A 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 repulsive 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). 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]-[6]

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 [7], an effect that was 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 speculated that this effect might aid biomolecules such as proteins in the adoption of correct conformations and in intermolecular recognition.

This paper presents further studies of this effect in a simplified system that is amenable to complete and thorough analytic examination. 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. The system studied here can be considered a simplified model of two molecular surfaces during the process of binding or aggregation. 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). 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 [7]-[9] to obtain the density of surface charge induced on the two surfaces.

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FIG. 1: 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 $\varepsilon_0$. 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 $\varepsilon_1$ 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 $\varepsilon_2$ 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.

II. THE GENERAL SITUATION

Consider a slab of material of thickness $2d$, infinite in the other directions, with dielectric constant $\varepsilon_0$ sandwiched between two half-spaces filled with materials of dielectric constant $\varepsilon_1$ and $\varepsilon_2$ respectively. A charge $q_1$ lies within the external material with dielectric constant $\varepsilon_1$ a distance $s_1$ from the internal material (dielectric constant $\varepsilon_0$); a charge $q_2$ lies within the other external material (with dielectric constant $\varepsilon_2$) 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 coordinates 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. Because of the symmetry of the system, cylindrical coordinates ($\rho$, $\phi$, and $z$) will be used.

We wish to find the electric potential ($\Phi$), 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 $\Phi$ is independent of $\phi$. The symbols $\Phi_0$, $\Phi_1$, and $\Phi_2$ 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. $\Phi \rightarrow 0$ as $z \rightarrow \pm\infty$
2. $\Phi_0(z = d) = \Phi_1(z = d)$
3. $\Phi_2(z = -d) = \Phi_0(z = -d)$
4. $\varepsilon_0 \frac{\partial \Phi_0}{\partial z} \bigg|_{z=d} = \varepsilon_1 \frac{\partial \Phi_1}{\partial z} \bigg|_{z=d}$
5. $\varepsilon_2 \frac{\partial \Phi_2}{\partial z} \bigg|_{z=-d} = \varepsilon_0 \frac{\partial \Phi_0}{\partial z} \bigg|_{z=-d}$

The appropriate general solution of Laplace’s equation is

$$\Phi = \sum_{n=0}^{\infty} \int_{0}^{\infty} J_m(k\rho)(ae^{kz} + be^{-kz})(c\sin m\phi + d\cos m\phi) \, dk \rightarrow \int_{0}^{\infty} J_0(k\rho)(ae^{kz} + be^{-kz}) \, dk,$$

because of the azimuthal symmetry. The appropriate form of the potential of a point charge at $\rho = 0$ and $z = z'$ is

$$\frac{1}{\sqrt{\rho^2 + (z - z')^2}} = \int_{0}^{\infty} e^{-k|z-z'|} J_0(k\rho) \, dk.$$

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:

$$\Phi_1 = \int_{0}^{\infty} B_1(k)e^{-kz} J_0(k\rho) \, dk + \frac{q_1}{\varepsilon_1} \int_{0}^{\infty} e^{-k|z-d-s_1|} J_0(k\rho) \, dk,$$

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

$$\Phi_2 = \int_{0}^{\infty} A_2(k)e^{kz} J_0(k\rho) \, dk + \frac{q_2}{\varepsilon_2} \int_{0}^{\infty} e^{-k|z+d+s_2|} J_0(k\rho) \, dk.$$  

The potential in the interior material is

$$\Phi_0 = \int_{0}^{\infty} (A_0(k)e^{kz} + B_0(k)e^{-kz})J_0(k\rho) \, dk.$$  

Boundary conditions 2-5 determine the coefficients:

$$B_1(k) = e^{k(d-s_1-s_2)} \frac{e^{k\xi_2}(\xi_0 + \xi_1)(\xi_0 - \xi_2)q_1 - e^{k(4d+s_2)}(\xi_0 - \xi_1)(\xi_0 + \xi_2)q_1 + 4e^{k(2d+s_1)}e^{\xi_0(1)q_2} - (\xi_0 - \xi_1)\xi_1(\xi_0 - \xi_2) + e^{4kd}\xi_1(\xi_0 + \xi_1)(\xi_0 + \xi_2)}{-(\xi_0 - \xi_1)\xi_1(\xi_0 - \xi_2) + e^{4kd}\xi_1(\xi_0 + \xi_1)(\xi_0 + \xi_2)}$$

$$A_0(k) = 2e^{k(d-s_1-s_2)} \frac{e^{k(4d+s_2)}(\xi_0 + \xi_2)q_1 + e^{k\xi_1}(\xi_0 - \xi_1)q_2}{-(\xi_0 - \xi_1)\xi_1(\xi_0 - \xi_2) + e^{4kd}\xi_1(\xi_0 + \xi_1)(\xi_0 + \xi_2)}$$

$$B_0(k) = 2e^{k(d-s_1-s_2)} \frac{e^{k\xi_2}(\xi_0 - \xi_2)q_1 + e^{k(2d+s_1)}(\xi_0 + \xi_1)q_2}{-(\xi_0 - \xi_1)\xi_1(\xi_0 - \xi_2) + e^{4kd}\xi_1(\xi_0 + \xi_1)(\xi_0 + \xi_2)}$$

$$A_2(k) = e^{k(d-s_1-s_2)} \frac{4e^{k(2d+s_1)}\xi_0\xi_2q_1 - e^{k(4d+s_1)}(\xi_0 + \xi_1)(\xi_0 - \xi_2)q_2 + e^{k\xi_1}(\xi_0 - \xi_1)(\xi_0 + \xi_2)q_2}{-(\xi_0 - \xi_1)\xi_1(\xi_0 - \xi_2) + e^{4kd}\xi_1(\xi_0 + \xi_1)(\xi_0 + \xi_2)}.$$  

Not surprisingly, interchanging the indices 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:

$$U = \frac{1}{2} \int \rho f \phi = \frac{q_1}{2} \Phi_1'(\rho = 0, z = d + s_1) + \frac{q_2}{2} \Phi_2'(\rho = 0, z = -d - s_2).$$
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 Eq. (1), Eq. (2), and Eq. (4) into Eq. (5) yields

\[
U = \frac{4q_1 q_2 \varepsilon_0}{(\varepsilon_0 + \varepsilon_1)(\varepsilon_0 + \varepsilon_2)} \int_0^\infty e^{-k(2d+q_1+q_2)} \frac{1}{1 - \alpha_1 \alpha_2 e^{-4kd}} \, dk + \frac{q_1^2}{2 \varepsilon_1} \int_0^\infty e^{-2ks_2 (1 - \alpha_1) \alpha_2} \frac{1}{1 - \alpha_1 \alpha_2 e^{-4kd}} \, dk
\]

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 materials 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 \( 2d \):

\[
\vec{F} = -\frac{\partial U}{\partial (2d)} \hat{z},
\]

or in scalar form for the magnitude

\[
F = -\frac{1}{2} \frac{\partial U}{\partial d}.
\]

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

\[
F = \frac{4q_1 q_2 \varepsilon_0}{(\varepsilon_0 + \varepsilon_1)(\varepsilon_0 + \varepsilon_2)} \int_0^\infty e^{-k(2d+q_1+q_2)} \frac{1}{1 - \alpha_1 \alpha_2 e^{-4kd}} \, dk + \frac{q_1^2 \alpha_1 (1 - \alpha_1^2)}{\varepsilon_1} \int_0^\infty e^{-k(2s_1+4d)} \frac{1}{1 - \alpha_1 \alpha_2 e^{-4kd}} \, dk + \frac{q_2^2 \alpha_2 (1 - \alpha_2^2)}{\varepsilon_2} \int_0^\infty e^{-k(2s_2+4d)} \frac{1}{1 - \alpha_1 \alpha_2 e^{-4kd}} \, dk.
\]

We now examine two particular cases.

### III. TWO IDENTICAL CHARGES IN IDENTICAL MEDIA

Let \( q_1 = q_2 = q \), \( \varepsilon_1 = \varepsilon_2 = \varepsilon_e \), \( \varepsilon_0 = \varepsilon_i \), and \( s_1 = s_2 = s \). We are now considering a slab of material (thickness \( 2d \) and infinite in the other directions) with dielectric constant \( \varepsilon_i \) sandwiched between two half-spaces filled with a material of dielectric constant \( \varepsilon_e \). (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. 2 with the positive charge chosen. The potential, the energy, and the force follow upon making the appropriate substitutions in Eqs. (1), Eq. (3), and Eq. (7) respectively. (Alternatively, it is a simple matter to set up and solve the boundary value problem for this particular situation.)

Making the appropriate substitutions in Eq. (6), letting \( \alpha = (\varepsilon_1 - \varepsilon_e)/(\varepsilon_1 + \varepsilon_e) \), and using the identity \((4\varepsilon_1 \varepsilon_e/((\varepsilon_1 + \varepsilon_e)^2) = 1 - \alpha^2 \), one finds the energy:

\[
U = \frac{q^2}{\varepsilon_e} \int_0^\infty e^{-2ks} e^{-2kd}(4\varepsilon_1 \varepsilon_e/(\varepsilon_1 - \varepsilon_e)^2) + \alpha e^{-4kd} - 1) \, dk
\]

\[
= \frac{q^2}{\varepsilon_e} \int_0^\infty e^{-2k(s+d)} \frac{1 - \alpha^2 e^{-4kd}}{1 - \alpha e^{-2kd}} \, dk.
\]
FIG. 2: 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 $\varepsilon_e$. The dielectric constant of the shaded slab is now referred to as $\varepsilon_i$.

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

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

$$= \frac{q^2}{2\varepsilon_e} \sum_{n=0}^\infty \left( \frac{\alpha^n}{s + (n+1)d} - \frac{\alpha^{n+1}}{s + nd} \right)$$

$$= \frac{q^2(1-\alpha^2)}{2\varepsilon_e\alpha s} \sum_{n=0}^\infty \frac{\alpha^n}{s + nd} - \frac{q^2}{2\varepsilon_e\alpha s}$$

$$= \frac{q^2(1-\alpha^2)}{2\varepsilon_e\alpha s} \, _2F_1 \left( \frac{s}{d}, 1; \frac{s}{d} + 1; \alpha \right) - \frac{q^2}{2\varepsilon_e\alpha s}.$$  (9)

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
FIG. 3: 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 $\varepsilon_e$ and $\varepsilon_i$) 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.

infinite sequence of image charges. The charges have separations $2s + 2nd$ 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.\[11\]

Because the dielectric constant of water ($\approx 80$\[12\]) is much larger than the dielectric constant of protein ($\approx 4$\[13\]), we are most interested in screening situation: $0 \leq \alpha \leq 1$. In the limit $\alpha \rightarrow 1$, the interior slab becomes metallic. In this case we find that $U = -q^2/(\varepsilon_e 2s)$, which is just the interaction 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 $d \rightarrow \infty$, $U \rightarrow -(q^2 \alpha)/(\varepsilon_e 2s) < 0$. 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 Fig. 3 and Fig. 4.

Making the appropriate substitutions in Eq. (7) and again using the identity $(4\varepsilon_1\varepsilon_e)/(\varepsilon_1 + \varepsilon_e)^2 = 1 - \alpha^2$, one finds the force:

$$F = \frac{q^2(1 - \alpha^2)}{\varepsilon_e} \int_0^\infty \frac{ke^{-2kd}}{(1 - \alpha e^{-2kd})^2} \, dk.$$

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

$$F = -\frac{q^2 \alpha (1 - \alpha^2)}{\varepsilon_e} \sum_{n=0}^\infty \frac{n \alpha^n}{(2s + n2d)^2}$$

$$= \frac{q^2 (1 - \alpha^2)}{4\varepsilon_e \alpha} \sum_{n=0}^\infty \frac{n \alpha^n}{(s + nd)^2}.$$

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 $F = q^2/(\varepsilon_e(2s+2d)^2)$,
FIG. 4: Graphs of the energy as a function of $\varepsilon_i$, 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 $\varepsilon_e$ and $\varepsilon_i$) is shown. The calculations are for $2s + 2d = 5$, $\varepsilon_e = 1$, $s = 1$, and $q = 1$.

the force between two identical charges in an infinite dielectric medium. On the other hand, if $d = 0$ we find the curious result $F = (q^2 \varepsilon_i)/((\varepsilon_e^2 4s^2))$. When $d = 0$ one might expect $F$ not to depend on $\varepsilon_i$. However, $F(d)$ samples $U(d)$ in the vicinity of $d$, and even when $d = 0$ a dependence is generated on $\varepsilon_i$, which characterizes the material that would fill the gap if one were to draw the two outer regions apart. Indeed, for $d = 0$ and $\varepsilon_i \rightarrow 1$, the force becomes infinite, i.e., the energy changes discontinuously at $d = 0$ if $\alpha = 1$. The behavior just summarized can be seen in Fig. 5 and Fig. 6.

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

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

Notice that $\Delta U \leq 0$ in the case of screening ($\alpha > 0$), which 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 $\Delta F$ corresponding to $\Delta U$ can be obtained either from the expression for $\Delta U$ or the expression for $F$:

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

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 $\Delta F$. Clearly $\Delta F = 0$ if $\alpha = 0$. The behavior of $\Delta F$ for small but non-zero
FIG. 5: 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 $\varepsilon_e$ and $\varepsilon_i$) 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.

FIG. 6: Graphs of the force as a function of $\varepsilon_i$, 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 $\varepsilon_e$ and $\varepsilon_i$) is shown. The calculations are for $2s + 2d = 5$, $\varepsilon_e = 1$, $s = 1$, and $q = 1$. 
\( \alpha \) may be deduced from the series expression for \( F \):

\[
\Delta F = \frac{q^2}{4\varepsilon_0} \sum_{n=1}^{\infty} \frac{\alpha(1 - \alpha^2)\alpha^n}{\alpha(s + nd)^2} - \frac{q^2}{4\varepsilon_0(s + d)^2}
\]

\[
> \frac{q^2}{4\varepsilon_0} \sum_{n=1}^{\infty} \frac{(1 - \alpha^2)\alpha^n}{\alpha(ns + nd)^2} - \frac{q^2}{4\varepsilon_0(s + d)^2}
\]

\[
= \frac{q^2}{4\varepsilon_0(s + d)^2} \left(\frac{1}{\alpha} \sum_{n=1}^{\infty} \frac{\alpha^n}{n} - \frac{q^2}{4\varepsilon_0(s + d)^2}\right)
\]

\[
= \frac{q^2}{4\varepsilon_0(s + d)^2} \frac{\alpha}{2} + O(\alpha^2).
\]

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 \( \varepsilon_e \). Upon letting \( \varepsilon_e \to 1 \) (see Fig. 3 and Fig. 4), 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

\[
U = \frac{q^2}{2\varepsilon_2} \int_0^\infty e^{-2ks} \frac{\alpha_1}{1 - \alpha_1} e^{-2kd} \, dk
\]

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

and

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

Each factor of \( \alpha_1 \) (\( \alpha_2 \)) indicates an image reflection across the surface of the material with dielectric constant \( \varepsilon_1 \) (\( \varepsilon_2 \)). Notice that the induced charge of the leading term (proportional to \( \alpha_1 \)) 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.

Now consider the energy and force differences (\( \Delta U \) and \( \Delta F \)) when the comparison is made to the interaction with the \( \varepsilon_1 \) material everywhere. The energy difference in this case, \( \Delta U \), is

\[
\Delta \tilde{U} = \frac{q^2}{\varepsilon_1\varepsilon_\varepsilon} \int_0^\infty e^{-2k(s + d)} \left( \frac{1 - \alpha e^{-2kd}}{1 - \alpha e^{-2kd} - \varepsilon_\varepsilon} \right) \, dk
\]

\[
= \frac{q^2}{\varepsilon_1\varepsilon_\varepsilon} \int_0^\infty e^{-2k(s + d)} \left( \frac{\varepsilon_\varepsilon}{\varepsilon_\varepsilon} + \alpha \varepsilon_\varepsilon e^{-2kd} - \varepsilon_\varepsilon e^{-2kd} \right) \, dk.
\]

In order to understand the behavior of \( \Delta \tilde{U} \), we observe that \( \Delta \tilde{U}(d = 0) = (q^2(\varepsilon_\varepsilon - \varepsilon_e))/(\varepsilon_\varepsilon\varepsilon_\varepsilon 2s) \geq 0 \) with equality when \( \varepsilon_1 = \varepsilon_\varepsilon \) (i.e., \( \alpha = 0 \)). However, as \( d \to \infty \), \( \Delta \tilde{U} \to -(q^2\alpha)/(2\varepsilon_\varepsilon s) \leq 0 \). Evidently, for any positive \( \alpha \), \( \Delta \tilde{U} \) is positive for small \( d \) and becomes negative for sufficiently large \( d \). This behavior can be inferred from Fig. 3. Given that \( (\varepsilon_1/\varepsilon_\varepsilon)(1 - \alpha) = (1 + \alpha) \), \( \Delta \tilde{F} \) is

\[
\Delta \tilde{F} = \frac{q^2}{\varepsilon_1} \int_0^\infty ke^{-2k(s + d)} \left[ \frac{(\varepsilon_1/\varepsilon_\varepsilon)(1 - \alpha^2)}{(1 - \alpha e^{-2kd})^2} - 1 \right] \, dk
\]

\[
= \frac{q^2}{\varepsilon_1} \int_0^\infty ke^{-2k(s + d)} \left[ \frac{(1 + \alpha)^2}{(1 - \alpha e^{-2kd})^2} - 1 \right] \, dk
\]

\[
\geq \frac{q^2}{\varepsilon_1} \int_0^\infty ke^{-2k(s + d)} [(1 + \alpha)^2 - 1] \, dk \geq 0,
\]

which guarantees that \( \Delta \tilde{F} \geq 0 \), as would be expected based upon Figs. 3 and 4.
IV. TWO OPPOSITE CHARGES IN IDENTICAL MEDIA

Consider the same situation as in the previous section except that the two charges are of opposite sign. Namely, let \( q_1 \equiv q, q_2 = -q, \varepsilon_1 = \varepsilon_2 \equiv \varepsilon_\alpha, \varepsilon_0 \equiv \varepsilon, \) and \( s_1 = s_2 \equiv s. \) See Fig. 2 with the negative charge chosen. The potential, the energy, and the force follow upon making the appropriate substitutions in Eqs. (13), Eq. (6), and Eq. (7), respectively. (Alternatively, it is a simply matter to set up and solve the boundary value problem for this particular situation.)

Making the appropriate substitutions in Eq. (6), letting \( \alpha = (\varepsilon_1 - \varepsilon_e)/(\varepsilon_1 + \varepsilon_e), \) and using the identity \((4\varepsilon_1\varepsilon_e/(\varepsilon_1 - \varepsilon_e)^2) = 1 - \alpha^2,\) one finds the energy:

\[
U = \frac{q^2}{\varepsilon_e} \int_0^\infty e^{-2kd s} \left(1 - \frac{1 - \alpha^2}{1 - \alpha e^{-4kd}}\right) dk = -\frac{q^2}{\varepsilon_e} \int_0^\infty e^{-2k(s+d)} \frac{1 + \alpha e^{-2kd}}{1 + \alpha e^{-2kd}} dk.
\]

(16)

Again, we are most interested in screening situation: \( 0 \leq \alpha \leq 1. \) When \( \alpha = 1 \) (perfect screening), we find that \( U = -q^2/(\varepsilon_e 2s), \) which is just the interaction 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 \( d \rightarrow \infty, U \rightarrow -(q^2 \alpha)/(\varepsilon_e 2s) < 0. \) 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. Note that if \( \alpha \) is close to unity (e.g., a water solvent), \( U \) varies little as \( d \) goes from 0 to \( \infty. \) The behavior just summarized can be seen in Fig. 3 and Fig. 4. Comparing Eq. (16) with Eq. (5), one sees that the series for \( U \) is the series for identical charges with an overall minus sign and the substitution \( \alpha \rightarrow -\alpha. \)

Making the appropriate substitutions in Eq. (7) and again using the identity \((4\varepsilon_1\varepsilon_e/(\varepsilon_1 - \varepsilon_e)^2) = 1 - \alpha^2,\) one finds the force:

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

(17)

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 opposite charges in an infinite dielectric medium. If \( d = 0 \) we find the somewhat non-obvious result \( F = -q^2/(\varepsilon_e 4s^2), \) the explanation for which is the same as in the case of identical 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 behavior just summarized can be seen in Fig. 5 and Fig. 6. Comparing Eq. (17) with Eq. (10), one sees that the series for \( F \) is the series for identical charges with an overall minus sign and the substitution \( \alpha \rightarrow -\alpha. \)

The energy difference \( \Delta U \) is now calculated along the lines used in the case of identical charges:

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

(18)

\[
= -\frac{2q^2\alpha}{\varepsilon_e} \int_0^\infty e^{-2k(s+d)} \frac{\sinh 2kd}{1 + \alpha e^{-2kd}} dk \leq 0.
\]

Since \( U(d = 0) = -q^2/(\varepsilon_e (2s + 2d)) \) and \( U \rightarrow -q^2\alpha/(2\varepsilon_\alpha s) \) as \( d \rightarrow \infty, \) it is clear that \( \Delta U \) should be negative (see Fig. 3). As expected, the energy difference \( \Delta U \) vanishes both for \( d = 0 \) and for \( \alpha = 0. \) For \( \alpha = 1, \) each charge interacts with its image charge, and therefore \( \Delta U = -(q^2 d)/(2\varepsilon_e s(s + d)). \)

Now consider \( \Delta F \) for opposite charges:

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

(19)

The magnitude of the attractive force between opposite charges with a screening layer is always less than when both charges are in one uniform dielectric medium with dielectric constant \( \varepsilon_e. \) This agrees with intuition upon letting \( \varepsilon_e \rightarrow 1. \) As expected, \( \Delta F \) vanishes if \( \alpha = 0. \) Also, \( \Delta F = q^2/(\varepsilon_e (2s + 2d)^2) \) if \( \alpha = 1, \) which confirms that there is no
force between charges that have a metal between them. For \( d = 0 \), the force difference \( \Delta F = (q^2 \alpha)/(2 \varepsilon_e s^2 (1 + \alpha)) \) depends on \( \alpha \) for the reason noted in the case of identical charges.

The energy difference when the comparison is made to the interaction with the \( \varepsilon_i \) material everywhere is \( \Delta \tilde{U} \):

\[
\Delta \tilde{U} = \frac{q^2}{\varepsilon_i} \int_0^\infty e^{-2kd(s+d)} \left[ \frac{\varepsilon_e - \varepsilon_i}{\varepsilon_i} - \frac{1 + \alpha e^{2kd}}{1 + \alpha e^{-2kd}} \right] \frac{\varepsilon_e - \varepsilon_i}{\varepsilon_e (1 + \alpha e^{-2kd})^2} - \frac{1}{2} \right] \, dk \tag{20}
\]

As expected on the basis of Fig. 3, \( \Delta \tilde{U} \) is less than or equal to 0 since both terms within the square brackets are less than or equal to 0 in the case of screening \((0 \leq \alpha \leq 1)\). For \( \alpha = 0 \), the energy difference \( \Delta \tilde{U} \) vanishes, while for \( \alpha = 1 \) and \( d \to \infty \), \( \Delta \tilde{U} = -q^2/(\varepsilon_e 2s) \), the energy of interaction due to the presence of image charges. For \( d = 0 \), \( \Delta \tilde{U} = q^2(\varepsilon_e - \varepsilon_i)/(2\varepsilon_e \varepsilon_i s) \).

Now consider \( \Delta \tilde{F} \):

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

The attraction between unlike charges in our setting is always stronger than when the charges are in a uniform dielectric medium of dielectric constant \( \varepsilon_i \). Clearly, \( \Delta \tilde{F} \) vanishes when \( \alpha = 0 \) and when \( d = 0 \).

V. 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 \( \varepsilon_e \) baseline, which one is reduced more? This question is easily answered by considering

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

When \( \delta F > 0 \), there is a larger reduction of the attraction than of the repulsion, and vice versa. Using Eq. (13) for \( \Delta F_{\text{rep}} \) and Eq. (11) for \( \Delta F_{\text{att}} \), we find

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

For the case of the \( \varepsilon_i \) baseline, we see that \( \Delta \tilde{F} \) 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 \( \varepsilon_i \)). For identical charges we have \( \Delta \tilde{F} > 0 \), implying that the repulsion is always enhanced when compared to this baseline. One can consider

\[
\delta \tilde{F} \equiv \Delta \tilde{F}_{\text{att}} - (-\Delta \tilde{F}_{\text{rep}}) = \Delta \tilde{F}_{\text{att}} + \Delta \tilde{F}_{\text{rep}}.
\]

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

\[
\delta \tilde{F} = \Delta \tilde{F}_{\text{att}} + \Delta \tilde{F}_{\text{rep}} = \frac{q^2}{\varepsilon_i} \int_0^\infty e^{-2kd(s+d)} \left[ \frac{(1 + \alpha)^2}{(1 - \alpha e^{-2kd})^2} - \frac{(1 + \alpha)^2}{(1 + \alpha e^{-2kd})^2} \right] \, dk \geq 0.
\]
According to Fig. 5, 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 interaction is essential when considering biomolecular systems.

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APPENDIX: SURFACE CHARGE METHOD

The surface charge method\[7\]-\[9\] 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

\[
\Phi = \frac{q}{\varepsilon_e |\vec{r} - (d + s)\hat{z}|} + \frac{q}{\varepsilon_e |\vec{r} + (d + s)\hat{z}|} + \int_{z'=+d} \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS' + \int_{z'=-d} \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS'.
\]

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\[14\]

\[
f(\rho) = \int_0^{\infty} a(\beta) J_\nu(\beta \rho) \, d\beta
\]

\[
a(\beta) = \beta \int_0^{\infty} f(\rho) J_\nu(\beta \rho) \rho \, d\rho,
\]

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. (A.1) can also be expanded in Bessel functions\[11\]:

\[
\frac{1}{|\vec{r} - \vec{r}'|} = \sum_{m=-\infty}^{\infty} \int_0^{\infty} dk \, e^{im(\phi - \phi')} J_m(k \rho) J_m(k \rho') e^{-k(z_>-z_<)},
\]

where \( z_> = \max\{z, z'\} \) and \( z_> = \min\{z, z'\} \).

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

\[
\frac{q}{\varepsilon_e |\vec{r} - (d + s)\hat{z}|} = \frac{q}{\varepsilon_e} \int_0^{\infty} dk \, J_0(k \rho) e^{-k(d+s-z)}
\]

and

\[
\frac{q}{\varepsilon_e |\vec{r} + (d + s)\hat{z}|} = \frac{q}{\varepsilon_e} \int_0^{\infty} dk \, J_0(k \rho) e^{-k(z+d+s)}.
\]
The potential near the boundary at \( z = d \) due to the induced surface charge at \( z = d \) is

\[
\int_{z' = +d} \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS' = \int (\rho' \, d\rho' \, d\rho') \left[ \int_0^\infty S(\beta) J_\nu(\beta \rho') \, d\beta \right] \times \left[ \sum_{m = -\infty}^\infty \int_0^\infty dk \, e^{im(\phi - \phi')} J_m(k \rho) J_m(k \rho') e^{-k(z' - z)} \right]
\]

\[
= \int_0^\infty d\beta S(\beta) \int_0^\infty dk \, e^{-k(z' - z)} \sum_{m = -\infty}^\infty J_m(k \rho) \left( \int d\phi' e^{im(\phi - \phi')} \right) \times \left[ \int d\rho' \, J_\nu(\beta \rho') J_m(k \rho') \right]
\]

\[
= 2\pi \int_0^\infty d\beta S(\beta) \int_0^\infty dk \, e^{-k(z' - z)} J_\nu(k \rho) \left( \int d\rho' \, J_\nu(\beta \rho') J_m(k \rho') \right).
\]

Letting \( \nu = 0 \) turns the \( \rho' \) integral into a standard one, \[13\]

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

and therefore

\[
\int_{z' = +d} \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS' = 2\pi \int_0^\infty dk \, e^{-k(z' - z)} J_\nu(k \rho) S(k)/k.
\]

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

\[
2\pi \int_0^\infty dk \, e^{-k(z' - z)} J_\nu(k \rho) S(k)/k.
\]

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

\[
2\pi \int_0^\infty dk \, e^{-k(d - z)} J_\nu(k \rho) S(k)/k.
\]

For \( z' = -d \) and \( z \) near \( d \) one finds a similar formula that is valid either above or below interface:

\[
2\pi \int_0^\infty dk \, e^{-k(z' + d)} J_\nu(k \rho) S(k)/k.
\]

The boundary condition at \( z = d \) is

\[
\varepsilon_1 \frac{\partial \Phi_{z \leq d}}{\partial z} \bigg|_{z = d} = \varepsilon_\varepsilon \frac{\partial \Phi_{z \geq d}}{\partial z} \bigg|_{z = d}
\]

for every value of \( \rho \), which leads to an equation easily solved for \( S(k) \):

\[
S(k) = \frac{g \kappa e^{-ks} (e^{-2kd} - 1)}{2\pi \varepsilon_\varepsilon (1 - \alpha e^{-2kd})}.
\]

Therefore

\[
\sigma(\rho) = \int_0^\infty J_\nu(k \rho) S(k) \, dk
\]

\[
= \frac{g \kappa}{2\pi \varepsilon_\varepsilon} \int_0^\infty J_\nu(k \rho) \frac{ke^{-ks}(e^{-2kd} - 1)}{(1 - \alpha e^{-2kd})} \, dk
\]

\[
= -\frac{g \kappa}{2\pi \varepsilon_\varepsilon} \int_0^\infty J_\nu(k \rho) ke^{-ks} \left( 1 + \frac{(\alpha - 1)e^{-2kd}}{1 - \alpha e^{-2kd}} \right) \, dk
\]

\[
= -\frac{g \kappa}{2\pi \varepsilon_\varepsilon} \left[ \int_0^\infty J_\nu(k \rho) ke^{-ks} \, dk + \int_0^\infty J_\nu(k \rho) ke^{-k(s + 2d)} (\alpha - 1) \sum_{n=0}^\infty \alpha^n e^{-2kd} \, dk \right]
\]

\[
= -\frac{g \kappa}{2\pi \varepsilon_\varepsilon} \left[ \int_0^\infty J_\nu(k \rho) ke^{-ks} \, dk + \sum_{n=0}^\infty \alpha^n (\alpha - 1) \int_0^\infty J_\nu(k \rho) ke^{-k(s + 2(n + 1)d)} \, dk \right].
\]
Since all variables are real, we make use of the following integral\[16\]
\[ \int_0^\infty e^{-\alpha x} J_\nu(\beta x)x^{\nu+1} \, dx = \frac{(2\alpha)(2\beta)^\nu \Gamma(\nu + (3/2))}{\sqrt{\pi}(\alpha^2 + \beta^2)^{\nu+(3/2)}} \]
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
\[ \sigma(\rho) = -\frac{q\alpha}{2\pi\varepsilon_e} \left[ \frac{s}{(s^2 + \rho^2)^{3/2}} + \sum_{n=0}^\infty \alpha^n (\alpha - 1) \frac{s + 2(n + 1)d}{[(s + 2(n + 1)d)^2 + \rho^2]^{3/2}} \right], \]
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 \( \rho' = d, \rho = 0, \) and \( z = s + d, |\vec{r} - \vec{r}'|^2 = s^2 + \rho'^2 \).

Therefore
\[ \int \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS' = 2\pi \int \frac{\rho'\sigma(\rho')}{(s^2 + \rho'^2)^{1/2}} \, d\rho' = 2\pi \int \left( S(k) \int \frac{\rho'J_0(k\rho')}{(s^2 + \rho'^2)^{1/2}} \, d\rho' \right) \, dk. \]
The \( \rho' \) integral is found in tables\[17\] 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 \( \rho' = -d, \rho = 0, \) 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 \( \rho' = -d \) 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
\[ \Phi(\rho = 0, z = s + d) = \frac{q}{\varepsilon_e} \int_0^\infty \left( e^{-k(2s+2d)} + \frac{\alpha e^{-2ks}(e^{-2kd} - 1)}{1 - \alpha e^{-2kd}} + \frac{\alpha e^{-k(2s+2d)}(e^{-2kd} - 1)}{1 - \alpha e^{-2kd}} \right) \, dk \]
\[ = \frac{q}{\varepsilon_e} \int_0^\infty e^{-2k(s+d)} \frac{1 - \alpha e^{2kd}}{1 - \alpha e^{-2kd}} \, dk, \]
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 Section\[III\] But \( U \) agrees, everything that follows from \( U \) must also agree.

For opposite charges
\[ \Phi = \frac{q}{\varepsilon_e|\vec{r} - (d + s)\hat{z}|} - \frac{q}{\varepsilon_e|\vec{r} + (d + s)\hat{z}|} + \int_{\rho' = -d}^{\rho'} \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS' + \int_{\rho' = +d}^{\rho'} \frac{\sigma(\rho')}{|\vec{r} - \vec{r}'|} \, dS' \]
However, by symmetry \( \sigma_+ = -\sigma_-= \sigma \). The boundary condition yields
\[ S(k) = \frac{qk\alpha e^{-ks}(e^{-2kd} + 1)}{2\pi\varepsilon_e(1 + \alpha e^{-2kd})} \]
The surface charge density becomes

\[ \sigma(\rho) = \frac{q_0}{2\pi \varepsilon e} \left[ \frac{s}{(s^2 + \rho^2)^{3/2}} + \sum_{n=0}^{\infty} \frac{(-\alpha)^n(1-\alpha)}{(s+2(n+1)d)^{3/2} + \rho^2} \right] \]

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 Section IV.

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