PHYSICAL REVIEW E, VOLUME 63, 061804

Counterion evaporation

C. Fleck and H. H. von Grünberg
Fakultät für Physik, Universität Konstanz, 78457 Konstanz, Germany

(Received 27 July 2000; revised manuscript received 26 January 2001; published 22 May 2001)

We study the adsorption behavior of a highly charged rodlike polyelectrolyte approaching an oppositely charged planar wall in an unbounded electrolyte solution. The grand potential, the entropy, and the total number of screening particles are calculated as functions of the rod-wall distance, using input parameters that are typical of a DNA-molecule and charged lipid bilayers. It is found that counterions which are bound to the polyelectrolyte at infinite rod-wall distances will be released, or ''evaporated,'' as the DNA molecule moves closer to the charged wall. This effect can be regarded as the opposite of the ion-condensation process. The transition of ions from the system of screening ions into the reservoir of bulk ions can lead to an increase of the enthalpy. This gain of enthalpy for the whole system manifests itself as an attractive contribution to the effective interaction between the wall and the polyelectrolyte.

DOI: 10.1103/PhysRevE.63.061804 PACS number(s): 61.25.Hq, 68.03.Cd, 87.14.Gg

I. INTRODUCTION

The possible occurrence of a phenomenon known as counterion condensation is perhaps the most prominent feature of polyelectrolyte suspensions [1,2]. These chainlike macromolecules become charged, when solved in a liquid characterized by the Bjerrum length $\lambda_B = e^2/\epsilon kT$ (with e being the elementary charge, ϵ the dielectric constant of the solvent, and kT the thermal energy) [3]. This is due to the dissociation of certain molecules at their surface. The counterions leaving the surface can either stay in the vicinity and thus remain under the influence of the charged polymer (bound counterions), or they can free themselves from the field of the polyelectrolyte (free counterions). If d, the mean distance between two charges on the polyelectrolyte, is large compared to λ_B, the number of free counterions in the suspension will increase parallel with the line charge density $\tau = 1/d$. However, once the line charge density τ becomes so high that $\lambda_B \tau \geqslant 1$, i.e., $d \leqslant \lambda_B$, the number of free counterions ceases to grow with τ and remains constant. New counterions produced by further increasing τ, will now become bound counterions. This behavior is reminiscent of the coexistence of saturated vapor pressure and liquid in the usual condensation process, where any increase in the density leaves the number of molecules in the gas phase (the analogs in our case are the free ions) unaffected, and only changes the total amount of liquid (bound ions). This analogy explains the term ''ion condensation'' [1].

This paper is concerned with the question of whether a reverse process of condensation is possible, that is, if something like ''counterion evaporation'' can occur. Suppose some of the bound counterions could be freed, or evaporated, for example, by an additional external electric field of a charged wall. These ions then leave the system and enter the bulk reservoir of electrolyte ions. Here and in the following, the term ''system'' refers to all those ions that are involved in screening the fixed charges of the polyelectrolyte and the wall. The disappearance of ions leaves more space for the counterions remaining in the system, so that their entropy is increased. This can lead to a substantial reduction of the grand potential energy of the system. If the external field has a gradient, this mechanism should therefore result in an additional evaporation-induced force (or ''counterion-release force'') which pulls the whole polyelectrolyte in the direction of the growing field strengths. It is the aim and purpose of this paper to show that this counterion-release force indeed exists, and on what mechanism it is exactly based.

That there is energy to be gained from the release of counterions is a fact long known in the theory of polyelectrolyte-ligand binding [4]. Relatively new, however, is the incorporation of these ideas into a theory of polyelectrolyte adsorption by Sens and Joanny [5]. This work, as well as the current interest in counterion release, was triggered by a number of experiments by Rädler and co-workers on cationic lipid DNA condensation [6], and only recently a paper appeared where, for the first time, counterion release seems to have been observed directly [7].

A good theoretical model system to address these questions consists of an infinitely long, charged, cylindrical rod that is immersed in an unbounded electrolyte, and brought into the external field of an oppositely charged, planar wall [8,9]. This model system was studied in Ref. [5] where a counterion-release induced force was analyzed in the case of a weakly charged polyelectrolyte, $\lambda_B \tau < 1$, where the nonlinear Poisson-Boltzmann (PB) equation [10] can be treated perturbatively. Their perturbative treatment failed, however, for the case of highly charged polyelectrolytes ($\lambda_B \tau > 1$), a charge regime that is of considerable importance as a large number of biomolecules fall into this class of polyelectrolytes (for example, the DNA molecule for which $\lambda_B \tau \approx 4$). More importantly than this, $\lambda_B \tau > 1$ characterizes the charge regime where counterion condensation sets in, and where one thus would expect evaporation-induced forces to become most pronounced.

Here we focus on the case $\lambda_B \tau > 1$, and study the total grand potential energy of the system as a function of the distance h between the rod and the wall, a quantity which can be regarded as the effective wall-rod interaction potential. To this end, we choose a mean-field approach, and solve the nonlinear PB equation for a fixed wall-rod distance h in order to first find the electrostatic mean-field potential in the region G between the surfaces of the cylinder, ∂G_C, and the wall, ∂G_W. Using this potential to evaluate the grand potential and repeating this procedure for varying h, we obtain the effective potential as a function of h, which we then can analyze in regard to the counterion release force.

II. THEORY

We are faced with the following two-dimentional boundary value problem (BVP) for the electrostatic potential $\phi(\vec{r})$:

$$\begin{aligned} &\nabla^2\phi(\vec{r})=\kappa^2\sinh\phi(\vec{r}), && \vec{r}\in G,\\ &\vec{n}_W\cdot\vec{\nabla}\phi=-4\pi\lambda_B\sigma_W, && \vec{r}\in\partial G_W,\\ &\vec{n}_C\cdot\vec{\nabla}\phi=2\lambda_B\tau/r_0, && \vec{r}\in\partial G_C, \end{aligned} \tag{1}$$

where $\kappa^2=8\pi\lambda_B c_s$ is the usual screening constant characterizing the electrolyte, c_s is the bulk density of the electrolyte ions assumed to have a valency of 1, σ_W is the number of wall surface charges per unit area, r_0 is the radius of the cylinder, and $\vec{n}_W$ and $\vec{n}_C$ are two unit vectors directed normal to the surfaces of wall and rod, respectively. ϕ differs from the usual potential ψ by a factor $e\beta$, $\phi=e\beta\psi$, with $\beta=1/kT$. Furthermore, we require ϕ to vanish at infinity. Note that the wall is positively charged, while the charges on the cylinder are negative. Note also that, with the boundary condition at the wall, we have implicitly assumed that the ratio ϵ'/ϵ of the dielectric constants of the wall and solvent vanishes: an assumption that, for an aequous solution, is nearly always justifiable. Thus image charges of equal magnitude and polarity are fully included in the calculation [11]. To simplify the BVP of Eq. (1), we have subtracted the Gouy-Chapman solution, ϕ_G, from ϕ for a single charged wall in a symmetric electrolyte [12], and could then formulate a BVP for the potential difference $\delta\phi=\phi-\phi_G$. It is also convenient to choose a coordinate system that is adapted to the geometry of the problem; in our case this is a bicylindrical coordinate system, in which the region G is mapped on to a rectangular domain, with the two confining surfaces ∂G_W and ∂G_C becoming two opposing sides of the rectangle.

In writing the PB problem as in Eq. (1), we have implicitly adopted a grand-canonical description of our problem (c_s is fixed). This ensemble is best suited for our case, where we want to allow ions to leave or enter the system. Thus there is a ''system'' (ions involved in the screening process) and a bulk reservoir of ions. The number of particles in the system is not fixed but only their chemical potential. This is given by the bulk density c_s, $\beta\mu_s=\log c_s\Lambda^3$, with Λ^3 being the usual thermal wavelength. With the aid of the potential ϕ, we can now calculate the number density $\rho_-+\rho_+$, with $\rho_\pm=c_s\exp(\mp\phi)$, and hence the total number of particles in the system,

$$N=2c_s\int_G d\vec{r}\,\cosh\phi, \tag{2}$$

which is, of course, dependent on ϕ and thus on h. Let us now turn to the energy calculation. The functional

$$\beta\Omega^*[\phi^*]=-\frac{1}{8\pi\lambda_B}\int_G d\vec{r}(\nabla\phi^*)^2-\frac{\tau}{2\pi r_0}\int_{\partial G_C}d\vec{r}\phi^* +\sigma_W\int_{\partial G_W}d\vec{r}\phi^*-2c_s\int_G d\vec{r}\,\cosh\phi^* \tag{3}$$

is the generating functional for the PB equation in Eq. (1), i.e., the PB equation produces the function $\phi^*=\phi$ where $\delta\Omega^*[\phi^*]/\delta\phi^*(\vec{r})$ vanishes (the saddle-point approximation). We obtain the grand potential Ω of the system by inserting ϕ into Eq. (3), which after some rewriting becomes

$$\beta\Omega^*[\phi]=\beta\Omega=\frac{1}{8\pi\lambda_B}\int_G d\vec{r}(\nabla\phi)^2 +\sum_{\alpha=\pm}\int_G d\vec{r}\rho_\alpha(\log\rho_\alpha\Lambda^3-1)-\beta\mu_s N. \tag{4}$$

Taking $\partial_\beta\beta\Omega^*[\phi^*]$ at $\phi^*=\phi$, we find the internal energy U, while $-\partial_T\Omega^*[\phi^*]$ at $\phi^*=\phi$ leads to the entropy

$$S/k=\left(\frac{5}{2}-\beta\mu_s\right)N-\sum_{\alpha=\pm}\int_G d\vec{r}\rho_\alpha\log\rho_\alpha/c_s. \tag{5}$$

Defining the enthalpy $\beta H=S/k+\beta\mu_s N$, the grand potential $\beta\Omega$ of Eq. (4) can now be understood as the difference of two terms U and H, $\Omega=U-H$, where

$$\beta H=\frac{5}{2}N-\sum_{\alpha=\pm}\int_G d\vec{r}\rho_\alpha\log\rho_\alpha/c_s. \tag{6}$$

Now inserting the solution ϕ of Eq. (1) into Eqs. (2), (4), and (6) provides us with the particle number, the effective potential, and the enthalpy, all as functions of varying wall-rod distances h. In the following, we refer these three quantities to the entire system, with an uncharged rod at the same position, and introduce the tilde symbol for this difference: $\tilde{\Omega}=\Omega^\tau-\Omega^0$, $\tilde{H}=H^\tau-H^0$, and $\tilde{N}=N^\tau-N^0$ (superscript τ and 0 for charged and uncharged cylinders, respectively). All three quantities refer, furthermore, to a unit length of the polyelectrolyte rod; hence we give all three of them in units of $d=1/\tau$.

To be able to evaluate our expressions numerically, we choose a set of parameters typical of a DNA molecule ($\lambda_B\tau=4, r_0=1$ nm), keeping in mind a number of recent experiments where the DNA adsorption behavior on lipid bilayers [13,14] was studied [6,15]. To specify the surface charge density of the wall, it is convenient to introduce the dimensionless quantity $\lambda_B\zeta=2\pi r_0\lambda_B\sigma_W$, which gives the surface density in numbers that are directly comparable to $\lambda_B\tau$. Surface densities derived from typical values of the average area per lipid headgroup are then $\lambda_B\zeta=1.88$, 0.94, 0.31 , and 0.063.

III. RESULTS AND DISCUSSION

Let us now come to a discussion of our results. For illustrative reasons, in the inset of Fig. 1 we show the equipoten-

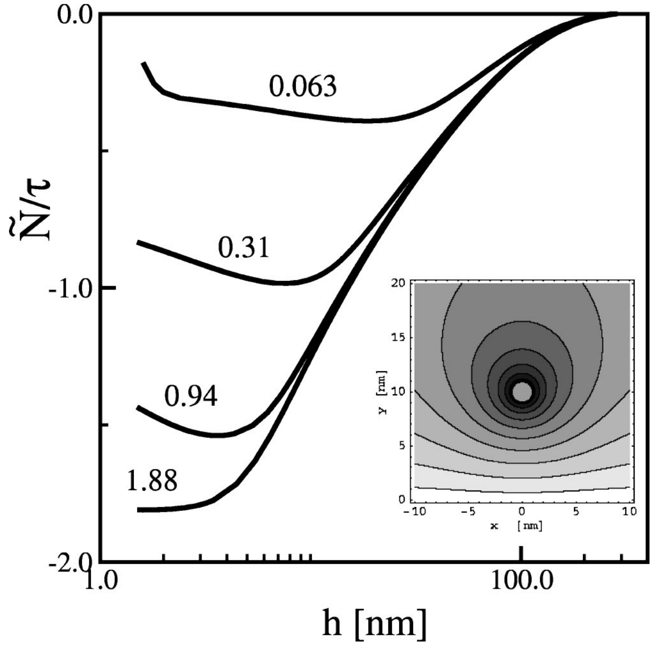

FIG. 1. Number $\tilde{N}$ of evaporated ions, as a function of the distance h between the wall and the polyelectrolyte (salt concentration $\kappa^{-1}=50$ nm). The parameters used in the calculation are typical of a rigid DNA molecule approaching a charged lipid bilayer. Labels specify the wall surface charge density $\lambda_B\zeta$. The inset shows the mean-field electrostatic potential ϕ for a fixed wall-rod distance of $h=10$ nm ($\lambda_B\zeta=0.94,\kappa^{-1}=50$ nm). The potential drops from $+5$ at the wall ($y=0$) to -5 at the cylinder surface.

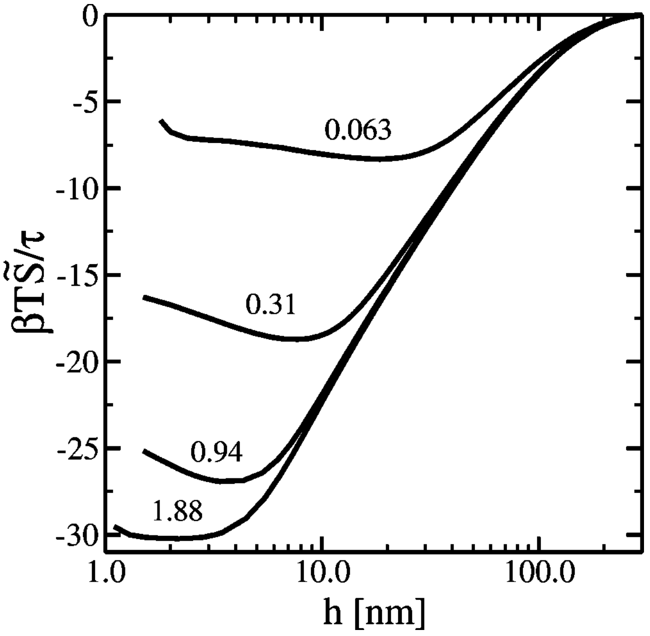

FIG. 2. The entropy $\beta T\tilde{S}$, calculated using the same parameters as in Fig. 1. The minima of $\beta T\tilde{S}$ correspond to the minima of $\tilde{N}$ in Fig. 1.

tial lines of ϕ for a typical wall-rod distance h. From a sequence of such potentials for various h, with Eq. (2) we obtain a change of the particle number $\tilde{N}$ between a system with charged and uncharged rods as a function of h; see Fig. 1. We observe that, on reducing h, ions leave the system and return to the reservoir. This can be interpreted as counterion evaporation. To understand the reason for this ion evaporation, one needs to recall that the total charge of a double layer surrounding either the wall or rod is equal to the total charge of the object (and is of opposite sign, of course). When two *oppositely* charged objects come sufficiently close to each other, the (fixed) surface charges of one object can help screen the charges of the other object, so that mobile ions of the atmosphere become useless and can leave the system. That $\tilde{N}$ in Fig. 1 decreases with decreasing h shows that the contribution of the fixed charges to the screening grows with decreasing h. Only for very small values of h, when the image charges of the cylinder charges—both have equal polarity and magnitude—become more important than the interfacial wall charges, there is again a demand for mobile electrolyte ions to help screen the image charges and $\tilde{N}$ again increases. Another way of looking at counterion release is that two double layers of different charge polarities dissolve each other if the wall-rod distance becomes short enough for these double layers to overlap. Returning to the language of the gas-liquid phase transition, the electric field strength of the wall charges here plays the role of the heat which one has to supply to transfer molecules from the liquid phase into the gas phase. In accordance with this picture, the total fraction of evaporated ions should grow with the increasing ''heat rate,'' that is, increasing $\lambda_B\sigma_W$, and the four curves of Fig. 1 reveal that this is indeed the case.

Evaluating the entropy expression of Eq. (5) as a function of h, one obtains the curves plotted in Fig 2. They look very similar to those of $\tilde{N}$ in Fig. 1. The entropy becomes increasingly negative when h is reduced, that is, the counterion-release causes a *loss of entropy* in the system. This is clear from Eq. (5), which shows that the entropy is governed by $-\beta\mu_s N(\beta\mu_s<0)$, and that thus a loss of particles leads to a loss of entropy in the system. However, the term $-\beta\mu_s N$ in the entropy is energetically not relevant, because it is canceled by the last term of Ω in Eq. (4). Those terms of the entropy that actually contribute to the grand potential are given by the sum $S/k+\beta\mu_s N$, i.e., by $\beta\tilde{H}$ of Eq. (6). This quantity is shown in Fig. 3 as a function of h. It increases when h becomes smaller. The second term in the enthalpy expression in Eq. (6), $-\Sigma_{\alpha=\pm}\int_G d\vec{r}\rho_\alpha \log\rho_\alpha/c_s$, can easily be seen to be identical to

$$\tilde{S}_p := \left(\frac{S^\tau}{N^\tau}-\frac{S^0}{N^0}\right)N^\tau \tag{7}$$

if $N^0\rightarrow\infty$. Thus $\beta\tilde{H}=5\tilde{N}/2+\tilde{S}_p/k$. The inset of Fig. 3 now shows that $\beta\tilde{H}$ is dominated by $\tilde{S}_p$, and that it increases because $\tilde{S}_p$ increases. What is the meaning of $\tilde{S}_p$ in Eq. (7)? N^τ and S^τ are the number of particles and the total entropy of the system if the rod is charged; hence S^τ/N^τ is the entropy per particle if the rod is charged, and S^0/N^0 that if it is uncharged. Its difference gives the entropy change per particle, where ''particle'' now refers only to those particles that

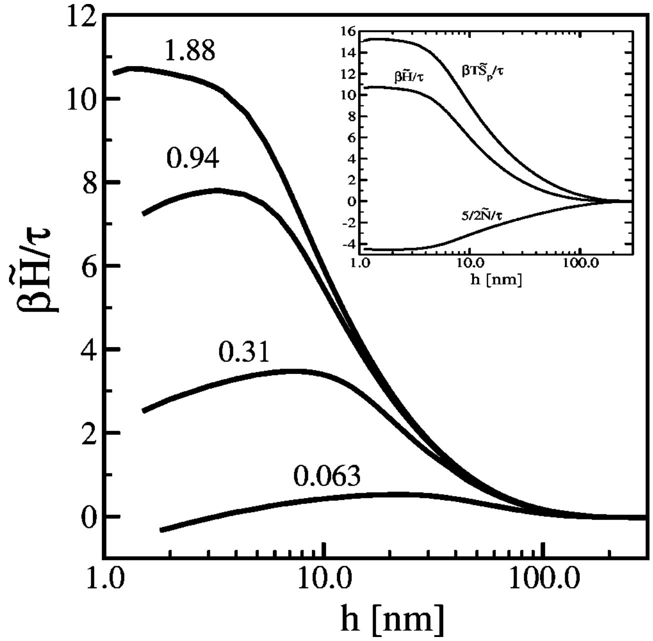

FIG. 3. The enthalpy $\beta\tilde{H}=5\tilde{N}/2+\tilde{S}_p/k$ as a function of the rod-wall distance h with the same parameters as in Fig. 1. The inset displays the two contributions to the enthalpy for $\lambda_B\zeta=1.88$, and demonstrates the dominance of the term $\tilde{S}_p$.

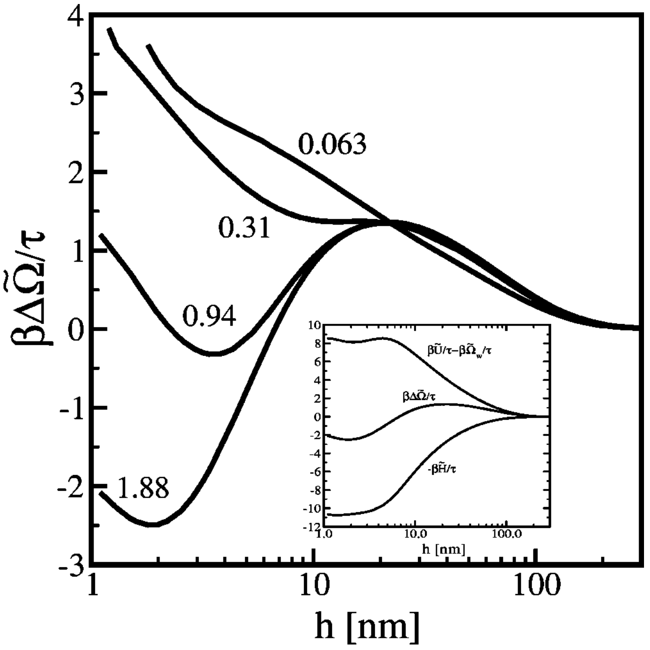

FIG. 4. The grand potential $\Delta\tilde{\Omega}=(\tilde{U}-\tilde{\Omega}_w)-\tilde{H}$ and in the inset $\Delta\tilde{\Omega}$ along with its two competing components $(\tilde{U}-\tilde{\Omega}_w)$ and $-\tilde{H}$ for $\lambda_B\zeta=1.88$ (same parameters as in Fig. 1). The inset shows that the minimum in $\Delta\tilde{\Omega}$ is due to the maximum of $\tilde{H}$.

remain in the system. Accordingly, $(S^\tau/N^\tau-S^0/N^0)N^\tau$ is *the total entropy change of all those ions remaining in the system.* This (and not the entropy as such) increases when ions evaporate. This increase, as we will see, is responsible for the counterion-release force. That the second term in Eq. (6) must increase when h becomes smaller can also be understood if one considers that the average volume per ion remaining in the system increases when ions disappear from the system.

Having learned that the release of ions causes an increase of $\beta\tilde{H}$, the relation $\Omega=U-H$ suggests an enthalpy-driven gain in energy when the cylinder approaches the wall. Let us therefore now consider the energy change $\tilde{\Omega}$. We first note that there will be always a trivial electrostatic attractive interaction between the fixed charges of the wall and rod, which tends to mask the attractive counterion-release contribution. Therefore, we separately calculate the trivial contribution arising from the attractive interaction of the bare charged cylinder in the *unperturbed* Gouy-Chapman layer (Gouy-Chapman potential ϕ_G), $\tilde{\Omega}_w=\Omega^{*\tau}[\phi_G]-\Omega^{*0}[\phi_G]$, and split the energy into two terms: $\tilde{\Omega}=\tilde{\Omega}_w+\Delta\tilde{\Omega}$. We can now concentrate on the more interesting contribution $\Delta\tilde{\Omega}$ coming from the interaction of the rod with the perturbation of the Gouy-Chapman layer.

Figure 4 shows $\Delta\tilde{\Omega}$ for a typical salt concentration of $\kappa^{-1}=50$ nm. This plot clearly reveals that a minimum in the self-energy forms when the surface density of the wall is increased. The first question must be if it is really the increase of enthalpy in the grand potential that is responsible for the creation of minimum. We demonstrate that this is so with the inset of Fig. 4, where we plotted $\Delta\tilde{\Omega}=(\tilde{U}-\tilde{\Omega}_w)-\tilde{H}$ along with its two competing components $(\tilde{U}-\tilde{\Omega}_w)$ and $-\tilde{H}$. Plots of other surface charges look similar. This then leads us to the main point of this paper: Evaporation of ions leads to an increase in enthalpy, which in turn is responsible for a net gain in energy. This explains the counterion-release force.

For low surface charges ($\lambda_B\zeta=0.063$), in Fig. 4 we observe that $\Delta\tilde{\Omega}$ is repulsive. This is the expected behavior: The existence of wall charges here is of minor importance, and the interaction is dominated solely by the hard wall, which is responsible for an energetically unfavorable distortion of the rod double layer from its perfect cylindrical symmetry. This confinement effect can also be obtained in linear theory, where we find that $\beta\Delta\tilde{\Omega}\approx\lambda_B\tau^2K_0(2\kappa h)$ (K_0 is the usual Bessel function). From Fig. 1 we see that, already for so low a surface charge density, there are ions disappearing from the system, but the gain in enthalpy (see Fig. 3) is not yet large enough to overcome the repulsive confinement effect.

This changes on increasing $\lambda_B\zeta$ to 0.94, when the loss of ions takes effect. Due to the evaporation the average volume per ion remaining in the system increases, so that their (and only their) entropy is increased. Remembering that $\Omega=U-H$, and acknowledging the fact that the internal energy is only very weakly affected by the loss of particles, we can infer that it is the evaporation-induced entropy gain of the ions remaining in the system, or more precisely, the enthalpy gain of the system as a whole, that is responsible for the attractive counterion-release interaction observed in Fig. 4. The position and depth of the minima in Fig. 4 match with the maxima of the enthalpy in the inset figure of Fig. 4. At very small h, Fig. 1 shows that the return of ions again costs enthalpy, so that $\Delta\tilde{\Omega}$ in Fig. 4, at these distances, goes up again. This is the repulsive interaction of the rod with its own image charge.

As pointed out above, it is essential for the occurrence of this effect that the wall and rod by oppositely charged. This implies that inevitably there will be another attractive interaction, namely, a direct interaction (in our case, the interaction of the bare charged cylinder with the unperturbed Gouy-Chapman layer). The corresponding force points in the same direction as the evaporation-induced force. Moreover, both forces grow in the same way (with increasing σ_W in our case). Thus, it is not easy to see how in an experiment one force could discriminate against the other. However, in an accurate quantitative measurement, it should be possible to identify the contribution of the evaporation-induced force; for instance, in DNA unbinding experiments as in Ref. [15] or in experimental adsorption studies of polyelectrolytes as in Ref. [8] (also see Ref. [9]). We have calculated the potential minimum for a variety of different σ_W and κ; it can easily reach a few kT per distance d, which should suffice to make a measurable effect.

In conclusion, we have clearly demonstrated that ions cannot only condense onto a polyelectrolyte, but may also evaporate again. Two oppositely charged objects, immersed in an electrolyte, can take part in screening each other if they are close enough for their double layers to overlap. This allows ions which are involved in the screening of the objects at infinite distances to leave the system. This loss of ions affects the effective interaction between both objects. Studying a DNA approaching a lipid bilayer, we have shown that, due to this evaporation, the whole system can gain a considerable amount of enthalpy, because the ions remaining in the system can increase their entropy, and this gain for the system manifests itself as an attractive contribution to the effective interaction between the polyelectrolyte and the wall. This can also be regarded as the energy that is gained if one allows two ion atmospheres of opposite polarity to overlap with and dissolve each other. The effective charge of the polyelectrolyte is, of course, also affected by the change in $\tilde{N}$. We will report on this and our related calculations for mobile wall surface charges elsewhere.

---

[1] F. Oosawa, *Polyelectrolytes* (Dekker, New York, 1971).

[2] G.S. Manning, J. Chem. Phys. **51**, 954 (1969).

[3] S. A. Rice and M. Nagasawa, *Polyelectrolyte Solution* (Academic Press, New York, 1961)

[4] M.T. Record, T.M. Lohman, and P. de Haseth, J. Mol. Biol. **107**, 145 (1976); P.L. de Haseth, T.M. Lohman, and M.T. Record, Biochemistry **16**, 4783 (1977); K.A. Sharp, R.A. Friedman, V. Misra, J. Hecht, and B. Honig, Biopolymers **36**, 245 (1995).

[5] P. Sens and J.F. Joanny, Phys. Rev. Lett. **84**, 4862 (2000).

[6] W. Firshein, Annu. Rev. Microbiol. **43**, 89 (1989); I.M. Verma and N. Somia, Nature (London) **389**, 239 (1997); J.P. Behr, Bioconjugate Chem. **5**, 382 (1994); B. Maier and J.O. Rädler, Phys. Rev. Lett. **82**, 1911 (1999); J.O. Rädler, I. Koltover, T. Salditt, and C.R. Safinya, Science **275**, 810 (1997); T. Sladitt, I. Koltover, J. Rädler, and C.R. Safinya, Phys. Rev. Lett. **79**, 2582 (1997).

[7] K. Wagner, D. Harris, S. May, V. Kahl, J.O. Rädler, and A. Ben-Shaul, Langmuir **26**, 303 (2000).

[8] R.J. Mashl, N. Gronbech-Jensen, M.R. Fitzsimmons, M. Lütt, and D. Li, J. Chem. Phys. **110**, 2219 (1999).

[9] R.J. Mashl and N. Gronbech-Jensen, J. Chem. Phys. **109**, 4617 (1998); R.R. Netz and J.F. Joanny, Macromolecules **32**, 9013 (1999); R. Menes, P. Pincus, R. Pittman, and N. Dan, Europhys. Lett. **44**, 393 (1998); R. Bruinsma and J. Mashl, *ibid.* **41**, 165 (1998).

[10] J.L. Barrat and J.F. Joanny, Adv. Chem. Phys. **94**, (1996).

[11] One can recognize this from Eq. (1), if one sets $\sigma_W = 0$. The first boundary condition then requires that the normal component of the electric field at the wall must vanish, which is only possible if there is a perfect mirror image at $z<0$ of the real charge distribution at $z>0$.

[12] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces and Membranes* (Addison-Wesley, Reading, M, 1994).

[13] E. Sackman, and R. Lipowsky, *Structure and Dynamic of Membranes* (North-Holland, Amsterdam, 1995).

[14] M. Shinitzky, *Biomembranes* (VCH, New York, 1993).

[15] B. Maier and J. Rädler (unpublished).