Simple electrostatic model applicable to biomolecular recognition

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An exact, analytic solution for a simple electrostatic model applicable to biomolecular recognition is presented. In the model, a layer of high-dielectric constant material (representative of the solvent, water), whose thickness may vary separates two regions of low-dielectric constant material (representative of proteins, DNA, RNA, or similar materials), in each of which is embedded a point charge. For identical charges, the presence of the screening layer always lowers the energy compared to the case of point charges in an infinite medium of low-dielectric constant. Somewhat surprisingly, the presence of a sufficiently thick screening layer also lowers the energy compared to the case of point charges in an infinite medium of *high*-dielectric constant. For charges of opposite sign, the screening layer always lowers the energy compared to the case of point charges in an infinite medium of either high or low dielectric constant. The behavior of the energy leads to a substantially increased repulsive force between charges of the same sign. The attractive force between charges of opposite signs is weaker than in an infinite medium of low dielectric constant material but stronger than in an infinite medium of high dielectric constant material. The presence of this behavior, which we name asymmetric screening, in the simple system presented here confirms the generality of the behavior that was established in a more complicated system of an arbitrary number of charged dielectric spheres in an infinite solvent.

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I. INTRODUCTION

The proper functioning of biomolecular systems depends upon the aggregation of multiple molecules embedded in a high-dielectric constant solvent (water). From the medical point of view, there are both normal complexes (such as ribosomes) and abnormal complexes (such as amyloid formations). The molecular contacts necessary for complex formation occur only when the surfaces of biomolecules approach each other closely. Given the importance of molecular contacts in biology, it is desirable to have a detailed understanding of the molecular forces in this situation. Understanding the microscopic mechanisms involved in the aggregation process would illuminate both normal and abnormal states, and could aid the modification of existing complexes or the design of new ones. This work examines the electrostatic interaction, among the most important interactions in biomolecular systems [1–7].

In previous research that developed a scheme for computing to known precision the energy and forces in a system of an arbitrary number of charged dielectric spheres embedded in an infinite solvent [8], an effect that called asymmetric screening was observed. Namely, the magnitude of attractive electrostatic interactions was decreased (relative to point charges in an infinite solvent) while the magnitude of repulsive electrostatic interactions was increased (again, relative to point charges in an infinite solvent). It was anticipated that this effect aids biomolecules such as proteins in the adoption of correct conformations and in intermolecular recognition. The effect is most pronounced at the short separations, i.e., when molecular surfaces approach each other. Therefore, a model involving planar surfaces is appropriate.

This paper further studies asymmetric screening in a simplified system. Instead of spheres, consider two half spaces, each with a single point charge embedded, separated by an infinite slab of high-dielectric constant material (water, for example). Amenable to complete and thorough analytic examination, this system models two molecular surfaces during the process of binding or aggregation because during a close approach of two biomolecules the curvature of their surfaces becomes less important and the surfaces appear locally planar. The simplicity of the model is an advantage in this case because one wishes to examine in more detail an effect that is already known to occur in the more general and less symmetric system of spheres mentioned above. A simplified model that can be solved completely analytically allows study of the fundamental origin of such generic physical features. If the dielectric constants are swapped, then one would have a model of, for example, a membrane in water. Separation of variables is used to obtain the potential, and from that the energy and the force between the two half spaces. It is more convenient to use the surface charge method [8–10] to obtain the density of surface charge induced on the two surfaces.

II. GENERAL SITUATION

Consider a slab of material of thickness $2d$, infinite in the other directions, with dielectric constant ε_0 sandwiched between two half spaces filled with materials of dielectric constant ε_1 and ε_2, respectively. A charge q_1 lies within the external material with dielectric constant ε_1 a distance s_1 from the internal material (dielectric constant ε_0); a charge q_2 lies within the other external material (with dielectric constant ε_2) a distance s_2 from the internal material and a distance s_1+s_2+2d from the charge q_1. Place the origin of co-

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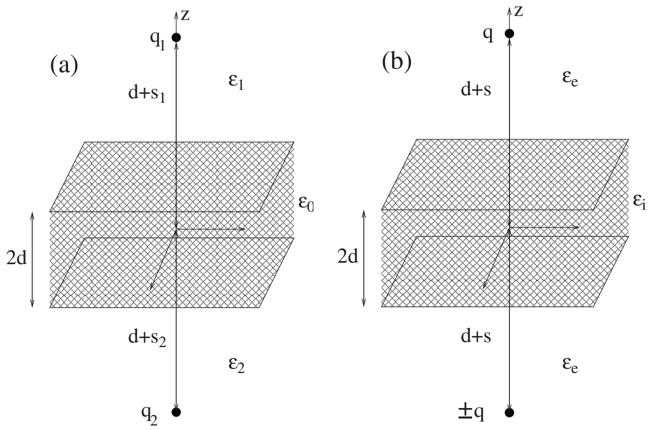

FIG. 1. (a) The most general situation under consideration. The shaded region is infinite in the x and y directions, has thickness $2d$ in the z direction, and is filled with a material with dielectric constant ε_0. The origin is chosen so that the distance from the origin to each surface of the shaded region is d. The unshaded region entirely in the $z>0$ half space is filled with a material with dielectric constant ε_1 and contains a charge q_1 on the positive z axis a distance $d+s_1$ from the origin and a fixed distance s_1 from the surface of the shaded region. The unshaded region entirely in the $z<0$ half space is filled with a material with dielectric constant ε_2 and contains a charge q_2 on the negative z axis a distance $d+s_2$ from the origin and a fixed distance s_2 from the surface of the shaded region. (b) A simplified situation considered in detail. The charges are now of equal magnitude and are constrained to be the same distance from the origin. The cases of identical charges and of opposite charges are both considered. Both unshaded regions have the same dielectric constant, referred to as ε_e. The dielectric constant of the shaded slab is now referred to as ε_i.

ordinates half way between the two charges. Place the z axis through the line joining the two charges, perpendicular to the surfaces of the internal slab of material, and with the positive z axis passing through the charge q_1, as in Fig. 1(a). Because of the symmetry of the system, cylindrical coordinates (ρ, ϕ, and z) will be used.

We wish to find the electric potential (Φ), the electrostatic energy (U), and the force ($\vec{F}$) required to pull the external materials apart. We begin by determining the potential in the general case. Azimuthal symmetry implies that the potential Φ is independent of ϕ. The symbols Φ_0, Φ_1, and Φ_2 will be used to indicate the potential in the interior material, in the material entirely in the positive z region, and in the material entirely in the negative z region, respectively. The boundary conditions are

(1) $\Phi \to 0$ as $z \to \pm\infty$

(2) $\Phi_0(z=d)=\Phi_1(z=d)$

(3) $\Phi_2(z=-d)=\Phi_0(z=-d)$

(4) $\varepsilon_0 \frac{\partial \Phi_0}{\partial z}\Big|_{z=d} = \varepsilon_1 \frac{\partial \Phi_1}{\partial z}\Big|_{z=d}$

(5) $\varepsilon_2 \frac{\partial \Phi_2}{\partial z}\Big|_{z=-d} = \varepsilon_0 \frac{\partial \Phi_0}{\partial z}\Big|_{z=-d}$.

The appropriate general solution of Laplace's equation is

$$\Phi = \sum_{m=0}^{\infty} \int_0^{\infty} J_m(k\rho)[a(k)e^{kz} + b(k)e^{-kz}][c(m)\sin m\phi + d(m)\cos m\phi]dk \to \int_0^{\infty} J_0(k\rho)[a(k)e^{kz} + b(k)e^{-kz}]dk,$$

because of the azimuthal symmetry. In Gaussian units (used throughout), the appropriate form of the potential of a point charge placed at position z' and $\rho'=0$ is [11]

$$\Phi_{\text{point charge}}(\rho,z) = \frac{q}{\epsilon(\rho'=0,z')\sqrt{\rho^2+(z-z')^2}} = \frac{q}{\epsilon(\rho'=0,z')}\int_0^{\infty} e^{-k|z-z'|}J_0(k\rho)dk.$$

The potential in the positive z region of exterior material is a solution of Laplace's equation plus the potential of the screened point source,

$$\Phi_1 = \int_0^{\infty} B_1(k)e^{-kz}J_0(k\rho)dk + \frac{q_1}{\varepsilon_1}\int_0^{\infty} e^{-k|z-d-s_1|}J_0(k\rho)dk, \tag{1}$$

where boundary condition (1) has deleted one of the exponentials in the solution of Laplace's equation. Similarly, the potential in the negative z region of exterior material is

$$\Phi_2 = \int_0^{\infty} A_2(k)e^{kz}J_0(k\rho)dk + \frac{q_2}{\varepsilon_2}\int_0^{\infty} e^{-k|z+d+s_2|}J_0(k\rho)dk. \tag{2}$$

The potential in the interior material is

$$\Phi_0 = \int_0^{\infty} [A_0(k)e^{kz} + B_0(k)e^{-kz}]J_0(k\rho)dk. \tag{3}$$

Boundary conditions (2)–(5) determine the coefficients,

$$B_1(k) = e^{k(d-s_1-s_2)}\frac{e^{ks_2}(\varepsilon_0+\varepsilon_1)(\varepsilon_0-\varepsilon_2)q_1 - e^{k(4d+s_2)}(\varepsilon_0-\varepsilon_1)(\varepsilon_0+\varepsilon_2)q_1 + 4e^{k(2d+s_1)}\varepsilon_0\varepsilon_1 q_2}{-(\varepsilon_0-\varepsilon_1)\varepsilon_1(\varepsilon_0-\varepsilon_2) + e^{4kd}\varepsilon_1(\varepsilon_0+\varepsilon_1)(\varepsilon_0+\varepsilon_2)},$$

$$A_0(k) = 2e^{k(d-s_1-s_2)}\frac{e^{k(2d+s_2)}(\varepsilon_0+\varepsilon_2)q_1 + e^{ks_1}(\varepsilon_0-\varepsilon_1)q_2}{-(\varepsilon_0-\varepsilon_1)(\varepsilon_0-\varepsilon_2) + e^{4kd}(\varepsilon_0+\varepsilon_1)(\varepsilon_0+\varepsilon_2)},$$

$$B_0(k) = 2e^{k(d-s_1-s_2)}\frac{e^{ks_2}(\varepsilon_0-\varepsilon_2)q_1 + e^{k(2d+s_1)}(\varepsilon_0+\varepsilon_1)q_2}{-(\varepsilon_0-\varepsilon_1)(\varepsilon_0-\varepsilon_2) + e^{4kd}(\varepsilon_0+\varepsilon_1)(\varepsilon_0+\varepsilon_2)},$$

$$A_2(k) = e^{k(d-s_1-s_2)} \frac{4e^{k(2d+s_2)}\varepsilon_0\varepsilon_2 q_1 - e^{k(4d+s_1)}(\varepsilon_0+\varepsilon_1)(\varepsilon_0-\varepsilon_2)q_2 + e^{ks_1}(\varepsilon_0-\varepsilon_1)(\varepsilon_0+\varepsilon_2)q_2}{-(\varepsilon_0-\varepsilon_1)\varepsilon_2(\varepsilon_0-\varepsilon_2) + e^{4kd}\varepsilon_2(\varepsilon_0+\varepsilon_1)(\varepsilon_0+\varepsilon_2)}. \quad (4)$$

Not surprisingly, interchanging the subscripts 1 and 2 in the expression for B_1 turns it into A_2.

The distribution of free charge (the two point charges) and the potential determine the energy,

$$U = \frac{1}{2}\int \rho_f(\vec{r})\Phi(\vec{r})d\vec{r} = \frac{q_1}{2}\Phi_1'(\rho=0, z=d+s_1) + \frac{q_2}{2}\Phi_2'(\rho=0, z=-d-s_2), \quad (5)$$

where the primes on the potentials indicate that the potential of the point charge in the corresponding region has been subtracted out in order to avoid infinite self-energies. Substitution of Eqs. (1)–(3) into Eq. (5) yields

$$U = \frac{4q_1q_2\varepsilon_0}{(\varepsilon_0+\varepsilon_1)(\varepsilon_0+\varepsilon_2)}\int_0^\infty \frac{e^{-k(2d+s_1+s_2)}}{1-\alpha_1\alpha_2 e^{-4kd}}dk + \frac{q_1^2}{2\varepsilon_1}\int_0^\infty \frac{e^{-2ks_1}(e^{-4kd}\alpha_2-\alpha_1)}{1-\alpha_1\alpha_2 e^{-4kd}}dk + \frac{q_2^2}{2\varepsilon_2}\int_0^\infty \frac{e^{-2ks_2}(e^{-4kd}\alpha_1-\alpha_2)}{1-\alpha_1\alpha_2 e^{-4kd}}dk, \quad (6)$$

where $\alpha_1 \equiv (\varepsilon_0-\varepsilon_1)/(\varepsilon_0+\varepsilon_1)$ and $\alpha_2 \equiv (\varepsilon_0-\varepsilon_2)/(\varepsilon_0+\varepsilon_2)$.

Because we imagine this situation to be a simplified model of two molecular surfaces separated by a layer of water, the force should be obtained by imagining that the charges are fixed with respect to the materials, in which they are embedded, but the thickness of the interior slab is allowed to vary. In other words, the force we are considering is the negative of the derivative of the energy with respect to $2d$,

$$\vec{F} = -\frac{\partial U}{\partial(2d)}\hat{z}.$$

When expressed in scalar form for the magnitude,

$$F = -\frac{1}{2}\frac{\partial U}{\partial d},$$

a positive (negative) force corresponds to repulsion (attraction). Clearly, this simple model neglects any internal rearrangement of the molecules during the process of interaction, an effect that is believed to be important in many cases. However, while a model designed to capture the behavior of specific molecules would need to include such an effect, our purpose is only to investigate one particular interaction, the very important electrostatic interaction, and so this point is not a concern here. The force is

$$F = \frac{4q_1q_2\varepsilon_0}{(\varepsilon_0+\varepsilon_1)(\varepsilon_0+\varepsilon_2)}\int_0^\infty e^{-k(2d+s_1+s_2)}k\frac{1+\alpha_1\alpha_2e^{-4kd}}{(1-\alpha_1\alpha_2e^{-4kd})^2}dk + \frac{q_1^2}{\varepsilon_1}\alpha_2(1-\alpha_1^2)\int_0^\infty \frac{e^{-k(2s_1+4d)}k}{(1-\alpha_1\alpha_2e^{-4kd})^2}dk + \frac{q_2^2}{\varepsilon_2}\alpha_1(1-\alpha_2^2)\int_0^\infty \frac{e^{-k(2s_2+4d)}k}{(1-\alpha_1\alpha_2e^{-4kd})^2}dk. \quad (7)$$

We now examine two particular cases.

III. TWO CHARGES IN IDENTICAL MEDIA

Let $q_1=q_2\equiv q$, $\varepsilon_1=\varepsilon_2\equiv\varepsilon_e$, $\varepsilon_0\equiv\varepsilon_i$, and $s_1=s_2\equiv s$. We are now considering a slab of material (thickness $2d$ and infinite in the other directions) with dielectric constant ε_i sandwiched between two half spaces filled with a material of dielectric constant ε_e. Internal material is indicated by the subscript "i," and external material is indicated by subscript "e." A charge q lies in the external material a distance s from the internal material. An identical charge q lies in the other semi-infinite external material a distance s from the internal material and a distance $2s+2d$ from the other charge. See Fig. 1(b), with the positive charge chosen. The potential, the energy, and the force follow upon making the appropriate substitutions in Eqs. (1)–(3), (6), and (7), respectively. (Alternatively, it is a simple matter to setup and solve the boundary value problem for this particular situation.)

Making the appropriate substitutions in Eq. (6), letting $\alpha=(\varepsilon_i-\varepsilon_e)/(\varepsilon_i+\varepsilon_e)$, and using the identity $(4\varepsilon_i\varepsilon_e/(\varepsilon_i+\varepsilon_e)^2)=1-\alpha^2$, one finds the energy,

$$U = \frac{q^2}{\varepsilon_e}\int_0^\infty e^{-2ks}\frac{e^{-2kd}(4\varepsilon_i\varepsilon_e/(\varepsilon_i-\varepsilon_e)^2)+\alpha(e^{-4kd}-1)}{1-\alpha^2e^{-4kd}}dk = \frac{q^2}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{1-\alpha e^{2kd}}{1-\alpha e^{-2kd}}dk. \quad (8)$$

One may evaluate the integral by expanding the denominator in a series,

$$U = \frac{q^2}{\varepsilon_e}\int_0^\infty \sum_{n=0}^\infty (\alpha^n e^{-2k(s+(n+1)d)} - \alpha^{n+1}e^{-2k(s+nd)})dk = \frac{q^2}{2\varepsilon_e}\sum_{n=0}^\infty\left(\frac{\alpha^n}{s+(n+1)d} - \frac{\alpha^{n+1}}{s+nd}\right) = \frac{q^2(1-\alpha^2)}{2\varepsilon_e\alpha}\sum_{n=0}^\infty\frac{\alpha^n}{s+nd} - \frac{q^2}{2\varepsilon_e\alpha s} = \frac{q^2(1-\alpha^2)}{2\varepsilon_e\alpha s}{}_2F_1\left(\frac{s}{d},1;\frac{s}{d}+1;\alpha\right) - \frac{q^2}{2\varepsilon_e\alpha s}. \quad (9)$$

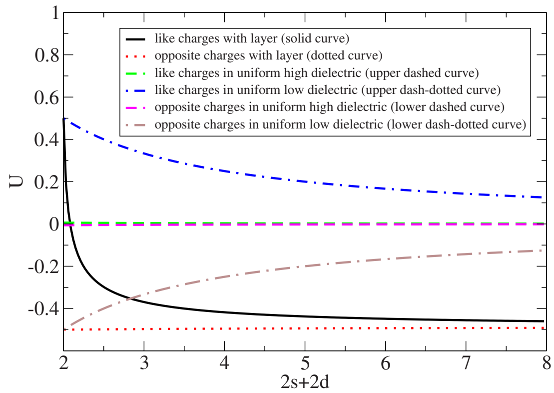

FIG. 2. (Color online) Graphs of the energy as a function of separation, both for identical charges and for opposite charges. For comparison, the energy of point charges, both identical and opposite, in an infinite uniform medium (both ε_e and ε_i) is shown. The calculations are for $\varepsilon_e=1$, $\varepsilon_i=80$, $s=1$, and $q=1$. For opposite charges separated by a high-dielectric layer, the energy varies little. For like charges separated by a high-dielectric layer, the energy at small separations changes rapidly.

where ${}_2F_1$ is a Gauss hypergeometric function.

Even though the series in Eq. (9) was obtained by separation of variables, it can be interpreted as the effect of an infinite sequence of image charges. The charges are located at $2s+2nd$ for $n=0,1,2,\ldots$. The magnitude of the image charges can be read off from the coefficients of $q/[\varepsilon_e(2s+2nd)]$ with appropriate care taken to separate out the direct interaction of the free charges. This interpretation brings to mind recent work that used an approximate series of image charges to study a pair of membranes in a solvent of water and ions [12]. (Of course, the image charges are a computational convenience: the physical charge is induced at the surface and is calculated in the Appendix.)

Because the dielectric constant of water (≈ 80 [13]) is much larger than the dielectric constant of protein (≈ 4 [14]), we are most interested in screening situations: $0\le\alpha\le 1$. In the limit $\alpha\to 1$, the interior slab becomes metallic. In this case we find that $U=-q^2/(\varepsilon_e 2s)$, which is just the interaction

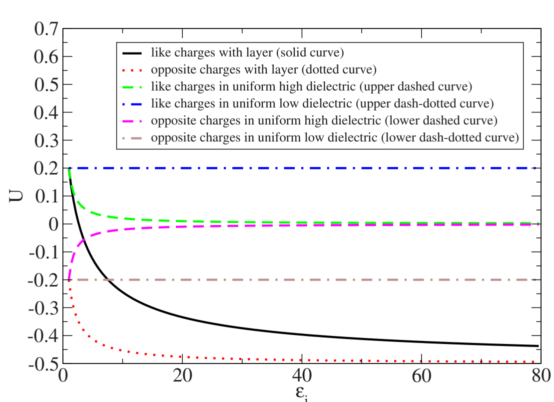

FIG. 3. (Color online) Graphs of the energy as a function of ε_i, both for identical charges and for opposite charges. For comparison, the energy of point charges, both identical and opposite, in an infinite uniform medium (both ε_e and ε_i) is shown. The calculations are for $2s+2d=5$, $\varepsilon_e=1$, $s=1$, and $q=1$.

energy of each free charge with its image charge due to the metal; the two free charges do not "feel" each other. If the media all have the same dielectric constant, then $\alpha=0$ and $U=q^2/[\varepsilon_e 2(s+d)]$, which is simply the energy of two charges in an infinite dielectric medium. Similarly, if $d=0$ we find the obvious result $U=q^2/(\varepsilon_e 2s)$. Finally, in the limit that $d\to\infty$, $U\to-(q^2\alpha)/(\varepsilon_e 2s)<0$. In this case, the two fixed charges do not see each other, but each point charge can still induce a charge density on the nearby surface, and this process will always reduce the energy. Therefore U is negative in this limit. The behavior just summarized can be seen in Figs. 2 and 3.

Making the appropriate substitutions in Eq. (7) and again using the identity $(4\varepsilon_i\varepsilon_e/(\varepsilon_i+\varepsilon_e)^2)=1-\alpha^2$, one finds the force,

$$F=\frac{q^2(1-\alpha^2)}{\varepsilon_e}\int_0^\infty \frac{ke^{-2k(d+s)}}{(1-\alpha e^{-2kd})^2}dk. \tag{10}$$

Rather than performing a similar procedure with series to evaluate the integral, one may simply differentiate the series for U:

$$\begin{aligned}F&=-\frac{q^2\alpha(1-\alpha^{-2})}{\varepsilon_e}\sum_{n=0}^{\infty}\frac{n\alpha^n}{(2s+n2d)^2}\\&=\frac{q^2(1-\alpha^2)}{4\varepsilon_e\alpha}\sum_{n=0}^{\infty}\frac{n\alpha^n}{(s+nd)^2}\\&=\frac{q^2(1-\alpha^2)}{4\varepsilon_e s^2}{}_3F_2\left(2,\frac{s}{d}+1,\frac{s}{d}+1;\frac{s}{d}+2,\frac{s}{d}+2;\alpha\right).\end{aligned} \tag{11}$$

As noted above, for the case of complete screening (i.e., $\alpha=1$) the free charges do not "feel" each other. As expected, the force vanishes in this case. If the media all have the same dielectric constant, then $\alpha=0$ and $F=q^2/[\varepsilon_e(2s+2d)^2]$, the force between two identical charges in an infinite dielectric medium. On the other hand, letting $d\to 0$ we find the curious result $F=(q^2\varepsilon_i)/(\varepsilon_e^2 4s^2)$. When $d\to 0$ one might expect F not to depend on ε_i. However, $F(d)$ samples $U(d)$ in the vicinity of d, and even when $d\to 0$ a dependence is generated on ε_i, which characterizes the material that would fill the gap if one were to draw the two outer regions apart. Indeed, for $d\to 0$ and $\varepsilon_i\to 1$, the force becomes infinite, i.e., the energy changes discontinuously as $d\to 0$ if $\alpha=1$. The behavior just summarized can be seen in Figs. 4 and 5.

The difference between U and the energy of two point charges in an infinite medium of dielectric constant ε_e is defined to be ΔU. (This could not be calculated in the general case because in that case there is no single exterior material.) One finds

$$\begin{aligned}\Delta U&=\frac{q^2}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\left(\frac{1-\alpha e^{2kd}}{1-\alpha e^{-2kd}}-1\right)dk\\&=-\frac{q^2\alpha}{\varepsilon_e}\int_0^\infty e^{-2ks}\frac{1-e^{-4kd}}{1-\alpha e^{-2kd}}dk.\end{aligned} \tag{12}$$

Notice that $\Delta U\le 0$ in the case of screening ($\alpha>0$), which

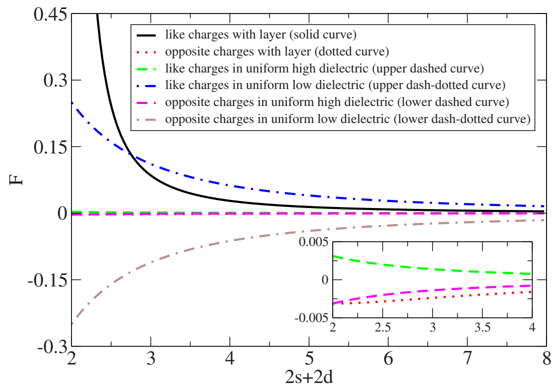

FIG. 4. (Color online) Graphs of the force as a function of separation, both for identical charges and for opposite charges. For comparison, the force between point charges, both identical and opposite, in an infinite uniform medium (both ε_e and ε_i) is shown. The calculations are for $\varepsilon_e=1$, $\varepsilon_i=80$, $s=1$, and $q=1$. The inset is a close-up of the three curves near the x axis for small separations.

makes sense because the energy should be lowered by replacing a portion of the low-dielectric constant material with higher dielectric constant material. If $\alpha=0$, the energy U is the same as the term we have just subtracted off, so $\Delta U=0$. Similarly, if $d=0$, then $\Delta U=0$.

The force difference ΔF corresponding to ΔU can be obtained either from the expression for ΔU or the expression for F:

$$\Delta F = \frac{q^2}{\varepsilon_e}\int_0^\infty k e^{-2k(d+s)}\left[\frac{(1-\alpha^2)}{(1-\alpha e^{-2kd})^2}-1\right]dk. \tag{13}$$

In the case of $d=0$ we find that $\Delta F=\frac{q^2\alpha}{2\varepsilon_e s^2(1-\alpha)}$. If $\alpha=1$, then $\Delta F=-q^2/[\varepsilon_e(2s+2d)^2]<0$ which, as expected, is just the term we subtracted off to form ΔF. Clearly $\Delta F=0$ if $\alpha=0$. The behavior of ΔF for small but nonzero α may be deduced from the series expression for F:

$$\begin{aligned}\Delta F &= \frac{q^2}{4\varepsilon_e}\sum_{n=1}^{\infty}\frac{n(1-\alpha^2)\alpha^n}{\alpha(s+nd)^2}-\frac{q^2}{4\varepsilon_e(s+d)^2}\\ &> \frac{q^2}{4\varepsilon_e}\sum_{n=1}^{\infty}\frac{n(1-\alpha^2)\alpha^n}{\alpha(ns+nd)^2}-\frac{q^2}{4\varepsilon_e(s+d)^2}\\ &= \frac{q^2}{4\varepsilon_e(s+d)^2}\frac{(1-\alpha^2)}{\alpha}\sum_{n=1}^{\infty}\frac{\alpha^n}{n}-\frac{q^2}{4\varepsilon_e(s+d)^2}\\ &= \frac{q^2}{4\varepsilon_e(s+d)^2}\frac{\alpha}{2}+\cdots .\end{aligned}$$

When $\Delta F>0$, the repulsion between identical charges is stronger than the case when both identical charges are in one uniform medium with dielectric constant ε_e. Upon letting $\varepsilon_e\to 1$ (see Figs. 4 and 5), we see that one can have a repulsion larger than in vacuum, a counter-intuitive conclusion. The origin of this behavior can be deduced by returning to Eq. (6), the energy for the more general situation first described. Setting $q_1=0$, $q_2=q$, and $s_2=s$ but retaining distinct dielectric constants in each region, we find

$$\begin{aligned}U &= \frac{q^2}{2\varepsilon_2}\int_0^\infty \frac{e^{-2ks}(e^{-4kd}\alpha_1-\alpha_2)}{1-\alpha_1\alpha_2 e^{-4kd}}dk\\ &= \frac{q^2}{2\varepsilon_2}\sum_{n=0}^{\infty}\alpha_1^n\alpha_2^n\left[\frac{\alpha_1}{2s+4(n+1)d}-\frac{\alpha_2}{2s+4nd}\right],\end{aligned}$$

and

$$F=\frac{q^2}{\varepsilon_2}\sum_{n=0}^{\infty}\alpha_1^n\alpha_2^n\left\{\frac{(n+1)\alpha_1}{[2s+4(n+1)d]^2}-\frac{n\alpha_2}{(2s+4nd)^2}\right\}.$$

Each factor of α_1 (α_2) indicates an image reflection across the surface of the material with dielectric constant ε_1 (ε_2). Notice that the induced charge of the leading term (proportional to α_1) is the same sign as the free charge because the image charge is located on the low dielectric side of the interface. If the image charge were located on the high dielectric side of the interface ($\varepsilon_0<\varepsilon_1$ and $\varepsilon_0<\varepsilon_2$) then the induced charge would have the opposite sign leading to an attractive force similar to the more familiar case of a charge near a conductor.

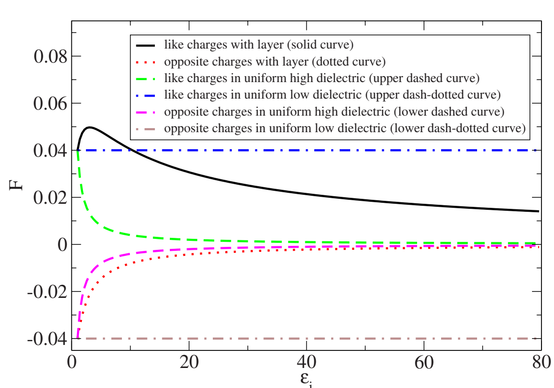

FIG. 5. (Color online) Graphs of the force as a function of ε_i, both for identical charges and for opposite charges. For comparison, the force between point charges, both identical and opposite, in an infinite uniform medium (both ε_e and ε_i) is shown. The calculations are for $2s+2d=5$, $\varepsilon_e=1$, $s=1$, and $q=1$.

Now consider the energy and force differences ($\widetilde{\Delta U}$ and $\widetilde{\Delta F}$) when the comparison is made to the interaction with the ε_i material everywhere. The energy difference in this case, $\widetilde{\Delta U}$, is

$$\begin{aligned}\widetilde{\Delta U} &= \frac{q^2}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\left(\frac{1-\alpha e^{2kd}}{1-\alpha e^{-2kd}}-\frac{\varepsilon_e}{\varepsilon_i}\right)dk\\ &= \frac{q^2}{\varepsilon_i\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{(\varepsilon_i-\varepsilon_e)+\alpha(\varepsilon_e e^{-2kd}-\varepsilon_i e^{2kd})}{1-\alpha e^{-2kd}}dk.\end{aligned} \tag{14}$$

In order to understand the behavior of $\widetilde{\Delta U}$, we observe that $\widetilde{\Delta U}(d=0)=(q^2(\varepsilon_i-\varepsilon_e))/(\varepsilon_i\varepsilon_e 2s)\geq 0$ with equality when $\varepsilon_i=\varepsilon_e$ (i.e., $\alpha=0$). However, as $d\to\infty$, $\widetilde{\Delta U}\to-(q^2\alpha)/(2\varepsilon_e s)$

≤ 0. Evidently, for any positive α, $\widetilde{\Delta U}$ is positive for small d and becomes negative for sufficiently large d. This behavior can be inferred from Fig. 2 Given that $(\varepsilon_i/\varepsilon_e)(1-\alpha)=(1+\alpha)$, $\widetilde{\Delta F}$ is

$$\widetilde{\Delta F} = \frac{q^2}{\varepsilon_i}\int_0^\infty ke^{-2k(s+d)}\left[\frac{(\varepsilon_i/\varepsilon_e)(1-\alpha^2)}{(1-\alpha e^{-2kd})^2}-1\right]dk = \frac{q^2}{\varepsilon_i}\int_0^\infty ke^{-2k(s+d)}\left[\frac{(1+\alpha)^2}{(1-\alpha e^{-2kd})^2}-1\right]dk \geq \frac{q^2}{\varepsilon_i}\int_0^\infty ke^{-2k(s+d)}[(1+\alpha)^2-1]dk \geq 0, \tag{15}$$

which guarantees that $\widetilde{\Delta F}\geq 0$, as would be expected based upon Figs. 4 and 5.

For the case of equal and opposite charges in Fig. 1(b), results for U, F, ΔU, ΔF, $\widetilde{\Delta U}$, and $\widetilde{\Delta F}$ may be obtained using the same methods that yielded Eqs. (8)–(15). As can be seen in Fig. 2, the energy in this case,

$$U = -\frac{q^2}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{1+\alpha e^{2kd}}{1+\alpha e^{-2kd}}dk = \frac{q^2(1-\alpha^2)}{2\varepsilon_e\alpha}\sum_{n=0}^\infty\frac{(-\alpha)^n}{s+nd}-\frac{q^2}{2\varepsilon_e\alpha s}, \tag{16}$$

which is the same as the series for like charges with an overall minus sign and the substitution $\alpha\to-\alpha$, varies little as d goes from 0 to ∞. As a consequence, the magnitude of the force,

$$F = -\frac{q^2(1-\alpha^2)}{\varepsilon_e}\int_0^\infty\frac{ke^{-2k(d+s)}}{(1+\alpha e^{-2kd})^2}dk = \frac{q^2(1-\alpha^2)}{4\varepsilon_e\alpha}\sum_{n=0}^\infty\frac{n(-\alpha)^n}{(s+nd)^2}, \tag{17}$$

is suppressed compared to the case of like charges. The behavior of the force in the case of opposite charges is more consistent with naive intuition: the force with a high dielectric layer is somewhere in between the force with low dielectric everywhere and the force with high dielectric everywhere. The energy differences (with definitions parallel to those for like charges) ΔU

$$\Delta U = -\frac{2q^2\alpha}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{\sinh 2kd}{1+\alpha e^{-2kd}}dk \leq 0, \tag{18}$$

and $\widetilde{\Delta U}$,

$$\widetilde{\Delta U} = \frac{q^2}{\varepsilon_e\varepsilon_i}\int_0^\infty e^{-2k(s+d)}\left[\frac{(\varepsilon_e-\varepsilon_i)+\alpha(\varepsilon_e e^{-2kd}-\varepsilon_i e^{2kd})}{1+\alpha e^{-2kd}}\right]dk \leq 0, \tag{19}$$

are always negative in this case, as can been seen in Figs. 2 and 3. The corresponding force differences ΔF,

$$\Delta F = \frac{q^2}{\varepsilon_e}\int_0^\infty ke^{-2k(s+d)}\left[\frac{\alpha^2-1}{(1+\alpha e^{-2kd})^2}+1\right]dk \geq 0, \tag{20}$$

and $\widetilde{\Delta F}$,

$$\widetilde{\Delta F} = -\frac{q^2}{\varepsilon_i}\int_0^\infty ke^{-2k(s+d)}\left[\frac{(1+\alpha)^2}{(1+\alpha e^{-2kd})^2}-1\right]dk \leq 0, \tag{21}$$

are positive and negative, respectively. The behavior of opposite charges is evidently simpler and more consistent with intuition.

IV. COMMENTS

The energy and force for the case of two point charges in a dielectric medium with a layer of differing dielectric between them has been compared with two baselines: point charges in a uniform medium having the dielectric constant of the separating layer and point charges in a uniform medium having the dielectric constant of the exterior medium. In the latter case, we find that for opposite charges, $\Delta F>0$ always, implying a weakened attraction when compared to the baseline. For identical charges, however, there are cases for which the repulsion is actually enhanced compared to this baseline. Since it is possible to let $\varepsilon_e\to 1$, this situation corresponds to an effective repulsion that is stronger than the vacuum case, a counter-intuitive result. We refer to this behavior as "asymmetric screening."

When both repulsion and attraction are weakened compared to the ε_e baseline, which one is reduced more? This question is easily answered by considering

$$\delta F \equiv \Delta F_{att} - (-\Delta F_{rep}) = \Delta F_{att} + \Delta F_{rep}.$$

When $\delta F>0$, there is a larger reduction of the attraction than of the repulsion, and vice versa. Using Eq. (13) for ΔF_{rep} and Eq. (20) for ΔF_{att}, we find

$$\delta F = \Delta F_{att}+\Delta F_{rep} = \frac{q^2}{\varepsilon_e}\int_0^\infty ke^{-2k(s+d)}\left[\frac{1-\alpha^2}{(1-\alpha e^{-2kd})^2} - \frac{1-\alpha^2}{(1+\alpha e^{-2kd})^2}\right]dk \geq 0.$$

For the case of the ε_i baseline, we see that $\widetilde{\Delta F}$ is always negative for opposite charges. This indicates an enhanced attraction compared to the baseline (when both charges are in a uniform medium of dielectric constant ε_i). For identical charges we have $\widetilde{\Delta F}>0$, implying that the repulsion is always enhanced when compared to this baseline. One can consider

$$\widetilde{\delta F} \equiv \widetilde{\Delta F}_{att} - (-\widetilde{\Delta F}_{rep}) = \widetilde{\Delta F}_{att} + \widetilde{\Delta F}_{rep}.$$

When $\widetilde{\delta F}>0$, the repulsion of identical charges is enhanced more than the attraction of opposite charges is. Using Eq. (15) for $\widetilde{\Delta F}_{rep}$ and Eq. (21) for $\widetilde{\Delta F}_{att}$, we find

$$\widetilde{\delta F} = \widetilde{\Delta F}_{\text{att}} + \widetilde{\Delta F}_{\text{rep}} = \frac{q^2}{\varepsilon_{\text{i}}}\int_0^\infty ke^{-2k(s+d)}\left[\frac{(1+\alpha)^2}{(1-\alpha e^{-2kd})^2} - \frac{(1+\alpha)^2}{(1+\alpha e^{-2kd})^2}\right]dk \geq 0.$$

According to Fig. 4, asymmetric screening is quite pronounced at short ranges, and we expect the phenomenon to play an important role in biomolecular recognition and in the adoption of the native conformation of proteins. Particularly pronounced is the enhanced repulsion between charges of the same sign. This behavior should exert a rather strong veto on poor matching of charges as one part of a molecule interacts with another part or as two molecules interact with each other. Therefore, accurate calculation of electrostatic interactions is essential when considering biomolecular systems.

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APPENDIX: SURFACE CHARGE METHOD

The surface charge method [8–10] provides a relatively easy path to the induced surface charge. In the case of two identical charges, symmetry implies that the induced surface charge densities on the two surfaces are identical functions in the plane. Therefore we may write

$$\Phi = \frac{q}{\varepsilon_{\text{e}}|\vec{r}-(d+s)\hat{z}|} + \frac{q}{\varepsilon_{\text{e}}|\vec{r}+(d+s)\hat{z}|} + \int_{z'=+d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' + \int_{z'=-d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS'. \tag{A1}$$

The induced surface charge density $\sigma(\rho)$ is unknown, but can be expanded in a complete set of functions. Because of the cylindrical symmetry, Bessel functions are the obvious choice in this case. Any reasonably well-behaved function $f(\rho)$ gives rise to the pair of transforms [15],

$$f(\rho) = \int_0^\infty a(\beta)J_\nu(\beta\rho)d\beta,$$

$$a(\beta) = \beta\int_0^\infty f(\rho)J_\nu(\beta\rho)\rho d\rho,$$

allowing us to write the surface charge as

$$\sigma(\rho) = \int_0^\infty S(\beta)J_\nu(\beta\rho)d\beta.$$

Furthermore, the denominator of the integrals in Eq. (A1) can also be expanded in Bessel functions [11],

$$\frac{1}{|\vec{r}-\vec{r}'|} = \sum_{m=-\infty}^{\infty}\int_0^\infty dke^{im(\phi-\phi')}J_m(k\rho)J_m(k\rho')e^{-k|z-z'|}.$$

In the vicinity of the surfaces, the potentials of the point charges are

$$\frac{q}{\varepsilon_{\text{e}}|\vec{r}-(d+s)\hat{z}|} = \frac{q}{\varepsilon_{\text{e}}}\int_0^\infty dkJ_0(k\rho)e^{-k(d+s-z)}$$

and

$$\frac{q}{\varepsilon_{\text{e}}|\vec{r}+(d+s)\hat{z}|} = \frac{q}{\varepsilon_{\text{e}}}\int_0^\infty dkJ_0(k\rho)e^{-k(z+d+s)}.$$

The potential near the boundary at $z=d$ due to the induced surface charge at $z=d$ is

$$\begin{aligned}
\int_{z'=+d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS'
&= \int(\rho' d\phi' d\rho')\left[\int_0^\infty \mathcal{S}(\beta)J_\nu(\beta\rho')d\beta\right] \times \left[\sum_{m=-\infty}^{\infty}\int_0^\infty dke^{im(\phi-\phi')}J_m(k\rho)J_m(k\rho')e^{-k|z-z'|}\right]\\
&= \int_0^\infty d\beta\mathcal{S}(\beta)\int_0^\infty dke^{-k|z-z'|}\sum_{m=-\infty}^{\infty}J_m(k\rho) \times\left[\int d\phi' e^{im(\phi-\phi')}\right]\times\left[\int d\rho'\rho' J_\nu(\beta\rho')J_m(k\rho')\right]\\
&= 2\pi\int_0^\infty d\beta\mathcal{S}(\beta)\int_0^\infty dke^{-k|z-z'|}J_0(k\rho) \times\left[\int d\rho'\rho' J_\nu(\beta\rho')J_0(k\rho')\right].
\end{aligned}$$

Letting $\nu=0$ turns the ρ' integral into a standard one [16],

$$\int_0^\infty J_\nu(\beta\rho)J_\nu(\beta'\rho)\rho d\rho = \frac{\delta(\beta-\beta')}{\beta} \quad (v > -1/2),$$

and therefore

$$\int_{z'=+d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' = 2\pi\int_0^\infty dke^{-k|z-z'|}J_0(k\rho)\mathcal{S}(k)/k.$$

So for $z'=+d$ and $z>d$ (just above the top interface)

$$\int_{z'=+d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' = 2\pi\int_0^\infty dke^{-k(z-d)}J_0(k\rho)\mathcal{S}(k)/k.$$

For $z'=+d$ and $z<d$ (just below the top interface)

$$\int_{z'=+d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' = 2\pi\int_0^\infty dke^{-k(d-z)}J_0(k\rho)\mathcal{S}(k)/k.$$

For $z'=-d$ and z near d one finds a similar formula that is valid either above or below interface,

$$\int_{z'=-d}\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' = 2\pi\int_0^\infty dke^{-k(z+d)}J_0(k\rho)\mathcal{S}(k)/k.$$

The boundary condition at $z=d$ is

$$\varepsilon_i \left.\frac{\partial \Phi_{z\le d}}{\partial z}\right|_{z=d} = \varepsilon_e \left.\frac{\partial \Phi_{z\ge d}}{\partial z}\right|_{z=d},$$

for every value of ρ, which leads to an equation easily solved for $\mathcal{S}(k)$,

$$\mathcal{S}(k) = \frac{qk\alpha e^{-ks}(e^{-2kd}-1)}{2\pi\varepsilon_e(1-\alpha e^{-2kd})}.$$

Therefore

$$\begin{aligned}\sigma(\rho) &= \int_0^\infty J_0(k\rho)\mathcal{S}(k)dk \\ &= \frac{q\alpha}{2\pi\varepsilon_e}\int_0^\infty J_0(k\rho)\frac{ke^{-ks}(e^{-2kd}-1)}{(1-\alpha e^{-2kd})}dk \\ &= -\frac{q\alpha}{2\pi\varepsilon_e}\int_0^\infty J_0(k\rho)ke^{-ks}\left[1+\frac{(\alpha-1)e^{-2kd}}{(1-\alpha e^{-2kd})}\right]dk \\ &= -\frac{q\alpha}{2\pi\varepsilon_e}\left[\int_0^\infty J_0(k\rho)ke^{-ks}dk \right.\\ &\quad \left. + \int_0^\infty J_0(k\rho)ke^{-k(s+2d)}(\alpha-1)\sum_{n=0}^\infty \alpha^n e^{-2knd}dk\right] \\ &= -\frac{q\alpha}{2\pi\varepsilon_e}\left\{\int_0^\infty J_0(k\rho)ke^{-ks}dk \right.\\ &\quad \left. + \sum_{n=0}^\infty \alpha^n(\alpha-1)\int_0^\infty J_0(k\rho)ke^{-k[s+2(n+1)d]}dk\right\}.\end{aligned}$$

Since all variables are real, we make use of the following integral [17]

$$\int_0^\infty e^{-\alpha x}J_\nu(\beta x)x^{\nu+1}dx = \frac{(2\alpha)(2\beta)^\nu\Gamma(\nu+(3/2))}{\sqrt{\pi}(\alpha^2+\beta^2)^{\nu+(3/2)}}$$

for $\nu>-1$ and $\alpha>0$. Recall that $\Gamma(n+(1/2))=\sqrt{\pi}(2n-1)!!2^{-n}$, so that $\Gamma(3/2)=\sqrt{\pi}/2$. Therefore, the surface charge density is

$$\begin{aligned}\sigma(\rho) = -\frac{q\alpha}{2\pi\varepsilon_e}&\left[\frac{s}{(s^2+\rho^2)^{3/2}}\right.\\ &\left.+\sum_{n=0}^\infty \alpha^n(\alpha-1)\frac{s+2(n+1)d}{\{[s+2(n+1)d]^2+\rho^2\}^{3/2}}\right],\end{aligned}$$

from which it is easy to verify that $\int\sigma(\rho)2\pi\rho d\rho=0$.

This charge density can be used to recover same energy and force as before. To compute the energy (and then the force), $\Phi(\rho=0,z=s+d)$ must be computed from $\sigma(\rho)$. For $z'=d$, $\rho=0$, and $z=s+d$, $|\vec{r}-\vec{r}'|^2=s^2+\rho'^2$. Therefore,

$$\begin{aligned}\int\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' &= 2\pi\int\frac{\rho'\sigma(\rho')}{(s^2+\rho'^2)^{1/2}}d\rho' \\ &= 2\pi\int\left[\mathcal{S}(k)\int\frac{\rho' J_0(k\rho')}{(s^2+\rho'^2)^{1/2}}d\rho'\right]dk.\end{aligned}$$

The ρ' integral is found in tables [18] to be

$$\int_0^\infty \frac{xJ_0(xy)}{(a^2+x^2)^{1/2}}dx = \frac{e^{-ay}}{y},$$

and so

$$\int\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' = \frac{q\alpha}{\varepsilon_e}\int_0^\infty e^{-2ks}\frac{e^{-2kd}-1}{1-\alpha e^{-2kd}}dk.$$

For $z'=-d$, $\rho=0$, and $z=s+d$, $|\vec{r}-\vec{r}'|^2=(s+2d)^2+\rho'^2$. The contribution to the potential from the induced surface charge at $z'=-d$ is

$$\int\frac{\sigma(\rho')}{|\vec{r}-\vec{r}'|}dS' = \frac{q\alpha}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{e^{-2kd}-1}{1-\alpha e^{-2kd}}dk.$$

The potential at $\rho=0$ and $z=s+d$ is

$$\begin{aligned}\Phi(\rho=0,z=s+d) &= \frac{q}{\varepsilon_e}\int_0^\infty\left[e^{-k(2s+2d)}+\frac{\alpha e^{-2ks}(e^{-2kd}-1)}{1-\alpha e^{-2kd}}\right.\\ &\quad\left.+\frac{\alpha e^{-k(2s+2d)}(e^{-2kd}-1)}{1-\alpha e^{-2kd}}\right]dk \\ &= \frac{q}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{1-\alpha e^{2kd}}{1-\alpha e^{-2kd}}dk,\end{aligned}$$

and therefore

$$U = \frac{q^2}{\varepsilon_e}\int_0^\infty e^{-2k(s+d)}\frac{1-\alpha e^{2kd}}{1-\alpha e^{-2kd}}dk,$$

in agreement with Sec. III. Because U agrees, everything that follows from U must also agree.

For opposite charges

$$\begin{aligned}\Phi &= \frac{q}{\varepsilon_e|\vec{r}-(d+s)\hat{z}|}-\frac{q}{\varepsilon_e|\vec{r}+(d+s)\hat{z}|}+\int_{z'=+d}\frac{\sigma_+(\rho')}{|\vec{r}-\vec{r}'|}dS' \\ &\quad+\int_{z'=-d}\frac{\sigma_-(\rho')}{|\vec{r}-\vec{r}'|}dS'.\end{aligned}$$

However, by symmetry $\sigma_+=-\sigma_-\equiv\sigma$. The boundary condition yields

$$\mathcal{S}(k) = \frac{qk\alpha e^{-ks}(e^{-2kd}+1)}{2\pi\varepsilon_e(1+\alpha e^{-2kd})}.$$

The surface charge density becomes

$$\begin{aligned}\sigma(\rho) = \frac{q\alpha}{2\pi\varepsilon_e}&\left[\frac{s}{(s^2+\rho^2)^{3/2}}\right.\\ &\left.+\sum_{n=0}^\infty(-\alpha)^n(1-\alpha)\frac{s+2(n+1)d}{\{[s+2(n+1)d]^2+\rho^2\}^{3/2}}\right].\end{aligned}$$

Again, it is easy to verify that $\int\sigma(\rho)2\pi\rho d\rho=0$ and that the energy U reproduces the result in Sec. III.

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