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Geometrical and Topological Aspects of Electric Double Layers near Curved Surfaces

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The properties of electric double layers near closed-curved surfaces of arbitrary shape and genus are obtained exactly within the Debye-Hückel approximation by means of multiple-scattering expansions. Geometric and topological features of the electrostatics and thermodynamics emerge in a straightforward way through convergent expansions in powers of the ratio of the screening length to the principal radii of curvature. Some consequences of these results for the electrostatic contribution to the stability of structures of various shapes are considered.

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A simply stated, but as yet incompletely solved problem in the physics of colloidal systems is as follows: What is the free energy of a set of closed-curved surfaces of arbitrary shape interacting through screened Coulomb interactions? This question appears in a variety of contexts, from the study of colloidal crystals[1] and flexible polyelectrolytes,[2] to the theory of size and shape distributions of micellar aggregates in self-assembling amphiphilic solutions[3] and the polymorphism of charged lyotropic mesophases.[4] The related issues of the distribution of screening ions and of electric fields near modulated surfaces arise in a variety of electrochemical contexts.[5,6] Of particular interest is the regime in which the radii of curvature of the surfaces are large compared to the electrostatic screening length, where one expects certain rather general geometric and topological features of those surfaces to enter.

At the level of the Gouy-Chapman theory of electric double layers,[7] the answer to the question posed above reduces to the solution of the Poisson-Boltzmann equation with specified boundary conditions, a difficult *nonlinear* problem even for simple surface geometries. As a first step toward such a complete solution it is clearly desirable that there be a formally exact solution to the *linearized* (i.e., Debye-Hückel) theory in the strong electrolyte regime. Existing approaches to this linear problem fall generally into two classes; exact solutions for particular, highly symmetric closed surfaces[8-11] (e.g., cylinders, spheres, etc.), and perturbative solutions[12-14] for nearly planar shapes. Here, we present the exact solution to the Debye-Hückel equation in the presence of boundary surfaces of arbitrary shapes and topologies.

We may summarize our findings by noting that within the Debye-Hückel approximation the excess free energy associated with the ionic atmosphere is expressed in terms of the electrostatic potential $\phi(r)$ as

$$\mathcal{F}(\phi) = -\frac{\epsilon}{8\pi}\int_V d^3r[(\nabla\phi)^2+\kappa^2\phi^2]$$
$$=\frac{\epsilon}{8\pi}\int_S \phi^+\frac{\partial\phi^+}{\partial n}dS\,, \tag{1}$$

with ϵ the electrolyte bulk dielectric constant, κ the inverse screening length, V the volume bounded by the surfaces S, and $\partial\phi^+/\partial n$ the *inward* normal derivative to the surface. The second expression is a functional of the surface potential only and follows from the Debye-Hückel equation obeyed by ϕ,

$$(\nabla^2-\kappa^2)\phi(r)=0\,, \tag{2}$$

and an integration by parts. In Eq. (1) the superscript + means that the surface is approached by continuity from the bulk electrolyte, and takes care of possible discontinuities at the surface.

Observe that Eq. (2) is simply a scalar version, for *imaginary frequencies*, of the wave equation of classical electrodynamics, also known as the Helmholtz equation. Solutions of the latter for arbitrary geometries and rather general boundary conditions (Neumann, Dirichlet, or mixed) are known[15] in the form of "multiple-scattering expansions." These results are related to a famous method of Neumann in electrostatics,[16] and essentially generalize the method of images to nontrivial geometries. Such techniques have proven useful in the study of Casimir forces between conductors of arbitrary shapes.[17]

Adapting these techniques to the screened electrostatic problem we obtain the free energy of a set of surfaces of arbitrary shape in the Debye-Hückel regime. The convergence of the resulting power series in the ratio of κ^{-1} to the radii of curvature of the surface is assured[15] for

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real κ. As an illustration of the method, we obtain the exact form of the second-order curvature corrections to the free energy,

$$\mathcal{F} = f_0 \int dS \left[1 + \frac{a}{\kappa} H + \frac{b}{\kappa^2} H^2 + \frac{c}{\kappa^2} K + \cdots \right], \quad (3)$$

where f_0 is an amplitude, and a, b, and c are universal dimensionless quantities associated only with the boundary conditions. The mean and Gaussian curvatures are defined in terms of the principal radii of curvature R_1 and R_2 as $H = \frac{1}{2}(1/R_1 + 1/R_2)$ and $K = 1/R_1 R_2$.

We consider three important physical situations: (i) *conducting* surfaces held at fixed potential—the Dirichlet problem; (ii) *insulating* "opaque" boundaries with specified surface charge densities and for which the fields do not penetrate into the interior—the Neumann problem; (iii) *insulating* thin "transparent" boundaries with specified discontinuity of the electric field across the two sides. In cases (i) and (ii) the near surface potential satisfies $\partial\phi^+/\partial n = -4\pi\sigma/\epsilon$, with σ the local surface charge density, while in case (iii) $\partial\phi^+/\partial n - \partial\phi^-/\partial n = -4\pi\sigma/\epsilon$. In all cases, we first determine ϕ and then the free energy (1).

The Dirichlet problem.—For fixed potentials $\phi^+|_S = \phi_0$, the multiple-scattering expansion is obtained[15] by writing ϕ as a *double-layer potential*[16] due to an as yet unknown surface dipole density μ,

$$\phi(r) = \int_S \frac{\partial G_0}{\partial n_\alpha}(r\alpha)\mu(\alpha)dS_\alpha, \quad (4)$$

where α is a point on the surface, and

$$G_0(rr') \equiv (1/4\pi|r-r'|)\exp(-\kappa|r-r'|)$$

is the free-space Green's function satisfying $(\nabla^2-\kappa^2) \times G_0(rr') = -\delta^3(r-r')$. Hereafter, we use the normal derivative $\partial/\partial n_\alpha = \mathbf{n}_\alpha \cdot \nabla_\alpha$, where $\mathbf{n}_\alpha$ is the inward normal vector. It is readily verified that ϕ satisfies the homogeneous Helmholtz equation (2) for *r inside* the electrolyte bulk. To enforce the boundary condition $\phi(r \to \beta^+) = \phi_0$, where *r approaches* the surface point β from the interior of V, we recall the fundamental singular property of the normal derivative of G_0,[15,16]

$$\partial G_0(\beta^+\alpha)/\partial n_\alpha = \partial G_0(\beta\alpha)/\partial n_\alpha + \tfrac{1}{2}\delta_S(\alpha-\beta); \quad (5)$$

i.e., the left-hand side of (5) contains a surface distribution $\frac{1}{2}\delta_S$ (normalized with dS_α) in addition to the value of $\partial G_0(\beta\alpha)/\partial n_\alpha = \mathbf{n}_\alpha \cdot \nabla_\alpha G_0(\beta\alpha)$ at the surface. Calculation of $\phi(\beta^+)$ from (4) and (5) yields the exact integral equation for μ,

$$\mu(\beta) = 2\phi_0 - 2\int_S \frac{\partial G_0}{\partial n_\alpha}(\beta\alpha)\mu(\alpha)dS_\alpha s. \quad (6)$$

Standard vector calculus then yields the surface free energy (1) for the Dirichlet problem,

$$\begin{aligned}\mathcal{F}(\phi_0) &= -\frac{\epsilon\phi_0\kappa^2}{8\pi}\int_S dS_\alpha dS_\beta \mathbf{n}_\alpha\cdot\mathbf{n}_\beta G_0(\alpha\beta)\mu(\beta)\\ &= -\frac{\epsilon\phi_0^2\kappa^2}{4\pi}\int_S dS_\alpha dS_\beta \mathbf{n}_\alpha\cdot\mathbf{n}_\beta G_0(\alpha\beta)\left[1 - 2\int_S dS_\gamma \frac{\partial G_0}{\partial n_\gamma}(\beta\gamma) + 2^2\int_S dS_\gamma dS_\delta \frac{\partial G_0}{\partial n_\gamma}(\beta\gamma)\frac{\partial G_0}{\partial n_\delta}(\gamma\delta) - 2^3 \cdots\right], \quad (7)\end{aligned}$$

where iterative use was made of (6).

The Neumann problem.—For specified surface charges, it is mathematically convenient to represent ϕ as a *single-layer potential,*

$$\phi(r) = \int_S G_0(r\beta)\Sigma(\beta)dS_\beta, \quad (8)$$

the auxiliary charge density Σ being determined by the boundary condition $\partial\phi^+(\alpha)/\partial n_\alpha = -4\pi\sigma(\alpha)/\epsilon$ in terms of the imposed surface charge density $\sigma(\alpha)$. An integral equation for Σ is constructed by determining the contact normal derivative of (8), using the *dual* of Eq. (5) in which a change of sign of the distribution part occurs. We obtain

$$\Sigma(\alpha) = \frac{8\pi}{\epsilon}\sigma(\alpha) + 2\int_S \frac{\partial G_0}{\partial n_\alpha}(\alpha\beta)\Sigma(\beta)dS_\beta. \quad (9)$$

The free energy for fixed-charge problems is simply the surface integral

$$\mathcal{F}(\sigma) = \tfrac{1}{2}\int_S \sigma\phi\, dS, \quad (10)$$

that is, the Legendre transform of (1) appropriate to fixed potentials. For uniform charge density σ_0 on all surfaces, iteration of (9) with (8) yields the free-energy expansion

$$\tilde{\mathcal{F}}(\sigma_0) = \frac{4\pi\sigma_0^2}{\epsilon}\int_S dS_\alpha dS_\beta G_0(\alpha\beta)\left[1 + 2\int_S dS_\gamma \frac{\partial G_0}{\partial n_\beta}(\beta\gamma) + 2^2\int_S dS_\gamma dS_\delta \frac{\partial G_0}{\partial n_\beta}(\beta\gamma)\frac{\partial G_0}{\partial n_\gamma}(\gamma\delta) + 2^3 \cdots\right], \quad (11)$$

which is very similar to that of the Dirichlet case (7), up to the presence of $\mathbf{n}_\alpha\cdot\mathbf{n}_\beta$ there, and alternating signs in the scatterings.[15]

For the transparent case in which, in addition, Eq. (2) holds on both sides, the problem is equivalent to one extended to the full space, for a particular distribution of sources σ on the surfaces; hence the Green's function is G_0 and the potential ϕ is still given by the screened Coulomb (Yukawa) form (8), with Σ simply replaced by σ, which in turn obeys the required discontinuity equation $\sigma = -(\epsilon/4\pi)(\partial\phi^+/\partial n - \partial\phi^-/\partial n)$. The free energy is given again by (10), and for uniform charge density σ_0 reads

$$\tilde{\mathcal{F}}_t(\sigma_0) = \frac{4\pi\sigma_0^2}{\epsilon}\int_S dS_\alpha dS_\beta G_0(\alpha\beta)\,. \tag{12}$$

The absence of a multiple-scattering expansion arises from the transparency of the membrane. The free energy corresponds to that stored in the electrolyte on both sides of the surface.

Curvature expansion.— From the forms of (7) and (11) we see that these expansions are ideally suited to the study of weakly curved surfaces. Observe that the scattering kernel reads $\partial G_0(\alpha\beta)/\partial n_\alpha = \mathbf{n}_\alpha \cdot \mathbf{u}_{\alpha\beta} G_0'(\alpha\beta)$, where $\mathbf{u}_{\alpha\beta}$ is the unit vector joining β to α, and a prime indicates differentiation. For a strictly planar surface all normal vectors $\mathbf{n}_\alpha$ are orthogonal to vectors $\mathbf{u}_{\alpha\beta}$ connecting points on the surface and the expansions for the free energies terminate after the first term. To evaluate the various integrals that appear in (7) and (11) in the limit of large radii of curvature relative to screening length, note first that near any given point α on the surface, we may construct a local coordinate system (Fig. 1) with the z axis parallel to the normal $\mathbf{n}_\alpha$, and coordinates x and y in the tangent plane along the directions of the principal radii of curvature. In that local set of coordinates the surface itself is described as

$$z_\alpha(x,y) = \tfrac{1}{2}[x^2/R_1(\alpha) + y^2/R_2(\alpha)] + \cdots\,, \tag{13}$$

the differential of the surface area is $dS_\beta = \sqrt{g}\,dx\,dy$, with $g = 1 + [\nabla z_\alpha(x,y)]^2$, and the scalar product of normals is $\mathbf{n}_\alpha \cdot \mathbf{n}_\beta = g^{-1/2}$. Then the convergent multiple-scattering expansions (7) and (11) appear as expansions in powers of the curvature, valid for $\kappa R_1, \kappa R_2 \gg 1$.[15]

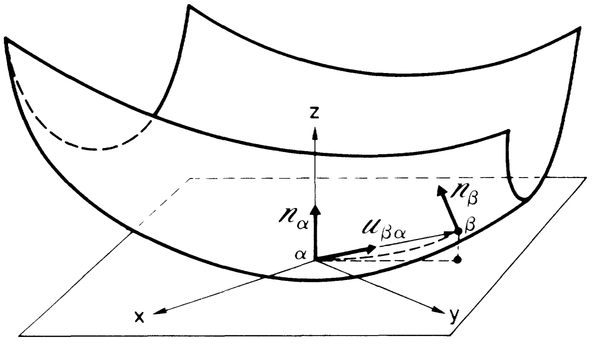

FIG. 1. A local coordinate system on a curved surface.

With these results and careful systematic Taylor expansions of G_0 and its derivative in (7), (11), and (12) along the same lines as in Refs. 15 and 17, we arrive at the form (3) of the free energy with the quantities f_0 and the dimensionless triads (a,b,c) given by $f_0 = -\epsilon\kappa\phi_0^2/8\pi$, $(-1, -\frac{1}{2}, \frac{1}{2})$; $f_0 = 2\pi\sigma_0^2/\epsilon\kappa$, $(1, \frac{3}{2}, -\frac{1}{2})$; $f_0 = \pi\sigma_0^2/\epsilon\kappa$, $(0, \frac{1}{2}, -\frac{1}{2})$, respectively, for the conducting, opaque, and transparent surfaces.

For weakly curved surfaces, one of the most immediate results of the present analysis is a direct computation of the electrostatic contribution to the bending energy of membranes,[8-14] a general expression for which is the quadratic form[18] suggested by Winterhalter and Helfrich,[8]

$$\mathcal{F}_{\mathrm{el}} = \int dS \left\{ \frac{1}{2}k_c \left[\frac{1}{R_1} + \frac{1}{R_2} - \frac{1}{R_0} \right]^2 + \bar{k}_c \frac{1}{R_1 R_2} + \cdots \right\}, \tag{14}$$

the integral running over the surface(s), with R_0 the spontaneous curvature radius. From the general expansion (3), we obtain $k_c = f_0 b/2\kappa^2$, $\bar{k}_c = f_0 c/\kappa^2$, and $1/R_0 = -a\kappa/b$. For the three types of boundary conditions, this yields

$$k_c = \frac{\epsilon\phi_0^2}{32\pi\kappa},\quad \bar{k}_c = -\frac{\epsilon\phi_0^2}{16\pi\kappa},\quad \frac{1}{R_0} = -2\kappa \quad \text{(conducting)}\,, \tag{15a}$$

$$k_c = \frac{3\pi\sigma_0^2}{2\epsilon\kappa^3},\quad \bar{k}_c = -\frac{\pi\sigma_0^2}{\epsilon\kappa^3},\quad \frac{1}{R_0} = -\frac{2\kappa}{3} \quad \text{(opaque)}\,, \tag{15b}$$

$$k_c = \frac{\pi\sigma_0^2}{4\epsilon\kappa^3},\quad \bar{k}_c = -\frac{\pi\sigma_0^2}{2\epsilon\kappa^3},\quad \frac{1}{R_0} = 0 \quad \text{(transparent)}\,, \tag{15c}$$

corroborating partial results obtained by different methods.[8-14] Note that the spontaneous curvature term $1/R_0$ is directly linked to the contribution linear in H in (3), and arises from the consideration of the electrolyte energy on one side of the membrane only. If we add the internal and external contributions with changes of signs of the normals, these linear curvature contributions cancel, so $1/R_0 = 0$ as in (15c), while the second-order terms are simply *doubled.*

Topological equilibrium shapes.— As a consequence of the Gauss-Bonnet theorem,

$$\frac{1}{4\pi}\int dS \frac{1}{R_1 R_2} = n_c - n_h\,, \tag{16}$$

where n_c is the number of connected surfaces and n_h is the number of handles (genus), we obtain information about the electrostatic contribution to topological aspects of double-layer thermodynamics.[19] For a single closed membrane immersed in the same electrolyte on both sides, the total curvature energy is $\mathcal{F}_{\mathrm{el}}=|f_0|\kappa^{-2}\psi$, with ψ a dimensionless quantity,

$$\psi=2\pi(b'\tau+c'\chi)\,, \tag{17}$$

where $\tau=(1/2\pi)\int_S dS\,H^2$ is the total mean-square curvature, and $\chi=2(1-n_h)$ is the Euler characteristic of the membrane. For the three physical cases listed above we have $(b',c')=(1,-1);(3,-1);(1,-1)$ (the fixed potential and transparent cases are the same). With (17) we may draw some conclusions about the kinds of shapes and topologies favored by electrostatic energies. Considering all possible topologies, we note that for any closed orientable surface of arbitrary genus, τ satisfies[20] $\tau\geq 2$, the equality being obtained for the round sphere only; hence, $\psi\geq\psi_{\mathrm{sph}}-4\pi c' n_h$. Since $c'<0$, clearly the sphere is the absolute minimum. If we constrain the topology, some interesting results appear,[21] since the free energy now depends only on τ, and $\tau\propto\int dS/R^2$ is a *conformal invariant;* it is conserved by dilations of the surface and also by *all conformal mappings* in *three*-dimensional space. From this, it may be shown that the equilibrium shapes of a membrane with the torus topology form a continuum, and, in the absence of other effects, this degeneracy would lead to the phenomenon of *continuous conformal shape fluctuations.* For the spherical topology, no such degeneracy exists, since conformal maps of course conserve the round sphere and fix the equilibrium shape uniquely.

In summary, we have obtained exact, convergent multiple-scattering expansions for the electrostatic and thermodynamic properties of charged and conducting surfaces within the Debye-Hückel regime, and derived from them geometric and topological information about the role of electrostatics in the elastic properties and stability of such surfaces. The formalism allows for a systematic study of the nonlinear corrections to Debye-Hückel theory, and promises to yield information about the shape dependence of interactions between charged or conducting surfaces. By its generality, it is applicable to any solvent-mediated force between surfaces in which the degree of freedom polarized by the boundaries is described by a massive Gaussian scalar free energy.

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[1] D. Hone, S. Alexander, P. M. Chaikin, and P. Pincus, J. Chem. Phys. **79**, 1474 (1983).

[2] T. Odijk, J. Polym. Sci. Polym. Phys. Ed. **15**, 477 (1977); J. Skolnik and M. Fixman, Macromolecules **10**, 944 (1977).

[3] P. J. Missel, N. A. Mazer, G. B. Benedek, C. Y. Young, and M. C. Carey, J. Phys. Chem. **84**, 1044 (1980).

[4] G. Cevc and D. Marsh, *Phospholipid Bilayers. Physical Principles and Models* (Wiley, New York, 1987); see also S. M. Gruner, J. Phys. Chem. **93**, 7562 (1989), and references therein.

[5] K. S. Cole, *Membranes, Ions, and Impulses* (Univ. of California Press, Berkeley, 1969).

[6] T. C. Halsey, Phys. Rev. A **36**, 5877 (1987), and references therein.

[7] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948); R. J. Hunter, *Foundations of Colloid Science* (Clarendon, Oxford, 1987).

[8] M. Winterhalter and W. Helfrich, J. Phys. Chem. **92**, 6865 (1988).

[9] H. N. W. Lekkerkerker, Physica (Amsterdam) **159A**, 319 (1989).

[10] D. J. Mitchell and B. W. Ninham, Langmuir **5**, 1121 (1989).

[11] M. Kiometzis and H. Kleinert, Phys. Lett. A **140**, 520 (1989).

[12] R. E. Goldstein, A. I. Pesci, and V. Romero-Rochin, Phys. Rev. A **41**, 5504 (1990).

[13] D. Bensimon, F. David, S. Leibler, and A. Pumir (to be published).

[14] P. Pincus, J. F. Joanny, and D. Andelman (to be published).

[15] R. Balian and C. Bloch, Ann. Phys. (N.Y.) **60**, 401 (1970); **84**, 559 (1974).

[16] R. Dautray and J. L. Lyons, *Analyse Mathématique et Calcul Numérique pour les Sciences et les Techniques* (Masson, Paris, 1984), Vol. 1

[17] R. Balian and B. Duplantier, Ann. Phys. (N.Y.) **104**, 300 (1977); **117**, 165 (1978).

[18] W. Helfrich, Z. Naturforsch. **28c**, 693 (1973).

[19] S. Leibler and D. A. Huse, J. Phys. (Paris) **49**, 605 (1988).

[20] T. J. Willmore, *Total Curvature in Riemannian Geometry* (Ellis Horwood Ltd., Chichester, 1982).

[21] B. Duplantier, Service de Physique Théorique Report No. SPhT 90/022 (unpublished).