The forces between surfaces of mobile, orientable dipoles. The method of reflection coefficients

Phil Attard and D. John Mitchell
Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, Canberra, ACT 2601, Australia

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The interaction free energy between two planar bodies interacting across a uniform dielectric, expressed as a sum over allowed electrodynamic modes, is interpreted in terms of reflection coefficients. It is proved that, within the approximations implied by this modal approach, the force between identical bodies interacting across a uniform dielectric is always attractive. Explicit electrostatic results for interacting dipolar surfaces are obtained and these are applicable to the measured long range attractive forces between polar lipid bilayers.

I. INTRODUCTION

Interest in the forces between dipolar surfaces has been stimulated by comparatively recent experimental advances. At short separations, large, approximately exponentially decaying repulsive forces have been measured between zwitter-ionic bilayers.1–6 At larger separations, the attractive forces4–6 differ in magnitude and rate of decay from that predicted by the usual Lifshitz theory of van der Waals forces.

The open question is whether the repulsive “hydration” forces can arise within a continuum electrostatic model of the dipolar headgroups interacting across a uniform aqueous phase. Initially Jönsson and Wennerström7 analyzed this image charge model and answered in the affirmative. However, Kjellander and Marcelja8 found, in the case of perpendicularly constrained dipoles, from hypernetted chain calculations, that the image repulsion is dominated at short separations by the correlational attraction between dipoles on different surfaces. A similar result was obtained by Attard and Mitchell9 for orientable dipoles using a perturbation theory. Further, Jönsson, Attard, and Mitchell10 found that the total force (including the van der Waals force) is attractive over all separations. These results were obtained numerically, for a limited set of parameters, using a perturbation theory. Thus it remains unclear whether the exact primitive model can give rise to a repulsive force. The contribution of the surface dipoles can be substantial, and they do appear responsible for the measured attractive forces between the polar lipid bilayers at large separations.11

Previous authors have used a modal approach12 to obtain the Lifshitz result for van der Waals forces. It is shown here how to interpret that method in terms of reflection coefficients. It is then proven analytically that, within the continuum electrostatic model, with the approximation that the reflection coefficients are independent of separation, there can never be a repulsive force between identical planar bodies interacting across a uniform dielectric medium. In addition, the method is applied to the specific problem of the interacting dipolar surfaces of the image charge model. This is the first full derivation of the asymptotic formulas used previously.2–11 The expressions for the interaction free energy are useful in analyzing measured forces between polar lipid bilayers.

Section II, besides the interpretation of the modal approach in terms of reflection coefficients, contains the proof that the force between identical bodies is attractive. In Sec. III the Lifshitz results for interacting dielectric half-spaces and for triple films are derived as a simple illustration of the method. The reflection coefficient of dipolar surfaces, located either in the central dielectric or in the outer media, are derived in Sec. IV. The long wavelength limit of the correlation functions are found in Sec. V, and this is used to obtain asymptotic expansions for the free energy (Sec. VI). Finally, in Sec. VII estimates for the susceptibility in the low coupling regime are given.

II. METHOD OF REFLECTION COEFFICIENTS

The Lifshitz results for the van der Waals force between planar bodies can be found most simply via the modal method of Van Kampen, Nijboer, and Schrama.12 In this approach the interaction free energy is expressed as the change in the free energies of the electromagnetic surface modes (treated as independent harmonic oscillators) allowed by the particular boundary conditions of the specific problem. Explicitly, the interaction free energy per unit area (in the nonretarded limit) is [Eq. (5.53) of Ref. 13]:

$$F_{\text{int}} = \frac{k_B T}{4\pi^2} \sum_{\sigma} \int d k \ln \mathcal{G}_{\text{int}}(k).$$  

(1)

Here $k_B$ is the Boltzmann constant, $T$ the temperature, and $k$ the two-dimensional Fourier wave vector. The interaction part of the secular determinant $\mathcal{G}_{\text{int}}(k)$ is an implicit function of the dielectric constants of the system $\epsilon(iq_{\sigma})$ evaluated at the discrete imaginary frequencies $i\omega_{\sigma} = 2\pi nk_{\parallel}T/h$. The prime on the summation indicates that the zero frequency term is to be halved. The interaction secular determinant, which by suitable choice of a multiplicative factor goes to one as the separation $h \to \infty$, gives the allowed modes and follows from the boundary conditions appropriate to each problem.

The interaction part of the secular determinant has a simple physical interpretation in terms of reflection coefficients. Consider two arbitrary bodies (passive, uncharged dielectrics), 2 and 2', interacting across a central uniform dielectric medium, 1, of width $h$. Then the electric potential satisfies the Laplace equation $\nabla^2 \psi(r,z) = 0$, $|z| < h/2$, which
in the two-dimensional Fourier space appropriate for this planar geometry, may be written
\[
\frac{d^2 \hat{\psi}(k,z)}{dz^2} - k^2 \hat{\psi}(k,z) = 0, \tag{2}
\]
with solution
\[
\hat{\psi}(k,z) = A \exp k(z - h/2) + B \exp - k(z + h/2). \tag{3}
\]

The first term of the potential represents the reaction of the right-hand body to the second term considered as an external field. Similarly the second term represents the reaction of the left-hand body to the first term. Thus, if the reflection coefficient of each body is defined as the ratio of the reflected (reaction) potential to the incident potential (evaluated at the boundary), then at the left-hand boundary one can write
\[
B = R_{12} A e^{-kh}, \tag{4a}
\]
where \(R_{12}\) is the reflection coefficient of the left-hand body, and at the right-hand boundary
\[
A = R_{12} B e^{-kh}, \tag{4b}
\]
where \(R_{12}\) is the reflection coefficient of the right-hand body. The allowed potentials which satisfy these conditions are those for which the determinant of the coefficients vanishes. This gives the secular determinant
\[
\mathcal{D}^\text{int}(k) = 1 - R_{12} R_{21} e^{-2kh}. \tag{5}
\]

The reflection coefficients can be determined from linear response theory and each is assumed independent of the other body (i.e., they do not depend on \(h\)). Lifshitz theory is based upon these approximations since Maxwell's equations in media assume a linear response of dielectric media to external fields, a response given by local dielectric constants.

From the above it follows that, for a symmetric system \([R(k) = R_{12} = R_{21}\)], the interaction free energy per unit area is
\[
F^\text{int} = \frac{k_B T}{4\pi^2} \sum_{n=0}^{\infty} \int d k \ln \left\{ 1 - R^2(k) e^{-2kh} \right\}. \tag{6}
\]
Taking the negative derivative of this with respect to separation yields for the pressure
\[
P = -\frac{k_B T}{4\pi^2} \sum_{n=0}^{\infty} \int d k \frac{2k R^2(k) e^{-2kh}}{1 - R^2(k) e^{-2kh}}. \tag{7}
\]

Clearly the theory will only yield sensible (real and finite) results if the argument of the logarithm in Eq. (6) is positive. Thus within the regime of validity of the theory, Eq. (7) will always yield a negative pressure. Two identical planar bodies interacting across a uniform dielectric medium must always attract each other. This result is rigorous within the context of the usual approximations of continuum electrostatics including that the reflection coefficients are independent of separation \(h\). This attractive interaction results from all the dipolar fluctuations of the dielectric media. The bodies have been taken to be uncharged, the central medium to be uniform, and thus only the van der Waals/Lifshitz contribution to the pressure has been considered.

### III. Examples

It is convenient to illustrate this procedure with some well-known examples, especially since the results will prove useful later. Take the left-hand body to be a semiinfinite half-space of dielectric constant \(\epsilon_2\). The potential in the central medium (of dielectric \(\epsilon_1\)) is
\[
\hat{\psi}(k,z) = Ae^{kz} + Be^{-kz}, \tag{8a}
\]
and that transmitted across the boundary is
\[
\hat{\psi}(k,z) = Ce^{kz}. \tag{8b}
\]
Now the continuity of \(\psi\) and \(\epsilon\psi'\) gives the boundary conditions \((z=0)\)
\[
A + B = C, \quad \epsilon_1 k (B - A) = - \epsilon_2 k C. \tag{9}
\]
The reflection coefficient, which is the ratio of the response to the applied potential at the boundary, is
\[
R(k) = B/A = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} = \Delta_{12}. \tag{10}
\]

The usual Lifshitz interaction between two dielectric half-spaces is now apparent, from either of Eqs. (6) or (7). Note that the transmission coefficient (which will be required later) follows from Eq. (9) and is
\[
T_{12}(k) = C/A = \frac{2\epsilon_1}{\epsilon_1 + \epsilon_2}. \tag{11}
\]

To generalize this result, one may consider a medium of dielectric constant \(\epsilon_3\) and of thickness \(w\) adsorbed to another body, a black box with reflection coefficient \(R_{2B}(k)\). Then the potential in the central medium 1 is again given by Eq. (8a), while that in the adsorbed layer is now
\[
\hat{\psi}(k,z) = Ce^{k(z+w)} + R_{2B}(k)Ce^{-k(z+w)}. \tag{12}
\]

Solving the boundary conditions as above, one obtains for the full reflection coefficient
\[
R(k) = B/A = \frac{\Delta_{12} + R_{2B}(k)e^{-2kw}}{1 + \Delta_{12} R_{2B}(k)e^{-2kw}}. \tag{13}
\]

To obtain the triple layer result, take the black box to be a half-space with dielectric constant \(\epsilon_3\), and then \(R_{2B}(k) = \Delta_{35}\) from above. The results for the general multilayer\(^{14}\) follow by repeated use of Eq. (13). These results are readily extended to include anisotropic multilayers.\(^{15}\)

### IV. Dipolar Surfaces

#### A. Dipoles in central medium

The method of reflection coefficients will now be used to obtain the electrostatic free energy between two interacting planar surfaces, each containing mobile orientable dipoles. The surfaces, a distance \(h\) apart, are embedded in a central uniform dielectric \(\epsilon_1\), and a distance \(w\) behind each is a semi-infinite dielectric half-space, \(\epsilon_2\). The separation between the half-spaces at \(d = h + 2w\). Since one cannot ascribe a bulk macroscopic dielectric constant to the dipolar surface, it is necessary to determine the analogous microscopic quantity. The polarization–polarization correlation function for the isolated body (i.e., surface plus dielectric discontinuity) can, in principle, be found at nonzero frequencies using quantum statistical mechanics. However, if only the \(n = 0\)
(electrostatic) term in Eq. (6) is required, then it suffices to use classical statistical mechanics, which restricted the problem we address henceforth.

Let us describe the dipolar fluid by the polarization operator, a three component vector with component \( \alpha \) being

\[
P^\alpha(r) = \sum_{i=1}^{N} \mu_{i\alpha} \delta(r - r_i).
\]  

(14)

Here the Dirac delta chooses the \( i \)th dipole (\( r \) is the cylindrical radius vector) which has moment \( \mu_{i\alpha} \) in the \( \alpha = x, y, \) or \( z \) direction and the asterisk denotes an operator. Ensemble averages of operators are denoted by dropping the asterisk, and for isolated bodies have a zero appended. In linear response theory, the excess polarization \( P^\alpha(r) = P(r) - P^0(r) \) induced by an external field \( E^\alpha(r) \) is given by

\[
P^\alpha(r) = \beta \int G^0(r - s - E^\alpha(s)) \, ds,
\]

(15)

where \( \beta = 1/k_B T \). The polarization-correlation function is

\[
G^0(r - s) = \langle P^\alpha(r)P^\alpha(s) \rangle^0 - P^\alpha(r)P^\alpha(s).
\]

(16)

In order to find the reflected potential, one requires the potential arising from an induced polarization of the dipolar surface at \( z = 0 \). One can show (e.g., by considering a dipole oriented in the \( x \) direction) that the direct potential due to the \( x \) component of polarization is

\[
\hat{\Phi}_{\alpha}^{\text{dir}}(k,z) = \frac{2\pi i}{\epsilon_1 k} e^{-k|z|} k_x \hat{P}_{\alpha}^{\text{ex}}(k),
\]

(17)

where \( k_x \) is the \( x \) component of \( k \). Note that this is the potential due to an ideal dipole; it is straightforward to extend the analysis to zwitterions. Since Eq. (10) enables one to find the potential reflected by the dielectric half-space, it follows that the total potential due to the \( x \) component of polarization is

\[
\hat{\Phi}_{\alpha}^{\text{ref}}(k,z) = \frac{2\pi i}{\epsilon_1 k} (1 + \Delta_{12} e^{-2kw}) e^{-k|z|} k_x \hat{P}_{\alpha}^{\text{ex}}(k), \quad z > 0.
\]

(18)

An entirely analogous expression holds for a \( y \) component. However, the potential due to a \( z \) component of polarization is given by

\[
\hat{\Phi}_{\alpha}^{\text{ref}}(k,z) = \frac{2\pi i}{\epsilon_1} (1 - \Delta_{12} e^{-2kw}) e^{-kz} k_z \hat{P}_{\alpha}^{\text{ex}}(k), \quad z > 0.
\]

(19)

Now a source to the right of the surface gives a potential

\[
\hat{\Phi}_{\alpha}^{\text{dir}}(r,z) = \epsilon_1 e^{kz} e^{-\alpha \sigma}
\]

(20)

which has an associated electric field (in Fourier space)

\[
\hat{E}^{\alpha}(k,z) = (ik_z - k) \epsilon_1 e^{kz}.
\]

(21a)

This is the direct field from the source. There is also the usual reflected field from the dielectric half-space

\[
\hat{E}^{\text{ref}}(k,z) = (ik_z + k) \epsilon_1 e^{-kz}.
\]

(21b)

Using the convolution theorem, Eq. (15) gives for the induced polarization

\[
\hat{P}^\alpha(k) = \beta \hat{G}^0(k) [\hat{E}^{\text{dir}}(k) + \hat{E}^{\text{ref}}(k)]
\]

(22a)

and hence for the \( \alpha \) component at \( z = 0 \),

\[
\hat{P}_{\alpha}^\alpha(k) = \beta \left\{ i [k_x \hat{G}_{\alpha x}^0(k) + k_y \hat{G}_{\alpha y}^0(k)](1 + \Delta_{12} e^{-2kw}) - k_z \hat{G}_{\alpha z}^0(k)(1 - \Delta_{12} e^{-2kw}) \right\}.
\]

(22b)

Since Eqs. (18) and (19) give the potential from an induced polarization, the total reflected potential is

\[
\hat{\Phi}_{\alpha}^{\text{ref}}(k,z) = \frac{2\pi i}{\epsilon_1 k} [k_x \hat{G}_{\alpha x}^0(k) + k_y \hat{G}_{\alpha y}^0(k)] e^{-kz}.
\]

(23)

It follows immediately, using the fact that \( \hat{G}^0(k) \) is Hermitian, that

\[
R(k) = \Delta_{12} e^{-2kw} - \frac{2\pi \beta}{\epsilon_1 k} [k_x \hat{G}_{\alpha x}^0(k) + k_y \hat{G}_{\alpha y}^0(k)](1 + \Delta_{12} e^{-2kw})^2 + k_z \hat{G}_{\alpha z}^0(k)(1 - \Delta_{12} e^{-2kw})^2
\]

\[
+ 2k_x k_z \hat{G}_{\alpha y}^0(k)(1 + \Delta_{12} e^{-2kw})^2 + 2ik_z [k_x \hat{G}_{\alpha x}^0(k) + k_y \hat{G}_{\alpha y}^0(k)](1 - \Delta_{12}^2 e^{-4kw}).
\]

(24)

Finally, the classical (zero frequency) interaction free energy for these interacting dipolar surfaces is

\[
F_{\text{int}} = \frac{k_B T}{8\pi^2} \int d^2 k \ln \left\{ 1 - R^2(k) e^{-2\hbar k} \right\}.
\]

(25)

\[\text{B. Dipoles in outer media}\]

Now consider dipolar surfaces embedded in the outer dielectric half-spaces \( \epsilon_2 \), with separation between the surfaces \( h = d + 2w \) (\( d \) is still the thickness of the central medium \( \epsilon_1 \)). A source to the right of the surfaces, \( \Phi = \epsilon_2 e^{kz} \) is transmitted across the dielectric boundary, with a coefficient given by Eq. (11), and produces a field

\[
\hat{E}^{\text{trans}}(k) = (ik_z - k) T_{12} e^{kz}.
\]

(26)

The induced polarization is then \( \hat{P}^\alpha(k) = \beta \hat{G}^0(k) \epsilon_1 e^{kz} \hat{E}^{\text{trans}}(k) \), or in component form

\[
\hat{P}_{\alpha}(k) = \beta \left\{ ik_x \hat{G}_{\alpha x}(k) + ik_y \hat{G}_{\alpha y}(k) - k_z \hat{G}_{\alpha z}(k) \right\} A(1 + \Delta_{12}) e^{-kw},
\]

(27)

where \( T_{12} = 1 + \Delta_{12} \) has been used. Each component of polarization gives rise to a direct potential [cf. Eq. (17)] which
is transmitted across the boundary with coefficient $T_{12} = 1 - \Delta_{12}$. Hence the total reflected potential is

$$\hat{\Phi}_{\text{ref}}(kz) = A\Delta_{12} e^{-kz} + (1 - \Delta_{12}) e^{-kz} - \frac{2\pi}{\varepsilon_k} e^{-kz} (ik_x \hat{P}_x(k) + ik_y \hat{P}_y(k) + k \hat{P}_z(k)).$$

(28)

This yields for the reflection coefficient $R(k) = \Delta_{12} - (1 - \Delta_{12}) e^{-2kz} - \frac{2\pi\beta}{\varepsilon_k} e^{-kz} (ik_x \hat{G}_x^0(k) + ik_y \hat{G}_y^0(k) + k \hat{G}_z^0(k))$.

(29)

which when inserted in Eq. (25) gives the interaction free energy between dipolar surfaces embedded in the outer di-electric half-spaces, provided the present distance between the boundaries, $d$ (rather than $h$) is used in the exponential.

V. LONG WAVELENGTH APPROXIMATION

The expression for the classical interaction free energy requires the polarization correlations as functions of $k$. A considerable simplification (with little loss of accuracy) results if the small $k$ limit of $\hat{G}^0(k)$ is taken instead, since this reduces the requirement to just two parameters, the susceptibilities. For large separations between the surfaces one expects that only the long wavelength correlations will contribute to the interaction free energy. And indeed the factor $e^{-2kz}$ does damp the large $k$ behavior of $R(k)$ and hence $\hat{G}^0(k)$. The limiting result is here derived for the dipolar surfaces in the central medium. The analogous expressions for the dipoles in the outer media follow by interchanging the subscripts 1 and 2.

The polarization–polarization correlation function gives the induced polarization in terms of the applied field, Eq. (15). One can define a response function $\tau$ which gives it in terms of the mean field:

$$\tau(r) = \beta \int \tau(r-s) E_{\text{mean}}(s) \, ds.$$  

(30)

The usual expression for the mean field is

$$E_{\text{mean}}(r) = E^{\text{int}}(r) + \int T(r-s) P^{\text{ext}}(s) \, ds,$$  

(31)

where $T$ is the dipole field tensor which here implicitly includes hard core or other short range effects. These equations [(15), (30), and (31)] may be solved in Fourier space:

$$\hat{G}^0(k) = [1 - \beta \tilde{\tau}(k) \hat{T}(k)]^{-1} \tilde{\tau}(k).$$  

(32)

Now it has previously been shown\(^a\) that $\tau(r)$ is a short ranged function (it is related to the short range part of the Ornstein–Zernike direct correlation function). It then follows that its Fourier transform possesses a Taylor series about $k = 0$, $\tilde{\tau}(k) = \tilde{\tau}(0) + \mathcal{O}(k^2)$. From the symmetry of the problem, $\tilde{\tau}(0)$ is diagonal with only two independent entries (the parallel components being equal). On the other hand, the dipole field tensor is long ranged, its components decaying as inverse cubics in $r$, and hence its Fourier transform has a mod $k$ singularity at the origin. It therefore follows that the required small $k$ expansion for the correlation function is

$$\hat{G}^0(k) \sim \hat{G}^0(0) + \beta \hat{G}^0(k) \hat{T}(k) \hat{G}^0(k) + \mathcal{O}(k^2).$$  

(33)

The typical components of the long range part of the interaction tensor $\hat{T}'(k)$ (which is Hermitian) are

$$\hat{T}'_{xx}(k) = -\frac{2\pi\kappa_{xx}}{\varepsilon_k} (1 + \Delta_{12} e^{-2kz}),$$  

(34a)

$$\hat{T}'_{zz}(k) = -\frac{2\pi i\kappa_{zz}}{\varepsilon_k} \Delta_{12} e^{-2kz},$$  

(34b)

$$\hat{T}'_{zz}(k) = \frac{2\pi \kappa_{zz}}{\varepsilon_k} (1 - \Delta_{12} e^{-2kz}).$$  

(34c)

These equations show that, like the dipole field tensor itself, the correlation function has a mod $k$ singularity. It is therefore long ranged in real space, decaying as $r^{-3}$ along the surface. This result is analogous to known results for three-dimensional homogeneous fluids\(^a\) where the isothermal compressibility $\kappa_T$ replaces the susceptibility $\hat{G}^0(0)$ above. The problem now only involves two parameters—the parallel $\hat{G}_{xx}^0(0)$ and perpendicular $\hat{G}_{zz}^0(0)$ components of the susceptibility.

VI. ASYMPTOTIC RESULTS

The long wavelength limit of the correlation function can be inserted into the reflection coefficient and the interaction free energy determined numerically from Eq. (25). However, since the contribution from long wavelengths becomes increasingly dominant at larger separations, one could argue that an asymptotic expansion in powers of separation would be more consistent. To obtain this, one expands the logarithm in Eq. (25), and collects from each term coefficients with the same power of $k$.

First for the case of the dipolar surfaces embedded in the central dielectric medium ($n = d - 2u$). Using the long wavelength limit of the correlations [Eq. (33)] in the formula for the reflection coefficient [Eq. (24)], one obtains the first several terms in the asymptotic expansion. The leading term is

$$P_{\text{int}} = -\frac{k_B T}{8\pi^3} \sum_{n=1}^{\infty} \frac{1}{n} \int d k \Delta_{12}^2 e^{-2kz} \left( -\frac{k_B T}{16\pi^3} \xi_3(\Delta_{12}^2) \right),$$  

(35a)

where $\xi_3(x) = \Sigma x^3/n^3$ is a generalized Riemann zeta function. This is the usual Lifshitz zero frequency result for the interaction between two half-spaces; it is independent of the dipolar surfaces. The next order term, where the coefficients contribute a factor of $k$,
\[ F_{10}^{\text{int}} = \frac{1}{e_1} \int_0^{\infty} k^3 \Delta_{12} e^{-2kd} e^{-\frac{kh}{1 - \Delta_{12}^2 e^{-2kd}}} \left\{ XW_+^2 + ZW_-^2 \right\} \, dk . \]  

(35b)

Here and after we use the notation \( X \equiv \hat{G} \gamma_0(0), Z \equiv \hat{G} \zeta_0(0), \)
\( W_+ \equiv 1 + \Delta_{12}^2 e^{-2kw} \). This term corresponds to the first order perturbation theory, keeping only the terms linear in \( k \). Asymptotically, this term decays as an inverse cubic in separation.

To obtain the terms which asymptotically go like \( h^{-4} \), one must collect coefficients quadratic in \( k \). Then one obtains

\[ F_{11}^{\text{int}} = -\frac{2\pi\beta}{\epsilon_1} \int_0^{\infty} k^3 \Delta_{12} e^{-2kd} e^{-\frac{kh}{1 - \Delta_{12}^2 e^{-2kd}}} \times \left\{ (XW_+ + ZW_-)^2 \Delta_{12} e^{-2kw} + X^2 W_-^2 - Z^2 W_-^2 \right\} \, dk , \]  

(35c)

\[ F_{20}^{\text{int}} = -\frac{\pi\beta}{\epsilon_1} \int_0^{\infty} k^3 \left( 1 + \Delta_{12}^2 e^{-2kd} \right) e^{-\frac{kh}{1 - \Delta_{12}^2 e^{-2kd}}} \times \left\{ (XW_+ + ZW_-)^2 \right\} \, dk . \]  

(35d)

The first of these arises in first order perturbation theory, from that part of the polarization correlation function linear in \( k \), Eq. (33). The other comes from second order perturbation theory with only the \( k^0 \) susceptibility. Of the above, this term is the only one nonzero if \( \epsilon_1 = \epsilon_2 \), since it includes the direct correlational attraction between the two dipolar surfaces.

For the dipolar surfaces embedded in the outer dielectric media \( (h = d + 2w) \), the corresponding results are

\[ F_{10}^{\text{int}} = \frac{X + Z}{\epsilon_2} \int_0^{\infty} k^2 \Delta_{12} e^{-2kd} \left( \frac{1}{1 - \Delta_{12}^2} e^{-2kw} \right) \, dk , \]  

(36a)

\[ F_{11}^{\text{int}} = -\frac{2\pi\beta}{\epsilon_2} \int_0^{\infty} k^3 \Delta_{12}^2 e^{-2kd} \left( \frac{1}{1 - \Delta_{12}^2} e^{-2kw} \right) \times \left\{ X^2 - Z^2 - (X - Z)^2 \Delta_{12}^2 e^{-2kw} \right\} \, dk , \]  

(36b)

\[ F_{20}^{\text{int}} = -\frac{\pi\beta}{\epsilon_2} \frac{(X + Z)^2}{1 - \Delta_{12}^2} \int_0^{\infty} k^3 \Delta_{12}^2 e^{-2kd} \left( \frac{1}{1 - \Delta_{12}^2} e^{-2kw} \right) \times \left( 1 - \Delta_{12}^2 \right) e^{-2kw} \, dk . \]  

(36c)

The long wavelength form of the correlation function is an exact result and yields the correct interaction free energy asymptotically. To obtain the strict asymptotic results, one should expand all the \( e^{-2kw} \) in powers of \( w/h \). However, the results presented in this section are more accurate than the strict asymptotic form over separations of the order of angstroms that one is usually interested in. Similarly, the full logarithm expression for the free energy equation (25) (which is rather more compact than the expansions) turns out to be accurate down to quite small separations.

\section*{VII. LOW COUPLING APPROXIMATION}

The long wavelength approximation requires two parameters—the parallel and perpendicular components of the susceptibility. These have been found by hypernetted chain calculations and by Monte Carlo simulations. However, in the low coupling regime, one can make useful estimates of these quantities. In obtaining Eq. (33) from Eq. (30), the susceptibility implicitly satisfied

\[ \hat{G}_0(0) = [I - \beta \hat{T}(0)]^{-1} \hat{T}(0) . \]  

(37)

The short ranged response function \( \tau \) is not only independent of the long range tail of the interaction potential, but is approximately determined by the system interacting with a truncated potential. Therefore, to a first approximation, its value is given by that of an ideal dipolar gas in which all orientations are equally likely

\[ \hat{\rho}_{zz}(0) = \hat{\rho}_{yy}(0) = \hat{\rho}_{xx}(0) = \frac{1}{2} \rho_{\text{mu}}^2 . \]  

(38)

This approximation is analogous to the usual Debye–Hückel theory of electrolytes. The dipole field tensor \( \hat{T} \) includes short range potentials, and these contribute to \( \hat{T}(0) \). If the system is not too highly coupled, then the core repulsions may be neglected. There then remains an electrostatic term in the \( zz \) component. Zwiterner of length \( a \) (and fixed moment \( \mu \)) have \( \hat{T}_{zz}(0) = -4\pi\epsilon/a^2 \). Hence, for freely orientable dipoles one has the approximations

\[ \hat{G}_0^{\text{xx}}(0) = \hat{G}_0^{\text{yy}}(0) \approx \frac{1}{3} \rho_{\text{mu}}^2 , \quad \hat{G}_0^{\text{zz}}(0) \approx \frac{\rho_{\text{mu}}^2/3}{1 + 4\pi\beta\rho_{\text{mu}}^2/\epsilon a} . \]  

(39a)

and for perpendicularly constrained dipoles one has

\[ \hat{G}_0^{\text{zz}}(0) \approx \hat{G}_0^{\text{xy}}(0) \equiv 0 , \quad \hat{G}_0^{\text{zz}}(0) \approx \frac{\rho_{\text{mu}}^2}{1 + 4\pi\beta\rho_{\text{mu}}^2/\epsilon a} . \]  

(39b)

Note that this approximation predicts that the \( zz \) component of the susceptibility goes to zero in the limit of point dipoles. This limit is a high coupling limit (since the charge must increase if the dipole moment \( \mu = qa \) is held fixed) and in actual fact the susceptibility becomes constant at sufficiently high coupling. For example, for perpendicular zwiterner with \( \mu = 1 \text{eA, } a = 1 \text{A, } \epsilon = 80, \text{ and } \rho^{-1} = 75 \text{A}^2 \), hypernetted chain calculations give a susceptibility \( \chi_{zz} \approx 0.707 \) [define the nondimensional form \( \chi \equiv G_{\text{zz}}(0) / \rho_{\text{mu}}^2 \)], and the above approximation gives \( \chi_{zz} \approx 0.46 \). The agreement becomes better as the length of the zwiterner is increased (at fixed \( \mu \)). However for smaller lengths, HNC calculations show that the susceptibility is almost constant. This explains why Monte Carlo simulations with point dipoles \( \chi_{zz} \equiv 0.72 \) appear in such good agreement with the HNC calculations for zwiterner. For \( \mu = 5 \text{eA} \) perpendicular zwiterner \( (a = 5 \text{A, } \epsilon = 80, \rho^{-1} = 75 \text{A}^2) \) the HNC gives \( \chi_{zz} \approx 0.205 \), the low coupling approximation gives \( \chi_{zz} \approx 0.15 \) and the MC gives \( \chi_{zz} \approx 0.19 \). For orientable dipoles, the above estimates for the parallel components are in reasonable agreement with Monte Carlo simulations provided the coupling (including the effect of hard cores) is not too high. The effects of dielectric discontinuities do not enter into the above estimates. Indeed, the HNC and MC results are, to a good approximation, independent of the near images and so the value of \( \hat{G}_0 \) (which can be taken as that for an infinite dielectric medium.  

VIII. CONCLUSION

It has been shown (in the linear continuum electrostatic approximation) that similar dielectric bodies interacting across a uniform dielectric medium must always attract each other. While the result does not prove that the primitive model can never give a repulsion for this system (the independence of the reflection coefficients of separation precludes absolute rigor), it now appears unlikely that continuum electrostatics can account for the repulsive hydration force at short separations. Nevertheless, the specific results obtained for interacting dipolar surfaces are applicable to the large separation attractive forces which have been measured.

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19In Ref. 9, an exponential factor and a minus sign is missing from the $xz$ term of $\Delta F_z$. This does not affect the numerical results presented in that paper.