0.1 配分函数

考虑三维自由空间中的n条由N段聚合物片段组成的聚合物系统。假定n条聚合物链都有相似的结构，即由连续的n_A段A型聚合物和n_B段B型聚合物组成。有体系不可压缩，既有体积$V = nN/\rho$，且有$f = n_A/N = f_A$，$f_B = n_B/N$。尝试写出系统正则系综下的配分函数：

$$Z = \int \mathcal{D}[\boldsymbol{R}(\boldsymbol{s})] \exp\left[-\beta(\mathcal{H}_0 + \mathcal{H}_e)\right] \times \delta\left[\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r}) - 1\right] \tag{1}$$

其中$\mathcal{H}_0$表示聚合物的键连哈密顿量，$\mathcal{H}_e$则表示非键连相互作用引起的哈密顿量变化，$\delta\left[\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r}) - 1\right]$为系统不可压缩条件，$\beta = 1/kT$。特别地，体系配分函数在形式上与单类型片段聚合物链并无差别，具体差异在于如何求解$\mathcal{H}_0$和$\mathcal{H}_e$。按照高斯链的一般形式，可得：

$$\frac{\mathcal{H}_0}{k_B T} = \frac{3}{2b^2} \sum_{i=1}^{n} \int_0^N \mathrm{d}s \left[\frac{\mathrm{d}\mathbf{R}_i(s)}{\mathrm{d}s}\right]^2 \tag{2}$$

$$\frac{\mathcal{H}_E}{k_B T} = \chi \rho_0 \int \mathrm{d}\mathbf{r}\, \hat{\phi}_A(\mathbf{r}) \hat{\phi}_B(\mathbf{r}) \tag{3}$$

其中$\alpha = A, B$表示A、B两种聚合物片段类型，且有密度算符定义为：

$$\rho_0 \hat{\phi}_\alpha(\mathbf{r}) \equiv \sum_{i=1}^{n} \int_0^{Nf_\alpha} \mathrm{d}s \delta\left[\mathbf{r} - \mathbf{R}_i(s)\right] \tag{4}$$

一般地，由δ函数的傅里叶变换，有恒等式：

$$\begin{aligned} \delta\left[\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r}) - 1\right] &= \delta\left[1 - (\hat{\phi}_A(\mathbf{r}) + \hat{\phi}_B(\mathbf{r}))\right] \\ &= \frac{1}{(2\pi)^V} \int^{(V)} \mathcal{D}[\xi] \mathrm{e}^{i\xi[1-(\hat{\phi}_A(\mathbf{r})+\hat{\phi}_B(\mathbf{r}))]} \end{aligned} \tag{5}$$

$$\begin{aligned} 1 &= c_\alpha^{-1} \int \mathcal{D}[\phi_\alpha] \delta(\phi_\alpha - \widehat{\phi}_\alpha) \\ &= c_\alpha^{-1} \int \mathcal{D}[\phi_\alpha] \frac{1}{(2\pi)^V} \int^{(V)} \mathcal{D}[\omega_\alpha] \mathrm{e}^{i\omega_\alpha(\phi_\alpha - \widehat{\phi}_\alpha)} \end{aligned} \tag{6}$$

其中c_α表示对应α组分在系统中的占比，已经由公式(5)引入了限制条件，作为常系数在以下推导中省略。下面在配分函数(1)中继续引入恒等式(5)进行场论推导，既有：

$$
\begin{aligned}
Z =& \int \mathcal{D}[\boldsymbol{R(s)}]\exp\left[-\beta(\mathcal{H}_0+\mathcal{H}_e)\right] \times \delta\left[\hat{\phi}_A(\mathbf{r})+\hat{\phi}_B(\mathbf{r})-1\right] \\
=& \int \mathcal{D}[\boldsymbol{R(s)}] \iint \frac{\mathcal{D}[\phi_A]\mathcal{D}[\phi_B]}{(2\pi)^{2V}} \\
& \int \mathcal{D}[\omega_A]\exp[i\omega_A((\phi_A-\widehat{\phi}_A))] \int \mathcal{D}[\omega_B]\exp[i\omega_B((\phi_B-\widehat{\phi}_B))] \\
& \times \frac{1}{(2\pi)^V}\int^{(V)} \mathcal{D}[\xi]\mathrm{e}^{i\xi[1-(\hat{\phi}_A(\mathbf{r})+\hat{\phi}_B(\mathbf{r}))]} \\
=& \int \mathcal{D}[\boldsymbol{R(s)}] \iint \frac{\mathcal{D}[\phi_A]\mathcal{D}[\phi_B]}{(2\pi)^{2V}} \\
& \int \mathcal{D}[\omega_A]\exp[i\omega_A((\phi_A-\widehat{\phi}_A))] \int \mathcal{D}[\omega_B]\exp[i\omega_B((\phi_B-\widehat{\phi}_B))] \\
& \times \frac{1}{(2\pi)^{NV}}\int^{(V)} \mathcal{D}[\xi]\exp\{\int \mathrm{d}r\, i\xi[1-(\hat{\phi}_A(\mathbf{r})+\hat{\phi}_B(\mathbf{r}))]\}
\end{aligned}
\tag{7}
$$

一般地，有$exp\{\int dr\, i\xi[1-(\hat{\phi}_A(\mathbf{r})+\hat{\phi}_B(\mathbf{r}))]\}$作为附加密度场的限制条件，$\xi$场在计算时用来控制系统的精准程度，因此为推导方便，关于ξ场的部分可以作为常数项，即可单位化为1。从而进一步推导配分函数为（交换积分次序，Z_0和分母系数等不受泛函积分影响的项重写入泛函中）：

$$
\begin{aligned}
Z =& \int \mathcal{D}[\phi_A,\phi_B]\mathrm{e}^{-\beta\mathcal{H}^E} \int \frac{\mathcal{D}[\omega_A,\omega_B]}{(2\pi)^{(N+2)V}}\mathrm{e}^{\{i(\omega_A\phi_A+\omega_B\phi_B)\}} \int \mathcal{D}[\boldsymbol{R}(s)]\mathrm{e}^{-\beta\mathcal{H}^0}\mathrm{e}^{-i(\omega_A\hat{\phi}_A+\omega_B\hat{\phi}_B)} \\
=& \int \mathcal{D}[\phi_A,\phi_B]\mathrm{e}^{-\beta\mathcal{H}^E} \int \frac{\mathcal{D}[\omega_A,\omega_B]}{(2\pi)^{(N+2)V}}\mathrm{e}^{\{i(\omega_A\phi_A+\omega_B\phi_B)\}} Q Z_0 \\
=& \frac{Z_0}{(2\pi)^{(N+2)V}} \int \mathcal{D}[\phi_A,\omega_A,\phi_B,\omega_B]\mathrm{e}^{-\mathcal{F}[\phi_A,\omega_A,\phi_B,\omega_B]} \\
=& \int \mathcal{D}[\phi_A,\omega_A,\phi_B,\omega_B]\mathrm{e}^{-\mathcal{F}[\phi_A,\omega_A,\phi_B,\omega_B]}
\end{aligned}
\tag{8}
$$

其中有单链组成系统的的配分函数定义为（$\alpha = A, B$）：

$$Q \equiv Z_0^{-1} \int \mathcal{D}\left\{\mathbf{R}(s)\right\} \exp\left\{\int \mathrm{d}s \left[\frac{\mathrm{d}\mathbf{R}(s)}{\mathrm{d}s}\right]^2 - \sum_{\alpha} \int \mathrm{d}s\, \omega_\alpha \left[\mathbf{R}(s)\right]\right\} \tag{9}$$

$$Z_0 = \int \mathcal{D}\left\{\mathbf{R}(s)\right\} \exp\left\{\int \mathrm{d}s \left[\frac{\mathrm{d}\mathbf{R}(s)}{\mathrm{d}s}\right]^2\right\} \tag{10}$$

而自由能：

$$\begin{aligned}\mathcal{F}[\phi_A, \omega_A, \phi_B, \omega_B] =& \beta\mathcal{H}^E - i(\omega_A\phi_A + \omega_B\phi_B) - \ln Q \\ =& \chi\rho_0 \int \mathrm{d}\boldsymbol{r} \hat{\phi}_A(\mathbf{r})\hat{\phi}_B(\mathbf{r}) - i\int \mathrm{d}\boldsymbol{r}[\omega_A(\boldsymbol{r})\phi_A(\boldsymbol{r}) + \omega_B(\boldsymbol{r})\phi_B(\boldsymbol{r})] - \ln Q \\ =& \chi\rho_0 \int \mathrm{d}\boldsymbol{r} \phi_A(\mathbf{r})\phi_B(\mathbf{r}) - i\int \mathrm{d}\boldsymbol{r}[\omega_A(\boldsymbol{r})\phi_A(\boldsymbol{r}) + \omega_B(\boldsymbol{r})\phi_B(\boldsymbol{r})] - \ln Q\end{aligned} \tag{11}$$

其中由于δ函数的限制作用可认为$\hat{\phi}_\alpha = \phi_\alpha$。

0.2 自洽场求解

根据定义有单链的配分函数为：

$$\begin{aligned}Q^0 =& Z_0^{-1} \exp\left\{\int \mathrm{d}s \left[\frac{\mathrm{d}\mathbf{R}(s)}{\mathrm{d}s}\right]^2 - \sum_{\alpha} \int \mathrm{d}s\, \omega_\alpha \left[\mathbf{R}(s)\right]\right\} \\ \equiv& \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, N-s; [w]) \exp[w_A(\mathbf{r})] \exp[w_B(\mathbf{r})] q(\mathbf{r}, s; [w])\end{aligned} \tag{12}$$

其中考虑q的计算时需要区分A、B链，同时有：

$$\begin{aligned}\frac{\mathcal{F}[\phi_A, \omega_A, \phi_B, \omega_B]}{N\rho_0} =& \chi N \int \mathrm{d}\mathrm{r}\, \phi_A(\mathbf{r})\phi_B(\mathbf{r}) - i\int d\boldsymbol{r}[\omega_A(\boldsymbol{r})\phi_A(\boldsymbol{r}) + \omega_B(\boldsymbol{r})\phi_B(\boldsymbol{r})] \\ & - \ln Q^0\end{aligned} \tag{13}$$

根据自由能公式(11)即可求解自洽场方程,从而得到平均场$\{\omega_\alpha^*, \phi_\alpha^*\}$，即满足以下条件：

$$\left.\frac{\delta\mathcal{F}}{\delta\omega_\alpha}\right|_{\omega_\alpha = \omega_\alpha^*, \phi_\alpha = \phi_\alpha^*} = \left.\frac{\delta\mathcal{F}}{\delta\phi_\alpha}\right|_{\omega_\alpha = \omega_\alpha^*, \phi_\alpha = \phi_\alpha^*} = 0 \tag{14}$$

则有对其在平均场$\{\omega_\alpha^*, \phi_\alpha^*\}$附近展开有：

$$\frac{\delta \mathcal{F}}{\delta i\omega_A} = \phi_A^* - \frac{N}{Q^0[i\omega_A^*]}\frac{\delta Q^0}{\delta i\omega_A} = \phi_A^* - \frac{N}{Q^0[i\omega_A^*]}\exp\left[i\omega_A^*(\mathbf{r})\right]\int \mathrm{d}s\ \exp\left[i\omega_B^*(\mathbf{r})\right]q(\boldsymbol{r},s)q(\boldsymbol{r},N-s) \tag{15}$$

$$\frac{\delta \mathcal{F}}{\delta i\omega_B} = \phi_B^* - \frac{N}{Q^0[i\omega_B^*]}\frac{\delta Q^0}{\delta i\omega_B} = \phi_B^* - \frac{N}{Q^0[i\omega_B^*]}\exp\left[i\omega_B^*(\mathbf{r})\right]\int \mathrm{d}s\ \exp\left[i\omega_A^*(\mathbf{r})\right]q(\boldsymbol{r},s)q(\boldsymbol{r},N-s) \tag{16}$$

$$\frac{\delta \mathcal{F}}{\delta \phi_A} = i\omega_A^* + \chi\rho_0\phi_B^* \tag{17}$$

$$\frac{\delta \mathcal{F}}{\delta \phi_B} = i\omega_B^* + \chi\rho_0\phi_A^* \tag{18}$$

即可得到以下解：

$$\phi_A^* = \frac{N}{Q^0[i\omega_A^*]}\exp\left[i\omega_A^*(\mathbf{r})\right]\int \mathrm{d}s\ \exp\left[i\omega_B^*(\mathbf{r})\right]q(\boldsymbol{r},s)q(\boldsymbol{r},N-s) \tag{19}$$

$$\phi_B^* = \frac{N}{Q^0[i\omega_B^*]}\exp\left[i\omega_B^*(\mathbf{r})\right]\int \mathrm{d}s\ \exp\left[i\omega_A^*(\mathbf{r})\right]q(\boldsymbol{r},s)q(\boldsymbol{r},N-s) \tag{20}$$

$$i\omega_A^* = -\chi\rho_0\phi_B^* \tag{21}$$

$$i\omega_B^* = -\chi\rho_0\phi_A^* \tag{22}$$

0.3 高斯涨落

为研究系统的相分离性质，还需要考虑系统在平均场附近的涨落，即引入：

$$\phi_\alpha(\mathbf{r}) = \phi_\alpha^* + \delta\phi_\alpha(\mathbf{r}) \tag{23}$$

$$\omega_\alpha(\mathbf{r}) = \omega_\alpha^* + \delta\omega_\alpha(\mathbf{r}) \tag{24}$$

则有自由能$\mathcal{F}$可在平均场附近展开为：$\mathcal{F} \approx \mathcal{F}^* + \mathcal{F}^{(1)} + \mathcal{F}^{(2)}$。而由于平均场的稳定性要求，需要满足$\mathcal{F}^{(1)} = 0$。而剩余项中有$\mathcal{F}^*$表示平均场自由能，$\mathcal{F}^{(2)}$则表示由高

斯涨落引起的自由能变化。其形式上可写为（可令$i\omega=\omega$）：

$$
\begin{aligned}
\frac{\mathcal{F}^{(2)}}{N\rho_0} = \int \mathrm{d}\mathbf{r}\left[\chi N \delta\phi_A(\mathbf{r})\delta\phi_B(\mathbf{r}) - \sum_\alpha \delta\omega_\alpha(\mathbf{r})\delta\phi_\alpha(\mathbf{r})\right] \\
- \frac{1}{2}\sum_{\alpha,\beta}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' C_{\alpha,\beta}\left(\mathbf{r},\mathbf{r}'\right)\delta\omega_\alpha(\mathbf{r})\delta\omega_\beta\left(\mathbf{r}'\right)
\end{aligned}
\tag{25}
$$

其中最后一项来自于公式(23)和(24)对单链配分函数Q^0的影响。

可定义链内关联函数为：

$$
C_{\alpha\beta}\left(\mathbf{r},\mathbf{r}'\right) \equiv \frac{\delta^2 \ln Q^0}{\delta\omega_\alpha\delta\omega_\beta} \tag{26}
$$

并定义$\delta\phi(\mathbf{r}) \equiv \delta\phi_A(\mathbf{r}) - \delta\phi_B(\mathbf{r})$和$\delta\mu_\pm(\mathbf{r}) \equiv \left[\delta\omega_A(\mathbf{r}) \pm \delta\omega_B(\mathbf{r})\right]/2$以使关联函数正交化。即可得到：

$$
\begin{aligned}
\frac{\mathcal{F}^{(2)}}{N\rho_0} =& \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\left\{\frac{\chi N}{2}\delta\phi(\mathbf{r})\delta\phi\left(\mathbf{r}'\right)\delta\left(\mathbf{r}-\mathbf{r}'\right)\right. \\
& - 2\delta\mu_-(\mathbf{r})\delta\phi\left(\mathbf{r}'\right)\delta\left(\mathbf{r}-\mathbf{r}'\right) \\
& - C\left(\mathbf{r},\mathbf{r}'\right)\delta\mu_-(\mathbf{r})\delta\mu_-\left(\mathbf{r}'\right) - \Sigma\left(\mathbf{r},\mathbf{r}'\right)\delta\mu_+(\mathbf{r})\delta\mu_+\left(\mathbf{r}'\right) \\
& \left. -\Delta\left(\mathbf{r},\mathbf{r}'\right)\left[\delta\mu_-(\mathbf{r})\delta\mu_+\left(\mathbf{r}'\right) + \delta\mu_+(\mathbf{r})\delta\mu_-\left(\mathbf{r}'\right)\right]\right\}
\end{aligned}
\tag{27}
$$

其中使用的符号有：

$$
\begin{aligned}
& C\left(\mathbf{r},\mathbf{r}'\right) \equiv C_{AA}\left(\mathbf{r},\mathbf{r}'\right) - 2C_{AB}\left(\mathbf{r},\mathbf{r}'\right) + C_{BB}\left(\mathbf{r},\mathbf{r}'\right) \\
& \Delta\left(\mathbf{r},\mathbf{r}'\right) \equiv C_{AA}\left(\mathbf{r},\mathbf{r}'\right) - C_{BB}\left(\mathbf{r},\mathbf{r}'\right) \\
& \Sigma\left(\mathbf{r},\mathbf{r}'\right) \equiv C_{AA}\left(\mathbf{r},\mathbf{r}'\right) + 2C_{AB}\left(\mathbf{r},\mathbf{r}'\right) + C_{BB}\left(\mathbf{r},\mathbf{r}'\right)
\end{aligned}
\tag{28}
$$

附：有上式拆分的逆过程：

$$
\phi(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\phi(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') \tag{29}
$$

$$
4\delta\mu_-(\mathbf{r})\delta\mu_-\left(\mathbf{r}'\right) = \delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') - \delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') - \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}') \tag{30}
$$

$$
4\delta\mu_+(\mathbf{r})\delta\mu_+\left(\mathbf{r}'\right) = \delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}') \tag{31}
$$

$$
\begin{aligned}
&4\delta\mu_-(\mathbf{r})\delta\mu_+(\mathbf{r}') + 4\delta\mu_+(\mathbf{r})\delta\mu_-(\mathbf{r}') \\
&= \delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') - \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}') - \delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}') \\
&\quad + \delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') - \delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}') - \delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}') \\
&= 2\delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') - 2\delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}')
\end{aligned} \tag{32}
$$

$$
\begin{aligned}
&C(\mathbf{r},\mathbf{r}')\,\delta\mu_-(\mathbf{r})\delta\mu_-(\mathbf{r}') + \Sigma(\mathbf{r},\mathbf{r}')\,\delta\mu_+(\mathbf{r})\delta\mu_+(\mathbf{r}') + \Delta(\mathbf{r},\mathbf{r}')\,[\delta\mu_-(\mathbf{r})\delta\mu_+(\mathbf{r}') + \delta\mu_+(\mathbf{r})\delta\mu_-(\mathbf{r}')] \\
&= \frac{1}{4}(C_{AA} - 2C_{AB} + C_{BB}) \times [\delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') - \delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') - \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}')] \\
&\quad + \frac{1}{4}(C_{AA} + 2C_{AB} + C_{BB}) \times [\delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}')] \\
&\quad + \frac{1}{4}(C_{AA} - C_{BB}) \times [2\delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') - 2\delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}')] \\
&= C_{AA}\delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') + C_{BB}\delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}') + C_{AB}[\delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') + \delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}')] \\
&= C_{AA}\delta\omega_A(\mathbf{r})\delta\omega_A(\mathbf{r}') + C_{BB}\delta\omega_B(\mathbf{r})\delta\omega_B(\mathbf{r}') + C_{AB}\delta\omega_A(\mathbf{r})\delta\omega_B(\mathbf{r}') + C_{BA}\delta\omega_B(\mathbf{r})\delta\omega_A(\mathbf{r}')
\end{aligned} \tag{33}
$$

对于二嵌段聚合物，有对关联函数为：

$$C_{AA}(x) = g_D(x) \tag{34}$$

$$C_{BB}(x) = g_D(x) \tag{35}$$

$$C_{AB}(x) = C_{BA}(x) = F(x) \tag{36}$$

其中有：

$$g_D(x) = \frac{2}{x^2}[\mathrm{e}^{-x} - 1 + x] \tag{37}$$

$$F(x) = \frac{1}{x^2}[\mathrm{e}^{-2x} - 2\mathrm{e}^{-x} + 1] \tag{38}$$

即可以重写配分函数为：

$$\mathcal{Z} \approx \exp\left(-\mathcal{F}^*\right) \int \mathcal{D}\left\{\delta\mu_\pm, \delta\phi\right\} \exp\left\{-\mathcal{F}^{(2)}\left[\delta\phi, \delta\mu_\pm\right]\right\} \tag{39}$$

其中高斯涨落自由能可用RPA关联函数表示为（定义有$\tilde{C} \equiv C - \Delta \cdot \Sigma^{-1} \cdot \Delta$）：

$$\frac{\mathcal{F}^{(2)}}{N\rho_0} = \frac{1}{2} \int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \delta\phi(\mathbf{r}) C_{RPA}^{-1}\left(\mathbf{r}, \mathbf{r}'\right) \delta\phi\left(\mathbf{r}'\right) \tag{40}$$

$$C_{RPA}^{-1}\left(\mathbf{r}, \mathbf{r}'\right) \equiv \left[\tilde{C}^{-1} - \frac{\chi N}{2} I\right]\left(\mathbf{r}, \mathbf{r}'\right) = \left[\frac{C_{AA} + 2C_{AB} + C_{BB}}{4C_{AA}C_{BB} - 4C_{AB}^2} - \frac{\chi N}{2}\right]\left(\mathbf{r}, \mathbf{r}'\right) \tag{41}$$