Thermodynamics of Rough Colloidal Surfaces

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In Debye-Hückel theory, the free energy of an electric double layer near a colloidal (or any other) surface can be related to the statistics of random walks near that surface. We present a numerical method based on this correspondence for the calculation of the double-layer free energy for an arbitrary charged or conducting surface. For self-similar surfaces, we propose a scaling law for the behavior of the free energy as a function of the screening length and the surface dimension. This scaling law is verified by numerical computation. Capacitance measurements on rough surfaces of, e.g., colloids can test these predictions.

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In colloidal physics (and elsewhere) one is faced with the problem of determining the free energy of electric double layers near surfaces of arbitrary shape.[1] In the strong-screening limit, where the Debye-Hückel screening length λ_D is much smaller than any scale of roughness in the surface, this problem can be solved for charged or conducting surfaces using a perturbative expansion in powers of λ_D/R, where R is a typical surface radius of curvature. This perturbation expansion has been successfully performed (for linear screening) about a flat surface, using exact results for various special shapes, and, most generally, using a multiple-scattering formalism.[2–6]

Unfortunately, the perturbative approach is of little use in the *weak-screening* regime, where $R \ll \lambda_D$, or in the *intermediate-screening* regime, where $R \sim \lambda_D$. While the free energy is essentially a local property of the surface in the strong-screening regime, in these other cases nonlocal effects will become important.

In this Letter, we seek to deal with this problem by introducing a general nonperturbative method for calculating double-layer free energies near arbitrary surfaces bounded by electrolytes. This method is based upon the well-known analogy between random walks and the properties of the Laplace operator; the novelty in our method is that we have exploited this analogy to generate an extremely fast and accurate numerical algorithm.[7–9] We show that for conducting surfaces, the free energy is determined by the first-passage time for random walks near the surface, while, for charged surfaces, the free energy is determined by the mean return time for such random walks.

The analogy with random walks only works in the linear screening regime, in which the potential in the electrolyte satisfies the linearized Poisson-Boltzmann equation,

$$\Delta\phi - \lambda_D^{-2}\phi = 0 . \tag{1}$$

The screening length λ_D is given in terms of the temperature T, dielectric constant ϵ, ionic concentration c, and charge e^* by $\lambda_D^2 = \epsilon k_B T/8\pi c e^{*2}$. The linear approximation is valid for surface potentials $\phi_0 \ll \epsilon k_B T/e^*$ or surface charges per unit area $\sigma \ll \epsilon k_B T/\lambda_D e^*$.

A simple case in which our numerical results can be compared with theoretical ideas is that of self-similar surfaces of (Minkowski) dimension D_M, which display roughness over a large range of length scales, offering a near-ideal test of our method. Using simple scaling ideas, we propose that for conducting surfaces at potential ϕ_0, the free energy scales with λ_D as $\mathcal{F} \sim \phi_0^2 \lambda_D^{d-2-D_M}$, while for charged surfaces with surface charge density σ_0, the free energy scales as $\mathcal{F} \sim \sigma_0^2 \lambda_D^{D_M - d + 2}$. These laws are in excellent agreement with our numerical results, and can, in principle, be tested experimentally.

Suppose we have a domain $\mathcal{D}$ bounded by a surface $\mathcal{S}$, which is held at constant potential ϕ_0. The Green's function G_ϕ for Eq. (1) satisfies

$$(\Delta - \lambda_D^{-2}) G_\phi(r,r';\lambda_D^{-1}) = -\delta(r-r') . \tag{2}$$

Here $G_\phi = 0$ when one of its arguments is a point $r = w$ on the boundary. If $\hat{n}(w)$ is the inward normal to the surface at the point w, then the free energy $\mathcal{F}$ in the Debye-Hückel limit may be written in terms of G_ϕ as

$$\mathcal{F}(\phi_0;\lambda_D^{-1}) = \frac{\epsilon\phi_0^2}{8\pi} \int dw \int dw' \, \partial_{\hat{n}(w)} \partial_{\hat{n}(w')} G_\phi(w,w';\lambda_D^{-1}) , \tag{3}$$

where the surface points w, w' are approached from the interior of the domain $\mathcal{D}$.[6]

We will now relate this result to properties of random walkers. Random walkers obey the diffusion equation, whose Green's function Γ is given by

$$\left(\frac{\partial}{\partial t} - D\Delta_r \right) \Gamma(r,r';t) = \delta(r-r')\delta(t) , \tag{4}$$

where D is the diffusion constant and, without loss of generality, we have set the initial time to zero. $\Gamma(r,r';t)$ is the probability that a random walk beginning at time $t=0$ from the point r' reaches the point r at time t. To ensure the correspondence with the constant-potential problem, we use absorbing boundary conditions, with $\Gamma_A(r=w,r';t)=0$ when r is a point w on the boundary. Laplace transforming with respect to time, we obtain

$$-D\left(\Delta_r-\frac{s}{D}\right)\tilde{\Gamma}_A(r,r';s)=\delta(r-r')\,, \tag{5}$$

so the electrostatic and random-walk propagators are related by

$$D\tilde{\Gamma}_A(r,r';s=D\lambda_D^{-2})=G_\phi(r,r';\lambda_D^{-1})\,. \tag{6}$$

The outward flux of probability at w due to a walk that began at the point r' is simply $D\partial_{\hat{n}(w)}\Gamma_A(w,r';t)dw$, and the total probability that the walker is absorbed at time t is the integral of that flux around the boundary. Thus we define $P(t,r')=D\int dw\,\partial_{\hat{n}(w)}\Gamma_A(w,r';t)$, the first-passage-time probability for a random walker starting at r'.

Suppose that we consider random walkers released a small distance a away from the surface, this length being the ultraviolet cutoff of the theory. Let us consider a finite-difference approximation to one of the normal derivatives in Eq. (3). We obtain the free energy

$$\mathcal{F}(\phi_0;\lambda_D^{-1})=\frac{\epsilon\phi_0^2}{8\pi}\lim_{a\to 0^+}\frac{1}{a}\int dw\left(\int dw'\,\partial_{\hat{n}(w)}G_\phi(w,w'+a\hat{n}(w');\lambda_D^{-1})-1\right). \tag{7}$$

From the above, we conclude that the electrostatic free energy can be written in terms of the Laplace transform $\tilde{P}(s)$ of the first-passage-time probability $P(t)$ as

$$\mathcal{F}(\phi_0;\lambda_D^{-1})=-\lim_{a\to 0}\frac{\epsilon\phi_0^2}{8\pi}\frac{1}{a}\int dw[1-\tilde{P}(s=D\lambda_D^{-2};w+a\hat{n})]\equiv-\lim_{a\to 0}\frac{\epsilon\phi_0^2}{8\pi}\frac{1}{a}S[1-\tilde{\mathcal{P}}(s=D\lambda_D^{-2})]\,, \tag{8}$$

where S is the area of the surface $\mathcal{S}$, and we have defined the averaged-return-time probability $\mathcal{P}$. In terms of random walks, the integral over $\mathcal{S}$ is the surface average of the first-passage-time probability, i.e., a sum over all random walks released with uniform distribution near the surface.

For a surface with a specified constant charge density σ_0, the potential will satisfy $\partial_{\hat{n}(w)}\phi(w)=4\pi\sigma_0/\epsilon$, and the associated Green's function G_σ has a vanishing normal derivative at the surface. The free energy can then be written in terms of G_σ as

$$\bar{\mathcal{F}}(\sigma_0;\lambda_D^{-1})=\frac{\sigma_0^2}{8\pi\epsilon}\int dw\int dw'\,G_\sigma(w,w';\lambda_D^{-1})\,. \tag{9}$$

For this problem, we use the diffusive Green's function Γ_R, with reflecting boundary conditions at the boundary $\mathcal{S}$, so that at a boundary point w we have $\partial_{\hat{n}(w)}\Gamma_R(w,r';t)=0$. We then define the probability per unit time $Q(t,r')=(D/a)\int dw\,\Gamma_R(w,r';t)$ that the random walker will strike the surface at time t. The UV cutoff factor a must appear for dimensional reasons.[10] Following similar arguments to the above, we obtain that the free energy $\bar{\mathcal{F}}$ is given in terms of the Laplace transform $\tilde{Q}(s)$ of $Q(t)$ by

$$\begin{aligned}\bar{\mathcal{F}}(\sigma_0;\lambda_D^{-1})&=\lim_{a\to 0}\frac{\sigma_0^2 a}{8\pi\epsilon}\int dw\,\tilde{Q}(s=D\lambda_D^{-2},w)\\&\equiv\lim_{a\to 0}\frac{\sigma_0^2 a}{8\pi\epsilon}S\tilde{Q}(s)\,.\end{aligned} \tag{10}$$

Note that in both Eqs. (8) and (10) it is necessary to make a somewhat arbitrary choice of the UV cutoff. Fortunately, the free energy can be determined exactly in the large-λ_D limit. Thus the appropriate UV cutoff can be determined directly from the numerical results.

In general, the free energy of the system will be of the order of magnitude of the typical potential times a typical charge density integrated over the region of the electrolyte in which the screening charge is concentrated. In the Debye-Hückel approximation, the electrolyte charge density $q=-(\epsilon\phi/4\pi\lambda_D^2)$.

Suppose that we have a conducting surface in d dimensions, which is also self-similar. We expect that the potential will be screened within a distance λ_D of the surface. The total electrolyte volume within this distance is $V(\lambda_D)\sim\lambda_D^d(L/\lambda_D)^{D_M}$, where D_M is the Minkowski dimension of the surface (usually the same as the Hausdorff dimension) and L is the macroscopic scale of the surface.[11] The characteristic value of the potential in this volume will be ϕ_0, the surface potential. The characteristic value of the charge density will be $q\sim\phi_0/\lambda_D^2$. Thus we expect that

$$\mathcal{F}\sim\phi_0^2\lambda_D^{d-2}(L/\lambda_D)^{D_M}\,. \tag{11}$$

For a charged surface with total surface charge Q, we have $q\sim Q/V(\lambda_D)$, and $\phi\sim Q\lambda_D^2/V(\lambda_D)$. Thus

$$\bar{\mathcal{F}}\sim Q^2\lambda_D^{2-d}(\lambda_D/L)^{D_M}\,. \tag{12}$$

Suppose that the domain $\mathcal{D}$ is closed. Then in the limit where λ_D is larger than the scale of the domain, we can solve for the leading behavior of the free energy, finding results that are natural extensions of Eqs. (11) and (12). Suppose the surface is conducting, at potential ϕ_0. Then we can write $\phi(r)=\phi_0+\phi_1(r)$, where $\phi_1\to 0$ as $\lambda_D\to\infty$. To lowest order in λ_D^{-1}, we can write $\mathcal{F}\propto\int dw\,\phi_0\partial_{\hat{n}(w)}\phi_1$. Using $\Delta\phi_1=\lambda_D^{-2}\phi_0+O(\lambda_D^{-4})$, we ob-

tain directly $\mathcal{F} \propto -\phi_0^2 \lambda_D^{-2} V_{\mathcal{D}}$, where $V_{\mathcal{D}}$ is the domain volume, in agreement with the arguments leading to Eq. (11). For the case of constant charge Q, similar arguments yield $\bar{\mathcal{F}} \propto Q^2 \lambda_D^2 / V_{\mathcal{D}}$, which is consistent with Eq. (12).

We can use these results to test a numerical algorithm based upon random walks. It is computationally inefficient to employ random walks of a fixed step size (say, equal to the cutoff length a); this would require enormous numbers of individual steps to span a domain of sufficient size to reveal the various scaling regimes. Random-walk computations are greatly accelerated by the use of variable-step-length walks in which the length of each step is chosen to be as large as possible while remaining less than the minimum distance to the nearest point on the surface.[12]

Given a sequence of such steps, exact information has been lost regarding the true elapsed time t of the total trajectory. However, if we view each step of length l of the trajectory as a random walk to the edge of a region of radius l, then the probability distribution $P(t)$ for the total elapsed time of a sequence of steps can be written in terms of the quantity $P_0(t;l)$, the first-passage-time probability for a walk from the center of a region of radius l to the edge. If the walk begins at point r_0, and passes through the N intermediate points $r_1, \ldots, r_N$, then $P(t)$ is a convolution over the unknown intermediate times $t_1, \ldots, t_N$ at which it arrived at those points:

$$P(t;\{r_i\}) = \int_0^t dt_N \int_0^{t_N} dt_{N-1} \cdots \int_0^{t_2} dt_1 P_0(t-t_N;l_N) \times P_0(t_N - t_{N-1};l_{N-1}) \cdots P_0(t_1;l_1), \quad (13)$$

where $l_n = |r_n - r_{n-1}|$ is the step length of the associated walk.

Although Eq. (13) appears computationally difficult, fortunately, we need only the Laplace transform of this convolution, which satisfies $\tilde{P}(s;\{l_i\}) = \prod_{i=1}^{N} \tilde{P}_0(s;l_i)$. At this point, the particular temporal order of the individual steps of the walk is irrelevant, so we may group together all steps of a given length to obtain $\tilde{P}(s;\{l_i\}) = \prod_j [\tilde{P}_0(s;ja)]^{n_j}$, where we assume that the step lengths are integral multiples of the cutoff a and n_j is the total number of steps of length ja. Thus, we need only know the quantities $\tilde{P}_0(s;ja)$ for the walk to the edge of the region of radius ja. These may be calculated by a simple eigenfunction expansion; in two dimensions the result is $\tilde{P}_0(s;l) = 1/I_0(l\sqrt{s/D})$, with I_0 a Bessel function.

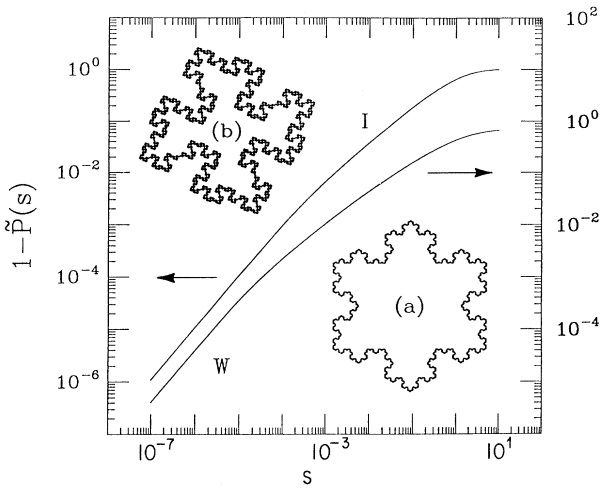

FIG. 1. Laplace-transformed first-passage-time probability $1-\tilde{\mathcal{P}}$ for two fractal domains, as a function of the Laplace transform variable s. In the weak-screening (W) regime ($L \ll \lambda_D$, where L is the domain scale) we find $1-\tilde{\mathcal{P}} \propto s^{\psi}$, with $\psi = 1$; in the intermediate-screening (I) regime ($a \ll \lambda_D \ll L$, where a is the UV cutoff) we find $\psi = D_M/2$, where D_M is the Minkowski dimension of the surface.

From a particular random walk, one obtains the sequence $\{l_i\}$. Note that from a set of such walks, one can calculate the free energy for any value of λ_D. This is the great advantage of this method over conventional relaxation techniques for partial differential equations, in which the entire computation must be performed separately for every value of λ_D.[13] In the results discussed below, we typically used 10^5 random walks for systems with $L/a \sim 10^3$, which we found to give excellent numerical results.

To calculate the return-time distribution, we realize that the probability $\mathcal{Q}(t)$ that a walker strikes the surface at time t may be resolved into contributions from walks with differing numbers of bounces off of the surface,

$$\mathcal{Q}(t) = \mathcal{P}^{(0)}(t) + \int_0^t dt' \mathcal{P}^{(1)}(t-t')\mathcal{P}^{(0)}(t') + \int_0^t dt' \int_0^{t'} dt'' \mathcal{P}^{(2)}(t-t')\mathcal{P}^{(1)}(t'-t'')\mathcal{P}^{(0)}(t'') + \cdots . \quad (14)$$

Here, $\mathcal{P}^{(n)}(t)$ is the probability that the walk occurring between bounce numbers n and $n+1$ took time t. Laplace transformation yields a simple continued product, each of whose terms can be computed using the methods for calculating $\tilde{\mathcal{P}}(s)$.

Figure 1 illustrates the numerical results obtained for the Laplace transform of the average-first-passage-time probability $\mathcal{P}$ for random walks inside two two-dimensional domains of scale L: a Koch curve (a) with $D_M = \ln(4)/\ln(3) \approx 1.26$, and a second fractal domain (b) with $D_M = \frac{3}{2}$. There are three regimes—weak screening, intermediate screening, and cutoff dominated—the first two displaying power-law behavior $1-\tilde{\mathcal{P}} \propto s^{\psi}$. Equation (11) implies that in the intermediate-screening case ($a \ll \lambda_D \ll L$), $\psi = D_M/2$, while the exact result for the weak-screening limit ($L \ll \lambda_D$) implies $\psi = 1$. These predictions are in excellent agree-

ment with the numerical results. For the Koch cure we find $\psi = 0.62 \pm 0.02$ for intermediate screening, and $\psi = 0.99 \pm 0.02$ for weak screening. For the second fractal domain we find $\psi = 0.74 \pm 0.02$ for intermediate screening, and $\psi = 1.00 \pm 0.02$ for weak screening. For $\lambda_D \lesssim a$, the random-walk method breaks down.

We obtain comparable numerical results for the Laplace transform of the return-time probability Q for the same two domains.[10] In this case, we expect $Q(s) \propto s^{\psi}$, with $\psi = -D_M/2$ for intermediate screening, and $\psi = -1$ for weak screening. These predictions are also in good agreement with the numerical results.

Of course, the shape of interesting surfaces will not always be well modeled by fractal geometry. Thus the scaling laws derived above will not always be relevant. Nevertheless, the numerical method can be used to determine the free energy of any surface, given a reliable model for its geometry.

Furthermore, the free energy of a conducting or charged surface defines its effective capacitance. The scaling laws Eqs. (11) and (12) imply that the static capacitance of a fractally rough electrode varies as a power law with the ionic concentration c of the electrolyte. Fractally rough electrodes can be generated by electrodeposition; their capacitance will offer a test of this theory.[14] In the more general case, the numerical method can still determine the dependence of the capacitance upon c. The ability to tune the screening length over wide ranges by varying c suggests the capacitance measurement as a useful probe of rough surfaces.

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