Equilibrium Distribution of Linear Micellar Aggregates in a Gravitational or Centrifugal Field

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The behavior of linear micelles subjected to external fields is a topic of current interest (see e.g. refs 1–10). Aggregates sedimenting under gravity or in a centrifugal field have apparently not been treated theoretically so we focus on the equilibrium case which is relatively straightforward. We first recall the thermodynamics of a dilute incompressible solution (whose solute need not be micellar) in a gravitational field which allows us to formulate the relevant variational principle for a suitably chosen thermodynamic potential. We then calculate the equilibrium size distribution and the concentration profile of a dilute suspension of linear aggregates under gravity or in a centrifuge.

We present a modified version of Kirkwood and Oppenheim's analysis[11] of a dilute suspension sedimenting in an external field (either gravitational or centrifugal). The potential $\Psi(z)$ of the field is defined per unit mass and acts in the z direction of our Cartesian coordinate system whose origin is chosen at the upper surface of the solution. The positive z half-space is situated above the surface. We chose $\Psi(0)$ equal to zero, i.e., $\Psi = gz$, for a gravitational field, with g being the gravitational acceleration or $\Psi = {}^1/_2\omega(R^2(0) - R^2(z))$ in a centrifuge where ω is the angular velocity of rotation and $R(z)$ the distance of a point in the solution to the axis of rotation. The solution is in equilibrium with a reservoir which has a constant temperature and exerts a constant pressure p_{ex} on the solution (Figure 1). We divide the solution into a very large number $\mathcal{N}$ of layers aligned perpendicularly to the field. If the thickness of each layer is macroscopically small so that it is much smaller than the scale of variation of the potential $\Psi(z)$, we may regard each layer as homogeneous. This enables us to write the differential of the internal energy U_k of one such layer labeled k as

$$dU_k = T_k\, dS_k - p_k\, dV_k + \mu_k\, dN_k + \mu_{w,k}\, dN_{w,k} \quad (1)$$

where T_k is the absolute temperature, S_k the entropy, p_k the pressure, and V_k the volume of the layer. The chemical potential $\mu_k = \mu_k(p_k,T_k,z_k) = \mu'(p_k,T_k) + m\Psi(z_k)$ of a solute molecule of mass m is the sum of the chemical potential μ' in the absence of the field and the increase in its potential energy in the gravitational field; likewise we have an analogous relation $\mu_{w,k} = \mu'_{w,k}(p_k,T_k) + m_w\Psi(z_k)$ for the
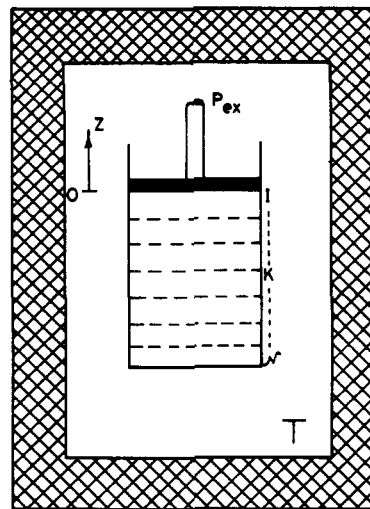
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Figure 1. A reservoir which fixes the temperature and the external pressure on a solution. The solution is divided into $\mathcal{N}$ homogeneous layers perpendicular to the direction (z) of the field.

chemical potential of a solvent molecule. The number of solute molecules in the kth layer is N_k and the number of solvent molecules $N_{w,k}$. For the reservoir of entropy S_r and volume V_r, the differential of the internal energy U_r reads

$$dU_r = T\, dS_r - p_{ex}\, dV_r \quad (2)$$

Since the internal energy of a closed system in stable equilibrium is a minimum, we obtain the equilibrium conditions of the solution plus reservoir by equating the first variation of the total internal energy ($=U_r + \Sigma U_k$) to zero. This variation is subject to the following constraints: the total entropy ($=S_r + \Sigma S_k$) and the total number of particles ($N = \Sigma N_k, N_w = \Sigma N_{w,k}$) are conserved; the volume of each layer is fixed except for that of the first layer which is allowed to vary so that the system may adjust to the fixed external pressure ($dV_1 = -dV_r, dV_k = 0$ for $k \neq 1$). The differential of the total internal energy U_{tot} is now written as

$$dU_{tot} = (p_{ex} - p_1)dV_1 + \sum_k (T_k - T)dS_k + \mu_k\, dN_k +$$
$$\mu_{w,k}\, dN_{w,k} \quad (3)$$

As dU_{tot} must vanish for arbitrary variations we have the following conditions for equilibrium

$$p_1 = p_{ex}; \quad T_k = T; \quad \mu_k = \mu \text{ and } \mu_{w,k} = \mu_w \text{ are uniform} \quad (4)$$

These conditions should be supplemented with stability criteria to ascertain that the equilibrium is stable, but they will not be discussed here.

In the theory of micellar growth it is often useful to employ a variational principle, especially when there are complicated interactions present.[12-14] For the system at hand we have a minimum principle for Φ:

$$\Phi = \Phi(N,N_w,p_{ex},T,\Psi(z)) \equiv N\mu + N_w\mu_w \quad (5)$$

If we keep in mind that all the volumes of the layers are constrained except the first, we have on using eqs 1, 2, and 4

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$$d\Phi = p_{ex}\,dV_1 + \sum_k (dU_k - T\,dS_k)$$

$$= dU_r + \sum_k dU_k \tag{6}$$

The differential $d\Phi$ is therefore equal to zero in equilibrium provided the uppermost layer of the solution has a constant pressure p_{ex}. We will not pause to formulate the consequences of $d^2\Phi > 0$ which ensures that the extremum is indeed a minimum.

At this stage we take the continuum limit ($\mathcal{N}$ extremely large) so that the chemical potential becomes

$$\mu = \mu(p(z),T,X(z),\Psi(z)) = \mu'(p(z),T,X(z)) + m\Psi(z)$$

$$= \mu'_0(p(z),T) + k_B T \log X(z) + m\Psi(z)$$

$$= \mu'_0(p_{ex},T) + (p(z) - p_{ex})v + k_B T \log X(z) + m\Psi(z)$$

$$\simeq \mu'_0(p_{ex},T) + k_B T \log X(z) + (m - \rho_w v)\Psi(z) \tag{7}$$

with k_B being Boltzmann's constant. Here we have used the fact that the solution is dilute (mole fraction $X(z) \equiv N(z)/(N(z) + N_w(z)) \ll 1$), the solute is incompressible ($v = \partial\mu'/\partial p$ = volume of a solute molecule; $\partial v/\partial p = 0$), and the pressure increment is given in terms of the external field ($p(z) - p_{ex} = -\rho_s \Psi(z) \simeq -\rho_w \Psi(z)$ where the solution density $\rho_s \simeq$ solvent density ρ_w for a dilute solution). The chemical potential in equilibrium is uniform so we immediately obtain the usual barometric distribution under gravity ($\Psi(z) = gz$), corrected for buoyancy.

Next we remark that the formal part of the preceding analysis does not need modification for a dilute solution of incompressible linear micelles in a similar external field. In units of $k_B T \equiv \beta^{-1}$ the chemical potential of one amphiphile within a linear aggregate consisting of s such species is then

$$\mu = \mu'(p_{ex},T,s,X(s,z)) + \beta m_b \Psi(z)$$

$$= \mu_0(p_{ex},T) + Ks^{-1} + s^{-1} \log X(s,z) -$$

$$ns^{-1} \log(s) + \beta m_b \Psi(z) \tag{8}$$

for s larger than some minimum aggregation number s_0. The chemical potential μ' in the absence of the external field is given by the standard form[15-17] and consists of the following contributions: (a) μ_0 is the chemical potential of a surfactant molecule if the aggregates were infinitely long; (b) K is the free energy of formation of two end caps; (c) a term arising from the ideal entropy of mixing which is dependent on the mole fraction $X(s,z)$ of the amphiphiles in the state of aggregation indexed s; (d) the surfactant loses a certain number of degrees of freedom on micellization. If this loss is associated with the mixing entropy only, we would set n equal to unity;[15] other researchers have argued that n may be larger than unity.[16,17] The term depending on the external potential $\Psi(z)$ is independent of s: the increment in the potential energy of an amphiphile is exactly proportional to its mass corrected for buoyancy. In particular, n is independent of Ψ. The corrected mass $m_b = m - \rho_w v$ where m is the mass and v the volume of one amphiphile which is incompressible.

In equilibrium the chemical potential of one surfactant molecule is independent of the height and its state of aggregation. From eq 8 we obtain the equilibrium distribution

$$X(s,z) = s^n \exp(-K - s\eta - s\beta m_b \Psi(z)) \tag{9}$$

where $\eta = \eta(p_{ex},T)$ is a constant assumed to be positive. It depends on the magnitude of the external field for the total number of surfactant molecules is conserved in a sedimentation experiment. In order to arrive at the total mole fraction solely as a function of height z, we sum over s in the continuum limit and apply Laplace's method:[18]

$$X(z) = \left(\frac{2\pi}{n}\right)^{1/2} \left(\frac{n}{\eta + \beta m_b \Psi(z)}\right)^{n+1} \exp(-K - n) \tag{10}$$

The ith moment of the distribution $X(s,z)$ is defined by

$$S_i(z) \equiv \frac{\sum_{s \geq s_0} s^i X(s,z)}{X(z)} \tag{11}$$

These moments are easily calculated using ref 18. The first moment, the mean aggregation number, is given by

$$S_1(z) = \frac{(n + 1)^{n+3/2}}{n^{n+1/2}} e^{-1} (\eta + \beta m_b \Psi(z))^{-1} \tag{12}$$

Note that there is a connection between $X(z)$ and $S_1(z)$ which is independent of the external potential

$$(n + 1) \log S_1(z) = K + n + c(n) + \log X(z) \tag{13}$$

Here $c(n)$ is a slowly varying function of order unity. The independence of Ψ comes about because the total external potential is purely extensive in nature. A way to see this immediately is by using the variational principle outlined earlier: $\partial\mu/\partial s = 0$. The resulting expression for $s(z)$ does not coincide with eq 13 precisely, since the distribution in eq 9 is not peaked very sharply.

Equation 10 is interesting for it shows that the sedimentation of linear aggregates depends on the influence of the centrifugal field on one surfactant molecule only. Nonetheless, the typical values of the potential Ψ needed to perturb thermal equilibrium in zero field are quite low because η is very small compared to unity for elongated micelles. A numerical example bears this out: setting $n = 1$ (the viewpoint adopted in ref 15), $K = 30$, and the total mole fraction equal to 10^{-6}, we have $\eta \simeq 3 \times 10^{-4}$ and $S_1 \simeq 9000$ (inversely proportional to η) in the absence of the field. Characteristic values of m_b and z are 30 g/mol and 1 cm, respectively, so at room temperature sedimentation is experimentally discernible for a centrifugal field of order 100 g. In a practical experiment it will often not be straightforward to calculate η from the total mole fraction (i.e., via a spatial average of eq 10), since the cell geometry may be complicated. However, a measurement of the profile via the refractive index should allow an unambiguous characterization of the micellar aggregation parameters K and n provided the solution remains dilute. In fact, adjusting K, n, and η in eq 10 to fit the experimental data should not pose any problems for n appears in the exponent. As yet few experimental investigations have focused on ultracentrifugation in equilibrium.[19]

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(18) To approximate summations of the type $J = \sum_{s \geq s_0}^{\infty} s^m e^{-ps}$ where $p > 0$, we write J as an integral: $\int_{s_0}^{\infty} ds \, s^m e^{-ps}$. For a fairly monodisperse sample of long aggregates (i.e., $m \gg p s_0$) we can use Laplace's method to asymptotically approximate the above integral by $J \simeq (2\pi/m)^{1/2}(m/p)^{m+1} e^{-m}$.

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