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Modeling of equilibrium hollow objects stabilized by electrostatics

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Abstract
The equilibrium size of two largely different kinds of hollow objects behave qualitatively differently with respect to certain experimental conditions. Yet, we show that they can be described within the same theoretical framework. The objects we consider are ‘minivesicles’ of ionic and nonionic surfactant mixtures, and shells of Keplerate-type polyoxometalates. The finite-size of the objects in both systems is manifested by electrostatic interactions. We emphasize the importance of constant charge and constant potential boundary conditions. Taking these conditions into account, indeed, leads to the experimentally observed qualitatively different behavior of the equilibrium size of the objects.

1. Introduction

Electrostatics is fundamental in the stabilization of equilibrium structures such as microemulsions [1–3], which is one of the several fields where Lekkerkerker provided important contributions. More recent examples where electrostatics is a determining factor are anomalously large colloidal and protein clusters [4, 5], virus capsids [6], and polyoxometalate shells [7]. The equilibrium sizes of these objects are dictated by the competition between cohesive energies such as hydrophobic interactions, depletion forces, or hydrogen bonds, and, on the other hand, (repulsive) electrostatic interactions. In this work we focus on hollow, spherical objects. The electrostatic interactions can be regulated by experimental parameters such as ionic strength, dielectric constant of the medium, and pH. These parameters therefore influence the size of the hollow object. Here we present a theory that correctly accounts for the electrostatic contribution and quantitatively predicts the equilibrium size of hollow objects. The approach is similar to that taken in Verhoeff et al [8], but here we show the generality of the model, at least as long as the proper boundary conditions are taken into account.

Colloidal systems that are stabilized by electrostatics such as Pickering emulsions [9], colloidal and protein clusters [4, 5] predominantly lie in between constant charge and constant potential limits, demanding a detailed calculation of electrostatic energy by solving the Poisson–Boltzmann equation in a cell model [10] or by using site-binding type models [4]. If a given model system falls either under constant potential or constant charge limits, one may wonder if there is a simple model that treats these limiting conditions, avoiding the explicit models mentioned above. This is the question we address in this paper.

To illustrate the importance of electrostatics in the stability of hollow objects, we consider two examples: minivesicles formed by a mixture of nonionic and ionic surfactants, and shell-like objects formed by nanosized polyoxometalates. The experiments by Oberdisse and Porte showed that the charge–neutral bilayers formed by nonionic surfactants spontaneously bend to form thermodynamically stable unilamellar vesicles, when a small amount of ionic surfactant is added [11, 12]. The driving force for bending comes from the negative contribution of Gaussian curvature rigidity modulus due to electrostatic interactions. Interestingly, it was shown that the size of the minivesicles can be modulated by varying the amount of ionic surfactants in a narrow range of values, and that beyond this range the minivesicle phase becomes unstable to a micellar phase or onion phase (multilamellar vesicles) [12]. A schematic of the phase boundaries of a minivesicle phase is shown in figure 1. Oberdisse and Porte numerically solved the full Poisson–Boltzmann (PB) equation to calculate the charge distribution in a minivesicle, and showed good agreement with the experimental data on minivesicle size [11]. The data are...
2. Theory

Consider a spherical shell of radius $R$ that consists of monomeric building blocks. The free energy ($F_p$) of formation of the shell in the limit of constant charge density (CCL) can be written as

$$
\frac{F_p}{k_B T} = 4\pi \gamma R^2 + 4\pi (2K + \bar{K}) + \frac{\lambda Z^2}{2R(1 + \kappa R)}.
$$

(1)

In this equation, $k_B$ denotes Boltzmann’s constant, $T$ the temperature, $\gamma$ the surface tension, $K$ and $\bar{K}$ the mean and Gaussian rigidity modulus, $\lambda = e^2 / 4\pi \varepsilon_0 k_B T$ the Bjerrum length, $Z$ the number of charges and $\kappa = (8\pi \lambda \rho)^{1/2}$ the inverse of the Debye screening length, with $e$ the unit charge, $\varepsilon_0$ the permittivity of vacuum, $\varepsilon$ the relative dielectric constant of the medium, and $\rho$ the number density of the 1:1 electrolyte. The first term is the surface free energy of the shell, which is extensive in the aggregation number and will not show up in the equilibrium size of the object. The second term denotes the energy required for bending, which is derived from the Helfrich expression for a spherical shape with zero spontaneous curvature [16]. The third term gives the self-energy of a uniformly charged hollow object in the Debye–Huckel limit [17].

Recasting equation (1) in terms of charge density, defined as $\sigma = Z / 4\pi R^2$, and minimizing the free energy per unit area gives the equilibrium radius of the shell as

$$
R^* = \left( \frac{2K + \bar{K}}{\pi \lambda \sigma^2} \right)^{1/3}
$$

(2)

where we take $\kappa R \ll 1$. It is important to note that $R^*$ scales with $\sigma$ and $\varepsilon$ as $\sigma^{-2/3}$ and $\varepsilon^{1/3}$, respectively, in the CCL. A similar relation was also obtained by Oberdisse [13].

If the monomers are highly charged, like the POMs, the surface potential becomes constant and charge renormalization sets in [10]. In this case, the electrostatic interactions should be treated in the constant potential limit (CPL). In the CPL, the free energy ($F_p$) of formation of the shell is given by the Legendre transformation [8]

$$
\frac{F_p}{k_B T} = \frac{F_p}{k_B T} - \psi Z.
$$

(3)

In this equation, $\psi$ is the surface potential. The relation between $Z$ and $\psi$ is obtained by minimizing $F_p$ with respect to $Z$, and it is given by

$$
Z = \psi \frac{R(1 + \kappa R)}{\lambda}.
$$

(4)

Substituting equation (4) in equation (3) and minimizing free energy per unit area, we get

$$
R^* = \frac{16\pi \lambda \left(2K + \bar{K}\right)}{\psi^2}. \quad \text{(5)}
$$

Note that $R^*$ is proportional to $\psi^{-2}$ and $\varepsilon^{-1}$. These predictions are qualitatively different from the CCL. The
Figure 2. A schematic representation of the self-assembly of [Mo72Fe30]-type spherical POMs (left) into a large, hollow, single-layered shell-like structure (right).

(This figure is in colour only in the electronic version)

model is applicable, in principle, to any equilibrium shell-like objects that are stabilized by electrostatic effects. In particular, the conditions for the applicability of the model are: (1) hollow spherical objects, (2) no preferred curvature, (3) very low chargeable group densities for constant charge limit, and (4) the CPL is expected to be the best approximation for relatively high chargeable group densities. Condition (2), in principle, applies to symmetric bilayers like surfactant bilayers. It is somewhat of a surprise that the behavior of POM shells, being curved monolayers, is consistent with this condition, as will be shown in section 3.

The mean field theory presented in this paper applies to an assembly of monomers in a shell-like structure, and not at the level of an individual monomer. Therefore, we have ignored any additional effects that arise from the discrete nature of the charges in these monomers, which should be addressed using an entirely different framework such as Monte Carlo or molecular dynamics simulation methods [18]. The merit of the theory is justified by predicting experimental data of not one but two broadly different systems, as shown in section 3, implying that the assumptions invoked in the model are valid.

3. Comparison of theory and experiment

We compare the predictions from the theory with the experimental results published elsewhere. Oberdisse and Porte reported that the size of the minivesicles formed by nonionic surfactant (Triton X) and neutral cosurfactant (octanol) could be controlled by the addition of a small amount of ionic surfactants (cetylpyridinium chloride [CPC]) [11]. They reported the size of the minivesicles as a function of CPC concentration. These data can be readily compared with equation (2), which is derived for CCL. In the experiments, a parameter $\Gamma$ is defined as $\Gamma = [\text{CPC}]/([\text{CPC}]+[\text{Triton X}]+[\text{octanol}])$. We can express the charge density $\sigma$ in terms of $\Gamma$ to directly compare the experimental data. We can rewrite $\Gamma$ as $\Gamma = Z/(Z + N)$, and define the surface area occupied by a surfactant molecule as $a = 4\pi R^2/N$, where $N$ is the total amount of surfactants (Triton X and octanol). By combining the expressions for $\Gamma$, $a$ and $\sigma$, we get

$$\sigma = \frac{1}{a} \left( \frac{\Gamma}{1 - \Gamma} \right) \approx \frac{\Gamma}{a} \quad \text{(if $\Gamma \ll 1$).} \quad (6)$$

Substituting equation (6) in equation (2), we get

$$R^* = \left( \frac{2K + \bar{K}}{\pi \lambda a^{-2}} \right)^{1/3} \Gamma^{-2/3}. \quad (7)$$

Figure 3 shows the comparison between experimental data [11] and theoretical predictions. We observe excellent match between the two, demonstrating the accuracy of the model. The fit to the data yields $R^* = 0.708 \times \Gamma^{-2/3}$ from which we obtain $2K + \bar{K} = 4.4k_BT$ using $\lambda = 0.7$ nm and $a \approx 0.5$ nm$^2$. Oberdisse and Porte [11] reported $2K + \bar{K} = 5.4k_BT$ from their numerical calculations, a value quite similar
equation (5) with the experimental fit, we find was observed in between 0 and 0.4 mM added monovalent salt. A significant influence of ionic strength on the equilibrium radius is consistent with the findings in table III in [11], where no dependence on the Debye length in our approximation. This $\kappa R \ll 1$ compares well to experiments. Also note that the equilibrium radius $R^*$ does not depend on the Debye length in our approximation. This is in consistent with the findings in table III in [11], where no significant influence of ionic strength on the equilibrium radius was observed in between 0 and 0.4 mM added monovalent salt. Equation (7) is strictly valid when $\kappa R \ll 1$, i.e. $\kappa^{-1} \gg R$. The Debye length corresponding to the maximum concentration of salt (0.4 mM) used in the experiment is $\sim 15$ nm, and the average radius of the minivesicle observed in this set of experiments was $5.5-6.8$ nm. Nevertheless, the condition $\kappa R \ll 1$ compares well to experiments.

As an example for the CPL, we refer to recent work by two of us [8] and we summarize it as follows. Consider the shell-like structures formed by spherical POM molecules. These POMs are highly charged nanometer-sized particles, thus will serve as the right candidates for testing the theory. From equation (5), we see that the shell size scales with the inverse of the dielectric constant (as $\lambda \propto 1/\varepsilon$) and inverse square of the surface potential. In the experiments, $\varepsilon$ is varied by using mixtures of solvents (e.g. acetone–water mixture), and it was observed that the shell size is very sensitive to $\varepsilon$. Figure 4 shows the comparison between experimental data and theory. The model and experimental data remarkably match each other. The fit to the data gives the relation $R^* = \frac{228}{\varepsilon}$.

Assuming hexagonal packing and Euler’s theorem, the bending energy $4\pi(2K + \bar{K})$ is in fact the defect energy of a closed surface, given by $-12u$, where $u$ is the cohesive binding energy between the POM particles [8]. Using the measured surface potential of $\psi = -2.24$ [8], and a comparison of equation (5) with the experimental fit, we find $u = -6.8k_BT$.

4. Conclusions

We have shown that the qualitatively different behavior of the equilibrium size of minivesicles and that of aggregates of Keplerate-type POMs can be explained within the same theoretical framework. The key is to take into account the appropriate boundary conditions: constant charge and constant potential. The importance of this distinction has (critically) been discussed already by Verwey and Overbeek [19] and again recently in [20].

In the constant charge limit, we showed that the equilibrium size of the minivesicles as a function of charge density is quantitatively explained. Analysis yields a value for effective bending modulus $2K + \bar{K} = 4.4k_BT$. The theory also explains the experimental finding that the size of the minivesicles is independent of the Debye screening length. In addition, we showed that in the other limit, that is at constant potential, the theory compares well with the equilibrium size of the polyoxometalate based shell-like structure as a function of dielectric constant of the medium.

References