

# Notes on Polymer Self-Consistent Field Theory

*by Qiang (David) Wang*  
*Department of Chemical and Biological Engineering*  
*Colorado State University, USA*

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# 1 Propagators and Correlation Functions of an Ideal Homopolymer Chain in an External Field

## 1.1 Lattice Polymer

Consider an ideal homopolymer chain (non-interacting with itself) of  $N$  segments on a lattice. The propagator  $g_s(\mathbf{r}, \mathbf{r}_0)$ , corresponding to the probability of finding a partial chain of  $s$  segments that starts at lattice site  $\mathbf{r}_0$  and ends at  $\mathbf{r}$  in an external field  $\omega(\mathbf{r})$ , is defined as

$$g_s(\mathbf{r}|\mathbf{r}_0) \equiv \sum_{\mathbf{R}_s} \delta_{\mathbf{R}_s, \mathbf{r}} \exp[-\omega(\mathbf{R}_s)] \prod_{k=1}^{s-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] \delta_{\mathbf{R}_1, \mathbf{r}_0}, \quad (1)$$

where  $\mathbf{R}_k$  denotes the lattice position of the  $k^{\text{th}}$  ( $1 \leq k \leq s$ ) segment on this partial chain and  $\delta_{\mathbf{r}, \mathbf{r}_0}$  the Kronecker  $\delta$ -function. It satisfies the recursive relation

$$\begin{aligned} g_{s=1}(\mathbf{r}|\mathbf{r}_0) &= \exp[-\omega(\mathbf{r})] \delta_{\mathbf{r}, \mathbf{r}_0} \\ g_{s+1}(\mathbf{r}|\mathbf{r}_0) &= \exp[-\omega(\mathbf{r})] \sum_{\mathbf{r}'} \Phi(\mathbf{r} - \mathbf{r}') g_s(\mathbf{r}'|\mathbf{r}_0) \\ &= \frac{\exp[-\omega(\mathbf{r})]}{z} \sum_{\mathbf{r}_n} g_s(\mathbf{r}_n|\mathbf{r}_0) \quad 1 \leq s \leq N-1, \end{aligned} \quad (2)$$

where  $z$  is the lattice coordination number,  $\mathbf{r}_n$  denotes a nearest neighbor of  $\mathbf{r}$  on the lattice, and the normalized bond transition probability

$$\Phi(\mathbf{b}) \equiv \frac{\exp[-\beta u(\mathbf{b})]}{\sum_{\mathbf{b}} \exp[-\beta u(\mathbf{b})]}. \quad (3)$$

Note that  $\Phi(\mathbf{b}) = 1/z$  if  $\mathbf{b}$  is one of the allowed bond vectors on the lattice (i.e.,  $\beta u(\mathbf{b}) = 0$ ) and 0 otherwise (i.e.,  $\beta u(\mathbf{b}) = \infty$ ), and that  $\Phi(\mathbf{b}) = \Phi(-\mathbf{b})$ .

The one-end-integrated propagator  $q_s(\mathbf{r})$ , corresponding to the probability of finding a partial chain of  $s$  segments that starts anywhere in the system and ends at  $\mathbf{r}$  in the external field, is defined as

$$\begin{aligned} q_s(\mathbf{r}) &\equiv \sum_{\mathbf{r}_0} g_s(\mathbf{r}|\mathbf{r}_0) = \sum_{\mathbf{r}_1} g_s(\mathbf{r}_1|\mathbf{r}) \\ &= \sum_{\mathbf{R}_s} \delta_{\mathbf{R}_s, \mathbf{r}} \exp[-\omega(\mathbf{R}_s)] \prod_{k=1}^{s-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)], \end{aligned} \quad (4)$$

and satisfies the recursive relation

$$\begin{aligned}
q_{s=1}(\mathbf{r}) &= \exp[-\omega(\mathbf{r})] \\
q_{s+1}(\mathbf{r}) &= \exp[-\omega(\mathbf{r})] \sum_{\mathbf{r}'} \Phi(\mathbf{r} - \mathbf{r}') q_s(\mathbf{r}') \\
&= \frac{\exp[-\omega(\mathbf{r})]}{z} \sum_{\mathbf{r}_n} q_s(\mathbf{r}_n) \quad 1 \leq s \leq N - 1.
\end{aligned} \tag{5}$$

For a constant external field  $\omega(\mathbf{r}) = C$ , we have  $q_s(\mathbf{r}) = \exp(-Cs)$ . Also note that

$$\begin{aligned}
\frac{\delta q_s(\mathbf{r})}{\delta \omega(\mathbf{r}')} &= \sum_{s'=1}^s \frac{\delta q_s(\mathbf{r})}{\delta \omega(\mathbf{R}_{s'})} \frac{\delta \omega(\mathbf{R}_{s'})}{\delta \omega(\mathbf{r}')} \\
&= \sum_{s'=1}^s \sum_{\mathbf{R}_s} \delta_{\mathbf{R}_s, \mathbf{r}} \exp[-\omega(\mathbf{R}_s)] \prod_{k=s'}^{s-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] (-1) \\
&\quad \cdot \prod_{k=1}^{s'-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] \cdot \delta_{\mathbf{R}_{s'}, \mathbf{r}'} \\
&= - \sum_{s'=1}^s \sum_{\mathbf{R}_s} \delta_{\mathbf{R}_s, \mathbf{r}} \exp[-\omega(\mathbf{R}_s)] \prod_{k=s'}^{s-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] \cdot \delta_{\mathbf{R}_{s'}, \mathbf{r}'} \\
&\quad \cdot \underbrace{e^{\omega(\mathbf{r}')} \sum_{\mathbf{R}_{s'}} \delta_{\mathbf{R}_{s'}, \mathbf{r}'} e^{-\omega(\mathbf{R}_{s'})}}_{=1} \cdot \prod_{k=1}^{s'-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] \\
&= - \sum_{s'=1}^s \underline{g_{s-s'+1}(\mathbf{r}|\mathbf{r}') e^{\omega(\mathbf{r}')} q_{s'}(\mathbf{r}')}, \tag{6}
\end{aligned}$$

where the underlined term inserted above is simply 1.

The single-chain partition function in the external field is defined as

$$\begin{aligned}
Q &\equiv \frac{1}{V} \sum_{\mathbf{r}} q_N(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{r}_1} \sum_{\mathbf{r}_0} g_N(\mathbf{r}_1|\mathbf{r}_0) \\
&= \frac{1}{V} \sum_{\mathbf{R}_N} \exp[-\omega(\mathbf{R}_N)] \prod_{k=1}^{N-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] = \frac{Z_0}{\mathcal{G}}, \tag{7}
\end{aligned}$$

where  $V$  is the total number of lattice sites,

$$\mathcal{Z}_0 \equiv \prod_{s=1}^N \sum_{\mathbf{R}_s} \cdot \exp \left[ -\beta h^C - \sum_{s=1}^N \omega(\mathbf{R}_s) \right] \quad (8)$$

is the canonical-ensemble partition function of an ideal homopolymer chain of  $N$  segments in the external field,  $h^C \equiv \sum_{s=1}^{N-1} u(\mathbf{b}_s)$  is the Hamiltonian due to the chain connectivity with  $\mathbf{b}_s \equiv \mathbf{R}_{s+1} - \mathbf{R}_s$ , and

$$\mathcal{G} \equiv V \prod_{s=1}^{N-1} \sum_{\mathbf{b}_s} \cdot \exp [-\beta h^C] = V z^{N-1} \quad (9)$$

is the partition function of an ideal chain without the external field. Note that

$$\begin{aligned} Q &= \frac{1}{V} \sum_{\mathbf{R}_N} \exp[-\omega(\mathbf{R}_N)] \underbrace{\prod_{k=s}^{N-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)] \cdot e^{\omega(\mathbf{R}_s)}}_{\cdot e^{-\omega(\mathbf{R}_s)} \prod_{k=1}^{s-1} \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_{k+1} - \mathbf{R}_k) \exp[-\omega(\mathbf{R}_k)]} \\ &= \frac{1}{V} \sum_{\mathbf{R}_s} \exp[-\omega(\mathbf{R}_s)] \underbrace{\sum_{\mathbf{R}_{k=s+1}} \Phi(\mathbf{R}_k - \mathbf{R}_s) \exp[-\omega(\mathbf{R}_k)]}_{\cdot \prod_{k=s+2}^N \sum_{\mathbf{R}_k} \Phi(\mathbf{R}_k - \mathbf{R}_{k-1}) \exp[-\omega(\mathbf{R}_k)] \cdot e^{\omega(\mathbf{R}_s)} \cdot q_s(\mathbf{R}_s)} \\ &= \frac{1}{V} \sum_{\mathbf{R}_s} \exp[-\omega(\mathbf{R}_s)] \sum_{\mathbf{R}_{t=N-s}} \Phi(\mathbf{R}_t - \mathbf{R}_s) \exp[-\omega(\mathbf{R}_t)] \\ &\quad \cdot \prod_{t=1}^{N-s-1} \sum_{\mathbf{R}_t} \Phi(\mathbf{R}_{t+1} - \mathbf{R}_t) \exp[-\omega(\mathbf{R}_t)] \cdot e^{\omega(\mathbf{R}_s)} \cdot q_s(\mathbf{R}_s) \\ &= \frac{1}{V} \sum_{\mathbf{R}_s} q_{N-s+1}(\mathbf{R}_s) e^{\omega(\mathbf{R}_s)} q_s(\mathbf{R}_s) = \frac{1}{V} \sum_{\mathbf{r}} q_{N-s+1}(\mathbf{r}) e^{\omega(\mathbf{r})} q_s(\mathbf{r}), \end{aligned} \quad (10)$$

where the two underlined terms above are the same but written in the opposite order of  $k, t \equiv N - k + 1$ , and we have used Eq. (4).

Finally,

$$\begin{aligned}\frac{\delta Q}{\delta\omega(\mathbf{r})} &= \frac{1}{V} \sum_{\mathbf{r}_1} \frac{\delta q_N(\mathbf{r}_1)}{\delta\omega(\mathbf{r})} = -\frac{1}{V} \sum_{\mathbf{r}_1} \sum_{s=1}^N g_{N-s+1}(\mathbf{r}_1|\mathbf{r}) e^{\omega(\mathbf{r})} q_s(\mathbf{r}) \\ &= -\frac{\exp[\omega(\mathbf{r})]}{V} \sum_{s=1}^N q_{N-s+1}(\mathbf{r}) q_s(\mathbf{r}).\end{aligned}\tag{11}$$

## 1.2 Discrete and Continuous Gaussian Chain in Continuum

In continuum, the above summation over lattice sites is replaced by an integral over space, i.e.,  $\sum_{\mathbf{r}} \rightarrow \int d\mathbf{r}$ , and the Kronecker  $\delta$ -function is replaced by the Dirac  $\delta$ -function, i.e.,  $\delta_{\mathbf{r},\mathbf{r}_0} \rightarrow \delta(\mathbf{r} - \mathbf{r}_0)$ .

For a discrete Gaussian chain (DGC) of  $N$  segments,  $\beta u(\mathbf{b}) = 3|\mathbf{b}|^2/2a^2$  with  $a$  denoting the average (or effective) bond length; all the above results therefore still apply (except, of course, those containing  $z$ ), with the normalized bond transition probability given by

$$\Phi(\mathbf{b}) = \left(\frac{3}{2\pi a^2}\right)^{d/2} \exp\left(-\frac{3|\mathbf{b}|^2}{2a^2}\right),\tag{12}$$

where  $d$  denotes the system dimensionality.

In the limit of  $N \rightarrow \infty$  while keeping  $R_{g,0} \equiv \sqrt{Na^2/6}$  finite, DGC becomes the continuous Gaussian chain (CGC). In this case, the variable  $s$  along the chain contour becomes continuous, i.e.,  $s \in [0, 1]$ ; the above summation over  $s$  is therefore replaced by an integral, i.e.,  $\frac{1}{N} \sum_{s=1}^N \rightarrow \int_0^1 ds$ . For simplicity, we also re-scale variables according to  $\mathbf{r}/R_{g,0} \rightarrow \mathbf{r}$  and  $N\omega(\mathbf{r}) \rightarrow \omega(\mathbf{r})$  hereafter. Finally, we write the propagators as  $g(\mathbf{r}, s|\mathbf{r}_0)$  and  $q(\mathbf{r}, s)$  for CGC.

For CGC, the recursive relation Eq. (2) becomes the Chapman-Kolmogorov equation (CKE)

$$g(\mathbf{r}, s + ds|\mathbf{r}_0) = \exp[-\omega(\mathbf{r})ds] \int d\mathbf{r}' \Phi(\mathbf{r} - \mathbf{r}') g(\mathbf{r}', s|\mathbf{r}_0), \quad g(\mathbf{r}, s = 0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0)\tag{13}$$

where

$$\Phi(\mathbf{r} - \mathbf{r}') = \left(\frac{1}{4\pi ds}\right)^{d/2} \exp\left(-\frac{|\mathbf{r} - \mathbf{r}'|^2}{4ds}\right)\tag{14}$$

is the probability for CGC to propagate from  $\mathbf{r}'$  to  $\mathbf{r}$  over an infinitesimal chain length of  $ds$ . Substituting the Taylor expansion

$$\begin{aligned} g(\mathbf{r}, s + ds|\mathbf{r}_0) &\approx g(\mathbf{r}, s|\mathbf{r}_0) + \frac{\partial g(\mathbf{r}, s|\mathbf{r}_0)}{\partial s} ds \\ \exp[-\omega(\mathbf{r})ds] &\approx 1 - \omega(\mathbf{r})ds \\ g(\mathbf{r}', s|\mathbf{r}_0) &\approx g(\mathbf{r}, s|\mathbf{r}_0) + \nabla g(\mathbf{r}, s|\mathbf{r}_0) \cdot (\mathbf{r}' - \mathbf{r}) + \frac{1}{2} \nabla \nabla g(\mathbf{r}, s|\mathbf{r}_0) : (\mathbf{r}' - \mathbf{r})(\mathbf{r}' - \mathbf{r}) \end{aligned} \quad (15)$$

into Eq. (13), and using

$$\begin{aligned} \int d\mathbf{r}' \Phi(\mathbf{r}, \mathbf{r}') &= 1 \\ \int d\mathbf{r}' \Phi(\mathbf{r}, \mathbf{r}') (\mathbf{r}' - \mathbf{r}) &= \mathbf{0} \\ \int d\mathbf{r}' \Phi(\mathbf{r}, \mathbf{r}') (\mathbf{r}' - \mathbf{r})(\mathbf{r}' - \mathbf{r}) &= 2ds\mathbf{I} \end{aligned} \quad (16)$$

where  $\mathbf{0}$  is the zero-vector and  $\mathbf{I}$  the identity matrix (with all diagonal elements being 1 and others being 0), we then obtain

$$\frac{\partial g(\mathbf{r}, s|\mathbf{r}_0)}{\partial s} ds = \nabla \nabla g(\mathbf{r}, s|\mathbf{r}_0) : ds\mathbf{I} - \omega(\mathbf{r})ds [g(\mathbf{r}, s|\mathbf{r}_0) + \nabla \nabla g(\mathbf{r}, s|\mathbf{r}_0) : ds\mathbf{I}]. \quad (17)$$

With  $\nabla \nabla g(\mathbf{r}, s|\mathbf{r}_0) : \mathbf{I} = \nabla^2 g(\mathbf{r}, s|\mathbf{r}_0)$  and ignoring again the  $(ds)^2$  term, we obtain the modified diffusion equation (MDE)

$$\frac{\partial}{\partial s} g(\mathbf{r}, s|\mathbf{r}_0) = \nabla^2 g(\mathbf{r}, s|\mathbf{r}_0) - \omega(\mathbf{r})g(\mathbf{r}, s|\mathbf{r}_0), \quad g(\mathbf{r}, s = 0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0). \quad (18)$$

The same CKE and MDE can be obtained for  $q(\mathbf{r}, s)$ , with a different initial condition  $q(\mathbf{r}, s = 0) = 1$ . Finally, Eqs. (10) and (11) become

$$Q = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, 1 - s) q(\mathbf{r}, s), \quad (19)$$

$$\frac{\delta Q}{\delta \omega(\mathbf{r})} = -\frac{1}{V} \int_0^1 ds q(\mathbf{r}, 1 - s) q(\mathbf{r}, s). \quad (20)$$

Efficient algorithms are available for solving MDE with high accuracy. Note, however, that CGC (and DGC) can be stretched infinitely, while lattice polymers cannot be stretched beyond their contour length.

## 2 Compressible Homopolymer Melts

### 2.1 Model System

We consider  $n$  homopolymer chains each of  $N$  segments on a lattice of totally  $V$  sites. The canonical-ensemble partition function of this system is given by

$$\mathcal{Z} = \frac{1}{n!} \prod_{k=1}^n \prod_{s=1}^N \sum_{\mathbf{R}_{k,s}} \cdot \exp \left( -\beta \sum_{k=1}^n h_k^C - \beta \mathcal{H}^E \right). \quad (21)$$

Here  $\mathbf{R}_{k,s}$  denotes the lattice position of the  $s^{\text{th}}$  segment on the  $k^{\text{th}}$  chain, and  $\beta \equiv 1/k_B T$  with  $k_B$  denoting the Boltzmann constant and  $T$  the absolute temperature.  $h_k^C$  is the Hamiltonian of the  $k^{\text{th}}$  chain due to its chain connectivity;  $\beta h_k^C = 0$  if the chain connectivity is maintained and  $\infty$  otherwise.  $\mathcal{H}^E$  is the system Hamiltonian due to non-bonded interactions; for our model system of compressible homopolymer melts with Kronecker  $\delta$ -function interactions, we have

$$\beta \mathcal{H}^E[\hat{\rho}] = \frac{1}{2\kappa\rho_0} \sum_{\mathbf{r}} [\hat{\rho}(\mathbf{r}) - \rho_0]^2, \quad (22)$$

where  $\rho_0 \equiv nN/V$  is the average segmental density,  $\hat{\rho}(\mathbf{r}) \equiv \sum_{k=1}^n \sum_{s=1}^N \delta_{\mathbf{r},\mathbf{R}_{k,s}}$  is the microscopic segmental density at lattice site  $\mathbf{r}$  with  $\delta_{\mathbf{r},\mathbf{R}_{k,s}}$  denoting the Kronecker  $\delta$ -function, and  $\kappa$  denotes the Helfand compressibility of the polymer melts (or equivalently, the quality of an implicit, good solvent); when  $\kappa = 0$ , the melts are incompressible.

### 2.2 Field Theory

With the Hubbard-Stratonovich transformation, i.e., inserting the identity  $1 = \int d\boldsymbol{\rho} \frac{d\boldsymbol{\omega}}{(2\pi)^V} \exp \{i\boldsymbol{\omega} \cdot (\boldsymbol{\rho} - \hat{\boldsymbol{\rho}})\}$  into Eq. (21), where  $\boldsymbol{\rho} \equiv \{\rho(\mathbf{r})\}$  is the density field constrained to  $\hat{\boldsymbol{\rho}} \equiv \{\hat{\rho}(\mathbf{r})\}$  and  $\boldsymbol{\omega} \equiv \{\omega(\mathbf{r})\}$  is the conjugate field imposing the constraint ( $\hat{\boldsymbol{\rho}}$  in Eq. (22) is therefore replaced by  $\boldsymbol{\rho}$ ), we can re-write the partition function as

$$\begin{aligned} \mathcal{Z} &= \frac{1}{n!} \prod_{k=1}^n \prod_{s=1}^N \sum_{\mathbf{R}_{k,s}} \cdot \int d\boldsymbol{\rho} \frac{d\boldsymbol{\omega}}{(2\pi)^V} \exp \{i\boldsymbol{\omega} \cdot (\boldsymbol{\rho} - \hat{\boldsymbol{\rho}})\} \exp \left\{ -\beta \sum_{k=1}^n h_k^C - \beta \mathcal{H}^E[\boldsymbol{\rho}] \right\} \\ &= \exp \{ -\beta \mathcal{F}^{id} \} \int d\boldsymbol{\rho} \exp \{ -\beta \mathcal{H}^E[\boldsymbol{\rho}] \} \int \frac{d\boldsymbol{\omega}}{(2\pi)^V} \exp \{ -\beta \mathcal{F}^{en}[i\boldsymbol{\omega}, \boldsymbol{\rho}] \}, \end{aligned} \quad (23)$$

where  $\beta \mathcal{F}^{id} \equiv -\ln(\mathcal{G}^n/n!)$  is the free energy of ideal chains, and  $\beta \mathcal{F}^{en}[i\boldsymbol{\omega}, \boldsymbol{\rho}] \equiv -i\boldsymbol{\omega} \cdot \boldsymbol{\rho} - n \ln Q[i\boldsymbol{\omega}]$  is the excess entropic contribution from chain configurations with

$Q[i\omega] \equiv \mathcal{Z}_0[i\omega]/\mathcal{G}$  denoting the single-chain partition function for a given conjugate field  $\omega$ . Note that  $\omega$  here is real and the above transformation is exact. This de-couples the many-chain interactions into those between an ideal chain and the (fluctuating) conjugate field.

### 2.3 Self-Consistent Field Theory (SCFT)

The SCF solution of the system  $(\omega^*, \rho^*)$  is obtained under the saddle-point approximation

$$\begin{aligned} \left. \frac{\delta\beta\mathcal{F}^{en}[i\omega, \rho]}{\delta i\omega} \right|_{\omega=\omega^*, \rho=\rho^*} = 0 &\Rightarrow \rho^*(\mathbf{r}) = \frac{n \exp[i\omega^*(\mathbf{r})]}{VQ[i\omega^*]} \sum_{s=1}^N q_s(\mathbf{r}) q_{N+1-s}(\mathbf{r}) \\ \left. \frac{\delta\beta(\mathcal{H}^E[\rho] + \mathcal{F}^{en}[i\omega, \rho])}{\delta \rho} \right|_{\omega=\omega^*, \rho=\rho^*} = 0 &\Rightarrow i\omega^*(\mathbf{r}) = \frac{\rho^*(\mathbf{r}) - \rho_0}{\kappa\rho_0}, \end{aligned} \quad (24)$$

where the propagator  $q$  is computed using Eq. (5) with  $i\omega^*$ . These two SCF equations need to be solved simultaneously (self-consistently); this is how the theory got its name. SCFT considers only a single configuration  $\omega^*$  of the conjugate field, and replaces the integral in Eq. (23) by the extremum of its integrand. SCFT therefore ignores the fluctuations and correlations in the system, and is a mean-field theory.

For a homogeneous system, we obtain  $\rho^*(\mathbf{r}) = \rho_0$ ,  $i\omega^*(\mathbf{r}) = 0$ ,  $q_s(\mathbf{r}) = 1$ , and  $Q[i\omega^*] = 1$ . SCFT therefore gives the Helmholtz free energy per chain

$$\beta f_c(N/\kappa) \equiv -\frac{\ln \mathcal{Z}(N/\kappa)}{n} = \frac{\beta\mathcal{F}^{id}}{n} = -\ln \mathcal{G} + \frac{\ln n!}{n}, \quad (25)$$

and the internal energy per chain

$$\beta u_c(N/\kappa) \equiv \frac{\beta\mathcal{H}^E[\rho^*]}{n} = 0. \quad (26)$$

For a given conjugate field  $\omega$ , the mean-square chain radius of gyration can be computed in the field theory as

$$R_g^2 = \frac{1}{N^2} \sum_{s'=1}^{N-1} \sum_{s=s'+1}^N \frac{\sum_{\mathbf{r}} \sum_{\mathbf{r}'} |\mathbf{r} - \mathbf{r}'|^2 \exp[i\omega(\mathbf{r}) + i\omega(\mathbf{r}')] q_{N-s+1}(\mathbf{r}) g_{s-s'+1}(\mathbf{r}, \mathbf{r}') q_{s'}(\mathbf{r}')}{VQ[i\omega]} \quad (27)$$

where the propagator  $g$  is computed using Eq. (2) with  $i\omega$ , and the term in the double summation (over  $s'$  and  $s$ ) with  $s' = 1$  and  $s = N$  gives the mean-square chain end-to-end distance  $R_e^2$ . For a homogeneous system, SCFT gives random walk, i.e.,  $R_e^2 = N - 1$  and  $R_g^2 = (N^2 - 1)/6N$ , regardless of  $N/\kappa$ . (The reason for using of  $N/\kappa$  instead of  $\kappa$  here is seen in the next section.)

### 3 1D Homopolymer Brush in an Implicit, Good Solvent

Here we consider a homopolymer brush on a one-dimensional (1D) lattice of totally  $V = L$  sites. The first segment of all chains is grafted at  $x = 1$ , and an impenetrable wall is placed at  $x = 0$  which cannot be occupied by polymer segments. Our model system is the same as above, with  $\mathbf{R}_{k,s} \rightarrow x_{k,s}$  and  $\mathbf{r} \rightarrow x$ . Note that  $\kappa$  denotes the solvent quality;  $N/\kappa = 0$  corresponds to the  $\theta$ -solvent, while a positive value corresponds to a good solvent.

Inserting in Eq. (21) the identity  $1 = \int \mathcal{D}\phi \mathcal{D}\omega \exp \left\{ \sum_{x=1}^L \omega(x) [\rho_0 \phi(x) - \hat{\rho}(x)] \right\}$ , where  $\phi(x)$  is the normalized segmental density constrained to  $\hat{\rho}(x)/\rho_0$ , and  $\omega(x)$  is the (purely imaginary) conjugate field imposing the constraint, we finally have

$$\mathcal{Z} = \int \mathcal{D}\phi \mathcal{D}\omega \exp \{-n\beta f_c[\phi, \omega]\} \quad (28)$$

with

$$\beta f_c = \frac{1}{L} \sum_{x=1}^L \left\{ \frac{N}{2\kappa} [\phi(x) - 1]^2 - \omega(x) \phi(x) \right\} - \ln(\mathcal{G}Q[\omega]) + \frac{\ln n!}{n}, \quad (29)$$

where we have re-scaled variables according to  $N\omega(x) \rightarrow \omega(x)$ .

Similar to Eq. (24), the SCF equations are obtained by setting  $\delta\beta f_c/\delta\phi(x) = \delta\beta f_c/\delta\omega(x) = 0$  and given by

$$\begin{aligned} \omega(x) &= \frac{N}{\kappa} [\phi(x) - 1] \\ \phi(x) &= \frac{\exp[\omega(x)/N]}{NQ} \sum_{s=1}^N q_s(x) q_{N+1-s}^*(x), \end{aligned} \quad (30)$$

where the propagator  $q_s(x)$  corresponds to the probability of finding a partial chain of  $s$  segments starting from the grafted end (where  $s = 1$ ) and ending at  $x$  in the system,

and  $q_t^*(x)$  corresponds to the probability of finding a partial chain of  $t \equiv N + 1 - s$  segments starting from the free end (where  $s = N$ ) and ending at  $x$ . According to the chain connectivity, we have the recursive relations analogous to Eq. (5):

$$q_{s+1}(x) = \exp\left[-\frac{\omega(x)}{N}\right] \frac{q_s(x-1) + q_s(x+1)}{2}, \quad q_{s=1}(x) = \exp\left[-\frac{\omega(x)}{N}\right] \delta_{x,1} \quad (31)$$

where the  $\delta$ -function fixes the grafted segment at  $x = 1$ , and

$$q_{t+1}^*(x) = \exp\left[-\frac{\omega(x)}{N}\right] \frac{q_t^*(x-1) + q_t^*(x+1)}{2}, \quad q_{t=1}^*(x) = \exp\left[-\frac{\omega(x)}{N}\right]. \quad (32)$$

The boundary conditions for the propagators are  $q_s(x) = q_t^*(x) = 0$  for  $x < 1$  and  $x > L$ . Finally, based on Eq. (10),  $Q = q_{t=N}^*(x=1)/L$ .

**Practice:** It is instructive to work out the exact results for  $N = 3$  with finite  $n$ ; one then sees that SCFT corresponds to the limit of  $n \rightarrow \infty$ .

## 4 Incompressible Diblock Copolymer Melts

Here we consider incompressible diblock copolymer melts consisting of  $n$  diblock copolymer chains on a lattice of totally  $V$  sites. Each copolymer chain has  $N_A$  segments of type A followed by  $N_B$  segments of B, and  $N \equiv N_A + N_B$ . The canonical-ensemble partition function is

$$\mathcal{Z} = \frac{1}{n!} \prod_{k=1}^n \prod_{s=1}^N \sum_{\mathbf{R}_{k,s}} \cdot \exp\left(-\beta \sum_{k=1}^n h_k^C - \beta \mathcal{H}^E\right) \cdot \prod_{\mathbf{r}} \delta_{\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}), \rho_0}. \quad (33)$$

Here we again use Kronecker  $\delta$ -function interactions with

$$\beta \mathcal{H}^E[\hat{\rho}_A, \hat{\rho}_B] = \frac{\chi}{2\rho_0} \sum_{\mathbf{r}} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r}), \quad (34)$$

where the Flory-Huggins  $\chi$  parameter denotes the repulsion between A and B segments at the same lattice site, and the microscopic densities of A and B segments at lattice site  $\mathbf{r}$  are defined as  $\hat{\rho}_A(\mathbf{r}) \equiv \sum_{k=1}^n \sum_{s=1}^{N_A} \delta_{\mathbf{r}, \mathbf{R}_{k,s}}$  and  $\hat{\rho}_B(\mathbf{r}) \equiv \sum_{k=1}^n \sum_{s=N_A+1}^N \delta_{\mathbf{r}, \mathbf{R}_{k,s}}$ , respectively. Finally, the last term (with the Kronecker  $\delta$ -function) in Eq. (33) imposes the incompressibility constraint at all lattice sites.

Inserting in Eq. (33) the identity  $1 = \prod_{j=A,B} \int \mathcal{D}\phi_j \mathcal{D}\omega_j \exp \{ \sum_{\mathbf{r}} \omega_j(\mathbf{r}) [\rho_0 \phi_j(\mathbf{r}) - \hat{\rho}_j(\mathbf{r})] \}$  where  $\phi_j(\mathbf{r})$  is the normalized density field constrained to  $\hat{\rho}_j(\mathbf{r})/\rho_0$  and  $\omega_j(\mathbf{r})$  is the (purely imaginary) conjugate field interacting with the species  $j$  ( $=A,B$ ) to impose the constraint, and substituting the following integral form of the  $\delta$ -function into Eq. (33)

$$\prod_{\mathbf{r}} \delta_{\rho_0[\phi_A(\mathbf{r})+\phi_B(\mathbf{r})],\rho_0} = \int \mathcal{D}\eta \exp \left\{ -\rho_0 \sum_{\mathbf{r}} \eta(\mathbf{r}) [\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) - 1] \right\} \quad (35)$$

where  $\eta(\mathbf{r})$  is a (purely imaginary) conjugate field enforcing the incompressibility, we finally have

$$\mathcal{Z} = \int \mathcal{D}\phi_A \mathcal{D}\omega_A \mathcal{D}\phi_B \mathcal{D}\omega_B \mathcal{D}\eta \exp \{ -n\beta f_c[\phi_A, \phi_B, \omega_A, \omega_B, \eta] \} \quad (36)$$

with

$$\beta f_c = \frac{1}{V} \sum_{\mathbf{r}} \left\{ \chi N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - \phi_A(\mathbf{r}) \omega_A(\mathbf{r}) - \phi_B(\mathbf{r}) \omega_B(\mathbf{r}) + \eta(\mathbf{r}) [\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) - 1] \right\} - \ln Q, \quad (37)$$

where the single-chain partition function  $Q[\omega_A, \omega_B] \equiv \sum_{\{\mathbf{R}_s\}} \exp[-\beta h^C - \sum_{s=1}^{N_A} \omega_A(\mathbf{R}_s)/N - \sum_{s=N_A+1}^N \omega_B(\mathbf{R}_s)/N] / \mathcal{G}$ . Note that we have omitted a constant factor in  $\mathcal{Z}$  and re-scaled variables according to  $N\omega_j(\mathbf{r}) \rightarrow \omega_j(\mathbf{r})$  and  $N\eta(\mathbf{r}) \rightarrow \eta(\mathbf{r})$ .

The SCF equations are obtained by setting  $\delta\beta f_c/\delta\phi_j(\mathbf{r}) = \delta\beta f_c/\delta\omega_j(\mathbf{r}) = \delta\beta f_c/\delta\eta(\mathbf{r}) = 0$  and given by

$$\begin{aligned} \omega_A(\mathbf{r}) &= \chi N \phi_B(\mathbf{r}) + \eta(\mathbf{r}) \\ \omega_B(\mathbf{r}) &= \chi N \phi_A(\mathbf{r}) + \eta(\mathbf{r}) \\ \phi_A(\mathbf{r}) &= \frac{\exp[\omega_A(\mathbf{r})/N]}{NQ} \sum_{s=1}^{N_A} q_s(\mathbf{r}) q_{N+1-s}^*(\mathbf{r}) \\ \phi_B(\mathbf{r}) &= \frac{\exp[\omega_B(\mathbf{r})/N]}{NQ} \sum_{s=N_A+1}^N q_s(\mathbf{r}) q_{N+1-s}^*(\mathbf{r}) \\ 1 &= \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}). \end{aligned} \quad (38)$$

Here the propagator  $q_s(\mathbf{r})$  corresponds to the probability of finding a partial copolymer chain of  $s$  segments starting from the A-end (where  $s = 1$ ) anywhere in the system and ending at  $\mathbf{r}$ ; according to the chain connectivity, we have the recursive relation

$$\begin{aligned} q_{s=1}(\mathbf{r}) &= \exp[-\omega_A(\mathbf{r})/N] \\ q_{s+1}(\mathbf{r}) &= \begin{cases} \exp[-\omega_A(\mathbf{r})/N] \sum_{\mathbf{r}_n} q_s(\mathbf{r}_n)/z & \text{for } 1 \leq s \leq N_A - 1 \\ \exp[-\omega_B(\mathbf{r})/N] \sum_{\mathbf{r}_n} q_s(\mathbf{r}_n)/z & \text{for } N_A \leq s \leq N - 1 \end{cases}. \end{aligned} \quad (39)$$

Similarly,  $q_t^*(\mathbf{r})$  corresponds to the probability of finding a partial copolymer chain of  $t \equiv N + 1 - s$  segments starting from the B-end (where  $s = N$ ) anywhere in the system and ending at  $\mathbf{r}$ ; we have the recursive relation

$$q_{t=1}^*(\mathbf{r}) = \exp[-\omega_B(\mathbf{r})/N]$$

$$q_{t+1}^*(\mathbf{r}) = \begin{cases} \exp[-\omega_B(\mathbf{r})/N] \sum_{\mathbf{r}_n} q_t^*(\mathbf{r}_n)/z & \text{for } 1 \leq t \leq N_B - 1 \\ \exp[-\omega_A(\mathbf{r})/N] \sum_{\mathbf{r}_n} q_t^*(\mathbf{r}_n)/z & \text{for } N_B \leq t \leq N - 1 \end{cases} \quad (40)$$

For microphase-separated structures in bulk, periodic boundary conditions for these propagators are used. Finally,

$$Q = \begin{cases} \sum_{\mathbf{r}} \exp[\omega_A(\mathbf{r})/N] q_s(\mathbf{r}) q_{N+1-s}^*(\mathbf{r})/V & \text{for } 1 \leq s \leq N_A \\ \sum_{\mathbf{r}} \exp[\omega_B(\mathbf{r})/N] q_s(\mathbf{r}) q_{N+1-s}^*(\mathbf{r})/V & \text{for } N_A + 1 \leq s \leq N \end{cases} \quad (41)$$

**Practice:** Show that, if  $(\boldsymbol{\omega}_A^*, \boldsymbol{\omega}_B^*)$  is a solution to Eq. (38), then  $(\boldsymbol{\omega}_A^* + c, \boldsymbol{\omega}_B^* + c)$  is also a solution, where  $c$  is an arbitrary constant. That is, they result in the same  $(\boldsymbol{\phi}_A^*, \boldsymbol{\phi}_B^*)$  and mean-field free energy (of mixing) per chain  $\beta f_c$ . In general, the conjugate fields in SCFT for an incompressible system can be shifted by an arbitrary constant; this requires some attention on how to obtain a unique solution when solving SCF equations numerically.