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

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

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

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

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), $\chi_{m\mathrm{J}}=0$ for all m, $\omega_\mathrm{J}(\mathbf{r})=0$, 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 $\hat{g}(\mathbf{q}) \equiv \int \mathrm{d}\mathbf{r} \exp\left(-\sqrt{-1}\mathbf{q}\bullet\mathbf{r}\right) g(\mathbf{r}) \big/ V$ denotes the Fourier transform of a spatially periodic function g($\mathbf{r}$) with $\mathbf{q}$ being the wavevector and V the system volume; Eq. (1) then gives $\hat{\boldsymbol{\omega}}(\mathbf{q}=\mathbf{0}) = \mathbf{X}\bar{\boldsymbol{\phi}}$, where $\hat{\boldsymbol{\omega}}(\mathbf{q})$ and $\bar{\boldsymbol{\phi}} = \hat{\boldsymbol{\phi}}(\mathbf{q}=\mathbf{0})$ are column vectors with their m^{th} (m=1,…,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 $\hat{\boldsymbol{\omega}}(\mathbf{q}\neq\mathbf{0})$ taken as the independent variables, the residual of Eq. (1) is calculated as $\boldsymbol{\varepsilon}(\mathbf{q}\neq\mathbf{0}) = \mathbf{X}\hat{\boldsymbol{\phi}}(\mathbf{q}\neq\mathbf{0}) - \left(\mathbf{I} - \mathbf{1}\mathbf{1}^T\mathbf{X}^{-1} \big/ \mathbf{1}^T\mathbf{X}^{-1}\mathbf{1}\right)\hat{\boldsymbol{\omega}}(\mathbf{q}\neq\mathbf{0})$, 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 $\hat{\boldsymbol{\phi}}(\mathbf{q}\neq\mathbf{0})$ is obtained from the (one-end-integrated) propagators at given $\hat{\boldsymbol{\omega}}(\mathbf{q})$.[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 $\begin{bmatrix} \mathbf{X} & \mathbf{1} \\ \mathbf{1}^T & 0 \end{bmatrix} \begin{bmatrix} \hat{\boldsymbol{\phi}}(\mathbf{q}) \\ \hat{\xi}(\mathbf{q}) \end{bmatrix} = \begin{bmatrix} \hat{\boldsymbol{\omega}}(\mathbf{q}) \\ \delta_{\mathbf{q},\mathbf{0}} \end{bmatrix}$; different from $\mathbf{X}$, the (n_m+1)×(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 $\hat{\boldsymbol{\omega}}(\mathbf{q}\neq\mathbf{0})$ taken as the independent variables, the residual of Eq. (1) is then calculated as $\boldsymbol{\varepsilon}(\mathbf{q}\neq\mathbf{0}) = \hat{\boldsymbol{\phi}}(\mathbf{q}\neq\mathbf{0}) - \mathbf{A}\hat{\boldsymbol{\omega}}(\mathbf{q}\neq\mathbf{0})$; as in PSCF, here we set $\hat{\xi}(\mathbf{q}=\mathbf{0})=0$ and obtain $\hat{\boldsymbol{\phi}}(\mathbf{q}\neq\mathbf{0})$ from the propagators at given $\hat{\boldsymbol{\omega}}(\mathbf{q})$.

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.