Equations to be Solved in Polymer Self-Consistent Field (SCF) Calculations

1. In a canonical ensemble

Here we consider a model system of n_c components of ***flexible*** and ***acyclic*** block copolymers (BCPs) in volume V at thermodynamic temperature T. The BCP component c ($=1,\ldots,n_c$) consists of $n_{\mathrm{B},c}$ blocks connected via a given chain architecture, with block i ($=1,\ldots,n_{\mathrm{B},c}$) being a linear homopolymer of $N_{i,c}$ segments of type m (which depends on the values of i and c). For simplicity, PSCF+ assumes that all blocks in the system have the same chain model, and that all segments in the system have the same volume (except the **joint segments** having no excluded-volume interaction, *i.e.*, no volume); see `Models.pdf` for details.

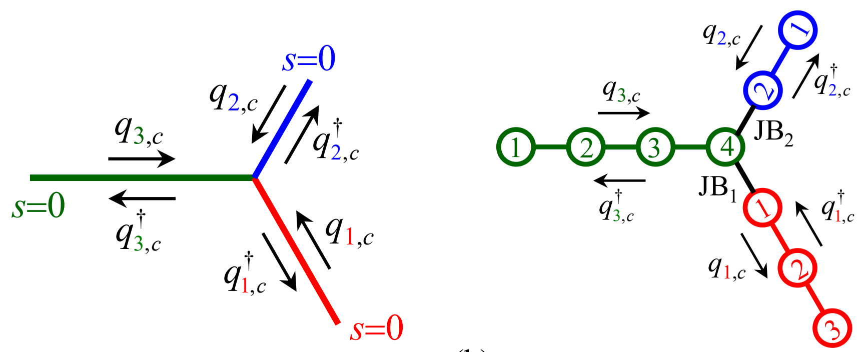
Block i of component c has two (one-end-integrated) propagators: the forward propagator $q_{i,c}(\mathbf{r},s)$ and the backward propagator $q^\dagger_{i,c}(\mathbf{r},s)$, where $\mathbf{r}$ denotes the spatial position and s the block-contour position. For the **continuous-Gaussian-chain (CGC)** model (see `Models.pdf` for details), $q_{i,c}(\mathbf{r},s)$ satisfies the **modified diffusion equation (MDE)**

$$\frac{\partial q_{i,c}}{\partial s} = \frac{b_{i,c}^{\ 2}}{6}\nabla^2 q_{i,c} - \omega_m(\mathbf{r}) q_{i,c} \tag{1}$$

for (continuous) $s\in[0,N_{i,c}]$, where $b_{i,c}$ denotes the effective bond length of the block (strictly speaking, $N_{i,c}\to\infty$ and $b_{i,c}\to 0$, and it is $\sqrt{N_{i,c}}b_{i,c}$ that matters in the CGC model) and $\omega_m(\mathbf{r})$ the conjugate field interacting with the segments on the block, and $q^\dagger_{i,c}(\mathbf{r},s)$ satisfies a similar MDE

$$-\frac{\partial q^\dagger_{i,c}}{\partial s} = \frac{b_{i,c}^{\ 2}}{6}\nabla^2 q^{?}_{i,c} - \omega_m(\mathbf{r}) q^\dagger_{i,c}\,. \tag{2}$$

The MDE has the initial condition of $q_{i,c}(\mathbf{r},s=0)=1$ ($q^\dagger_{i,c}(\mathbf{r},s=N_{i,c})=1$) if the segment $s=0$ ($s=N_{i,c}$) is a free chain end, and otherwise that given by the product of the propagators that "flow into" the



(a) (b)

Figure 1. For a three-arm star BCP (*i.e.*, component c) of (a) the CGC model and (b) a discrete-chain model, where the three blocks are shown in red, blue and green, respectively, the initial condition of the backward propagator for block i=3 is $q^\dagger_{3,c}(\mathbf{r},s=N_{3,c}) = q_{1,c}(\mathbf{r},s=N_{1,c})q_{2,c}(\mathbf{r},s=N_{2,c})$ in (a) and $q^\dagger_{3,c}(\mathbf{r},s=4)=\exp\left(-\omega_m(\mathbf{r})\right)\int \mathrm{d}\mathbf{r}'\Phi_{\mathrm{JB}_1}(|\mathbf{r}-\mathbf{r}'|)q^\dagger_{1,c}(\mathbf{r}',s=1)\int \mathrm{d}\mathbf{r}''\Phi_{\mathrm{JB}_2}(|\mathbf{r}-\mathbf{r}''|)q_{2,c}(\mathbf{r}'',s=2)$ in (b), where m denotes the segment type of the block i=3, and $\Phi_{\mathrm{JB}_1}(r)$ and $\Phi_{\mathrm{JB}_2}(r)$ are the transition probabilities of the two JBs shown in black.

joint segment s=0 (s=$N_{i,c}$) over all other blocks connected to the segment; see Fig. 1(a) for an example. Note that labeling of the two ends of a block (as s=0 and $N_{i,c}$, respectively) can be chosen ***arbitrarily*** in PSCF+ but determines the "flow" direction of propagators; that is, the forward (backward) propagator of a block "flows" in its direction of increasing (decreasing) s. For BCP self-assembly in bulk, periodic boundary conditions are used for the calculation cell; see `SavMem.pdf` for details of solving the MDEs in PSCF+. The volume-fraction field of segments of type m is then given by

$$\phi_m(\mathbf{r}) = \sum_{\{i,c\}\in m} \frac{\bar{\phi}_c}{N_c Q_c} \int_0^{N_{i,c}} \mathrm{d}s\, q_{i,c}(\mathbf{r},s) q_{i,c}^{\dagger}(\mathbf{r},s)\,, \tag{3}$$

where the summation is over all the blocks i and components c whose segment type is m, $\bar{\phi}_c$ is the ***specified*** overall volume fraction of component c in the system satisfying $\sum_{c=1}^{n_c} \bar{\phi}_c = 1$, $Q_c = \hat{q}_{i,c}(\mathbf{q}=\mathbf{0}, s=N_{i,c})$ for any block i of component c whose last segment (*i.e.*, s=$N_{i,c}$) is a free chain end is the normalized single-BCP partition function, $\hat{g}(\mathbf{q}) \equiv \int \mathrm{d}\mathbf{r} \exp\left(-\sqrt{-1}\mathbf{q}\bullet\mathbf{r}\right) g(\mathbf{r}) \big/ V$ denotes the Fourier transform of a ***spatially periodic*** function g($\mathbf{r}$) with $\mathbf{q}$ being the wavevector, and $N_c \equiv \sum_{i=1}^{n_{\mathrm{B},c}} N_{i,c}$ is the total chain length of c; see `RI.pdf` for details of calculating the integral over s in PSCF+.

For **discrete-chain models** (see `Models.pdf` for details), the $n_{\mathrm{B},c}$ blocks are connected by $n_{\mathrm{J},c}$=$n_{\mathrm{B},c}$−1 **joint bonds (JBs)**, and $N_{i,c}$≥1 must be an integer. $q_{i,c}(\mathbf{r},s)$ satisfies the **Chapman-Kolmogorov equation (CKE)**

$$q_{i,c}(\mathbf{r},s+1) = \exp\left(-\omega_m(\mathbf{r})\right) \int \mathrm{d}\mathbf{r}' \Phi_m(|\mathbf{r}-\mathbf{r}'|) q_{i,c}(\mathbf{r}',s) \tag{4}$$

for (integer) s∈[1,$N_{i,c}$−1], where $\Phi_m(r)$ is the bond transition probability of block i of component c satisfying $4\pi\int_0^{\infty} \mathrm{d}r r^2 \Phi_m(r) = 1$ (see `Models.pdf` for details), and $q_{i,c}^{\dagger}(\mathbf{r},s)$ satisfies a similar CKE

$$q_{i,c}^{\dagger}(\mathbf{r},s-1) = \exp\left(-\omega_m(\mathbf{r})\right) \int \mathrm{d}\mathbf{r}' \Phi_m(|\mathbf{r}-\mathbf{r}'|) q_{i,c}^{\dagger}(\mathbf{r}',s) \tag{5}$$

for (integer) s∈[2,$N_{i,c}$]. The CKE has the initial condition of $q_{i,c}(\mathbf{r},s=1) = \exp\left(-\omega_m(\mathbf{r})\right)$ ($q_{i,c}^{\dagger}(\mathbf{r},s=N_{i,c}) = \exp\left(-\omega_m(\mathbf{r})\right)$) if the segment s=1 (s=$N_{i,c}$) is a free chain end, and otherwise that given by the product of the end-segment propagators that "flow into" the segment s=1 (s=$N_{i,c}$) over all other blocks connected to the segment, each convoluted with the transition probability of the connecting JB, with $\exp\left(-\omega_m(\mathbf{r})\right)$; see Fig. 1(b) for an example. The convolutions in CKEs are readily calculated with the fast Fourier transforms; see `SavMem.pdf` for more details. One then has

$$\phi_m(\mathbf{r}) = \exp\left(\omega_m(\mathbf{r})\right) \sum_{\{i,c\}\in m} \frac{\bar{\phi}_c}{N_c Q_c} \sum_{s=1}^{N_{i,c}} q_{i,c}(\mathbf{r},s) q_{i,c}^{\dagger}(\mathbf{r},s)\,; \tag{6}$$

note that joint segments having no excluded-volume interaction (see `Models.pdf` for details) are excluded from the above summations over i.

For **incompressible** systems, one has

$$\omega_m(\mathbf{r}) = \xi(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\beta u_0(|\mathbf{r}-\mathbf{r}'|)\sum_{m'=1}^{n_m}\chi_{mm'}\phi_{m'}(\mathbf{r}'),\tag{7}$$

where $\xi(\mathbf{r})$ is the conjugate field enforcing the incompressibility constraint

$$\sum_{m=1}^{n_m}\phi_m(\mathbf{r}) = 1,\tag{8}$$

$\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant, n_m denotes the total number of segment types in the system, and the normalized non-bonded pair potential between segments $u_0(r)$ and interaction parameters $\chi_{mm'}$ are defined in [Models.pdf]; note that, for joint segments (see [Models.pdf] for details) having no non-bonded interactions (denoted by type J), $\chi_{m\mathrm{J}}=0$ for all m, $\omega_\mathrm{J}(\mathbf{r})=0$, and J is excluded from the above summations over m and m'. See [SlvSCF.pdf] for details of solving the SCF Eqs. (7) and (8) in PSCF+.

For **compressible** systems, one has the SCF equation

$$\omega_m(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\beta u_0(|\mathbf{r}-\mathbf{r}'|)\sum_{m'=1}^{n_m}\left(\frac{1}{\kappa}+\chi_{mm'}\right)\phi_{m'}(\mathbf{r}') - \frac{1}{\kappa},\tag{9}$$

where the excluded-volume interaction parameter κ is defined in [Models.pdf]; joint segments are again excluded from the above summation over m'. In PSCF+, Eq. (9) is iteratively solved in the reciprocal space with $\hat{\omega}_m(\mathbf{q})$ for all m and wavevectors $\mathbf{q}$ (denoted by $\{\hat{\omega}_m(\mathbf{q})\}$) taken as the independent variables and $\{\hat{\phi}_m(\mathbf{q})\}$ calculated from the propagators at given $\{\hat{\omega}_m(\mathbf{q})\}$.

After the above SCF equations are solved, the (mean-field) dimensionless Helmholtz free energy per chain of N segments can be calculated as

$$\beta f_{ch} = -\frac{N}{2V}\int \mathrm{d}\mathbf{r}\sum_{m=1}^{n_m}\omega_m(\mathbf{r})\phi_m(\mathbf{r}) - N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\left(\ln Q_c + 1\right) + N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\beta\mu_c^{\mathrm{ig}}\tag{10}$$

for both incompressible and compressible systems, where $\beta\mu_c^{\mathrm{ig}} \equiv \ln\left(\rho_0\bar{\phi}_c/N_c\right)$ is the ***ideal-gas*** contribution to the dimensionless chain chemical potential $\beta\mu_c$ of component c due to the ***chain*** translational entropy of component c; since ρ_0 is not specified in SCF theory, PSCF+ calculates (as in PSCF)

$$\beta f_{ch}^* \equiv \beta f_{ch} - N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\beta\mu_c^{\mathrm{ig},*} = -\frac{N}{2V}\int \mathrm{d}\mathbf{r}\sum_{m=1}^{n_m}\omega_m(\mathbf{r})\phi_m(\mathbf{r}) - N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\left(\ln\frac{Q_c}{\bar{\phi}_c}+1\right)\tag{11}$$

instead of βf_{ch}, where $\beta\mu_c^{\mathrm{ig},*} \equiv \beta\mu_c^{\mathrm{ig}} - \ln\bar{\phi}_c = \ln\left(\rho_0/N_c\right)$, and $\beta\mu_c^* \equiv \beta\mu_c - \beta\mu_c^{\mathrm{ig},*} = \beta\mu_c^{\mathrm{ex}} + \ln\bar{\phi}_c$, where $\beta\mu_c^{\mathrm{ex}} = -\ln Q_c$ is the dimensionless excess chain chemical potential of component c.

For spatially periodic structures in bulk, βf_{ch} (or, equivalently, βf_{ch}^*) needs to be minimized with respect to up to six parameters (denoted by $\boldsymbol{\theta}$) controlling the size and shape of the calculation cell; this gives

$$\frac{\mathrm{d}\beta f_{ch}}{\mathrm{d}\boldsymbol{\theta}} = \sum_{\mathbf{q}}\frac{\partial q}{\partial\boldsymbol{\theta}}\frac{\mathrm{d}\beta\hat{u}_0(q)}{\mathrm{d}q}\sum_{m=1}^{n_m}\hat{\phi}_m(-\mathbf{q})\left(\frac{N}{2}\sum_{m'=1}^{n_m}\chi_{mm'}\hat{\phi}_{m'}(\mathbf{q})+C(\mathbf{q})\right) - N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c Q_c}\frac{\partial Q_c}{\partial\boldsymbol{\theta}} = 0,\tag{12}$$

where $\partial/\partial\boldsymbol{\theta}$ is taken at fixed $\{\hat{\omega}_m(\mathbf{q})\}$, $q\equiv|\mathbf{q}|$ is the wavenumber, $\hat{u}_0(q) = \left(4\pi/q\right)\int_0^\infty \mathrm{d}r\,r\sin(qr)u_0(r)$ is the 3D Fourier transform of $u_0(r)$, $C(\mathbf{q})=0$ for

incompressible systems and $\frac{N}{\kappa}\left(\frac{1}{2}\sum_{m'=1}^{n_m}\hat{\phi}_{m'}(\mathbf{q})-\delta_{\mathbf{q},\mathbf{0}}\right)$ for **compressible** systems, and finally for the **CGC models** $\frac{\partial Q_c}{\partial \boldsymbol{\theta}}=\sum_{\mathbf{q}}\frac{\partial q}{\partial \boldsymbol{\theta}}\sum_{i=1}^{n_{B,c}}\frac{\mathrm{d}\hat{\Phi}_{i,c}(q)}{\mathrm{d}q}\int_0^{N_{i,c}}\mathrm{d}s\hat{q}_{i,c}(\mathbf{q},s)\hat{q}_{i,c}^{\dagger}(-\mathbf{q},s)$ with $\hat{\Phi}_{i,c}(q)=(4\pi/q)\int_0^{\infty}\mathrm{d}rr\sin(qr)\Phi_{i,c}(r)$ being the 3D Fourier transform of the bond transition probability $\Phi_{i,c}(r)$ of the block i of component c, while for the **discrete-chain models** it is given by the summation of $\sum_{\mathbf{q}}\frac{\partial q}{\partial \boldsymbol{\theta}}\frac{\mathrm{d}\hat{\Phi}_b(q)}{\mathrm{d}q}\hat{q}'(\mathbf{q},s_b)\hat{q}'(-\mathbf{q},s_b')$ over each bond b (which connects segments s_b and s_b') in a BCP molecule of component c with $\hat{\Phi}_b(q)$ being the 3D Fourier transform of the bond transition probability of b and $\hat{q}'(\mathbf{q},s_b)$ and $\hat{q}'(-\mathbf{q},s_b')$ being that of the two (either forward or backward) propagators "flowing" into b (as an example, for the three-arm star BCP shown in Fig. 1(b) one has

$$\frac{\partial Q_c}{\partial \boldsymbol{\theta}}=\sum_{\mathbf{q}}\frac{\partial q}{\partial \boldsymbol{\theta}}\left[\begin{array}{l}\frac{\mathrm{d}\hat{\Phi}_1(q)}{\mathrm{d}q}\left(\hat{q}_{1,c}^{\dagger}(\mathbf{q},s=3)\hat{q}_{1,c}(-\mathbf{q},s=2)+\hat{q}_{1,c}^{\dagger}(\mathbf{q},s=2)\hat{q}_{1,c}(-\mathbf{q},s=1)\right)\\ +\frac{\mathrm{d}\hat{\Phi}_{\mathrm{JB}_1}(q)}{\mathrm{d}q}\hat{q}_{1,c}^{\dagger}(\mathbf{q},s=1)\hat{q}_{3,c}(-\mathbf{q},s=4)+\frac{\mathrm{d}\hat{\Phi}_2(q)}{\mathrm{d}q}\hat{q}_{2,c}(\mathbf{q},s=1)\hat{q}_{2,c}^{\dagger}(-\mathbf{q},s=2)\\ +\frac{\mathrm{d}\hat{\Phi}_{\mathrm{JB}_2}(q)}{\mathrm{d}q}\hat{q}_{2,c}(\mathbf{q},s=2)\hat{q}_{3,c}(-\mathbf{q},s=4)\\ +\frac{\mathrm{d}\hat{\Phi}_3(q)}{\mathrm{d}q}\left(\begin{array}{l}\hat{q}_{3,c}(\mathbf{q},s=1)\hat{q}_{3,c}^{\dagger}(-\mathbf{q},s=2)+\hat{q}_{3,c}(\mathbf{q},s=2)\hat{q}_{3,c}^{\dagger}(-\mathbf{q},s=3)\\ +\hat{q}_{3,c}(\mathbf{q},s=3)\hat{q}_{3,c}^{\dagger}(-\mathbf{q},s=4)\end{array}\right)\end{array}\right]$$

); note that $\frac{\mathrm{d}\beta\hat{u}_0(q)}{\mathrm{d}q}=0$ when $\beta u_0(r)=\delta(r)$ (*i.e.*, for zero-range non-bonded interactions; see Models.pdf for details). In PSCF+, Eq. (12) is solved simultaneously with the SCF equations (*i.e.*, Eqs. (7) and (8) or Eq. (9)) via the Anderson mixing[1]; see Ref. 2 for details.

2. In a grand-canonical ensemble

Here we specify $\beta\mu_c^*$, and replace Eqs. (3) and (6) by

$$\phi_m(\mathbf{r})=\sum_{\{i,c\}\in m}\frac{\exp(\beta\mu_c^*)}{N_c}\int_0^{N_{i,c}}\mathrm{d}sq_{i,c}(\mathbf{r},s)q_{i,c}^{\dagger}(\mathbf{r},s) \tag{13}$$

and

$$\phi_m(\mathbf{r})=\exp(\omega_m(\mathbf{r}))\sum_{\{i,c\}\in m}\frac{\exp(\beta\mu_c^*)}{N_c}\sum_{s=1}^{N_{i,c}}q_{i,c}(\mathbf{r},s)q_{i,c}^{\dagger}(\mathbf{r},s), \tag{14}$$

respectively; all other SCF equations remain unchanged. After these SCF equations are solved, the (mean-field) dimensionless grand potential per chain of N segments can be calculated as

$$\beta\omega_{ch} = -\frac{N}{2V}\int \mathrm{d}\mathbf{r}\sum_{m=1}^{n_m}\omega_m(\mathbf{r})\phi_m(\mathbf{r}) - N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c} \tag{15}$$

with $\bar{\phi}_c = Q_c \exp\left(\beta\mu_c^*\right)$, which is related to βf_{ch} via the Legendre transform as $\beta\omega_{ch} = \beta f_{ch} - N\sum_{c=1}^{n_c}\beta\mu_c\bar{\phi}_c / N_c$. For spatially periodic structures in bulk, minimizing $\beta\omega_{ch}$ with respect to $\boldsymbol{\theta}$ then gives

$$\frac{\mathrm{d}\beta\omega_{ch}}{\mathrm{d}\boldsymbol{\theta}} = \sum_{\mathbf{q}}\frac{\partial q}{\partial\boldsymbol{\theta}}\frac{\mathrm{d}\beta\hat{u}_0(q)}{\mathrm{d}q}\sum_{m=1}^{n_m}\hat{\phi}_m(-\mathbf{q})\left(\frac{N}{2}\sum_{m'=1}^{n_m}\chi_{mm'}\hat{\phi}_{m'}(\mathbf{q}) + C(\mathbf{q})\right) - N\sum_{c=1}^{n_c}\frac{\exp\left(\beta\mu_c^*\right)}{N_c}\frac{\partial Q_c}{\partial\boldsymbol{\theta}} = 0, \tag{16}$$

similar to Eq. (12). Note that we will implement the grand-canonical-ensemble calculations of compressible systems later.

References:

1. Matsen, M. W., Fast and accurate SCFT calculations for periodic block-copolymer morphologies using the spectral method with Anderson mixing. *Eur. Phys. J. E* **2009,** *30* (4), 361-369.
2. Arora, A.; Morse, D. C.; Bates, F. S.; Dorfman, K. D., Accelerating self-consistent field theory of block polymers in a variable unit cell. *J. Chem. Phys.* **2017,** *146* (24), 244902.