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### Short Communication

## Growth of charged micelles

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**Résumé.** — On considère les propriétés électrostatiques de micelles cylindriques chargées ayant des extrémités de forme sphérique. En régime semidilué (fraction volumique  $\phi \ll 1$ ) et sans addition de sel, le modèle, qui prend en considération les non-linéarités, suggère que les interactions coulombiennes impliquent une contribution supplémentaire à l'énergie libre d'une extrémité et modifie la loi de croissance de la micelle. Dans quelques cas, la taille de la micelle varie à peu près comme  $\phi^{(1/2)(1+\Lambda)}$  où  $\Lambda$  dépend de la charge coulombienne renormalisée. Ces résultats pourraient aider à expliquer des anomalies récemment observées expérimentalement dans le comportement dynamique de micelles quand il y a de petites concentrations de sel.

**Abstract.** — We consider the electrostatics of charged, cylindrical micelles with spherical end-caps. In the semidilute regime (volume fraction  $\phi \ll 1$ ), and with no added salt, a model calculation which includes nonlinearities suggests that Coulomb interactions result in an additional contribution to the free energy of an end-cap that modifies the growth law for the average micelle size. In some cases, the micelle size varies approximately as  $\phi^{(1/2)(1+\Lambda)}$ , where  $\Lambda > 0$  depends on the renormalized coulomb charge of an end cap. These results may help explain anomalies, seen at low added salt, in recent experiments on the dynamics of worm-like micelles.

Recent studies of elongated micelles of ionic surfactant in water show that in some systems flexible, worm-like cylinders are formed whose properties resemble those of polymer solutions [1 – 6]. While the osmotic compressibility and cooperative diffusion constant scale as power laws with the volume fraction of surfactant,  $\phi$ , in accord with the predictions of polymer theory [7], the dynamical properties of these systems are more complex [6, 8, 9]. There are two reasons for this: firstly, the average degree of polymerization,  $N$ , is itself a function of  $\phi$  in these self-assembling systems, with  $N \sim \phi^{1/2}$  expected for long semi-flexible cylinders with spherical endcaps [10]. Secondly, the process of micellar disentanglement is enhanced by the presence of breaking and

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recombination reactions. A recent theory [11], which takes into account both effects, predicts a dependence on  $\phi$  of the viscosity, stress relaxation time [8] and the self-diffusion constant [9] that is in reasonable agreement with experiments on CTAB/KBr when the concentration of added salt is high. In particular, the theory predicts [11] for the viscosity  $\eta \sim N\phi^3 \sim \phi^\alpha$  where  $\alpha \simeq 3.5$ . The experimental results are close to this prediction at high salt ( $[\text{KBr}] \geq 0.25 \text{ M}$ ) but the measured exponent increases smoothly to about  $\alpha \simeq 5.0$  at  $[\text{KBr}] \leq 0.1 \text{ M}$ . One way to reconcile this deviation with the analysis of reference [11], is to suggest that the usual  $N \sim \phi^{1/2}$  behavior may be modified in charged systems. This provides the motivation for the present study of the effects of electrostatics on the growth of locally cylindrical micelles [12].

In this note, we show that the electrostatic interactions increase the rate of growth of  $N$  with  $\phi$ . In some cases, these effects can still lead to a power-law growth, but with a new effective exponent relating  $N$  and  $\phi$ . This result arises because the average degree of polymerization,  $N$ , of the wormlike micelles is controlled by the excess free energy,  $\Delta\mu$ , of a pair of end-caps relative to the cylindrical interior regions, according to [11, 13]

$$N \sim \left[ \phi e^{\Delta\mu/kT} \right]^{1/2} \quad (1)$$

Below, we derive an approximate expression for  $\Delta\mu$  for charged, elongated micelles in the limit of no added salt. For practical purposes, in which data is collected over a relatively narrow range of  $\phi$  (about one decade [8, 9]) our result may resemble an effective power law  $N \sim \phi^{(1/2)(1+\Lambda)}$ , where the usual exponent of 1/2 is corrected by a term  $\Lambda$ , which is weakly  $\phi$ -dependent and is related to the fraction of "unbound" counterions in solution.

The physical origin of the increased growth exponent is that the electrostatic free energy contributions favor the end-caps over the cylindrical regions. This effect leads to *smaller* micelles; however, we find that the bias towards end cap formation is a decreasing function of  $\phi$ , resulting in an *increased* micellar growth exponent. This statement is valid when the surface charge density on the micelles is high; we focus on this limit here. In this regime, the end-cap energy is dependent on the renormalized (effective) charge  $Z^*$  on a cap, whose value depends logarithmically on the ambient charge density and hence the micellar volume fraction. The correction term  $\Lambda$  should tend to zero at high added salt, when the effective charge is controlled by the ambient salt level rather than the surfactant concentration.

One contribution to the end-cap energy is the difference in the energy per unit length between an infinite and finite cylinder, even with no rearrangement of the charge at the ends. This contribution was discussed in reference [12] by Odijk in the context of micelle growth with increasing salt concentration. Carrying over his results to the case of zero added salt [14] implies that  $\Delta\mu \sim \phi^{-1/2}$ . Equation (1) then predicts an exponentially strong increase in the growth as  $\phi$  is decreased. This effect will dominate at very small values of  $\phi$  and will be the major contribution to the initial growth from a state of small micelles. For larger values of  $\phi$ , this term tends to zero, and the effects of charge rearrangement at the ends of the micelles, which are assumed to be terminated by spherical end-caps, will be important.

In this regime we find  $\Delta\mu$ , for the limit of zero added salt, by estimating the free energy difference between (i)  $N_c$  surfactants molecules in a semidilute array of infinite cylinders at volume fraction  $\phi$  and (ii)  $N_c$  surfactants, constituting one half of a spherical micelle, immersed in a medium with an ambient counterion charge density appropriate to the same cylindrical array. The semidilute limit is defined formally by  $\phi \rightarrow 0$ ,  $N \rightarrow \infty$  with  $\phi N^2 \gg 1$ ;  $N_c$  denotes the number of surfactants in a hemispherical end-cap.

This estimate is motivated by the idea that for long micelles, the end-caps are extremely dilute "species" in a semi-dilute environment of locally cylindrical objects; a reasonable guess for the energy of a highly curved end cap can presumably be obtained by considering the simpler

geometry of a spherical micelle in the same environment. All short-ranged, local effects will then contribute to a  $\phi$ -independent part,  $\Delta\mu_0$ , where we write

$$\Delta\mu = \Delta\mu_0 + \Delta\mu_1(\phi). \tag{2}$$

Our calculations, outlined below, indicate that for semi-dilute cylinders there are contribution to  $\Delta\mu_1$  which vary as  $\log \phi$  and cannot be neglected even as  $\phi \rightarrow 0$ . All higher virial contributions (terms in  $\phi, \phi^2 \dots$ ), which may have both electrostatic and short-ranged components, are negligible in the semi-dilute regime discussed here.

We now consider the mean-field free energy of a system of fixed charges on a set of immobile colloidal particles (i.e. the micelles) with mobile counterions in a solution of dielectric constant  $\epsilon$ . For example, in the case of a single spherical particle of radius  $R$ , the free energy in units of  $kT$ ,  $F$ , is given by

$$F = \frac{1}{2} \ell \int \text{drdr}' n(\mathbf{r})n(\mathbf{r}') V(\mathbf{r} - \mathbf{r}') - \ell Z \int \text{dr} n(\mathbf{r}) V(r - R) + \int \text{dr} n(\mathbf{r}) \ln[n(\mathbf{r})v_0] \tag{3}$$

where  $V(\mathbf{r}) = \frac{1}{|\mathbf{r}|}$  and  $\ell = \frac{e^2}{\epsilon kT}$  is the Bjerrum length. The first term in equation (3) represents the Coulomb interactions of the counterions whose density is given by  $n(\mathbf{r})$ . The second term accounts for the interactions of the counterions with the fixed number of surface charges per unit area,  $\sigma_0$ , located on the sphere described by  $r = R$ . The total charge is  $Z = 4\pi\sigma_0R^2$ . The last term in equation (3) is the entropy of the counterions (in the dilute limit) where  $v_0$  is the molecular volume of a counterion. The usual Poisson-Boltzmann equation may be derived by functionally minimizing  $F$  with respect to the charge distribution  $n(\mathbf{r})$ , with the constraint of charge neutrality.

While exact solutions exist [15] for the charge density and potential for an array of infinite, charged cylinders whose counterions are solubilized in the intervening solvent, no such treatment exists for spheres [16]. Most studies [17] have focused on the case of high salt concentration  $n_{\text{salt}}$  and hence short-screening lengths,  $\kappa^{-1} = [8\pi\ell n_{\text{salt}}]^{-1/2}$ . In that regime, an expansion in  $(\kappa R)^{-1}$ , where  $R$  is the sphere radius, can be performed. However, it is precisely the limit of *long* screening lengths that is of interest here.

To obtain a consistent, analytic estimate for the  $\phi$  dependence of the free energy in both spherical and cylindrical geometries, we have calculated the charge density and free energy in either case using a unified variational approximation. Charge neutrality is enforced within a cylindrical or spherical Wigner-Seitz cell as appropriate. The variational ansatz for the counterion density is motivated by the form of the charge distribution around an infinite sheet [16]: most of the charge is localized in a small region near the sheet (the inner region, of order  $(\sigma_0\ell)^{-1}$ ), with the remainder spread nearly uniformly in the remainder of the Wigner-Seitz cell (outer region) [18].

We first consider an array of spheres, for which we take as our variational charge density profile within each cell a charge  $(Z - Z^*)$  uniformly distributed in an inner region  $R < r < R(1 + \delta)$ , with charge  $Z^*$  uniformly distributed in the outer region  $R < r < R_b$ , as shown in figure 1.

(Here  $R_b$  denotes the radius of the Wigner-Seitz cell.) The form of  $n(\mathbf{r})$  is thus written :

$$\begin{aligned} n(r) &= \frac{(Z - Z^*)}{V_1} + \frac{Z^*}{V} & R < r < R(1 + \delta) \\ n(r) &= \frac{Z^*}{V} & R(1 + \delta) < r < R_b \end{aligned} \tag{4}$$

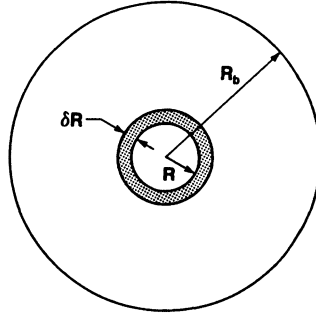


Fig. 1. — The Wigner-Seitz cell of radius  $R_b$  contains the micelle of radius  $R$ . The inner region of high charge density occupies a shell of thickness  $\delta R$ . The geometry shown applies, in two and three dimensions, to cylindrical and spherical cases respectively.

where  $V_1 = \frac{4\pi R^3}{3} [(1+\delta)^3 - 1]$  and  $V = \frac{4\pi}{3} (R_b^3 - R^3)$  are the volumes of the inner region and the entire Wigner-Seitz cell respectively. The variational parameters are thus  $Z^*$  and  $\delta$ . Note that equation (4) automatically satisfies the conservation condition  $\int_V d\mathbf{r} n(\mathbf{r}) = Z$ .

For the case of spherical symmetry and a spherical Wigner-Seitz cell, the integrals in equation (3) are readily performed (e.g., by use of Gauss' theorem). The results are best expressed in terms of the free energy per unit charge,  $f = \frac{F}{Z}$ , which depends on  $\lambda = 2\pi\sigma_0\ell R$  (a dimensionless measure of the surface charge density) and on the volume fraction of the spheres,  $\phi_s = (R/R_b)^3$ .

We first discuss the high charge limit where the region of enhanced charge density is a small fraction of  $R$ , i.e.  $\delta \ll 1$ . In the dilute limit, where we neglect terms of  $O(\phi_s)$ , one can then write to  $O(\delta)$

$$f \approx f_0 + \lambda \left[ (1-\beta)^2 \left( 1 - \frac{2\delta}{3} \right) - (1-\beta)(2-\delta) \right] + \beta \ln[\phi_s \beta] + (1-\beta) \ln \left( \frac{1-\beta}{3\delta} \right) \quad (5)$$

where  $\beta = Z^*/Z$ . The terms proportional to  $\lambda$  are the electrostatic energies,  $f_0$  is a constant that depends only on  $Z$  and  $R$ , and the remaining terms are the entropies of the "unbound" and "bound" counterions respectively. In the limit  $\phi_s \rightarrow 0$ , minimizing with respect to  $\delta$  yields

$$\delta \approx \left[ \frac{\lambda}{3} (1+2\beta) \right]^{-1} \quad (6)$$

so that for high charge ( $\lambda \gg 1$ ),  $\delta \ll 1$  as was assumed in writing equation (5).

Minimization of equation (5) with respect to  $\beta$  yields :

$$\ln[(1-\beta)/\beta] - \ln(3\delta\phi_s) - 2\lambda\beta = 0. \quad (7)$$

We now consider the case of small  $Z^*/Z$  ( $\beta \ll 1$ ) although we continue to assume a high bare charge density ( $\lambda \gg 1$ ). In this case, most of the charge is localized near the surface and the

fraction of delocalized charge,  $\beta = Z^*/Z$  is given from equation (7) as  $\beta \approx -\left(\frac{1}{2\lambda}\right) \ln(3\delta\phi_s\beta)$ . This result is in qualitative agreement with an heuristic argument presented in reference [16]. The fraction of delocalized charge increases as the system becomes more dilute, since the entropy of unbound counterions becomes more important. The  $\phi_s$  dependent part of the free energy per charge,  $\Delta f_s$ , is then

$$\Delta f_s = -\beta^2\lambda - \beta \approx -\frac{1}{4\lambda} (\ln [3\delta\beta\phi_s])^2. \tag{8}$$

In the case of a cylindrical array, a similar calculation can be performed ; the electrostatic integral, performed using Gauss' theorem with cylindrical symmetry, results in a term  $V$  of equation (3) that is logarithmic in the radial distance. For cylinders of radius  $R$ , we find that in the high charge limit, the inner region has an extent given by  $\delta_c = \left[\frac{\lambda}{3}\right]^{-1}$ , for small values of  $\beta$ . As above,  $\lambda = 2\pi\ell R\sigma_0$  and the parameter  $\delta_c$  approaches the same value as for spheres. However, in contrast to the spherical case, there is for cylinders no limit in which both  $\lambda \gg 1$  and the charge is also delocalized [19]. Instead,  $\beta = \beta_c$  is always  $\ll 1$  for the case of high charge. This can be seen from the following variational result for the fraction of delocalized charge  $\beta_c$  as a function of the volume fraction of cylinders,  $\phi_c = (R/R_b)^2$ :

$$\beta_c \approx \left[\frac{1}{\lambda}\right] \frac{\ln [2\delta_c\beta_c\phi_c]}{(1 + \ln \phi_c)} \approx \frac{1}{\lambda} \tag{9}$$

where the second form holds at low volume fractions  $\phi_c$  [20]. For the high charge limit considered here, the free energy dependence on  $\phi_c$  is given in the cylindrical case by

$$\Delta f_c \approx \frac{1}{2\lambda} \frac{(\ln [2\delta_c\beta_c\phi_c])^2}{(\ln \phi_c + 1)} - \beta_c \tag{10}$$

at the level of our variational approximation [20].

We now use these results to estimate the end-cap energy,  $\Delta\mu$  of equation (2), due to the charge rearrangement at the ends of the spherical endcaps. We consider a single sphere in a background of charge density,  $n_c$ , arising from the unbound charge ( $Z_c^* = \beta Z \approx Z/\lambda$ ) of the semidilute array of cylinders (We assume the high charge limit is the one of experimental relevance). The background charge density,  $n_c$ , is calculated by distributing the cylinders' effective (unbound) countercharges uniformly in space (consistent with our variational description of the outer zone). This gives

$$n_c \approx \frac{\phi}{\pi R^2 \ell} \tag{11}$$

where  $R$  is the cylinder radius and  $\phi$  the volume fraction of cylinders.

The calculation of electrostatic energy of the added sphere proceeds as above, with two modifications, as follows : (i) the Wigner-Seitz cell radius  $R_b$ , within which charge neutrality holds, is taken as  $\kappa^{-1} = [4\pi\ell n_c]^{-1/2}$ , the screening length appropriate to the ambient charge density  $n_c$ ; (ii) the entropy of counterions at density  $n(r)$  in the outer region must be corrected for the presence of the extra countercharges at density  $n_c$ . Thus the last term in equation (3) must be replaced by

$$\Delta S = \int dr \{ (n(r) + n_c) \ln [(n(r) + n_c) v_0] - n_c \ln [n_c v_0] \}. \tag{12}$$

In the inner region,  $R < r < R(1 + \delta)$ ,  $n_c \ll n(r)$  and the value of  $\delta \sim 1/\lambda$  is unaffected by this modification. In the outer region,  $n_c \gg n(r)$  and the resulting contribution to equation

(12) is well approximated as  $\int n(r) \ln [n_c v_0] dr$ . In equation (5), this corresponds to replacing the factor  $\ln [\beta \phi_s]$  on the right by  $\ln [\zeta \phi / 3\delta]$  where  $\phi = \phi_c$  is the volume fraction of micelles and  $\zeta = 4R\delta/\ell$ . In physical terms, the entropy per charge of the unbound counterions arising from a spherical micelle, in a semi-dilute array of cylinders, is fixed by the ambient counterion density  $n_c$  within the Wigner-Seitz cell, arising from the cylinders, rather than by the density of the micellar counterions themselves.

We now estimate the free energy of a pair of hemispherical end caps as that of sphere of radius  $R$  as described above. By minimizing the free energy, the effective charge  $Z^*/2$  on an end cap is found to obey  $Z^* = Z\beta_e \approx -Z \left( \frac{1}{2\lambda} \right) \ln(\zeta\phi)$ . For the  $\phi$ -dependent part of the free energy per charge of the pair of end-caps we find

$$\Delta f_e \approx -\beta_e^2 \lambda \approx -\frac{1}{4\lambda} [\ln(\zeta\phi)]^2. \quad (13)$$

From this we may subtract the corresponding expression for cylinders, equation (10), to obtain the free energy difference per charge between the end-cap and cylindrical environments:

$$\Delta f_e - \Delta f_c \approx -\frac{1}{4\lambda} [\ln(\zeta\phi)]^2 - \frac{1}{2\lambda} \frac{(\ln[\zeta'\phi])^2}{\ln\phi + 1} \quad (14)$$

where  $\zeta' = 2\delta_c/\lambda$ . According to our identification of the sphere as a pair of end-caps, this expression is simply  $\Delta\mu_1/(2ZkT)$  with  $Z = N_c$ .

For the leading behaviour at low  $\phi$  we obtain from (14)

$$\Delta\mu_1/kT = -\frac{1}{2} \frac{Z}{\lambda} [\ln(\zeta\phi)]^2 = \frac{1}{2} Z^* \ln(\zeta\phi). \quad (15)$$

Inserting this in equation (1) yields

$$N \sim \phi^{1/2} \exp [-(Z/4\lambda)(\ln[\zeta\phi])^2]. \quad (16)$$

As discussed in the introduction, for practical purposes, this form may resemble an effective power law

$$N \sim \phi^{(1/2)(1+\Lambda)} \quad (17)$$

where the usual exponent of  $\frac{1}{2}$  is corrected by a term in  $\Lambda = Z^*$ . (This value for effective exponent may be checked by taking the logarithmic derivative of equation (16) with respect to  $\phi$ .) Typical values of  $N_c \approx 20$  and  $\beta \approx 0.05$  [1, 12, 16] suggest an increase of order one in the growth law exponent. Again, we note that the effective power law discussed here is only relevant when the term in  $\Delta\mu$  proportional to  $\phi^{-1/2}$ , arising from the energy of finite cylinders with no charge rearrangement, becomes small.

It would be premature to attempt a quantitative explanation of the viscosity data of reference [8] on the basis of this result. Qualitatively, however, it is significant in demonstrating how electrostatic interactions can change the micellar growth law at low salt, giving an effective exponent for the volume fraction dependence that is greater than  $\frac{1}{2}$ . More work (both theory and experiment) will be necessary to determine whether this can indeed explain the discrepancy between the viscosity and self diffusion data on wormlike micelles [8, 9] and the theory of reference [11]. In addition, the crossover from the effects due to charge rearrangement (which give the effective power law growth) to the contribution of the finite cylinder electrostatics (which gives

$N \sim \exp(-1/\phi^{1/2})$  at very small values of  $\phi$ ) has yet to be delineated [14]. Another contributing factor could be the dependence of the persistence length on salt, as arises in ordinary polyelectrolytes. However, the characteristic growth law exponent, the focus of the present work, is an effect unique to self-assembling micellar systems.

In summary, we have demonstrated that for charged spherocylindrical micelles, in the absence of added salt, the end-cap free energy has a term which depends logarithmically on the volume fraction of surfactant,  $\phi$ . In an intermediate regime of  $\phi$ , this free energy contribution modifies the growth law for the degree of polymerization of these micelles, with an effective power law exponent that depends on the effective charge  $Z^*$  of the end-cap. This effect may be relevant in understanding the strong dependence of the viscosity and self-diffusion constant on  $\phi$  in the case of worm-like micelles with low added salt [8, 9, 14]. At high salt, the Coulomb interactions are screened and there is no  $\phi$ -dependent contribution to the end-cap free energy; the standard growth law,  $N \sim \phi^{1/2}$  is then expected to hold.

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### References

- [1] PORTE G., APPELL J., POGGI Y., *J. Phys. Chem.* **84** (1980) 3105; *J. Coll. Int. Sci.* **87** (1982) 492.
- [2] HOFFMANN H., REHAGE H., *Faraday Discuss. Chem. Soc.* **76** (1983) 363; *J. Phys. Chem.* **92** (1988) 5172.
- [3] SHIKATA T., HIRATA H., KOTAKA T., *Langmuir* **4** (1988) 354.
- [4] WARR G. MAGID L., CAPONETTI E., MARTIN C., *Langmuir* **4** (1988) 813.
- [5] IMAE T., *J. Phys. Chem.* **92** (1988) 5721.
- [6] CANDAU S.J., HIRSCH E., ZANA R., *J. Phys. France* **45** (1984) 1263; *J. Colloid Int. Sci.* **105** (1985) 521; *Physics of Complex and Supermolecular Fluids*, Eds. S.A. Safran and N. Clark (Wiley, New York) 1987 p.569.
- [7] SAFRAN S.A., TURKEVICH L.A. and PINCUS P.A., *J. Phys. Lett. France* **45** (1984) L19.
- [8] CANDAU S.J., HIRSCH E., ZANA R., ADAM M., *J. Coll. Int. Sci.* **122** (1988) 430; CANDAU S.J., HIRSCH E., ZANA R., DELSANTI M., *Langmuir* (in press).
- [9] MESSENGER R., OTT A., CHATENAY D., URBACH W., LANGEVIN D., *Phys. Rev. Lett.* **60** (1988) 1410.
- [10] SHEU E. and CHEN S.H., *J. Phys. Chem.* **92** (1988) 4466 have measured a growth law which is apparently slower than  $\phi^{1/2}$ . However, these results reflect an increase of the aggregation number of only a factor of 2 from the minimum spherical micelle. Our discussion focuses on the case of long, cylindrical micelles which are much larger than the minimum spherical micelle.
- [11] CATES M.E., *Macromolecules* **20** (1987) 2289; *Europhys. Lett.* **4** (1987) 497; *J. Phys. France* **49** (1988) 1593.
- [12] Studies of the salt dependence at fixed surfactant volume fraction,  $\phi$ , have been discussed by PORTE G., *Surfactants in Solution*, Eds. K.L. Mittal and B. Lindman (Plenum, New York) 1984, p.805 and by ODIJK T., *J. Phys. Chem.* **93** (1989) 3888.
- [13] ISRAELACHVILI J.N., MITCHELL D.J., NINHAM B.W., *J. Chem. Soc. Faraday Trans. II* **72** (1976) 1525.
- [14] MACKINTOSH F.M., SAFRAN S.A., PINCUS P., to be published.
- [15] FUOSS R.M., KATCHALSKY A., LIFSON S., *Proc. Natl. Acad. Sci.* **37** (1951) 579.



- [16] ALEXANDER S., CHAIKIN P.M., GRANT P., MORALES G.J., PINCUS P. and HONE D., *J. Chem Phys.* **80** (1984) 5776 ;  
 PINCUS P., SAFRAN S.A., ALEXANDER S., HONE D., *Physics of Finally Divided Matter*, Eds. N. Boccara and M. Daoud (Springer-Verlag, New York) 1986, p.40.
- [17] MITCHELL D.J., NINHAM B.W., *J. Phys. Chem.* **87** (1983) 2996 ;  
 EVANS D.F., MITCHELL D.J., NINHAM B.W., *J. Chem. Phys.* **88** (1984) 6344.
- [18] See "Polyelectrolytes", by OOSAWA F. (Marcel Dekker, New York) 1971.
- [19] Even for an isolated, charge cylinder, a large fraction of the counterions condense near the surface. For polyelectrolytes, this is termed Manning condensation.
- [20] This result scales correctly with  $\lambda$  when compared with the exact [15] expression for the charge on the Wigner-Seitz cell boundary in the high charge limit. In addition, the qualitative  $\phi_c$  dependence is similar ;  $\beta_c$  increases as  $\phi_c$  increases. (The exact [15] result for the fractional charge density at the Wigner-Seitz cell boundary is, in the high charge limit,  $\left(\frac{1}{\lambda}\right) \exp\left(\frac{\pi^2}{s^2}\right)$  with  $s = \left(\frac{1}{2}\right) \ln \phi_c$ ). A comparison of the results in the high charge limit ( $\lambda \gg 1$ ) for the planar, cylindrical, and spherical geometries highlights the interplay of the geometry and the counterion energy. In the planar case, a calculation similar to that presented above yields an effective charge,  $Z^* = \beta_p Z$  with  $\beta_p \sim \phi_p$  where the Wigner-Seitz cell is of size  $\phi_p^{-1}$ . The effective charge thus *decreases* as  $\phi_p \rightarrow 0$ . In contrast, the increased counterion entropy around a sphere results in  $\beta \approx -\ln [3\delta\phi_s\beta]/\lambda$  for  $\beta \ll 1$ , so that  $Z^*$  increases as the cell size increases ( $\phi_s$  decreases). When  $\phi_s \ll \lambda e^{-\lambda}$  the charge is completely unbound and  $Z^* \approx Z$  as can be seen from equation (7). The cylinder is the marginal case where  $\beta \sim 1/\lambda$ , is approximately constant as the system is made more dilute.