Free-Energy Decomposition

1. In a canonical ensemble

In general, the (mean-field) dimensionless Helmholtz free energy per chain of N segments (see SCFeqs.pdf for details) calculated in PSCF+ can be decomposed as

$$
\begin{aligned}
\beta f_{ch}^{*} &= \beta u_{ch}^{\chi} + \underline{\beta u_{ch}^{\kappa}} - \underline{\underline{s_{ch}/k_B}} \\
&= \frac{1}{2V}\sum_{m=1}^{n_m}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_m(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\sum_{m'=1}^{n_m}\chi_{mm'}N\phi_{m'}(\mathbf{r}') + \underline{\frac{1}{2V}\sum_{m=1}^{n_m}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_m(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\frac{N}{\kappa}\left(\sum_{m'=1}^{n_m}\phi_{m'}(\mathbf{r}')-1\right)} \\
&\quad - \underline{\underline{\left[\frac{N}{V}\sum_{m=1}^{n_m}\int \mathrm{d}\mathbf{r}\,\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)\right]}} \\
&= \frac{1}{2}\sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\sum_{c'=1}^{n_c}\sum_{i'=1}^{n_{\mathrm{B},c'}}\frac{\chi_{mm'}N}{V}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{c,i}(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\phi_{c',i'}(\mathbf{r}') \\
&\quad + \underline{\frac{1}{2}\sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\sum_{c'=1}^{n_c}\sum_{i'=1}^{n_{\mathrm{B},c'}}\frac{N}{\kappa V}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{c,i}(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\left(\phi_{c',i'}(\mathbf{r}')-\bar{\phi}_{c',i'}\right)} \\
&\quad - \underline{\underline{\left[\frac{N}{V}\sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\int \mathrm{d}\mathbf{r}\,\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\left(\ln\frac{Q_c}{\bar{\phi}_c}+1\right)\right]}} \\
&= \frac{1}{2}\sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\sum_{c'=1}^{n_c}\sum_{i'=1}^{n_{\mathrm{B},c'}}\left(\beta u_{c,i,c',i'}^{\chi} + \beta u_{c,i,c',i'}^{\kappa}\right) - \underline{\underline{\left[\frac{N}{V}\sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\int \mathrm{d}\mathbf{r}\,\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\left(\ln\frac{Q_c}{\bar{\phi}_c}+1\right)\right]}},
\end{aligned}
$$

where $\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant and T the thermodynamic temperature of the system, $\beta u_{ch}^{\chi} \equiv \frac{1}{2V}\sum_{m=1}^{n_m}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_m(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\sum_{m'=1}^{n_m}\chi_{mm'}N\phi_{m'}(\mathbf{r}')$ and $\beta u_{ch}^{\kappa} \equiv \frac{1}{2V}\sum_{m=1}^{n_m}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_m(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\frac{N}{\kappa}\left(\sum_{m'=1}^{n_m}\phi_{m'}(\mathbf{r}')-1\right)$ are the dimensionless internal energy per chain due to the Flory-Huggins-type and the excluded-volume interactions, respectively, V is the system volume, n_m is the number of segment types in the system, $\phi_m(\mathbf{r}) \equiv \sum_{c=1}^{n_c}\sum_{\substack{i=1\\ i\in m}}^{n_{\mathrm{B},c}}\phi_{c,i}(\mathbf{r})$ with the summation including ***only*** blocks of segment type m (thus $\sum_{m=1}^{n_m}\phi_m(\mathbf{r}) = \sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\phi_{c,i}(\mathbf{r})$) is the volume fraction of segments of type m at spatial position $\mathbf{r}$, n_c is the number of components in the system, $n_{\mathrm{B},c}$ is the number of blocks of component c, $\phi_{c,i}(\mathbf{r})$ is the volume fraction of segments on block i of component c at $\mathbf{r}$, $\beta u_0(r)$ is the normalized non-bonded pair potential between two segments satisfying $\int \mathrm{d}\mathbf{r}\beta u_0(|\mathbf{r}|) = 1$, $\chi_{mm'}$ is the generalized Flory-Huggins interaction parameter between two segments of type m and m' (with χ_{mm}=0), κ is the generalized Helfand excluded-volume interaction parameter between any two segments (see Models.pdf for details),

$s_{ch}/k_B = \frac{N}{V}\sum_{m=1}^{n_m}\int d\mathbf{r}\,\omega_m(\mathbf{r})\phi_m(\mathbf{r}) + N\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{N_c}\left(\ln\frac{Q_c}{\bar{\phi}_c}+1\right)$ is the dimensionless entropy per chain, $\omega_m(\mathbf{r})$ is the conjugate field interacting with the segments on block i of component c (whose segment type is m) at $\mathbf{r}$, $\bar{\phi}_c \equiv \sum_{i=1}^{n_{B,c}}\bar{\phi}_{c,i}$ is the overall volume fraction of component c satisfying $\sum_{c=1}^{n_c}\bar{\phi}_c = 1$, $\bar{\phi}_{c,i} \equiv (1/V)\int d\mathbf{r}\,\phi_{c,i}(\mathbf{r})$ is the overall volume fraction of segments on block i of component c (thus $\sum_{c=1}^{n_c}\sum_{i=1}^{n_{B,c}}\bar{\phi}_{c,i} = 1$ and $\frac{1}{V}\sum_{m=1}^{n_m}\int d\mathbf{r}\,\phi_m(\mathbf{r}) = 1$), N_c is the total number of segments of component c, Q_c is the normalized single-chain partition function of component c, and $\beta u^{\chi}_{c,i,c',i'} \equiv (\chi_{mm'}N/V)\int d\mathbf{r}d\mathbf{r}'\,\phi_{c,i}(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\phi_{c',i'}(\mathbf{r}')$ and $\beta u^{\kappa}_{c,i,c',i'} \equiv (N/\kappa V)\int d\mathbf{r}d\mathbf{r}'\,\phi_{c,i}(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\left(\phi_{c',i'}(\mathbf{r}') - \bar{\phi}_{c',i'}\right)$ are the dimensionless internal energy per chain due to the Flory-Huggins-type and the excluded-volume interactions, respectively, between block i of component c (whose segment type is m) and block i' of component c' (whose segment type is m'). Note that for incompressible systems, $N/\kappa\to\infty$ and $\beta u^{\kappa}_{c,i,c',i'} = 0$ (thus $\beta u^{\kappa}_{ch} = 0$).

For the **continuous-Gaussian-chain** (CGC) model (see Models.pdf for details), $N\to\infty$, $N_c\to\infty$ (at finite and non-zero $r_c \equiv N_c/N$), $\chi_{mm'}\to 0$ (at finite $\chi_{mm'}N$), a joint (where at least two blocks meet) belongs to all the blocks, and s_{ch}/k_B can be further decomposed as

$$
\begin{aligned}
s_{ch}/k_B &= \sum_{c=1}^{n_c}\sum_{j=1}^{n_{V,c}}\frac{s^{V}_{c,j}}{k_B} + \underline{C} + \underline{\underline{\sum_{c=1}^{n_c}\sum_{i=1}^{n_{B,c}}\frac{s_{c,i}}{k_B}}} \\
&= -\sum_{c=1}^{n_c}\sum_{j=1}^{n_{V,c}}\frac{\bar{\phi}_c}{n_{V,c}r_cV}\int d\mathbf{r}\left(\frac{1}{Q_c}\prod_{i=1}^{n_{B,j,c}}q_{c,i}(\mathbf{r},j)\right)\ln\left(\frac{1}{Q_c}\prod_{i'=1}^{n_{B,j,c}}q_{c,i'}(\mathbf{r},j)\right) + \underline{\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{r_c}\left(1-\ln\bar{\phi}_c\right)} \\
&\quad + \underline{\underline{\sum_{c=1}^{n_c}\sum_{i=1}^{n_{B,c}}\left\{\frac{N}{V}\int d\mathbf{r}\,\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + \frac{\bar{\phi}_c}{n_{V,c}r_cV}\int d\mathbf{r}\left[\begin{array}{l}\left(\frac{1}{Q_c}\prod_{b=1}^{n_{B,j,c}}q_{c,b}(\mathbf{r},j)\right)\ln q_{c,i}(\mathbf{r},j) \\ +\left(\frac{1}{Q_c}\prod_{b'=1}^{n_{B,j',c}}q_{c,b'}(\mathbf{r},j')\right)\ln q_{c,i}(\mathbf{r},j')\end{array}\right]\right\}}} \\
&= \cancel{-\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{n_{V,c}r_cVQ_c}\sum_{j=1}^{n_{V,c}}\int d\mathbf{r}\left(\prod_{i=1}^{n_{B,j,c}}q_{c,i}(\mathbf{r},j)\right)\sum_{i'=1}^{n_{B,j,c}}\ln q_{c,i'}(\mathbf{r},j)} + \sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{r_c}\ln Q_c + \underline{\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{r_c}\left(1-\ln\bar{\phi}_c\right)} \\
&\quad + \underline{\underline{\frac{N}{V}\sum_{m=1}^{n_m}\int d\mathbf{r}\,\omega_m(\mathbf{r})\phi_m(\mathbf{r}) + \sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{n_{V,c}r_cVQ_c}\sum_{i=1}^{n_{B,c}}\int d\mathbf{r}\cancel{\left[\begin{array}{l}\left(\prod_{b=1}^{n_{B,j,c}}q_{c,b}(\mathbf{r},j)\right)\ln q_{c,i}(\mathbf{r},j) \\ +\left(\prod_{b'=1}^{n_{B,j',c}}q_{c,b'}(\mathbf{r},j')\right)\ln q_{c,i}(\mathbf{r},j')\end{array}\right]}}},
\end{aligned}
$$

where $n_{\mathrm{V},c}$ is the number of **vertices** (including both joints and free chain ends) of component c, $s^{\mathrm{V}}_{c,j}/k_B \equiv -\left(\bar{\phi}_c/n_{\mathrm{V},c}r_cV\right)\int \mathrm{d}\mathbf{r}\rho^{\mathrm{V}}_{c,j}(\mathbf{r})\ln\rho^{\mathrm{V}}_{c,j}(\mathbf{r})$ is the dimensionless ***translational*** entropy per chain of vertex j of component c, $\rho^{\mathrm{V}}_{c,j}(\mathbf{r}) \equiv \frac{1}{Q_c}\prod_{i=1}^{n_{\mathrm{B},j,c}} q_{c,i}(\mathbf{r},j)$ is the normalized number density of vertex j of component c at $\mathbf{r}$, $n_{\mathrm{B},j,c}$ is the number of blocks ***connected*** to vertex j of component c, $q_{c,i}(\mathbf{r},j)$ is the propagator of vertex j on block i of component c at $\mathbf{r}$ that propagates ***into*** the vertex (note that $Q_c = \frac{1}{V}\int \mathrm{d}\mathbf{r}\prod_{i=1}^{n_{\mathrm{B},j,c}} q_{c,i}(\mathbf{r},j)$, thus $(1/V)\int \mathrm{d}\mathbf{r}\rho^{\mathrm{V}}_{c,j}(\mathbf{r})=1$), $C \equiv \sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{r_c}\left(1-\ln\bar{\phi}_c\right)$ is a constant, and $s_{c,i}/k_B \equiv (N/V)\int \mathrm{d}\mathbf{r}\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + \left(\bar{\phi}_c/n_{\mathrm{V},c}r_cV\right)\int \mathrm{d}\mathbf{r}\left(\rho^{\mathrm{V}}_{c,j}(\mathbf{r})\ln q_{c,i}(\mathbf{r},j) + \rho^{\mathrm{V}}_{c,j'}(\mathbf{r})\ln q_{c,i}(\mathbf{r},j')\right)$ is the dimensionless ***conformational*** entropy per chain of block i of component c.

For **discrete-chain models** (see Models.pdf for details), a joint (including a joint segment) belongs only to one block, s_{ch}/k_B can therefore be further decomposed as

$$s_{ch}/k_B = \frac{N}{V}\sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\int \mathrm{d}\mathbf{r}\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + \sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{r_c}\ln Q_c + \underline{\sum_{c=1}^{n_c}\frac{\bar{\phi}_c}{r_c}\left(1-\ln\bar{\phi}_c\right)}$$

$$= \sum_{c=1}^{n_c}\left(\sum_{i=1}^{n_{\mathrm{B},c}}\frac{N}{V}\int \mathrm{d}\mathbf{r}\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + \frac{\ln Q_c}{r_c}\sum_{i=1}^{n_{\mathrm{B},c}}\bar{\phi}_{c,i}\right) + \underline{C} = \sum_{c=1}^{n_c}\sum_{i=1}^{n_{\mathrm{B},c}}\frac{s_{c,i}}{k_B} + \underline{C},$$

where $s_{c,i}/k_B \equiv (N/V)\int \mathrm{d}\mathbf{r}\omega_m(\mathbf{r})\phi_{c,i}(\mathbf{r}) + \bar{\phi}_{c,i}\ln Q_c/r_c$ is the dimensionless entropy per chain of block i of component c.

In addition to the converged profiles $\{\omega_m(\mathbf{r})\}$ and $\{\phi_m(\mathbf{r})\}$, the corresponding ***adjustable*** unit-cell parameters, and thermodynamic quantities (including βf^*_{ch}, βu^{χ}_{ch}, βu^{κ}_{ch} (only for compressible systems), s_{ch}/k_B, C, and the dimensionless chain chemical potential $\beta\mu^*_c$ of component c (see SCFeqs.pdf for details)), PSCF+ also outputs the corresponding profiles $\phi_{c,i}(\mathbf{r})$, $\rho^{\mathrm{J}}_{c,j}(\mathbf{r})$ (only for the CGC model), and thermodynamic quantities $(1/V)\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_{c,i}(\mathbf{r})\beta u_0(|\mathbf{r}-\mathbf{r}'|)\phi_{c',i'}(\mathbf{r}')$, $s^{\mathrm{V}}_{c,j}/k_B$ (only for the CGC model) and $s_{c,i}/k_B$ for user-specified c, i, j, c' and i' (for ***each*** of these quantities); for the automated calculation along a path (ACAP), user can also specify whether ***each*** of these quantities is output only at the end of the path (***by default***) or for all the converged cases during the ACAP.

2. In a grand-canonical ensemble

Here we specify $\beta\mu^*_c$ and calculate $\bar{\phi}_c = Q_c\exp\left(\beta\mu^*_c\right)$. So the only difference from the above canonical ensemble is that in the output, βf^*_{ch} and $\beta\mu^*_c$ are replaced by the (mean-field) dimensionless grand potential per chain of N segments $\beta\omega_{ch} = \beta f^*_{ch} - \sum_{c=1}^{n_c}\beta\mu^*_c\bar{\phi}_c/r_c$ and $\bar{\phi}_c$, respectively.