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Transition from small to big charged unilamellar vesicles

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Abstract. The transition from small to big unilamellar vesicles predicted by a Poisson-Boltzmann Cell Model for the thermodynamics of a dilute phase of unilamellar charged vesicles is characterized. The radius as a function of experimental parameters is calculated and the coexistence region of small and big vesicles is identified. We further investigate the physical meaning in terms of simplified models, which allow for an identification of the role of parameters like the surface charge density or the Debye-length. Connections to experiments are discussed.

PACS. 05.70.Ce Thermodynamic functions and equations of state – 82.65.Dp Thermodynamics of surfaces and interfaces – 82.70.Dd Colloids

1 Introduction

In recent years several sophisticated models for the thermodynamics of vesicle formation have been proposed in the literature. The authors of these articles are usually interested in a general description of the thermodynamics of equilibrium vesicle phases, leading to a detailed modelling of the different contributions to the free energy, like electrostatics, entropies of chain conformation or undulation modes of the membrane [1–6]. Studies of curvature expansions for the electrostatics of large vesicles in relatively concentrated regimes have been undertaken using a cell model [7], as well as calculations under physiological conditions [8].

Motivated by evidences for the spontaneous formation of (uni- and multilamellar) vesicles in different experimental systems [9,10], we have studied the effect of ionic surfactants on the bending properties of an initially nonionic membrane. One of the results was the emergence of a phase of unilamellar vesicles of surprisingly small radius at high dilution [11]. It was possible to reproduce the observed radius dependence on the experimental parameters in terms of a Poisson-Boltzmann cell model [12]. We also reported on an unexpected prediction of the model: for a specific choice of the experimental parameters it predicts a coexistence of small and big vesicles. The issue of the present article is to further investigate this result in terms of simpler but more intuitive models.

2 Wigner-Seitz cell

The confinement of ions and counter-ions in a Wigner-Seitz cell is crucial. We define the geometric characteristics of a vesicle in a spherically symmetric cell. The discussion is restricted to unilamellar vesicles of mean radius R and membrane thickness δ:

$$\begin{aligned} R &= \frac{R_i + R_o}{2} \\ \delta &= R_o - R_i \end{aligned} \tag{1}$$

where R_i (resp. R_o) is the inner (resp. outer) radius of the vesicle. In numerical evaluations, we use the experimental bilayer thickness of 30 Å. The radius of the cell is chosen such that the volume fraction in the cell equals the global volume fraction Φ:

$$R_{cell} = \sqrt[3]{\frac{R_o^3 - R_i^3}{\Phi}} \,. \tag{2}$$

This leads to a maximum vesicle size R_o^{max}:

$$R_o^{max} = \frac{\delta}{1 - \sqrt[3]{1-\Phi}} \,. \tag{3}$$

For a vesicle with $R_o > R_o^{max}$ the volume fraction is necessarily below Φ.

Finally, the total electric charge of the cell is zero, which implies a vanishing electric field at the surface of the Wigner-Seitz cell. The number of charged surfactant molecules on the vesicle can be calculated from the mean size of the vesicles, if one knows the surface charge density. Throughout this article we will assume a constant surface charge density σ, independent of the radius of the vesicle.

3 Small-to-big vesicle transition

We start with the theoretical prediction of coexisting small and big charged vesicles. A detailed description of the

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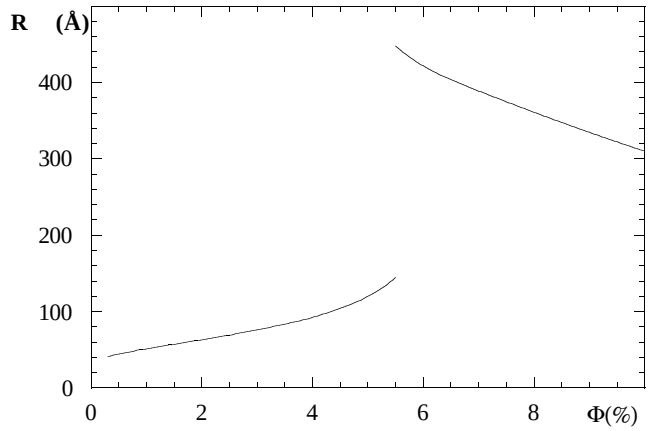

Fig. 1. Prediction of Poisson-Boltzmann cell model: mean vesicle radius as a function of volume fraction Φ ($\tilde{\kappa} = 2.9\,k_BT$, $\Gamma = 5.0\%$).

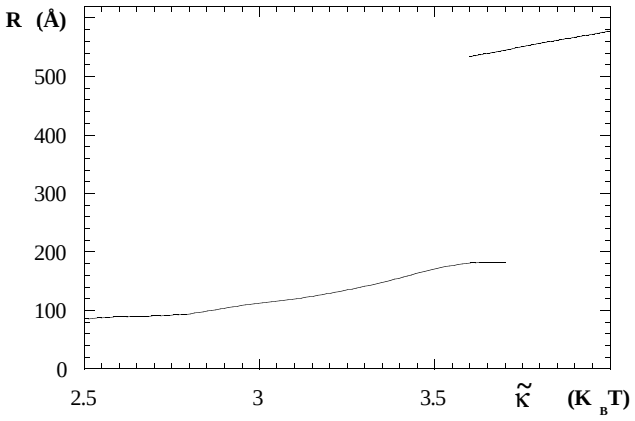

Fig. 2. Prediction of Poisson-Boltzmann cell model: mean vesicle radius as a function of the bending constant $\tilde{\kappa}$ ($\Phi = 4.5\%$, $\Gamma = 5.0\%$).

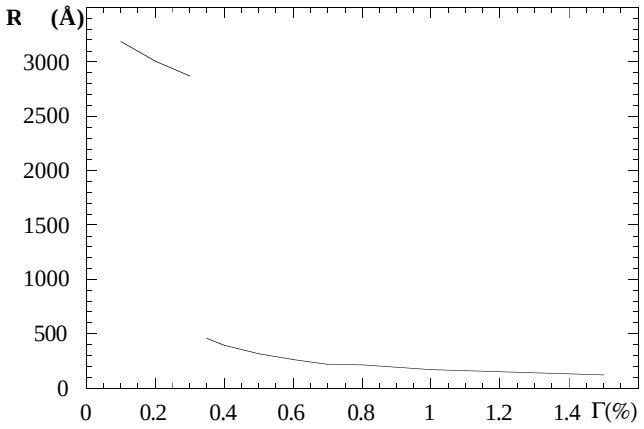

Fig. 3. Prediction of Poisson-Boltzmann cell model: mean vesicle radius as a function of Γ the ratio of the mass of charged surfactant molecules to the total mass of surfactant molecules, which is closely related to the surface charge density σ ($\Phi = 1.0\%$, $\tilde{\kappa} = 2.7\,k_BT$)

model can be found elsewhere [12]. It is based on the calculation of the distribution of ions in a Wigner-Seitz cell containing a vesicle of mean radius R using the framework of the (non-linearized) Poisson-Boltzmann equation. A free energy F_{el} of the electrostatic double layer is then associated with this vesicle. The second contribution is the curvature energy of the symmetric neutral bilayer, estimated by the Helfrich Hamiltonian and thus introducing the only free parameter of the model, $\tilde{\kappa}$ [12,13]. One might argue that there is a second parameter, the spontaneous curvature c_0 with a non-zero value due to the redistribution of charged amphiphilic molecules between the inner and the outer monolayer. However, the experimental parameter Γ – the mass ratio [charged surfactant]/[total surfactant] – is of the order of a few percent, *i.e.* the charge density σ is very small. The steric contribution of this small number of charged molecules is thus not expected to change the spontaneous curvature (the electrostatics being taken care of by the Poisson-Boltzmann Cell Model). The competition between the electrostatic contribution to the free energy, the curvature energy of the neutral bilayer and the entropy of mixing of the vesicles (using an ideal gas approximation) yields a minimum in the total free energy, at a given radius R_{opt}.

Finally, the size distribution function $N(R)dR$ – the number density of vesicles of mean radius between R and $R + dR$ – reads:

$$N(R) = N_0 \exp\left[\frac{-\left(\frac{F_{el}(R)+8\pi\tilde{\kappa}}{V(R)} - \mu\right) V(R)}{k_BT}\right] \qquad (4)$$

where μ is the Lagrange multiplier associated with conservation of volume of bilayer (*i.e.* the chemical potential). $F_{el}(R)$ is the free energy of the electrostatic double layer of a vesicle of radius R, $V(R)$ the volume of its bilayer, and $\tilde{\kappa}$ is the intrinsic bending constant of the symmetric neutral bilayer. In the harmonic approximation, the bending energy is $8\pi\tilde{\kappa}$ for a spherical vesicle and is size-independent.

We have written equation (4) in this form in order to illustrate the fact that the maximum of $N(R)$ is close to the minimum of $\frac{F_{el}(R)+8\pi\tilde{\kappa}}{V(R)}$, deviations towards smaller radii being due to the entropy of mixing of vesicles. For qualitative discussions it is thus sufficient to study the minima of $\frac{F_{el}(R)+8\pi\tilde{\kappa}}{V(R)}$.

Following our calculations using the Poisson-Boltzmann equation, a certain number of situations showing coexisting small and big vesicle phases are found. In Figures 1–3 we present the theoretical prediction – deduced from the maxima of $N(R)$ – for the radius as a function of concentration (at fixed charge density σ and bending constant $\tilde{\kappa}$), of the bending constant (at fixed charge density σ and concentration), and finally of charge density σ (at fixed concentration and $\tilde{\kappa}$). Remarkably, the transition from small to big vesicles is present in the three cases. We will now turn to the physical origin of this transition.

As assumed in our model the very small size of vesicles (first population) is a compromise between bending energy and the free energy of the electrostatic double layer. The existence of a second population implies thus – given the monotoneously decreasing bending energy contribution $\frac{8\pi\tilde{\kappa}}{V(R)}$ – that there must be a second minimum due to a plateau or minimum in the electrostatic contribution itself. As the situation is somewhat obscure due to the "black box" of the numerical integration of the Poisson-Boltzmann equation (and of the free energy), we try to gain physical insight by developing simpler models for the electrostatic free energy and for an interpretation of the two-population problem.

3.1 Coulomb model

In a zero-order approach, we estimate the electrostatic contribution to the free energy F_{el} by the energy U_{el} of a charge Q on a shell of radius R. Any counter-ion contribution is ignored, and the total charge on the two monolayers can be estimated by:

$$Q = 2 \times 4\pi R^2 \sigma. \tag{5}$$

We deduce for the electric energy of the vesicle of radius R:

$$U_{el} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{Q^2}{R} \tag{6}$$

where ε is the dielectric constant of the solvent and ε_0 the vacuum permittivity. The contribution per unit volume is then:

$$\frac{U_{el}}{V_{cell}} = 4\frac{\sigma^2 \Phi R}{\varepsilon\varepsilon_0\delta} \tag{7}$$

where V_{cell} is the volume of the Wigner-Seitz cell. In this last equation (7) we have used the conservation of the bilayer volume fraction (Eq. (2)) simplified for $R \gg \delta$:

$$\Phi = \frac{3\delta R^2}{R_{cell}^3}\,. \tag{8}$$

As can be seen from equation (7), the electric energy per unit volume U_{el}/V_{cell} decreases with decreasing vesicle radius. It thus favors the formation of small vesicles. This tendency is in competition with the bending energy of the bilayer per unit volume U_{bend}/V_{cell}. The conservation of volume implies that the bending energy of smaller vesicles is higher because more vesicles are formed. This leads to the following dependence on the mean vesicle radius R:

$$\frac{U_{bend}}{V_{cell}} = 2\frac{\Phi\tilde{\kappa}}{R^2\delta}\,. \tag{9}$$

Minimizing the sum of equations (7, 9) yields the optimum mean radius:

$$R_{opt} \propto \tilde{\kappa}^{1/3}\left(\frac{\varepsilon\varepsilon_0}{\sigma^2}\right)^{1/3}. \tag{10}$$

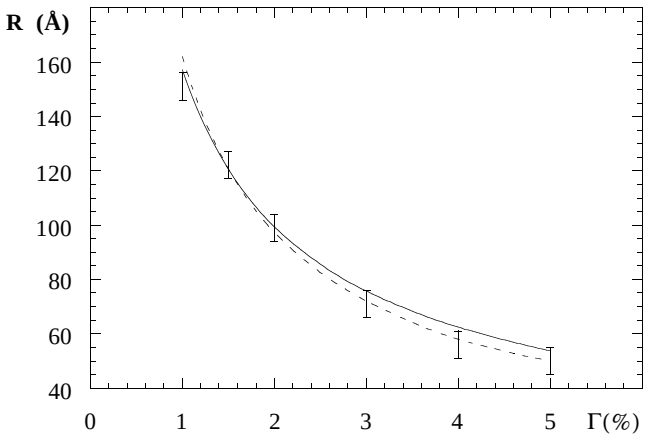

Fig. 4. Comparison to experiment: mean vesicle radius R as a function of relative amount of charge Γ (*cf.* Fig. 3). Full line: Coulomb model. Dotted line: Homogeneous counter-ion distribution.

This scaling law for the optimum mean radius compares fairly well with the experiment reported in [12], see the full line in Figure 4. However, there is no prediction for the evolution of the radius with concentration or salinity. We have no data to discuss the predicted dependence of the radius on the bending constant $\tilde{\kappa}$.

This rather basic model completely neglects the counter-ions. This has two important consequences. First of all their entropic contribution is ignored. The spatial reorganization of the counter-ions as a function of experimental parameters is not described, and subtle effects arising from this rearrangement – *e.g.* the effect of screening by added salt – are excluded. The second consequence is that the Wigner-Seitz cell itself is not electrically neutral: one of the fundamental concepts of electrostatics is ignored. Therefore we propose a second model which overcomes this difficulty.

3.2 Homogeneous counter-ion distribution

In this second simple model we impose electroneutrality for the Wigner-Seitz cells. This is done by homogenously distributing the counter-ions in the cell (except the membrane), see Figure 5 for a schematic representation. The number of counter-ions N is equal to the number of charged surfactant molecules in the membrane $N = \frac{Q}{e} = 4\pi(R_i^2 + R_o^2)\frac{\sigma}{e}$, and their number density n is:

$$n = \frac{N}{\frac{4\pi}{3}\left(R_{cell}^3 - (R_o^3 - R_i^3)\right)}\,. \tag{11}$$

For simplicity we suppose a vanishing electric field within the membrane. Then the number of charged molecules in the inner (resp. outer) monolayer equals the number of counter-ions inside (resp. outside) the vesicle (*i.e.* we assume a conducting bilayer).

Using Gauss' theorem the electric field (only the radial component is non-zero for symmetry reasons) can be

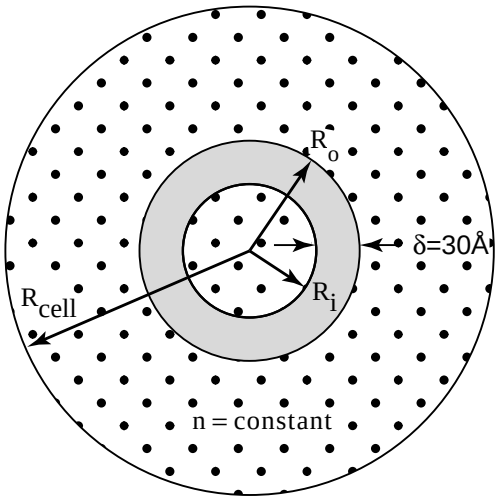

Fig. 5. Schematic representation of the vesicle in its Wigner-Seitz cell with homogeneous counter-ion distribution.

found anywhere in the cell:

$$E(r) = \frac{1}{4\pi\varepsilon\varepsilon_0 r^2} Q_{tot}(r) \tag{12}$$

where $Q_{tot}(r)$ is the total charge within a sphere of radius r (centered at the origin), ε is the dielectric constant of the solvent and ε_0 the vacuum permittivity. For negative counter-ions the charge obtained inside ($r < R_i$) the vesicle is:

$$Q_{tot}(r) = \frac{4\pi}{3}(-e)n\, r^3. \tag{13}$$

And outside ($R_o < r < R_{cell}$):

$$Q_{tot}(r) = \frac{4\pi}{3}(-e)n\left(r^3 - \left(R_o^3 - R_i^3\right)\right) + Ne \tag{14}$$

where the last term (Ne) is due to the ions on the bilayer. As usual, the electric energy is given by:

$$U_{el} = \frac{\varepsilon\varepsilon_0}{2}\int |E(r)|^2 d^3r. \tag{15}$$

The integral (15) can be evaluated analytically. For a given vesicle, the energy reads:

$$U_{el} = \frac{e^2N^2}{4\pi\varepsilon\varepsilon_0}\left(\frac{1}{1-\Phi}\right)^2\left[\frac{1}{10}\frac{R_{cell}^5 - (R_o^5 - R_i^5)}{R_{cell}^6} - \frac{1}{2}\left(\frac{1}{R_{cell}} - \frac{1}{R_o}\right) - \frac{1}{2}\frac{R_{cell}^2 - R_o^2}{R_{cell}^3}\right]. \tag{16}$$

As we are interested in what happens at comparatively large radii ($R \gg \delta$), *i.e.* the in the big vesicle population, we express this last equation (16) in terms of the mean radius R only, and keep only the lowest-order terms in δ/R. The result (per unit volume) is of the form:

$$\frac{U_{el}}{V_{cell}} = \frac{2\sigma^2}{\varepsilon\varepsilon_0}\frac{\Phi}{(1-\Phi)^2}\left[c_1(\Phi)\left(\frac{\delta}{R}\right)^{-2} - c_2(\Phi)\left(\frac{\delta}{R}\right)^{-4/3} + c_3(\Phi)\left(\frac{\delta}{R}\right)^{-1} + O\left(\frac{\delta}{R}\right)\right] \tag{17}$$

where

$$\begin{aligned} c_1(\Phi) &= \frac{\Phi}{3}\left(1 - \frac{\Phi}{3}\right) \\ c_2(\Phi) &= \frac{9}{5}\sqrt[3]{\frac{\Phi}{3}} \\ c_3(\Phi) &= 1 + \frac{\Phi}{3} \end{aligned} \tag{18}$$

are positive prefactors.

Note that the linear term (with prefactor c_3 in Eq. (17)) is simply the transcription of the electrostatic energy in our first model, equation (7). Not surprisingly, the experimentally measured evolution of the mean radius R as a function of relative amount of charge Γ is reproduced with about the same accuracy as in the first simple model, *cf.* the dotted line in Figure 4. The value of the only free parameter of the model, the bending constant $\tilde{\kappa}$ of the neutral bilayer, is $5.6 \pm 0.2\, k_BT$[1].

One can see from the prefactors c_i (c_1 and c_2 tend to zero as $\Phi \to 0$), that the other two terms are consequences of the condition of electroneutrality imposed on the finite-size Wigner-Seitz cell. They translate in terms of energy – in a mean field approximation – the action of surrounding vesicles: the confinement of ions in a cell.

A closer look at equation (16) allows for an interpretation of the transition of small to big vesicles. In this picture, very small vesicles result from the competition between the linear term in the free energy of the electrostatic double layer and the bending energy, given by equation (9). However, due to the finite size of the cell, further contributions appear: the R^2 and the – $R^{4/3}$ term will produce a secondary minimum, which is this time of purely electrostatic origin (*i.e.* totally independent of the bending elasticity). This is illustrated in Figures 6 and 7, where we change the volume fraction and plot U_{el} per unit volume as a function of mean vesicle radius R (using Eq. (16)). At small R the electrostatic energy favors small vesicles – this is mainly due to the linear term – but the secondary minimum at $R = 600$ Å ($\Phi = 5\%$, Fig. 6) is clearly visible. Upon increasing the concentration to $\Phi = 8.3\%$ (Fig. 7), the Wigner-Seitz cell shrinks, the secondary minimum is shifted to smaller R, and becomes more pronounced. At $\Phi \approx 8\%$ it becomes comparable to the primary minimum, and a two population coexistence is predicted[2].

[1] The deviation from the value obtained with the Poisson-Boltzmann cell ($\approx 3\, k_BT$) model is due to the neglected entropy of counter-ions.

[2] Strictly speaking the entropy of mixing of the vesicles will always favor the smaller objects, *i.e.* the secondary minimum has to be deeper than the first in order to host a population comparable in number.

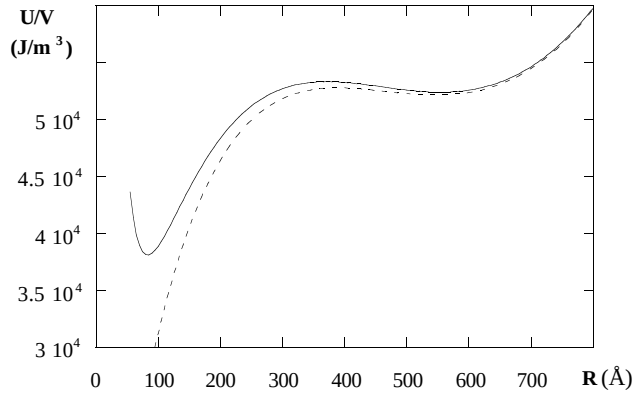

Fig. 6. Dotted line: Electrostatic energy per unit volume as a function of mean vesicle radius R (calculated for the homogeneous counter-ion distribution) for $\Phi = 5.0\%$, $\Gamma = 3.55\%$. Scale: 5×10^4 J/m^3 corresponds to approximately $2\,k_BT$ per ion. Full line: Electrostatic energy plus energy of curvature ($\tilde{\kappa} = 5.6\,k_BT$).

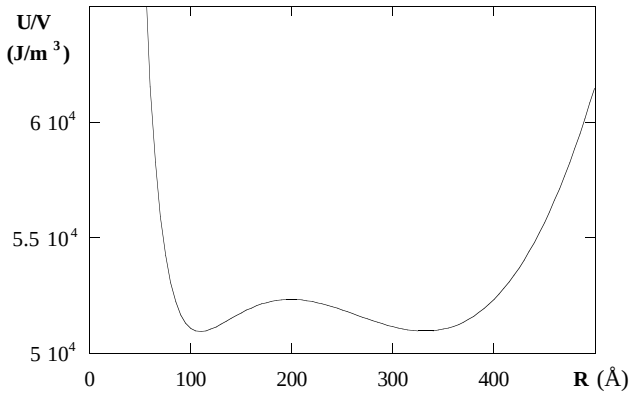

Fig. 7. Electrostatic energy per unit volume as a function of mean vesicle radius R (calculated for the homogeneous counter-ion distribution) for $\Phi = 8.3\%$, $\Gamma = 3.55\%$, $\tilde{\kappa} = 5.6\,k_BT$.

Furthermore, the influence of the other experimental parameters can now be understood. In this model, the electrostatic energy is simply proportional to σ^2, thus varying σ or $\tilde{\kappa}$ will change the relative depth of the two minima: this explains why and how a specific choice of the experimental parameters leads to the coexistence of small and big vesicles.

3.3 Debye-Hückel model

The simple model of a homogeneous charge distribution is unrealistic in the sense that it ignores the fundamental electrostatic length scale: the thickness of the electrostatic double layer given by the Debye length λ_D. Indeed, the electrostatic potential $\Psi(r)$ decays exponentially (or of Yukawa form in spherical symmetry) inside and outside the vesicle. In the range $R \gg \lambda_D$ and $(R_{cell} - R) \gg \lambda_D$ the electrostatic double layer is not perturbed by the centre or the surface of the Wigner-Seitz cell. The free energy of the electrostatic double layer per unit volume of bilayer is then expected to be independent of vesicle radius R.

In the limit of low surface potentials ($\Psi \ll \frac{k_BT}{e} \approx$ 25 mV at room temperature) the Poisson-Boltzmann equation can be linearized. The resulting Debye-Hückel equation

$$\Delta\Psi = k^2\Psi \tag{19}$$

where Δ is the Laplace operator and $k = \frac{1}{\lambda_D}$, possesses an analytical solution in spherical symmetry:

$$\Psi(r) = A\frac{e^{-kr}}{r} + B\frac{e^{kr}}{r} \tag{20}$$

where A and B are constants of integration.

The same analysis as presented in [12] can then be carried through with this analytical solution. This is straightforward but tedious, as three regions of space (inside, bilayer, and outside the vesicle) have to be connected. We therefore propose a version which contains the physics of the decaying electrostatic double layers, but ignores the quantitatively unimportant contribution of the electric field in bilayer. The bilayer of thickness δ is replaced by an infinitely thin spherical shell with surface charge density 2σ (without changing R_{cell}). The form of the potential Ψ_o outside ($R < r < R_{cell}$) the shell is then given by equation (20). In order to assure a zero electrical field at the center its form inside the shell ($r < R$) is given by:

$$\Psi_i(r) = C\frac{\sinh(k\,r)}{r}\,. \tag{21}$$

A, B, and C are determined by the following boundary conditions:

$$\Psi_i(R) = \Psi_o(R), \tag{22a}$$

$$\left.\frac{d\Psi_i}{dr}\right|_{r\to R^-} - \left.\frac{d\Psi_o}{dr}\right|_{r\to R^+} = \frac{2\sigma}{\varepsilon\varepsilon_0}, \tag{22b}$$

$$\left.\frac{d\Psi_o}{dr}\right|_{r\to R_{cell}} = 0. \tag{22c}$$

The solution of the system is straightforward. According to [14] the free energy of the electrostatic double layer per unit of bilayer area is given by:

$$\int_0^\sigma \Psi(R,\sigma')d\sigma'. \tag{23}$$

We deduce the free energy F_{DH} of the electrostatic double layer per unit volume

$$\frac{F_{DH}}{V_{cell}} = \frac{2\sigma^2\Phi}{\varepsilon\varepsilon_0\delta k} f(kR,\, kR_{cell}), \tag{24a}$$

$$f(kR,\, kR_{cell}) = \frac{e^{2kR_{cell}}\ \frac{kR_{cell}-1}{kR_{cell}+1} + e^{2kR}}{e^{2kR_{cell}}\ \frac{kR_{cell}-1}{kR_{cell}+1}[\coth(kR)+1] + e^{2kR}[\coth(kR)-1]}\,. \tag{24b}$$

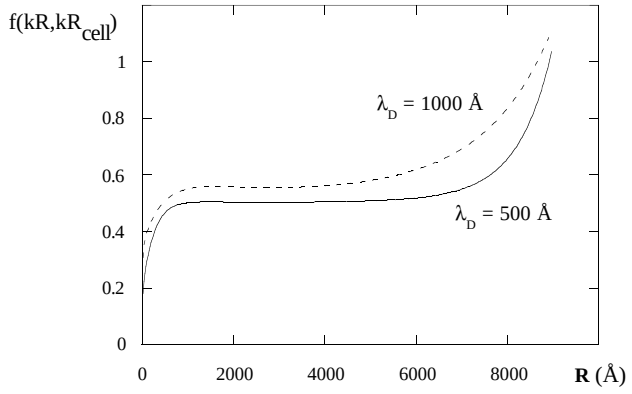

Fig. 8. $f(kR,\, kR_{cell})$ (electrostatic energy per unit volume in reduced units, *cf.* Eq. (24)) as a function of mean vesicle radius R (calculated for the Debye-Hückel model) for $\Phi = 1.0\%$. The maximum radius of the Wigner-Seitz cell (Eq. (3)) is 8970 Å.

A typical result for $\Phi = 1\%$ and $\lambda_D = 500$ Å is plotted in Figure 8. Note the plateau, and the perturbations induced by the center and the boundary of the Wigner-Seitz cell. For small radii we find the Coulomb-type dependence, *cf.* equation (7) (and also Eq. (17)), which is responsible for the formation of microvesicles.

As one increases the Debye-length, the electrostatic double layer is further perturbed by to the cell boundary and the center of the cell, and the plateau shrinks (see also Fig. 8 for $\lambda_D = 1000$ Å).

The presence of the plateau expressed the fact that there is – in this range – no preference for electrostatical reasons for bigger or smaller vesicles. The competition between entropy of mixing and bending energy as discussed by Safran *et al.* [15] will lead to very big vesicles (and very polydisperse in size) which exist only at very low concentration. If the first population (located in the Coulomb part of the free energy at very small radii) can compete energetically, coexistence of two populations is expected.

4 Discussion

The size of the very small vesicles ($R < 100$ Å) observed by SANS has been previously accounted for in terms of the Poisson-Boltzmann Cell Model. We have now shown that a pure Coulomb form for the contribution of the electrostatic double layer to the free energy is appropriate for a description of these small vesicles, at least as far as the evolution of the radius with charge density is concerned. However, the transition from small to big unilamellar vesicles – as predicted by the Poisson-Boltzmann Cell Model – can not be attributed to the Coulomb term. We have studied in detail its occurrence as one varies the experimental parameters. It seems to be related to weak charges, high bending rigidity or high concentration. Unfortunately, the numerical integration of the Poisson-Boltzmann equation makes a deeper understanding difficult.

Therefore a model with a homogeneous distribution of counter-ions within the Wigner-Seitz cell has been proposed. Here, the leading term at small radii can be easily identified in the analytical expressions, and the transition is still observed: this illustrates that it is not a feature of the nonlinearity of the Poisson-Boltzmann framework itself. Moreover, it could be shown that it is a consequence of the electroneutrality condition imposed on the Wigner-Seitz cell, *i.e.* it is a finite-concentration effect. This simplified model with a homogeneous charge distribution can be thought of as a model with a very big Debye length. The center and the cell boundary are always "felt" by the electrostatic double layer. In the more realistic description using the Debye-Hückel equation, a plateau is found, which will allow for a second population of big vesicles if the solution is sufficiently dilute and if the intrinsic bending modulus is not too high.

The models we have presented in this article are appropriate for unilamellar vesicles only. In this geometry, the transition from small to large unilamellar vesicles is interesting, as coexistence has been found *e.g.* in cat-anionic systems [16] and in biological model systems [17]. In other experiments, however, onion like structures (multilamellar vesicles) are often found as one increases the concentration [9,11], although it is not established if it is really a phase at thermal equilibrium. In a recent article, Bergmeier *et al.* [18] report on preparing without shear a fluid charged lamellar phase which on gently shaking becomes a viscoelastic onion phase. The input of mechanical energy breaks up the (previously quasi-infinite) planar bilayers, and – from an electrostatic point of view – one can speculate on the formation of small vesicles (first population). These vesicles could then serve as core for the formation of onions, as every additional layer has the same energetical cost per unit bilayer volume due to the free energy plateau (Eq. (24)), at least as long as the interlamellar distance is greater than the Debye-length.

As a last point, we would like to mention that Gradzielski *et al.* have recently found a cubic phase of vesicles [19] in a mixture of ionic surfactant and nonionic cosurfactant at high cosurfactant-to-surfactant ratio in an intermediate concentration region: $\Phi = 0.05{-}0.15$. From Small Angle Neutron Scattering and freeze fracture experiments the structural parameters of the phase are determined. It turns out that the vesicles are in close contact, which is one of the characteristics of the big vesicle population predicted here.

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References

1. M. Bergström, Langmuir **12**, 2454 (1996); M. Bergström, J.C. Eriksson, Langmuir **12**, 624 (1996).
2. D.C. Morse, S.T. Milner, Europhys. Lett. **26**, 565 (1994); D.C. Morse, S.T. Milner, Phys. Rev. E **52**, 5918 (1995).

3. P.K. Yuet, D. Blankschtein, Langmuir **11**, 1925 (1995); P.K. Yuet, D. Blankschtein, Langmuir **12**, 3802 (1996); P.K. Yuet, D. Blankschtein, Langmuir **12**, 3819 (1996).
4. H.N.W. Lekkerkerker, Physica A **159**, 319 (1989).
5. D.J. Mitchell, B.W. Ninham, Langmuir **5**, 1121 (1989).
6. M. Winterhalter, W. Helfrich, J. Phys. Chem. **92**, 6865 (1988).
7. A. Fogden, J. Daicic, D.J. Mitchell, B.W. Ninham, Physica A **234**, 167 (1996); J. Daicic, A. Fogden, I. Carlsson, H. Wennerstrom, B. Jönsson, Phys. Rev. E **54**, 3984 (1996); A. Fogden, I. Carlsson, J. Daicic, Phys. Rev. E (accepted).
8. T. Chou, M.V. Jaric, E.D. Siggia, Biophys. J. **72**, 2042 (1997).
9. H. Hoffmann, C. Thunig, P. Schmiedel, U. Munkert, Langmuir **10**, 3972 (1994); Würtz, H. Hoffmann, J. Colloid Interface Sci. **175**, 304 (1995); H. Hoffmann, U. Munkert, C. Thunig, M. Valiente, J. Colloid Interface Sci. **163**, 217 (1994).
10. L.L. Brasher, K.L. Herrington, E.W. Kaler, Langmuir **11**, 4267 (1995); E.W. Kaler, A.K. Murthy, B. Rodriguez, J.A.N. Zasadzinski, Science **245**, 1371 (1989); E.W. Kaler, K.L. Herrington, A.K. Murthy, J.A.N. Zasadzinski, J. Phys. Chem. **96**, 6698 (1992).
11. J. Oberdisse, C. Couve, J. Appell, J.F. Berret, C. Ligoure, G. Porte, Langmuir **12**, 1212 (1996).
12. J. Oberdisse, G. Porte, Phys. Rev. E **56**, 1965 (1997).
13. W. Helfrich, Z. Naturforsch **28c**, 693 (1973).
14. E.J.M. Verwey, J.T.G. Overbeek, *Theory of Stability of Lyophobic Colloids* (Elsevier, 1948).
15. S.A. Safran, P.A. Pincus, D. Andelman, F.C. MacIntosh, Phys. Rev. A **43**, 1071 (1991).
16. E. Marques, A. Khan, unpublished results.
17. S. Beugin, C. Grabrielle-Madelmont, M. Paternostre, M. Ollivon, S. Lesieur, Prog. Coll. Polym. Sci. **98**, 206 (1995).
18. M. Bergmeier, H. Hoffmann, C. Thunig, J. Phys. Chem. B **101**, 5767 (1997).
19. M. Gradzielski, M. Bergmeier, M. Müller, H. Hoffmann, J. Phys. Chem. B **101**, 1719 (1997).