_\alpha e^{i\mathbf{q}\cdot\mathbf{x}_\alpha}\right\rangle\\
&= \left\langle \sum_\alpha e^{i\mathbf{q}\cdot\mathbf{x}_\alpha} \int d^d x_1 e^{-i\mathbf{q}\cdot\mathbf{x}_1} \sum_\alpha \delta(\mathbf{x}_1-\mathbf{x}_\alpha)\right\rangle\\
&= \left\langle \sum_\alpha e^{i\mathbf{q}\cdot\mathbf{x}_\alpha} \sum_\alpha \int d^d x_1 e^{-i\mathbf{q}\cdot\mathbf{x}_1} \delta(\mathbf{x}_1-\mathbf{x}_\alpha)\right\rangle\\
&= \left\langle \sum_\alpha e^{i\mathbf{q}\cdot\mathbf{x}_\alpha} \sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha}\right\rangle\\
&= \left\langle \sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \sum_\alpha e^{-i(-\mathbf{q})\cdot\mathbf{x}_\alpha}\right\rangle\\
&= \left\langle n(\mathbf{q})n(-\mathbf{q})\right\rangle\\
&= I(\mathbf{q})
\end{aligned} \tag{29}$$

In a periodic solid, the ensemble average of density operator can be decomposed into Fourier components with wave vectors in the reciprocal lattice:

$$\left\langle n(\mathbf{x})\right\rangle = \sum_{\mathbf{G}} \left\langle n_{\mathbf{G}}\right\rangle e^{i\mathbf{G}\cdot\mathbf{x}} \tag{30}$$

Thus, the average number density in a periodic solid is fully specified by its Fourier components $\langle n_{\mathbf{G}}\rangle$ at reciprocal lattice vectors **G**.

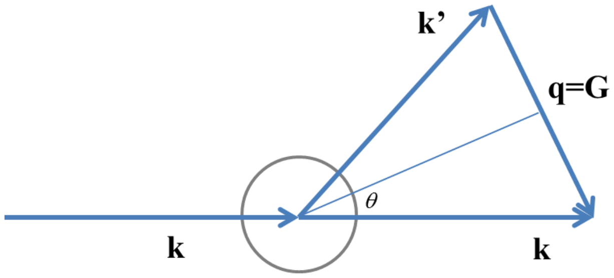


Figure 4

If scatterers are rigidly fixed at sites on a periodic lattice, the scattering matrix element (eq. 18) becomes

$$M_{\mathbf{k},\mathbf{k'}} = V\sum_{\mathbf{G}} U_{\mathbf{G}}\delta_{\mathbf{q},\mathbf{G}} \tag{31}$$

This can be seen from

$$\begin{aligned} M_{\mathbf{k},\mathbf{k'}} &= \sum_{\alpha} U_{\alpha}(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{x}_{\alpha}} \\ &= \sum_{\mathbf{G}}\sum_{\alpha} U_{\alpha}(\mathbf{q})e^{-i\mathbf{G}\cdot\mathbf{x}_{\alpha}}e^{i(\mathbf{G}-\mathbf{q})\cdot\mathbf{x}_{\alpha}} \\ &= \begin{cases} 0, & \text{if } \mathbf{q} \neq \mathbf{G} \\ \sum_{\mathbf{G}}\sum_{\alpha} U_{\alpha}(\mathbf{G})e^{-i\mathbf{G}\cdot\mathbf{x}_{\alpha}}, & \text{if } \mathbf{q} = \mathbf{G} \end{cases} \\ &= V\sum_{\mathbf{G}} U_{\mathbf{G}}\delta_{\mathbf{q},\mathbf{G}} \end{aligned} \tag{32}$$

The scattering cross-section then becomes

$$\frac{d^2\sigma}{d\Omega} = V^2\sum_{\mathbf{G}} \left|U_{\mathbf{G}}\right|^2 \delta_{\mathbf{q},\mathbf{G}} \tag{33}$$

Thus, there will be peaks in the scattering pattern at every reciprocal lattice vector with intensity proportional to the square of the volume of the sample and to the square of the Fourier component of the scattering potential at wave vector **G**. These are the Bragg scattering peaks of the solid. The scattering into Bragg peaks is elastic so that the magnitude of the incident and scattered wave vectors is the same, i.e.,

$$\left|\mathbf{k}\right|^2 = \left|\mathbf{k}'\right|^2 \tag{34}$$

This leads to a variation of Bragg's law, known as the Laue condition. We have the relation

$$\mathbf{q} = \mathbf{k} - \mathbf{k}' \tag{35}$$

At the Bragg scattering peaks, we also have

$$\mathbf{q} = \mathbf{G} \tag{36}$$

Combining eq. 35 and eq. 36 arrive at

$$\mathbf{k}' = \mathbf{k} - \mathbf{G} \tag{37}$$

Squaring the left and right hand side of eq. 37, we have

$$\left|\mathbf{k}'\right|^2 = \left|\mathbf{k}\right|^2 + \left|\mathbf{G}\right|^2 - 2\mathbf{k}\cdot\mathbf{G} \tag{38}$$

Using eq. 34 and rearranging eq. 38, we have

$$\left|\frac{\mathbf{G}}{2}\right|^2 = \mathbf{k}\cdot\left(\frac{\mathbf{G}}{2}\right) \tag{39}$$

As shown in Figure 4, the right hand of above equation can be evaluated as

$$\mathbf{k}\cdot\left(\frac{\mathbf{G}}{2}\right) = \left|\mathbf{k}\right|\left|\frac{\mathbf{G}}{2}\right|\sin\theta \tag{40}$$

Now eq. 39 can be simplified to be

$$\left|\mathbf{G}\right| = 2\left|\mathbf{k}\right|\sin\theta \tag{41}$$

This relation is equivalent to the Bragg condition as can be seen by substituting

$$\left|\mathbf{G}\right| = \frac{2\pi}{d} \tag{42}$$

and

$$\left|\mathbf{k}\right| = \frac{2\pi}{\lambda} \tag{43}$$

into eq. 41:

$$2d\sin\theta = \lambda \tag{44}$$

where d is the distance between adjacent planes and λ is the wave length of incident wave.

6. Excluded volume and incompressibility

The interaction between hard core A and B is

$$U = \int d^d r d^d r' \phi_{\mathrm{A}}(\mathbf{r}) V(\mathbf{r}-\mathbf{r}') \phi_{\mathrm{B}}(\mathbf{r}') \tag{45}$$

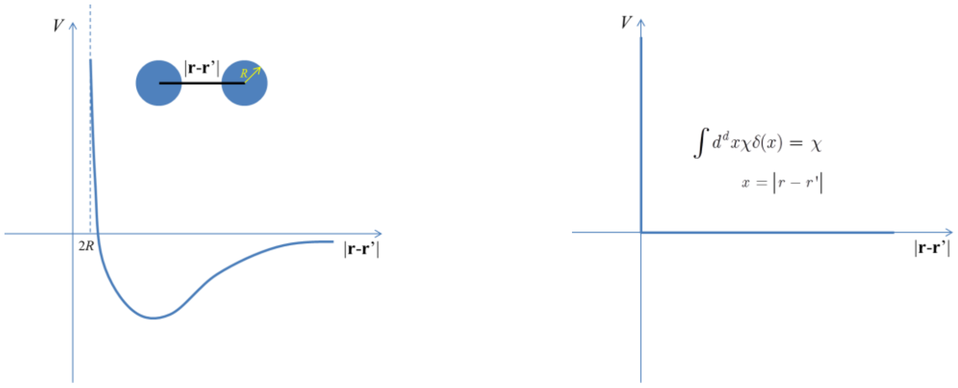
For Flory-Huggins interactions, V has the form

$$V(\mathbf{r}-\mathbf{r}') = \chi\delta(\mathbf{r}-\mathbf{r}') \tag{46}$$

where χ is Flory-Huggins interaction parameter. This leads to the well-known interaction energy

$$\begin{aligned} U &= \int d^d r d^d r' \phi_{\mathrm{A}}(\mathbf{r}) V(\mathbf{r}-\mathbf{r}') \phi_{\mathrm{B}}(\mathbf{r}') \\ &= \int d^d r d^d r' \phi_{\mathrm{A}}(\mathbf{r}) \chi\delta(\mathbf{r}-\mathbf{r}') \phi_{\mathrm{B}}(\mathbf{r}') \\ &= \chi\int d^d r \phi_{\mathrm{A}}(\mathbf{r}) \int d^d r' \phi_{\mathrm{B}}(\mathbf{r}') \delta(\mathbf{r}-\mathbf{r}') \\ &= \chi\int d^d r \phi_{\mathrm{A}}(\mathbf{r}) \phi_{\mathrm{B}}(\mathbf{r}) \end{aligned} \tag{47}$$

In general, V includes the information of excluded volume effect. However, the approximation of eq. 46 ignores the exclusive hard core interactions (any interaction is set to 0 when A and B are not in identical location), which can be seen in Figure 5. To avoid unphysical results from this



(a) (b)

Figure 5

approximation, the incompressibility condition is introduced.

7. Structure factor for single ideal Gaussian chain and Debye function (For more details, see Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p32-33; M. Doi, *Introduction to Polymer Physics*, 1996, p9-10.)

Origin of the term structure factor. In section 5, we introduce the structure function in eq. 22. The bracket denotes averaging over all possible configurations. For a system of N atoms, $I(\mathbf{q})$ contains a sum of N^2 complex numbers with phases determined by the positions of all N particles. If the relative positions of the atoms are random (as for an ideal gas) then the only terms that do not average to zero are those with a = a’ for which $\sum_{\alpha,\alpha'} \to \sum_{\alpha}$. In this case, $I(\mathbf{q})$ increases linearly with N (rather than with N^2), i.e., $I(\mathbf{q})$ is extensive. For fluid phases, where relative positions are not random for some close neighbor particles, $I(\mathbf{q})$ remains extensive. An intensive version of the structure function (independent of N) is obtained by dividing $I(\mathbf{q})$ by N or V. The resulting function,

$$S(\mathbf{q}) = N^{-1} I(\mathbf{q}) \tag{48}$$

or

$$S(\mathbf{q}) = V^{-1} I(\mathbf{q}) \tag{49}$$

is called the structure factor. Most experimental data are presented in the first (dimensionless) form.

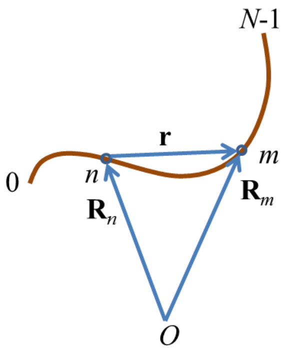


Figure 6

The structure factor of a single ideal Gaussian chain. The Gaussian chain has N segments which are indexed from 0 to *N*-1. As illustrated in Figure 6, *n* and *m* are independent indexes. Therefore, the structure factor can be calculated as

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N}\left\langle \sum_{n,m} e^{-i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \right\rangle \\ &= \frac{1}{N}\sum_{n}\sum_{m}\left\langle e^{-i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \right\rangle \end{aligned} \tag{50}$$

the ensemble average according to Gaussian distribution:

$$\begin{aligned} &\left\langle e^{-i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \right\rangle \\ &= \left\langle e^{-i\mathbf{q}\cdot\mathbf{r}} \right\rangle \\ &= \int d^3 r e^{-i\mathbf{q}\cdot\mathbf{r}} \left[\frac{3}{2\pi\left|n-m\right|b^2}\right]^{\frac{3}{2}} e^{-\frac{3r^2}{2\left|n-m\right|b^2}} \end{aligned} \tag{51}$$

Using the following relations

$$\mathbf{r} = (x, y, z) \tag{52}$$

$$r^2 = x^2 + y^2 + z^2 \tag{53}$$

$$\mathbf{q}\cdot\mathbf{r} = q_x x + q_y y + q_z z \tag{54}$$

the above integral can be split into three parts:

$$\begin{aligned} &\left\langle e^{-i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \right\rangle \\ &= \int dx e^{-iq_x x} \left[\frac{3}{2\pi\left|n-m\right|b^2}\right]^{\frac{1}{2}} e^{-\frac{3x^2}{2\left|n-m\right|b^2}} \\ &\times \int dy e^{-iq_y y} \left[\frac{3}{2\pi\left|n-m\right|b^2}\right]^{\frac{1}{2}} e^{-\frac{3y^2}{2\left|n-m\right|b^2}} \\ &\times \int dz e^{-iq_z z} \left[\frac{3}{2\pi\left|n-m\right|b^2}\right]^{\frac{1}{2}} e^{-\frac{3z^2}{2\left|n-m\right|b^2}} \\ &= I_x I_y I_z \end{aligned} \tag{55}$$

The first integral is calculated as

$$
\begin{aligned}
I_x &= \int dx e^{-iq_x x} \left[\frac{3}{2\pi \left| n - m \right| b^2} \right]^{\frac{3}{2}} e^{-\frac{3x^2}{2\left|n-m\right|b^2}} \\
&= \left[\frac{3}{2\pi \left| n - m \right| b^2} \right]^{\frac{3}{2}} \int dx e^{-\frac{3x^2}{2\left|n-m\right|b^2} - iq_x x} \\
&= \left(\frac{\sigma^2}{\pi} \right)^{\frac{3}{2}} \int dx e^{-\sigma^2 x^2 - iq_x x} \\
&= \left(\frac{\sigma^2}{\pi} \right)^{\frac{3}{2}} \int dx e^{-\sigma^2 (x - \frac{-iq_x}{2\sigma^2})^2 + \frac{-iq_x}{4\sigma^2}} \\
&= \left(\frac{\sigma^2}{\pi} \right)^{\frac{3}{2}} \int dx e^{-\sigma^2 (x - \frac{-iq_x}{2\sigma^2})^2 + \frac{(-iq_x)^2}{4\sigma^2}} \\
&= \left(\frac{\sigma^2}{\pi} \right)^{\frac{3}{2}} e^{\frac{(-iq_x)^2}{4\sigma^2}} \int dt e^{-\sigma^2 t^2} \\
&= \left(\frac{\sigma^2}{\pi} \right)^{\frac{1}{2}} e^{-\frac{{q_x}^2}{4\sigma^2}} \left(\frac{\pi}{\sigma^2} \right)^{\frac{1}{2}} \\
&= e^{-\frac{{q_x}^2}{4\sigma^2}} \\
&= e^{-\frac{{q_x}^2}{6}\left|n-m\right|b^2}
\end{aligned}
\tag{56}
$$

Here we use the Gaussian integral

$$
\int_{-\infty}^{\infty} dt e^{-\sigma^2 t^2} = \sqrt{\frac{\pi}{\sigma^2}}
\tag{57}
$$

I_y and I_z are similarly obtained:

$$
I_y = e^{-\frac{{q_y}^2}{6}\left|n-m\right|b^2}
\tag{58}
$$

$$
I_z = e^{-\frac{{q_z}^2}{6}\left|n-m\right|b^2}
\tag{59}
$$

Substitute eq. 56, 58 and 59 into 55, we have

$$
\left\langle e^{-i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \right\rangle = e^{-\frac{q^2}{6}\left|n-m\right|b^2}
\tag{60}
$$

where

$$
q^2 = q_x^2 + q_y^2 + q_z^2
\tag{61}
$$

Substitute eq. 60 into eq. 50, and let $N \rightarrow \infty$,

$$
\begin{aligned}
S(\mathbf{q}) &= \frac{1}{N} \int_0^N dn \int_0^N dm \; e^{-\frac{q^2}{6}\left|n-m\right|b^2} \\
&= \frac{N^2}{N} \int_0^1 dn \int_0^1 dm \; e^{-\frac{q^2}{6}\left|n-m\right|Nb^2} \\
&= N \int_0^1 dn \int_0^1 dm \; e^{-q^2 R_g^2 \left|n-m\right|}
\end{aligned}
\tag{62}
$$

In last line, n and m are rescaled in the range of 0 to 1, and the radius of gyration R_g2=Nb^2/6.

$$
\begin{aligned}
&\int_0^1 dm\ e^{-q^2R_g^2|n-m|} \\
&= \int_0^n dm\ e^{-q^2R_g^2(n-m)} + \int_n^1 dm\ e^{-q^2R_g^2(m-n)} \\
&= e^{-q^2R_g^2 n}\int_0^n dm\ e^{q^2R_g^2 m} + e^{q^2R_g^2 n}\int_n^1 dm\ e^{-q^2R_g^2 m} \\
&= \left(\frac{1}{q^2R_g^2}e^{-q^2R_g^2 n}\right) e^{q^2R_g^2 n} - e^{q^2R_g^2 0} - \left(\frac{1}{q^2R_g^2}e^{q^2R_g^2 n}\right) e^{-q^2R_g^2 1} - e^{-q^2R_g^2 n} \\
&= \frac{1}{x^2}e^{-x^2 n}\left(e^{x^2 n} - 1\right) - \frac{1}{x^2}e^{x^2 n}\left(e^{-x^2} - e^{-x^2 n}\right) \\
&= \frac{1}{x^2} - \frac{1}{x^2}e^{-x^2 n} - \frac{1}{x^2}e^{x^2(n-1)} + \frac{1}{x^2} \\
&= \frac{2}{x^2} - \frac{1}{x^2}e^{-x^2 n} - \frac{e^{-x^2}}{x^2}e^{x^2 n}
\end{aligned} \tag{63}
$$

where

$$
x = qR_g \tag{64}
$$

Substitute above result into eq. 62, we have

$$
\begin{aligned}
S(\mathbf{q}) &= N\int_0^1 dn\left(\frac{2}{x^2} - \frac{1}{x^2}e^{-x^2 n} - \frac{e^{-x^2}}{x^2}e^{x^2 n}\right) \\
&= N\int_0^1 dn\frac{2}{x^2} - N\int_0^1 dn\frac{1}{x^2}e^{-x^2 n} - N\int_0^1 dn\frac{e^{-x^2}}{x^2}e^{x^2 n} \\
&= N\frac{2}{x^2} \\
&\quad -N\frac{1}{x^2}\left(\frac{1}{-x^2}\right)\int_0^1 d(-x^2 n)e^{-x^2 n} \\
&\quad -N\frac{e^{-x^2}}{x^2}\left(\frac{1}{x^2}\right)\int_0^1 d(x^2 n)e^{x^2 n} \\
&= N\frac{2}{x^2} + N\frac{1}{x^4}\ e^{-x^2} - 1\ - N\frac{e^{-x^2}}{x^4}\ e^{x^2} - 1 \\
&= N\left(\frac{2e^{-x^2}}{x^4} - \frac{2}{x^4} + \frac{2}{x^2}\right) \\
&= N\frac{2}{x^4}\left(e^{-x^2} - 1 + x^2\right) \\
&= Ng(x)
\end{aligned} \tag{65}
$$

The Debye function. The Debye function is

$$
g(x) = \frac{2}{x^4}\ e^{-x^2} - 1 + x^2 \tag{66}
$$

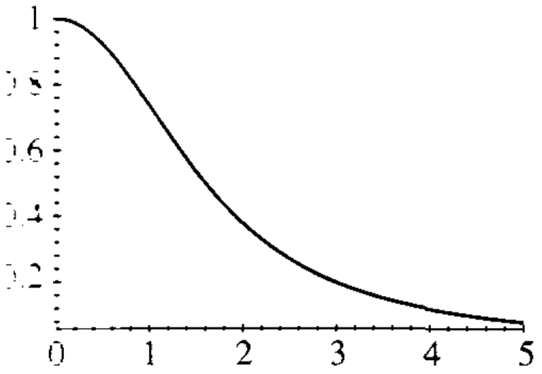


Figure 7

Debye function has two asymptotic forms. When x→∞,

$$g(x) = \frac{2}{x^2} \tag{67}$$

$$S(\mathbf{q}) = \frac{2N}{q^2 R_g^2} \tag{68}$$

And when x→0,

$$g(x) = \frac{2}{x^4}\left(1 - x^2 + \frac{x^4}{2} - 1 + x^2\right) = 1 \tag{69}$$

$$S(\mathbf{q}) = N \tag{70}$$

8. **Response function and fluctuation-dissipation theorem** (For more details, see M. Doi, *Introduction to Polymer Physics*, 1996, p29-32; Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p35.)

In statistical mechanics, the probability density function is

$$P \propto e^{-\beta U_0} \tag{71}$$

The ensemble average of any physical quantity (take density as an example) can be evaluated

$$\left\langle \phi \right\rangle = \frac{Tr\left[\phi e^{-\beta U_0}\right]}{Tr\left[e^{-\beta U_0}\right]} = \frac{\int D\phi \phi e^{-\beta U_0}}{\int D\phi e^{-\beta U_0}} \tag{72}$$

Here *Tr* represents trace, which denotes integrating over all possible configurations. The external potential is

$$U_{ext} = \int d^3 r \phi(\mathbf{r}) U(\mathbf{r}) \tag{73}$$

Under the external potential, the ensemble average of density will deviate from <ϕ>:

$$\left\langle \phi \right\rangle_U = \frac{\int D\phi \phi e^{-\beta(U_0 + U_{ext})}}{\int D\phi e^{-\beta(U_0 + U_{ext})}} \neq \left\langle \phi \right\rangle \tag{74}$$

If the external field is small, the deviation

$$\overline{\delta\phi(\mathbf{r})} \equiv \left\langle \phi \right\rangle_U - \left\langle \phi \right\rangle \tag{75}$$

can be written as a linear function of the external potential:

$$\overline{\delta\phi(\mathbf{r})} = -\int d^3 r\,'\, \Gamma(\mathbf{r},\mathbf{r}\,') U_{ext}(\mathbf{r}\,') \tag{76}$$

where Γ(**r**,**r**’) is called the response function. It can be calculated

$$\Gamma(\mathbf{r},\mathbf{r}\,') = -\frac{\delta\left[\overline{\delta\phi(\mathbf{r})}\right]}{\delta U_{ext}(\mathbf{r}\,')} \tag{77}$$

It is related to the Ursell function S_{nn}(**r**,**r**’) as follows:

$$\Gamma(\mathbf{r},\mathbf{r}\,') = \beta S_{nn}(\mathbf{r},\mathbf{r}\,') \tag{78}$$

The above equation is the fluctuation-dissipation theorem. Below we will give an illustrative proof.

The Ursell function can be derived from two-point density-density operator or density fluctuation as follows:

$$\begin{aligned} S_{nn}(\mathbf{r},\mathbf{r}\,') &= C_{nn}(\mathbf{r},\mathbf{r}\,') - \left\langle \phi(\mathbf{r}) \right\rangle \left\langle \phi(\mathbf{r}\,') \right\rangle \\ &= \left\langle \phi(\mathbf{r})\phi(\mathbf{r}\,') \right\rangle - \left\langle \phi(\mathbf{r}) \right\rangle \left\langle \phi(\mathbf{r}\,') \right\rangle \\ &= \left\langle \phi(\mathbf{r})\phi(\mathbf{r}\,') \right\rangle + \left\langle \phi(\mathbf{r}) \right\rangle \left\langle \phi(\mathbf{r}\,') \right\rangle - \left\langle \phi(\mathbf{r}) \left\langle \phi(\mathbf{r}\,') \right\rangle \right\rangle - \left\langle \phi(\mathbf{r}\,') \left\langle \phi(\mathbf{r}) \right\rangle \right\rangle \\ &= \left\langle \left[\phi(\mathbf{r}) - \left\langle \phi(\mathbf{r}) \right\rangle \right] \left[\phi(\mathbf{r}\,') - \left\langle \phi(\mathbf{r}\,') \right\rangle \right] \right\rangle \\ &= \left\langle \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}\,') \right\rangle \end{aligned} \tag{79}$$

The ensemble average of density under external potential can be rewritten in the term of equilibrium ensemble average as

$$\begin{aligned} \left\langle \phi \right\rangle_U &= \frac{\int D\phi \phi e^{-\beta(U_0 + U_{ext})}}{\int D\phi e^{-\beta(U_0 + U_{ext})}} \\ &= \frac{\int D\phi \phi e^{-\beta U_{ext}} e^{-\beta U_0}}{\int D\phi e^{-\beta U_0}} \frac{\int D\phi e^{-\beta U_0}}{\int D\phi e^{-\beta U_{ext}} e^{-\beta U_0}} \\ &= \frac{\left\langle \phi e^{-\beta U_{ext}} \right\rangle}{\left\langle e^{-\beta U_{ext}} \right\rangle} \end{aligned} \tag{80}$$

Under weak external field, i.e. in the limit

$$\beta U_{ext} \to 0 \tag{81}$$

the exponential terms can be expanded to the first order term,

$$\begin{aligned}\langle \phi \rangle_U &= \frac{\langle \phi e^{-\beta U_{ext}} \rangle}{\langle e^{-\beta U_{ext}} \rangle} \\ &= \frac{\langle \phi\left(1-\beta U_{ext}\right) \rangle}{\langle 1-\beta U_{ext} \rangle} \\ &= \frac{\langle \phi \rangle - \beta \langle \phi U_{ext} \rangle}{1-\beta \langle U_{ext} \rangle} \\ &= \left(\langle \phi \rangle - \beta \langle \phi U_{ext} \rangle\right)\left(1+\beta \langle U_{ext} \rangle\right) \\ &= \langle \phi \rangle - \beta \langle \phi U_{ext} \rangle + \beta \langle \phi \rangle \langle U_{ext} \rangle\end{aligned} \tag{82}$$

where the second order term of $<U_{ext}>^2$ is ignored. From above equation, the density deviation is

$$\begin{aligned}\overline{\delta\phi(\mathbf{r})} &= -\beta \langle \phi U_{ext} \rangle + \beta \langle \phi \rangle \langle U_{ext} \rangle \\ &= -\beta \left\langle \phi(\mathbf{r}) \int d^3r' \phi(\mathbf{r}')U(\mathbf{r}') \right\rangle + \beta \langle \phi(\mathbf{r}) \rangle \left\langle \int d^3r' \phi(\mathbf{r}')U(\mathbf{r}') \right\rangle \\ &= -\beta \int d^3r' \langle \phi(\mathbf{r})\phi(\mathbf{r}') \rangle U(\mathbf{r}') + \beta \langle \phi(\mathbf{r}) \rangle \int d^3r' \langle \phi(\mathbf{r}') \rangle U(\mathbf{r}') \\ &= -\beta \int d^3r' \langle \phi(\mathbf{r})\phi(\mathbf{r}') \rangle U(\mathbf{r}') + \beta \int d^3r' \langle \phi(\mathbf{r}) \rangle \langle \phi(\mathbf{r}') \rangle U(\mathbf{r}') \\ &= -\int d^3r' \beta \left[\langle \phi(\mathbf{r})\phi(\mathbf{r}') \rangle - \langle \phi(\mathbf{r}) \rangle \langle \phi(\mathbf{r}') \rangle \right] U(\mathbf{r}')\end{aligned} \tag{83}$$

Compare eq. 83 with eq. 76, we find the response function

$$\Gamma(\mathbf{r},\mathbf{r}') = \beta \left[\langle \phi(\mathbf{r})\phi(\mathbf{r}') \rangle - \langle \phi(\mathbf{r}) \rangle \langle \phi(\mathbf{r}') \rangle \right] \tag{84}$$

Compare eq. 84 with eq. 79, the term inside the square bracket in eq. 84 is just Ursell function. Therefore, the proof is completed.

9. Random phase approximation (RPA) (For more details, see M. Doi, *Introduction to Polymer Physics*, 1996, p29-35; Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p38-39.)

Let us consider a mixture of two polymers A and B, having degrees of polymerization N_A and N_B, respectively. Let ϕ_A, ϕ_B be the overall volume fractions of each type of segment, with

$$\phi_A + \phi_B = 1 \tag{85}$$

The density operators for A and B also satisfy the relation for incompressible system:

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1 \tag{86}$$

Letting <…> denote an equilibrium ensemble average, then

$$\langle \phi_A(\mathbf{r}) \rangle = \phi_A \tag{87}$$

$$\langle \phi_B(\mathbf{r}) \rangle = \phi_B \tag{88}$$

The deviation of the segmental density is defined by

$$\delta\phi_{\mathrm{A}}(\mathbf{r}) = \phi_{\mathrm{A}}(\mathbf{r}) - \phi_{\mathrm{A}} \tag{89}$$

$$\delta\phi_{\mathrm{B}}(\mathbf{r}) = \phi_{\mathrm{B}}(\mathbf{r}) - \phi_{\mathrm{B}} \tag{90}$$

From this definition, the following relation is held

$$\begin{aligned} \delta\phi_{\mathrm{A}}(\mathbf{r}) + \delta\phi_{\mathrm{B}}(\mathbf{r}) &= \phi_{\mathrm{A}}(\mathbf{r}) - \phi_{\mathrm{A}} + \phi_{\mathrm{B}}(\mathbf{r}) - \phi_{\mathrm{B}} \\ &= \left[\phi_{\mathrm{A}}(\mathbf{r}) + \phi_{\mathrm{B}}(\mathbf{r})\right] - \left[\phi_{\mathrm{A}} + \phi_{\mathrm{B}}\right] \\ &= 1 - 1 \\ &= 0 \end{aligned} \tag{91}$$

So

$$\delta\phi_{\mathrm{A}}(\mathbf{r}) = -\delta\phi_{\mathrm{B}}(\mathbf{r}) \tag{92}$$

The fluctuation is characterized by the Ursell functions of $\delta\phi_{\mathrm{A}}(\mathbf{r})$ and $\delta\phi_{\mathrm{B}}(\mathbf{r})$ as follows:

$$S_{\mathrm{AA}}(\mathbf{r},\mathbf{r}') = \left\langle \delta\phi_{\mathrm{A}}(\mathbf{r})\delta\phi_{\mathrm{A}}(\mathbf{r}')\right\rangle \tag{93}$$

$$S_{\mathrm{AB}}(\mathbf{r},\mathbf{r}') = \left\langle \delta\phi_{\mathrm{A}}(\mathbf{r})\delta\phi_{\mathrm{B}}(\mathbf{r}')\right\rangle \tag{94}$$

$$S_{\mathrm{BA}}(\mathbf{r},\mathbf{r}') = \left\langle \delta\phi_{\mathrm{B}}(\mathbf{r})\delta\phi_{\mathrm{A}}(\mathbf{r}')\right\rangle \tag{95}$$

$$S_{\mathrm{BB}}(\mathbf{r},\mathbf{r}') = \left\langle \delta\phi_{\mathrm{B}}(\mathbf{r})\delta\phi_{\mathrm{B}}(\mathbf{r}')\right\rangle \tag{96}$$

Using eq. 92, we have

$$S_{\mathrm{AA}} = S_{\mathrm{BB}} = -S_{\mathrm{AB}} = -S_{\mathrm{BA}} \tag{97}$$

Let us consider weak external potentials $u_{\mathrm{A}}(\mathbf{r})$, $u_{\mathrm{B}}(\mathbf{r})$ which act respectively on the segments of A and B polymers. The change in the system's potential energy is

$$U_{ext} = \int d^3r\left[\phi_{\mathrm{A}}(\mathbf{r})u_{\mathrm{A}}(\mathbf{r}) + \phi_{\mathrm{B}}(\mathbf{r})u_{\mathrm{B}}(\mathbf{r})\right] \tag{98}$$

Then the linear response theory implies

$$\overline{\delta\phi_{\alpha}(\mathbf{r})} = -\sum_{\beta}\int d^3r'\,\Gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}')u_{\beta}(\mathbf{r}') \tag{99}$$

where subscripts α and β run over A and B. Applying fluctuation-dissipation theorem, we have

$$\Gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \beta S_{\alpha\beta}(\mathbf{r},\mathbf{r}') \tag{100}$$

Homogeneous mixture of A and B polymers is fluid which is spatially homogeneous and rotationally isotropic. This means that the average environment of any point in a fluid is identical to that any other point and independent of direction. Thus the average properties of a fluid are invariant with respect to spatially uniform translations through any vector **R** and with respect to arbitrary rotations about any axis. Translational invariance implies

$$S_{\alpha\beta}(\mathbf{r},\mathbf{r}') = S_{\alpha\beta}(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R}) \tag{101}$$

In particular, we can choose **R** to be equal to –**r**’ so that

$$S_{\alpha\beta}(\mathbf{r},\mathbf{r}') = S_{\alpha\beta}(\mathbf{r}-\mathbf{r}',0) \equiv S_{\alpha\beta}(\mathbf{r}-\mathbf{r}') \tag{102}$$

depends only on **r-r**’. Similarly, other spatial quantities also depend on **r-r**’, such as

$$\Gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \Gamma_{\alpha\beta}(\mathbf{r}-\mathbf{r}') \tag{103}$$

In this form of Ursell function and response function, eq. 76 is a convolution

$$\overline{\delta\phi(\mathbf{r})} = -\beta\int d^3r'\, S(\mathbf{r}-\mathbf{r}')u(\mathbf{r}') \tag{104}$$

which is most convenient in Fourier space. Using Fourier transform to eq. 104, the left hand side is

$$\int d^3r\,\overline{\delta\phi(\mathbf{r})}e^{-i\mathbf{q}\cdot\mathbf{r}} = \overline{\delta\phi(\mathbf{q})} \tag{105}$$

and the right hand side is

$$\begin{aligned}
&\int d^3r\left[-\beta\int d^3r'\, S(\mathbf{r}-\mathbf{r}')u(\mathbf{r}')\right]e^{-i\mathbf{q}\cdot\mathbf{r}}\\
&= -\beta\int d^3r\int d^3r'\, S(\mathbf{r}-\mathbf{r}')u(\mathbf{r}')e^{-i\mathbf{q}\cdot\mathbf{r}}\\
&= -\beta\int d^3r'\, u(\mathbf{r}')\int d^3r\, S(\mathbf{r}-\mathbf{r}')e^{-i\mathbf{q}\cdot\mathbf{r}}\\
&= -\beta\int d^3r'\, u(\mathbf{r}')\int d^3R\, S(\mathbf{R})e^{-i\mathbf{q}\cdot(\mathbf{r}'+\mathbf{R})}\\
&= -\beta\int d^3r'\, u(\mathbf{r}')e^{-i\mathbf{q}\cdot\mathbf{r}'}\int d^3R\, S(\mathbf{R})e^{-i\mathbf{q}\cdot\mathbf{R}}\\
&= -\beta\int d^3r'\, u(\mathbf{r}')e^{-i\mathbf{q}\cdot\mathbf{r}'}S(\mathbf{q})\\
&= -\beta S(\mathbf{q})\int d^3r'\, u(\mathbf{r}')e^{-i\mathbf{q}\cdot\mathbf{r}'}\\
&= -\beta S(\mathbf{q})u(\mathbf{q})
\end{aligned} \tag{106}$$

Thus, in Fourier space, the convolution is just a multiplication

$$\overline{\delta\phi(\mathbf{q})} = -\beta S(\mathbf{q})u(\mathbf{q}) \tag{107}$$

In the above context, we first outline the basic RPA procedure as follows. In general, if an external filed *u*(**q**) is applied to the system, the resulting change in the concentration is given by

$$\overline{\delta\phi} = -\beta S^{(0)}u \tag{108}$$

Hereafter (**q**) is dropped from all related physical quantities for simplicity. Now, in reality there are interactions between components, which we will take into account through the mean-field approximation. The interaction *u* changes to an effective interaction

$$u_{eff} = u + w\overline{\delta\phi} \tag{109}$$

where $\overline{\delta\phi}$ is different from the one in eq. 108, it satisfies

$$\begin{aligned}\overline{\delta\phi} &= -\beta S^{(0)} u_{eff} \\ &= -\beta S^{(0)} \quad u + w\overline{\delta\phi}\end{aligned} \tag{110}$$

Re-express above equation in the form

$$\overline{\delta\phi} = -\beta S^{RPA} u \tag{111}$$

We finally obtain the Ursell function under external potential u_{eff}:

$$S^{RPA} = \frac{S^{(0)}}{1 + \beta S^{(0)} w} \tag{112}$$

The Ursell function for the mixture of A and B polymers can be calculated by following the RPA procedure. First of all, let us consider the case where the polymers A and B are placed on the lattice at random, without excluded volume effects or interaction energies. In this case,

$$S^{(0)}_{\mathrm{AB}}(\mathbf{r} - \mathbf{r}') = \left\langle \delta\phi_{\mathrm{A}}(\mathbf{r})\delta\phi_{\mathrm{B}}(\mathbf{r}') \right\rangle = 0 \tag{113}$$

$$S^{(0)}_{\mathrm{BA}}(\mathbf{r}, \mathbf{r}') = \left\langle \delta\phi_{\mathrm{B}}(\mathbf{r})\delta\phi_{\mathrm{A}}(\mathbf{r}') \right\rangle = 0 \tag{114}$$

but

$$S^{(0)}_{\mathrm{AA}}(\mathbf{r} - \mathbf{r}') = \left\langle \delta\phi_{\mathrm{A}}(\mathbf{r})\delta\phi_{\mathrm{A}}(\mathbf{r}') \right\rangle \neq 0 \tag{115}$$

$$S^{(0)}_{\mathrm{BB}}(\mathbf{r} - \mathbf{r}') = \left\langle \delta\phi_{\mathrm{B}}(\mathbf{r})\delta\phi_{\mathrm{B}}(\mathbf{r}') \right\rangle \neq 0 \tag{116}$$

since the segments of the polymers are linked together. According to linear response theory, the change of concentration is given by (using eq. 99)

$$\begin{aligned}\overline{\delta\phi_{\mathrm{A}}(\mathbf{r})} &= -\beta\int d^3r' S^{(0)}_{\mathrm{AA}}(\mathbf{r} - \mathbf{r}')u_{\mathrm{A}}(\mathbf{r}') - \beta\int d^3r' S^{(0)}_{\mathrm{AB}}(\mathbf{r} - \mathbf{r}')u_{\mathrm{B}}(\mathbf{r}') \\ &= -\beta\int d^3r' S^{(0)}_{\mathrm{AA}}(\mathbf{r} - \mathbf{r}')u_{\mathrm{A}}(\mathbf{r}')\end{aligned} \tag{117}$$

In Fourier space,

$$\overline{\delta\phi_{\mathrm{A}}} = -\beta S^{(0)}_{\mathrm{AA}} u_{\mathrm{A}} \tag{118}$$

Similarly,

$$\overline{\delta\phi_{\mathrm{B}}} = -\beta S^{(0)}_{\mathrm{BB}} u_{\mathrm{B}} \tag{119}$$

Now, in reality there are interactions between the chains. Through the mean-filed approximation, the molecular fields acting on the segments are given by

$$w_{\mathrm{A}}(\mathbf{r}) = -z\left[\varepsilon_{\mathrm{AA}}\phi_{\mathrm{A}}(\mathbf{r}) + \varepsilon_{\mathrm{AB}}\phi_{\mathrm{B}}(\mathbf{r})\right] \tag{120}$$

$$w_{\mathrm{B}}(\mathbf{r}) = -z\big[\varepsilon_{\mathrm{BA}}\phi_{\mathrm{A}}(\mathbf{r}) + \varepsilon_{\mathrm{BB}}\phi_{\mathrm{B}}(\mathbf{r})\big] \tag{121}$$

Further, there is the conservation of volume condition (impressible condition eq. 86), which can be represented in the following potential form (which can also be viewed as a Lagrange multiplier):

$$U_{excl} = \int d^3r V(\mathbf{r})\big[\phi_{\mathrm{A}}(\mathbf{r}) + \phi_{\mathrm{B}}(\mathbf{r})\big] \tag{122}$$

Here *V*(**r**) is a potential determined from the volume conservation condition. The mean fields acting on segments A and B are, respectively, w_A+V and w_B+V, and so the changes of concentration are given by the following (in Fourier space):

$$\overline{\delta\phi_{\mathrm{A}}} = -\beta S^{(0)}_{\mathrm{AA}} \quad u_{\mathrm{A}} + w_{\mathrm{A}} + V \tag{123}$$

$$\overline{\delta\phi_{\mathrm{B}}} = -\beta S^{(0)}_{\mathrm{BB}} \quad u_{\mathrm{B}} + w_{\mathrm{B}} + V \tag{124}$$

where w_A and w_B are Fourier transform of $w_A(\mathbf{r})$ and $w_B(\mathbf{r})$, which can be calculated as

$$\begin{aligned} w_{\mathrm{A}} &= -z\Big[\varepsilon_{\mathrm{AA}}\int d^3r\phi_{\mathrm{A}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} + \varepsilon_{\mathrm{AB}}\int d^3r\phi_{\mathrm{B}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}\Big] \\ &= -z \quad \varepsilon_{\mathrm{AA}}\overline{\delta\phi_{\mathrm{A}}} + \varepsilon_{\mathrm{AB}}\overline{\delta\phi_{\mathrm{B}}} \end{aligned} \tag{125}$$

$$\begin{aligned} w_{\mathrm{B}} &= -z\Big[\varepsilon_{\mathrm{BA}}\int d^3r\phi_{\mathrm{A}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} + \varepsilon_{\mathrm{BB}}\int d^3r\phi_{\mathrm{B}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}\Big] \\ &= -z \quad \varepsilon_{\mathrm{BA}}\overline{\delta\phi_{\mathrm{A}}} + \varepsilon_{\mathrm{BB}}\overline{\delta\phi_{\mathrm{B}}} \end{aligned} \tag{126}$$

where we use the relation

$$\begin{aligned} \overline{\delta\phi_{\mathrm{A}}} &= \int d^3r\overline{\delta\phi_{\mathrm{A}}(\mathbf{r})}e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \int d^3r\big[\phi_{\mathrm{A}}(\mathbf{r}) - \phi_{\mathrm{A}}\big]e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \int d^3r\phi_{\mathrm{A}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} \end{aligned} \tag{127}$$

$$\begin{aligned} \overline{\delta\phi_{\mathrm{B}}} &= \int d^3r\overline{\delta\phi_{\mathrm{B}}(\mathbf{r})}e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \int d^3r\big[\phi_{\mathrm{B}}(\mathbf{r}) - \phi_{\mathrm{B}}\big]e^{-i\mathbf{q}\cdot\mathbf{r}} \\ &= \int d^3r\phi_{\mathrm{B}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} \end{aligned} \tag{128}$$

Substitute eq. 125 and 126 into eq. 123 and 124, we have

$$\overline{\delta\phi_{\mathrm{A}}} = -\beta S^{(0)}_{\mathrm{AA}}\Big[u_{\mathrm{A}} - z \quad \varepsilon_{\mathrm{AA}}\overline{\delta\phi_{\mathrm{A}}} + \varepsilon_{\mathrm{AB}}\overline{\delta\phi_{\mathrm{B}}} \quad + V\Big] \tag{129}$$

$$\overline{\delta\phi_{\mathrm{B}}} = -\beta S^{(0)}_{\mathrm{BB}}\Big[u_{\mathrm{B}} - z \quad \varepsilon_{\mathrm{BA}}\overline{\delta\phi_{\mathrm{A}}} + \varepsilon_{\mathrm{BB}}\overline{\delta\phi_{\mathrm{B}}} \quad + V\Big] \tag{130}$$

Moving the term before the square brackets in the above two equations to the left hand, and then subtracting the first equation from the second equation, we have

$$\frac{\overline{\delta\phi_{\mathrm{A}}}}{-\beta S^{(0)}_{\mathrm{AA}}} - \frac{\overline{\delta\phi_{\mathrm{B}}}}{-\beta S^{(0)}_{\mathrm{BB}}} = u_{\mathrm{A}} - u_{\mathrm{B}} - z\Big[\ \varepsilon_{\mathrm{AA}} - \varepsilon_{\mathrm{BA}} \quad \overline{\delta\phi_{\mathrm{A}}} + \ \varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{BB}} \quad \overline{\delta\phi_{\mathrm{B}}}\Big] \tag{131}$$

With the following relation

$$\overline{\delta\phi_{\mathrm{A}}} = -\overline{\delta\phi_{\mathrm{B}}} \tag{132}$$

$$\varepsilon_{\mathrm{AB}} = \varepsilon_{\mathrm{BA}} \tag{133}$$

we can rewrite eq. 131 to be

$$-\frac{1}{\beta}\left(\frac{1}{S_{\mathrm{AA}}^{(0)}} + \frac{1}{S_{\mathrm{BB}}^{(0)}}\right)\overline{\delta\phi_{\mathrm{A}}} = \ u_{\mathrm{A}} - u_{\mathrm{B}} \ - z \ \ \varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}} - 2\varepsilon_{\mathrm{AB}} \ \ \overline{\delta\phi_{\mathrm{A}}} \tag{134}$$

Further rearrangement leads to

$$\overline{\delta\phi_{\mathrm{A}}} = -\beta\left[\frac{1}{S_{\mathrm{AA}}^{(0)}} + \frac{1}{S_{\mathrm{BB}}^{(0)}} - 2\chi\right]^{-1} \ u_{\mathrm{A}} - u_{\mathrm{B}} \tag{135}$$

where χ is the Flory-Huggins interaction parameter which is defined as

$$\chi = \frac{z}{k_B T}\left(\frac{\varepsilon_{\mathrm{AA}} + \varepsilon_{\mathrm{BB}}}{2} - \varepsilon_{\mathrm{AB}}\right) \tag{136}$$

From eq. 107 and eq. 135 the Fourier transform of the concentration fluctuations is given as follows:

$$\frac{1}{S(\mathbf{q})} = \frac{1}{S_{\mathrm{AA}}^{(0)}(\mathbf{q})} + \frac{1}{S_{\mathrm{BB}}^{(0)}(\mathbf{q})} - 2\chi \tag{137}$$

The above approximation has used the completely random state as a base, and has estimated the effect of interactions through a perturbation calculation. Therefore, this model is not applicable to systems with strong correlation effects, for example a solution near *c** where there are large fluctuations in the concentration. However, the accuracy of this approximation improves as the concentration increases, and it holds quite well for polymer blends.

10. Landau theory and phase transition

See Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p151-188.

11. Variational mean-field theory (For more details, see Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p198-201, p.204-205)

Variational mean-field is a mean-field theory valid for all ranges of temperatures for systems with order parameters of essentially arbitrary complexity. This variational method is based upon approximating the total equilibrium density matrix by a product of local site or particle density matrices and if often referred to as Trρlnρ mean-field theory.

Let ϕ be any random variable, which can be either continuous or discrete, and let

$$P(\phi) \geq 0 \tag{138}$$

be its associated probability distribution. Then the expectation value of any function $f(\phi)$ is

$$\left\langle f(\phi) \right\rangle = \mathrm{Tr}\left[P(\phi) f(\phi) \right] \tag{139}$$

where Tr signifies a sum or integral over all possible values of ϕ. The inequality

$$\left\langle e^{-\lambda\phi} \right\rangle \geq e^{-\lambda\left\langle \phi \right\rangle} \tag{140}$$

valid for any probability distribution, may be proved as follows. Consider the following function

$$F(\phi) = e^{\phi} - 1 - \phi \tag{141}$$

Its first-order derivative is

$$F'(\phi) = e^{\phi} - 1 \tag{142}$$

When ϕ=0,

$$F(0) = 0 \tag{143}$$

When ϕ>0,

$$F'(\phi) > 0 \tag{144}$$

i.e. $F(\phi)$ is an increasing function. Thus, $F(\phi)$>0. When ϕ<0,

$$F'(\phi) < 0 \tag{145}$$

i.e. $F(\phi)$ is a decreasing function. Thus, $F(\phi)$>0. In summary, for all ϕ, $F(\phi)$>0. So we have the inequality

$$e^{\phi} \geq 1 + \phi \tag{146}$$

Therefore,

$$\begin{aligned} e^{-\lambda\phi} &= e^{-\lambda\left\langle \phi \right\rangle} e^{-\lambda \;\; \phi - \left\langle \phi \right\rangle} \\ &\geq e^{-\lambda\left\langle \phi \right\rangle} \left[1 - \lambda \;\; \phi - \left\langle \phi \right\rangle \;\; \right] \end{aligned} \tag{147}$$

which, when averaged over $P(\phi)$, implies

$$\begin{aligned} \left\langle e^{-\lambda\phi} \right\rangle &\geq \left\langle e^{-\lambda\left\langle \phi \right\rangle} \left[1 - \lambda \;\; \phi - \left\langle \phi \right\rangle \;\; \right] \right\rangle \\ &= e^{-\lambda\left\langle \phi \right\rangle} \left\langle 1 - \lambda \;\; \phi - \left\langle \phi \right\rangle \;\; \right\rangle \\ &= e^{-\lambda\left\langle \phi \right\rangle} \;\; 1 - \left\langle \lambda\phi \right\rangle + \left\langle \lambda \left\langle \phi \right\rangle \right\rangle \\ &= e^{-\lambda\left\langle \phi \right\rangle} \;\; 1 - \lambda\left\langle \phi \right\rangle + \lambda\left\langle \phi \right\rangle \\ &= e^{-\lambda\left\langle \phi \right\rangle} \end{aligned} \tag{148}$$

which establishes eq. 140.

Now consider a classical Hamiltonian H that is a function of a discrete or continuous classical field ϕ. Let $\rho(\phi)$ be any classical probability distribution satisfying

$$\mathrm{Tr}\rho = 1 \tag{149}$$

and

$$\rho(\phi) \geq 0 \tag{150}$$

The canonical partition function can be written as

$$\begin{aligned} Z &= \mathrm{Tr}\Big[e^{-\beta H[\phi]} \Big] \\ &\equiv \mathrm{Tr}\Big[\rho \frac{1}{\rho} e^{-\beta H[\phi]} \Big] \\ &= \mathrm{Tr}\Big[\rho e^{-\ln\rho} e^{-\beta H[\phi]} \Big] \\ &= \mathrm{Tr}\Big[\rho e^{-\beta H[\phi] - \ln\rho} \Big] \\ &= \Big\langle e^{-\beta H[\phi] - \ln\rho} \Big\rangle_\rho \\ &= e^{-\beta F} \end{aligned} \tag{151}$$

where $< >_\rho$ signifies an average with respect to the density matrix ρ and where F is the free energy (or more precisely the thermodynamic potential) associated with H. Thus, using eq. 151 and the inequality in eq. 140, we obtain

$$\begin{aligned} e^{-\beta F} &= \Big\langle e^{-\beta H[\phi] - \ln\rho} \Big\rangle_\rho \\ &\geq e^{-\beta \langle H \rangle_\rho - \langle \ln\rho \rangle_\rho} \end{aligned} \tag{152}$$

or

$$\begin{aligned} F &\leq F_\rho \\ &= \big\langle H \big\rangle_\rho + k_B T \big\langle \ln\rho \big\rangle_\rho \\ &= \mathrm{Tr}\big[\rho H \big] + k_B T \mathrm{Tr}\big[\rho \ln\rho \big] \end{aligned} \tag{153}$$

where F_ρ is an approximating free energy associated with the density matrix ρ. is a minimum with respect to variations in r subject to the constraint

$$\mathrm{Tr}\rho = 1 \tag{154}$$

when

$$\rho = \frac{1}{Z} e^{-\beta H} \tag{155}$$

is the actual equilibrium density matrix. This can be seen from the equation

$$\frac{\delta F_\rho}{\delta \rho} = H + k_B T(\ln\rho + 1) = \varsigma \tag{156}$$

where ζ is a Lagrange multiplier whose value is chosen to impose the constraint eq. 154. Thus, at its minimum with respect to ρ is the actual free energy F.

* Equilibrium state: the system has a free energy that corresponds to the maximum number of possible configurations. Note that each configuration has the same probability to appear. To simply understand this, use a two dices experiment as an example. Sum of the points of these two dices ⇔ free energy. A certain combination of two points on these two dices ⇔ configuration. The equilibrium state ⇔ when the sum = 7: it has six configurations {1,6}{6,1}{2,5}{5,2}{3,4}{4,3}.

The mean-field approximation. The inequality, Eq. 153, provides the basis for variational approximations to the free energy that can be implemented as follows: a functional form with free unspecified parameters is chosen for a trial density matrix ρ to approximate the actual density matrix. The trial density matrix with the chosen functional form that best approximates the actual density matrix is obtained by minimizing the approximate free energy F_ρ with respect to the free parameters in ρ. Mean-field theory is obtained by a trial density matrix that is a product of independent single matrices. If ρ_α is the single particle density matrix depending only on the degree of freedom of particle α, the mean-field density matrix is

$$\rho = \prod_\alpha \rho_\alpha \tag{157}$$

and the variational mean-field free energy is

$$F_\rho = \left\langle H \right\rangle_\rho + k_B T \sum_\alpha \mathrm{Tr}\left[\rho_\alpha \ln \rho_\alpha\right] \tag{158}$$

The precise form of $<H>_\rho$ will, of course, depend on H. The second term in eq. 158 is obtained as follows:

$$\begin{aligned}
\left\langle \ln \rho \right\rangle_\rho &= \mathrm{Tr}\left[\rho \ln \rho\right] \\
&= \mathrm{Tr}\left[\prod_\alpha \rho_\alpha \ln \prod_\beta \rho_\beta\right] \\
&= \mathrm{Tr}\left[\prod_\alpha \rho_\alpha \sum_\beta \ln \rho_\beta\right] \\
&= \mathrm{Tr}\left[\ \rho_1\rho_2\rho_3\cdots \quad \ln\rho_1 + \ln\rho_2 + \ln\rho_3 + \cdots\ \right] \\
&= \mathrm{Tr}\left[\ \rho_1\rho_2\rho_3\cdots\ \ln\rho_1 +\ \rho_1\rho_2\rho_3\cdots\ \ln\rho_2 +\ \rho_1\rho_2\rho_3\cdots\ \ln\rho_3 + \cdots\right] \\
&= \mathrm{Tr}\left[\ \rho_2\rho_3\cdots\ \rho_1 \ln\rho_1\right] \\
&\quad + \mathrm{Tr}\left[\ \rho_1\rho_3\cdots\ \rho_2 \ln\rho_2\right] \\
&\quad + \mathrm{Tr}\left[\ \rho_1\rho_2\rho_4\cdots\ \rho_3 \ln\rho_3\right] + \cdots \\
&= \mathrm{Tr}\left[\rho_1 \ln\rho_1\right] + \mathrm{Tr}\left[\rho_2 \ln\rho_2\right] + \mathrm{Tr}\left[\rho_3 \ln\rho_3\right] + \cdots \\
&= \sum_\alpha \mathrm{Tr}\left[\rho_\alpha \ln \rho_\alpha\right]
\end{aligned} \tag{159}$$

We can connect the single particle density matrix with density operator by

$$\mathrm{Tr}\left[\phi_\alpha \rho_\alpha\right] = \left\langle \phi_\alpha \right\rangle \tag{160}$$

Example: derivation of Flory-Huggins theory for mixture of small molecules A and B. In the mixture, there are N_A molecules A and N_B molecules B. Let $x_A{}^\alpha$ denote the positions of components A and $x_B{}^\beta$ denote the positions of components B, where α and β are indexes varies from 0 to N_A-1 and 0 to N_B-1, respectively. The density operators are

$$n_\sigma(\mathbf{x}) = \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\sigma^\alpha) \tag{161}$$

where σ runs over A and B. With the mean-field density matrix is

$$\rho = \prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \prod_\beta \rho_\mathrm{B}(\mathbf{x}_\mathrm{B}^\beta) \tag{162}$$

the average number density of molecules A can be calculated according to eq. 160:

$$\begin{aligned}
\left\langle n_\mathrm{A}(\mathbf{x}) \right\rangle &= \left\langle \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^\alpha) \right\rangle \\
&= \mathrm{Tr}\left[\rho \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^\alpha) \right] \\
&= \mathrm{Tr}\left[\prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \prod_\beta \rho_\mathrm{B}(\mathbf{x}_\mathrm{B}^\beta) \sum_{\alpha'} \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \mathrm{Tr}\left[\prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \prod_\beta \rho_\mathrm{B}(\mathbf{x}_\mathrm{B}^\beta) \sum_{\alpha'} \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \mathrm{Tr}\left[\prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \sum_{\alpha'} \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \mathrm{Tr}\left[\prod_\beta \rho_\mathrm{B}(\mathbf{x}_\mathrm{B}^\beta) \right] \\
&= \mathrm{Tr}\left[\prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \sum_{\alpha'} \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \mathrm{Tr}\left[\sum_{\alpha'} \prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \sum_{\alpha'} \mathrm{Tr}\left[\prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \sum_{\alpha'} \mathrm{Tr}\left[\prod_\alpha \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \sum_{\alpha'} \mathrm{Tr}\left[\prod_{\alpha \neq \alpha'} \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^\alpha) \right] \mathrm{Tr}\left[\rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^{\alpha'}) \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \sum_{\alpha'} \mathrm{Tr}\left[\rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^{\alpha'}) \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \right] \\
&= \sum_{\alpha'} \int d^3 x_\mathrm{A}^{\alpha'} \rho_\mathrm{A}(\mathbf{x}_\mathrm{A}^{\alpha'}) \delta(\mathbf{x} - \mathbf{x}_\mathrm{A}^{\alpha'}) \\
&= \sum_{\alpha'} \rho_\mathrm{A}(\mathbf{x}) \\
&= N_\mathrm{A} \rho_\mathrm{A}(\mathbf{x})
\end{aligned} \tag{163}$$

similarly,

$$\left\langle n_\mathrm{B}(\mathbf{x}) \right\rangle = N_\mathrm{B} \rho_\mathrm{B}(\mathbf{x}) \tag{164}$$

The Hamiltonian of this system is

$$H = \frac{1}{2}\sum_{\alpha,\beta}\sum_{\sigma,\sigma'} V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}_{\sigma'}^{\beta}) \tag{165}$$

where V is the molecular interaction between two molecules either of type A or type B. The Hamiltonian can be re-expressed in the term of density operator:

$$H = \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x d^3x' n_{\sigma}(\mathbf{x}) V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') n_{\sigma'}(\mathbf{x}') \tag{166}$$

This can be proved by substituting eq. 161 into eq. 166 as follows:

$$\begin{aligned}
H &= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x d^3x' n_{\sigma}(\mathbf{x}) V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') n_{\sigma'}(\mathbf{x}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x d^3x' \sum_{\alpha} \delta(\mathbf{x} - \mathbf{x}_{\sigma}^{\alpha}) V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') n_{\sigma'}(\mathbf{x}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x' n_{\sigma'}(\mathbf{x}') \int d^3x V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') \sum_{\alpha} \delta(\mathbf{x} - \mathbf{x}_{\sigma}^{\alpha}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x' n_{\sigma'}(\mathbf{x}') \sum_{\alpha} \int d^3x V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') \delta(\mathbf{x} - \mathbf{x}_{\sigma}^{\alpha}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x' n_{\sigma'}(\mathbf{x}') \sum_{\alpha} V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{\alpha}\int d^3x' n_{\sigma'}(\mathbf{x}') V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{\alpha}\int d^3x' \sum_{\beta} \delta(\mathbf{x}' - \mathbf{x}_{\sigma'}^{\beta}) V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{\alpha}\sum_{\beta}\int d^3x' V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}') \delta(\mathbf{x}' - \mathbf{x}_{\sigma'}^{\beta}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{\alpha}\sum_{\beta} V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}_{\sigma'}^{\beta}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{\alpha,\beta} V_{\sigma,\sigma'}(\mathbf{x}_{\sigma}^{\alpha} - \mathbf{x}_{\sigma'}^{\beta})
\end{aligned} \tag{167}$$

Note that in the above derivation, indexes α and β are smart enough that they can run over from 0 to N_A-1 when σ=A, and from 0 to N_B-1 when σ=B. Using the linear property of summation and integral operator in eq. 166, the ensemble average of H respect to ρ is easily obtained as

$$\begin{aligned}
\langle H \rangle &= \left\langle \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x d^3x' n_{\sigma}(\mathbf{x}) V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') n_{\sigma'}(\mathbf{x}') \right\rangle \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3x d^3x' \langle n_{\sigma}(\mathbf{x}) \rangle V_{\sigma,\sigma'}(\mathbf{x} - \mathbf{x}') \langle n_{\sigma'}(\mathbf{x}') \rangle
\end{aligned} \tag{168}$$

The ensemble average of lnρ is calculated as

$$
\begin{aligned}
\left\langle \ln\rho \right\rangle_\rho &= \mathrm{Tr}\left[\rho\ln\rho\right]\\
&= \mathrm{Tr}\left[\prod_\alpha \rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\prod_\beta \rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\beta)\ln\prod_\alpha \rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\prod_\beta \rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\beta)\right]\\
&= \mathrm{Tr}\left\{\prod_\alpha \rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\prod_\beta \rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\beta)\left[\sum_\alpha \ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)+\sum_\beta \ln\rho_{\mathrm{B}}(\mathbf{x}_{B}^\beta)\right]\right\}\\
&= \mathrm{Tr}\left[\prod_\alpha \rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\prod_\beta \rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\beta)\sum_\alpha \ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\right]\\
&\quad +\mathrm{Tr}\left[\prod_\alpha \rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\prod_\beta \rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\beta)\sum_\beta \ln\rho_{\mathrm{B}}(\mathbf{x}_{B}^\beta)\right]\\
&= \sum_\alpha \mathrm{Tr}\left[\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\right]+\sum_\beta \mathrm{Tr}\left[\rho_{\mathrm{B}}(\mathbf{x}_{B}^\beta)\ln\rho_{\mathrm{B}}(\mathbf{x}_{B}^\beta)\right]
\end{aligned}
\tag{169}
$$

The first term in the last line can be further simplified as

$$
\begin{aligned}
&\mathrm{Tr}\left[\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\right]\\
&= \int d^3x_{\mathrm{A}}^\alpha \rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\\
&= \int d^3x_{\mathrm{A}}^\alpha \left[\int d^3x\rho_{\mathrm{A}}(\mathbf{x})\delta(\mathbf{x}_{\mathrm{A}}^\alpha-\mathbf{x})\right]\ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\\
&= \int d^3x\rho_{\mathrm{A}}(\mathbf{x})\int d^3x_{\mathrm{A}}^\alpha \ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\delta(\mathbf{x}_{\mathrm{A}}^\alpha-\mathbf{x})\\
&= \int d^3x\rho_{\mathrm{A}}(\mathbf{x})\int d^3x_{\mathrm{A}}^\alpha \ln\rho_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}}^\alpha)\delta(\mathbf{x}-\mathbf{x}_{\mathrm{A}}^\alpha)\\
&= \int d^3x\rho_{\mathrm{A}}(\mathbf{x})\ln\rho_{\mathrm{A}}(\mathbf{x})
\end{aligned}
\tag{170}
$$

Similarly, the second term in the last line of eq. 169 is

$$
\mathrm{Tr}\left[\rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\alpha)\ln\rho_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}}^\alpha)\right]=\int d^3x\rho_{\mathrm{B}}(\mathbf{x})\ln\rho_{\mathrm{B}}(\mathbf{x})
\tag{171}
$$

Substituting eq. 163, 164, 170 and 171 into 169, we have

$$
\begin{aligned}
\left\langle \ln\rho \right\rangle_\rho &= \sum_\alpha \int d^3x\rho_{\mathrm{A}}(\mathbf{x})\ln\rho_{\mathrm{A}}(\mathbf{x})+\sum_\beta \int d^3x\rho_{\mathrm{B}}(\mathbf{x})\ln\rho_{\mathrm{B}}(\mathbf{x})\\
&= N_{\mathrm{A}}\int d^3x\rho_{\mathrm{A}}(\mathbf{x})\ln\rho_{\mathrm{A}}(\mathbf{x})+N_{\mathrm{B}}\int d^3x\rho_{\mathrm{B}}(\mathbf{x})\ln\rho_{\mathrm{B}}(\mathbf{x})\\
&= \int d^3xN_{\mathrm{A}}\frac{\left\langle n_{\mathrm{A}}(\mathbf{x})\right\rangle}{N_{\mathrm{A}}}\ln\frac{\left\langle n_{\mathrm{A}}(\mathbf{x})\right\rangle}{N_{\mathrm{A}}}+\int d^3xN_{\mathrm{B}}\frac{\left\langle n_{\mathrm{B}}(\mathbf{x})\right\rangle}{N_{\mathrm{B}}}\ln\frac{\left\langle n_{\mathrm{B}}(\mathbf{x})\right\rangle}{N_{\mathrm{B}}}\\
&= \int d^3x\left[\left\langle n_{\mathrm{A}}(\mathbf{x})\right\rangle\ln\frac{\left\langle n_{\mathrm{A}}(\mathbf{x})\right\rangle}{N_{\mathrm{A}}}+\left\langle n_{\mathrm{B}}(\mathbf{x})\right\rangle\frac{\left\langle n_{\mathrm{B}}(\mathbf{x})\right\rangle}{N_{\mathrm{B}}}\right]
\end{aligned}
\tag{172}
$$

Therefore the variational free energy is

$$
\begin{aligned}
F_\rho &= \frac{1}{2}\sum_{\sigma,\sigma'}\int d^3xd^3x'\left\langle n_\sigma(\mathbf{x})\right\rangle V_{\sigma,\sigma'}(\mathbf{x}-\mathbf{x}')\left\langle n_{\sigma'}(\mathbf{x}')\right\rangle\\
&\quad +k_BT\int d^3x\left[\left\langle n_{\mathrm{A}}(\mathbf{x})\right\rangle\ln\frac{\left\langle n_{\mathrm{A}}(\mathbf{x})\right\rangle}{N_{\mathrm{A}}}+\left\langle n_{\mathrm{B}}(\mathbf{x})\right\rangle\frac{\left\langle n_{\mathrm{B}}(\mathbf{x})\right\rangle}{N_{\mathrm{B}}}\right]
\end{aligned}
\tag{173}
$$

A similar example about derivation of Debye-Hückel theory for plasma is demonstrated in the book: Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p198-201, p.204-205.

12. Perturbation theory

Here we take the simplest Landau free energy as an example. The local free energy density is

$$f = \frac{1}{2} r\phi^2 + u\phi^4 \tag{174}$$

and the gradient energy is

$$\frac{c}{2}\ \nabla\phi\ ^2 \tag{175}$$

Thus the Hamiltonian is

$$H\left[\phi\right] = \int d^3x \left[\frac{1}{2} r\phi^2 + \frac{c}{2}\ \nabla\phi\ ^2 + u\phi^4\right] \tag{176}$$

The partition function is

$$Z = \int D\phi e^{-\beta H\left[\phi\right]} \tag{177}$$

To calculate Z, we first calculate Z_0 which can be explicitly integrated:

$$Z_0 = \int D\phi e^{-\beta H_0} \tag{178}$$

with H_0 being

$$H_0 = \int d^3x \left[\frac{1}{2} r\phi^2 + \frac{c}{2}\ \nabla\phi\ ^2\right] \tag{179}$$

Then rewrite eq. 177 to be

$$\begin{aligned} Z &= \frac{Z_0}{Z_0}\int D\phi e^{-\beta H_0 - \beta V} \\ &= Z_0 \frac{\int D\phi e^{-\beta V} e^{-\beta H_0}}{\int D\phi e^{-\beta H_0}} \\ &= Z_0 \left\langle e^{-\beta V}\right\rangle \end{aligned} \tag{180}$$

If βV<<1, we have

$$\begin{aligned} \left\langle e^{-\beta V}\right\rangle &= \left\langle 1 - \beta V + \frac{1}{2}\beta^2 V^2 + \cdots\right\rangle \\ &= 1 - \beta\left\langle V\right\rangle + \cdots \end{aligned} \tag{181}$$

Here V is

$$V\left[\phi\right] = \int d^3x\ \ u\phi^4 \tag{182}$$

and

$$\left\langle V\right\rangle = \left\langle \phi\phi\phi\phi\right\rangle \tag{183}$$

The generating function:

$$
\begin{aligned}
Z[J] &= \int D\phi e^{-\beta H_0 - \int d^3x J(x)\phi(x)} \\
&= Z_0 e^{-\frac{1}{2} J G^{(0)} J}
\end{aligned}
\tag{184}
$$

The cumulant expansion. The free energy in SCFT is

$$
F[\phi, w] = \frac{\rho_0 R_g^3}{N}\left\{\int d^3r\left[\chi N \phi_{\mathrm{A}}\phi_{\mathrm{B}} - \sum_\alpha \phi_\alpha w_\alpha\right] - V \ln Q_c[w_\alpha]\right\}
\tag{185}
$$

$$
Q_c[w_\alpha] = \frac{1}{V}\int D\mathbf{R} P_0[\mathbf{R}(s)] e^{-\sum_\alpha \int d^3x H_\alpha[\mathbf{R}_\alpha(s)]}
\tag{186}
$$

Perturbation expansion:

$$
w_\alpha = w_\alpha^{(0)} + \delta w_\alpha
\tag{187}
$$

$$
\begin{aligned}
Q_c &= Q_c^{(0)} + Q_c^{(1)} + Q_c^{(2)} + \cdots \\
&= Q_c^{(0)} + \frac{1}{V}\sum_{n=1}^{\infty}\sum_{\alpha_1,\alpha_2,\alpha_3\cdots}(-1)^n \int d^3r_1 \cdots d^3r_n C^{(n)}_{\alpha_1,\alpha_2,\alpha_3\cdots}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n)\delta w_{\alpha_1}\delta w_{\alpha_2}\cdots\delta w_{\alpha_n}
\end{aligned}
\tag{188}
$$

or

$$
\begin{aligned}
V \ln Q_c &= V \ln Q_c^{(0)} \\
&\quad + \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\sum_{\alpha_1,\alpha_2,\alpha_3\cdots}\int d^3r_1 \cdots d^3r_n C^{(n)}_{\alpha_1,\alpha_2,\alpha_3\cdots}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n)\delta w_{\alpha_1}\delta w_{\alpha_2}\cdots\delta w_{\alpha_n}
\end{aligned}
\tag{189}
$$

13. Weak segregation theory and strong segregation theory

The density field and its conjugated potential field is divided into two parts, the average and the deviation:

$$
\phi = \phi^{(0)} + \delta\phi
\tag{190}
$$

$$
w = w^{(0)} + \delta w
\tag{191}
$$

Weak segregation theory (WST). The average value of ϕ and w are chosen to be

$$
\phi_\alpha^{(0)} = f_\alpha
\tag{192}
$$

$$
w_\alpha^{(0)} = 0
\tag{193}
$$

In this case,

$$
Q_\alpha \ \ \mathbf{r}, s \mid \mathbf{r}
\tag{194}
$$

can be integrated to obtain $F^{(0)}$:

$$F^{(0)} = f(1-f)\chi N \tag{195}$$

The free energy is

$$\begin{aligned} \frac{N}{\rho_0 R_g^3 V} F &= F^{(0)} + F^{(1)} + F^{(2)} + \cdots \\ &= f(1-f)\chi N \\ &+ \frac{1}{V}\int d^3 r \left[\chi N \delta\phi_\mathrm{A} \delta\phi_\mathrm{B} - \sum_\alpha \phi_\alpha \delta w_\alpha \right] \\ &- \frac{1}{2V}\sum_{\alpha,\beta}\int d^3 r d^3 r' C_{\alpha,\beta} \quad \mathbf{r},\mathbf{r}' \quad \delta w_\alpha(\mathbf{r}) \delta w_\beta(\mathbf{r}') \\ &+ \cdots \end{aligned} \tag{196}$$

where $F^{(1)}$=0 is applied to the second line. In above expression, only first two order terms are shown. The WST should expand F to the 4th-order:

$$\frac{N}{\rho_0 R_g^3 V} F = F^{(0)} + F^{(1)} + F^{(2)} + F^{(3)} + F^{(4)} + \cdots \tag{197}$$

Using variation to eliminate *w* in eq. 196:

$$\frac{\delta F}{\delta w_\alpha} = 0 \tag{198}$$

which leads to a set of equations

$$-\delta\phi_\alpha - C_{\alpha\beta}\delta w_\beta - C_{\alpha\cdots}\delta w_{\cdots} - \cdots = 0 \tag{199}$$

Solving above equation to obtain δw:

$$\delta w_\beta = \frac{-1}{C_{\alpha\beta}} \delta\phi_\alpha + \cdots \tag{200}$$

Retaining only the first term of eq.200 leads to RPA, while retaining more terms leads to Leibler theory.

Strong segregation theory. In strong segregation limit, the interface between two phases is clear. The free energy can be divided into two parts: bulk and interface. The interfacial free energy is proportional to the interfacial area *A*:

$$\frac{F_\mathrm{in}}{k_B T} = \rho_0 A \sqrt{\frac{\chi}{6}} \tag{201}$$

The interfacial area is inverse proportional to the phase size:

$$A \propto \frac{1}{d} \tag{202}$$

SST has a clear physical picture. However, it cannot explain:

(1) $N \to \infty$

(2) The joint can move around at the interface, which introduce extra entropy.

14. Saddle point approximation (For more details, see Fredrickson, The Equilibrium Theory of Inhomogeneous Polymers, 2006, p203-205; Chaikin and Lubensky, *Principles of Condensed Matter Physics*, 1995, p198-201, p200-201.)

The partition function can be approximated by the maximum term in the integral

$$\begin{aligned} Z &= \int D\phi e^{-\beta H[\phi]} \\ &\approx e^{-\beta H[\phi^*]} \end{aligned} \tag{203}$$

where ϕ^* is determined by solving the following variation equation

$$\frac{\delta H}{\delta \phi}\Big|_{\phi=\phi^*} = 0 \tag{204}$$

It seems that the saddle point approximation can be viewed as one of approaches to determine variational minima to eq. 153 in section 11. First, we choose a parametrization of ρ in terms of the order parameter $<\phi>$ of a phase transition. This parametrization must satisfy the constraints:

$$\mathrm{Tr}\rho = 1 \tag{205}$$

and

$$\mathrm{Tr}\ \ \rho\phi\ \ = \langle \phi \rangle \tag{206}$$

The variational parameter is simply the order parameter $<\phi>$. If there is no external field in H coupling linearly to ϕ, then F_ρ is simply the Helmholtz free energy $F(<\phi>)$. Then eq. 156 turns to be the form of eq. 191.