

Supplementary Information

Light Scattering from Mixtures of Interacting, Nonionic Micelles with Hydrophobic Solutes

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S1. Thermodynamic fluctuation theory

1.1 Derivation of δS_T and symmetry relations for $[G]$

In this section the total entropy fluctuation δS_T , given by eqn (7)–(9), is derived for an n -component mixture at constant temperature and volume using either the Gibbs thermodynamic framework at constant pressure, corresponding to typical experimental conditions, or, equivalently, the McMillan-Mayer framework at constant solvent chemical potential, which defines the chemical potential fluctuations of a mixture with a force-free solvent. We begin with eqn (7)

$$-2T\delta S_T = \sum_{i=1}^n \delta\mu_i \delta N_i = \sum_{i=1}^{n-1} \delta\mu_i \delta N_i + \delta\mu_n \delta N_n . \quad (S.1)$$

According to the Gibbs framework, the total fluctuation differential of the extensive Gibbs free energy is given by

$$\delta g = -S\delta T + V\delta p + \sum_{i=1}^{n-1} \mu_i \delta N_i + \mu_n \delta N_n , \quad (S.2)$$

and the chemical potentials are defined as

$$\mu_i = \left(\frac{\partial g}{\partial N_i} \right)_{p,T,N_{k \neq i}} \quad \text{for } i = 1, 2, \dots, n. \quad (S.3)$$

and N_i is the number of moles of component i . Furthermore, using the constant volume constraint, we have

$$\delta V = \sum_{i=1}^n \bar{V}_i \delta N_i = \sum_{i=1}^{n-1} \bar{V}_i \delta N_i + \bar{V}_n \delta N_n = 0 , \quad (S.4)$$

where \bar{V}_i is the molar volume of species i , which is assumed to be constant. Solving for the fluctuation δN_n in eqn (S.4) provides

$$\delta N_n = - \sum_{i=1}^{n-1} \frac{\bar{V}_i}{\bar{V}_n} \delta N_i . \quad (S.5)$$

Eqn (S.1) and (S.5), combine to yield

$$\sum_{i=1}^n \delta\mu_i \delta N_i = \sum_{i=1}^{n-1} \left(\delta\mu_i - \frac{\bar{V}_i}{\bar{V}_n} \delta\mu_n \right) \delta N_i . \quad (S.6)$$

Now, using the Gibbs-Duhem relation at constant temperature, pressure, and volume, we have

$$\sum_{j=1}^n N_j \delta\mu_j = \sum_{j=1}^{n-1} N_j \delta\mu_j + N_n \delta\mu_n = 0 . \quad (S.7)$$

Solving for the solvent fluctuation $\delta\mu_n$ in eqn (S.7) provides

$$\delta\mu_n = - \sum_{j=1}^{n-1} \frac{V N_j}{V N_n} \delta\mu_j = - \sum_{j=1}^{n-1} \frac{C_j}{C_n} \delta\mu_j . \quad (S.8)$$

Eqn (S.6) and (S.8) combine with the solvent volume fraction

$$C_n \bar{V}_n = 1 - \phi . \quad (S.9)$$

to provide

$$\sum_{i=1}^n \delta\mu_i \delta N_i = \sum_{i=1}^{n-1} \left(\delta\mu_i + \frac{\bar{V}_i}{1 - \phi} \sum_{j=1}^{n-1} C_j \delta\mu_j \right) \delta N_i . \quad (S.10)$$

At constant temperature and pressure, the species chemical potentials $\mu_i = \mu_i(T, p, C_k, \dots, C_{n-1})$ are expanded via the chain rule

$$\delta\mu_i = - \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial C_k} \right)_{p,T,N_{i \neq k}} \delta C_k , \quad (S.11)$$

and eqn (S.1), (S.10) and (S.11) combine to give

$$-2T\delta S_T = V \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} G_{ik} \delta C_i \delta C_k , \quad (S.12)$$

where

$$G_{ik} = \left(\frac{\partial \mu_i}{\partial C_k} \right)_{p,T,C_{i \neq k}} + \frac{\bar{V}_i}{1 - \phi} \sum_{j=1}^{n-1} C_j \left(\frac{\partial \mu_j}{\partial C_k} \right)_{p,T,C_{i \neq k}} \quad \text{for } i, k = 1, 2, \dots, n - 1 . \quad (S.13)$$

Now, using the McMillan-Mayer framework, we will first show that $[G]$ is symmetric, followed by a derivation for the total entropy fluctuation δS_T . The extensive McMillan-Mayer free energy for an n -component mixture is given by a Legendre transform of the Helmholtz free energy $A(V, T, N_1, \dots, N_n)$.^{1,2}

$$\tilde{F}(V, T, N_1, \dots, N_{n-1}, \bar{\mu}_n) = A(V, T, N_1, \dots, N_n) - N_n \bar{\mu}_n , \quad (S.14)$$

and the total fluctuation differential of \tilde{F} is given by

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$$\delta\tilde{F} = -S\delta T - p\delta V + \sum_{i=1}^{n-1} \mu_i \delta N_i - N_n \delta \mu_n, \quad (\text{S.15})$$

where the chemical potential of component i at constant volume is defined according to

$$\mu_i = \left(\frac{\partial \tilde{F}}{\partial N_i} \right)_{T, \mu_n, V, N_{k \neq i}} \quad \text{for } i = 1, 2, \dots, n-1. \quad (\text{S.16})$$

At constant volume, temperature, and solvent chemical potential, mixed partial derivatives of the McMillan-Mayer free energy are given by

$$\left(\frac{\partial^2 \tilde{F}}{\partial N_k \partial N_i} \right)_{T, \mu_n, V, C_{k \neq i}} = \left(\frac{\partial^2 \tilde{F}}{\partial N_i \partial N_k} \right)_{T, \mu_n, V, C_{k \neq i}} \quad \text{for } i, k = 1, 2, \dots, n-1. \quad (\text{S.17})$$

Multiplying eqn (S.17) through and by constant volume V yields

$$\left(\frac{\partial^2 \tilde{F}}{\partial C_k \partial N_i} \right)_{T, \mu_n, V, C_{k \neq i}} = \left(\frac{\partial^2 \tilde{F}}{\partial C_i \partial N_k} \right)_{T, \mu_n, V, C_{k \neq i}} \quad \text{for } i, k = 1, 2, \dots, n-1, \quad (\text{S.18})$$

and eqn (S.16) and (S.18) combine to provide

$$\left(\frac{\partial \mu_i}{\partial C_k} \right)_{T, \mu_n, V, C_{k \neq i}} = \left(\frac{\partial \mu_k}{\partial C_i} \right)_{T, \mu_n, V, C_{k \neq i}} \quad \text{for } i, k = 1, 2, \dots, n-1. \quad (\text{S.19})$$

Furthermore, at constant V , T , and μ_n , eqn (S.1) reduces to

$$-2T\delta S_T = \sum_{i=1}^{n-1} \delta \mu_i \delta N_i. \quad (\text{S.20})$$

and the species chemical potentials $\mu_i = \mu_i(T, \mu_n, C_k, \dots, C_{n-1})$ are expanded via the chain rule

$$\delta \mu_i = \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial C_k} \right)_{T, \mu_n, V, C_{k \neq i}} \delta C_k. \quad (\text{S.21})$$

Eqn (S.20) and (S.21) combine to give

$$-2T\delta S_T = V \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial C_k} \right)_{T, \mu_n, V, C_{k \neq i}} \delta C_k \delta C_i. \quad (\text{S.22})$$

Finally, combination of eqn (S.12), (S.13), and (S.22) yield

$$G_{ik} = \left(\frac{\partial \mu_i}{\partial C_k} \right)_{T, \mu_n, V, C_{k \neq i}} = \left(\frac{\partial \mu_i}{\partial C_k} \right)_{p, T, C_{i \neq k}} + \frac{\bar{V}_i}{1-\phi} \sum_{j=1}^{n-1} C_j \left(\frac{\partial \mu_j}{\partial C_k} \right)_{p, T, C_{i \neq k}} \quad \text{for } i, k = 1, 2, \dots, n-1. \quad (\text{S.23})$$

1.2 Diagonalization of $[\mathbf{G}]$

In this section, the modal matrix $[\mathbf{P}]$ for the diffusivity matrix $[\mathbf{D}]$ is shown to diagonalize the chemical potential derivative matrix $[\mathbf{G}]$ via

$$[\hat{\mathbf{G}}] = [\mathbf{P}]^T [\mathbf{G}] [\mathbf{P}]. \quad (\text{S.24})$$

To begin, note that for a ternary mixture, the matrix $[\hat{\mathbf{G}}]$ is diagonal if

$$\hat{G}_{as} = \hat{G}_{sa} = 0. \quad (\text{S.25})$$

Furthermore, $[\mathbf{G}]$ is symmetric,³ so that

$$G_{as} = G_{sa}. \quad (\text{S.26})$$

Combining eqn (S.24)–(S.26) provides

$$G_{aa} P_{aa} P_{as} + G_{as} (P_{aa} P_{ss} + P_{as} P_{sa}) + G_{ss} P_{sa} P_{ss} = 0. \quad (\text{S.27})$$

Eqn (S.27) and (34) combine to yield

$$G_{aa} D_{as}^2 + G_{as} (D_+ + D_- - 2D_{aa}) D_{as} + G_{ss} \{D_+ D_- - D_{aa} (D_+ + D_-) + D_{aa}^2\} = 0. \quad (\text{S.28})$$

The following relations for the trace

$$D_+ + D_- = D_{aa} + D_{ss}. \quad (\text{S.29})$$

and the determinant

$$D_+ D_- = D_{ss} D_{aa} - D_{as} D_{sa}. \quad (\text{S.30})$$

of $[\mathbf{D}]$ are then combined with eqn (S.28) to give

$$D_{aa} G_{as} + D_{sa} G_{ss} = G_{aa} D_{as} + G_{as} D_{ss}, \quad (\text{S.31})$$

which is the Onsager Reciprocal relation.³ Hence, eqn (S.25) is satisfied and $[\hat{\mathbf{G}}]$ is diagonal.

1.3 Derivations of \mathbf{B} and R_{90}

In this section, we begin with eqn (15), generalized for an n -component mixture at constant temperature and pressure

$$P(\delta \mathbf{x}) = \Omega_0^{-1} \exp \left\{ -\frac{V}{2k_B T} \left(\sum_{i=1}^{n-1} \hat{G}_i \delta \hat{C}_i^2 \right) \right\}. \quad (\text{S.32})$$

Using the product rule for exponents, we can write

$$P(\delta \mathbf{x}) = P_1(\delta \hat{C}_1) P_2(\delta \hat{C}_2) \cdots P_{n-1}(\delta \hat{C}_{n-1}), \quad (\text{S.33})$$

where,

$$P_i(\delta \hat{C}_i) = \Omega_i^{-1} e^{\left(-\frac{V}{2k_B T} \hat{G}_i \delta \hat{C}_i^2 \right)}. \quad (\text{S.34})$$

Eqn (S.33) and (S.34) indicate that the decoupled concentration fluctuations $\delta \hat{C}_i$ are statistically uncorrelated with a fluctuation probability $P_i(\delta \hat{C}_i)$ that obeys a Gaussian distribution. The constants Ω_i are determined via integration of the fluctuation probability over all possible fluctuations,

$$\Omega_i = \langle \delta \hat{C}_i \rangle = \int_{-\infty}^{\infty} d(\delta \hat{C}_i) e^{\left(-\frac{V}{2k_B T} \hat{G}_i \delta \hat{C}_i^2 \right)} = \left(\frac{2\pi k_B T}{V \hat{G}_i} \right)^{\frac{1}{2}}, \quad (\text{S.35})$$

Using eqn (S.34), the mean-square fluctuation in concentration is given by

$$\begin{aligned} \langle \delta \hat{C}_i^2 \rangle &= \int_{-\infty}^{\infty} d(\delta \hat{C}_i) \delta \hat{C}_i^2 P_i(\delta \hat{C}_i) \\ &= \Omega_i^{-1} \int_{-\infty}^{\infty} d(\delta \hat{C}_i) \delta \hat{C}_i^2 e^{\left(-\frac{V}{2k_B T} \hat{G}_i \delta \hat{C}_i^2\right)} \\ &= \Omega_i^{-1} \left(\frac{2\pi k_B T}{V \hat{G}_i} \right)^{\frac{1}{2}} \frac{k_B T}{V \hat{G}_i}, \end{aligned} \quad (\text{S.36})$$

and eqn (S.35) and (S.36) combine to yield

$$\langle \delta \hat{C}_i^2 \rangle = \frac{k_B T}{V \hat{G}_i}. \quad (\text{S.37})$$

In order to determine the field autocorrelation function, defined by eqn (19), we invoke non-equilibrium thermodynamics and expand the total fluctuation of the local dielectric constant $\varepsilon = \varepsilon(T, p, \hat{C}_1, \hat{C}_i, \dots, \hat{C}_{n-1})$, expressed here as function of $n + 1$ intensive variables.⁴ The chain rule at constant T and p provides

$$\delta \varepsilon(\mathbf{q}, t) = \sum_{i=1}^{n-1} \left(\frac{\partial \varepsilon}{\partial \hat{C}_i} \right)_{T,p} \delta \hat{C}_i(\mathbf{q}, t), \quad (\text{S.38})$$

where, $\delta \hat{C}_i(\mathbf{q}, t)$ is the Fourier transform of the decoupled local concentration fluctuation $\delta \hat{C}_i(\mathbf{r}, t)$, given by

$$\delta \hat{C}_i(\mathbf{q}, t) = \frac{1}{V} \int_V d\mathbf{r}^3 e^{i\mathbf{q}\cdot\mathbf{r}} \delta \hat{C}_i(\mathbf{r}, t). \quad (\text{S.39})$$

The time correlation function for fluctuations in $\varepsilon(\mathbf{q}, t)$ is given by

$$\begin{aligned} &\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, t) \rangle \\ &= \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \left(\frac{\partial \varepsilon}{\partial \hat{C}_i} \right)_{T,p} \left(\frac{\partial \varepsilon}{\partial \hat{C}_j} \right)_{T,p} \langle \delta \hat{C}_i^*(\mathbf{q}, 0) \delta \hat{C}_j(\mathbf{q}, t) \rangle. \end{aligned} \quad (\text{S.40})$$

The concentration fluctuations $\delta \hat{C}_i(\mathbf{q}, t)$ are statistically uncorrelated, consistent with eqn (S.33) and the Siegert relation, so that

$$\langle \delta \hat{C}_i^*(\mathbf{q}, 0) \delta \hat{C}_j(\mathbf{q}, t) \rangle = \langle \delta \hat{C}_i^*(\mathbf{q}, 0) \delta \hat{C}_j(\mathbf{q}, t) \rangle \delta_{ij}, \quad (\text{S.41})$$

where δ_{ij} is the Kronecker delta. Eqn (S.40), (S.41), and (25) combine to yield

$$\begin{aligned} &\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, t) \rangle \\ &= \sum_{i=1}^{n-1} \left(\frac{\partial \varepsilon}{\partial \hat{C}_i} \right)_{T,p}^2 \langle \delta \hat{C}_i^*(\mathbf{q}, 0) \delta \hat{C}_i(\mathbf{q}, 0) \rangle \exp(-q^2 \bar{D}_i t). \end{aligned} \quad (\text{S.42})$$

In order to relate the static correlation function $\langle \delta \hat{C}_i^*(\mathbf{q}, 0) \delta \hat{C}_i(\mathbf{q}, 0) \rangle$ in eqn (S.42) with the mean-square fluctuation $\langle \delta \hat{C}_i^2 \rangle$, given by eqn (S.37), we note that in the limit $qR_{i^*} \rightarrow 0$, q is small compared with the position vector \mathbf{r} that

spans the region enclosed by the scattering volume V , so that $\mathbf{q} \cdot \mathbf{r} = 0$ in the limit $qR_{i^*} \rightarrow 0$. Hence, we can write

$$\delta \hat{C}_i(\mathbf{q}, t) = \lim_{qR_{i^*} \rightarrow 0} \frac{1}{V} \int_V d\mathbf{r}^3 e^{i\mathbf{q}\cdot\mathbf{r}} \delta \hat{C}_i(\mathbf{r}, t) = \frac{1}{V} \int_V d\mathbf{r}^3 \delta \hat{C}_i(\mathbf{r}, t). \quad (\text{S.43})$$

Now, setting $t = 0$ in eqn (S.43), the static autocorrelation function of $\delta \hat{C}_i(\mathbf{q}, 0)$ in the limit $qR_{i^*} \rightarrow 0$ is related to $\langle \delta \hat{C}_i^2 \rangle$ according to

$$\lim_{qR_{i^*} \rightarrow 0} \langle \delta \hat{C}_i^*(\mathbf{q}, 0) \delta \hat{C}_i(\mathbf{q}, 0) \rangle = \left\langle \left[\frac{1}{V} \int_V d\mathbf{r}^3 \delta \hat{C}_i(\mathbf{r}, 0) \right]^2 \right\rangle = \langle \delta \hat{C}_i^2 \rangle, \quad (\text{S.44})$$

which describes mean-square fluctuations in concentration that occur via mass exchange between the liquid enclosed within the scattering volume V and the surrounding bath. Eqn (S.37), (S.42), and (S.44) combine to provide

$$\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, t) \rangle = \sum_{i=1}^{n-1} \left(\frac{\partial \varepsilon}{\partial \hat{C}_i} \right)_{T,p}^2 \frac{k_B T}{V \hat{G}_i} \exp(-q^2 \bar{D}_i t). \quad (\text{S.45})$$

For a non-magnetic, non-absorbing material, the solution refractive index is related to the dielectric constant via

$$\varepsilon = n^2, \quad (\text{S.46})$$

so that eqn (S.45) becomes

$$\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, t) \rangle = 4n^2 \sum_{i=1}^{n-1} \hat{R}_i^2 \frac{k_B T}{V \hat{G}_i} \exp(-q^2 \bar{D}_i t), \quad (\text{S.47})$$

where the refractive index increments are given by

$$\hat{R}_i = \left(\partial n / \partial \hat{C}_i \right)_{T,p}, \quad (\text{S.48})$$

Eqn (19), (22), and (S.47) combine to yield the absolute value of the normalized field correlation function for a n -component mixture at constant temperature and pressure

$$|g^{(1)}(\mathbf{q}, t)| = \frac{\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, t) \rangle}{\langle |\delta \varepsilon(\mathbf{q}, 0)|^2 \rangle} = \sum_{i=1}^{n-1} \left\{ \frac{\exp(-q^2 \bar{D}_i t)}{\sum_{j=1}^{n-1} \left(\frac{\hat{R}_j}{\hat{R}_i} \right)^2 \frac{G_j}{\hat{G}_i}} \right\}. \quad (\text{S.49})$$

Note, by taking the absolute value, the term $e^{-i\omega_i t}$ has been eliminated from eqn (22). For a ternary mixture ($n = 3$), eqn (S.49) reduces to

$$|g^{(1)}(\mathbf{q}, t)| = \left(\frac{B}{1+B} \right) \exp(-q^2 \bar{D}_1 t) + \left(\frac{1}{1+B} \right) \exp(-q^2 \bar{D}_2 t), \quad (\text{S.50})$$

where the mode amplitude ratio equals

$$B = \left(\frac{\hat{R}_1}{\hat{R}_2} \right)^2 \left(\frac{\hat{G}_2}{\hat{G}_1} \right). \quad (\text{S.51})$$

In order to determine the Rayleigh ratio R_{90} for an n -component mixture at constant temperature and pressure, we combine eqn (37) and (S.47) and set $t = 0$, $\varepsilon^2 = n^4$, and $k_f \approx 2\pi n/\lambda_0$ to provide

$$R_{90} = \frac{I(\mathbf{q})R^2}{I_0V} = \frac{4\pi^2n^2}{\lambda_0^4} \sum_{i=1}^{n-1} \hat{R}_i^2 \frac{k_B T}{V\hat{G}_i} . \quad (\text{S.52})$$

For a ternary mixture ($n = 3$), we have

$$R_{90} = \frac{4\pi^2n^2}{\lambda_0^4} \hat{R}_2^2 \left(\frac{k_B T}{\hat{G}_2} \right) (1 + B) . \quad (\text{S.53})$$

S2. Refractive index derivatives, chemical potentials, thermodynamic driving forces, and diffusion coefficients for multicomponent micellar solutions

2.1 Refractive index derivatives

The solution refractive index for a ternary, single phase mixture can be defined as a function of four independent, intensive variables $n = n(T, p, C_a, C_s) = n(T, p, C_a/C_s, \phi)$.⁴ Thus, at constant temperature T and pressure p , which are the typical conditions under which measurements are performed, the total differential of the solution refractive index is given by

$$\begin{aligned} dn &= \left(\frac{\partial n}{\partial C_a} \right)_{p,T,C_s} dC_a + \left(\frac{\partial n}{\partial C_s} \right)_{p,T,C_a} dC_s \\ &= \left\{ \frac{\partial n}{\partial (C_a/C_s)} \right\}_{p,T,\phi} d \left(\frac{C_a}{C_s} \right) + \left(\frac{\partial n}{\partial \phi} \right)_{p,T,C_a/C_s} d\phi . \end{aligned} \quad (\text{S.54})$$

Total differentials for the solute to surfactant molar ratio and the volume fraction are given by

$$d \left(\frac{C_a}{C_s} \right) = \frac{1}{C_s} dC_a - \frac{C_a}{C_s^2} dC_s \quad (\text{S.55})$$

and

$$d\phi = \bar{V}_a dC_a + \bar{V}_{hs} dC_s . \quad (\text{S.56})$$

Combining eqn (S.54)–(S.56) with $R_i = (\partial n / \partial C_i)_{T,p}$ yields,

$$R_a = \bar{V}_a \left(\frac{\partial n}{\partial \phi} \right)_{p,T,C_a/C_s} + \frac{1}{C_s} \left\{ \frac{\partial n}{\partial (C_a/C_s)} \right\}_{p,T,\phi} \quad (\text{S.57})$$

and

$$R_s = \bar{V}_{hs} \left(\frac{\partial n}{\partial \phi} \right)_{p,T,C_a/C_s} - \frac{\bar{V}_{hs} C_a / C_s}{(\phi - \phi_a)} \left\{ \frac{\partial n}{\partial (C_a/C_s)} \right\}_{p,T,\phi} . \quad (\text{S.58})$$

2.2 Local equilibrium relations

Consider an n -component mixture comprised of free water, free molecular solute, hydrated surfactant monomer, and a distribution of N different micelle types, comprised of various numbers of solute and hydrated surfactant molecules. During a typical light scattering measurement, fluctuations in the

concentrations of the mixture components occur and then relax by diffusion. As diffusion occurs, it is assumed the local equilibrium is achieved on a time scale much faster than that of diffusion. Hence, one may define the total free energy minimum for a mixture within a fixed, local control volume (sometimes described as material point) at constant temperature T and pressure p . The re-equilibration process via self-assembly occurs very quickly, therefore, the system may be considered isolated (no mass or energy transfer into or out of the material point) on the time scale of equilibration. Hence, the total molar Gibbs free energy differential at constant volume, temperature, and pressure, is given by

$$dg = \mu_a dC_{a,free} + \mu_s dC_{mon} + \mu_n dC_n + \sum_{k=1}^N \mu_k dC_k = 0 , \quad (\text{S.59})$$

where $C_{a,free}$, C_{mon} , C_n , and C_k are molar concentrations for free solute, hydrated surfactant, solvent, and micelles of type k , respectively.

For an incompressible fluid at constant volume, we have

$$\bar{V}_a dC_{a,free} + \bar{V}_{hs} dC_{mon} + \bar{V}_n dC_n + \sum_{k=1}^N \bar{V}_k dC_k = 0 . \quad (\text{S.60})$$

Here, \bar{V}_n is the partial molar volume of the solvent. Solving eqn (S.60) for dC_n yields,

$$dC_n = -\frac{\bar{V}_a}{\bar{V}_n} dC_{a,free} - \frac{\bar{V}_{hs}}{\bar{V}_n} dC_{mon} - \sum_{k=1}^N \frac{\bar{V}_k}{\bar{V}_n} dC_k = 0 . \quad (\text{S.61})$$

The total concentrations of solute (a) and surfactant (s) are conserved, so that

$$dC_a = dC_{a,free} + \sum_{k=1}^N n_k dC_k = 0 \quad (\text{S.62})$$

and

$$dC_s = dC_{mon} + \sum_{k=1}^N m_k dC_k = 0 . \quad (\text{S.63})$$

Combining eqn (S.59) and (S.61)–(S.63) yields

$$\mu_k - n_k \mu_a - m_k \mu_s = \bar{V}_k - n_k \bar{V}_a - m_k \bar{V}_{hs} . \quad (\text{S.64})$$

Since the molar volume of a micelle type k is given by $\bar{V}_k = n_k \bar{V}_a + m_k \bar{V}_{hs}$, eqn (E.6) yields

$$\begin{aligned} \mu_k &= n_k \mu_a + m_k \mu_s \\ \text{for } k &= 1, 2, \dots, N . \end{aligned} \quad (\text{S.65})$$

In eqn (S.65) the chemical potentials are not uniquely defined, and may be expressed, for instance, according to

$$\mu_k = \left(\frac{\partial g}{\partial C_k} \right)_{p,T,C_{i \neq k}} = \left(\frac{\partial \tilde{F}}{\partial C_k} \right)_{T,\mu_n,V,C_{i \neq k}} = \left(\frac{\partial A}{\partial C_k} \right)_{T,V,C_{i \neq k}} , \quad (\text{S.66})$$

where \tilde{F} and A are the extensive McMillan-Mayer and Helmholtz free energies, respectively.

2.3 Osmotic pressure derivatives

Mixtures of nonionic surfactants and hydrophobic solutes can be modelled as either ternary, single phase mixtures comprised of solute, surfactant, and solvent, or as n-component mixtures of free molecular solute, monomer surfactant, and a distribution of aggregates, containing various numbers of solute and surfactant molecules. Hence, the osmotic pressure of these mixtures can be defined as a function of either four or $n + 1$ independent, intensive variables according to $\Pi = \Pi(T, \mu_n, C_a, C_s) = \Pi(T, \mu_n, C_1, C_2, \dots, C_{n-1})$. Using the chain rule, the gradient in the osmotic pressure can be expanded at constant T, μ_n

$$(\nabla \Pi)_{T, \mu_n} = \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} \nabla C_a + \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} \nabla C_s. \quad (S.67)$$

Eqn (S.67) and the Gibbs-Duhem equation at constant T, μ_n combine to yield

$$\left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} \nabla C_a + \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} \nabla C_s = \sum_{j=1}^{n-1} C_j (\nabla \mu_j)_{T, \mu_n}. \quad (S.68)$$

Similarly, the micelle species chemical potentials can also be expressed as a function of either four or $n + 1$ independent, intensive variables, according to $\mu_j = \mu_j(T, \mu_n, C_a, C_s) = \mu_j(T, \mu_n, C_1, C_2, \dots, C_{n-1})$ and the gradients in μ_j can also be expanded using the chain rule at constant T, μ_n

$$(\nabla \mu_j)_{T, \mu_n} = \left(\frac{\partial \mu_j}{\partial C_a} \right)_{T, \mu_n} \nabla C_a + \left(\frac{\partial \mu_j}{\partial C_s} \right)_{T, \mu_n} \nabla C_s. \quad (S.69)$$

Combination of eqn (S.67)–(S.69) and expansion using the chain rule provides

$$\left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} = \sum_{k=1}^{n-1} \sum_{j=1}^{n-1} C_k \left(\frac{\partial \mu_k}{\partial C_j} \right)_{T, \mu_n} \left(\frac{\partial C_j}{\partial C_a} \right) \quad (S.70)$$

and

$$\left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} = \sum_{k=1}^{n-1} \sum_{j=1}^{n-1} C_k \left(\frac{\partial \mu_k}{\partial C_j} \right)_{T, \mu_n} \left(\frac{\partial C_j}{\partial C_s} \right) \quad (S.71)$$

In this work, the concentrations of free molecular solute and surfactant monomer are vanishingly small, so that eqn (S.70) and (S.71) reduce to summations over N micellar species

$$\left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} = \sum_{k=1}^N \sum_{j=1}^N C_k \left(\frac{\partial \mu_k}{\partial C_j} \right)_{T, \mu_n} \left(\frac{\partial C_j}{\partial C_a} \right) \quad (S.72)$$

and

$$\left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} = \sum_{k=1}^N \sum_{j=1}^N C_k \left(\frac{\partial \mu_k}{\partial C_j} \right)_{T, \mu_n} \left(\frac{\partial C_j}{\partial C_s} \right) \quad (S.73)$$

2.4 Chemical potential derivatives and driving forces for diffusion

The driving force for diffusion of component i in an n-component, single phase, incompressible mixture may be written as

$$X_i = -\nabla \mu_i, \quad (S.74)$$

where the chemical potential μ_i of species i is a function of $n + 1$ other independent, intensive variables $\mu_i = \mu_i(T, p, C_1, C_2, \dots, C_{n-1}) = \mu_i(T, \mu_n, C_1, C_2, \dots, C_{n-1})$,⁴ and μ_n is the chemical potential of the solvent. Using the chain rule, one can expand eqn (S.74) according to

$$X_i = -\left(\frac{\partial \mu_i}{\partial T} \right)_{p, C} \nabla T - \left(\frac{\partial \mu_i}{\partial p} \right)_{T, C} \nabla p - (\nabla \mu_i)_{p, T} \quad (S.75)$$

or, equivalently,

$$X_i = -\left(\frac{\partial \mu_i}{\partial T} \right)_{\mu_n, C} \nabla T - \left(\frac{\partial \mu_i}{\partial \mu_n} \right)_{T, C} \nabla \mu_n - (\nabla \mu_i)_{T, \mu_n}. \quad (S.76)$$

In eqn (S.75) and (S.76), the subscript $C = [C_1, C_2, \dots, C_{n-1}]$ indicates that the vector of component concentrations is held fixed. For an incompressible mixture, one can show

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T, C} = \bar{V}_i \quad (S.77)$$

and by using a chain rule expansion we have

$$\left(\frac{\partial \mu_i}{\partial \mu_n} \right)_{T, C} = \frac{(\partial \mu_i / \partial p)_{T, C}}{(\partial \mu_n / \partial p)_{T, C}} = \frac{\bar{V}_i}{\bar{V}_n}. \quad (S.78)$$

Eqn (S.75)–(S.78) combine to produce

$$\begin{aligned} X_i &= -\left(\frac{\partial \mu_i}{\partial T} \right)_{p, C} \nabla T - \bar{V}_i \nabla p - (\nabla \mu_i)_{p, T} \\ &= -\left(\frac{\partial \mu_i}{\partial T} \right)_{\mu_n, C} \nabla T - \frac{\bar{V}_i}{\bar{V}_n} \nabla \mu_n - (\nabla \mu_i)_{T, \mu_n}. \end{aligned} \quad (S.79)$$

At constant T, μ_n , eqn (S.79) provides

$$(\nabla \mu_i)_{p, T} = (\nabla \mu_i)_{T, \mu_n} - \bar{V}_i (\nabla p)_{T, \mu_n}, \quad (S.80)$$

and according to the Gibbs-Duhem equation at constant T, μ_n , the total pressure gradient in the mixture is given by

$$(\nabla p)_{T, \mu_n} = (\nabla \Pi)_{T, \mu_n} = \sum_{j=1}^{n-1} C_j (\nabla \mu_j)_{T, \mu_n}. \quad (S.81)$$

Per McMillan-Mayer solution theory,^{1, 2} eqn (S.81) describes a total pressure gradient within a multicomponent mixture that is separated from pure solvent by a semi-permeable membrane, which is permeable to only the solvent. The total pressure p of the mixture is equal to the osmotic pressure Π , plus the pressure of the pure solvent p_w , which is held constant with μ_n . Hence $(\nabla p)_{T, \mu_n} = [\nabla(p_w + \Pi)]_{T, \mu_n} = (\nabla \Pi)_{T, \mu_n}$. Eqn (S.80) and (S.81) combine to give

$$-(\nabla\mu_i)_{p,T} = -(\nabla\mu_i)_{T,\mu_n} + \bar{V}_i \sum_{j=1}^{n-1} C_j (\nabla\mu_j)_{T,\mu_n} . \quad (S.82)$$

Now, using eqn (S.78), hold T, p constant, so that

$$-(\nabla\mu_i)_{T,\mu_n} = -(\nabla\mu_i)_{p,T} + \frac{\bar{V}_i}{\bar{V}_n} (\nabla\mu_n)_{p,T} . \quad (S.83)$$

Per the Gibbs-Duhem eqn at constant T, p

$$(\nabla\mu_n)_{p,T} = - \sum_{j=1}^{n-1} \frac{C_j}{C_n} (\nabla\mu_j)_{p,T} . \quad (S.84)$$

Combine eqn (S.83) and (S.84) with the solvent volume fraction $C_n \bar{V}_n = 1 - \phi$ to find

$$-(\nabla\mu_i)_{T,\mu_n} = -(\nabla\mu_i)_{p,T} - \frac{\bar{V}_i}{1-\phi} \sum_{j=1}^{n-1} C_j (\nabla\mu_j)_{p,T} . \quad (S.85)$$

According to the chain rule, we have

$$(\nabla\mu_i)_{p,T} = \sum_{k=1}^{n-1} \left(\frac{\partial\mu_i}{\partial C_k} \right)_{p,T} \nabla C_k \quad (S.86)$$

and

$$(\nabla\mu_i)_{T,\mu_n} = \sum_{k=1}^{n-1} \left(\frac{\partial\mu_i}{\partial C_k} \right)_{T,\mu_n} \nabla C_k . \quad (S.87)$$

Combine eqn (S.82), (S.86), and (S.87), so that

$$\left(\frac{\partial\mu_i}{\partial C_k} \right)_{p,T} = \left(\frac{\partial\mu_i}{\partial C_k} \right)_{T,\mu_n} - \bar{V}_i \sum_{j=1}^{n-1} C_j \left(\frac{\partial\mu_j}{\partial C_k} \right)_{T,\mu_n} . \quad (S.88)$$

Now, combine eqn (S.85)–(S.87) to provide the elements of $[\mathbf{G}]$

$$G_{ik} = \left(\frac{\partial\mu_i}{\partial C_k} \right)_{T,\mu_n} = \left(\frac{\partial\mu_i}{\partial C_k} \right)_{p,T} + \frac{\bar{V}_i}{1-\phi} \sum_{j=1}^{n-1} C_j \left(\frac{\partial\mu_j}{\partial C_k} \right)_{p,T} \quad \text{for } i, k = 1, 2, \dots, n-1 . \quad (S.89)$$

Eqn (S.88) and (S.89) combine to yield

$$\left(\frac{\partial\mu_i}{\partial C_k} \right)_{p,T} = (1-\phi) \left(\frac{\partial\mu_i}{\partial C_k} \right)_{T,\mu_n} \quad \text{for } i, k = 1, 2, \dots, n-1 . \quad (S.90)$$

Following de Groot and Mazur,⁵ the rate of entropy produced irreversibly by diffusion in an isothermal, non-reacting, multicomponent mixture with no externally applied forces is defined by

$$T\sigma = - \sum_{i=1}^n J_i^a \cdot (\nabla\mu_i)_{p,T} \geq 0 . \quad (S.91)$$

Here, the molar species flux of component i is given by

$$J_i^a = C_i (\mathbf{v}_i - \mathbf{v}^a) , \quad (S.92)$$

and is defined relative to an arbitrary reference velocity

$$\mathbf{v}^a = \sum_{i=1}^n a_i \mathbf{v}_i , \quad (S.93)$$

where \mathbf{v}_i and a_i are the respective velocity and normalized weighting factor for species i .

The forces $-(\nabla\mu_i)_{p,T}$ and fluxes J_i^a in eqn (S.91) are not independent, since the flux and chemical potential gradient of the solvent, denoted by the subscript n , can be eliminated using the Gibbs-Duhem equation

$$(\nabla\mu_n)_{p,T} = - \sum_{k=1}^{n-1} \frac{C_k}{C_n} (\nabla\mu_k)_{p,T} \quad (S.94)$$

and the following relation between the fluxes

$$J_n^a = - \sum_{k=1}^{n-1} \frac{C_n a_i}{C_i a_n} J_i^a . \quad (S.95)$$

Eqn (S.91), (S.94), and (S.95) combine to provide the rate of entropy production in terms of independent driving forces and fluxes

$$T\sigma = - \sum_{i=1}^{n-1} J_i^a \cdot \mathbf{X}_i^a . \quad (S.96)$$

where

$$\mathbf{X}_i^a = - \sum_{k=1}^{n-1} A_{ik}^a (\nabla\mu_k)_{p,T} , \quad (S.97)$$

and

$$A_{ik}^a = \delta_{ik} + \frac{a_i C_k}{a_n C_i} . \quad (S.98)$$

The independent fluxes and driving forces, described by eqn (S.92), (S.93), (S.97) and (S.98), are linked via the normalized reference velocity weighting factor a_i and are therefore often referred to as conjugate pairs.

By setting the weighing factor equal to the species volume fraction $a_i = \phi_i$, one can define the following mean volume reference velocity,

$$\mathbf{v} = \sum_{i=1}^n \phi_i \mathbf{v}_i , \quad (S.99)$$

which is equal to zero for an incompressible mixture relative to a fixed-volume reference frame. Eqn (S.92), (S.97), and (S.98) combine with $a_i = \phi_i$ and $\mathbf{v}^a = \mathbf{v} = \mathbf{0}$ to provide the driving force,

$$\mathbf{X}_i = - \sum_{k=1}^{n-1} \left(\delta_{ik} + \frac{C_k \bar{V}_i}{C_n \bar{V}_n} \right) (\nabla\mu_k)_{p,T} , \quad (S.100)$$

and conjugate diffusive flux

$$J_i = C_i \mathbf{v}_i , \quad (S.101)$$

defined relative to a volume-fixed reference frame, which closely approximates the fixed-laboratory frame in which experimental data is acquired. Eqn (S.100) combines with $C_n \bar{V}_n = 1 - \phi$ to provide

$$\mathbf{X}_i = -(\nabla \mu_i)_{p,T} - \frac{\bar{V}_i}{1 - \phi} \sum_{k=1}^{n-1} C_k (\nabla \mu_k)_{p,T} , \quad (\text{S.102})$$

which is identical to the result provided by Batchelor⁶ (cf. eqn (4.1) of his work). Finally, eqn (S.85) and (S.102) combine to yield

$$\mathbf{X}_i = -(\nabla \mu_i)_{T, \mu_n} , \quad (\text{S.103})$$

which describes the driving force for the diffusion of species i in a multicomponent liquid, relative to a reference frame in which the net flux of material volume is zero, and the solvent is force-free according to

$$\mathbf{X}_n = -(\nabla \mu_n)_{T, \mu_n} = 0 . \quad (\text{S.104})$$

The summation in eqn (S.102) accounts for a contribution to the driving force that acts on component i caused by solvent backflow, which inevitably occurs when a solute gradient is established in an incompressible mixture at constant temperature and pressure in a constant volume diffusion cell. Interestingly, when the same diffusion process is described using the McMillan-Mayer framework, the driving force on component i is given by eqn (S.103) and the solvent backflow contribution is accounted for via an osmotic pressure gradient. One may imagine a 1-dimensional diffusion cell, separated by a semipermeable membrane (permeable only to the solvent) oriented parallel to the flux direction along the diffusion pathway. In this scenario, the membrane separates the multicomponent mixture at each local point from pure solvent, thereby maintaining a constant solvent chemical potential at each point along the diffusion path, so that the solvent is force-free. Here, solvent passes through the membrane into the diffusion cell from the pure solvent reservoir and raises the osmotic pressure locally in proportion with the local solute concentration, thereby enhancing the thermodynamic driving force on component i via a gradient in osmotic pressure, rather than by backflow of solvent at constant pressure. We note that the McMillan Mayer framework is useful here because of the simplicity of eqn (S.103) as compared with (S.102).

2.5 Diffusivities

2.5.1 Diffusion coefficient matrix [D]

In this section, the main solute diffusivity D_{aa} , given by eqn (75), is derived starting with eqn (69). Eqn (76)–(78) can be similarly derived to yield the complete matrix [D]. Note, this appendix is a generalization of our previous derivation for D_{aa} applied to dilute locally monodisperse micellar solutions.⁷ We begin with eqn (69)

$$D_{aa} = \sum_{i=1}^N n_i D_i^0 \left\{ \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) \frac{\partial C_i}{\partial C_a} + \phi_i \sum_{j=1}^N h_{ij} \frac{\partial C_j}{\partial C_a} \right\} . \quad (\text{S.105})$$

Here, n_i and D_i^0 are independent of C_a , enabling the following rearrangement of eqn (S.105)

$$D_{aa} = \sum_{i=1}^N \frac{\partial (n_i D_i^0 C_i)}{\partial C_a} \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) + \sum_{i=1}^N n_i D_i^0 \phi_i \left(\sum_{j=1}^N h_{ij} \frac{\partial C_j}{\partial C_a} \right) . \quad (\text{S.106})$$

The derivatives $\partial (n_i D_i^0 C_i) / \partial C_a (1 + \sum_{k=1}^N f_{ik} \phi_k)$ and $\sum_{j=1}^N h_{ij} \partial C_j / \partial C_a$ in eqn (H.2) are then rearranged using the product rule to yield

$$D_{aa} = \frac{\partial}{\partial C_a} \left\{ \sum_{i=1}^N n_i D_i^0 C_i \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) - \sum_{i=1}^N n_i D_i^0 C_i \frac{\partial}{\partial C_a} \left(\sum_{k=1}^N f_{ik} \phi_k \right) + \sum_{i=1}^N n_i D_i^0 \phi_i \left\{ \frac{\partial}{\partial C_a} \left(\sum_{j=1}^N h_{ij} C_j \right) - \sum_{j=1}^N C_j \frac{\partial h_{ij}}{\partial C_a} \right\} \right\} . \quad (\text{S.107})$$

For narrow micelle size distributions, the local species concentrations and volume fractions can be approximated using $C_i = C_{tot} \delta_{ii^*}$ and $\phi_i = \phi \delta_{ii^*}$, where C_{tot} is the total micelle concentration and δ_{ii^*} is a Kronecker delta function. The function δ_{ii^*} is nonzero when $i = i^*$, corresponding to a micelle species i^* that represents the distribution mean and has \bar{n} solutes, \bar{m} surfactants, radius R_{i^*} , and local concentration C_{tot} . Inserting the Kronecker distribution to eqn (S.107) and using the sifting property, which selects a single micelle type i^* from the distribution, provides

$$D_{aa} = \frac{\partial (C_a D_{i^*}^0)}{\partial C_a} (1 + f \phi) + C_a D_{i^*}^0 \phi h \frac{\partial \ln C_{tot}}{\partial C_a} + C_a D_{i^*}^0 \phi L_a . \quad (\text{S.108})$$

Similarly, one can derive

$$D_{as} = C_a \frac{\partial D_{i^*}^0}{\partial C_s} (1 + f \phi) + C_a D_{i^*}^0 \phi h \frac{\partial \ln C_{tot}}{\partial C_s} + C_a D_{i^*}^0 \phi L_s . \quad (\text{S.109})$$

$$D_{sa} = C_s \frac{\partial D_{i^*}^0}{\partial C_a} (1 + f \phi) + C_s D_{i^*}^0 \phi h \frac{\partial \ln C_{tot}}{\partial C_a} + C_s D_{i^*}^0 \phi L_a . \quad (\text{S.110})$$

and

$$D_{ss} = \frac{\partial (C_s D_{i^*}^0)}{\partial C_s} (1 + f \phi) + C_s D_{i^*}^0 \phi h \frac{\partial \ln C_{tot}}{\partial C_s} + C_s D_{i^*}^0 \phi L_s . \quad (\text{S.111})$$

where

$$L_a = \frac{\partial f}{\partial C_a} + \left[\frac{\partial (h_{ii^*} - f_{ii^*})}{\partial C_a} \right]_{i=i^*} - \left(\frac{\partial h_{ij}}{\partial C_a} \right)_{j=i^*} . \quad (\text{S.112})$$

and

$$L_s = \frac{\partial f}{\partial C_s} + \left[\frac{\partial(h_{ii^*} - f_{ii^*})}{\partial C_s} \right]_{i=i^*} - \left(\frac{\partial h_{ij}}{\partial C_s} \right)_{j=i=i^*}. \quad (\text{S.113})$$

In eqn (S.108–S.113), $f = f_{i^*i^*}$ and $h = h_{i^*i^*}$ account for interactions between micelles of the same type. For a ternary, single phase mixture in local equilibrium, f_{ij} and h_{ij} can be written as functions of intensive state variables according to $f_{ij} = f_{ij}(T, \mu_n, C_a, C_s) = f_{ij}(T, \mu_n, C_a/C_s, \phi)$ and $h_{ij} = h_{ij}(T, \mu_n, C_a, C_s) = h_{ij}(T, \mu_n, C_a/C_s, \phi)$. Using the chain rule, the partial derivatives for f_{ij} with respect to C_a and C_s are given by

$$\frac{\partial f_{ij}}{\partial C_a} = \frac{\partial f_{ij}}{\partial(C_a/C_s)} \frac{\partial(C_a/C_s)}{\partial C_a} + \frac{\partial f_{ij}}{\partial \phi} \frac{\partial \phi}{\partial C_a}, \quad (\text{S.114})$$

and

$$\frac{\partial f_{ij}}{\partial C_s} = \frac{\partial f_{ij}}{\partial(C_a/C_s)} \frac{\partial(C_a/C_s)}{\partial C_s} + \frac{\partial f_{ij}}{\partial \phi} \frac{\partial \phi}{\partial C_s}. \quad (\text{S.115})$$

In eqn (S.114) and S.115), the volume fraction and molar ratio derivatives are evaluated to provide

$$C_a \frac{\partial f_{ij}}{\partial C_a} = \frac{C_a}{C_s} \frac{\partial f_{ij}}{\partial(C_a/C_s)} + \frac{\partial f_{ij}}{\partial \phi} \phi_a, \quad (\text{S.116})$$

and

$$C_s \frac{\partial f_{ij}}{\partial C_s} = -\frac{C_a}{C_s} \frac{\partial f_{ij}}{\partial(C_a/C_s)} + \frac{\partial f_{ij}}{\partial \phi} (\phi - \phi_a). \quad (\text{S.117})$$

Eqn (S.116) and (S.117) combine to give

$$C_a \frac{\partial f_{ij}}{\partial C_a} + C_s \frac{\partial f_{ij}}{\partial C_s} = \phi \frac{\partial f_{ij}}{\partial \phi}. \quad (\text{S.118})$$

Similarly, one finds

$$C_a \frac{\partial h_{ij}}{\partial C_a} + C_s \frac{\partial h_{ij}}{\partial C_s} = \phi \frac{\partial h_{ij}}{\partial \phi}. \quad (\text{S.119})$$

Eqn (S.112), (S.113), (S.118), and (S.119) combine to yield

$$C_a L_a + C_s L_s = \phi L. \quad (\text{S.120})$$

where

$$L = \frac{\partial f}{\partial \phi} + \left[\frac{\partial(h_{ii^*} - f_{ii^*})}{\partial \phi} \right]_{i=i^*} - \left(\frac{\partial h_{ij}}{\partial \phi} \right)_{j=i=i^*}. \quad (\text{S.121})$$

Differentiating the Stokes Einstein equation $D_{i^*}^0 = k_B T / (6\pi\eta R_{i^*})$, one finds

$$\frac{\partial \ln D_{i^*}^0}{\partial \ln C_a} = -\frac{\partial \ln R_{i^*}}{\partial \ln C_a}. \quad (\text{S.122})$$

and

$$\frac{\partial \ln D_{i^*}^0}{\partial \ln C_s} = \frac{\partial \ln R_{i^*}}{\partial \ln C_a}. \quad (\text{S.123})$$

Furthermore, the total micelle concentration is differentiated according to

$$\frac{\partial \ln C_{tot}}{\partial \ln C_a} = \frac{\phi_a}{\phi} - 3 \frac{\partial \ln R_{i^*}}{\partial \ln C_a}. \quad (\text{S.124})$$

and

$$\frac{\partial \ln C_{tot}}{\partial \ln C_s} = 1 - \frac{\phi_a}{\phi} + 3 \frac{\partial \ln R_{i^*}}{\partial \ln C_a}. \quad (\text{S.125})$$

Finally, eqn (S.108)–(S.111), (S.120), and (S.122)–(S.125) yield

$$\frac{D_{aa}}{D_{i^*}^0} = 1 + f\phi - \mathcal{M}, \quad (\text{S.126})$$

$$\frac{D_{as}}{D_{i^*}^0} = \frac{C_a}{C_s} \{ (\tilde{A} + g)\phi + [(f + g)\tilde{A} + L]\phi^2 + \mathcal{M} \}, \quad (\text{S.127})$$

$$\frac{D_{sa}}{D_{i^*}^0} = -\frac{C_s}{C_a} \mathcal{M}, \quad (\text{S.128})$$

and

$$\frac{D_{ss}}{D_{i^*}^0} = 1 + (\tilde{A} + f + g)\phi + [(f + g)\tilde{A} + L]\phi^2 + \mathcal{M}, \quad (\text{S.129})$$

where the function \mathcal{M} is given by

$$\mathcal{M} = \frac{\partial \ln R_{i^*}}{\partial \ln C_a} [1 + (f + 3h)\phi] - h\phi_a - C_a L_a \phi, \quad (\text{S.130})$$

and

$$h = \tilde{A} + g + (f + g)\tilde{A}\phi, \quad (\text{S.131})$$

2.5.2 Long-time self (D_s) and gradient (D_c) diffusivities

In this section, gradient and long-time self diffusion coefficients (D_c and D_s , respectively) for a monodisperse particle suspension are derived by evaluating the diffusive flux for a polydisperse colloidal suspension comprising N different particle types and subsequently applying a delta distribution function. We begin by considering a polydisperse colloidal suspension comprising N different particle types. The total diffusive flux \mathbf{J} is determined by summing over all of the species fluxes \mathbf{J}_i according to

$$-\mathbf{J} = -\sum_{i=1}^N \mathbf{J}_i = \sum_{i=1}^N \sum_{j=1}^N D_{ij} \nabla \phi_j. \quad (\text{S.132})$$

where the diffusion coefficient matrix D_{ij} is given by combining eqn (49), (59), and (66) to provide

$$\frac{D_{ij}}{D_i^0} = \delta_{ij} \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) + h_{ij} \phi_i. \quad (\text{S.133})$$

With the function h_{ij} given by

$$\frac{h_{ij}}{\lambda_{ij}^3} = \tilde{A}_{ij} + g_{ij} + \sum_{k=1}^N (\tilde{A}_{ij} f_{ik} + g_{ik} \tilde{A}_{kj}) \phi_k. \quad (\text{S.134})$$

The species concentration gradient is expanded using the chain rule: $\nabla \phi_j = \partial \phi_j / \partial \phi \nabla \phi$ and combined with eqn (S.132)–(S.134) to yield

$$-J = \sum_{i=1}^N D_i^0 \left\{ \delta_{ij} \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) \frac{\partial \phi_i}{\partial \phi} + \phi_i \sum_{j=1}^N h_{ij} \frac{\partial \phi_j}{\partial \phi} \right\} \nabla \phi .$$

(S.135)

Here, D_i^0 is independent of ϕ , enabling the following re-arrangement of eqn (I.4)

$$-J = \sum_{i=1}^N \frac{\partial(D_i^0 \phi_i)}{\partial \phi} \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) \nabla \phi + \sum_{i=1}^N D_i^0 \phi_i \left(\sum_{j=1}^N h_{ij} \frac{\partial \phi_j}{\partial \phi} \right) \nabla \phi .$$

(S.136)

The derivatives $\partial(D_i^0 \phi_i)/\partial \phi (1 + \sum_{k=1}^N f_{ik} \phi_k)$ and $\sum_{j=1}^N h_{ij} \partial \phi_j / \partial \phi$ in eqn (S.136) are then re-arranged using the product rule to provide

$$-J = \frac{\partial}{\partial \phi} \left\{ \sum_{i=1}^N D_i^0 \phi_i \left(1 + \sum_{k=1}^N f_{ik} \phi_k \right) \right\} \nabla \phi - \sum_{i=1}^N D_i^0 \phi_i \frac{\partial}{\partial \phi} \left(\sum_{k=1}^N f_{ik} \phi_k \right) \nabla \phi + \sum_{i=1}^N D_i^0 \phi_i \left\{ \frac{\partial}{\partial \phi} \left(\sum_{j=1}^N h_{ij} \phi_j \right) - \sum_{j=1}^N \phi_j \frac{\partial h_{ij}}{\partial \phi} \right\} \nabla \phi .$$

(S.137)

The Kronecker delta distribution $\phi_i = \phi \delta_{ii^*}$ is combined with eqn (S.137) to provide

$$-J = D_{i^*}^0 \{ 1 + (\tilde{A} + f + g)\phi + [(f + g)\tilde{A} + L]\phi^2 \} \nabla \phi , \quad (S.138)$$

where

$$L = \frac{\partial f}{\partial \phi} + \left[\frac{\partial(h_{ii^*} - f_{ii^*})}{\partial \phi} \right]_{i=i^*} - \left(\frac{\partial h_{ij}}{\partial \phi} \right)_{j=i=i^*} . \quad (S.139)$$

Eqn (S.138) describes gradient diffusion in a monodisperse colloidal dispersion according to the diffusivity D_c ,

$$\frac{D_c}{D_{i^*}^0} = 1 + (\tilde{A} + f + g)\phi + [(f + g)\tilde{A} + L]\phi^2 , \quad (S.140)$$

To determine the long-time self diffusion coefficient D_s , again consider a multicomponent mixture with N distinct colloidal species. However, in this scenario, a thermodynamic driving forces acts only on the species i , which is present in vanishingly small amount such that $\phi_i = 0$, and the remaining species are force free. The flux of species i for this case is given by

$$-J_i = D_s \nabla \phi_i = \sum_{j=1}^N D_{ij} \nabla \phi_j . \quad (S.141)$$

Eqn (S.133) and (S.141) combine with $\phi_i = 0$ to provide

$$\frac{D_s}{D_i^0} = 1 + \sum_{k=1}^N f_{ik} \phi_k . \quad (S.142)$$

For mixtures of monodisperse particles $f_{ik} = f$, so that the long-time self diffusion coefficient at arbitrary concentration is given by

$$\frac{D_s}{D_i^0} = 1 + f\phi , \quad (S.143)$$

S3 Derivations for limiting special cases

3.1 Scattering functions B and R_{90} for locally monodisperse micelles

In this section, the mode amplitude ratio B , and the Rayleigh ratio R_{90} are derived in the limit as the local micelle polydispersity approaches zero. First, eqn (34)–(36) and (51)–(53) combine to produce the elements of the diagonalized chemical potential derivative matrix $[\hat{G}]$

$$C_a \hat{G}_a = \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} + \frac{C_a}{C_s} P_{sa}^2 \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} - C_s G_{sa} \left(\frac{C_a}{C_s} P_{sa} - 1 \right)^2 \quad (S.144)$$

and

$$C_s \hat{G}_s = \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} + \frac{C_s}{C_a} P_{as}^2 \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} - C_a G_{sa} \left(\frac{C_s}{C_a} P_{as} - 1 \right)^2 \quad (S.145)$$

In the limit as the local micelle polydispersity approaches zero, $G_{sa} \rightarrow -\infty$, so that eqn (27), (85), (90), (S.144) and (S.145) combine to yield the ratio

$$B = 0 , \quad (S.146)$$

and eqn (26), (84), and (S.146) provide the field correlation function

$$|g^{(1)}(\mathbf{q}, t)| = \exp\{-q^2 D_i^0 [1 + (f + h)\phi + L\phi^2]t\} , \quad (S.147)$$

Now, turning our attention toward the Rayleigh ratio, a general form for the osmotic pressure in a mixture of monodisperse micelles is given by

$$\frac{\Pi}{N_A k_B T} = C_{tot} Z(\phi) , \quad (S.148)$$

Differentiating eqn (S.148) with respect to either C_a or C_s and combining the results with eqn (85) and (S.145) yields

$$C_s^2 \hat{G}_s = C_a \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} + C_s \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} + Z(\phi) \left(\frac{\partial \ln C_{tot}}{\partial \ln C_a} + \frac{\partial \ln C_{tot}}{\partial \ln C_s} \right) \quad (S.149)$$

Differentiation of the total micelle concentration $C_{tot} = C_s / \bar{m}$ provides

$$\frac{\partial \ln C_{tot}}{\partial \ln C_a} = - \frac{\partial \ln \bar{m}}{\partial \ln C_a} \quad (S.150)$$

and

$$\frac{\partial \ln C_{tot}}{\partial \ln C_s} = 1 - \frac{\partial \ln \bar{m}}{\partial \ln C_s} \quad (S.151)$$

As argued in our previous work,⁷ if the aggregation number is a univariate function of the solute to surfactant molar ratio C_a/C_s at constant temperature and pressure, then the aggregation number derivatives are related via

$$\frac{\partial \ln \bar{m}}{\partial \ln C_s} = - \frac{\partial \ln \bar{m}}{\partial \ln C_a} \quad (S.152)$$

Hence, eqn (S.150)–(S.152) combine to give

$$\frac{\partial \ln C_{tot}}{\partial \ln C_a} + \frac{\partial \ln C_{tot}}{\partial \ln C_s} = 1 \quad (S.153)$$

Furthermore, the compressibility factor derivatives in eqn (S.149) can be expanded using the chain rule, so that

$$\frac{\partial Z(\phi)}{\partial \ln C_a} + \frac{\partial Z(\phi)}{\partial \ln C_s} = \phi \frac{dZ(\phi)}{d\phi} \left(\frac{\partial \ln \phi}{\partial \ln C_a} + \frac{\partial \ln \phi}{\partial \ln C_s} \right) \quad (S.154)$$

Differentiation of the volume fraction $\phi = C_a \bar{V}_a + C_s \bar{V}_{hs}$ with respect to C_a gives

$$\frac{\partial \ln \phi}{\partial \ln C_a} = \frac{\phi_a}{\phi} \quad (S.155)$$

Now, differentiating with respect to C_s and using $C_s \bar{V}_{hs} = \phi - \phi_a$, we have

$$\frac{\partial \ln \phi}{\partial \ln C_s} = 1 - \frac{\phi_a}{\phi} \quad (S.156)$$

Hence, eqn (S.155) and (S.156) combine to provide

$$\frac{\partial \ln \phi}{\partial \ln C_a} + \frac{\partial \ln \phi}{\partial \ln C_s} = 1 \quad (S.157)$$

Eqn (S.149), (S.153), and (S.157) combine to produce

$$\frac{C_s^2 \hat{G}_s}{C_{tot} N_A k_B T} = \phi \frac{dZ(\phi)}{d\phi} + Z(\phi) = \frac{d[\phi Z(\phi)]}{d\phi} \quad (S.158)$$

The diagonalized refractive index increment \hat{R}_s is evaluated using eqn (31)–(33) and (85)

$$\hat{R}_s = \frac{\phi}{C_s} \left(\frac{\partial n}{\partial \phi} \right)_{p, T, C_a / C_s} \quad (S.159)$$

Finally, eqn (39), (S.146), (S.158), (S.159), and $\phi = N_A C_s / m_0 V_i^*$ yield

$$R_{90} = \frac{4\pi^2 n^2}{\lambda_0^4} \left(\frac{\partial n}{\partial \phi} \right)_{p, T, C_a / C_s}^2 V_i^* \phi \left(\frac{d[\phi Z(\phi)]}{d\phi} \right)^{-1} \quad (S.160)$$

3.2 Onsager matrix [L] for locally monodisperse micelles

The main Onsager coefficient L_{aa} in eqn (99) is derived in this appendix. Eqn (100) and (101) can be derived using a similar approach to provide the complete Onsager matrix [L]. We begin by evaluating the determinant of the chemical potential derivative matrix [G] using eqn (51)–(53)

$$C_a C_s |G| = \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} - G_{sa} \left\{ C_a \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} + C_s \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} \right\} \quad (S.161)$$

Eqn (53), (95), and (S.161) combine in the limit as the local micelle polydispersity approaches zero, so that $G_{sa} \rightarrow -\infty$, to produce

$$L_{aa} = \frac{C_a^2 D_{aa} + C_a C_s D_{as}}{C_a \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} + C_s \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n}} \quad (S.162)$$

Per eqn (S.149) and (S.158)

$$C_a \left(\frac{\partial \Pi}{\partial C_a} \right)_{T, \mu_n} + C_s \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_n} = C_{tot} N_A k_B T \left(\frac{d[\phi Z(\phi)]}{d\phi} \right) \quad (S.163)$$

Eqn (S.162) and (S.163) combine with $C_a = \bar{n} C_{tot}$ to give

$$L_{aa} = \frac{\bar{n}^2 C_{tot}}{N_A k_B T} \left(D_{aa} + \frac{C_s}{C_a} D_{as} \right) \left(\frac{d[\phi Z(\phi)]}{d\phi} \right)^{-1} \quad (S.164)$$

Using eqn (75)–(78), (84), we have

$$D_{aa} + \frac{C_s}{C_a} D_{as} = D_{ss} + \frac{C_a}{C_s} D_{sa} = D_+ \quad (S.165)$$

As discussed in the main text, and in section 2.5.2 of SI, the eigenvalue D_+ is equal to the gradient diffusion coefficient for monodisperse particle dispersions. Hence, D_+ can be described using the following generalized Stokes-Einstein equation

$$D_+ = D_i^0 K(\phi) \frac{d[\phi Z(\phi)]}{d\phi} \quad (S.166)$$

Eqn (S.164)–(S.166) combine to yield

$$L_{aa} = \frac{\bar{n}^2 C_{tot} D_i^0}{N_A k_B T} K(\phi) \quad (S.167)$$

This approach may be used to derive the remaining Onsager coefficients, applicable to locally monodisperse mixtures at arbitrary concentration:

$$L_{as} = L_{sa} = \bar{n}\bar{m}C_{tot} \left(\frac{D_{i^*}^0}{N_A k_B T} \right) K(\phi) \quad (S.168)$$

and

$$L_{ss} = \bar{m}^2 C_{tot} \left(\frac{D_{i^*}^0}{N_A k_B T} \right) K(\phi). \quad (S.169)$$

3.3 [G] in the tracer limit

In this section, we provide a detailed derivation for [G] in the tracer limit, given by eqn (128)–(130). We begin with eqn (52)

$$G_{sa} = \left(\frac{N_A k_B T}{m_1} \right) \left\{ \frac{1}{C_a} \frac{\partial \ln C_1}{\partial \ln C_a} + \sum_{j=1}^N A_{1j} \left(\frac{\partial C_j}{\partial C_a} \right) \right\}. \quad (S.170)$$

The derivation in this section is simplified by introducing the following function

$$\tilde{A}_{1j} = (1 - \phi) A_{1j}, \quad (S.171)$$

so that eqn (S.170) can be rewritten as

$$\frac{m_1(1 - \phi)G_{sa}}{N_A k_B T} = \frac{(1 - \phi)}{C_a} \frac{\partial \ln C_1}{\partial \ln C_a} + \sum_{j=1}^N \tilde{A}_{1j} \left(\frac{\partial C_j}{\partial C_a} \right). \quad (S.172)$$

The summation in eqn (S.172) is then rearranged, using the product rule, to the following more amenable form:

$$\sum_{j=1}^N \tilde{A}_{1j} \left(\frac{\partial C_j}{\partial C_a} \right) = \frac{\partial}{\partial C_a} \left(\sum_{j=1}^N C_j \tilde{A}_{1j} \right) - \sum_{j=1}^N C_j \left(\frac{\partial \tilde{A}_{1j}}{\partial C_a} \right). \quad (S.173)$$

For micelle distributions that are monomodal and narrow, the micelle distribution function can be reasonable approximated using a Kronecker delta distribution function $C_j = C_{tot} \delta_{jj^*}$. According to this definition, C_j is nonzero only when the index $j = j^*$, which denotes a micelle type representative of the distribution mean and characterized as having \bar{n} solutes, \bar{m} surfactants, radius R_{j^*} , and concentration C_{tot} , all of which are functions of composition (C_a/C_s). Inserting the Kronecker distribution into eqn (S.173) yields,

$$\sum_{j=1}^N \tilde{A}_{1j} \left(\frac{\partial C_j}{\partial C_a} \right) = \frac{\partial}{\partial C_a} \left(\sum_{j=1}^N C_{tot} \delta_{jj^*} \tilde{A}_{1j} \right) - \sum_{j=1}^N C_{tot} \delta_{jj^*} \left(\frac{\partial \tilde{A}_{1j}}{\partial C_a} \right). \quad (S.174)$$

Using the sifting property, which selects a micelle type j^* from a set of N different micelle types, the summations on the right-hand side of eqn (S.174) are evaluated to give

$$\sum_{j=1}^{N-1} \tilde{A}_{1j} \left(\frac{\partial C_j}{\partial C_a} \right) = \frac{\partial}{\partial C_a} (C_{tot} \tilde{A}_{1j^*}) - C_{tot} \left(\frac{\partial \tilde{A}_{1j}}{\partial C_a} \right)_{j=j^*}. \quad (S.175)$$

The derivative $\partial(C_{tot} \tilde{A}_{1j^*})/\partial C_a$ in eqn (S.175) can be expanded with the product rule to provide

$$\sum_{j=1}^N \tilde{A}_{1j} \left(\frac{\partial C_j}{\partial C_a} \right) = \tilde{A}_{1j^*} \frac{\partial C_{tot}}{\partial C_a} + C_{tot} \left\{ \frac{\partial \tilde{A}_{1j^*}}{\partial C_a} - \left(\frac{\partial \tilde{A}_{1j}}{\partial C_a} \right)_{j=j^*} \right\}. \quad (S.176)$$

In order to determine the first term on the right-hand side of eqn (S.176) we start by combining eqn (49), (125), and (S.171) with $k = 1$ to give

$$\begin{aligned} \tilde{A}_{1j} = \frac{\pi}{6} \{ & d_1^3 + d_j^3 + d_1^3 d_j^3 \eta_0 \\ & + 3d_1 d_j [d_1(1 + d_1 \eta_2)(1 + d_j^2 \eta_1) \\ & + d_j(1 + d_j \eta_2)(1 + d_1^2 \eta_1)] \\ & + 9d_1^2 d_j^2 \eta_2(1 + d_1 \eta_2)(1 + d_j \eta_2) \}. \end{aligned} \quad (S.177)$$

where d_1 and d_j are the respective diameters of a solute-free and a type j particle,

$$\eta_v = \frac{\xi_v}{1 - \phi}, \quad (S.178)$$

and

$$\xi_v = \sum_{i=1}^N \phi_i d_i^{v-3}. \quad (S.179)$$

Using the Kronecker distribution, so that $C_j = C_{tot} \delta_{jj^*}$ and $\phi_i = C_{tot} N_A V_i \delta_{ii^*}$, eqn (S.177)–(S.179) combine to yield

$$\begin{aligned} & \frac{\tilde{A}_{1j}}{\frac{\pi}{6} d_1^3} \\ & = \left(\frac{d_j}{d_1} \right)^3 + \frac{\left\{ 1 + \left[\left(\frac{d_j}{d_{j^*}} \right)^3 - 1 \right] \phi \right\}}{(1 - \phi)} \\ & + 3 \left(\frac{d_j}{d_1} \right) \frac{\left[1 + \left(\frac{d_1}{d_{j^*}} - 1 \right) \phi \right] \left\{ 1 + \left[\left(\frac{d_j}{d_{j^*}} \right)^2 - 1 \right] \phi \right\}}{(1 - \phi)^2} \\ & + 3 \left(\frac{d_j}{d_1} \right)^2 \frac{\left[1 + \left(\frac{d_j}{d_{j^*}} - 1 \right) \phi \right] \left\{ 1 + \left[\left(\frac{d_1}{d_{j^*}} \right)^2 - 1 \right] \phi \right\}}{(1 - \phi)^2} \\ & + 9\phi \left(\frac{d_j^2}{d_1 d_{j^*}} \right) \frac{\left[1 + \left(\frac{d_1}{d_{j^*}} - 1 \right) \phi \right] \left[1 + \left(\frac{d_j}{d_{j^*}} - 1 \right) \phi \right]}{(1 - \phi)^3}. \end{aligned} \quad (S.180)$$

Imposing $j = j^*$ onto eqn (S.180) provides

$$\begin{aligned} \frac{\tilde{A}_{0j^*}}{\frac{\pi}{6} d_1^3} = & \left(\frac{d_{j^*}}{d_1} \right)^3 + \frac{1}{(1 - \phi)} + 3 \left(\frac{d_{j^*}}{d_1} \right) \frac{\left[1 + \left(\frac{d_1}{d_{j^*}} - 1 \right) \phi \right]}{(1 - \phi)^2} \\ & + 3 \left(\frac{d_{j^*}}{d_1} \right)^2 \frac{\left\{ 1 + \left[\left(\frac{d_1}{d_{j^*}} \right)^2 - 1 \right] \phi \right\}}{(1 - \phi)^2} \\ & + 9\phi \left(\frac{d_{j^*}}{d_1} \right) \frac{\left[1 + \left(\frac{d_1}{d_{j^*}} - 1 \right) \phi \right]}{(1 - \phi)^3}. \end{aligned} \quad (S.181)$$

With the aid of Mathematica, eqn (S.181) simplifies to

$$\frac{\tilde{A}_{1j^*}}{\frac{\pi}{6}d_1^3} = \lambda^3 + \frac{3\lambda^2}{(1-\phi)} + \frac{3\lambda(1+\phi-2\phi^2)}{(1-\phi)^3} + \frac{(1+2\phi)^2}{(1-\phi)^3}, \quad (S.182)$$

where $\lambda = d_{j^*}/d_1$ is a micelle size ratio. Multiplying eqn (S.182) by λ^{-3} provides

$$\frac{\tilde{A}_{1j^*}}{\frac{\pi}{6}d_{j^*}^3} = 1 + \frac{3\lambda^{-1}}{(1-\phi)} + \frac{3\lambda^{-2}(1+\phi-2\phi^2)}{(1-\phi)^3} + \frac{\lambda^{-3}(1+2\phi)^2}{(1-\phi)^3} \quad (S.183)$$

Furthermore, using eqn (S.150) and eqn (A.16) from Appendix A in our previous work,⁷ we find

$$\frac{\partial \ln C_{tot}}{\partial \ln C_a} = \frac{\phi_a}{\phi} - 3 \frac{\partial \ln R_{j^*}}{\partial \ln C_a}. \quad (S.184)$$

Eqn (S.183), (S.184), and $\phi = C_{tot}N_A\pi/6d_{j^*}^3$ combine to provide the first term on the right-hand side of eqn (S.176),

$$\tilde{A}_{1j^*} \frac{\partial C_{tot}}{\partial C_a} = \frac{1}{C_a} \left\{ 1 + \frac{3\lambda^{-1}}{(1-\phi)} + \frac{3\lambda^{-2}(1+\phi-2\phi^2)}{(1-\phi)^3} + \frac{\lambda^{-3}(1+2\phi)^2}{(1-\phi)^3} \right\} \left(\phi_a - 3\phi \frac{\partial \ln R_{j^*}}{\partial \ln C_a} \right). \quad (S.185)$$

Now, focusing on the second term of eqn (S.176), differentiation of eqn (S.180) and (S.182) with respect to solute concentration C_a is accomplished via symbolic computation performed using Mathematica to provide

$$C_{tot} \left\{ \frac{\partial \tilde{A}_{1j^*}}{\partial C_a} - \left(\frac{\partial \tilde{A}_{1j}}{\partial C_a} \right)_{j=j^*} \right\} = \frac{1}{C_a} \left\{ 1 + \frac{\lambda^{-1}(2-3\phi+\phi^3)}{(1-\phi)^3} + \frac{\lambda^{-2}(1+6\phi-6\phi^2-\phi^3)}{(1-\phi)^3} + \frac{\lambda^{-3}\phi(2+\phi)^2}{(1-\phi)^3} \right\} 3\phi \frac{\partial \ln R_{j^*}}{\partial \ln C_a}, \quad (S.186)$$

where we have used $\partial \ln R_{j^*}/\partial \ln C_a = \partial \ln d_{j^*}/\partial \ln C_a$. Combination of eqn (S.172), (S.176), (S.185), and (S.186), again via symbolic computation using Mathematica, yield

$$\frac{m_1(1-\phi)G_{sa}}{N_A k_B T} = (1-\phi) \frac{1}{C_a} \frac{\partial \ln C_0}{\partial \ln C_a} + \tilde{A}(\lambda, \phi) \frac{\phi_a}{C_a} - \tilde{B}(\lambda, \phi) \frac{1}{C_a} \frac{\partial \ln R_{j^*}}{\partial \ln C_a} \quad (S.187)$$

where

$$\tilde{A}(\lambda, \phi) = 1 + \frac{3\lambda^{-1}}{(1-\phi)} + \frac{3\lambda^{-2}(1+\phi-2\phi^2)}{(1-\phi)^3} + \frac{\lambda^{-3}(1+2\phi)^2}{(1-\phi)^3} \quad (S.188)$$

and

$$\tilde{B}(\lambda, \phi) = 3\phi \left\{ \lambda^{-1} + \frac{\lambda^{-2}(2+\phi)}{(1-\phi)} + \frac{\lambda^{-3}(1+\phi+\phi^2)}{(1-\phi)^2} \right\}. \quad (S.189)$$

To evaluate the solute-free micelle derivative in eqn (S.187), consider the Poisson distribution, given by

$$C_i = \frac{C_s \bar{n}^{n_i}}{\bar{m} n_i!} \exp(-\bar{n}). \quad (S.190)$$

where \bar{n} , the average number of solutes per micelle, is equal to the distribution variance. The Poisson distribution, which is derived assuming ideal mixing between solute and surfactant within micelles, and is considered valid when $\bar{n} \ll \bar{m}$,^{8,9} is useful here because the Poisson variance approaches zero $\bar{n} \rightarrow 0$ in the tracer limit as $C_a \rightarrow 0$, causing eqn (S.190) to approach a Kronecker delta function

$$\lim_{C_a \rightarrow 0} \frac{C_s \bar{n}^{n_i}}{\bar{m} n_i!} \exp(-\bar{n}) = \frac{C_s}{m_1} \delta_{i1}. \quad (S.191)$$

Hence, in the tracer limit, the Poisson distribution becomes consistent with the delta distribution applied earlier in this derivation to evaluate the summation given by eqn (S.173). Differentiation of eqn (S.191) for $i = 1$ yields

$$\frac{\partial \ln C_1}{\partial \ln C_a} = 1 - (\bar{n} + 1) \left(1 + \frac{\partial \ln \bar{m}}{\partial \ln C_a} \right). \quad (S.192)$$

Combining eqn (S.192) with eqn (A.16) from Appendix A in our previous work,⁷ we have

$$\frac{\partial \ln C_1}{\partial \ln C_a} = 1 - (\bar{n} + 1) \left(1 + 3 \frac{\partial \ln R_{j^*}}{\partial \ln C_a} - \frac{\phi_a}{\phi} \right). \quad (S.193)$$

Eqn (S.187) and (S.193) combine to provide

$$\frac{m_1(1-\phi)G_{sa}}{N_A k_B T} = -(1-\phi) \frac{\bar{n}}{C_a} + \left[\tilde{A}(\lambda, \phi) + \frac{(1-\phi)(\bar{n}+1)}{\phi} \right] \frac{\phi_a}{C_a} - [\tilde{B}(\lambda, \phi) + 3(1-\phi)(\bar{n}+1)] \frac{1}{C_a} \frac{\partial \ln R_{j^*}}{\partial \ln C_a} \quad (S.194)$$

In the limit as $C_a \rightarrow 0$, for which $\lambda \rightarrow 1$, $\bar{n} \rightarrow 0$, $\bar{n}/C_a \rightarrow m_1/C_s$, $1/C_a (\partial \ln R_{j^*}/\partial \ln C_a) \rightarrow a_1/(R_1 C_s)$, $\phi \rightarrow C_s \bar{V}_{hs}$, and $\phi_a/C_a \rightarrow \bar{V}_a$, with the aid of Mathematica, eqn (S.188), (S.189), and (S.194) simplify to

$$\frac{C_s G_{sa}}{N_A k_B T} = -1 + \frac{\bar{V}_a}{m_1 \bar{V}_{hs}} \frac{(1+2\phi)^2}{(1-\phi)^4} - \frac{3a_1}{m_1 R_1} \frac{(1+\phi+\phi^2)}{(1-\phi)^3} \quad (S.195)$$

In order to determine the remaining elements of the matrix $[\mathbf{G}]$, defined by eqn (51) and (53), one must evaluate the osmotic pressure derivatives $(\partial \Pi / \partial C_a)_{T, \mu_n}$ and $(\partial \Pi / \partial C_s)_{T, \mu_n}$. Imposing the delta distribution $C_j = C_{tot} \delta_{jj^*}$ on eqn (124) provides the Percus-Yevick result for monodisperse hard spheres

$$\frac{\Pi}{N_A k_B T} = C_{tot} \frac{(1+\phi+\phi^2)}{(1-\phi)^3}. \quad (S.196)$$

Differentiation of eqn (S.196) with respect to C_a provides

$$\frac{(\partial\Pi/\partial C_a)_{T,\mu_n}}{N_A k_B T} = \frac{C_{tot}}{C_a} \left\{ \frac{(1-\phi^3)}{(1-\phi)^4} \frac{\partial \ln C_{tot}}{\partial \ln C_a} + \frac{(2+\phi)^2}{(1-\phi)^4} \phi \frac{\partial \ln \phi}{\partial \ln C_a} \right\} \quad (S.197)$$

Using eqn (S.197), (S.155), and (S.184) with $C_{tot} = C_s/\bar{m}$, we have

$$\frac{(\partial\Pi/\partial C_a)_{T,\mu_n}}{N_A k_B T} = \frac{C_s/C_a}{\bar{m}\phi(1-\phi)^4} \left\{ (1+2\phi)^2 \phi_a - 3\phi(1-\phi^3) \frac{\partial \ln R_{j^*}}{\partial \ln C_a} \right\}. \quad (S.198)$$

The osmotic pressure derivative with respect to surfactant concentration C_s is similarly derived, using eqn (S.153) and (S.157),

$$\frac{(\partial\Pi/\partial C_s)_{T,\mu_n}}{N_A k_B T} = \frac{1}{\bar{m}\phi(1-\phi)^4} \left\{ (1+2\phi)^2 (\phi - \phi_a) + 3\phi(1-\phi^3) \frac{\partial \ln R_{j^*}}{\partial \ln C_a} \right\}. \quad (S.199)$$

In the tracer limit, as $(\partial \ln R_{j^*} / \partial \ln C_a) \rightarrow 0$, $1/C_a (\partial \ln R_{j^*} / \partial \ln C_a) \rightarrow a_1/(R_1 C_s)$, $\phi_a \rightarrow 0$, $\phi_a/C_a \rightarrow \bar{V}_a$, and $\phi \rightarrow C_s \bar{V}_{hs}$, eqn (S.198) and (S.199) reduce to

$$\frac{(\partial\Pi/\partial C_a)_{T,\mu_n}}{N_A k_B T} = \frac{\bar{V}_a}{m_1 \bar{V}_{hs}} \frac{(1+2\phi)^2}{(1-\phi)^4} - \frac{3a_1}{m_1 R_1} \frac{(1-\phi^3)}{(1-\phi)^4}, \quad (S.200)$$

and

$$\frac{(\partial\Pi/\partial C_s)_{T,\mu_n}}{N_A k_B T} = \frac{(1+2\phi)^2}{m_1 (1-\phi)^4}. \quad (S.201)$$

Finally, eqn (51), (53), (S.195), (S.200), and (S.201) yield $[\mathbf{G}]$ in the tracer limit, with elements given by

$$\frac{C_a G_{as}}{N_A k_B T} = 1, \quad (S.202)$$

$$\frac{C_s G_{as}}{N_A k_B T} = \frac{C_s G_{sa}}{N_A k_B T} = -1 - \frac{3a_1}{m_1 R_1} \frac{(1+\phi+\phi^2)}{(1-\phi)^3} + \frac{\bar{V}_a}{m_1 \bar{V}_{hs}} \frac{(1+2\phi)^2}{(1-\phi)^4}, \quad (S.203)$$

and

$$\frac{C_s G_{ss}}{N_A k_B T} = \frac{1}{m_1} \frac{(1+2\phi)^2}{(1-\phi)^4}. \quad (S.204)$$

3.4 $[\mathbf{G}]$, \mathbf{R}_{90} , \mathbf{B}_{LL} , and $[\mathbf{L}]$ for the label limit

In this section, the micelle chemical potential derivative matrix $[\mathbf{G}]$, the Rayleigh ratio \mathbf{R}_{90} , and the mode amplitude ratio \mathbf{B}_{LL} are derived for the label limit, where solute behaves as a volume-less label in a mixture of equally sized micelles with $\phi_a = 0$, $\bar{m} = m_1$, and $R_{j^*} = R_1$, where m_1 and R_1 are the solute-free micelle aggregation number and radius, respectively. Starting with our derivation for $[\mathbf{G}]$, we begin with eqn (52)

$$\frac{m_1 G_{as}}{N_A k_B T} = \frac{m_1 G_{sa}}{N_A k_B T} = \frac{1}{C_a} \frac{\partial \ln C_1}{\partial \ln C_a} + \sum_{j=1}^N A_{1j} \left(\frac{\partial C_j}{\partial C_a} \right). \quad (S.205)$$

For the label limit, micelles are distinguished only by the number of solubilize labels, which do not affect the interaction potentials between various micelle types. Hence, $A_{1j} = A$, and eqn (S.205) combines with $\partial C_{tot}/\partial C_a = 0$ to provide,

$$\frac{m_1 G_{sa}}{N_A k_B T} = \frac{1}{C_a} \frac{\partial \ln C_1}{\partial \ln C_a}. \quad (S.206)$$

The osmotic pressure derivatives are determined using eqn (47)–(49), (45), $A_{kj} = A$, and $\partial C_{tot}/\partial C_a = 0$, yielding

$$\left(\frac{\partial \Pi}{\partial C_a} \right)_{T,\mu_n} = 0. \quad (S.207)$$

Using (S.207) with (S.163), we have

$$\frac{m_1 (\partial \Pi / \partial C_s)_{T,\mu_n}}{N_A k_B T} = \frac{d[\phi Z(\phi)]}{d\phi}. \quad (S.208)$$

Eqn (51)–(53), (S.206)–(S.208), and $\phi_a = 0$ combine to generate $[\mathbf{G}]$ in the label limit, equal to

$$G_{aa} = -\frac{N_A k_B T}{\bar{n} C_a} \frac{\partial \ln C_1}{\partial \ln C_a}, \quad (S.209)$$

$$G_{as} = G_{sa} = \frac{N_A k_B T}{\bar{n} C_s} \frac{\partial \ln C_1}{\partial \ln C_a}, \quad (S.210)$$

and

$$G_{ss} = \frac{N_A k_B T}{m_0 C_s} \left\{ \frac{d[\phi Z(\phi)]}{d\phi} - \frac{\partial \ln C_1}{\partial \ln C_a} \right\}, \quad (S.211)$$

Derivations for R_{90} and B_{LL} for labelled micelles are similar that those in section 3.1. We begin by combining eqn (S.144) and (S.145) with (145), and (S.206)–(S.208) to yield the diagonalized elements of $[\mathbf{G}]$ in the label limit

$$\frac{C_a \hat{G}_a}{N_A k_B T} = -\frac{C_s}{C_a} \frac{\partial \ln C_1}{\partial \ln C_a} \quad (S.212)$$

and

$$\frac{m_1 C_s \hat{G}_s}{N_A k_B T} = \frac{d[\phi Z(\phi)]}{d\phi}. \quad (S.213)$$

The diagonalized refractive index increments are evaluated using eqn (30)–(33), (145), and $\bar{V}_a = 0$ to give

$$\hat{R}_a = \frac{1}{C_s} \left\{ \frac{\partial n}{\partial (C_a/C_s)} \right\}_{p,T,\phi} \quad (S.214)$$

and

$$\hat{R}_s = \frac{\phi}{C_s} \left(\frac{\partial n}{\partial \phi} \right)_{p,T,C_a/C_s}. \quad (S.215)$$

Eqn (27), (39), (S.212)–(S.215), and $\phi = N_A C_s / m_1 V_1$ combine to yield the Rayleigh ratio

$$R_{90} = \frac{4\pi^2 n^2}{\lambda_0^4} \left(\frac{\partial n}{\partial \phi} \right)_{p,T,C_a/C_s}^2 V_1 \phi \left\{ \frac{d[\phi Z(\phi)]}{d\phi} \right\}^{-1} (1 + B_{LL}), \quad (\text{S.216})$$

Where V_1 is the volume of a solute-free micelle and the mode amplitude ratio is given by

$$B_{LL} = \left\{ \frac{[\partial n / \partial (C_a / C_s)]_{p,T,\phi}}{\phi (\partial n / \partial \phi)_{p,T,C_a/C_s}} \right\}^2 \frac{(C_a / C_s)^2}{(-\partial \ln C_1 / \partial \ln C_a)} \frac{d[\phi Z(\phi)]}{d\phi}. \quad (\text{S.217})$$

In order to derive the Onsager coefficient matrix $[\mathbf{L}]$, we start by evaluating the determinant of $[\mathbf{G}]$ using eqn (S.161), (S.207), (S.208), (S.210), and $\bar{n}C_s = m_1 C_a$

$$|\mathbf{G}| = \left(\frac{N_A k_B T}{\bar{n}C_s} \right)^2 \left(-\frac{\partial \ln C_1}{\partial \ln C_a} \right) \frac{d[\phi Z(\phi)]}{d\phi}. \quad (\text{S.218})$$

Eqn (95) and (133)–(141), and (S.218) combine to provide

$$L_{aa} = \bar{n}^2 C_{tot} \left(\frac{D^0}{N_A k_B T} \right) \left[K(\phi) + \frac{1 + f\phi}{(-\partial \ln C_1 / \partial \ln C_a)} \right], \quad (\text{S.219})$$

Similar arguments yield the remaining Onsager coefficients:

$$L_{as} = L_{sa} = \bar{n} m_1 C_{tot} \left(\frac{D^0}{N_A k_B T} \right) K(\phi) \quad (\text{S.220})$$

and

$$L_{ss} = m_1^2 C_{tot} \left(\frac{D^0}{N_A k_B T} \right) K(\phi). \quad (\text{S.221})$$

3.5 R_{90} for binary mixtures of monodisperse micelles with crowding-induced dehydration

In this section, we derive the Rayleigh ratio for a binary mixture of hydrated surfactant (s) and water (w) with a concentration dependent hydration index $n_H = n_H(T, p, C_s)$ and a constant aggregation number m_1 . For this system, the total entropy fluctuation at constant temperature T and scattering volume V is given by

$$\delta S_T = -\frac{1}{2T} (\delta \mu_w \delta N_w + \delta \mu_s \delta N_s), \quad (\text{S.222})$$

where μ_w and μ_s are the chemical potentials for water and hydrated surfactant and N_w and N_s are the respective numbers of moles in the scattering volume V . Imposing constant volume, we have

$$\delta V = \delta [\bar{V}_w N_w + (\bar{V}_s + n_H \bar{V}_w) N_s] = 0. \quad (\text{S.223})$$

Solving eqn (S.223) for the fluctuation in the number of moles of water provides

$$\delta N_w = -N_s \delta n_H - \frac{(\bar{V}_s + n_H \bar{V}_w)}{\bar{V}_w} \delta N_s. \quad (\text{S.224})$$

At constant temperature, pressure, and volume, the total fluctuation differential in the hydration index is given by

$$\delta n_H = \frac{V}{V} \left(\frac{\partial n_H}{\partial N_s} \right)_{p,T} \delta N_s = \left(\frac{\partial n_H}{\partial C_s} \right)_{p,T} \delta C_s, \quad (\text{S.225})$$

and eqn (S.224) and (S.225) combine to yield

$$\delta N_w = -V \left\{ C_s \left(\frac{\partial n_H}{\partial C_s} \right)_{p,T} + \frac{(\bar{V}_s + n_H \bar{V}_w)}{\bar{V}_w} \right\} \delta C_s, \quad (\text{S.226})$$

which indicates that hydrated surfactant displaces free water at constant volume and adds to N_w via the transfer of bound water from hydrated surfactant to bulk water via dehydration.

Now, using the Gibbs-Duhem relation at constant temperature, pressure, and volume, and solving for the free water fluctuation $\delta \mu_w$ provides

$$\delta \mu_w = -\frac{V N_s}{V N_w} \delta \mu_s = -\frac{C_s}{C_w} \delta \mu_s. \quad (\text{S.227})$$

The total fluctuation differential in hydrated surfactant chemical potential at constant temperature, pressure, and volume is given by

$$\delta \mu_s = \frac{V}{V} \left(\frac{\partial \mu_s}{\partial N_s} \right)_{p,T} \delta N_s = \left(\frac{\partial \mu_s}{\partial C_s} \right)_{p,T} \delta C_s, \quad (\text{S.228})$$

and eqn (S.227) and (S.228) combine

$$\delta \mu_w = -\frac{C_s}{C_w} \left(\frac{\partial \mu_s}{\partial C_s} \right)_{p,T} \delta C_s. \quad (\text{S.229})$$

Now, eqn (S.222), (S.226), and (S.229) combine with $\phi = C_s (\bar{V}_s + n_H \bar{V}_w)$ and $1 - \phi = C_w \bar{V}_w$ to provide

$$\delta S_T = -\frac{V}{2T} \left(\frac{1}{1 - \phi} \right) \left(\frac{\partial \mu_s}{\partial C_s} \right)_{p,T} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p,T} \right] \delta C_s^2. \quad (\text{S.230})$$

Eqn (S.90) reduces for a binary mixture to provide

$$\left(\frac{1}{1 - \phi} \right) \left(\frac{\partial \mu_s}{\partial C_s} \right)_{p,T} = \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T,\mu_w}, \quad (\text{S.231})$$

and eqn (S.230) and (S.231) yield

$$\delta S_T = -\frac{V}{2T} \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T,\mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p,T} \right] \delta C_s^2. \quad (\text{S.232})$$

The master formula for fluctuation theory provides the probability for a fluctuation δC_s in the scattering volume V

$$P(\delta C_s) = \Omega^{-1} e^{\left\{ -\frac{V}{2k_B T} \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T,\mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p,T} \right] \delta C_s^2 \right\}}, \quad (\text{S.233})$$

and is integrated over all possible fluctuations to determine the normalization constant

$$\begin{aligned}\Omega = \langle \delta C_s \rangle &= \int_{-\infty}^{\infty} d(\delta C_s) e^{\left\{ -\frac{V}{2k_B T} \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right] \delta C_s^2 \right\}} \\ &= \left\{ \frac{2\pi k_B T}{V \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]} \right\}^{\frac{1}{2}},\end{aligned}\quad (S.234)$$

Using eqn (S.233) and (S.234), the mean-square fluctuation in the surfactant concentration is given by

$$\begin{aligned}\langle \delta C_s^2 \rangle &= \int_{-\infty}^{\infty} d(\delta C_s) \delta C_s^2 P(\delta C_s) \\ &= \Omega^{-1} \int_{-\infty}^{\infty} d(\delta C_s) \delta C_s^2 e^{\left\{ -\frac{V}{2k_B T} \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right] \delta C_s^2 \right\}} \\ &= \frac{k_B T}{V \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]},\end{aligned}\quad (S.235)$$

In order to determine the Rayleigh ratio, we will need the fluctuation in the dielectric constant $\varepsilon = \varepsilon[T, p, C_s, n_H(T, p, C_s)]$, which is expanded in reciprocal space at constant temperature and pressure to provide

$$\delta \varepsilon(\mathbf{q}, t) = \left(\frac{\partial \varepsilon}{\partial n_H} \right)_{p, T, C_s} \delta n_H(\mathbf{q}, t) + \left(\frac{\partial \varepsilon}{\partial C_s} \right)_{p, T, n_H} \delta C_s(\mathbf{q}, t), \quad (S.236)$$

In eqn (S.236), $\delta C_s(\mathbf{q}, 0)$ is the Fourier transform of the local surfactant concentration fluctuation $\delta C_s(\mathbf{r}, 0)$, given by

$$\delta C_s(\mathbf{q}, 0) = \frac{1}{V} \int_V d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \delta \hat{C}_s(\mathbf{r}, 0). \quad (S.237)$$

Eqn (S.225) and (S.236) combine to yield

$$\delta \varepsilon(\mathbf{q}, t) = \left[\left(\frac{\partial \varepsilon}{\partial C_s} \right)_{p, T, n_H} + \left(\frac{\partial \varepsilon}{\partial n_H} \right)_{p, T, C_s} \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right] \delta C_s(\mathbf{q}, t), \quad (S.238)$$

Using eqn (S.238), the ensemble averaged time correlation function for fluctuations in ε is given by

$$\begin{aligned}\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, t) \rangle &= \left[\left(\frac{\partial \varepsilon}{\partial C_s} \right)_{p, T, n_H} + \left(\frac{\partial \varepsilon}{\partial n_H} \right)_{p, T, C_s} \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]^2 \\ &\quad \times \langle \delta C_s^*(\mathbf{q}, 0) \delta C_s(\mathbf{q}, t) \rangle.\end{aligned}\quad (S.239)$$

Now, setting $t = 0$ and using eqn (S.237) in the limit $qR_i^* \rightarrow 0$, the mean square fluctuation in surfactant concentration is given by

$$\langle \delta C_s^*(\mathbf{q}, 0) \delta C_s(\mathbf{q}, 0) \rangle = \left\langle \left[\frac{1}{V} \int_V d\mathbf{r} \delta C_s(\mathbf{r}, 0) \right]^2 \right\rangle = \langle \delta C_s^2 \rangle. \quad (S.240)$$

Eqn (S.235), (S.239) and (S.240) combine with $t = 0$ to provide

$$\langle \delta \varepsilon^*(\mathbf{q}, 0) \delta \varepsilon(\mathbf{q}, 0) \rangle = \frac{k_B T \left[\left(\frac{\partial \varepsilon}{\partial C_s} \right)_{p, T, n_H} + \left(\frac{\partial \varepsilon}{\partial n_H} \right)_{p, T, C_s} \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]^2}{V \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w} \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]}. \quad (S.241)$$

The Rayleigh ratio R_{90} at constant temperature and pressure is determined by combining eqn (37) and (S.241) and $\varepsilon^2 = n^4$, and $k_f \approx 2\pi n/\lambda_0$ to provide

$$\begin{aligned}R_{90} = \frac{I(\mathbf{q})R^2}{I_0 V} &= \frac{4\pi^2 n^2 \left[\left(\frac{\partial n}{\partial C_s} \right)_{p, T, n_H} + \left(\frac{\partial n}{\partial n_H} \right)_{p, T, C_s} \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]^2}{\lambda_0^4 \left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]} \\ &\quad \times \frac{k_B T}{V \left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w}}.\end{aligned}\quad (S.242)$$

The surfactant chemical potential derivative $(\partial \mu_s / \partial C_s)_{T, \mu_w}$ is determined using (S.73), reduced for a binary mixture

$$\left(\frac{\partial \mu_s}{\partial C_s} \right)_{T, \mu_w} = \frac{1}{C_s} \left(\frac{\partial \Pi}{\partial C_s} \right)_{T, \mu_w}, \quad (S.243)$$

and a general form for the osmotic pressure in a mixture of monodisperse micelles

$$\frac{\Pi}{N_A k_B T} = C_{tot} Z(\phi). \quad (S.244)$$

where $Z(\phi)$ is the compressibility factor. Eqn (S.242)–(S.244) and $C_{tot} = C_s/m_1$ combine to yield

$$R_{90} = \frac{4\pi^2 n^2}{\lambda_0^4} \frac{\left(\frac{\partial n}{\partial C_s} \right)_{T, p}^2}{\left[1 + C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \right]} \frac{C_s m_1 \left\{ \frac{d[C_s Z(\phi)]}{dC_s} \right\}^{-1}}{N_A}, \quad (S.245)$$

where, according to the chain rule,

$$\left(\frac{\partial n}{\partial C_s} \right)_{T, p} = \left(\frac{\partial n}{\partial C_s} \right)_{p, T, n_H} + \left(\frac{\partial n}{\partial n_H} \right)_{p, T, C_s} \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T}. \quad (S.246)$$

Furthermore, using eqn (94), we have

$$\begin{aligned}\frac{d[C_s Z(\phi)]}{dC_s} &= \frac{(1 + 2\phi)^2 - \phi^3(4 - \phi)}{(1 - \phi)^4} \\ &\quad - C_s^2 \bar{V}_w \left(\frac{\partial n_H}{\partial C_s} \right)_{p, T} \frac{(4 + 4\phi - 2\phi^2)}{(1 - \phi)^4}\end{aligned}\quad (S.247)$$

A check for the results given by eqn (S.245)–(S.247) is provided by removing dehydration, so that $(\partial n_H / \partial C_s)_{p, T} = 0$ and the hydrated surfactant molar volume $\bar{V}_{hs} = \bar{V}_s + n_H \bar{V}_w$ is constant. As a result, using $\phi = C_s \bar{V}_{hs}$ and $m_1 \bar{V}_{hs} / N_A = V_1$, eqn (S.245) reduces to

$$R_{90} = \frac{4\pi^2 n^2}{\lambda_0^4} \left(\frac{\partial n}{\partial \phi} \right)_{T,p}^2 V_1 \phi \left\{ \frac{d[\phi Z(\phi)]}{d\phi} \right\}^{-1}, \quad (\text{S.248})$$

which is consistent with R_{90} or a binary mixture of monodisperse hard spheres.

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