Chain Models (with Non-Bonded Interactions) and Chain Architecture

The model system in PSCF+ can be a mixture of ***flexible*** and ***acyclic*** block copolymers (BCPs) of different chain lengths and/or architectures. 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 $1/\rho_0$ (except the **joint segments** having no excluded-volume interaction as described below).

To explain the various chain models in PSCF+, let us first focus on one **block** in a BCP, which is a linear homopolymer of $N \geq 1$ segments of type m. In this case, a chain model is characterized by the ***functional forms*** of both its bonding potential $u_m^{\mathrm{b}}(r)$, where r denotes the distance between two segments, and its non-bonded (excluded-volume) interaction. Note that we shift $\beta u_m^{\mathrm{b}}(r)$ by a constant such that $4\pi\int_0^\infty \mathrm{d}r r^2 \Phi_m(r) = 1$, where $\beta \equiv 1/k_B T$ with k_B denoting the Boltzmann constant and T the thermodynamic temperature of the system, and $\Phi_m(r) \equiv \exp\left(-\beta u_m^{\mathrm{b}}(r)\right)$ is the bond transition probability; for example, $\Phi_m^{\mathrm{FJC}}(r) = \delta(r - b_m)/4\pi {b_m}^2$ for the **freely jointed chain (FJC)** of a fixed bond length b_m, and $\Phi_m^{\mathrm{DGC}}(r) = \left(3/2\pi {b_m}^2\right)^{3/2} \exp\left(-3r^2/2{b_m}^2\right)$ for the **discrete Gaussian chain (DGC)** of an effective bond length b_m. Both of these become the **continuous Gaussian chain (CGC)** in the limit of $N \to \infty$ and $b_m \to 0$ at finite $\sqrt{N-1}\, b_m > 0$.

On the other hand, the excluded-volume interaction of the system can be described either by the many-body incompressibility constraint enforced at all spatial position **r** in the system (that is, the system is ***incompressible***), or by a non-bonded pair potential $u^\kappa(r)$ between polymer segments, which must be soft (*i.e.*, allow complete overlap of segments) and integrable (*i.e.*, $4\pi\int_0^\infty \mathrm{d}r r^2 \beta u^\kappa(r)$ is finite) in the polymer self-consistent field theory (in this case, the system is ***compressible***). In the latter case, we take $u^\kappa(r) = u_0(r)/\kappa\rho_0$, where $4\pi\int_0^\infty \mathrm{d}r r^2 \beta u_0(r) = 1$ and the dimensionless parameter $\kappa > 0$ controls the potential strength (thus the system compressibility). We have implemented in PSCF+ the **soft-sphere (SS) potential** $\beta u_0^{\mathrm{SS}}(r) = 3/4\pi\sigma^3$ for $r < \sigma$ and 0 otherwise with $\sigma > 0$ being the potential cut-off, the **dissipative particle dynamics (DPD) potential** $\beta u_0^{\mathrm{DPD}}(r) = \left(15/2\pi\sigma^3\right)\left(1 - r/\sigma\right)^2$ for $r < \sigma$ and 0 otherwise, and the **Gaussian (G) potential** $\beta u_0^{\mathrm{G}}(r) = \exp\left(-r^2/\sigma^2\right)\Big/\left(\sqrt{\pi}\sigma\right)^3$ with $\sigma > 0$ controlling the potential range; all of these are purely repulsive and in the limit of $\sigma \to 0$ become the **Dirac δ-function potential**.

The **tangent soft-sphere chain (TSSC) model** therefore refers to the combination of FJC and SS potential, and the **dissipative particle dynamics chain (DPDC) model** refers to that of DGC and DPD potential; while other combinations (*i.e.*, chain models) are possible, we note that those of discrete chains with the Dirac δ-function potential lead to unphysical results for BCP self-assembly (see figure 1 and related text in Ref. 1 for details). In PSCF+, the excluded-volume interaction of the system can also be modelled via the incompressibility constraint, which corresponds to the limit of $\kappa \to 0$.

For a bond connecting two blocks of segment type m and m', respectively, PSCF+ uses the

parameter $b_{mm'} \equiv \sqrt{b_m b_{m'}}$ for its bonding potential. Note that, based on the symmetry consideration for discrete-chain models, one can introduce in PSCF+ a **joint segment (JS)** of N=1, and simply use b_m for the bond connecting it to a block of segment type m; Fig. 1 gives an example of compositionally symmetric star triblock terpolymer, where the joint segment shown in black is needed. PSCF+ also assumes that $u^{\kappa}(r)$ is the same for all segments regardless of their types (except joint segments, which ***can*** have no excluded-volume interaction).

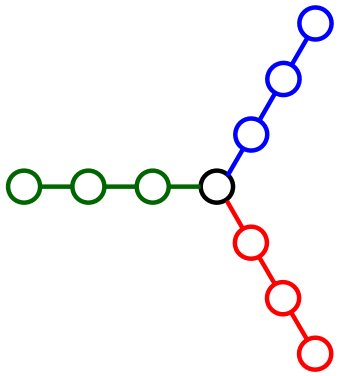

Figure 1. A discrete chain model of compositionally symmetric star triblock terpolymer consisting of three arms (shown in red, blue and green) each having three segments connected to a joint segment (shown in black). In PSCF+, the three arms can have different effective bond lengths (represented in different colors), and the non-bonded interactions of the joint segment can be set to 0.

For BCP self-assembly, non-bonded repulsion between segments of different types are needed in addition to the above excluded-volume interaction, and are taken to be $u^{\chi}_{mm'}(r) = u_0(r)\chi_{mm'}/\rho_0$, where the dimensionless parameter $\chi_{mm'} \geq 0$ controls the repulsion strength between two segments of type m and m', respectively, with χ_{mm}=0. The **"standard" model** (*i.e.*, an incompressible melt of CGCs interacting with the Dirac δ-function repulsion) for BCP self-assembly is therefore recovered in the limit of $N\to\infty$ and $b_m\to 0$ at finite $\sqrt{N-1}b_m > 0$ for all blocks (except joint blocks, which always have N=1 with only $b_m\to 0$ taken for the limit), $\kappa\to 0$ and $\sigma\to 0$.

Finally, <u>for CGC models</u> a BCP consists of $n_B \geq 1$ **blocks** connecting $n_V = n_B + 1$ **vertices**, including both joints (where at least two blocks meet) and free ends, and its chain architecture is described by specifying the vertices j and $k \in [0, n_B]$ connected by each block i (=0,…,n_B−1). <u>For discrete-chain models</u> a BCP consists of $n_B \geq 1$ **blocks** connected by $n_J = n_B - 1$ **joint bonds (JBs)** each connecting two end-segments of ***different*** blocks. Each block i has $N_i \geq 1$ segments. A block of N_i=1 (*i.e.*, a JS) is considered as a vertex, and the two end-segments of a block of $N_i \geq 2$ are considered as two vertices connected by a **block bond (BB)** of $N_i \equiv N_i - 2$; a **vertex** can be either a joint (which is connected by at least two joint or block bonds, and is not necessarily a JS) or a free end (which is connected by only one JB or BB), and has at most one BB connected to it. The chain then consists of $n_b \geq 1$ **v-bonds**, including both JBs (for which $N_{i'}$=0) and BBs each characterized by its $N_{i'}$ and effective bond length $b_{i'}$ (i'=0,…,n_b−1), connecting $n_V = n_b + 1$ vertices, and its chain architecture is described by specifying the vertices j and $k \in [0, n_b]$ connected by each v-bond i'.

References:

1. Sandhu, P.; Zong, J.; Yang, D.; Wang, Q., On the comparisons between dissipative particle dynamics simulations and self-consistent field calculations of diblock copolymer microphase separation. *J. Chem. Phys.* **2013,** *138* (19), 194904.