Electronic Supplementary Material (ESI) for Soft Matter.

Supplemental text

A cluster size distribution theory to study the thermodynamics and phase behavior of multi-bonding single site solutes in patchy colloidal mixtures

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S.1. DERIVATION OF CHEMICAL POTENTIAL

Below we provide a complete derivation of the chemical potential.

For a mixture of multi-bonding single site solutes and patchy solvent molecules, the Helmholtz free energy due to association is

$$\frac{A^{AS}}{Vk_{\mathrm{B}}T} = \rho^{(p)} \left(\sum_{A\in\Gamma^{(p)}} \ln X_A^{(p)} + \frac{1}{2}\left(1 - X_A^{(p)}\right) \right) + \rho^{(\sigma)} \left(\ln X_0^{(\sigma)} + \sum_{n=1}^{N_{bond}^{max}} \frac{n}{2} X_n^{(\sigma)} \right) \tag{S.1}$$

The chemical potential of the solute and solvent molecules is obtained by taking the derivative of the free energy with respect to the density of the respective species

$$\beta\Delta\mu_{(k)}^{AS} = \frac{\partial}{\partial\rho^{(k)}} \left(\frac{A^{AS}}{Vk_{\mathrm{B}}T} \right) \tag{S.2}$$

$$\begin{aligned} \beta\Delta\mu_{(k)}^{AS} = {} & \frac{\partial\rho^{(p)}}{\partial\rho^{(k)}} \left(\sum_{A\in\Gamma^{(p)}} \ln X_A^{(p)} + \frac{1}{2}\left(1 - X_A^{(p)}\right) \right) + \rho^{(p)} \left(\sum_{A\in\Gamma^{(p)}} \frac{\partial \ln X_A^{(p)}}{\partial\rho^{(k)}} - \frac{1}{2}\frac{\partial X_A^{(p)}}{\partial\rho^{(k)}} \right) \\ & + \frac{\partial\rho^{(\sigma)}}{\partial\rho^{(k)}} \left(\ln X_0^{(\sigma)} + \sum_{n=1}^{N_{bond}^{max}} \frac{n}{2} X_n^{(\sigma)} \right) + \rho^{(\sigma)} \left(\frac{\partial \ln X_0^{(\sigma)}}{\partial\rho^{(k)}} + \sum_{n=1}^{N_{bond}^{max}} \frac{n}{2} \frac{\partial X_n^{(\sigma)}}{\partial\rho^{(k)}} \right) \end{aligned} \tag{S.3}$$

To simplify the above expression, we start with the equation for $c_A^{(p)}$ and take the derivative with respect to $\rho^{(k)}$

$$c_A^{(p)} = \sum_{M\in\Gamma^{(p)}} \rho^{(p)} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho} + \sum_{n=1}^{N_{bond}^{max}} \rho^{(\sigma)} n \cdot X_0^{(\sigma)} \left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p \right)^{n-1} \cdot \frac{F_{\theta_{(c,\sigma)}}^{(n)} \bar{f}_\sigma \cdot \kappa_p}{\rho^n} \tag{S.4}$$

$$c_A^{(p)} = \sum_{M\in\Gamma^{(p)}} \rho^{(p)} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho} + \sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} n \cdot X_n^{(\sigma)} \cdot \bar{f}_\sigma \cdot \kappa_p}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p \right)} \tag{S.5}$$

taking derivative with respect to $\rho^{(k)}$ we get,

$$\frac{\partial c_A^{(p)}}{\partial \rho^{(k)}} = \sum_{M\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho} + \sum_{M\in\Gamma^{(p)}} \rho^{(p)} \frac{\partial X_M^{(p)}}{\partial \rho^{(k)}} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho}$$
$$+ \sum_{M\in\Gamma^{(p)}} \rho^{(p)} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{\partial n_{avg}^{HS}}{\partial \rho^{(k)}} \frac{1}{\rho}$$
$$- \sum_{M\in\Gamma^{(p)}} \rho^{(p)} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho^2} + \sum_{n=1}^{N_{bond}^{max}} \frac{\partial \rho^{(\sigma)}}{\partial \rho^{(k)}} \frac{n \cdot X_n^{(\sigma)} \cdot \bar{f}_\sigma \cdot \kappa_p}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)}$$
$$+ \sum_{n=1}^{N_{bond}^{max}} \frac{\partial X_n^{(\sigma)}}{\partial \rho^{(k)}} \frac{\rho^{(\sigma)} \cdot n \cdot \bar{f}_\sigma \cdot \kappa_p}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)}$$
$$- \sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} \cdot n \cdot X_n^{(\sigma)} \cdot \bar{f}_\sigma \cdot \kappa_p}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)^2} \left(\sum_{A\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p + \sum_{A\in\Gamma^{(p)}} \rho^{(p)} \frac{\partial X_A^{(p)}}{\partial \rho^{(k)}} \bar{f}_\sigma \cdot \kappa_p \right) \tag{S.6}$$

Multiplying the above equation by $\rho^{(p)} X_A^{(p)}$ and taking summation over the sites A, using Eq. S.5 and rearranging we get

$$\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \frac{\partial c_A^{(p)}}{\partial \rho^{(k)}} = \sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \sum_{M\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho}$$
$$+ \sum_{A\in\Gamma^{(p)}} \rho^{(p)} \frac{\partial X_A^{(p)}}{\partial \rho^{(k)}} \cdot c_A^{(p)}$$
$$- 2 \cdot \sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} \cdot n \cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)} \left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \frac{\partial X_A^{(p)}}{\partial \rho^{(k)}} \bar{f}_\sigma \cdot \kappa_p \right)$$
$$+ \sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \sum_{M\in\Gamma^{(p)}} x^{(p)} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \left(\frac{\partial n_{avg}^{HS}}{\partial \rho^{(k)}} - \frac{n_{avg}^{HS}}{\rho} \right)$$
$$+ \sum_{n=1}^{N_{bond}^{max}} \frac{\partial \rho^{(\sigma)}}{\partial \rho^{(k)}} \cdot n \cdot X_n^{(\sigma)} + \sum_{n=1}^{N_{bond}^{max}} \frac{\partial X_n^{(\sigma)}}{\partial \rho^{(k)}} \rho^{(\sigma)} \cdot n$$
$$- \sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} \cdot n \cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)} \left(\sum_{A\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p \right) \tag{S.7}$$

also

$$X_A^{(p)} = \frac{1}{1 + c_A^{(p)}} \tag{S.8}$$

or

$$\ln X_A^{(p)} = -\ln(1 + c_A^{(p)}) \tag{S.9}$$

$$\frac{1}{X_A^{(p)}}\frac{\partial X_A^{(p)}}{\partial \rho^{(k)}} = -X_A^{(p)}\frac{\partial c_A^{(p)}}{\partial \rho^{(k)}} \tag{S.10}$$

Eq. S.7 can be rearranged as

$$\begin{aligned}
\sum_{A\in\Gamma^{(p)}} \rho^{(p)}\frac{\partial X_A^{(p)}}{\partial \rho^{(k)}}\cdot\left(\frac{1}{X_A^{(p)}}-\frac{1}{2}\right) + \frac{1}{2}\sum_{n=1}^{N_{bond}^{max}}\frac{\partial X_n^{(\sigma)}}{\partial \rho^{(k)}}\rho^{(\sigma)}\cdot n \\
= -\frac{1}{2}\sum_{A\in\Gamma^{(p)}}\rho^{(p)}X_A^{(p)}\sum_{M\in\Gamma^{(p)}}\frac{\partial \rho^{(p)}}{\partial \rho^{(k)}}X_M^{(p)}\kappa_{AM}f_{AM}^{(p,p)}\frac{n_{avg}^{HS}}{\rho} \\
+ \sum_{n=1}^{N_{bond}^{max}}\frac{\rho^{(\sigma)}\cdot n\cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}}\rho^{(p)}X_A^{(p)}\bar{f}_\sigma\cdot\kappa_p\right)}\left(\sum_{A\in\Gamma^{(p)}}\rho^{(p)}\frac{\partial X_A^{(p)}}{\partial \rho^{(k)}}\bar{f}_\sigma\cdot\kappa_p\right) \\
- \frac{1}{2}\sum_{A\in\Gamma^{(p)}}\rho^{(p)}X_A^{(p)}\sum_{M\in\Gamma^{(p)}}x^{(p)}X_M^{(p)}\kappa_{AM}f_{AM}^{(p,p)}\left(\frac{\partial n_{avg}^{HS}}{\partial \rho^{(k)}}-\frac{n_{avg}^{HS}}{\rho}\right) \\
- \frac{1}{2}\sum_{n=1}^{N_{bond}^{max}}\frac{\partial \rho^{(\sigma)}}{\partial \rho^{(k)}}\cdot n\cdot X_n^{(\sigma)} \\
+ \frac{1}{2}\sum_{n=1}^{N_{bond}^{max}}\frac{\rho^{(\sigma)}\cdot n\cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}}\rho^{(p)}X_A^{(p)}\bar{f}_\sigma\cdot\kappa_p\right)}\left(\sum_{A\in\Gamma^{(p)}}\frac{\partial \rho^{(p)}}{\partial \rho^{(k)}}X_A^{(p)}\bar{f}_\sigma\cdot\kappa_p\right)
\end{aligned} \tag{S.11}$$

now we consider the monomer fraction of the multi-bonding solute

$$\ln X_0^{(\sigma)} = -\ln\left(1+\sum_{n=1}^{N_{bond}^{max}}\left(\sum_{A\in\Gamma^{(p)}}\rho^{(p)}\cdot X_A^{(p)}\cdot f_{BA}^{(\sigma,p)}\cdot\kappa_p\right)^n\cdot\frac{F_{\theta_{c,\sigma}}^{(n)}}{\rho^n}\right) \tag{S.12}$$

by taking derivative with respect to $\rho^{(k)}$ we get,

$$\rho^{(\sigma)} \frac{\partial \ln X_0^{(\sigma)}}{\partial \rho^{(k)}} = -\sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} \cdot n \cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)} \left(\sum_{A\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)$$
$$- \sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} \cdot n \cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)} \left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \frac{\partial X_A^{(p)}}{\partial \rho^{(k)}} \bar{f}_\sigma \cdot \kappa_p\right)$$
$$- \sum_{n=1}^{N_{bond}^{max}} \rho^{(\sigma)} X_0^{(\sigma)} \left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \cdot X_A^{(p)} \cdot f_{BA}^{(\sigma,p)} \cdot \kappa_p\right)^n \cdot \left(\frac{1}{\rho^n} \frac{\partial F_{\theta_{c,\sigma}}^{(n)}}{\partial \rho^{(k)}} - \frac{n \cdot F_{\theta_{c,\sigma}}^{(n)}}{\rho^{n+1}}\right) \tag{S.13}$$

using Eqs. S.11 and S.13

$$\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \frac{\partial X_A^{(p)}}{\partial \rho^{(k)}} \cdot \left(\frac{1}{X_A^{(p)}} - \frac{1}{2}\right) + \rho^{(\sigma)} \left(\sum_{n=1}^{N_{bond}^{max}} \frac{n}{2} \frac{\partial X_n^{(\sigma)}}{\partial \rho^{(k)}} + \frac{\partial \ln X_0^{(\sigma)}}{\partial \rho^{(k)}}\right)$$
$$= -\frac{1}{2} \sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \sum_{M\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \frac{n_{avg}^{HS}}{\rho}$$
$$- \frac{1}{2} \sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \sum_{M\in\Gamma^{(p)}} x^{(p)} X_M^{(p)} \kappa_{AM} f_{AM}^{(p,p)} \left(\frac{\partial n_{avg}^{HS}}{\partial \rho^{(k)}} - \frac{n_{avg}^{HS}}{\rho}\right)$$
$$- \frac{1}{2} \sum_{n=1}^{N_{bond}^{max}} \frac{\partial \rho^{(\sigma)}}{\partial \rho^{(k)}} \cdot n \cdot X_n^{(\sigma)}$$
$$- \frac{1}{2} \sum_{n=1}^{N_{bond}^{max}} \frac{\rho^{(\sigma)} \cdot n \cdot X_n^{(\sigma)}}{\left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)} \left(\sum_{A\in\Gamma^{(p)}} \frac{\partial \rho^{(p)}}{\partial \rho^{(k)}} X_A^{(p)} \bar{f}_\sigma \cdot \kappa_p\right)$$
$$- \sum_{n=1}^{N_{bond}^{max}} \rho^{(\sigma)} X_0^{(\sigma)} \left(\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \cdot X_A^{(p)} \cdot f_{BA}^{(\sigma,p)} \cdot \kappa_p\right)^n \cdot \left(\frac{1}{\rho^n} \frac{\partial F_{\theta_{c,\sigma}}^{(n)}}{\partial \rho^{(k)}} - \frac{n \cdot F_{\theta_{c,\sigma}}^{(n)}}{\rho^{n+1}}\right) \tag{S.14}$$

Using Eq. S.14, the chemical potential equation in Eq. S.3 can be simplified. For the solute molecules we get

$$\beta \Delta \mu_{(\sigma)}^{AS} = \ln X_0^{(\sigma)} - \sum_{n=1}^{N_{bond}^{max}} \left[\rho^{(\sigma)} \cdot X_0^{(\sigma)} \left(\sum_{A\in\Gamma^{(p)}} x^{(p)} X_A^{(p)} f_{BA}^{(\sigma,p)} \kappa_p\right)^n \cdot \left(\frac{\partial F_{\theta_{c,\sigma}}^{(n)}}{\partial \rho^{(\sigma)}} - \frac{n \cdot F_{\theta_{c,\sigma}}^{(n)}}{\rho}\right)\right]$$
$$- \frac{1}{2} \left[\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \cdot X_A^{(p)} \sum_{B\in\Gamma^{(p)}} x^{(p)} \cdot X_B^{(p)} \left(f_{AB}^{(p,p)} \kappa_{AB}\right) \cdot \left(\frac{\partial n_{avg}^{HS}}{\partial \rho^{(\sigma)}} - \frac{n_{avg}^{HS}}{\rho}\right)\right] \tag{S.15}$$

and for the solvent molecules

$$\beta\Delta\mu_{(p)}^{AS} = \ln X_0^{(p)} - \sum_{n=1}^{N_{bond}^{max}} \left[\rho^{(\sigma)} \cdot X_0^{(\sigma)} \left(\sum_{A\in\Gamma^{(p)}} x^{(p)} X_A^{(p)} f_{BA}^{(\sigma,p)} \kappa_p\right)^n \cdot \left(\frac{\partial F_{\theta_{c,\sigma}}^{(n)}}{\partial \rho^{(p)}} - \frac{n \cdot F_{\theta_{c,\sigma}}^{(n)}}{\rho}\right)\right]$$
$$- \frac{1}{2}\left[\sum_{A\in\Gamma^{(p)}} \rho^{(p)} \cdot X_A^{(p)} \sum_{B\in\Gamma^{(p)}} x^{(p)} \cdot X_B^{(p)} \left(f_{AB}^{(p,p)} \kappa_{AB}\right) \cdot \left(\frac{\partial n_{avg}^{HS}}{\partial \rho^{(p)}} - \frac{n_{avg}^{HS}}{\rho}\right)\right] \tag{S.16}$$