[pex50] Spherical aggregates of colloids

Consider a colloidal dispersion with a tendency for aggregation. The differential in mass density between colloids and dispersion medium is so small that any effects of gravity can be ignored. The colloids are monodisperse and have volume v. The interfacial energy, $E_{\text{int}} = 4\pi r^2\gamma$, between aggregate and dispersion medium adds to the cost of aggregation. Therefore, if the energy of association for one colloid to an aggregate of infinite size is ϵ_∞, then the energy of association of m colloids to one spherical aggregate is $\epsilon_m = \epsilon_\infty + E_{\text{int}}/m$ for each of these colloids.
(a) Show that this energy of association can be written in the form

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_{\text{B}} T}{m^{1/3}}, \quad \alpha \doteq \frac{4\pi\gamma}{k_{\text{B}}T}\left(\frac{3v}{4\pi}\right)^{2/3}. \tag{1}$$

The parameter α decreases with increasing T not only because of the factor T in the denominator but also because the interface tension γ is expected to decrease. As in [pex40]-[pex42] we use the expression

$$X_m \propto m \exp\left(\frac{m(\mu - \epsilon_m)}{k_{\text{B}}T}\right), \quad m = 1, 2, \ldots \tag{2}$$

for volume fractions of size-m aggregates at thermal equilibrium.
(b) Infer from expressions (1) and (2) the relation

$$X_m = m\Big[X_1 e^{\alpha}\Big]^m e^{-\alpha m^{2/3}}, \tag{3}$$

by eliminating the chemical potential μ.
(c) Compute the concentration of size-m aggregates, X_m, and the total concentration of colloids, $\phi \doteq \sum_m X_m$, as functions of the variable α and the parameter X_1 (the concentration of colloids in dispersion). Use a cut-off $m_{\max}$ in the sum large enough that its effect on the results is negligible. The concentration of aggregated colloids is $X_{\text{agg}} \doteq \phi - X_1$. Plot (parametrically) curves of X_1 and X_{agg} versus ϕ. Use several values of the energy constant in the range $1 < \alpha < 7$. For each choice of α, zoom into the range of ϕ where interesting physical phenomena take place such as (more or less abrupt) changes in the concentrations of free and aggregated colloids.
(d) Identify data points for the critical aggregation concentration (CAC). Try to fit these data point to a model expression for $\phi_c(\alpha)$.

[adapted from Jones 2002]

Solution: