Ray-theory approach to electrical-double-layer interactions

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(Received 21 October 2014; published 18 February 2015)

A novel approach is presented for analyzing the double-layer interaction force between charged particles in electrolyte solution, in the limit where the Debye length is small compared with both interparticle separation and particle size. The method, developed here for two planar convex particles of otherwise arbitrary geometry, yields a simple asymptotic approximation limited to neither small zeta potentials nor the "close-proximity" assumption underlying Derjaguin's approximation. Starting from the nonlinear Poisson-Boltzmann formulation, boundary-layer solutions describing the thin diffuse-charge layers are asymptotically matched to a WKBJ expansion valid in the bulk, where the potential is exponentially small. The latter expansion describes the bulk potential as superposed contributions conveyed by "rays" emanating normally from the boundary layers. On a special curve generated by the centers of all circles maximally inscribed between the two particles, the bulk stress—associated with the ray contributions interacting nonlinearly—decays exponentially with distance from the center of the smallest of these circles. The force is then obtained by integrating the traction along this curve using Laplace's method. We illustrate the usefulness of our theory by comparing it, alongside Derjaguin's approximation, with numerical simulations in the case of two parallel cylinders at low potentials. By combining our result and Derjaguin's approximation, the interaction force is provided at arbitrary interparticle separations. Our theory can be generalized to arbitrary three-dimensional geometries, nonideal electrolyte models, and other physical scenarios where exponentially decaying fields give rise to forces.

DOI: 10.1103/PhysRevE.91.022307 PACS number(s): 82.70.Dd, 47.57.E−, 47.57.jd

I. INTRODUCTION

Solid surfaces become charged when brought in contact with an electrolyte solution. Ionic diffuse-charge layers, where counterions are in excess, concurrently form in the adjacent liquid phase through a balance between electromigration and ionic diffusion. Two such surfaces in proximity experience a force due to the interaction between their diffuse layers. While this force generally decays exponentially with separation, it is well known that even a slight diffuse-layer overlap often gives rise to an appreciable effect [1,2]. Electrical-double-layer forces thus play a fundamental role in a wide range of physical scenarios including solution stability [3], particle dynamics near electrodes [4], colloidal crystals [5,6], atomic force microscopy measurements [7], coal flotation, swelling of clays [8], and numerous biological applications [9–12].

In the framework of mean-field dilute-solution theory, the interaction force may be calculated by solving a nonlinear Poisson-Boltzmann (PB) equation for the electric potential, followed by integration of the electric stress and hydrostatic (osmotic) pressure over the particle surface [13]. This problem is nonlinear and exhibits multiple scales in the common case where the Debye length is small compared to system dimensions. In particular, calculating the force requires resolving the electric potential to exponential order in both the thin diffuse layers and the bulk. The classical one-dimensional parallel-plate configuration is relatively simple to handle. A numerical solution becomes straightforward, and analytic solutions exist in some cases [14,15]; more importantly, simple approximations are available for low voltages, where the problem can be linearized, or for Debye lengths small compared with the distance between the plates, in which case the contributions of two opposing semi-infinite diffuse layers can be superposed.

In most practical scenarios, however, the geometry is nonplanar. For low voltages, the problem can be linearized, paving the way to simplified numerics and various analytic methods, though the latter tend to be rather cumbersome and limited to specific idealized geometries [16–18]. Much more useful is Derjaguin's (or Deryagin's) "close-proximity approximation," where the force between generic (convex) nonplanar surfaces is provided by multiplying the one-dimensional parallel-plate interaction potential by an "effective radius" depending on the local radii of curvature of the surfaces at minimum separation. The approximation holds when both the Debye length and the separation distance are small compared to the radii of curvature characteristic of the surfaces [19]. Toward having useful analytic formulas at hand, it is common to employ one of the approximate forms of the one-dimensional solution, thereby further limiting Derjaguin's approximation to either low voltages or diffuse layers thin compared with separation (the latter being still small compared with particle size) [1]. A popular descendant of Derjaguin's approximation is the surface element integration (SEI) method [20]. Its justification and the asymptotic nature of that approximation are not clear to this author; a stated assumption of the SEI method is that the traction acts normal to the surface, which is not in general the case in electrical-double-layer interactions.

We present here a new approach to analyzing double-layer interactions. It yields—for a general geometry and arbitrary potentials—a simple approximation not limited to close proximity. To this end, we systematically consider the limit where the Debye length is small compared with both the separation distance and the characteristic radii of curvature. The theory is developed for a general geometry consisting of two convex two-dimensional particles of otherwise arbitrary shape. Our methodology builds on what is known as the

superposition approximation, in which for thin double layers the potential is provided by adding single-particle potential distributions [13]. We further follow Refs. [21,22] where the latter distributions are constructed, in the special case of spheres, by matching a nonlinear boundary-layer solution to a linear approximation of the bulk. We introduce here two new ideas which together facilitate obtaining a closed-form approximation for a general geometry: (i) the bulk potential is described by a multidimensional WKBJ "ray solution" and (ii) a special surface is identified on which stress is localized, and thus the leading force is extracted using Laplace's integration method.

II. PROBLEM FORMULATION

Consider two planar convex particles of otherwise arbitrary shape, placed in an unbounded binary symmetric electrolyte of valency $\pm\mathcal{Z}$, far-field concentration c_*, and dielectric constant ϵ_* (Henceforth an asterisk denotes a dimensional quantity). We consider either of the following two surface-charge models [23]: (i) "fixed potential": a voltage ψ_{*i} is prescribed between the surface of particle $i = 1,2$ and the far-field potential; (ii) "fixed charge": a uniform surface-charge density σ_{*i} is prescribed. Our interest is in the force acting on the particles in the case where their position and orientation are prescribed and fixed. The fluid is then at rest, and the solid-electrolyte system attains a state of equilibrium wherein the ionic distributions are Boltzmann distributed [24].

We shall henceforth employ a dimensionless formulation wherein ionic concentrations are normalized by c_*; potentials by the thermal voltage $\varphi_* = k_*T_*/\mathcal{Z}e_*$ (k_*T_* being the Boltzmann temperature and e_* the fundamental charge); lengths by a_*, a typical length scale characteristic of the particles; and stresses and pressures by $\epsilon_*(\varphi_*/a_*)^2$. The dimensionless ionic concentrations and electric potential are, respectively, denoted as $c^{\pm}$ and φ. Taking the latter to decay at large distances, we substitute Boltzmann's distribution $c^{\pm} = e^{\mp\varphi}$ into Poisson's equation, yielding the nonlinear PB equation

$$\delta^2\nabla^2\varphi = \sinh\varphi, \tag{1}$$

where δ is the dimensionless Debye length given by

$$\delta = \lambda_*/a_*, \quad \lambda_*^2 = \frac{\epsilon_*\varphi_*}{2\mathcal{Z}e_*c_*}. \tag{2}$$

On the boundary of each particle ($i = 1,2$), we have one of the two conditions

$$\varphi = \psi_i \quad \text{or} \quad \frac{\partial\varphi}{\partial n} = -\delta^{-1}\sigma_i, \tag{3}$$

corresponding, respectively, to the cases of fixed potential and fixed charge. In the first, ψ_i is the normalized surface potential. In the second, $\sigma_i = \sigma_{*i}\lambda_*/\epsilon_*\varphi_*$ is the normalized surface charge [25]. The problem for the electric potential is closed by the decay condition $\varphi \to 0$ far away from both particles.

Once the potential is determined, the force per unit length (normalized by $\epsilon_*\varphi_*^2/a_*$) on particle i is found by integrating the stresses on the particle boundary $\mathcal{C}_i$,

$$\mathbf{F}_i = \oint_{\mathcal{C}_i} \hat{\mathbf{n}}\cdot\mathsf{T}\,ds. \tag{4}$$

Here $\hat{\mathbf{n}}$ is the local outer normal to $\mathcal{C}_i$, and T is the total stress tensor

$$\mathsf{T} = -p\mathsf{I} + \nabla\varphi\nabla\varphi - \tfrac{1}{2}|\nabla\varphi|^2\mathsf{I}, \tag{5}$$

which includes a hydrostatic pressure term and the electrical (Maxwell) stress tensor; I denotes the unit tensor. The pressure distribution is found in terms of the potential by integrating the momentum balance $\nabla\cdot\mathbf{T} = 0$, or $\nabla p = \nabla^2\varphi\nabla\varphi$, in conjunction with (1). Choosing the pressure to decay at large distances then yields

$$p = \delta^{-2}(\cosh\varphi - 1). \tag{6}$$

Since the total stress (5) is divergence free, the integration boundary in (4) can be deformed to any other closed boundary enclosing particle i that does not intersect or encloses the other particle.

III. THIN-DOUBLE-LAYER ANALYSIS

A. Single particle

We first consider the potential distribution around a single particle, dropping the i subscript for now. Our scheme is based upon exploiting the thin-double-layer limit $\delta \ll 1$. In this singular limit, a thin diffuse-charge layer of thickness $O(\delta)$ forms about the particle boundary. The leading-order boundary-layer solution of (1), in conjunction with (3), and with attenuation at distances $\gg \delta$ from the boundary, is well known [26–28]. It is given by $\varphi \sim \Psi + O(\delta)$, where

$$\tanh\frac{\Psi}{4} = e^{-l/\delta}\tanh\frac{\zeta}{4}. \tag{7}$$

Here $l = O(\delta)$ denotes the normal distance from the surface, and ζ is the leading-order voltage across the layer. A familiar feature of this thin-double-layer solution is that it is asymptotically insensitive to the choice of boundary condition in (3). We shall thus henceforth regard ζ as the prescribed surface property; it is asymptotic to the surface potential ψ and related to the surface charge σ by the Gouy-Chapman relation $\sigma = 2\sinh(\zeta/2)$.

Consider next the bulk domain outside the thin diffuse layer. The decay of the Debye-scale potential,

$$\Psi \sim 4e^{-l/\delta}\tanh\frac{\zeta}{4} \quad \text{as} \quad l/\delta \to \infty, \tag{8}$$

implies that the bulk potential is *exponentially* small in δ. We can therefore linearize (1):

$$\delta^2\nabla^2\varphi = \varphi, \quad \mathbf{x} \in \text{bulk}. \tag{9}$$

This linearity suggests expanding the *bulk* potential according to the WKBJ ansatz [29]

$$\varphi \sim [A(\mathbf{x}) + O(\delta)]\,e^{-u(\mathbf{x})/\delta}. \tag{10}$$

From (8), asymptotic matching of the bulk expansion with the nonlinear Debye-scale potential requires

$$u \sim l, \quad A \sim 4\tanh\frac{\zeta}{4}; \quad \delta \ll l \ll 1. \tag{11}$$

Substitution of (10) into (9) yields at leading order the "eikonal" equation

$$|\nabla u|^2 = 1. \tag{12}$$

This equation is typically solved by the method of characteristics (Charpit's method [30]). The present case is a trivial application of this method: The solution $u(\mathbf{x})$, satisfying the first matching condition given in (11), is just the minimum distance of $\mathbf{x}$ from the particle boundary. Explicitly, if the particle boundary and outer normal are respectively parametrized as $\mathbf{x} = \mathbf{x}_p(s)$ and $\hat{\mathbf{n}}_p(s)$, then the solution can be written parametrically as

$$u(s,l) = l \quad \text{on} \quad \mathbf{x}(s,l) = \mathbf{x}_p(s) + l\hat{\mathbf{n}}_p(s). \tag{13}$$

We say that, at any given boundary point, a straight ray emanates in the direction of the local outward normal. Since the particle is convex, there is a unique ray passing through any given point in the bulk.

The next order of (9) yields the "transport" equation

$$\nabla u \cdot \nabla A = -\frac{A}{2}\nabla^2 u. \tag{14}$$

By noting that $\nabla u = \hat{\mathbf{n}}_p(s)$, (14) can be written as

$$\nabla \cdot (A^2 \hat{\mathbf{n}}_p) = 0; \tag{15}$$

this, together with the matching condition (11), implies that [31]

$$A\,[\rho(s),l;\zeta] = 4\tanh\frac{\zeta}{4}\sqrt{\frac{\rho(s)}{\rho(s)+l}}, \tag{16}$$

with $\rho(s)$ denoting the local radius of curvature of the particle boundary at $x_0(s)$.

The leading-order potential distribution in the entire domain external to a single convex particle has been determined. As depicted in Fig. 1, it is given by the nonlinear distribution (7)

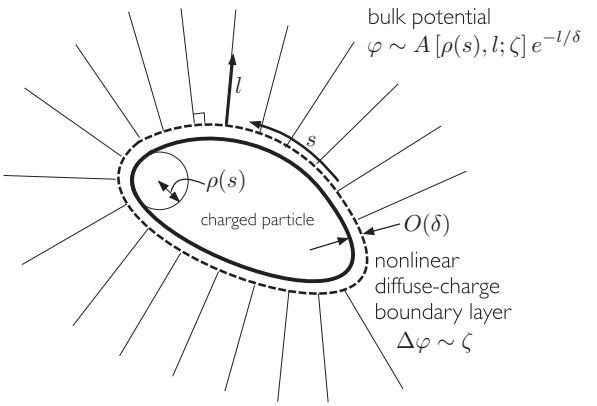

FIG. 1. Asymptotic solution for the electric potential around a single particle.

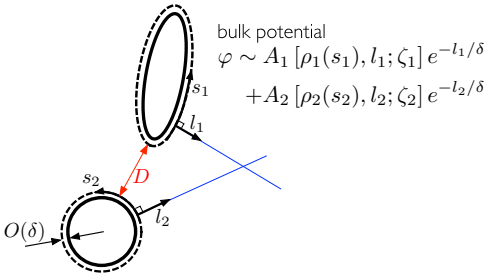

FIG. 2. (Color online) The thin-double-layer solution for two particles, with $\delta \ll D$, obtained by superposing two single-particle solutions.

within the thin diffuse layer and by the ray solution

$$\varphi \sim 4\tanh\frac{\zeta}{4}\sqrt{\frac{\rho(s)}{\rho(s)+l}}e^{-l/\delta} \tag{17}$$

in the bulk domain.

B. Two particles

We return now to the original problem of two convex particles, one of which we allow to extend to a wall. Our interest is in the thin-double-layer limit $\delta \ll 1$, with $D \gg \delta$. In this limit the asymptotic solution for the potential distribution in the bulk between the particles is obtained simply by superposing two ray solutions like (17),

$$\varphi \sim A_1\,[\rho_1(s_1),l_1;\zeta_1]\,e^{-l_1/\delta} + A_2\,[\rho_2(s_2),l_2;\zeta_2]\,e^{-l_2/\delta}, \tag{18}$$

where A_i is provided by, respectively, replacing s, l, ρ, and ζ, by s_i, l_i, ρ_i and ζ_i, in (16). This is valid because each of the two single-particle contributions separately satisfies (9), in an asymptotic sense, and since matching with the diffuse layer of one particle is unaffected by rays emanating from the other particle. The parametric construction of the solution is depicted in Fig. 2.

C. Interaction force

While the contributions to the bulk potential "carried" by the two families of rays superpose, the same does not apply for the stress (5) there, which is nonlinear in the potential. Upon substitution of the ray solution for the bulk potential (18)—with the pressure (6) accordingly expanded for small φ—we find three types of terms: (a) stresses generated by interaction of rays from particle 1 with rays from particles 2 and (b and c) stresses generated by self-interaction of the rays from a single particle, either 1 or 2. These terms are, respectively of order $\delta^{-2}e^{-(l_1+l_2)/\delta}$, $\delta^{-2}e^{-2l_1/\delta}$, and $\delta^{-2}e^{-2l_2/\delta}$; hence, their magnitudes vary immensely with position, and their asymptotic hierarchy is not spatially uniform. This apparent difficulty is avoided by choosing in (4) a special integration curve on which all three estimates are comparable. Such a curve is generated by the centers of all circles maximally inscribed between the two particles. This is because two rays meeting at any point along this curve have traversed the same distance $l_1 = l_2 = r$, r being the radius of the inscribed circle centered at that point (see Fig. 3). On this

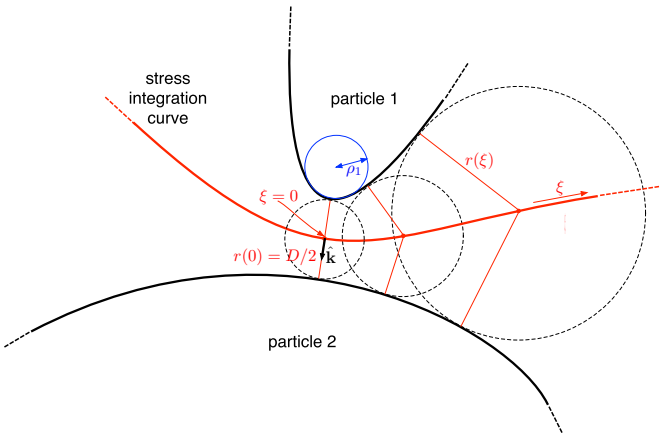

FIG. 3. (Color online) The interaction force calculated by integrating stresses on a bulk curve generated by the centers of all maximally inscribed circles.

curve, the leading stress reads

$$\mathsf{T} \sim \delta^{-2} e^{-2r/\delta} \{ -[A_1^2 + A_2^2 + (1 + \hat{\mathbf{n}}_{p1} \cdot \hat{\mathbf{n}}_{p2}) A_1 A_2] \mathsf{I} + A_1^2 \hat{\mathbf{n}}_{p1} \hat{\mathbf{n}}_{p1} + A_1 A_2 (\hat{\mathbf{n}}_{p1} \hat{\mathbf{n}}_{p2} + \hat{\mathbf{n}}_{p2} \hat{\mathbf{n}}_{p1}) + A_2^2 \hat{\mathbf{n}}_{p2} \hat{\mathbf{n}}_{p2} \}. \tag{19}$$

The stress (19) decays exponentially fast away from the center of the smallest maximally inscribed circle. We can thereby extract the dominant contribution to (4), which is localized about this center, using Laplace's method [33]. Consider without loss of generality the force acting on particle 1. To proceed, we parameterize the integration curve using the *arc-length* variable ξ, with $r(\xi = 0) = D/2$. As $\xi \to 0$, the outward normal to the integration surface is $\hat{\mathbf{n}} \sim \hat{\mathbf{k}}$, where $\hat{\mathbf{k}}$ is a unit vector parallel to the line of minimal distance connecting particle 1 to particle 2. Also in this limit, $\hat{\mathbf{n}}_{p1} \sim \hat{\mathbf{k}}$, $\hat{\mathbf{n}}_{p2} \sim -\hat{\mathbf{k}}$, and

$$A_i \sim 4 \tanh \frac{\zeta_i}{4} \sqrt{\frac{\rho_i}{\rho_i + D/2}}, \quad i = 1,2, \tag{20}$$

where hereafter ρ_i is understood to denote the radius of curvature of surface i at minimum separation (see Fig. 3). Finally, the exponent in (19) is expanded as

$$r(\xi) \sim \frac{D}{2} + \frac{1}{2} \left(\frac{d^2 r}{d\xi^2} \right)_{\xi=0} \xi^2 + \cdots. \tag{21}$$

The result

$$\left(\frac{d^2 r}{d\xi^2} \right)_{\xi=0} = \frac{1}{2} \left[\frac{1}{\rho_1 + D/2} + \frac{1}{\rho_2 + D/2} \right] \tag{22}$$

follows from a local geometric analysis of the separation region, as outlined in the Supplemental Material [34]. Substituting these approximations into (19), the force integral (4) reduces to a Gaussian integral, yielding

$$\mathbf{F}_1 \sim -32 \tanh \frac{\zeta_1}{4} \tanh \frac{\zeta_2}{4} \sqrt{\frac{2\pi \rho_1 \rho_2}{\rho_1 + \rho_2 + D}} \delta^{-3/2} e^{-D/\delta} \hat{\mathbf{k}}. \tag{23}$$

IV. DISCUSSION

Formula (23) provides the requisite leading-order approximation for the interaction force between two convex planar particles [35]. It is apparently the first simple, systematic, and general approximation to hold beyond close proximity. That is, it holds for arbitrary $D \gg \delta$, with $\delta \ll 1$; as demonstrated below, (23) is actually a good approximation when D is just a few times larger than δ. Thus the domain of validity of the new theory complements the validity regime of Derjaguin's approximation: $D \ll 1$ and $\delta \ll 1$. Notably, the validity regimes overlap when $\delta \ll D \ll 1$. It will be demonstrated below that the new approximation is more accurate in this overlap domain, which is of particular practical importance. Moreover, when Derjaguin's approximation can be given in closed form for all $D \ll 1$ (such as at low potentials), a uniformly valid closed-form approximation for arbitrary D may readily be obtained.

A key feature of (23) is that it depends solely on *local* physicochemical and geometrical properties of the particles. While this is a famous feature of Derjaguin's approximation, this is far from evident beyond "close proximity." The generalization is manifested through the dependence of the multiplicative prefactor in (23) on D. For $D \ll 1$, this dependence disappears, and (23) degenerates to the closed-form version of the Derjaguin approximation based on a thin-double-layer parallel-plate solution. The dependence on D also disappears, incidentally, in the case of a finite particle interacting with a plane wall, $\rho_2 \to \infty$. That Derjaguin's approximation fortuitously applies in this special case has been previously observed in direct numerical simulations [13].

A. Numerical example

To demonstrate the applicability of our theory, and to compare it with Derjaguin-type approximations, we have computed the interaction force numerically in what may be the simplest scenario: two identical parallel circular cylinders, whose surfaces are fixed at a low voltage, $\zeta = 0.3$; with this small value, and for the sake of comparison, it is sufficient to solve the linearized PB equation. Choosing a_* as the common radius, formula (23) degenerates to $\sim -2\sqrt{\pi}\zeta^2(1 + D/2)^{-1/2}\delta^{-3/2}e^{-D/\delta}$. In Fig. 4, this expression is shown (thick line) as a function of D, along with the numerical solution for several small values of δ (symbols). The agreement is excellent for D just a few times larger than δ, e.g., starting from $D \approx 0.3$ for $\delta = 0.1$. Also shown in the figure are two versions of the Derjaguin approximation. The first (thin line) is the closed-form expression based on the thin-double-layer solution of the parallel-plate configuration. As already mentioned, this is just the $D \ll 1$ limit of our approximation, and it is valid only in the narrow domain $\delta \ll D \ll 1$. The second (dotted lines) is the closed-form expression based on a linearized low-voltage solution of the parallel-plate configuration, valid for $D \ll 1$ including $D \sim O(\delta)$. This approximation is obtained by adding the term $2\sqrt{2\pi}\zeta^2\delta^{-3/2}e^{-2D/\delta}$ to the thin-double-layer Derjaguin approximation [36]. Note that by adding this term to our approximation instead, we obtain a uniform approximation for entirely arbitrary values of D.

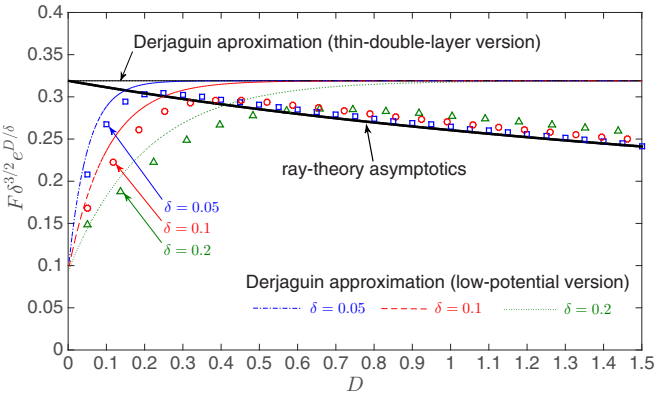

FIG. 4. (Color online) Dimensionless repulsion force F, scaled by $\delta^{-3/2}e^{-D/\delta}$, as a function of minimum separation D between two identical parallel cylinders held at a fixed low potential, $\zeta = 0.3$. See Sec. IV A for details regarding the data and approximations shown.

B. Generalizations

The method presented here can be considerably generalized. In three dimensions, a ray solution for the potential can be constructed in a similar fashion; in the attenuation formula (16) for the multiplicative factor A, planar curvatures are replaced by the respective Gaussian curvatures. The interaction force then follows by retracing the present calculation via Laplace's method, this time in two dimensions, generalizing the integration surface to the "medial surface" generated by the centers of all maximally inscribed *spheres*. Nonuniform zeta potentials are immediately accounted for; in fact, our theory remains valid with ζ in (16) understood to depend on s, and the ζ's appearing in (23) being those at minimum separation. We may also consider the case of nonconvex particles, where rays emanating from the same particle intersect. Because of the exponential decay, typically there would be a unique ray that dominates the contribution at any given point. Pathological cases, e.g., points where an infinite number of rays intersect with the same l, can be dealt with through local analysis in the spirit of the geometric theory of diffraction [37].

Other desirable extensions have to do with the physical model underlying our calculation. One possible generalization would be to consider multispecies and multivalent electrolytes. More fundamentally, it is well known that the Poisson-Boltzmann formulation breaks down at sufficiently high concentrations or surface charge densities and in other scenarios where ion-ion electrostatic interactions become appreciable [38–42]. Distributions of the ion concentrations and electric potential can often still be calculated based on modified continuum models that, similar to the Poisson-Boltzmann model, display exponential decay and which reduce in the bulk to linear equations. Nonideal behavior of that sort will be manifested in our scheme as a modification to the prefactor A. A potentially interesting situation arises in highly concentrated electrolytes or room-temperature ionic liquids, where the diffuse-layer potential oscillates while attenuating [43].

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