A Quick Guide to the Self-consistent Field Theory in Polymer Physics

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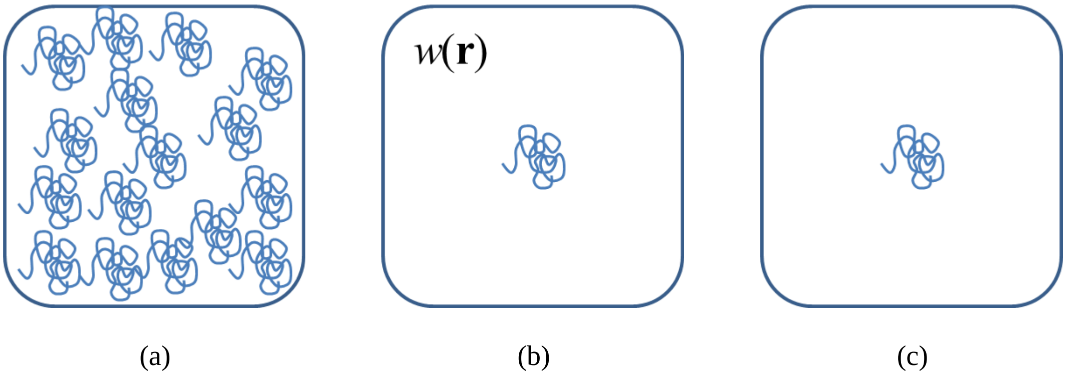
Equation Section 1Introduction

The self-consistent field theory (SCFT) for many-chain systems is obtained by imposing a mean-field approximation to simplify the statistical field theories. The statistical field theories can be constructed from the particle-based model by carrying out a particle-to-field transformation. The general approach for a particle-to-field transformation is to invoke formal techniques related to Hubbard-Stratonovich transformations, which have the effect of decoupling interactions among particles (or polymer segments) and replacing them with interactions between the particles and one or more auxiliary fields.



(a) (b) (c)

Figure 1

Fig.1a shows the particle description of a many-chain system. It can be simplified by applying a particle-to-field transformation leading to a single chain sitting in an external field $w(\mathbf{r})$ that is generated by all other interacting chains, as can be seen in Fig. 1b. Fig. 1c shows an isolated single chain which is the basis for constructing a field-theoretic model. In principle, any chain models will work. In this notes, the continuous Gaussian chain model is chosen in particular.

2. Continuous Gaussian chain model

As shown in Fig. 2, the configuration of the continuous Gaussian chain is specified by a space curve $\mathbf{r}(s)$ in which $s\in[0,N]$ is a contour variable that describes the location of a segment along the backbone of the chain. The position in space of segment *s* is given by **r**(*s*).

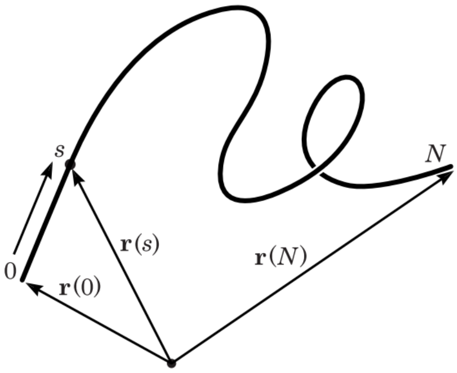


Figure 2

The configuration partition function of the continuous Gaussian chain can be written

$$Z_0 = \int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}]) \tag{1}$$

where the notation $\int \mathcal{D}\mathbf{r}$ indicates a functional integral or a path integral overall possible space curve **r**(*s*). The potential energy of the continuous Gaussian chain U_0 in eq. (1) can be written

$$U_0[\mathbf{r}] = \frac{3k_B T}{2b^2} \int_0^N ds \left| \frac{d\mathbf{r}(s)}{ds} \right|^2 \tag{2}$$

where the square bracket notation is used to indicate that U_0 is a functional of the space curve. It is important to note that *s* does not indicate arc length in the continuous Gaussian chain model, but is simply a parameter indexing the segments along the chain. Eq. (2) for the potential energy is commonly referred to as the “Edwards Hamiltonian.”

Here we adopt the stochastic process approach to explore the properties of the continuous Gaussian chain model introduced by Fredrickson in the book *The Equilibrium Theory of Inhomogeneous Polymers* (2006, p42-43). We also give a naive deduction of the Chapman-Kolmogorov equation which is directly given in Fredrickson’s book. In practice, we are mainly interested in the observable quantities, i.e. those ensemble averages over the configurational degrees of freedom of a single polymer. The single-chain average quantities of primary interest are segment densities, density-density correlations, and elastic stresses, all of which can be connected to observables in experiments. With the single-chain partition function defined in eq. (1), we can define the single-chain average of an arbitrary function *f*(**r**) of the space curve **r** by

$$\left\langle f(\mathbf{r})\right\rangle = \frac{\int \mathcal{D}\mathbf{r} f(\mathbf{r}) \exp(-\beta U_0[\mathbf{r}])}{\int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}])} \tag{3}$$

In particular, the average segment number density is defined by

$$\rho(\mathbf{r}) = \left\langle \hat{\rho}(\mathbf{r})\right\rangle = \frac{\int \mathcal{D}\mathbf{r} \hat{\rho}(\mathbf{r}) \exp(-\beta U_0[\mathbf{r}])}{\int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}])} \tag{4}$$

where the microscopic density $\hat{\rho}$ for a single continuous Gaussian chain is given by

$$\hat{\rho}(\mathbf{r}) = \int_0^N ds \delta\left[\mathbf{r}(s) - \mathbf{r}\right] \tag{5}$$

Substitute eq. (5) into eq. (4), we have

$$\begin{aligned}
\rho(\mathbf{r}) &= \frac{\int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}]) \int_0^N ds \delta\left[\mathbf{r}(s) - \mathbf{r}\right]}{\int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}])} \\
&= \frac{\int_0^N ds \int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}]) \delta\left[\mathbf{r}(s) - \mathbf{r}\right]}{\int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}])} \\
&= \frac{V^2 \left(\frac{2\pi b^2 \Delta s}{3}\right)^{\frac{3}{2}N_N} \int_0^N ds J(\mathbf{r}, s)}{\int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}])}
\end{aligned} \tag{6}$$

where V is the system volume, $\Delta s = N/N_N$, the chain contour is divided into N_N equally spaced parts, and $J(\mathbf{r},s)$ is defined to be

$$
\begin{aligned}
J(\mathbf{r},s) &= \frac{1}{V^2}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_N}\int \mathcal{D}\mathbf{r}\exp\left(-\int_0^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&= \frac{1}{V^2}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_N}\int \mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_s^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&\quad\times\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&= \frac{1}{V^2}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_N}\int \mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_s^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&\quad\times\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\times 1\\
&= \frac{1}{V^2}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_N}\int \mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_s^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&\quad\times\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\times\int d\mathbf{r}(s)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&= \frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int \mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&\quad\times\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_N-N_s)}\int \mathcal{D}\mathbf{r}\exp\left(-\int_s^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&= \frac{1}{V}q(\mathbf{r},s)\frac{1}{V}q(\mathbf{r},N-s) \qquad\qquad (7)\\
&= \frac{1}{V}q(\mathbf{r},s)\frac{1}{V}q^{*}(\mathbf{r},s)
\end{aligned}
$$

where N_s is the number of spaces that the 0~s part of chain has. The system volume V can be obtained by integrating over all positions

$$V=\int d\mathbf{r} \tag{8}$$

In eq. (7), $q(\mathbf{r},s)$ represents the statistical weight for a chain of 0~s part of chain to have its end at position $\mathbf{r}$, and $q(\mathbf{r},N\text{-}s)=q^{*}(\mathbf{r},s)$ is the propagator for a complementary chain with length N-s. This object is commonly referred to as a chain propagator. The coefficient before the integral of the first line of eq. (7) is added to ensure the propagator is normalized properly. It can be seen from

$$
\begin{aligned}
&\int d\mathbf{r}\,\frac{1}{V}\,q(\mathbf{r},s)\\
&=\int d\mathbf{r}\,\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int\mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\,\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&=\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int\mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\,\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\int d\mathbf{r}\,\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&=\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int\mathcal{D}\mathbf{r}\exp\left(-\int_0^s ds'\,\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&\approx\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{j=0}^{N_s}\int d\mathbf{r}_j\,\exp\left(-\frac{3}{2b^2\Delta s}\sum_{i=1}^{N_s}\left|\mathbf{r}_{i-1}-\mathbf{r}_i\right|^2\right)\\
&=\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int d\mathbf{r}_{N_s}\int d\mathbf{r}_0\,\exp\left(-\frac{3}{2b^2\Delta s}\left|\mathbf{r}_0-\mathbf{r}_1\right|^2\right)\int d\mathbf{r}_1\,\exp\left(-\frac{3}{2b^2\Delta s}\left|\mathbf{r}_1-\mathbf{r}_2\right|^2\right)\\
&\quad\cdots\int d\mathbf{r}_{N_s-1}\,\exp\left(-\frac{3}{2b^2\Delta s}\left|\mathbf{r}_{N_s-1}-\mathbf{r}_{N_s}\right|^2\right)\\
&=\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int d\mathbf{r}_{N_s}\left[\int d\mathbf{r}\exp\left(-\frac{3}{2b^2\Delta s}\left|\mathbf{r}\right|^2\right)\right]^{N_s}\\
&=\frac{1}{V}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\left[\iiint dx\,dy\,dz\exp\left(-\frac{3}{2b^2\Delta s}(x^2+y^2+z^2)\right)\right]^{N_s}\int d\mathbf{r}_{N_s}\\
&=\frac{1}{V}V\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\left[\int dx\exp\left(-\frac{3}{2b^2\Delta s}x^2\right)\int dy\exp\left(-\frac{3}{2b^2\Delta s}y^2\right)\int dz\exp\left(-\frac{3}{2b^2\Delta s}z^2\right)\right]^{N_s}\\
&=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\left[\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{1}{2}}\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{1}{2}}\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{1}{2}}\right]^{N_s}\\
&=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{3}{2}N_s}\\
&=1
\end{aligned}
\tag{9}
$$

To calculate the single-chain partition function, just integrate $J(\mathbf{r},s)$ respect to $\mathbf{r}$ and multiply it with an appropriate coefficient. It can be seen from

$$
\begin{aligned}
&V^2\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{3}{2}N_N}\int d\mathbf{r}\,J(\mathbf{r},s)\\
&=V^2\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{3}{2}N_N}\int d\mathbf{r}\,\frac{1}{V^2}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_N}\int\mathcal{D}\mathbf{r}\exp\left(-\int_0^N ds'\,\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&=\left[\int\mathcal{D}\mathbf{r}\exp\left(-\int_0^N ds'\,\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\right]\int d\mathbf{r}\,\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&=\int\mathcal{D}\mathbf{r}\exp\left(-\int_0^N ds'\,\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&=\int\mathcal{D}\mathbf{r}\exp(-\beta U_0[\mathbf{r}])\\
&=Z_0
\end{aligned}
\tag{10}
$$

Therefore, inserting eq. (7) and eq. (10) into eq. (6), we can evaluate average segment number density as

$$\rho(\mathbf{r})=\left\langle \tilde{\rho}(\mathbf{r})\right\rangle=\frac{\int_0^N dsq(\mathbf{r},s)q(\mathbf{r},N-s)}{\int_{-\infty}^{\infty} d\mathbf{r}\,q(\mathbf{r},s)q(\mathbf{r},N-s)} \tag{11}$$

It will be clear later that it is convenient to define a normalized single-chain partition function *Q* as

$$Q\left[w(\mathbf{r})=0\right]=\frac{Z\left[w(\mathbf{r})=0\right]}{Z_0} \tag{12}$$

In this case, the external field is *0* everywhere. Since $Z[w(\mathbf{r})=0]$ is just Z_0, eq. (12) is reduced to

$$Q\left[w(\mathbf{r})=0\right]=1 \tag{13}$$

As shown in eq. (45), Z0 can be evaluated analytically,

$$Z_0=V\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{3}{2}N_N} \tag{14}$$

Insert eq. (14) into eq. (10), we have

$$Z\left[w(\mathbf{r})=0\right]=VZ_0\int d\mathbf{r}\,J(\mathbf{r},s) \tag{15}$$

Thus, the single-chain partition function can be expressed as

$$Q\left[w(\mathbf{r})=0\right]=\frac{1}{V}\int d\mathbf{r}\,q(\mathbf{r},s)q(\mathbf{r},N-s) \tag{16}$$

with *J* replaced by the next to last line of eq. (7). And the average segment density can be written as

$$\rho(\mathbf{r})=\frac{1}{VQ[w(\mathbf{r})]}\int_0^N dsq(\mathbf{r},s)q(\mathbf{r},N-s) \tag{17}$$

by inserting eq. (16) into eq. (11). Actually, eq. (16) and eq. (17) is at least valid for any linear polymers as long as the continuous Gaussian chain model is used.

The propagator *q* is a central quantity in statistical field theory. The ensemble averages and the single-chain partition function can be derived from it. Below we will derive an equation to compute it conveniently.

First, we explicitly write the chain propagator *q* in the form:

$$q(\mathbf{r},s)=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \tag{18}$$

where we use the discrete approach to define a path integral, such as

$$\int \mathcal{D}\mathbf{r}=\prod_{t=0}^{s}\int d\mathbf{r}(t)\approx\prod_{i=0}^{N_s}\int d\mathbf{r}_i \tag{19}$$

Note the short hand notation for functional differential is used, and it should be understood that keeping the continuous form of U_0 in eq. (18) instead of discretization one is just for clarity in presentation (See Fredrickson, 2006 for more details about the definition and description of the path integral).

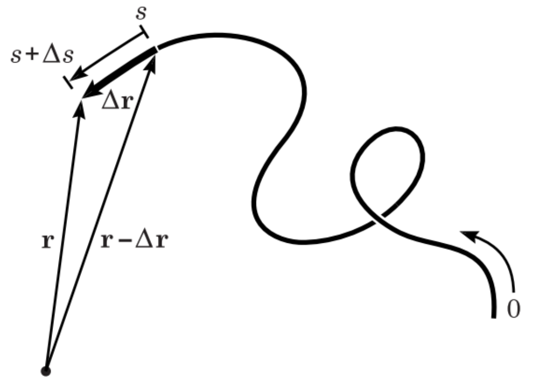


Figure 3

Then, the chain propagator after advancing a step along the chain contour from s to $s+\Delta s$ is given by

$$\begin{aligned}
&q(\mathbf{r},s+\Delta s)\\
&=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_s+1)}\prod_{t=0}^{s+\Delta s}\int d\mathbf{r}(t)\exp\left(-\int_0^{s+\Delta s}ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]\\
&=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_s+1)}\prod_{t=0}^{s+\Delta s}\int d\mathbf{r}(t)\exp\left(-\int_0^{s}ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_s^{s+\Delta s}ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&\times\delta\left[\mathbf{r}(s+\Delta s)-\mathbf{r}\right]\\
&=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_s+1)}\prod_{t=0}^{s}\int d\mathbf{r}(t)\prod_{t=s}^{s+\Delta s}\int d\mathbf{r}(t)\exp\left(-\int_0^{s}ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\\
&\times\exp\left(-\int_s^{s+\Delta s}ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\left[\mathbf{r}(s+\Delta s)-\mathbf{r}\right]
\end{aligned} \tag{20}$$

Let $\Delta s\rightarrow 0$, the last two lines in above equation can be simplified. The functional integral from s to $s+\Delta s$ can be evaluated as

$$
\begin{aligned}
&\prod_{t=s}^{s+\Delta s}\int d\mathbf{r}(t)\\
&\approx \iint\cdots\int d\mathbf{r}(s+\frac{1}{n}\Delta s)d\mathbf{r}(s+\frac{2}{n}\Delta s)\cdots d\mathbf{r}(s+\Delta s)\\
&= \int d\mathbf{r}(s+\Delta s)\\
&= \int d\big[\mathbf{r}(s)+\Delta\mathbf{r}\big]\\
&= \int d\Delta\mathbf{r}
\end{aligned}
\tag{21}
$$

From the second line to the third line, only one step is needed to advance from s to $s+\Delta s$ when Δs is sufficiently small. From the fourth line to the fifth line, $\mathbf{r}(s)$ is constant for a certain configuration. Note that the range of possible values of $\Delta\mathbf{r}$ is $(-\infty,+\infty)$ because the integrand approach 0 when $\Delta\mathbf{r}\rightarrow\pm\infty$. The delta functional can be evaluated as

$$
\begin{aligned}
\delta\big[\mathbf{r}(s+\Delta s)-\mathbf{r}\big] &= \delta\big[\mathbf{r}(s)+\Delta\mathbf{r}-\mathbf{r}\big]\\
&= \delta\big[\mathbf{r}(s)-(\mathbf{r}-\Delta\mathbf{r})\big]
\end{aligned}
\tag{22}
$$

And the second part of the potential energy can be evaluated as

$$
\begin{aligned}
&\int_{s}^{s+\Delta s} ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\\
&= \frac{3}{2b^2}\left|\frac{d\mathbf{r}(s)}{ds}\right|^2\\
&\approx \frac{3}{2b^2}\left|\frac{\mathbf{r}(s+\Delta s)-\mathbf{r}(s)}{\Delta s}\right|^2\Delta s\\
&= \frac{3}{2b^2}\frac{\Delta\mathbf{r}^2}{\Delta s^2}\Delta s\\
&= \frac{3}{2b^2\Delta s}\Delta\mathbf{r}^2
\end{aligned}
\tag{23}
$$

Through insertion of eq.(19), (20), and (21) into eq. (18), we can find the Chapman-Kolmogorov equation given in Fredrickson's book (eq. 2.58):

$$
\begin{aligned}
&q(\mathbf{r},s+\Delta s)\\
&= \left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_s+1)}\prod_{t=0}^{s}\int d\mathbf{r}(t)\int d\Delta\mathbf{r}\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\exp\left(-\frac{3}{2b^2\Delta s}\Delta\mathbf{r}^2\right)\\
&\times\delta\big[\mathbf{r}(s)-(\mathbf{r}-\Delta\mathbf{r})\big]\\
&= \int d\Delta\mathbf{r}\left\{\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right)\delta\big[\mathbf{r}(s)-(\mathbf{r}-\Delta\mathbf{r})\big]\right\}\\
&\times\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}}\exp\left(-\frac{3}{2b^2\Delta s}\Delta\mathbf{r}^2\right)\\
&= \int d\Delta\mathbf{r}\,q(\mathbf{r}-\Delta\mathbf{r},s)\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}}\exp\left(-\frac{3}{2b^2\Delta s}\Delta\mathbf{r}^2\right)\\
&= \int d\Delta\mathbf{r}\,\Phi(\Delta\mathbf{r})q(\mathbf{r}-\Delta\mathbf{r},s)
\end{aligned}
\tag{24}
$$

where Φ(Δ**r**) has a physical meaning of transition probability density, which describes the conditional probability of a displacement Δ**r** for a segment of chain of contour length Δ*s*, starting from the position **r**- Δ**r** at contour location *s*. Φ(Δ**r**) is given by

$$\Phi(\Delta\mathbf{r}) = \left(\frac{3}{2\pi b^2 \Delta s}\right)^{\frac{3}{2}} \exp\left(-\frac{3}{2b^2\Delta s}\Delta\mathbf{r}^2\right) \tag{25}$$

Note that this transition probability density is properly normalized due to the proper normalization of the propagator. A useful feature of continuous chain models is that Chapman-Kolmogorov integral equations can be reduced to partial differential equations, which are referred to in probability theory as Fokker-Planck equations and in quantum theory as Feynman-Kac formulas. We illustrate this by deriving the Fokker-Planck equation associated with eq. (24). The derivation proceeds by performing the Taylor expansion for both sides of eq. (24) in powers of Δ*s* and Δ**r**, treating each as small. It finally reduced to the Fokker-Planck equation:

$$\frac{\partial}{\partial s} q(\mathbf{r},s) = \frac{b^2}{6}\nabla^2 q(\mathbf{r},s) \tag{26}$$

Thus, the Fokker-Planck equation for the continuous Gaussian chain takes the form of a conventional diffusion equation with a diffusion coefficient given by $b^2/6$. The solution of this equation provides full information about the distribution of end segments, *q*(**r**,*s*). The full derivation is given by

$$q(\mathbf{r},s+\Delta s) = q(\mathbf{r},s) + \Delta s \frac{\partial}{\partial s} q(\mathbf{r},s) + O(\Delta s^2) \tag{27}$$

$$\begin{aligned}
&\int d\Delta\mathbf{r}\Phi(\Delta\mathbf{r})q(\mathbf{r}-\Delta\mathbf{r},s)\\
&= \left\langle q(\mathbf{r}-\Delta\mathbf{r},s)\right\rangle_\Phi\\
&= \left\langle q(\mathbf{r},s) - \Delta\mathbf{r}\cdot\nabla q(\mathbf{r},s) + \frac{1}{2!}\Delta\mathbf{r}\Delta\mathbf{r} : \nabla\nabla q(\mathbf{r},s) + O(\Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r})\right\rangle_\Phi\\
&= q(\mathbf{r},s) - \left\langle\Delta\mathbf{r}\right\rangle_\Phi\cdot\nabla q(\mathbf{r},s) + \frac{1}{2!}\left\langle\Delta\mathbf{r}\Delta\mathbf{r}\right\rangle_\Phi : \nabla\nabla q(\mathbf{r},s) + O(\left\langle\Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r}\right\rangle_\Phi)
\end{aligned} \tag{28}$$

where the Φ-average appearing in this equation are defined by

$$\left\langle f(\Delta\mathbf{r})\right\rangle_\Phi = \int d\Delta\mathbf{r}\Phi(\Delta\mathbf{r})f(\Delta\mathbf{r}) \tag{29}$$

The average on the right last line of eq. (28) can be evaluated as

$$
\begin{aligned}
\left\langle \Delta\mathbf{r} \right\rangle_{\Phi} &= \int d\Delta\mathbf{r} \left(\frac{3}{2\pi b^2 \Delta s} \right)^{\frac{3}{2}} \exp\left(-\frac{3}{2b^2\Delta s} \Delta\mathbf{r}^2 \right) \Delta\mathbf{r} \\
&= \frac{1}{2} \left(\frac{3}{2\pi b^2 \Delta s} \right)^{\frac{3}{2}} \int_{-\infty}^{\infty} d(\Delta\mathbf{r}^2) \exp\left(-\frac{3}{2b^2\Delta s} \Delta\mathbf{r}^2 \right) \\
&= \frac{1}{2} \left(\frac{3}{2\pi b^2 \Delta s} \right)^{\frac{3}{2}} \left(-\frac{2b^2\Delta s}{3} \right) \exp\left(-\frac{3}{2b^2\Delta s} \Delta\mathbf{r}^2 \right) \Bigg|_{-\infty}^{\infty} \\
&= 0
\end{aligned}
\tag{30}
$$

$$
\left\langle \Delta\mathbf{r}\Delta\mathbf{r} \right\rangle_{\Phi} = \left\langle \Delta\mathbf{r}_{\alpha}\Delta\mathbf{r}_{\beta} \right\rangle_{\Phi} = \frac{b^2\Delta s}{3}\delta_{\alpha\beta}
\tag{31}
$$

Insert eq. (30) and (31) into eq. (28), and equal it to eq. (27), we find

$$
q(\mathbf{r},s) + \Delta s \frac{\partial}{\partial s} q(\mathbf{r},s) + O(\Delta s^2) = q(\mathbf{r},s) + \Delta s \frac{b^2}{6} \nabla^2 q(\mathbf{r},s) + O(\left\langle \Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r} \right\rangle_{\Phi})
\tag{32}
$$

Let $\Delta s \to 0$, eq. (26) is finally obtained.

3. Single continuous Gaussian chain in external field

In this section, we want to discuss how the partition functions and distribution functions of the continuous Gaussian chain model are modified by the presence of an external field. The external field of primary interest is a spatially varying chemical potential field $w(\mathbf{r})$ that acts indiscriminately on the polymer segments of a continuous Gaussian chain. The potential energy generated by this external field is given by

$$
\beta U_1[\mathbf{r}, w] = \int_0^N ds w[\mathbf{r}(s)]
\tag{33}
$$

The potential energy without the presence of the external field is still given by eq. (2). Thus the single-chain partition function under an external field is given by

$$
Z[w] = \int \mathcal{D}\mathbf{r} \exp(-\beta U_0[\mathbf{r}] - \beta U_1[\mathbf{r}, w])
\tag{34}
$$

Similar to eq. (18), the propagator is defined as

$$
\begin{aligned}
q(\mathbf{r},s) = & \left(\frac{3}{2\pi b^2 \Delta s} \right)^{\frac{3}{2}N_s} \prod_{t=0}^{s} \int d\mathbf{r}(t) \exp\left(-\int_0^s ds' \frac{3}{2b^2} \left| \frac{d\mathbf{r}(s')}{ds'} \right|^2 - \int_0^s ds' w[\mathbf{r}(s')] \right) \\
& \times \delta\left[\mathbf{r}(s) - \mathbf{r} \right]
\end{aligned}
\tag{35}
$$

Then, the chain propagator after advancing a step along the chain contour from s to $s+\Delta s$ is given by

$$
\begin{aligned}
q(\mathbf{r}, s+\Delta s) = &\left(\frac{3}{2\pi b^2 \Delta s}\right)^{\frac{3}{2}(N_s+1)} \prod_{t=0}^{s} \int d\mathbf{r}(t) \prod_{t=s}^{s+\Delta s} \int d\mathbf{r}(t) \\
&\times \exp\left(-\int_0^s ds' \frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^s ds' w[\mathbf{r}(s')]\right) \\
&\times \exp\left(-\int_s^{s+\Delta s} ds' \frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2\right) \\
&\times \exp\left(-\int_s^{s+\Delta s} ds' w[\mathbf{r}(s')]\right) \delta\left[\mathbf{r}(s+\Delta s) - \mathbf{r}\right]
\end{aligned}
\tag{36}
$$

Inserting eq. (21), (22), (23), and the following equality

$$
\int_s^{s+\Delta s} ds' w[\mathbf{r}(s')] = w[\mathbf{r}(s)]\Delta s = w(\mathbf{r})\Delta s \tag{37}
$$

into eq. (36), we can find that

$$
q(\mathbf{r}, s+\Delta s) = e^{-w(\mathbf{r})\Delta s} \int d\Delta\mathbf{r} \Phi(\Delta\mathbf{r}) q(\mathbf{r} - \Delta\mathbf{r}, s) \tag{38}
$$

with the transition probability density function Φ still given by eq. (25). Using the same Taylor expansion strategy introduced in **section 3**, the left hand side of above equation is expanded into eq.(27), and the right hand side is expanded as

$$
\begin{aligned}
& e^{-w(\mathbf{r})\Delta s} \int d\Delta\mathbf{r} \Phi(\Delta\mathbf{r}) q(\mathbf{r} - \Delta\mathbf{r}, s) \\
&= \left[1 - w(\mathbf{r})\Delta s + O(\Delta s^2)\right] \\
&\times \left[q(\mathbf{r}, s) + \Delta s \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s) + O(\left\langle \Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r} \right\rangle_\Phi)\right] \\
&= q(\mathbf{r}, s) + \Delta s \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s) - \Delta s w(\mathbf{r}) q(\mathbf{r}, s) + O(\Delta s^2) + O(\left\langle \Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r} \right\rangle_\Phi)
\end{aligned}
\tag{39}
$$

Equating eq. (27) and eq. (39) and cancelling same terms and higher order terms leads to the final Fokker-Planck equation

$$
\frac{\partial}{\partial s} q(\mathbf{r}, s) = \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}) q(\mathbf{r}, s) \tag{40}
$$

which can be viewed as a generalization of eq. (26) to include an external potential. The Fokker-Planck equation is commonly referred to as a modified diffusion equation, and sometimes, by analogy with the path integral formulation of quantum mechanics, as a Feynman-Kac formula.

To find the initial condition, we first calculate the chain propagator which is just one step ahead, $q(\mathbf{r}, \Delta s)$, since q is well defined for at least one bond. $q(\mathbf{r}, \Delta s)$ is evaluated as follows

$$\begin{aligned}
q(\mathbf{r},\Delta s) &= \left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}} \int d\mathbf{r}(0)\int d\mathbf{r}(\Delta s) \\
&\quad \exp\left(-\int_0^{\Delta s} ds' \frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^{\Delta s} ds'\, w[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(\Delta s)-\mathbf{r}\right] \\
&= \left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}} \int d\mathbf{r}(0)\int d\mathbf{r}(\Delta s) \\
&\quad \exp\left(-\frac{3}{2b^2}\Delta s\left|\frac{\mathbf{r}(\Delta s)-\mathbf{r}(0)}{\Delta s}\right|^2 - \Delta s w[\mathbf{r}(\Delta s)]\right)\delta\left[\mathbf{r}(\Delta s)-\mathbf{r}\right] \qquad (41) \\
&= \left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}} \int d\mathbf{r}(0)\exp\left(-\frac{3}{2b^2}\Delta s\left|\frac{\mathbf{r}-\mathbf{r}(0)}{\Delta s}\right|^2 - \Delta s w(\mathbf{r})\right) \\
&= e^{-\Delta s w(\mathbf{r})}\int d\mathbf{r}(0)\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}}\exp\left[-\frac{3}{2b^2\Delta s}\left(\mathbf{r}-\mathbf{r}(0)\right)^2\right] \\
&= e^{-\Delta s w(\mathbf{r})}
\end{aligned}$$

At the continuum limit, i.e. Δ*s*→0,

$$q(\mathbf{r},0) = \lim_{\Delta s\to 0} q(\mathbf{r},\Delta s) = \lim_{\Delta s\to 0} e^{-\Delta s w(\mathbf{r})} = 1 \qquad (42)$$

The normalized single-chain partition function Q[*w*] can be expressed as a ratio of path integrals

$$Q[w] \equiv \frac{Z[w]}{Z_0} = \frac{\int \mathcal{D}\mathbf{r}\exp(-\beta U_0[\mathbf{r}] - \beta U_1[\mathbf{r},w])}{\int \mathcal{D}\mathbf{r}\exp(-\beta U_0[\mathbf{r}])} \qquad (43)$$

It can be shown by following the calculation in eq. (10)

$$Z[w] = V^2\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{3}{2}N_N} \int d\mathbf{r}\frac{1}{V}q(\mathbf{r},s)\frac{1}{V}q(\mathbf{r},N-s) \qquad (44)$$

And the single-chain partition function Z_0 is integrated to

$$
\begin{aligned}
& Z_0 \\
&= \int \mathcal{D}\mathbf{r} \exp\left(-\int_0^N ds' \frac{3}{2b^2} \left| \frac{d\mathbf{r}(s')}{ds'} \right|^2 \right) \\
&\approx \prod_{j=0}^{N_N} \int d\mathbf{r}_j \exp\left(-\frac{3}{2b^2 \Delta s} \sum_{i=1}^{N_N} \left| \mathbf{r}_{i-1} - \mathbf{r}_i \right|^2 \right) \\
&= \int d\mathbf{r}_{N_N} \int d\mathbf{r}_0 \exp\left(-\frac{3}{2b^2 \Delta s} \left| \mathbf{r}_0 - \mathbf{r}_1 \right|^2 \right) \int d\mathbf{r}_1 \exp\left(-\frac{3}{2b^2 \Delta s} \left| \mathbf{r}_1 - \mathbf{r}_2 \right|^2 \right) \\
& \cdots \int d\mathbf{r}_{N_N - 1} \exp\left(-\frac{3}{2b^2 \Delta s} \left| \mathbf{r}_{N_N - 1} - \mathbf{r}_{N_N} \right|^2 \right) \\
&= \int d\mathbf{r}_{N_N} \left[\int d\mathbf{r} \exp\left(-\frac{3}{2b^2 \Delta s} \left| \mathbf{r} \right|^2 \right) \right]^{N_N} \\
&= \left[\iiint dx dy dz \exp\left(-\frac{3}{2b^2 \Delta s} (x^2 + y^2 + z^2) \right) \right]^{N_s} \int d\mathbf{r}_{N_N} \\
&= V \left[\int dx \exp\left(-\frac{3}{2b^2 \Delta s} x^2 \right) \int dy \exp\left(-\frac{3}{2b^2 \Delta s} y^2 \right) \int dz \exp\left(-\frac{3}{2b^2 \Delta s} z^2 \right) \right]^{N_N} \\
&= V \left[\left(\frac{2\pi b^2 \Delta s}{3} \right)^{\frac{1}{2}} \left(\frac{2\pi b^2 \Delta s}{3} \right)^{\frac{1}{2}} \left(\frac{2\pi b^2 \Delta s}{3} \right)^{\frac{1}{2}} \right]^{N_N} \\
&= V \left(\frac{2\pi b^2 \Delta s}{3} \right)^{\frac{3}{2} N_N}
\end{aligned}
\tag{45}
$$

Therefore, the normalized partition function in the term of propagator *q* is obtained by substituting eq. (44) and (45) into (43):

$$
Q[w] = \frac{1}{V} \int d\mathbf{r}\, q(\mathbf{r}, s) q(\mathbf{r}, N - s) \tag{46}
$$

Particularly, let *s*=0 and invoke the initial condition given by eq. (42), we have

$$
Q[w] = \frac{1}{V} \int d\mathbf{r}\, q(\mathbf{r}, N) \tag{47}
$$

The modified diffusion equation together with the above equation fully describes the statistical mechanics of the continuous Gaussian chain in an external potential *w*(**r**).

With the definition of chain propagator, it is easy to verify that the average segment number density is still given by eq. (11):

$$
\begin{aligned}
&\frac{\int_0^N dsq(\mathbf{r},s)q(\mathbf{r},N-s)}{\int_{-\infty}^{\infty} d\mathbf{r}\,q(\mathbf{r},s)q(\mathbf{r},N-s)} \\
&= \frac{1}{VQ[w(\mathbf{r})]}\int_0^N ds\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^s ds'\,w[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \\
&\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_N-N_s)}\prod_{t=0}^{N-s}\int d\mathbf{r}(t)\exp\left(-\int_0^{N-s} ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^{N-s} ds'\,w[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \\
&= \frac{Z_0}{VZ}\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\int_0^N ds\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^s ds'\,w[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \\
&\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_N-N_s)}\prod_{t=s}^{N}\int d\mathbf{r}(t)\exp\left(-\int_s^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_s^N ds'\,w[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \\
&= \frac{1}{Z}\int_0^N ds\prod_{t=0}^{N}\int d\mathbf{r}(t)\exp\left(-\int_0^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^N ds'\,w[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \\
&= \frac{1}{Z}\prod_{t=0}^{N}\int d\mathbf{r}(t)\exp\left(-\int_0^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^N ds'\,w[\mathbf{r}(s')]\right)\int_0^N ds\delta\left[\mathbf{r}(s)-\mathbf{r}\right] \\
&= \frac{1}{Z}\prod_{t=0}^{N}\int d\mathbf{r}(t)\tilde{\rho}(\mathbf{r})\exp\left(-\int_0^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^N ds'\,w[\mathbf{r}(s')]\right) \\
&= \frac{\int \mathcal{D}\mathbf{r}\tilde{\rho}(\mathbf{r})\exp\left(-\int_0^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^N ds'\,w[\mathbf{r}(s')]\right)}{\int \mathcal{D}\mathbf{r}\exp\left(-\int_0^N ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^N ds'\,w[\mathbf{r}(s')]\right)} \\
&= \left\langle \tilde{\rho}(\mathbf{r})\right\rangle = \rho(\mathbf{r})
\end{aligned}
$$

(48)

From first equal sign to the second equal sign, eq. (43) is used, from the second equal sign to the third equal sign eq. (45) is used, and from the fifth equal sign to the sixth equal sign eq. (34) is used. Substituting eq. (46) into above equation, the average segment density can be evaluated using

$$\rho(\mathbf{r}) = \left\langle \tilde{\rho}(\mathbf{r})\right\rangle = \frac{1}{VQ[w(\mathbf{r})]}\int_0^N dsq(\mathbf{r},s)q(\mathbf{r},N-s) \tag{49}$$

4. Many-chain model for two-bead chains

In previous two sections, we deal with single-chain systems. From now on, we start to analyze the properties of many-chain systems. To construct a field theory for many-chain system, the particle-to-field transformation should be performed. The most important mathematical tool during the particle-to-field transformation is the delta functional, which is defined as

$$\int \mathcal{D}\rho F[\rho]\delta[\rho-\tilde{\rho}] = F[\tilde{\rho}] \tag{50}$$

for any functional $F[\rho]$. The delta functional can be viewed as an infinite-dimensional version of the Dirac delta function that vanishes unless the fields $\rho(\mathbf{r})$ and $\tilde{\rho}(\mathbf{r})$ are equal at all points **r** in the domain of interest. A useful complex exponential representation of the delta functional can be developed by temporarily discretizing space using M_g grid points according to

$$\begin{aligned}
\delta[\rho-\tilde{\rho}] &= \prod_{\mathbf{r}} \delta[\rho(\mathbf{r})-\tilde{\rho}(\mathbf{r})] \\
&= \prod_{i=1}^{M_g} \delta[\rho(\mathbf{r}_i)-\tilde{\rho}(\mathbf{r}_i)] \\
&= \prod_{i=1}^{M_g} \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} dw(\mathbf{r}_i) e^{iw(\mathbf{r}_i)[\rho(\mathbf{r}_i)-\tilde{\rho}(\mathbf{r}_i)]} \right\} \\
&= \left(\frac{1}{2\pi}\right)^{M_g} \int_{-\infty}^{\infty} dw(\mathbf{r}_1) e^{iw(\mathbf{r}_1)[\rho(\mathbf{r}_1)-\tilde{\rho}(\mathbf{r}_1)]} \int_{-\infty}^{\infty} dw(\mathbf{r}_2) e^{iw(\mathbf{r}_2)[\rho(\mathbf{r}_2)-\tilde{\rho}(\mathbf{r}_2)]} \\
&\quad \cdots \int_{-\infty}^{\infty} dw(\mathbf{r}_{M_g}) e^{iw(\mathbf{r}_{M_g})[\rho(\mathbf{r}_{M_g})-\tilde{\rho}(\mathbf{r}_{M_g})]} \\
&= \left(\frac{1}{2\pi}\right)^{M_g} \int_{-\infty}^{\infty} dw(\mathbf{r}_1) \int_{-\infty}^{\infty} dw(\mathbf{r}_2) \cdots \int_{-\infty}^{\infty} dw(\mathbf{r}_{M_g}) e^{i\sum_{j=1}^{M_g} w(\mathbf{r}_j)[\rho(\mathbf{r}_j)-\tilde{\rho}(\mathbf{r}_j)]} \\
&= \int \mathcal{D}w \; e^{i\int d\mathbf{r}\, w(\mathbf{r})[\rho(\mathbf{r})-\tilde{\rho}(\mathbf{r})]}
\end{aligned} \tag{51}$$

The third line of the above expression follows from the application of the representation of the one-dimensional delta function $\delta[\rho(\mathbf{r}_i)-\tilde{\rho}(\mathbf{r}_i)]$ at grid $\mathbf{r}_i$. The final expression results from restoring the continuum description and can be viewed as a formal definition of the functional integral $\int \mathcal{D}w$ over the auxiliary field $w(\mathbf{r})$. It is important to note that $w(\mathbf{r})$ is a real scalar field and that the functional integral in eq. (51) is taken along the whole real axis at each **r**.

Now, it is ready for us to examine the simplest many-chain model for diblock copolymers: two-bead model. In two-bead model, there are n chains in the system. Each chain has two beads A and B connected by a spring. The potential energy of this system has two sources of contribution: the intramolecular, short-ranged interferences and the intermolecular interactions among segments. The first energetic contribution is just sum of spring energies stored in all chains:

$$\beta U_0(\mathbf{r}^{2n}) = \sum_{j=1}^{n} \frac{\lambda}{2} \left| \mathbf{r}_{Ai} - \mathbf{r}_{Bi} \right|^2 \tag{52}$$

where $\mathbf{r}^{2n}=(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{2n})$ denotes the set of $2n$ bead positions, and λ is the spring constant. The second energetic contribution originates from the interaction between any of two beads in the system, whose general form is given by

$$
\begin{aligned}
\beta U_1(\mathbf{r}^{2n}) &= \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{\sigma=A,B}\sum_{\sigma'=A,B} u_{\sigma,\sigma'}(\left|\mathbf{r}_{\sigma j}-\mathbf{r}_{\sigma' k}\right|) \\
&= \frac{1}{2}\sum_{j,k}\sum_{\sigma,\sigma'} u_{\sigma,\sigma'}(\left|\mathbf{r}_{\sigma j}-\mathbf{r}_{\sigma' k}\right|)
\end{aligned}
\tag{53}
$$

where $u(r)$ is the familiar pair potential function. The factor of 1/2 in the expression corrects for the counting of each pair of particles twice in the double sum. If we define the microscopic density operators for bead A and bead B as

$$
\tilde{\rho}_{\sigma}(\mathbf{r}) = \sum_{j=1}^{n}\delta(\mathbf{r}-\mathbf{r}_{\sigma j}) \tag{54}
$$

where σ denotes either A or B. With this definition, it follows that

$$
\beta U_1(\mathbf{r}^{2n}) = \frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_{\sigma}(\mathbf{r})u_{\sigma,\sigma'}(\left|\mathbf{r}-\mathbf{r}'\right|)\tilde{\rho}_{\sigma'}(\mathbf{r}') \tag{55}
$$

The equality can be seen from

$$
\begin{aligned}
&\frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}d\mathbf{r}'\,\tilde{\rho}_{\sigma}(\mathbf{r})u_{\sigma,\sigma'}(\mathbf{r}-\mathbf{r}')\tilde{\rho}_{\sigma'}(\mathbf{r}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}d\mathbf{r}'\sum_{j}\delta(\mathbf{r}-\mathbf{r}_{\sigma j})u_{\sigma,\sigma'}(\mathbf{r}-\mathbf{r}')\tilde{\rho}_{\sigma'}(\mathbf{r}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}'\,\tilde{\rho}_{\sigma'}(\mathbf{r}')\int d\mathbf{r}\,u_{\sigma,\sigma'}(\mathbf{r}-\mathbf{r}')\sum_{j}\delta(\mathbf{r}-\mathbf{r}_{\sigma j}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}'\,\tilde{\rho}_{\sigma'}(\mathbf{r}')\sum_{j}\int d\mathbf{r}\,u_{\sigma,\sigma'}(\mathbf{r}-\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}_{\sigma j}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\int d\mathbf{r}'\,\tilde{\rho}_{\sigma'}(\mathbf{r}')\sum_{j}u_{\sigma,\sigma'}(\mathbf{r}_{\sigma j}-\mathbf{r}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{j}\int d\mathbf{r}'\,\tilde{\rho}_{\sigma'}(\mathbf{r}')u_{\sigma,\sigma'}(\mathbf{r}_{\sigma j}-\mathbf{r}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{j}\int d\mathbf{r}'\sum_{k}\delta(\mathbf{r}-\mathbf{r}_{\sigma' k})u_{\sigma,\sigma'}(\mathbf{r}_{\sigma j}-\mathbf{r}') \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{j}\sum_{k}\int d\mathbf{r}'\,u_{\sigma,\sigma'}(\mathbf{r}_{\sigma j}-\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}_{\sigma' k}) \\
&= \frac{1}{2}\sum_{\sigma,\sigma'}\sum_{j}\sum_{k}u_{\sigma,\sigma'}(\mathbf{r}_{\sigma j}-\mathbf{r}_{\sigma' k}) \\
&= \frac{1}{2}\sum_{j,k}\sum_{\sigma,\sigma'}u_{\sigma,\sigma'}(\mathbf{r}_{\sigma j}-\mathbf{r}_{\sigma' k})
\end{aligned}
\tag{56}
$$

In the two-bead model, the interaction energies between segments of different types separated by distance $\left|\mathbf{r}-\mathbf{r}'\right|$ are:

$$
u_{A,A}(\left|\mathbf{r}-\mathbf{r}'\right|) = u_{AA}\delta(\mathbf{r}-\mathbf{r}') \tag{57}
$$

$$
u_{B,B}(\left|\mathbf{r}-\mathbf{r}'\right|) = u_{BB}\delta(\mathbf{r}-\mathbf{r}') \tag{58}
$$

$$u_{A,B}(|\mathbf{r}-\mathbf{r}'|) = u_{B,A}(|\mathbf{r}-\mathbf{r}'|) = u_{AB}\delta(\mathbf{r}-\mathbf{r}') \tag{59}$$

where u_{AA}, u_{BB}, u_{AB} are the intersegment excluded volumes arising from the short range interactions, δ is the Dirac delta function. It follows that eq. (55) can be reduced to

$$\begin{aligned}
\beta U_1(\mathbf{r}^{2n}) &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{A,A}(|\mathbf{r}-\mathbf{r}'|)\tilde{\rho}_A(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{A,B}(|\mathbf{r}-\mathbf{r}'|)\tilde{\rho}_B(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r})u_{B,A}(|\mathbf{r}-\mathbf{r}'|)\tilde{\rho}_A(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r})u_{B,B}(|\mathbf{r}-\mathbf{r}'|)\tilde{\rho}_B(\mathbf{r}') \\
&= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{AA}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_A(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{AB}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_B(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r})u_{AB}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_A(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r})u_{BB}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_B(\mathbf{r}') \\
&= \frac{1}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\int d\mathbf{r}'\,u_{AA}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_A(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\int d\mathbf{r}'\,u_{AB}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_B(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})\int d\mathbf{r}'\,u_{AB}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_A(\mathbf{r}') \\
&+\frac{1}{2}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})\int d\mathbf{r}'\,u_{BB}\delta(\mathbf{r}-\mathbf{r}')\tilde{\rho}_B(\mathbf{r}') \\
&= \frac{1}{2}u_{AA}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + \frac{1}{2}u_{AB}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&+\frac{1}{2}u_{AB}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + \frac{1}{2}u_{BB}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= \frac{u_{AA}}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})^2 + \frac{u_{BB}}{2}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})^2 + u_{AB}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})
\end{aligned} \tag{60}$$

By applying the incompressible condition $\rho_0 = \tilde{\rho}_A(\mathbf{r}) + \tilde{\rho}_B(\mathbf{r})$, the first integral in the last line of above equation can be evaluated as

$$\begin{aligned}
&\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})^2 \\
&= \int d\mathbf{r}\left[\frac{1}{2}\;\tilde{\rho}_A(\mathbf{r}) + \tilde{\rho}_B(\mathbf{r})\;^2 - \frac{1}{2}\tilde{\rho}_B(\mathbf{r})^2 - \tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{1}{2}\tilde{\rho}_A(\mathbf{r})^2\right] \\
&= \int d\mathbf{r}\left[\frac{1}{2}{\rho_0}^2 - \tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{1}{2}\;\tilde{\rho}_A(\mathbf{r})^2 - \tilde{\rho}_B(\mathbf{r})^2\;\right] \\
&= \int d\mathbf{r}\left[\frac{1}{2}{\rho_0}^2 - \tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{1}{2}\;\tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\quad\tilde{\rho}_A(\mathbf{r}) + \tilde{\rho}_B(\mathbf{r})\;\right] \\
&= \int d\mathbf{r}\left[\frac{1}{2}{\rho_0}^2 - \tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{1}{2}\rho_0\left(\tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\right)\right] \\
&= \frac{1}{2}\int d\mathbf{r}\left({\rho_0}^2 + \rho_0\tilde{\rho}_A(\mathbf{r}) - \rho_0\tilde{\rho}_B(\mathbf{r})\right) - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= \frac{{\rho_0}^2}{2}\int d\mathbf{r} + \frac{\rho_0}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r}) - \frac{\rho_0}{2}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r}) - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= \frac{{\rho_0}^2 V}{2} + \frac{\rho_0}{2}\int d\mathbf{r}\sum_{j=1}^{n}\delta(\mathbf{r} - \mathbf{r}_{Aj}) - \frac{\rho_0}{2}\int d\mathbf{r}\sum_{j=1}^{n}\delta(\mathbf{r} - \mathbf{r}_{Bj}) - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= \frac{2n\rho_0}{2} + \frac{n\rho_0}{2} - \frac{n\rho_0}{2} - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= n\rho_0 - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})
\end{aligned} \tag{61}$$

The second integral is evaluated similary,

$$\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})^2 = n\rho_0 - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \tag{62}$$

Substituting eq (61) and (62) into eq (60), we have

$$\begin{aligned}
&\beta U_1(\mathbf{r}^{2n}) \\
&= \frac{u_{AA}}{2}\;n\rho_0 - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&+\frac{u_{BB}}{2}\;n\rho_0 - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&+u_{AB}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= \frac{2u_{AB} - u_{AA} - u_{BB}}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{u_{AA} + u_{BB}}{2}n\rho_0 \\
&= v_0\chi\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{u_{AA} + u_{BB}}{2}n\rho_0
\end{aligned} \tag{63}$$

where v_0=1/ρ_0 is the volume of a statistical segment (here the volume of the bead), and χ is just the Flory-Huggins interaction parameter:

$$\chi = \frac{2u_{AB} - u_{AA} - u_{BB}}{2v_0} \tag{64}$$

The constant term in eq 63 can be ignored since it has no thermodynamic consequence. Finally we have

$$\beta U_1(\mathbf{r}^{2n}) = v_0\chi\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \tag{65}$$

The canonical partition function for the two-bead system has the usual form

$$Z = \frac{1}{n!(\lambda_T^3)^{2n}} \int d\mathbf{r}^{2n} \exp\left[-\beta U_0(\mathbf{r}^{2n}) - \beta U_1(\mathbf{r}^{2n})\right] \delta\left[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\right] \tag{66}$$

where 1/*n*! corrects the fact of *n* indistinguishable two-bead chains and

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \tag{67}$$

is the thermal wavelength, *m* is the mass of an atom, and *h* is the Planck constant. The object $\delta\left[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\right]$ denotes a functional delta function that imposes a local incompressibility constraint. With the potential energies given in eq. (52) and (65), we can write the partition function as

$$Z = \frac{1}{n!(\lambda_T^3)^{2n}} \int d\mathbf{r}^{2n} \exp\left[-\sum_{j=1}^{n} \frac{\lambda}{2} \left|\mathbf{r}_{Ai} - \mathbf{r}_{Bi}\right|^2 - v_0 \chi \int d\mathbf{r} \tilde{\rho}_A(\mathbf{r}) \tilde{\rho}_B(\mathbf{r})\right] \delta\left[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\right]$$

(68)

To transform the canonical partition function in the above equation into statistical field theory, the Hubbard-Stratonovich transformation is performed. In eq. (68), $Z[\tilde{\rho}_A(\mathbf{r}), \tilde{\rho}_B(\mathbf{r})]$ is a functional of $\tilde{\rho}_A(\mathbf{r})$ and $\tilde{\rho}_B(\mathbf{r})$. By utilizing eq. (50) twice, we have

$$\begin{aligned} Z[\tilde{\rho}_A, \tilde{\rho}_B] &= \int \mathcal{D}\rho_A Z[\rho_A, \tilde{\rho}_B] \delta[\rho_A - \tilde{\rho}_A] \\ &= \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B Z[\rho_A, \rho_B] \delta[\rho_A - \tilde{\rho}_A] \delta[\rho_B - \tilde{\rho}_B] \end{aligned} \tag{69}$$

Inserting the functional form of *Z* in eq. (68) into the last line of eq. (69), we have

$$\begin{aligned} Z = &\frac{1}{n!(\lambda_T^3)^{2n}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int d\mathbf{r}^{2n} \exp\left[-\sum_{j=1}^{n} \frac{\lambda}{2} \left|\mathbf{r}_{Ai} - \mathbf{r}_{Bi}\right|^2 - v_0 \chi \int d\mathbf{r} \rho_A(\mathbf{r}) \rho_B(\mathbf{r})\right] \\ &\times \delta\left[\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})\right] \delta[\rho_A(\mathbf{r}) - \tilde{\rho}_A(\mathbf{r})] \delta[\rho_B(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})] \end{aligned} \tag{70}$$

The delta functionals in the above are then replaced by the complex exponential representation introduced in eq. (51), which leads to

$$
\begin{aligned}
Z &= \frac{1}{n!(\lambda_T^3)^{2n}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int d\mathbf{r}^{2n} \exp\left[-\sum_{j=1}^{n} \frac{\lambda}{2} \left| \mathbf{r}_{Ai} - \mathbf{r}_{Bi} \right|^2 - v_0 \chi \int d\mathbf{r} \rho_A(\mathbf{r}) \rho_B(\mathbf{r}) \right] \\
&\times \int \mathcal{D}\xi \exp \;\; i \int d\mathbf{r} \xi(\mathbf{r}) [1 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] \\
&\times \int \mathcal{D}w_A \exp \;\; i \int d\mathbf{r} w_A(\mathbf{r}) [\rho_A(\mathbf{r}) - \tilde{\rho}_A(\mathbf{r})] \\
&\times \int \mathcal{D}w_B \exp \;\; i \int d\mathbf{r} w_B(\mathbf{r}) [\rho_B(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})] \\
&= \frac{1}{n!(\lambda_T^3)^{2n}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int d\mathbf{r}^{2n} \exp\left[-\sum_{j=1}^{n} \frac{\lambda}{2} \left| \mathbf{r}_{Ai} - \mathbf{r}_{Bi} \right|^2 - v_0 \chi \int d\mathbf{r} \rho_A(\mathbf{r}) \rho_B(\mathbf{r}) \right] \\
&\int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}\xi \exp \left\{ i \int d\mathbf{r} \left[w_A(\mathbf{r}) \rho_A(\mathbf{r}) + w_B(\mathbf{r}) \rho_B(\mathbf{r}) + \xi(\mathbf{r}) [\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] \right] \right\} \\
&\times \exp \left\{ i \int d\mathbf{r} \left[w_A(\mathbf{r}) \tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r}) \tilde{\rho}_B(\mathbf{r}) \right] \right\}
\end{aligned}
\tag{71}
$$

The last line of above equation is $\mathbf{r}^{2n}$ dependent, which can be seen from

$$
\begin{aligned}
&\int d\mathbf{r} \left[w_A(\mathbf{r}) \tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r}) \tilde{\rho}_B(\mathbf{r}) \right] \\
&= \int d\mathbf{r} w_A(\mathbf{r}) \tilde{\rho}_A(\mathbf{r}) + \int d\mathbf{r} w_B(\mathbf{r}) \tilde{\rho}_B(\mathbf{r}) \\
&= \int d\mathbf{r} w_A(\mathbf{r}) \sum_{j=1}^{n} \delta(\mathbf{r} - \mathbf{r}_{Aj}) + \int d\mathbf{r} w_B(\mathbf{r}) \sum_{j=1}^{n} \delta(\mathbf{r} - \mathbf{r}_{Bj}) \\
&= \sum_{j=1}^{n} \int d\mathbf{r} w_A(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_{Aj}) + \sum_{j=1}^{n} \int d\mathbf{r} w_B(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_{Bj}) \\
&= \sum_{j=1}^{n} w_A(\mathbf{r}_{Aj}) + \sum_{j=1}^{n} w_B(\mathbf{r}_{Bj}) \\
&= \sum_{j=1}^{n} \left[w_A(\mathbf{r}_{Aj}) + w_B(\mathbf{r}_{Bj}) \right]
\end{aligned}
\tag{72}
$$

U_0 is also $\mathbf{r}^{2n}$ dependent and all other terms in eq. (71) are $\mathbf{r}^{2n}$ independent. Therefore, we can rearrange eq. (71) into two parts, one is $\mathbf{r}^{2n}$ dependent and the other is $\mathbf{r}^{2n}$ independent:

$$
\begin{aligned}
Z &= \frac{1}{n!(\lambda_T^3)^{2n}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}\xi \\
&\exp \;\; \int d\mathbf{r} \left[i w_A(\mathbf{r}) \rho_A(\mathbf{r}) + i w_B(\mathbf{r}) \rho_B(\mathbf{r}) + i\xi(\mathbf{r}) [\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] - v_0 \chi \rho_A(\mathbf{r}) \rho_B(\mathbf{r}) \right] \\
&\int d\mathbf{r}^{2n} \exp \left\{ -\sum_{j=1}^{n} \left[\frac{\lambda}{2} \left| \mathbf{r}_{Ai} - \mathbf{r}_{Bi} \right|^2 + i w_A(\mathbf{r}_{Aj}) + i w_B(\mathbf{r}_{Bj}) \right] \right\}
\end{aligned}
\tag{73}
$$

Now, let’s look closely at the last line of above equation. It can be evaluated as

$$
\begin{aligned}
&\int d\mathbf{r}^{2n} \exp \left\{ -\sum_{j=1}^{n} \left[\frac{\lambda}{2} \left| \mathbf{r}_{Ai} - \mathbf{r}_{Bi} \right|^2 + i w_A(\mathbf{r}_{Aj}) + i w_B(\mathbf{r}_{Bj}) \right] \right\} \\
&= \int d\mathbf{r}_{A1} d\mathbf{r}_{B1} \exp \left[-\frac{\lambda}{2} \left| \mathbf{r}_{A1} - \mathbf{r}_{B1} \right|^2 - i w_A(\mathbf{r}_{A1}) - i w_B(\mathbf{r}_{B1}) \right] \\
&\int d\mathbf{r}_{A2} d\mathbf{r}_{B2} \exp \left[-\frac{\lambda}{2} \left| \mathbf{r}_{A2} - \mathbf{r}_{B2} \right|^2 - i w_A(\mathbf{r}_{A2}) - i w_B(\mathbf{r}_{B2}) \right] \\
&\cdots \int d\mathbf{r}_{An} d\mathbf{r}_{Bn} \exp \left[-\frac{\lambda}{2} \left| \mathbf{r}_{An} - \mathbf{r}_{Bn} \right|^2 - i w_A(\mathbf{r}_{An}) - i w_B(\mathbf{r}_{Bn}) \right] \\
&= \left\{ \int d\mathbf{r}_A d\mathbf{r}_B \exp \left[-\frac{\lambda}{2} \left| \mathbf{r}_A - \mathbf{r}_B \right|^2 - i w_A(\mathbf{r}_A) - i w_B(\mathbf{r}_B) \right] \right\}^n
\end{aligned}
\tag{74}
$$

Remarkably, the integral in the last line is just the single-chain partition function in the external field that is internally generated in the many-chain two-bead systems:

$$Z_s = \int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right] \tag{75}$$

Since there are only two beads in a single chain, there is no need to go through the tedious procedures that are introduced in section 4 for long chain polymers. However, it is still convenient to define a normalized single-chain partition function

$$Q[iw_A, iw_B] = \frac{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]}{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2\right]} \tag{76}$$

where the denominator in the right hand side of above equation can be integrated analytically:

$$\begin{aligned}
&\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2\right] \\
&= \int d\mathbf{r}_B \int d\mathbf{r}_A \exp\left[-\frac{\lambda}{2}(\mathbf{r}_A - \mathbf{r}_B)^2\right] \\
&= \int d\mathbf{r}_B \int_{-\infty}^{\infty} d(\mathbf{r}_A - \mathbf{r}_B) \exp\left[-\frac{\lambda}{2}(\mathbf{r}_A - \mathbf{r}_B)^2\right] \\
&= \int d\mathbf{r}_B \int_{-\infty}^{\infty} d^3 r \exp\left(-\frac{\lambda}{2}\mathbf{r}^2\right) \\
&= \int d\mathbf{r}_B \left(\frac{2\pi}{\lambda}\right)^{\frac{3}{2}} \\
&= \left(\frac{2\pi}{\lambda}\right)^{\frac{3}{2}} \int d\mathbf{r}_B \\
&= V\left(\frac{2\pi}{\lambda}\right)^{\frac{3}{2}}
\end{aligned} \tag{77}$$

It follows that

$$Z_s = V\left(\frac{2\pi}{\lambda}\right)^{\frac{3}{2}} Q[iw_A, iw_B] \tag{78}$$

and

$$\begin{aligned}
(Z_s)^n &= \left[V\left(\frac{2\pi}{\lambda}\right)^{\frac{3}{2}} Q[iw_A, iw_B]\right]^n \\
&= \left[V\left(\frac{2\pi}{\lambda}\right)^{\frac{3}{2}}\right]^n \exp\quad n\ln Q[iw_A, iw_B]
\end{aligned} \tag{79}$$

Upon combining eq. (73) and eq. (79), the particle-to-field transformation is complete. The canonical partition function can be expressed as the following statistical field theory:

$$Z = Z_0 \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}\xi \exp(-H) \tag{80}$$

where the functional

$$H = \int d\mathbf{r} \left[v_0 \chi \rho_A(\mathbf{r})\rho_B(\mathbf{r}) - iw_A(\mathbf{r})\rho_A(\mathbf{r}) - iw_B(\mathbf{r})\rho_B(\mathbf{r}) - i\xi(\mathbf{r})[\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] \right] - n \ln Q[iw_A, iw_B] \tag{81}$$

is referred to as an "effective Hamiltonian", and the prefactor is

$$Z_0 = \frac{1}{n!(\lambda_T^3)^{2n}} \left[V \left(\frac{2\pi}{\lambda} \right)^{\frac{3}{2}} \right]^n \tag{82}$$

Before we proceed to calculate the average properties, among which the average local bead (A or B) number density $\langle \tilde{\rho}_\sigma(\mathbf{r}) \rangle$ of this two-bead chain system is of primary interest, we first establish a relation between the single-chain density operator $\tilde{\rho}_\sigma^1(\mathbf{r})$ and the normalized single-chain partition function *Q*. The definition of the single-chain density operator is

$$\tilde{\rho}_\sigma^1(\mathbf{r}) = \delta(\mathbf{r}_\sigma - \mathbf{r}) \tag{83}$$

The relation is given by

$$\tilde{\rho}_A^1(\mathbf{r}) = -\frac{\delta \ln Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}{\delta[iw_A(\mathbf{r})]} \tag{84}$$

$$\tilde{\rho}_B^1(\mathbf{r}) = -\frac{\delta \ln Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}{\delta[iw_B(\mathbf{r})]} \tag{85}$$

To verify above relation, we invoke one of the properties of functional derivatives:

$$\begin{aligned} \frac{\delta F[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r}')} &= \frac{\delta F[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \frac{\delta \rho(\mathbf{r}')}{\delta \rho(\mathbf{r})} \\ &= \frac{\delta F[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}') \end{aligned} \tag{86}$$

Thus, it is easy to show that eq. (84) is correct:

$$
\begin{aligned}
&-\frac{\delta \ln Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}{\delta[iw_A(\mathbf{r})]} \\
&= -\frac{1}{Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}\frac{\delta Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}{\delta[iw_A(\mathbf{r})]} \\
&= -\frac{\delta(\mathbf{r}_A-\mathbf{r})}{Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}\frac{\delta Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}{\delta[iw_A(\mathbf{r}_A)]} \\
&= -\frac{\delta(\mathbf{r}_A-\mathbf{r})}{Q[iw_A(\mathbf{r}_A), iw_B(\mathbf{r}_B)]}\frac{\delta\left\{\frac{1}{V}\left(\frac{2\pi}{\lambda}\right)^{-\frac{3}{2}}\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A-\mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]\right\}}{\delta[iw_A(\mathbf{r}_A)]} \\
&= -\frac{\frac{1}{V}\left(\frac{2\pi}{\lambda}\right)^{-\frac{3}{2}}\delta(\mathbf{r}_A-\mathbf{r})}{Q[w_A(\mathbf{r}_A), w_B(\mathbf{r}_B)]}\int d\mathbf{r}_A d\mathbf{r}_B \frac{\delta \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A-\mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]}{\delta[iw_A(\mathbf{r}_A)]} \\
&= -\frac{\frac{1}{V}\left(\frac{2\pi}{\lambda}\right)^{-\frac{3}{2}}\delta(\mathbf{r}_A-\mathbf{r})}{Q[w_A(\mathbf{r}_A), w_B(\mathbf{r}_B)]}\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A-\mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]\frac{\delta\left[-iw_A(\mathbf{r}_A)\right]}{\delta[iw_A(\mathbf{r}_A)]} \\
&= \frac{\delta(\mathbf{r}_A-\mathbf{r})}{Q[w_A(\mathbf{r}_A), w_B(\mathbf{r}_B)]}\int d\mathbf{r}_A d\mathbf{r}_B \frac{1}{V}\left(\frac{2\pi}{\lambda}\right)^{-\frac{3}{2}}\exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A-\mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right] \\
&= \frac{\delta(\mathbf{r}_A-\mathbf{r})}{Q[w_A(\mathbf{r}_A), w_B(\mathbf{r}_B)]}Q[w_A(\mathbf{r}_A), w_B(\mathbf{r}_B)] \\
&= \delta(\mathbf{r}_A-\mathbf{r}) \\
&= \tilde{\rho}_A^1(\mathbf{r})
\end{aligned} \tag{87}
$$

Eq. (85) can be proved similarly. The single-chain density operator $\tilde{\rho}_\sigma^1(\mathbf{r})$ is important because we can conveniently find its ensemble average based on the approach sketched in **section 3**. With the knowledge of the single-chain density operator, it is straightforward to calculate the average local bead number density using

$$\left\langle \tilde{\rho}_\sigma(\mathbf{r})\right\rangle = n\left\langle \tilde{\rho}_\sigma^1(\mathbf{r})\right\rangle \tag{88}$$

It is important to point out that the equality in eq. (88) is universal for any many-chain model with polymer chains described by the continuous Gaussian chain model whose ends are free. Therefore, the complex many-chain system is effectively reduced to the system of a single chain in external field. Note the external field here is generated internally due to long-range interactions.

To prove eq. (88), we will follow the approach presented in Fredrickson's book p.141-142. The partition function in eq. (66) is augmented with a "source term" involving a field *J*(**r**) that is conjugate to the microscopic density:

$$\begin{aligned} Z[J_A, J_B] = \frac{1}{n!(\lambda_T^3)^{2n}} & \int d\mathbf{r}^{2n} \exp\Big[-\beta U_0(\mathbf{r}^{2n}) - \beta U_1(\mathbf{r}^{2n})\Big] \\ & \times \exp\Big[-\int d\mathbf{r}\, J(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) - \int d\mathbf{r}\, J(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\Big] \\ & \times \delta\big[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\big] \end{aligned} \tag{89}$$

The logarithm of *Z* is a generating functional in the sense that functional derivatives with respect to $J_\sigma(\mathbf{r})$ provide expressions from the connected (cumulant) correlation functions of density. In particular,

$$\big\langle \tilde{\rho}_\sigma(\mathbf{r}) \big\rangle = -\frac{\delta \ln Z[J_A, J_B]}{\delta J_\sigma(\mathbf{r})}\Big|_{J_A=0, J_B=0} \tag{90}$$

In order to compute the derivatives on the right-hand side of the above equation, it is helpful to transform to a field-theoretic representation of *Z* by retracing that led from eq. (66) to eq. (80). One obtains the following field theory:

$$Z = Z_0 \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}\xi \exp\ -H[J_A, J_B] \tag{91}$$

$$\begin{aligned} H[J_A, J_B] = -\int d\mathbf{r} \big[& i w_A(\mathbf{r})\rho_A(\mathbf{r}) + i w_B(\mathbf{r})\rho_B(\mathbf{r}) + i\xi(\mathbf{r})[\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] - v_0 \chi \rho_A(\mathbf{r})\rho_B(\mathbf{r}) \big] \\ & - n \ln Q[i w_A + J_A, i w_B + J_B] \end{aligned}$$

(92)

where J_σ enters the effective Hamiltonian only as a shift in the argument of *Q*. It follows that

$$Z[J_A = 0, J_B = 0] = Z \tag{93}$$

$$H[J_A = 0, J_B = 0] = H \tag{94}$$

The right-hand side of eq. (88) can thus be evaluated as

$$\begin{aligned} \big\langle \tilde{\rho}_\sigma(\mathbf{r}) \big\rangle &= \left\langle -n \frac{\delta \ln Q[i w_A + J_A, i w_B + J_B]}{\delta J_\sigma}\Big|_{J_A=0, J_B=0} \right\rangle \\ &= \left\langle -n \frac{\delta \ln Q[i w_A + J_A, i w_B + J_B]}{\delta [i w_A + J_A]} \frac{\delta [i w_A + J_A]}{\delta J_\sigma}\Big|_{J_A=0, J_B=0} \right\rangle \\ &= \left\langle -n \frac{\delta \ln Q[i w_A + J_A, i w_B + J_B]}{\delta [i w_A + J_A]}\Big|_{J_A=0, J_B=0} \right\rangle \\ &= n \left\langle -\frac{\delta \ln Q[i w_A, i w_B]}{\delta [i w_A]} \right\rangle \end{aligned} \tag{95}$$

Inserting eq. (84) or eq. (85) into the above equation, eq. (88) is recovered.

Finally, It is easy to calculate the ensemble average of the single-chain density operator

$$
\begin{aligned}
\left\langle \tilde{\rho}_A^1(\mathbf{r}) \right\rangle &= \frac{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]\tilde{\rho}_A^1(\mathbf{r})}{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]} \\
&= \frac{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]\delta(\mathbf{r}_A - \mathbf{r})}{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]} \\
&= \frac{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}) - iw_B(\mathbf{r}_B)\right]}{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]} \\
&= \frac{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_B(\mathbf{r}_B)\right]}{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]}\exp\left[-iw_A(\mathbf{r})\right]
\end{aligned}
\tag{96}
$$

and similarly

$$
\left\langle \tilde{\rho}_B^1(\mathbf{r}) \right\rangle = \frac{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_B)\right]}{\int d\mathbf{r}_A d\mathbf{r}_B \exp\left[-\frac{\lambda}{2}\left|\mathbf{r}_A - \mathbf{r}_B\right|^2 - iw_A(\mathbf{r}_A) - iw_B(\mathbf{r}_B)\right]}\exp\left[-iw_B(\mathbf{r})\right] \tag{97}
$$

Now that we have the tools for calculating the ensemble average densities for A and B beads, we are ready to derive the self-consistent field theory. The self-consistent field theory is obtained by imposing the mean-field approximation to the statistical field theory. The mean-field SCF equations are obtained by the saddle-approximation, where one sets

$$
\frac{\delta H}{\delta \rho_A} = 0 \tag{98}
$$

$$
\frac{\delta H}{\delta \rho_B} = 0 \tag{99}
$$

$$
\frac{\delta H}{\delta \eta} = 0 \tag{100}
$$

It is easy to find all above variations which are

$$
w_A(\mathbf{r}) = v_0 \chi \rho_B(\mathbf{r}) + \xi(\mathbf{r}) \tag{101}
$$

$$
w_B(\mathbf{r}) = v_0 \chi \rho_A(\mathbf{r}) + \xi(\mathbf{r}) \tag{102}
$$

$$
\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r}) = 0 \tag{103}
$$

where all field variables are pure imaginary.

5. Many-chain model for A-B block copolymers

In this section, we will consider a more complicated system: A-B diblock copolymers (Model E in Fredrickson’s book p159-161). In principle, the techniques derived in the previous section are generally applicable. Practically, however, one must pay attention to the effect of joint point that connects A and B blocks which complicates the construction of the chain propagator.

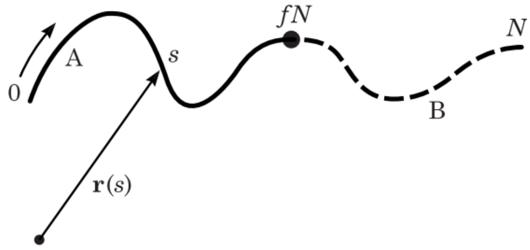


Figure 4

Here, a continuous Gaussian chain model of an A-B diblock copolymer is considered, as shown in Fig. 4. The copolymer has a total polymerization index of *N*; the section 0≤*s*≤*fN* (solid) being comprised of type A segments and the section *fN*≤*s*≤*N* (dashed) comprised of type B segments. The parameter *f* can be interpreted as the fraction of the copolymer that is type A. If the A and B segments are further defined to have equal volumes, then *f* corresponds to the average volume fraction of type A segments. We assume statistical segment lengths are the same for type A segments and type B segments.

By analogy to many-chain model for two-bead chain, we derive the statistical field theory as follows. The potential energy from intramolecular, short-ranged interferences is obtained by extending eq. (2) to an *n*-chain system:

$$U_0[\mathbf{r}^{nN}] = \frac{3k_BT}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 \tag{104}$$

The potential energy from intermolecular interactions among segments and the long-range interferences has the similar general form as eq. (53)

$$\beta U_1(\mathbf{r}^{nN}) = \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^N ds\int_0^N ds'\,u\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right) \tag{105}$$

The segment pair of same type has no pair interactions and the segment of type A interacting with the segment of type B is the same as the segment of type B interacting with the segment of type A. Thus, eq. (105) reduces to

$$\begin{aligned}\beta U_1(\mathbf{r}^{nN}) &= \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^{fN} ds\int_0^{fN} ds' u_{AA}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)\\ &+\frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^{fN} ds\int_{fN}^{N} ds' u_{AB}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)\\ &+\frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_{fN}^{N} ds\int_0^{fN} ds' u_{AB}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)\\ &+\frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_{fN}^{N} ds\int_{fN}^{N} ds' u_{BB}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)\end{aligned}\tag{106}$$

where $u_{A,B}$ denotes the pair interaction energy between segment of type A and segment of type B. With the definition of microscopic density operators

$$\tilde{\rho}_A(\mathbf{r}) = \sum_{j=1}^{n}\int_0^{fN} ds\delta[\mathbf{r}-\mathbf{r}_j(s)]\tag{107}$$

$$\tilde{\rho}_B(\mathbf{r}) = \sum_{j=1}^{n}\int_{fN}^{N} ds\delta[\mathbf{r}-\mathbf{r}_j(s)]\tag{108}$$

eq. (106) can be expresses as

$$\begin{aligned}\beta U_1(\mathbf{r}^{nN}) &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{AA}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\tilde{\rho}_B(\mathbf{r}')\\ &+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r})u_{BB}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\tilde{\rho}_B(\mathbf{r}')\\ &+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{AB}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\tilde{\rho}_B(\mathbf{r}')\\ &+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r})u_{AB}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\tilde{\rho}_A(\mathbf{r}')\end{aligned}\tag{109}$$

It can be seen from

$$\begin{aligned}&\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_A(\mathbf{r})u_{AB}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\tilde{\rho}_B(\mathbf{r}')\\ &= \int d\mathbf{r}\int d\mathbf{r}'\sum_{j=1}^{n}\int_0^{fN} ds\delta[\mathbf{r}-\mathbf{r}_j(s)]u_{AB}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\tilde{\rho}_B(\mathbf{r}')\\ &= \sum_{j=1}^{n}\int_0^{fN} ds\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r}')\int d\mathbf{r}\,u_{AB}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)\delta[\mathbf{r}-\mathbf{r}_j(s)]\\ &= \sum_{j=1}^{n}\int_0^{fN} ds\int d\mathbf{r}'\,\tilde{\rho}_B(\mathbf{r}')u_{A,B}\left(\left|\mathbf{r}_j(s)-\mathbf{r}'\right|\right)\\ &= \sum_{j=1}^{n}\int_0^{fN} ds\int d\mathbf{r}'\sum_{k=1}^{n}\int_{fN}^{N} ds'\,\delta[\mathbf{r}'-\mathbf{r}_k(s')]u_{AB}\left(\left|\mathbf{r}_j(s)-\mathbf{r}'\right|\right)\\ &= \sum_{j=1}^{n}\int_0^{fN} ds\sum_{k=1}^{n}\int_{fN}^{N} ds'\int d\mathbf{r}'\,u_{AB}\left(\left|\mathbf{r}_j(s)-\mathbf{r}'\right|\right)\delta[\mathbf{r}'-\mathbf{r}_k(s')]\\ &= \sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^{fN} ds\int_{fN}^{N} ds'\,u_{AB}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)\end{aligned}\tag{110}$$

If we further introduce the Flory-type pair interaction energy

$$u_{AA}(|\mathbf{r}-\mathbf{r}'|)=u_{AA}\delta(\mathbf{r}-\mathbf{r}') \tag{111}$$

$$u_{AB}(|\mathbf{r}-\mathbf{r}'|)=u_{AB}\delta(\mathbf{r}-\mathbf{r}') \tag{112}$$

$$u_{AB}(|\mathbf{r}-\mathbf{r}'|)=u_{AB}\delta(\mathbf{r}-\mathbf{r}') \tag{113}$$

Following the same procedure of eq (60), we have

$$\beta U_1(\mathbf{r}^{nN})=\frac{u_{AA}}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})^2+\frac{u_{BB}}{2}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})^2+u_{AB}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \tag{114}$$

By applying the incompressible condition $\rho_0=\tilde{\rho}_A(\mathbf{r})+\tilde{\rho}_B(\mathbf{r})$, the first integral can be evaluated as

$$\begin{aligned}
&\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})^2\\
&=\int d\mathbf{r}\left[\frac{1}{2}\left(\tilde{\rho}_A(\mathbf{r})+\tilde{\rho}_B(\mathbf{r})\right)^2-\frac{1}{2}\tilde{\rho}_B(\mathbf{r})^2-\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})+\frac{1}{2}\tilde{\rho}_A(\mathbf{r})^2\right]\\
&=\int d\mathbf{r}\left[\frac{1}{2}\rho_0{}^2-\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})+\frac{1}{2}\left(\tilde{\rho}_A(\mathbf{r})^2-\tilde{\rho}_B(\mathbf{r})^2\right)\right]\\
&=\int d\mathbf{r}\left[\frac{1}{2}\rho_0{}^2-\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})+\frac{1}{2}\left(\tilde{\rho}_A(\mathbf{r})-\tilde{\rho}_B(\mathbf{r})\right)\left(\tilde{\rho}_A(\mathbf{r})+\tilde{\rho}_B(\mathbf{r})\right)\right]\\
&=\int d\mathbf{r}\left[\frac{1}{2}\rho_0{}^2-\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})+\frac{1}{2}\rho_0\left(\tilde{\rho}_A(\mathbf{r})-\tilde{\rho}_B(\mathbf{r})\right)\right]\\
&=\frac{1}{2}\int d\mathbf{r}\left(\rho_0{}^2+\rho_0\tilde{\rho}_A(\mathbf{r})-\rho_0\tilde{\rho}_B(\mathbf{r})\right)-\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\\
&=\frac{\rho_0{}^2}{2}\int d\mathbf{r}+\frac{\rho_0}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})-\frac{\rho_0}{2}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})-\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\\
&=\frac{\rho_0{}^2V}{2}+\frac{\rho_0}{2}\int d\mathbf{r}\sum_{j=1}^{n}\int_0^{fN}ds\delta[\mathbf{r}-\mathbf{r}_j(s)]\\
&-\frac{\rho_0}{2}\int d\mathbf{r}\sum_{j=1}^{n}\int_{fN}^{N}ds\delta[\mathbf{r}-\mathbf{r}_j(s)]-\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\\
&=\frac{nN\rho_0}{2}+\frac{nfN\rho_0}{2}-\frac{n(N-fN)\rho_0}{2}-\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\\
&=fnN\rho_0-\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})
\end{aligned} \tag{115}$$

Similarly, the other integral can be evaluated to be

$$\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})^2=(1-f)nN\rho_0-\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \tag{116}$$

Substituting eq (115) and (116) into eq (114), we have

$$
\begin{aligned}
&\beta U_1(\mathbf{r}^{nN}) = \\
&\frac{u_{AA}}{2}\ fnN\rho_0 - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&+\frac{u_{BB}}{2}\Big[(1-f)nN\rho_0 - \int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\Big] \\
&+u_{AB}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
&= \frac{2u_{AB} - u_{AA} - u_{BB}}{2}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{fu_{AA} + (1-f)u_{BB}}{2}nN\rho_0 \\
&= v_0\chi\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + \frac{fu_{AA} + (1-f)u_{BB}}{2}nN\rho_0
\end{aligned}
\tag{117}
$$

The Flory-Huggins interaction parameter is again given by

$$
\chi = \frac{2u_{AB} - u_{AA} - u_{BB}}{2v_0}
\tag{118}
$$

and the constant term is ignored to give the final form of Flory-type energy

$$
\beta U_1(\mathbf{r}^{nN}) = v_0\chi\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})
\tag{119}
$$

The canonical partition function of diblock copolymers is again similar to that of two-bead chain system

$$
Z = \frac{1}{n!(\lambda_T^3)^{nN}}\int d\mathbf{r}^{nN}\exp\Big[-\beta U_0(\mathbf{r}^{nN}) - \beta U_1(\mathbf{r}^{nN})\Big]\delta\big[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\big]
\tag{120}
$$

Inserting eq. (104) and (119) into above equation, we have

$$
Z = \frac{1}{n!(\lambda_T^3)^{nN}}\int d\mathbf{r}^{nN}\exp\left[-\frac{3k_BT}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 - v_0\chi\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r})\right]\delta\big[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})\big]
\tag{121}
$$

Using the delta functionals, it changes to

$$
\begin{aligned}
Z = &\frac{1}{n!(\lambda_T^3)^{nN}}\int \mathcal{D}\rho_A\int \mathcal{D}\rho_B\int d\mathbf{r}^{nN}\exp\left[-\frac{3k_BT}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 - v_0\chi\int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r})\right] \\
&\times\delta\big[1 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})\big]\delta[\rho_A(\mathbf{r}) - \tilde{\rho}_A(\mathbf{r})]\delta[\rho_B(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})]
\end{aligned}
\tag{122}
$$

The delta functionals are then replaced by their complex exponential representations

$$
\begin{aligned}
Z = {} & \frac{1}{n!(\lambda_T^3)^{nN}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int d\mathbf{r}^{nN} \exp\left[-\frac{3k_BT}{2b^2} \sum_{j=1}^{n} \int_0^N ds \left| \frac{d\mathbf{r}_j(s)}{ds} \right|^2 - v_0\chi \int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r}) \right] \\
& \times \int \mathcal{D}\xi \exp \ \ i \int d\mathbf{r}\xi(\mathbf{r})[1 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] \\
& \times \int \mathcal{D}w_A \exp \ \ i \int d\mathbf{r} w_A(\mathbf{r})[\rho_A(\mathbf{r}) - \tilde{\rho}_A(\mathbf{r})] \\
& \times \int \mathcal{D}w_B \exp \ \ i \int d\mathbf{r} w_B(\mathbf{r})[\rho_B(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r})] \\
= {} & \frac{1}{n!(\lambda_T^3)^{2n}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int d\mathbf{r}^{2n} \exp\left[-\frac{3k_BT}{2b^2} \sum_{j=1}^{n} \int_0^N ds \left| \frac{d\mathbf{r}_j(s)}{ds} \right|^2 - v_0\chi \int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r}) \right] \\
& \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}\xi \exp \left\{ \int d\mathbf{r} \big[w_A(\mathbf{r})\rho_A(\mathbf{r}) + w_B(\mathbf{r})\rho_B(\mathbf{r}) + \xi(\mathbf{r})[\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] \big] \right] \\
& \times \exp \left\{ i \int d\mathbf{r} \big[w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \big] \right\}
\end{aligned}
$$

(123)

The last line of above function can be evaluated the same as eq. (72), which leads to

$$
\begin{aligned}
& \int d\mathbf{r} \big[w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \big] \\
& = \int d\mathbf{r} w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + \int d\mathbf{r} w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) \\
& = \int d\mathbf{r} w_A(\mathbf{r}) \sum_{j=1}^{n} \int_0^{fN} ds \delta[\mathbf{r} - \mathbf{r}_j(s)] + \int d\mathbf{r} w_B(\mathbf{r}) \sum_{j=1}^{n} \int_{fN}^{N} ds \delta[\mathbf{r} - \mathbf{r}_j(s)] \\
& = \sum_{j=1}^{n} \int_0^{fN} ds \int d\mathbf{r} w_A(\mathbf{r}) \delta[\mathbf{r} - \mathbf{r}_j(s)] + \sum_{j=1}^{n} \int_{fN}^{N} ds \int d\mathbf{r} w_B(\mathbf{r}) \delta[\mathbf{r} - \mathbf{r}_j(s)] \\
& = \sum_{j=1}^{n} \int_0^{fN} ds w_A(\mathbf{r}_j(s)) + \sum_{j=1}^{n} \int_{fN}^{N} ds w_B(\mathbf{r}_j(s))
\end{aligned}
\tag{124}
$$

Substitute above equation into eq. (123), we have

$$
\begin{aligned}
Z = {} & \frac{1}{n!(\lambda_T^3)^{nN}} \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}\xi \\
& \exp \ \ \int d\mathbf{r} \big[i w_A(\mathbf{r})\rho_A(\mathbf{r}) + i w_B(\mathbf{r})\rho_B(\mathbf{r}) + i\xi(\mathbf{r})[\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})] - v_0\chi\rho_A(\mathbf{r})\rho_B(\mathbf{r}) \big] \\
& \int d\mathbf{r}^{2n} \exp\left\{ -\sum_{j=1}^{n} \left[\frac{3k_BT}{2b^2} \sum_{j=1}^{n} \int_0^N ds \left| \frac{d\mathbf{r}_j(s)}{ds} \right|^2 + i \int_0^{fN} ds w_A(\mathbf{r}_j(s)) + i \int_{fN}^{N} ds w_B(\mathbf{r}_j(s)) \right] \right\}
\end{aligned}
$$

(125)

The last line of above equation is evaluated as

$$
\begin{aligned}
&\int d\mathbf{r}^{nN}\exp\left\{-\sum_{j=1}^{n}\left[\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2+i\int_0^{fN}dsw_A(\mathbf{r}_j(s))+i\int_{fN}^{N}dsw_B(\mathbf{r}_j(s))\right]\right\}\\
&=\int d\mathbf{r}_{A1}^{fN}d\mathbf{r}_{B1}^{N-fN}\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}_1(s)}{ds}\right|^2-i\int_0^{fN}dsw_A(\mathbf{r}_1(s))-i\int_{fN}^{N}dsw_B(\mathbf{r}_1(s))\right]\\
&\int d\mathbf{r}_{A2}^{fN}d\mathbf{r}_{B2}^{N-fN}\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}_2(s)}{ds}\right|^2-i\int_0^{fN}dsw_A(\mathbf{r}_2(s))-i\int_{fN}^{N}dsw_B(\mathbf{r}_2(s))\right]\\
&\cdots\int d\mathbf{r}_{An}^{fN}d\mathbf{r}_{Bn}^{N-fN}\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}_n(s)}{ds}\right|^2-i\int_0^{fN}dsw_A(\mathbf{r}_n(s))-i\int_{fN}^{N}dsw_B(\mathbf{r}_n(s))\right]\\
&=\left\{\int d\mathbf{r}_{A}^{fN}d\mathbf{r}_{B}^{N-fN}\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2-i\int_0^{fN}dsw_A(\mathbf{r}(s))-i\int_{fN}^{N}dsw_B(\mathbf{r}(s))\right]\right\}^n\\
&=\left\{\prod_{t=0}^{N}\int d\mathbf{r}(t)\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2-i\int_0^{fN}dsw_A(\mathbf{r}(s))-i\int_{fN}^{N}dsw_B(\mathbf{r}(s))\right]\right\}^n
\end{aligned}
\tag{126}
$$

The integral in the last line of above equation is just the single-chain partition function

$$
Z_s=\prod_{t=0}^{N}\int d\mathbf{r}(t)\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2-i\int_0^{fN}dsw_A(\mathbf{r}(s))-i\int_{fN}^{N}dsw_B(\mathbf{r}(s))\right]
\tag{127}
$$

The first term in the exponential is just the internal energy of a continuous Gaussian chain, the second term describes the interaction between A block and the corresponding external field which is generated internally, and the third term describes the interaction between B block and the corresponding external field.

The chain propagator is defined similarly to eq. (35). However, it has two forms depending on the value of *s*. For 0≤*s*≤*fN*, it is defined as

$$
q(\mathbf{r},s)=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_0^s ds'iw_A[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]
$$

(128)

Retracing the steps from eq. (36) to eq. (40), we can obtain the Fokker-Planck equation

$$
\frac{\partial}{\partial s}q(\mathbf{r},s)=\frac{b^2}{6}\nabla^2q(\mathbf{r},s)-iw_A(\mathbf{r})q(\mathbf{r},s)
\tag{129}
$$

Similarly, for *fN*≤*s*≤*N*, the chain propagator is defined as

$$
\begin{aligned}
q(\mathbf{r},s)=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}&\prod_{t=0}^{s}\int d\mathbf{r}(t)\\
\exp&\left(-\int_0^s ds'\frac{3}{2b^2}\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_0^{fN}ds'iw_A[\mathbf{r}(s')]-\int_{fN}^{s}ds'iw_A[\mathbf{r}(s')]\right)\delta\left[\mathbf{r}(s)-\mathbf{r}\right]
\end{aligned}
\tag{130}
$$

and the resulted Fokker-Planck equation is given by

$$\frac{\partial}{\partial s}q(\mathbf{r},s)=\frac{b^2}{6}\nabla^2 q(\mathbf{r},s)-iw_B(\mathbf{r})q(\mathbf{r},s) \tag{131}$$

The initial condition is

$$q(\mathbf{r},0)=1 \tag{132}$$

The normalized single-chain partition function is obtained by following the steps from eq. (43) to eq. (46)

$$Q[iw_A,iw_B]=\frac{1}{V}\int d\mathbf{r}\,q(\mathbf{r},s)q(\mathbf{r},N-s) \tag{133}$$

In particular, for *s*=0, *Q* is evaluated to be

$$Q[iw_A,iw_B]=\frac{1}{V}\int d\mathbf{r}\,q(\mathbf{r},N) \tag{134}$$

With the definition of *Q*, we now reach the final result of the statistical field theory for diblock copolymer melts:

$$Z=Z_0\int\mathcal{D}\rho_A\int\mathcal{D}\rho_B\int\mathcal{D}w_A\int\mathcal{D}w_B\int\mathcal{D}\xi\exp(-H) \tag{135}$$

where the effective Hamiltonian is

$$H=\int d\mathbf{r}\big[v_0\chi\rho_A(\mathbf{r})\rho_B(\mathbf{r})-iw_A(\mathbf{r})\rho_A(\mathbf{r})-iw_B(\mathbf{r})\rho_B(\mathbf{r})-i\xi(\mathbf{r})[\rho_0-\rho_A(\mathbf{r})-\rho_B(\mathbf{r})]\big]-n\ln Q[iw_A,iw_B] \tag{136}$$

and the explicit form of the prefactor Z_0 is unimportant.

The single-chain partition function describes a single chain in an external field. In light of **section 3**, we can define two single-chain density operators:

$$\tilde{\rho}_A^1(\mathbf{r})=\int_0^{fN}ds\delta[\mathbf{r}-\mathbf{r}(s)] \tag{137}$$

$$\tilde{\rho}_B^1(\mathbf{r})=\int_{fN}^{N}ds\delta[\mathbf{r}-\mathbf{r}(s)] \tag{138}$$

Invoking the universal relation (eq. (88)) between the average segment density and the average single-chain segment density established in **section 4**, we have

$$\left\langle\tilde{\rho}_A(\mathbf{r})\right\rangle=n\left\langle\tilde{\rho}_A^1(\mathbf{r})\right\rangle \tag{139}$$

$$\left\langle\tilde{\rho}_B(\mathbf{r})\right\rangle=n\left\langle\tilde{\rho}_B^1(\mathbf{r})\right\rangle \tag{140}$$

Therefore, we only need to calculate the average single-chain segment densities.

Since the external field exerting on A block is different from that exerting on B block, as can be seen in the single-chain partition function (eq. (127)), it is impossible to calculate the average single-chain segment densities from only *q* propagator. Taking $\left\langle \tilde{\rho}_A^1(\mathbf{r}) \right\rangle$ as an example, we see that

$$
\begin{aligned}
&\left\langle \tilde{\rho}_A^1(\mathbf{r}) \right\rangle \\
&= \frac{1}{Z}\prod_{t=0}^{N}\int d\mathbf{r}(t)\tilde{\rho}_A^1(\mathbf{r})\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 - i\int_0^{fN} dsw_A(\mathbf{r}(s)) - i\int_{fN}^{N} dsw_B(\mathbf{r}(s))\right] \\
&= \frac{1}{Z}\prod_{t=0}^{N}\int d\mathbf{r}(t)\int_0^{fN} ds\delta[\mathbf{r}-\mathbf{r}(s)] \\
&\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - i\int_0^{fN} ds'w_A(\mathbf{r}(s')) - i\int_{fN}^{N} dsw_B(\mathbf{r}(s'))\right] \\
&= \frac{1}{Z}\int_0^{fN} ds\prod_{t=0}^{N}\int d\mathbf{r}(t) \\
&\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - i\int_0^{fN} ds'w_A(\mathbf{r}(s')) - i\int_{fN}^{N} ds'w_B(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)] \\
&= \frac{1}{Z}\int_0^{fN} ds\prod_{t=0}^{N}\int d\mathbf{r}(t)\int d\mathbf{r}(s)\delta[\mathbf{r}-\mathbf{r}(s)] \\
&\exp\left[-\frac{3k_BT}{2b^2}\int_0^N ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - i\int_0^{fN} ds'w_A(\mathbf{r}(s')) - i\int_{fN}^{N} ds'w_B(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)] \\
&= \frac{1}{Z}\left(\frac{2\pi b^2\Delta s}{3}\right)^{\frac{3}{2}N_N}\int_0^{fN} ds \\
&\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left[-\frac{3k_BT}{2b^2}\int_0^s ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - i\int_0^{s} dsw_A(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)] \\
&\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_N-N_s)}\prod_{t=s}^{N}\int d\mathbf{r}(t)\exp\left[-\frac{3k_BT}{2b^2}\int_s^N ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - i\int_s^{fN} ds'w_A(\mathbf{r}(s')) - i\int_{fN}^{N} ds'w_B(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)] \\
&= \frac{Z_0}{ZV}\int_0^{fN} dsq(\mathbf{r},s) \\
&\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_N-N_s)}\prod_{t=s}^{N}\int d\mathbf{r}(t)\exp\left[-\frac{3k_BT}{2b^2}\int_s^N ds\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - i\int_s^{fN} ds'w_A(\mathbf{r}(s')) - i\int_{fN}^{N} ds'w_B(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)]
\end{aligned}
$$

(141)

The last line of above equation is neither *q*(**r**, *s*) nor *q*(**r**, *N*-*s*). However, we can rewrite it to

$$
\begin{aligned}
&\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}(N_N-N_s)}\prod_{t=0}^{N-s}\int d\mathbf{r}(t) \\
&\exp\left[-\frac{3k_BT}{2b^2}\int_0^{N-s} ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2 - \int_0^{(1-f)N} ds'iw_B(\mathbf{r}(s')) - \int_{(1-fN)}^{N-s} ds'iw_A(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(N-s)]
\end{aligned}
$$

(142)

This expression says it has the same structure of the chain propagator *q*, but instead of starting propagation from the end of block A, it starts at the end of block B. Note that the range of *N-s* in the eq. (142) is (1-*f*)*N*≤*s*≤*N*. So we can define a complementary chain propagator q^* when *s* is in the range of (1-*f*)*N*≤*s*≤*N*:

$$q^*(\mathbf{r},s)=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)$$
$$\exp\left[-\frac{3k_BT}{2b^2}\int_0^s ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_0^{(1-f)N}ds'\,iw_B(\mathbf{r}(s'))-\int_{(1-fN)}^{s}ds'\,iw_A(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)]$$

(143)

This q^* also satisfies a Fokker-Planck equation (for (1-*f*)*N*≤*s*≤*N*)

$$\frac{\partial}{\partial s}q^*(\mathbf{r},s)=\frac{b^2}{6}\nabla^2 q^*(\mathbf{r},s)-iw_A(\mathbf{r})q^*(\mathbf{r},s) \tag{144}$$

Using the definition q^* and invoking the definition of *Q*, eq. (141) becomes

$$\left\langle\tilde{\rho}_A^1(\mathbf{r})\right\rangle=\frac{1}{VQ[iw_A(\mathbf{r}),iw_B(\mathbf{r})]}\int_0^{fN}dsq(\mathbf{r},s)q^*(\mathbf{r},N-s) \tag{145}$$

The derivation of the above equation for the segment of type B is similar. By retracing the steps from eq. (141) to eq. (145), we can obtain the average single-chain segment density

$$\left\langle\tilde{\rho}_B^1(\mathbf{r})\right\rangle=\frac{1}{VQ[iw_A(\mathbf{r}),iw_B(\mathbf{r})]}\int_{fN}^{N}dsq(\mathbf{r},s)q^*(\mathbf{r},N-s) \tag{146}$$

In the above, the range for *N-s* is 0≤*s*≤(1-*f*)*N*, and the form of the complementary chain propagator q^* defined in this range is

$$q^*(\mathbf{r},s)=\left(\frac{3}{2\pi b^2\Delta s}\right)^{\frac{3}{2}N_s}\prod_{t=0}^{s}\int d\mathbf{r}(t)\exp\left[-\frac{3k_BT}{2b^2}\int_0^s ds'\left|\frac{d\mathbf{r}(s')}{ds'}\right|^2-\int_0^{s}ds'\,iw_B(\mathbf{r}(s'))\right]\delta[\mathbf{r}-\mathbf{r}(s)]$$

(147)

And it satisfies the following Fokker-Planck equation (for 0≤*s*≤(1-*f*)*N*)

$$\frac{\partial}{\partial s}q^*(\mathbf{r},s)=\frac{b^2}{6}\nabla^2 q^*(\mathbf{r},s)-iw_B(\mathbf{r})q^*(\mathbf{r},s) \tag{148}$$

As long as we find the tools for calculating the ensemble average densities for A and B beads, we are ready to derive the self-consistent field theory. The self-consistent field theory is obtained by imposing the mean-field approximation to the statistical field theory. The mean-field SCF equations are obtained by the saddle-approximation which has the same expressions as in eq. (101), eq. (102), and eq. (103), but with ensemble average densities according to this section.

6. Many-chain model for solutions of A-B diblock copolyelectrolytes

In this section, we will extend the many-chain model for diblock copolymer melts to charged systems. In particular, we will consider A-B diblock copolyelectrolytes in a solution of small-molecules, usually water, with presence of salt. We treat the solvent explicitly, which interacts with polymer segments with a Flory-type interaction. The chains are again taken to be continuous Gaussian chains and the charge distribution can be either smeared (corresponding to strongly dissociating polyelectrolytes, e.g. PAA) and annealed (corresponding to weakly dissociating polyelectrolytes, e.g. polyethylene-poly(acrylic acid) statistical copolymer). We also assume that the counterions dissociated from polyelectrolytes are identical to the ions form salt that carry the same type of charge, and denote cations by + and anions by -. Integer variables $v_+>0$, $v_- < 0$, and v_P are used to denote the valencies of cations, anions and the ions bounded to P (=A, B) polymer segments, respectively.

In this model, besides the potential energy for the continuous Gaussian chain and the potential energy from the intermolecular interactions among polymer segments and solvent molecules, there is an additional energetic contribution arisen from the long-ranged Coulomb interactions. The Coulomb interaction is the most distinctive feature for charged systems. The Coulomb potential acting between an ion with charge eZ_j and a second ion with charge eZ_k, separated by a distance r in a uniform dielectric medium, can be written

$$u_e(r) = \frac{e^2 Z_j Z_k}{\varepsilon r} \tag{149}$$

where cgs units are employed and ε is the dielectric constant. The Coulomb potential is often rewritten in the form

$$u_e(r) = k_B T \frac{l_B Z_j Z_k}{r} \tag{150}$$

where

$$l_B \equiv \frac{e^2}{\varepsilon k_B T} \tag{151}$$

is the so-called Bjerrum length. It defines a length scale at which the electrostatic interaction is comparable to the thermal energy $k_B T$.

The electrostatic interaction energy can be obtained by summing the electric potential of all pairs of charged species across the whole system, which also has the similar general form of eq. (53)

$$\begin{aligned}\beta U_e[\mathbf{r}^{nN+n_+ +n_-}] = {} & \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^N ds\int_0^N ds' u_e(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|) \\ & +\sum_{j=1}^{n}\sum_{k=1}^{n_+}\int_0^N ds u_e(\left|\mathbf{r}_j(s)-\mathbf{r}_k\right|) \\ & +\sum_{j=1}^{n}\sum_{k=1}^{n_-}\int_0^N ds u_e(\left|\mathbf{r}_j(s)-\mathbf{r}_k\right|) \\ & +\frac{1}{2}\sum_{j=1}^{n_+}\sum_{k=1}^{n_+} u_e(\left|\mathbf{r}_j-\mathbf{r}_k\right|) \\ & +\sum_{j=1}^{n_+}\sum_{k=1}^{n_-} u_e(\left|\mathbf{r}_j-\mathbf{r}_k\right|) \\ & +\frac{1}{2}\sum_{j=1}^{n_-}\sum_{k=1}^{n_-} u_e(\left|\mathbf{r}_j-\mathbf{r}_k\right|)\end{aligned} \tag{152}$$

where n, n_+ and n_- are the number of diblock copolymers, cations and anions, respectively. The first to the sixth lines of eq. (152) represent the Coulomb interactions between polymer segments, between polymer segments and cations, between polymer segments and anions, between cations, between cations and anions, and between anions, respectively. The singular interactions of each ion with itself included in eq. (152) only lead to a shift in chemical potential of each species that has no thermodynamic consequence. To write eq. (152) in a compact form, it is helpful to define a microscopic charge density

$$\tilde{\rho}_+(\mathbf{r}) = \sum_{j=1}^{n_+}\delta(\mathbf{r}-\mathbf{r}_j) \tag{153}$$

$$\tilde{\rho}_-(\mathbf{r}) = \sum_{j=1}^{n_-}\delta(\mathbf{r}-\mathbf{r}_j) \tag{154}$$

$$\begin{aligned}\tilde{\rho}_e(\mathbf{r}) = {} & v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN} ds\delta(\mathbf{r}-\mathbf{r}_j(s)) + v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N} ds\delta(\mathbf{r}-\mathbf{r}_j(s)) \\ & +v_+\tilde{\rho}_+(\mathbf{r}) + v_-\tilde{\rho}_-(\mathbf{r})\end{aligned} \tag{155}$$

where α_A and α_B are the degree of ionization for block A and block B, respectively. In writing eq. (155), we have assumed the smeared charge distribution. The charge density operator $\tilde{\rho}_e(\mathbf{r})$ is in units of e. The system satisfies the electroneutrality condition, thus

$$
\begin{aligned}
\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r}) &= \int d\mathbf{r} v_A \alpha_A \sum_{j=1}^{n} \int_0^{fN} ds\delta(\mathbf{r}-\mathbf{r}_j(s)) \\
&\quad + \int d\mathbf{r} v_B \alpha_B \sum_{j=1}^{n} \int_{fN}^{N} ds\delta(\mathbf{r}-\mathbf{r}_j(s)) \\
&\quad + \int d\mathbf{r} v_+ \sum_{j=1}^{n_+} \delta(\mathbf{r}-\mathbf{r}_j) \\
&\quad + \int d\mathbf{r} v_- \sum_{j=1}^{n_-} \delta(\mathbf{r}-\mathbf{r}_j) \\
&= v_A \alpha_A \sum_{j=1}^{n} \int_0^{fN} ds \int d\mathbf{r}\delta(\mathbf{r}-\mathbf{r}_j(s)) \\
&\quad + v_B \alpha_B \sum_{j=1}^{n} \int_{fN}^{N} ds \int d\mathbf{r}\delta(\mathbf{r}-\mathbf{r}_j(s)) \\
&\quad + v_+ \sum_{j=1}^{n_+} \int d\mathbf{r}\delta(\mathbf{r}-\mathbf{r}_j) \\
&\quad + v_- \sum_{j=1}^{n_-} \delta \int d\mathbf{r}(\mathbf{r}-\mathbf{r}_j) \\
&= v_A \alpha_A \sum_{j=1}^{n} \int_0^{fN} ds + v_B \alpha_B \sum_{j=1}^{n} \int_{fN}^{N} ds + v_+ \sum_{j=1}^{n_+} 1 + v_- \sum_{j=1}^{n_-} 1 \\
&= v_A \alpha_A nfN + v_B \alpha_B n(1-f)N + v_+ n_+ + v_- n_- \\
&= 0
\end{aligned}
\qquad (156)
$$

So we have the relation between the numbers of different species:

$$
v_A \alpha_A nfN + v_B \alpha_B n(1-f)N + v_+ n_+ + v_- n_- = 0 \qquad (157)
$$

The electrostatic interaction energy can thus be written

$$
\beta U_e[\mathbf{r}^{nN+n_+ +n_-}] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\, \tilde{\rho}_e(\mathbf{r}) \frac{l_B}{|\mathbf{r}-\mathbf{r}'|} \tilde{\rho}_e(\mathbf{r}') \qquad (158)
$$

This equality can be verified as follows

$$
\begin{aligned}
&\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\tilde{\rho}_e(\mathbf{r})\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\tilde{\rho}_e(\mathbf{r}')\\
&=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}-\mathbf{r}_j(s))+v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}-\mathbf{r}_j(s))+v_+\tilde{\rho}_+(\mathbf{r})+v_-\tilde{\rho}_-(\mathbf{r})\right]\\
&\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))+v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))+v_+\tilde{\rho}_+(\mathbf{r}')+v_-\tilde{\rho}_-(\mathbf{r}')\right]\\
&=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_+\tilde{\rho}_+(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_-\tilde{\rho}_-(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_+\tilde{\rho}_+(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}-\mathbf{r}_j(s))\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_-\tilde{\rho}_-(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_+\tilde{\rho}_+(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_+\tilde{\rho}_+(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_+\tilde{\rho}_+(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_+\tilde{\rho}_+(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_+\tilde{\rho}_+(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_-\tilde{\rho}_-(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_-\tilde{\rho}_-(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_A\alpha_A\sum_{j=1}^{n}\int_0^{fN}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_-\tilde{\rho}_-(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N}ds\delta(\mathbf{r}'-\mathbf{r}_j(s))\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_-\tilde{\rho}_-(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_+\tilde{\rho}_+(\mathbf{r}')\right]\\
&+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\left[v_-\tilde{\rho}_-(\mathbf{r})\right]\frac{l_B}{\left|\mathbf{r}-\mathbf{r}'\right|}\left[v_-\tilde{\rho}_-(\mathbf{r}')\right]
\end{aligned}
$$

(159)

The sum of 1st, 2nd, 3rd and 4th terms after the second equal sign in eq. (159) corresponds to the first term of the right-hand side of eq. (152). Similarly, the sum of 3rd, 7th, 9th, and 10th terms, 4th, 8th, 13th, and 14th terms, 11th terms, the sum of 12th and 15th terms, and 16th terms after the second equal sign in eq. (159) correspond to the 2nd, 3rd, 4th, 5th, and 6th of the right-hand side of eq. (152), respectively.

The potential energy from unperturbed continuous Gaussian chains is still given by (the same as eq. (104))

$$\beta U_0[\mathbf{r}^{nN}] = \frac{3}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 \tag{160}$$

The short-range (e.g. van der Waals) interaction energy of the system is approximated by the energy arisen from Flory-type interactions. Following the treatment analogous in section 5, we can express the short-range interaction energy as

$$\beta U_1(\mathbf{r}^{nN+n_S}) = v_0\chi_{AB}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + v_0\chi_{AS}\int d\mathbf{r}\tilde{\rho}_A(\mathbf{r})\tilde{\rho}_S(\mathbf{r}) + v_0\chi_{BS}\int d\mathbf{r}\tilde{\rho}_B(\mathbf{r})\tilde{\rho}_S(\mathbf{r}) \tag{161}$$

where χ_{AB} is the Flory-Huggins interaction parameter between polymer segments of type A and type B, χ_{AS} is that between the polymer segments of type A and the solvent molecules, and χ_{BS} is that between the polymer segments of type A and the solvent molecules. In the above equation, there are two additional terms describing the Flory-type interactions between polymer segments and solvent molecules compared to eq. (114). In eq. (161), the volumes of the statistical segment (either of type A or B) and the solvent molecule are assumed to be identical. The microscopic segment density and microscopic solvent density are defined to be

$$\tilde{\rho}_A(\mathbf{r}) = \sum_{j=1}^{n}\int_0^{fN} ds\delta[\mathbf{r} - \mathbf{r}_j(s)] \tag{162}$$

$$\tilde{\rho}_B(\mathbf{r}) = \sum_{j=1}^{n}\int_{fN}^{N} ds\delta[\mathbf{r} - \mathbf{r}_j(s)] \tag{163}$$

$$\tilde{\rho}_S(\mathbf{r}) = \sum_{j=1}^{n_S}\delta[\mathbf{r} - \mathbf{r}_j] \tag{164}$$

Combining the potential energies in eq. (158), (160) and (161), we can write the canonical partition function as

$$Z = \frac{1}{n!n_S!n_+!n_-!(\lambda_T^3)^{nN+n_S+n_++n_-}}\int d\mathbf{r}^{nN+n_S+n_++n_-}\exp\Big[-\beta U_0(\mathbf{r}^{nN}) - \beta U_1(\mathbf{r}^{nN+n_S}) - \beta U_e(\mathbf{r}^{nN+n_++n_-})\Big]$$
$$\delta\big[\rho_0 - \tilde{\rho}_A(\mathbf{r}) - \tilde{\rho}_B(\mathbf{r}) - \tilde{\rho}_S(\mathbf{r})\big]\delta\Big(\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\Big)$$

(165)

The next task is to perform a particle-to-field transformation to the above partition function. To present here more clearly, we will do the transformation separately. Since it is not necessary to do transformation on U_0, we first do the transformation for U_1. Upon using the identity involving a delta functional (eq. (50)), we have

$$\begin{aligned}
&\exp\left[-\beta U_1(\mathbf{r}^{nN+n_S})\right]\delta[\rho_0-\tilde{\rho}_A(\mathbf{r})-\tilde{\rho}_B(\mathbf{r})-\tilde{\rho}_S(\mathbf{r})]\\
&=\int\mathcal{D}\rho_A\int\mathcal{D}\rho_B\int\mathcal{D}\rho_S\\
&\exp\left[-v_0\chi_{AB}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r})-v_0\chi_{AS}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_S(\mathbf{r})-v_0\chi_{BS}\int d\mathbf{r}\rho_B(\mathbf{r})\rho_S(\mathbf{r})\right]\\
&\delta[\rho_A(\mathbf{r})-\tilde{\rho}_A(\mathbf{r})]\delta[\rho_B(\mathbf{r})-\tilde{\rho}_B(\mathbf{r})]\delta[\rho_S(\mathbf{r})-\tilde{\rho}_S(\mathbf{r})]\delta[\rho_0-\rho_A(\mathbf{r})-\rho_B(\mathbf{r})+\rho_S(\mathbf{r})]
\end{aligned}\tag{166}$$

And replacing the delta functionals with their complex exponential representations, it becomes

$$\begin{aligned}
&\exp\left[-\beta U_1(\mathbf{r}^{nN+n_S})\right]\delta[\rho_0-\tilde{\rho}_A(\mathbf{r})-\tilde{\rho}_B(\mathbf{r})]\\
&=\int\mathcal{D}\rho_A\int\mathcal{D}\rho_B\int\mathcal{D}\rho_S\\
&\exp\left[-v_0\chi_{AB}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r})-v_0\chi_{AS}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_S(\mathbf{r})-v_0\chi_{BS}\int d\mathbf{r}\rho_B(\mathbf{r})\rho_S(\mathbf{r})\right]\\
&\int\mathcal{D}w_A\exp\left[i\int d\mathbf{r}w_A(\mathbf{r})(\rho_A(\mathbf{r})-\tilde{\rho}_A(\mathbf{r}))\right]\\
&\int\mathcal{D}w_B\exp\left[i\int d\mathbf{r}w_B(\mathbf{r})(\rho_B(\mathbf{r})-\tilde{\rho}_B(\mathbf{r}))\right]\\
&\int\mathcal{D}w_S\exp\left[i\int d\mathbf{r}w_S(\mathbf{r})(\rho_S(\mathbf{r})-\tilde{\rho}_S(\mathbf{r}))\right]\\
&\int\mathcal{D}\eta\exp\left[i\int d\mathbf{r}w_S(\mathbf{r})(\rho_0-\rho_A(\mathbf{r})-\rho_B(\mathbf{r})-\rho_S(\mathbf{r}))\right]\\
&=\int\mathcal{D}\rho_A\int\mathcal{D}\rho_B\int\mathcal{D}\rho_S\int\mathcal{D}w_A\int\mathcal{D}w_B\int\mathcal{D}w_S\int\mathcal{D}\eta\\
&\exp\left[-v_0\chi_{AB}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r})-v_0\chi_{AS}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_S(\mathbf{r})-v_0\chi_{BS}\int d\mathbf{r}\rho_B(\mathbf{r})\rho_S(\mathbf{r})\right]\\
&\exp\left\{i\int d\mathbf{r}\left[w_A(\mathbf{r})\rho_A(\mathbf{r})+w_B(\mathbf{r})\rho_B(\mathbf{r})+w_S(\mathbf{r})\rho_S(\mathbf{r})+w_S(\mathbf{r})(\rho_0-\rho_A(\mathbf{r})-\rho_B(\mathbf{r})-\rho_S(\mathbf{r}))\right]\right\}\\
&\exp\left\{i\int d\mathbf{r}\left[w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r})+w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r})+w_S(\mathbf{r})\tilde{\rho}_S(\mathbf{r})\right]\right\}
\end{aligned}$$

(167)

The exponential term with U_e can be treated similarly. Upon using the identity involving the delta functional (eq. (50)), we have

$$\begin{aligned}
&\exp\left[-\beta U_e(\mathbf{r}^{nN+n_++n_-})\right]\delta\left(\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\right)\\
&=\int\mathcal{D}\rho_e\exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho_e(\mathbf{r})\frac{l_B}{|\mathbf{r}-\mathbf{r}'|}\rho_e(\mathbf{r}')\right]\delta\left[\rho_e(\mathbf{r})-\tilde{\rho}_e(\mathbf{r})\right]\delta\left(\int d\mathbf{r}\rho_e(\mathbf{r})\right)
\end{aligned}\tag{168}$$

Substituting the complex exponential form of the delta functional into above equation leads to

$$\begin{aligned}
&\exp\left[-\beta U_e(\mathbf{r}^{nN+n_+ +n_-})\right]\delta\left(\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\right)\\
&=\int\mathcal{D}\rho_e\exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho_e(\mathbf{r})\frac{l_B}{|\mathbf{r}-\mathbf{r}'|}\rho_e(\mathbf{r}')\right]\int\mathcal{D}\varphi\exp\left[i\int d\mathbf{r}\varphi(\mathbf{r})(\rho_e(\mathbf{r})-\tilde{\rho}_e(\mathbf{r}))\right]\int d\lambda\exp\left[i\lambda\int d\mathbf{r}\rho_e(\mathbf{r})\right]\\
&=\int\mathcal{D}\rho_e\int d\lambda\exp\left[i\lambda\int d\mathbf{r}\rho_e(\mathbf{r})\right]\int\mathcal{D}\varphi\exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho_e(\mathbf{r})\frac{l_B}{|\mathbf{r}-\mathbf{r}'|}\rho_e(\mathbf{r}')+i\int d\mathbf{r}\varphi(\mathbf{r})\rho_e(\mathbf{r})\right]\exp\left[-i\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\varphi(\mathbf{r})\right]\\
&=\int\mathcal{D}\varphi\int d\lambda\exp\left[-i\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\varphi(\mathbf{r})\right]\left\{\int\mathcal{D}\rho_e\exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho_e(\mathbf{r})\frac{l_B}{|\mathbf{r}-\mathbf{r}'|}\rho_e(\mathbf{r}')+i\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\rho_e(\mathbf{r})\right]\right]\right\}
\end{aligned}$$

(169)

Fortunately, the functional inside the curly bracket is a typical Gaussian functional which can be evaluated analytically. One of Gaussian integral formulas is (see Fredrickson's book p398-399)

$$\int\mathcal{D}f\exp\left[-\frac{1}{2}\int dx\int dx'f(x)A(x,x')f(x')+i\int dxJ(x)f(x)\right]=C_0\exp\left[-\frac{1}{2}\int dx\int dx'J(x)A^{-1}(x,x')J(x')\right]$$

(170)

where $A(x,x')$ is assumed to be real, symmetric, and positive definite. The functional inverse of A, A^{-1}, is defined by

$$\int dx'A(x,x')A^{-1}(x',x'')=\delta(x-x'') \tag{171}$$

and the constant C_0 is

$$C_0=\int\mathcal{D}f\exp\left[-\frac{1}{2}\int dx\int dx'f(x)A(x,x')f(x')\right] \tag{172}$$

In our case here, A is

$$A=\frac{l_B}{|\mathbf{r}-\mathbf{r}'|} \tag{173}$$

its functional inverse is

$$A^{-1}=-\frac{1}{4\pi l_B}\nabla^2\delta(\mathbf{r}-\mathbf{r}') \tag{174}$$

and J is

$$J=\varphi(\mathbf{r})+\lambda \tag{175}$$

It follows that

$$\begin{aligned}
&\int \mathcal{D}\rho_e \exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho_e(\mathbf{r})\frac{l_B}{|\mathbf{r}-\mathbf{r}'|}\rho_e(\mathbf{r}') + i\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\rho_e(\mathbf{r})\right] \\
&= C_0 \exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'(\varphi(\mathbf{r})+\lambda)\left(-\frac{1}{4\pi l_B}\nabla^2\delta(\mathbf{r}-\mathbf{r}')\right)(\varphi(\mathbf{r}')+\lambda)\right] \\
&= C_0 \exp\left[\frac{1}{8\pi l_B}\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\int d\mathbf{r}'\nabla^2\delta(\mathbf{r}-\mathbf{r}')(\varphi(\mathbf{r}')+\lambda)\right] \\
&= C_0 \exp\left[\frac{1}{8\pi l_B}\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\nabla^2\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')(\varphi(\mathbf{r}')+\lambda)\right] \\
&= C_0 \exp\left[\frac{1}{8\pi l_B}\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\nabla^2(\varphi(\mathbf{r})+\lambda)\right] \\
&= C_0 \exp\left[\frac{1}{8\pi l_B}\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\nabla^2\varphi(\mathbf{r})\right]
\end{aligned} \tag{176}$$

The integral in the above equation can be evaluated by integrating by part

$$\begin{aligned}
&\int d\mathbf{r}(\varphi(\mathbf{r})+\lambda)\nabla^2\varphi(\mathbf{r}) \\
&= \lambda\int d\mathbf{r}\nabla^2\varphi(\mathbf{r}) + \int d[\nabla\varphi(\mathbf{r})]\varphi(\mathbf{r}) \\
&= \lambda\nabla\varphi(\mathbf{r})\Big|_{-\infty}^{\infty} + \varphi(\mathbf{r})\nabla\varphi(\mathbf{r})\Big|_{-\infty}^{\infty} - \int d\varphi(\mathbf{r})\nabla\varphi(\mathbf{r}) \\
&= -\int d\varphi(\mathbf{r})\nabla\varphi(\mathbf{r}) \\
&= -\int d\mathbf{r}\nabla\varphi(\mathbf{r})\nabla\varphi(\mathbf{r}) \\
&= -\int d\mathbf{r}\left|\nabla\varphi(\mathbf{r})\right|^2
\end{aligned} \tag{177}$$

Inserting eq. (177) into eq. (176), we have

$$\int \mathcal{D}\rho_e \exp\left[-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho_e(\mathbf{r})\frac{l_B}{|\mathbf{r}-\mathbf{r}'|}\rho_e(\mathbf{r}') + i\int d\mathbf{r}\varphi(\mathbf{r})\rho_e(\mathbf{r})\right] = C_0\exp\left(-\frac{1}{8\pi l_B}\int d\mathbf{r}\left|\nabla\varphi(\mathbf{r})\right|^2\right) \tag{178}$$

Then the above equation is substituted into eq. (169), which leads to the final field form for electrostatic interaction energy

$$\begin{aligned}
\exp\left[-\beta U_e(\mathbf{r}^{nN+n_++n_-})\right] &= \int \mathcal{D}\varphi\int d\lambda C_0\exp\left[-i\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\varphi(\mathbf{r})\right]\exp\left(-\frac{1}{8\pi l_B}\int d\mathbf{r}\left|\nabla\varphi(\mathbf{r})\right|^2\right) \\
&= \int \mathcal{D}\varphi D_0\exp\left[-\int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})i\varphi(\mathbf{r}) + \frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2\right)\right]
\end{aligned} \tag{179}$$

where the integration result with respect to λ is absorbed into D_0. In literature, an effective Hamiltonian for electrostatic interaction energy is often used, which is just the integral inside the square bracket in the second line of eq. (179):

$$\beta H_e[\varphi] = \int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})i\varphi(\mathbf{r}) + \frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2\right) \tag{180}$$

Note that the real electric potential field φ is usually replaced by a pure imaginary variable ψ in literature. In this convention, the Hamiltonian is expressed as

$$\beta H_e[\psi] = \int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})\psi(\mathbf{r}) - \frac{1}{8\pi l_B}\left|\nabla\psi(\mathbf{r})\right|^2\right) \tag{181}$$

The negative sign is coming from the square of imaginary number *i*:

$$\begin{aligned}\beta H_e[\psi] &= \int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})i\varphi(\mathbf{r}) - (-1)\frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2\right)\\ &= \int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})i\varphi(\mathbf{r}) - i^2\frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2\right)\\ &= \int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})i\varphi(\mathbf{r}) - \frac{1}{8\pi l_B}\left|\nabla\ \ i\varphi(\mathbf{r})\ \ \right|^2\right)\\ &= \int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})\psi(\mathbf{r}) - \frac{1}{8\pi l_B}\left|\nabla\psi(\mathbf{r})\right|^2\right)\end{aligned} \tag{182}$$

It is now ready for us to finish the particle-to-field transformation. Substituting eq. (167), (179), the partition function is given by

$$\begin{aligned}Z = {}& \frac{1}{n!n_S!n_+!n_-!(\lambda_T^3)^{nN+n_S+n_++n_-}}\int d\mathbf{r}^{nN+n_S+n_++n_-}\\ & \exp\left[-\frac{3}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2\right]\\ & \int\mathcal{D}\rho_A\int\mathcal{D}\rho_B\int\mathcal{D}\rho_S\int\mathcal{D}w_A\int\mathcal{D}w_B\int\mathcal{D}w_S\\ & \exp\left[-v_0\chi_{AB}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r}) - v_0\chi_{AS}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_S(\mathbf{r}) - v_0\chi_{BS}\int d\mathbf{r}\rho_B(\mathbf{r})\rho_S(\mathbf{r})\right]\\ & \exp\left\{\int d\mathbf{r}\left[w_A(\mathbf{r})\rho_A(\mathbf{r}) + w_B(\mathbf{r})\rho_B(\mathbf{r}) + w_S(\mathbf{r})\rho_S(\mathbf{r}) + w_S(\mathbf{r})(\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r}) - \rho_S(\mathbf{r}))\right]\right.\\ & \exp\left\{i\int d\mathbf{r}\left[w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + w_S(\mathbf{r})\tilde{\rho}_S(\mathbf{r})\right]\right\}\\ & \int\mathcal{D}\varphi D_0\exp\left[-\int d\mathbf{r}\left(\tilde{\rho}_e(\mathbf{r})i\varphi(\mathbf{r}) + \frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2\right)\right]\end{aligned}$$

(183)

Rearranging the above equation in terms of $\mathbf{r}^{nN+n_S+n_++n_-}$ dependent and independent part, we have

$$
\begin{aligned}
Z = {} & \frac{D_0}{n!n_S!n_+!n_-!(\lambda_T^3)^{nN+n_S+n_++n_-}} \\
& \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int \mathcal{D}\rho_S \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}w_S \int \mathcal{D}\eta \int \mathcal{D}\varphi \\
& \exp\Big[-v_0\chi_{AB}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_B(\mathbf{r}) - v_0\chi_{AS}\int d\mathbf{r}\rho_A(\mathbf{r})\rho_S(\mathbf{r}) - v_0\chi_{BS}\int d\mathbf{r}\rho_B(\mathbf{r})\rho_S(\mathbf{r})\Big] \\
& \exp\ \ i\int d\mathbf{r}\big[w_A(\mathbf{r})\rho_A(\mathbf{r}) + w_B(\mathbf{r})\rho_B(\mathbf{r}) + w_S(\mathbf{r})\rho_S(\mathbf{r}) + \eta(\mathbf{r})(\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r}) - \rho_S(\mathbf{r}))\big] \\
& \exp\left[-\int d\mathbf{r}\left(\frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2\right)\right] \\
& \int d\mathbf{r}^{nN+n_S+n_++n_-} \\
& \exp\left[-\frac{3}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 - i\int d\mathbf{r}\big[w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + w_S(\mathbf{r})\tilde{\rho}_S(\mathbf{r})\big] - i\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\varphi(\mathbf{r})\right]
\end{aligned}
$$

(184)

The last two lines of the above equation can be evaluated by substituting back the definition of all microscopic density operators

$$
\begin{aligned}
&\int d\mathbf{r}^{nN+n_S+n_++n_-} \\
&\exp\left[-\frac{3}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 - i\int d\mathbf{r}\left[w_A(\mathbf{r})\tilde{\rho}_A(\mathbf{r}) + w_B(\mathbf{r})\tilde{\rho}_B(\mathbf{r}) + w_S(\mathbf{r})\tilde{\rho}_S(\mathbf{r})\right] - i\int d\mathbf{r}\tilde{\rho}_e(\mathbf{r})\varphi(\mathbf{r})\right] \\
&= \int d\mathbf{r}^{nN+n_S+n_++n_-}\exp\left[-\frac{3}{2b^2}\sum_{j=1}^{n}\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2\right] \\
&\exp\left[-i\int d\mathbf{r}\left[w_A(\mathbf{r})\sum_{j=1}^{n}\int_0^{fN} ds\delta[\mathbf{r}-\mathbf{r}_j(s)] + w_B(\mathbf{r})\sum_{j=1}^{n}\int_{fN}^{N} ds\delta[\mathbf{r}-\mathbf{r}_j(s)] + w_S(\mathbf{r})\sum_{j=1}^{n_S}\delta[\mathbf{r}-\mathbf{r}_j]\right]\right] \\
&\exp\left\{-i\int d\mathbf{r}\left[\begin{array}{l} v_A\alpha_A\displaystyle\sum_{j=1}^{n}\int_0^{fN} ds\delta(\mathbf{r}-\mathbf{r}_j(s)) + v_B\alpha_B\sum_{j=1}^{n}\int_{fN}^{N} ds\delta(\mathbf{r}-\mathbf{r}_j(s)) \\ +v_+\displaystyle\sum_{j=1}^{n_+}\delta(\mathbf{r}-\mathbf{r}_j) + v_-\sum_{j=1}^{n_-}\delta(\mathbf{r}-\mathbf{r}_j)\end{array}\right]\varphi(\mathbf{r})\right\} \\
&= \int d\mathbf{r}^{nN+n_S+n_++n_-}\exp\left\{\sum_{j=1}^{n}\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 \\ -i\displaystyle\int_0^{fN} ds\int d\mathbf{r}\left(w_A(\mathbf{r}) + v_A\alpha_A\varphi(\mathbf{r})\right)\delta[\mathbf{r}-\mathbf{r}_j(s)] \\ -i\displaystyle\int_{fN}^{N} ds\int d\mathbf{r}\left(w_B(\mathbf{r}) + v_B\alpha_B\varphi(\mathbf{r})\right)\delta[\mathbf{r}-\mathbf{r}_j(s)]\end{array}\right]\right\} \\
&\exp\left[\sum_{j=1}^{n_S}\left(-i\int d\mathbf{r}w_S(\mathbf{r})\delta[\mathbf{r}-\mathbf{r}_j]\right)\right] \\
&\exp\left[\sum_{j=1}^{n_+}\left(-i\int d\mathbf{r}v_+\varphi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_j)\right)\right] \\
&\exp\left[\sum_{j=1}^{n_-}\left(-i\int d\mathbf{r}v_-\varphi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_j)\right)\right] \\
&= \prod_{j=1}^{n}\int d\mathbf{r}^{nN}\exp\left\{\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}_j(s)}{ds}\right|^2 - i\int d\mathbf{r}\left(w_A(\mathbf{r}) + v_A\alpha_A\varphi(\mathbf{r})\right)\int_0^{fN} ds\delta[\mathbf{r}-\mathbf{r}_j(s)] \\ -i\displaystyle\int d\mathbf{r}\left(w_B(\mathbf{r}) + v_B\alpha_B\varphi(\mathbf{r})\right)\int_{fN}^{N} ds\delta[\mathbf{r}-\mathbf{r}_j(s)]\end{array}\right\} \\
&\prod_{j=1}^{n_S}\int d\mathbf{r}_j\exp\left[-iw_S(\mathbf{r}_j)\right]\prod_{j=1}^{n_+}\int d\mathbf{r}_j\exp\left[-iv_+\varphi(\mathbf{r}_j)\right]\prod_{j=1}^{n_-}\int d\mathbf{r}_j\exp\left[-iv_-\varphi(\mathbf{r}_j)\right] \\
&= \left\{\prod_{t=1}^{N}\int d\mathbf{r}(t)\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -i\displaystyle\int_0^{fN} ds\left(w_A[\mathbf{r}(s)] + v_A\alpha_A\varphi[\mathbf{r}(s)]\right) \\ -i\displaystyle\int_{fN}^{N} ds\left(w_B[\mathbf{r}(s)] + v_B\alpha_B\varphi[\mathbf{r}(s)]\right)\end{array}\right]\right\}^n \\
&\left\{\int d\mathbf{r}\exp\left[-iw_S(\mathbf{r})\right]\right\}^{n_S} \\
&\left\{\int d\mathbf{r}\exp\left[-iv_+\varphi(\mathbf{r})\right]\right\}^{n_+} \\
&\left\{\int d\mathbf{r}\exp\left[-iv_-\varphi(\mathbf{r})\right]\right\}^{n_-}
\end{aligned}
$$

(185)

The three integrals in the last three lines of above equations can be interpreted as single-particle partition functions for the solvent molecule, the cations, and the anions, respectively. Thus, we have

$$Z_S = \int d\mathbf{r} \exp\left[-iw_S(\mathbf{r})\right] \tag{186}$$

$$Z_+ = \int d\mathbf{r} \exp\left[-v_+ i\varphi(\mathbf{r})\right] \tag{187}$$

$$Z_- = \int d\mathbf{r} \exp\left[-v_- i\varphi(\mathbf{r})\right] \tag{188}$$

We then define the normalized partition functions as in section 5 accordingly,

$$Q_S = \frac{Z_S}{Z_{S0}} = \frac{\int d\mathbf{r} \exp\left[-iw_S(\mathbf{r})\right]}{\int d\mathbf{r} 1} = \frac{1}{V}\int d\mathbf{r} \exp\left[-iw_S(\mathbf{r})\right] \tag{189}$$

$$Q_+ = \frac{Z_+}{Z_{+0}} = \frac{\int d\mathbf{r} \exp\left[-v_+ i\varphi(\mathbf{r})\right]}{\int d\mathbf{r} 1} = \frac{1}{V}\int d\mathbf{r} \exp\left[-v_+ i\varphi(\mathbf{r})\right] \tag{190}$$

$$Q_- = \frac{Z_-}{Z_{-0}} = \frac{\int d\mathbf{r} \exp\left[-v_- i\varphi(\mathbf{r})\right]}{\int d\mathbf{r} 1} = \frac{1}{V}\int d\mathbf{r} \exp\left[-v_- \varphi(\mathbf{r})\right] \tag{191}$$

The ensemble average particle density for these three species can be calculated as

$$\begin{aligned}
\rho_S(\mathbf{r}) &= \left\langle \tilde{\rho}_S(\mathbf{r}) \right\rangle \\
&= n_S \left\langle \tilde{\rho}_S^1(\mathbf{r}) \right\rangle \\
&= n_S \frac{\int d\mathbf{r}' \tilde{\rho}_S^1(\mathbf{r}) \exp\left[-iw_S(\mathbf{r}')\right]}{\int d\mathbf{r}' \exp\left[-iw_S(\mathbf{r}')\right]} \\
&= n_S \frac{\int d\mathbf{r}' \delta[\mathbf{r}-\mathbf{r}'] \exp\left[-iw_S(\mathbf{r}')\right]}{\int d\mathbf{r}' \exp\left[-iw_S(\mathbf{r}')\right]} \\
&= \frac{n_S}{VQ_S} \exp\left[-iw_S(\mathbf{r})\right]
\end{aligned} \tag{192}$$

$$\begin{aligned}
\rho_+(\mathbf{r}) &= \left\langle \tilde{\rho}_+(\mathbf{r}) \right\rangle \\
&= n_+ \left\langle \tilde{\rho}_+^1(\mathbf{r}) \right\rangle \\
&= n_+ \frac{\int d\mathbf{r}' \tilde{\rho}_+^1(\mathbf{r}) \exp\left[-v_+ i\varphi(\mathbf{r}')\right]}{\int d\mathbf{r}' \exp\left[-v_+ i\varphi(\mathbf{r}')\right]} \\
&= n_+ \frac{\int d\mathbf{r}' \delta[\mathbf{r}-\mathbf{r}'] \exp\left[-v_+ i\varphi(\mathbf{r}')\right]}{\int d\mathbf{r}' \exp\left[-v_+ i\varphi(\mathbf{r}')\right]} \\
&= \frac{n_+}{VQ_+} \exp\left[-v_+ i\varphi(\mathbf{r})\right]
\end{aligned} \tag{193}$$

$$\begin{aligned}\rho_{\_}(\mathbf{r}) &= \left\langle \tilde{\rho}_{\_}(\mathbf{r}) \right\rangle \\ &= n_{\_} \left\langle \tilde{\rho}_{\_}^{1}(\mathbf{r}) \right\rangle \\ &= n_{\_} \frac{\int d\mathbf{r}'\tilde{\rho}_{\_}^{1}(\mathbf{r}) \exp\left[-v_{\_} i\varphi(\mathbf{r}')\right]}{\int d\mathbf{r}' \exp\left[-v_{\_} i\varphi(\mathbf{r}')\right]} \\ &= n_{\_} \frac{\int d\mathbf{r}'\delta[\mathbf{r}-\mathbf{r}'] \exp\left[-v_{\_} i\varphi(\mathbf{r}')\right]}{\int d\mathbf{r}' \exp\left[-iv_{\_} i\varphi(\mathbf{r}')\right]} \\ &= \frac{n_{\_}}{VQ_{\_}} \exp\left[-v_{\_} i\varphi(\mathbf{r})\right]\end{aligned} \tag{194}$$

where the relation of eq. (88) has been used.

Now, let’s turn to the first term after the last equal sign of eq. (185). It should be looked familiar though it is a rather complicated object at a first glance. In comparison with eq. (127), we immediately find that the integral in the curly bracket of that term is just the single-chain partition function for the charged diblock copolymer, which has the form

$$Z_C = \prod_{t=1}^{N} \int d\mathbf{r}(t) \exp\left[\begin{array}{l} -\frac{3}{2b^2}\int_0^N ds \left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -i\int_0^{fN} ds \quad w_A[\mathbf{r}(s)] + v_A \alpha_A \varphi[\mathbf{r}(s)] \\ -i\int_{fN}^{N} ds \quad w_B[\mathbf{r}(s)] + v_B \alpha_B \varphi[\mathbf{r}(s)] \\ \end{array}\right] \tag{195}$$

The only different between the single-chain partition functions of the neutral diblock copolymer and the charged diblock copolymer is the later has an additional field describing the electrostatic interactions. Therefore, there is no need to go through the steps from eq. (128) to eq. (148) to obtain expressions for calculating the normalized single-chain partition functions, chain propagators, and the ensemble average density of type A segments and type B segments. Just replacing w_A by

$$w_A + v_A \alpha_A \varphi \tag{196}$$

and replacing w_B by

$$w_B + v_B \alpha_B \varphi \tag{197}$$

Here, we only summarize the final results:

The statistical field theory for diblock copolyelectrolyte solutions is

$$Z = \int \mathcal{D}\rho_A \int \mathcal{D}\rho_B \int \mathcal{D}\rho_S \int \mathcal{D}w_A \int \mathcal{D}w_B \int \mathcal{D}w_S \int \mathcal{D}\eta \int \mathcal{D}\varphi \exp(-H) \tag{198}$$

where

$$\begin{aligned} H = \int d\mathbf{r}[& v_0\chi_{AB}\rho_A(\mathbf{r})\rho_B(\mathbf{r}) + v_0\chi_{AS}\rho_A(\mathbf{r})\rho_S(\mathbf{r}) + v_0\chi_{BS}\rho_B(\mathbf{r})\rho_S(\mathbf{r}) \\ & -iw_A(\mathbf{r})\rho_A(\mathbf{r}) - iw_B(\mathbf{r})\rho_B(\mathbf{r}) - iw_S(\mathbf{r})\rho_S(\mathbf{r}) \\ & -i\eta(\mathbf{r})(\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r}) - \rho_S(\mathbf{r})) \\ & + \frac{1}{8\pi l_B}\left|\nabla\varphi(\mathbf{r})\right|^2] \\ & -n\ln Q_C - n_S\ln Q_S - n_+\ln Q_+ - n_-\ln Q_- \end{aligned} \tag{199}$$

and the prefactor Z_0 is unimportant.

The normalized single-chain partition function can be calculated by

$$\begin{aligned} Q_C &= \frac{1}{V}\int d\mathbf{r}\, q(\mathbf{r},s)q(\mathbf{r},N-s) \\ &= \frac{1}{V}\int d\mathbf{r}\, q(\mathbf{r},N) \end{aligned} \tag{200}$$

or equivalently by

$$\begin{aligned} Q_C &= \frac{1}{V}\int d\mathbf{r}\, q^*(\mathbf{r},s)q^*(\mathbf{r},N-s) \\ &= \frac{1}{V}\int d\mathbf{r}\, q^*(\mathbf{r},N) \end{aligned} \tag{201}$$

where the propagator q is determined by the following modified diffusion functions

$$\frac{\partial q(\mathbf{r},s)}{\partial s} = \begin{cases} \frac{b^2}{6}\nabla^2 q(\mathbf{r},s) - [iw_A(\mathbf{r}) + v_A\alpha_A i\varphi(\mathbf{r})]q(\mathbf{r},s), \text{ if } s \le fN \\ \frac{b^2}{6}\nabla^2 q(\mathbf{r},s) - [iw_B(\mathbf{r}) + v_B\alpha_B i\varphi(\mathbf{r})]q(\mathbf{r},s), \text{ if } s \ge fN \end{cases} \tag{202}$$

and the complementary chain propagator q^* is determined similarly by

$$\frac{\partial}{\partial s}q^*(\mathbf{r},s) = \begin{cases} \frac{b^2}{6}\nabla^2 q^*(\mathbf{r},s) - [iw_B(\mathbf{r}) + v_B\alpha_B i\varphi(\mathbf{r})]q^*(\mathbf{r},s), \text{ if } s \le (1-fN) \\ \frac{b^2}{6}\nabla^2 q^*(\mathbf{r},s) - [iw_A(\mathbf{r}) + v_A\alpha_A i\varphi(\mathbf{r})]q^*(\mathbf{r},s), \text{ if } s \le (1-fN) \end{cases} \tag{203}$$

The ensemble average segment densities of A and B segments are constructed by composing forward and backward propagators (propagator and complementary propagator), giving rise to the expressions

$$\rho_A(\mathbf{r}) = \frac{1}{VQ_C}\int_0^{fN} ds\, q(\mathbf{r},s)q^*(\mathbf{r},N-s) \tag{204}$$

$$\rho_B(\mathbf{r}) = \frac{1}{VQ_C}\int_{fN}^{N} ds\, q(\mathbf{r},s)q^*(\mathbf{r},N-s) \tag{205}$$

Note that each field variable appearing in eq. (199), (202), and (203) is associated with the imaginary number *i*. Thus we can absorb *i* into field variables which results in pure imaginary fields. With these changes, eq. (199), (202), and (203) become

$$
\begin{aligned}
H = \int d\mathbf{r}[&v_0\chi_{AB}\rho_A(\mathbf{r})\rho_B(\mathbf{r}) + v_0\chi_{AS}\rho_A(\mathbf{r})\rho_S(\mathbf{r}) + v_0\chi_{BS}\rho_B(\mathbf{r})\rho_S(\mathbf{r}) \\
&-w_A(\mathbf{r})\rho_A(\mathbf{r}) - w_B(\mathbf{r})\rho_B(\mathbf{r}) - w_S(\mathbf{r})\rho_S(\mathbf{r}) \\
&-\eta(\mathbf{r})(\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r}) - \rho_S(\mathbf{r})) \\
&-\frac{1}{8\pi l_B}\left|\nabla\psi(\mathbf{r})\right|^2] \\
&-n\ln Q_C - n_S\ln Q_S - n_+\ln Q_+ - n_-\ln Q_-
\end{aligned}
\tag{206}
$$

$$
\frac{\partial q(\mathbf{r},s)}{\partial s} = \begin{cases} \frac{b^2}{6}\nabla^2 q(\mathbf{r},s) - [w_A(\mathbf{r}) + v_A\alpha_A\psi(\mathbf{r})]q(\mathbf{r},s), \text{ if } s \le fN \\ \frac{b^2}{6}\nabla^2 q(\mathbf{r},s) - [w_B(\mathbf{r}) + v_B\alpha_B\psi(\mathbf{r})]q(\mathbf{r},s), \text{ if } s \ge fN \end{cases}
\tag{207}
$$

$$
\frac{\partial}{\partial s}q^*(\mathbf{r},s) = \begin{cases} \frac{b^2}{6}\nabla^2 q^*(\mathbf{r},s) - [w_B(\mathbf{r}) + v_B\alpha_B\psi(\mathbf{r})]q^*(\mathbf{r},s), \text{ if } s \le (1-fN) \\ \frac{b^2}{6}\nabla^2 q^*(\mathbf{r},s) - [w_A(\mathbf{r}) + v_A\alpha_A\psi(\mathbf{r})]q^*(\mathbf{r},s), \text{ if } s \le (1-fN) \end{cases}
\tag{208}
$$

The self-consistent field theory is obtained by imposing the mean-field approximation to the statistical field theory. The mean-field SCF equations are obtained by the saddle-approximation, where one sets

$$\frac{\delta H}{\delta \rho_A} = 0 \tag{209}$$

$$\frac{\delta H}{\delta \rho_B} = 0 \tag{210}$$

$$\frac{\delta H}{\delta \rho_S} = 0 \tag{211}$$

$$\frac{\delta H}{\delta \eta} = 0 \tag{212}$$

$$\frac{\delta H}{\delta \psi} = 0 \tag{213}$$

The first four variations of in above equations can be easily done, leading to the following four equations

$$w_A(\mathbf{r}) = v_0\chi_{AB}\rho_B(\mathbf{r}) + v_0\chi_{AS}\rho_S(\mathbf{r}) + \eta(\mathbf{r}) - \frac{1}{8\pi}\frac{\partial\varepsilon(\mathbf{r})}{\partial\rho_A(\mathbf{r})}\left|\nabla\psi(\mathbf{r})\right|^2 \tag{214}$$

$$w_B(\mathbf{r}) = v_0\chi_{AB}\rho_A(\mathbf{r}) + v_0\chi_{BS}\rho_S(\mathbf{r}) + \eta(\mathbf{r}) - \frac{1}{8\pi}\frac{\partial\varepsilon(\mathbf{r})}{\partial\rho_B(\mathbf{r})}\left|\nabla\psi(\mathbf{r})\right|^2 \tag{215}$$

$$w_S(\mathbf{r}) = v_0\chi_{AS}\rho_A(\mathbf{r}) + v_0\chi_{BS}\rho_B(\mathbf{r}) + \eta(\mathbf{r}) - \frac{1}{8\pi}\frac{\partial\varepsilon(\mathbf{r})}{\partial\rho_S(\mathbf{r})}\left|\nabla\psi(\mathbf{r})\right|^2 \tag{216}$$

$$\rho_0 - \rho_A(\mathbf{r}) - \rho_B(\mathbf{r}) - \rho_S(\mathbf{r}) = 0 \tag{217}$$

while the last one is much more complicated. There are four terms in *H* of eq. (206) are ψ dependent, and their variations with respect to ψ are evaluated as follows

$$\begin{aligned}
&\delta\int d\mathbf{r}\left(-\frac{1}{8\pi l_B}\left|\nabla\psi(\mathbf{r})\right|^2\right)\\
&= -\frac{1}{8\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\left[\left|\nabla\ \ \psi(\mathbf{r}) + \delta\psi\ \ \right|^2\right] + \frac{1}{8\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\ \left|\nabla\psi(\mathbf{r})\right|^2\\
&= -\frac{1}{8\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\left[\left|\nabla\psi(\mathbf{r}) + \nabla\delta\psi\right|^2\right] + \frac{1}{8\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\ \left|\nabla\psi(\mathbf{r})\right|^2\\
&= -\frac{1}{8\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\left[\left|\nabla\psi(\mathbf{r})\right|^2 + 2\nabla\psi(\mathbf{r})\nabla\delta\psi + \left|\nabla\delta\psi\right|^2\right] + \frac{1}{8\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\ \left|\nabla\psi(\mathbf{r})\right|^2\\
&= -\frac{1}{4\pi}\int d\mathbf{r}\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})\nabla\delta\psi\\
&= -\frac{1}{4\pi}\int d\delta\psi\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})\\
&= -\frac{1}{4\pi}\left[\delta\psi\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})\ \big|_{-\infty}^{\infty}\ - \int\delta\psi d[\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})]\right]\\
&= \frac{1}{4\pi l_B}\int d\mathbf{r}\nabla[\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})]\delta\psi
\end{aligned} \tag{218}$$

It follows that

$$\frac{\delta}{\delta\psi}\int d\mathbf{r}\left(-\frac{1}{8\pi l_B}\left|\nabla\psi(\mathbf{r})\right|^2\right) = \frac{1}{4\pi}\nabla[\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})] \tag{219}$$

The other variations are

$$
\begin{aligned}
\frac{\delta}{\delta\psi}\ -n\ln Q_C \quad &= -\frac{n}{Q_C}\frac{\delta Q_C}{\delta\psi} \\
&= -\frac{n}{Q_C Z_{C0}}\frac{\delta}{\delta\psi}\int \mathcal{D}\mathbf{r}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds\ \ w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)] \\ -\displaystyle\int_{fN}^{N} ds\ \ w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)] \\ \end{array}\right] \\
&= -\frac{n}{Z}\int \mathcal{D}\mathbf{r}\,\frac{\delta}{\delta\psi}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds\ \ w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)] \\ -\displaystyle\int_{fN}^{N} ds\ \left(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\right) \\ \end{array}\right] \\
&= -\frac{n}{Z}\int \mathcal{D}\mathbf{r}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds\ \left(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\right) \\ -\displaystyle\int_{fN}^{N} ds\ \left(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\right) \\ \end{array}\right] \\
&\frac{\delta}{\delta\psi}\left[-\int_0^{fN} ds\ \left(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\right) - \int_{fN}^{N} ds\ \left(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\right)\right] \\
&= \frac{n}{Z}\int \mathcal{D}\mathbf{r}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds\ \left(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\right) \\ -\displaystyle\int_{fN}^{N} ds\ \left(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\right) \\ \end{array}\right] \\
&\frac{\delta}{\delta\psi}\left[\int_0^{fN} ds\ \left(w_A[\mathbf{r}(s)] + v_A\alpha_A\int d\mathbf{r}\psi(\mathbf{r})\delta[\mathbf{r}-\mathbf{r}(s)]\right) - \int_{fN}^{N} ds\ \left(w_B[\mathbf{r}(s)] + v_B\alpha_B\int d\mathbf{r}\psi(\mathbf{r})\delta[\mathbf{r}-\mathbf{r}(s)]\right)\right]
\end{aligned}
\tag{220}
$$

Continued by

$$
\begin{aligned}
&= \frac{n}{Z}\int \mathcal{D}\mathbf{r}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds \;\; w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)] \\ -\displaystyle\int_{fN}^{N} ds \;\; w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)] \end{array}\right] \\
&\frac{\delta}{\delta\psi}\int_0^{fN} ds v_A\alpha_A\int d\mathbf{r}\psi(\mathbf{r})\delta[\mathbf{r}-\mathbf{r}(s)] + \frac{\delta}{\delta\psi}\int_{fN}^{N} ds v_B\alpha_B\int d\mathbf{r}\psi(\mathbf{r})\delta[\mathbf{r}-\mathbf{r}(s)] \\
&= \frac{n}{Z}\int \mathcal{D}\mathbf{r}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds \;\; \Big(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\Big) \\ -\displaystyle\int_{fN}^{N} ds \;\; \Big(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\Big) \end{array}\right] \\
&\left[v_A\alpha_A\frac{\delta}{\delta\psi}\int d\mathbf{r}\psi(\mathbf{r})\int_0^{fN} ds\delta[\mathbf{r}-\mathbf{r}(s)] + v_B\alpha_B\frac{\delta}{\delta\psi}\int d\mathbf{r}\psi(\mathbf{r})\int_{fN}^{N} ds\delta[\mathbf{r}-\mathbf{r}(s)]\right] \\
&= \frac{n}{Z}\int \mathcal{D}\mathbf{r}\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds \;\; \Big(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\Big) \\ -\displaystyle\int_{fN}^{N} ds \;\; \Big(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\Big) \end{array}\right] \\
&\left[v_A\alpha_A\frac{\delta}{\delta\psi}\int d\mathbf{r}\psi(\mathbf{r})\tilde{\rho}_A^1(\mathbf{r}) + v_B\alpha_B\frac{\delta}{\delta\psi}\int d\mathbf{r}\psi(\mathbf{r})\tilde{\rho}_B^1(\mathbf{r})\right] \\
&= v_A\alpha_A\frac{n}{Z}\int \mathcal{D}\mathbf{r}\tilde{\rho}_A^1(\mathbf{r})\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds \;\; \Big(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\Big) \\ -\displaystyle\int_{fN}^{N} ds \;\; \Big(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\Big) \end{array}\right] \\
&+v_B\alpha_B\frac{n}{Z}\int \mathcal{D}\mathbf{r}\tilde{\rho}_B^1(\mathbf{r})\exp\left[\begin{array}{l} -\dfrac{3}{2b^2}\displaystyle\int_0^N ds\left|\frac{d\mathbf{r}(s)}{ds}\right|^2 \\ -\displaystyle\int_0^{fN} ds \;\; \Big(w_A[\mathbf{r}(s)] + v_A\alpha_A\psi[\mathbf{r}(s)]\Big) \\ -\displaystyle\int_{fN}^{N} ds \;\; \Big(w_B[\mathbf{r}(s)] + v_B\alpha_B\psi[\mathbf{r}(s)]\Big) \end{array}\right] \\
&= v_A\alpha_A\rho_A(\mathbf{r}) + v_B\alpha_B\rho_B(\mathbf{r})
\end{aligned}
\tag{221}
$$

and

$$\begin{aligned}
&\frac{\delta}{\delta\psi}\ -n_+\ln Q_+ \ \ = -\frac{n_+}{Q_+}\frac{\delta Q_+}{\delta\psi}\\
&= -\frac{n_+}{VQ_+}\frac{\delta}{\delta\psi}\int d\mathbf{r}\exp\big[-v_+\psi(\mathbf{r})\big]\\
&= -\frac{n_+}{VQ_+}\frac{\partial}{\partial\psi}\exp\big[-v_+\psi(\mathbf{r})\big]\\
&= -\frac{n_+}{VQ_+}\exp\big[-v_+\psi(\mathbf{r})\big]\frac{\partial}{\partial\psi}\big[-v_+\psi(\mathbf{r})\big]\\
&= v_+\frac{n_+}{VQ_+}\exp\big[-v_+\psi(\mathbf{r})\big]\\
&= v_+\rho_+(\mathbf{r})
\end{aligned} \tag{222}$$

and

$$\begin{aligned}
&\frac{\delta}{\delta\psi}\ -n_-\ln Q_- \ \ = -\frac{n_-}{Q_-}\frac{\delta Q_-}{\delta\psi}\\
&= -\frac{n_-}{VQ_-}\frac{\delta}{\delta\psi}\int d\mathbf{r}\exp\big[-v_-\psi(\mathbf{r})\big]\\
&= -\frac{n_-}{VQ_-}\frac{\partial}{\partial\psi}\exp\big[-v_-\psi(\mathbf{r})\big]\\
&= -\frac{n_-}{VQ_-}\exp\big[-v_-\psi(\mathbf{r})\big]\frac{\partial}{\partial\psi}\big[-v_-\psi(\mathbf{r})\big]\\
&= v_-\frac{n_-}{VQ_-}\exp\big[-v_-\psi(\mathbf{r})\big]\\
&= v_-\rho_-(\mathbf{r})
\end{aligned} \tag{223}$$

Combining eq. (206), eq. (213), eq. (219), (221), eq. (222), and eq. (223), we have

$$\frac{1}{4\pi}\nabla[\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})] = -\big[v_A\alpha_A\rho_A(\mathbf{r}) + v_B\alpha_B\rho_B(\mathbf{r}) + v_+\rho_+(\mathbf{r}) + v_-\rho_-(\mathbf{r})\big] \tag{224}$$

This is a Poisson-Boltzmann equation with variable coefficient in the Laplacian which is typical in equilibrium electrostatic systems.

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the derivation of Flory-Huggins interaction parameter

see Kumar, R.; Muthukumar, M. J. Chem. Phys., 2007, 126, 214902