

Solving Polymer Self-Consistent Field (SCF) Equations for an Incompressible System

Here we focus on the (linear) SCF equations given for an incompressible system as

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

where $\omega_m(\mathbf{r})$ is the conjugate field at spatial position \mathbf{r} interacting with segments of type m , $\xi(\mathbf{r})$ is the conjugate field enforcing the incompressibility constraint

$$\sum_{m=1}^{n_m} \phi_m(\mathbf{r}) = 1 \quad (2)$$

as in the “standard” model, n_m denotes the total number of segment types in the system, $\phi_m(\mathbf{r})$ is the volume fraction of segments of type m , and the non-bonded interaction parameters $\beta u_0(r)$ and $\chi_{mm'}$ are defined in [Models.pdf](#); note that, for joint segments (see [Models.pdf](#) for details) having no non-bonded interactions (denoted by type J), $\chi_{mJ}=0$ for all m , $\omega_J(\mathbf{r})=0$, and J is excluded from the summation in Eq. (2).

In PSCF, Eqs. (1) and (2) are solved via the Anderson mixing.¹ Note that, for incompressible systems, all the conjugate fields (*i.e.*, $\omega_m(\mathbf{r})$ for all m and $\xi(\mathbf{r})$) can be shifted by an arbitrary constant, which is fixed by setting $\hat{\xi}(\mathbf{q} = \mathbf{0}) = 0$ in PSCF, where $\hat{g}(\mathbf{q}) \equiv \int d\mathbf{r} \exp(-\sqrt{-1}\mathbf{q} \cdot \mathbf{r}) g(\mathbf{r}) / V$ denotes the Fourier transform of a spatially periodic function $g(\mathbf{r})$ with \mathbf{q} being the wavevector and V the system volume; Eq. (1) then gives $\hat{\omega}(\mathbf{q} = \mathbf{0}) = \mathbf{X}\bar{\phi}$, where $\hat{\omega}(\mathbf{q})$ and $\bar{\phi} = \hat{\phi}(\mathbf{q} = \mathbf{0})$ are column vectors with their m^{th} ($m=1, \dots, n_m$) element being $\hat{\omega}_m(\mathbf{q})$ and $\bar{\phi}_m = \hat{\phi}_m(\mathbf{q} = \mathbf{0})$, respectively, and \mathbf{X} is an $n_m \times n_m$ matrix with its (m, m') -element being $\chi_{mm'}$.¹ With $\hat{\omega}(\mathbf{q} \neq \mathbf{0})$ taken as the independent variables, the residual of Eq. (1) is calculated as $\boldsymbol{\varepsilon}(\mathbf{q} \neq \mathbf{0}) = \mathbf{X}\hat{\phi}(\mathbf{q} \neq \mathbf{0}) - (\mathbf{I} - \mathbf{1}\mathbf{1}^T \mathbf{X}^{-1} / \mathbf{1}^T \mathbf{X}^{-1} \mathbf{1})\hat{\omega}(\mathbf{q} \neq \mathbf{0})$, where \mathbf{I} denotes the $n_m \times n_m$ identity matrix, $\mathbf{1}$ denotes the column vector having n_m elements of 1, and the column vector $\hat{\phi}(\mathbf{q} \neq \mathbf{0})$ is obtained from the (one-end-integrated) propagators at given $\hat{\omega}(\mathbf{q})$.¹ Clearly, this approach used in PSCF requires \mathbf{X} be invertible, which is not satisfied when all the χ -parameters of some segment type (*e.g.*, J or an athermal solvent) are 0.

In PSCF+, to avoid the above problem we write Eqs. (1) **and** (2) in a block matrix form as $\begin{bmatrix} \mathbf{X} & \mathbf{1} \\ \mathbf{1}^T & 0 \end{bmatrix} \begin{bmatrix} \hat{\phi}(\mathbf{q}) \\ \xi(\mathbf{q}) \end{bmatrix} = \begin{bmatrix} \hat{\omega}(\mathbf{q}) \\ \delta_{\mathbf{q}, \mathbf{0}} \end{bmatrix}$; different from \mathbf{X} , the $(n_m+1) \times (n_m+1)$ matrix $\begin{bmatrix} \mathbf{X} & \mathbf{1} \\ \mathbf{1}^T & 0 \end{bmatrix}$ is always invertible, and we use \mathbf{A} to denote the $n_m \times n_m$ submatrix obtained by deleting the last row and the last column of $\begin{bmatrix} \mathbf{X} & \mathbf{1} \\ \mathbf{1}^T & 0 \end{bmatrix}^{-1}$. With $\hat{\omega}(\mathbf{q} \neq \mathbf{0})$ taken as the independent variables, the residual of Eq. (1) is then calculated as $\boldsymbol{\varepsilon}(\mathbf{q} \neq \mathbf{0}) = \hat{\phi}(\mathbf{q} \neq \mathbf{0}) - \mathbf{A}\hat{\omega}(\mathbf{q} \neq \mathbf{0})$; as in PSCF, here we set $\hat{\xi}(\mathbf{q} = \mathbf{0}) = 0$ and obtain $\hat{\phi}(\mathbf{q} \neq \mathbf{0})$ from the propagators at given $\hat{\omega}(\mathbf{q})$.

References:

1. 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.