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An Exact Calculation of the van der Waals Interaction between Two Spheres of Classical Dipolar Fluid

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An exact treatment of the van der Waals interaction between two spherical dielectric bodies possessing purely classical degrees of freedom is presented. The spheres are described by multipole expansions of their fluctuating charge distributions, and the correlation between the fluctuations are taken into account using classical electrostatics and statistical mechanics. The presented approach avoids both the assumption of pairwise additivity of Hamaker theory and the implicit linear response assumption of Lifshitz theory. The resulting equations are solved numerically for $D/a \geq 0.01$, where a is the radius of the spheres and D is their minimum separation, for a system with $\varepsilon = 80$, and the results are compared to the analytical Hamaker formula with a Hamaker constant calculated from Lifshitz theory.

Introduction

van der Waals forces are ubiquitous in nature and, despite their relative weakness, of great importance, playing a major role in such diverse areas as protein folding, colloidal stability, and the ability of the gecko lizard to climb glass walls.[1−3] One of the seminal contributions to the investigation of van der Waals forces between macroscopic bodies was given in the 1930s by Hamaker,[4] who developed formulas for the free energy of interaction $A(D)$ between bodies of different geometries as a function of their separation D. In particular, he found that the interaction free energy per unit area between two parallel planar surfaces is given by

$$A_{\text{plane}}(D) = -\frac{H}{12\pi D^2} \qquad (1)$$

where

$$H = \pi^2 C \rho_1 \rho_2 \qquad (2)$$

is the so-called Hamaker constant, which is related to the London dispersion force constant C and densities ρ_1 and ρ_2 of the interacting materials. Thus, C is a purely molecular property, and Hamaker's approach is based on an assumption of pairwise additivity of the interactions between the molecules of the two materials; an approximation that clearly does not hold for dense materials such as liquids and solids.

The treatment of van der Waals interactions between spherical bodies, which is of great interest in, for example, colloidal chemistry, is more cumbersome than between planes. Using the Hamaker formalism, the interaction energy between two equally sized spheres of radius a becomes[1]

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$$A_{\text{sphere}}(D) = -\frac{H}{3}\left[\frac{a^2}{D(4a+D)} + \frac{a^2}{(2a+D)^2} + \right.$$
$$\left. \frac{1}{2}\ln\left(1 - \frac{4a^2}{(2a+D)^2}\right)\right] \quad (3)$$

where D is the minimum separation between their surfaces. The limiting case

$$A_{\text{sphere}}(D) = -\frac{H}{12}\frac{a}{D} \qquad D \ll a \qquad (4)$$

is often used, for example, in the much-celebrated DLVO theory of colloidal stability.[5] This limit is also consistent with applying the Derjaguin approximation to eq 1.

The problem of pairwise additivity is avoided in the Lifshitz theory of van der Waals interaction, which is rather involved, at least in its original formulation.[6] The Lifshitz expression for $A_{\text{plane}}(D)$ is the same as that of eq 1 (except for an additional D dependence entering into the expression for H due to retardation screening), but the calculation of H is based on the dielectric properties of the materials rather than on their molecular properties. An approximate form valid for small values of ε for two identical media interacting across a vacuum is[2]

$$H \approx \frac{3}{4}kT\left[\frac{\varepsilon(0)-1}{\varepsilon(0)+1}\right]^2 + \frac{3\hbar}{2}\int_{kT/\hbar}^{\infty}\left[\frac{\varepsilon(i\xi)-1}{\varepsilon(i\xi)+1}\right]^2 d\xi \quad (5)$$

where $\varepsilon(i\xi)$ is the frequency dependent dielectric permittivity at the imaginary frequency $i\xi$. The first term of eq 5 is usually dominated by thermal contributions, corresponding to classical degrees of freedom such as molecular rotations, whereas the integral in the second term is usually assumed to be dominated by quantum-mechanical degrees of freedom, related to molecular polarization. However, as has been shown by Daicic, Ninham, and Wennerström,[7−9] this separation into "classical" and "quantum-mechanical" contributions to H is problematic, and therefore making mechanistic interpretations of the different energy contributions based on Lifshitz theory is not straightforward.

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Although Lifshitz theory is usually referred to as being exact within the dielectric continuum description of matter, Davies[10] showed that there is an inherent linear response assumption present in this and all related approaches. This is equivalent to a first-order perturbation treatment, where the unperturbed states of the two bodies are assumed not to be altered by their electrostatic coupling. Using a field-theoretical approach, Netz[11] went beyond the first-order perturbation approach by adding a second-order correction factor, although this was found to be small for nonionic systems.

The full many-body interaction between two spheres was solved by Langbein[12,13] in the 1970s using a formalism similar to that of Lifshitz theory, thus retaining the implicit linear response assumption but going beyond the assumption of pairwise additivity. Just as for Lifshitz theory, Langbein's approach makes use of the full dielectric spectra $\varepsilon(i\xi)$ of the interacting materials and thus does not allow for a straightforward mechanistic interpretation of the different contributions to the interaction. Unlike the Hamaker expression of eq 3, Langbein's solution does not yield any simple analytic distance dependence of the interaction. Furthermore, the resulting equations are slowly convergent and thus cumbersome to implement numerically. Because of this, the formalism has found little practical use, although several approximate and simplified procedures have been proposed.[14−16]

Although the functional form of eq 3 relies on the assumption of pairwise additivity, the Hamaker constant H can be calculated using Lifshitz theory (e.g., eq 5), thus taking many-body effects into account. Thus, it is possible to partially capture the many-body nature of the van der Waals interactions, but still using the simple closed form of eq 3.

In the present article, we will use a formalism based on multipole expansions of the fluctuating charge distributions of two dielectric spheres[17,18] to derive their effective interaction across a vacuum. Our approach differs from Langbein's theory in that it assumes the material to be purely classical and thus uses only its static dielectric constant $\varepsilon(0)$. Furthermore, we avoid the linear response approximation inherent in the theories due to Lifshitz and Langbein, thus putting no restriction on the strength of the interaction.

Theory

Lifshitz Theory for Classical Systems. Lifshitz theory describes the interaction between two bodies solely in terms of their dielectric properties, and no assumptions are made about thermal excitations and whether the different degrees of freedom are of classical or quantum-mechanical origin. Nevertheless, the theory remains valid for the particular case of a purely classical system. In such a system, the degrees of freedom related to the positions and momenta of the particles separate from each other, and the interaction between the bodies is determined solely by the configuration integral Z. Thus, the interaction energy is independent of the dynamics of the system under study. Within a dielectric description, this implies that the interactions are uniquely determined by the zero-frequency dielectric properties of the material, described through its static dielectric constant $\varepsilon(0)$.

The general Lifshitz expression for the Hamaker coefficient H between two identical half-spaces separated by a distance D interacting across a vacuum is (eq L2.1 of ref 1)

$$H = \frac{3}{2}kT\sum_{n=0}^{\infty}{}' \int_{r_n}^{\infty} x \ln[(1 - \tilde{\Delta}^2 e^{-x})(1 - \Delta^2 e^{-x})]\, dx \tag{6}$$

where the prime on the summation sign indicates that the $n = 0$ term should be multiplied by 1/2, $r_n = 2D\xi_n/c$ is a dimensionless factor quantifying the retardation screening, $\xi_n = 2\pi nkT/\hbar$ defines the eigenfrequencies at which ε should be evaluated, c is the velocity of light in vacuum,

$$\tilde{\Delta} = \frac{p\varepsilon(i\xi_n) - s}{p\varepsilon(i\xi_n) + s} \tag{7}$$

and

$$\Delta = \frac{p - s}{p + s} \tag{8}$$

In the above equations, $s = [p^2 - 1 + \varepsilon(i\xi_n)]^{1/2}$ and $p = x/r_n$. According to the above reasoning, we now take as a condition for a classical system that $\varepsilon(i\xi_n) = 1$ for $n \geq 1$, leading to that all terms with $n > 0$ vanish. Furthermore, since $\xi_0 = 0$, and thus $r_0 = 0$, $p \rightarrow \infty$ by virtue of its r_n^{-1} dependence, leading to $\tilde{\Delta} = (\varepsilon(0) - 1)/(\varepsilon(0) + 1)$ and $\Delta = 0$. An integration by parts and some additional manipulations now leads to

$$H = \frac{3}{8}kT \int_0^{\infty} x^2 \left[\left(\frac{\varepsilon(0) + 1}{\varepsilon(0) - 1}\right)^2 \exp(x) - 1 \right]^{-1} dx \tag{9}$$

Equation 9 is identical to eq 90.14 of ref 19 for the asymptotic ($D \rightarrow \infty$) retarded interaction between two general (i.e., not necessarily classical) bodies. This observation lends further support to the conjecture stated in refs 8 and 9 that interactions arising from classical and quantum-mechanical degrees of freedom are asymptotically equivalent. Using a standard relationship for the integral representation of polylogarithms,[20] eq 9 can be reformulated as

$$H = \frac{3}{4}kT \sum_{q=1}^{\infty} q^{-3} \left(\frac{\varepsilon(0) - 1}{\varepsilon(0) + 1}\right)^{2q} \tag{10}$$

where we can identify the $q = 1$ term as the "classical" term of eq 5, which again highlights the approximate nature of the latter equation for large values of $\varepsilon(0)$.

Interactions in Dipolar Fluids. For two subsystems labeled 1 and 2, each containing N dipoles, the configuration integral Z_{12} is formally expressed as

$$Z_{12} = \int \cdots \int \exp[-\beta V(\mathbf{x}_1^{(1)}\cdots\mathbf{x}_N^{(1)}, \mathbf{x}_1^{(2)}\cdots\mathbf{x}_N^{(2)})]\, d\mathbf{x}_1^{(1)}\cdots d\mathbf{x}_N^{(1)},$$
$$d\mathbf{x}_1^{(2)}\cdots d\mathbf{x}_N^{(2)} \tag{11}$$

where $\beta = (kT)^{-1}$ is the inverse thermal energy and $\mathbf{x}_i$ represents all degrees of freedom of the ith dipole. We now decompose the interaction potential V according to

$$V = V_{11}(\{\mathbf{x}_i^{(1)}\}) + V_{22}(\{\mathbf{x}_j^{(2)}\}) + V_{12}(\{\mathbf{x}_i^{(1)}\}, \{\mathbf{x}_j^{(2)}\}) \tag{12}$$

where the coupling V_{12} between the two subsystems, given by

$$V_{12}(\{\mathbf{x}_i^{(1)}\},\{\mathbf{x}_j^{(2)}\}) = \sum_{i,j=1}^{N} V^{(dd)}(\mathbf{x}_i^{(1)},\mathbf{x}_j^{(2)}) \qquad (13)$$

is purely dipolar, and the internal interaction potentials V_{11} and V_{22} of the two subsystems contain other short-range terms in addition to the dipole−dipole interactions.

At sufficiently large separations R between the subsystems, the coupling term is negligible and $Z_{12} = Z_1 Z_2$, where Z_1 and Z_2 are the configuration integrals of the isolated subsystems. The interaction free energy A_{int} between the subsystems is thus given by[24]

$$A_{int}(R) = -kT \ln \frac{Z_{12}}{Z_1 Z_2} = -kT \ln \langle \exp[-\beta V_{12}] \rangle_0 \qquad (14)$$

where the subscript 0 denotes that the average is taken over the unperturbed subsystems. We now express the free energy as a perturbation expansion to second order,

$$A_{int}(R) \approx \langle V_{12} \rangle_0 - \frac{\beta}{2}[\langle V_{12}^2 \rangle_0 - \langle V_{12} \rangle_0^2] = -\frac{\beta}{2}\langle V_{12}^2 \rangle_0 \qquad (15)$$

where the second equality follows from the fact that $\langle V_{12} \rangle_0$ is zero by symmetry. Thus, eq 15 gives the leading nonzero term of the interaction free energy. However, in dipolar systems there are typically strong orientational correlations between the molecules, and the averages over distributions are difficult to evaluate.

Lifshitz theory avoids the problem of handling orientational correlations by instead letting the properties of the material be reflected through its dielectric response properties and expressing the change in free energy of the intervening field. It is, however, possible to exactly describe the interaction from the point-of-view of the material if one makes a coordinate transformation in the configuration integral. By describing the dipolar system in terms of the collective multipole moments Q_{-m} of its charge distribution rather than through the molecular positions and orientations, i.e. $\{\mathbf{x}_i^{(1)}, \mathbf{x}_j^{(2)}\} \rightarrow \{Q_{1,lm}, Q_{2,lm}\}$, a number of simplifications appear:

1. Different multipole components, specified through the integers l (≥ 1) and m ($-l \leq m \leq l$), in the same subsystem are uncoupled for symmetry reasons.
2. The interaction between the two subsystems can be expressed in a reasonably simple way.
3. There is a convergence of the interaction in terms of increasing order l of the multipoles.
4. For a given value of l, the dominant contributions to the interactions come from small values of $|m|$.

Even though this approach is valid within a molecular description of matter, we will in the present contribution treat the subsystems as dielectric continua, since the fluctuations of the multipole moments can then be conveniently described by Gaussian probability distributions with widths determined by the dielectric constant $\varepsilon(0)$ of the material.

General Strategy. We will consider two dielectric spheres S_i and S_j, possessing only classical degrees of freedom. The fluctuating multipole moments Q_{lm} will be described by probability distributions $P(Q_{lm})$ according to the previously developed formalism,[17,18] and our starting point will be $P(Q_{lm})$ for an isolated dielectric sphere in a vacuum. When the two spheres
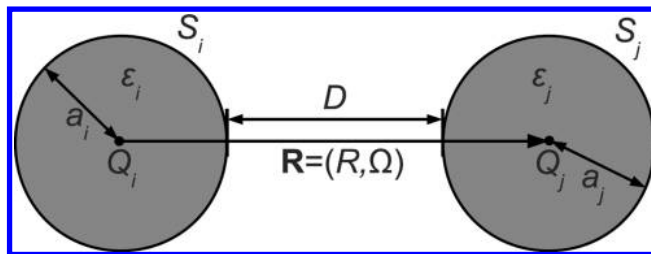
Figure 1. Definition of some parameters used to describe the model system.

are brought close to each other, the coupling between their electric moments will change their probability distributions. By carefully considering the coupling and resulting correlation between all fluctuating moments of the two spheres, we are able to deduce the total interaction free energy A_{int} of the two dielectric spheres.

As explained in Appendix A, we will only consider multipole moments Q_{lm} with $m \geq 0$ and treat separately the real and imaginary parts of Q_{lm}. We will throughout let the vector $\mathbf{R}$ connecting the centers of the two spheres define the z axis of the external coordinate system, where $\mathbf{R}$ points from S_i to S_j. Relevant parameters are defined in Figure 1.

One Dielectric Sphere. The unnormalized probability distribution $P(Q_{lm}^X)$ of the multipole moment component Q_{lm}^X of a dielectric sphere in vacuum (see Appendix A) is given by the Gaussian function

$$P(Q_{lm}^X) = \exp[-\alpha_l(2 - \delta_{m0})(Q_{lm}^X)^2] \qquad (16)$$

where δ is the Kronecker delta, $X \in \{R, I\}$ for $m \neq 0$ and $X = R$ for $m = 0$, and

$$Q_{lm}^R \equiv \text{Re}(Q_{lm}) \qquad (17a)$$

$$Q_{lm}^I \equiv \text{Im}(Q_{lm}) \qquad (17b)$$

Furthermore, the exponent α_l is given by[17,18]

$$\alpha_l = \frac{\beta[l(\varepsilon + 1) + 1]}{2l(\varepsilon - 1)a^{2l+1}} \qquad (18)$$

with a representing the radius of the sphere and ε its dielectric constant.

One Dielectric Sphere Coupled to a Permanent Charge Distribution. We now consider the corresponding probability distribution for the dielectric sphere S_i in the presence of a permanent charge distribution ρ_j of zero net charge, where $i, j \in \{1, 2\}$ and $i \neq j$. When $\mathbf{R}$ is parallel to the z axis, this probability distribution is given by (see Appendix A)

$$P(Q_{i,lm}^X;\rho_j) = P(Q_{i,lm}^X) \exp[-\beta U_{lm;\rho_j}] \qquad (19)$$

where the interaction energy $U_{lm;\rho_j}$ is given by[21]

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$$U_{l_i m; \rho_j} =$$
$$(-1)^{l_i+m}(2 - \delta_{m0})Q^X_{i,l_i m} \sum_{l_j} R^{-(L+1)} f(l_i,l_j,m,-m) Q^X_{\rho_j,l_j m} \quad (20)$$

In eq 20, $Q_{\rho_j,l_j m}$ are the spherical multipole moments of ρ_j defined by

$$Q_{\rho,lm} \equiv \int_V \rho(\mathbf{r}) r^l C_{lm}(\Omega) \, d\mathbf{r} \quad (21)$$

with $C_{lm}(\Omega)$ representing Racah's unnormalized spherical harmonics. Furthermore, the function f is given by

$$f(l_i,l_j,m_i,m_j) \equiv \left[\frac{(2L)!}{(2l_i)!(2l_j)!}\right]^{1/2} \sqrt{2L+1} \begin{pmatrix} l_i & l_j & L \\ m_i & m_j & -M \end{pmatrix} \quad (22)$$

with $L \equiv l_i + l_j$, $M \equiv m_i + m_j$, and $(\cdots)$ is the Wigner $3j$ symbol.[22] Finally, the summation limits are defined according to

$$\sum_l \equiv \sum_{l=\max\{1,m\}}^{\infty} \quad (23)$$

Using standard statistical-mechanical concepts, the interaction free energy $\langle A^{(X)}_{lm} \rangle$ between $Q^X_{i,lm}$ and ρ_j can be expressed as (see Appendix B)

$$\langle \beta A^{(X)}_{lm} \rangle = -\frac{(2 - \delta_{m0})}{4\alpha_{l_i}} \left[\beta \sum_{l_j} R^{-(L+1)} f(l_i,l_j,m,-m) Q^X_{\rho_j,l_j m} \right]^2 \quad (24)$$

The total interaction free energy A_{int} between S_i and ρ_j is now obtained by summing up all the contributions according to

$$\beta A_{\text{int}} = \sum_{l_i=1}^{\infty} \sum_{m=0}^{l_i} [\langle \beta A^{(R)}_{lm} \rangle + \langle \beta A^{(I)}_{lm} \rangle] \quad (25)$$

where it should be noted that $\langle \beta A^{(I)}_{l0} \rangle = 0$ since Q_{l0} is real.

Two Coupled Dielectric Spheres: Exact Approach. We now replace the permanent charge distribution by a fluctuating dielectric sphere S_j, and let $P(Q^X_{i,lm};S_j)$ represent the unnormalized probability distribution of the multipole component $Q^X_{i,lm}$ of S_i when this moment is coupled to *all* moments of S_j. This probability distribution is given by

$$P(Q^X_{i,lm};S_j) = P(Q^X_{i,lm}) \exp[-\beta \langle U_{l_i m;S_j} \rangle] \equiv$$
$$\exp[-\hat{\alpha}_{i,lm}(2 - \delta_{m0})(Q^X_{i,lm})^2] \quad (26)$$

which also defines $\hat{\alpha}_{i,lm}$. Furthermore, the mean interaction energy $\langle U_{l_i m; S_j} \rangle$ between $Q^X_{i,lm}$ and all moments of S_j is given by

$$\langle U_{l_i m;S_j} \rangle =$$
$$(-1)^{l_i+m}(2 - \delta_{m0})Q^X_{i,lm} \sum_{l_j} R^{-(L+1)} f(l_i,l_j,m,-m) \langle Q^X_{j,l_j m} \rangle_{Q^X_{i,l_i m}} \quad (27)$$

In eq 27, $\langle Q^X_{j,l_j m} \rangle_{Q^X_{i,l_i m}}$ is the mean value of $Q^X_{j,l_j m}$ in the presence of a *fixed* value of $Q^X_{i,l_i m}$. Formally, this mean value is given by the integral

$$\langle Q^X_{j,l_j m} \rangle_{Q^X_{i,l_i m}} = \frac{\int_{-\infty}^{\infty} Q^X_{j,l_j m} \mathscr{P}(Q^X_{j,l_j m};Q^X_{i,l_i m}) \, dQ^X_{j,l_j m}}{\int_{-\infty}^{\infty} \mathscr{P}(Q^X_{j,l_j m};Q^X_{i,l_i m}) \, dQ^X_{j,l_j m}} \quad (28)$$

where the conditional probability distribution of the multipole component $Q^X_{j,l_j m}$ of S_j in the presence of a fixed value of the multipole component $Q^X_{i,l_i m}$ of S_i, denoted by $\mathscr{P}(Q^X_{j,l_j m};Q^X_{i,l_i m})$, is given by

$$\mathscr{P}(Q^X_{j,l_j m};Q^X_{i,l_i m}) = \exp[-\tilde{\alpha}_{j,l_j l_i m}(2 - \delta_{m0})(Q^X_{j,l_j m})^2] \exp[-\beta U_{l_i m;l_j m}] \quad (29)$$

In eq 29, $\tilde{\alpha}_{j,l_j l_i m}$ represents the Gaussian exponent of the probability distribution of $Q^X_{j,l_j m}$ in the presence of S_i, but *excluding* the contribution coming from the coupling to $Q^X_{i,l_i m}$. This coupling is instead included explicitly through the interaction energy $U_{l_i m;l_j m}$ between the l_ith moment of S_i and the l_jth moment of S_j according to (see Appendix A)

$$U_{l_i m;l_j m} = (-1)^{l_i+m}(2 - \delta_{m0})R^{-(L+1)} f(l_i,l_j,m,-m) Q^X_{i,l_i m} Q^X_{j,l_j m} \quad (30)$$

Hence, $\mathscr{P}(Q^X_{j,l_j m};Q^X_{i,l_i m})$ is in general nonsymmetrical about $Q^X_{j,l_j m} = 0$ (except for when $Q^X_{i,l_i m} = 0$) and takes into account all correlations between $Q^X_{i,l_i m}$ and $Q^X_{j,l_j m}$, whereas the interaction with all the other multipole moments are averaged out, and included in the exponent $\tilde{\alpha}_{j,l_j l_i m}$. Inserting eqs 29 and 30 into eq 28, carrying out the integration, inserting the result into eq 27, and subsequent identification using eq 26 now gives

$$\hat{\alpha}_{i,lm} = \alpha_{i,l_i} - \frac{1}{2} \sum_{l_j} \frac{[\beta R^{-(L+1)} f(l_i,l_j,m,-m)]^2}{\tilde{\alpha}_{j,l_j l_i m}} \quad (31)$$

To proceed, we need to find a second relationship between $\hat{\alpha}$ and $\tilde{\alpha}$. As a starting point, we form the joint probability distribution $P(Q^X_{i,l_i m},Q^X_{j,l_j m})$ of the coupled multipole moments according to

$$P(Q^X_{i,l_i m},Q^X_{j,l_j m}) = \exp[-\tilde{\alpha}_{i,l_i l_j m}(2 - \delta_{m0})(Q^X_{i,l_i m})^2] \times$$
$$\exp[-\tilde{\alpha}_{j,l_j l_i m}(2 - \delta_{m0})(Q^X_{j,l_j m})^2] \exp[-\beta U_{l_i m;l_j m}] \quad (32)$$

We now make a comparison between eqs 26 and 32, using the relationship

$$P(Q^X_{i,l_i m};S_j) = \int_{-\infty}^{\infty} P(Q^X_{i,l_i m},Q^X_{j,l_j m}) \, dQ^X_{j,l_j m} \quad (33)$$

where it should be noted that all the degrees of freedom of S_j have been integrated out to form the probability distribution of the left-hand side. Carrying out the integration and using the equality of the exponents yields the set of equations

$$\hat{\alpha}_{i,l_jm} = \frac{4\tilde{\alpha}_{i,l_il_jm}\tilde{\alpha}_{j,l_il_jm} - [\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2}{4\tilde{\alpha}_{j,l_il_jm}} \qquad \forall l_j$$

(34)

where the right-hand side (RHS) is independent of l_j by the above argument. Solving eq 34 and the one obtained by permuting i and j yields the exponent $\tilde{\alpha}_{i,l_il_jm}$ according to

$$\tilde{\alpha}_{ij} = \frac{1}{2}\hat{\alpha}_i + \frac{1}{2}\sqrt{\hat{\alpha}_i^2 + [\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2\frac{\hat{\alpha}_i}{\hat{\alpha}_j}}$$

(35)

where we have introduced the simplified notations $\tilde{\alpha}_{ij} = \tilde{\alpha}_{i,l_il_jm}$ and $\hat{\alpha}_i = \hat{\alpha}_{i,l_im}$. Insertion of eq 35 into eq 31 now gives

$$\hat{\alpha}_i = \alpha_i - \sum_{l_j} \frac{[\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2}{\hat{\alpha}_j + \sqrt{\hat{\alpha}_j^2 + [\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2\frac{\hat{\alpha}_j}{\hat{\alpha}_i}}}$$

(36)

From eq 36 we find that $\hat{\alpha}_{i,l_im} \leq \alpha_{i,l_i}$, implying that there are larger charge fluctuations in a sphere in the coupled system compared to the uncoupled one. Furthermore, according to eq 35, $\tilde{\alpha}_{i,l_il_jm} \geq \hat{\alpha}_{i,l_im}$, consistent with the fact that $\tilde{\alpha}_{i,l_il_jm}$ does not include the widening due to the coupling with Q_{l_jm}, whereas $\hat{\alpha}_{i,l_im}$ includes all couplings. In both cases, the equalities hold in the limits of large separation ($R \rightarrow \infty$) or weakly polarizable materials ($\alpha_{l_i} \rightarrow \infty$).

Using the joint probability distribution of eq 32 together with basic statistical mechanics, we may now express the energetic part $\langle U_{l_il_jm}\rangle$ of the electrostatic interaction between the moments Q^X_{i,l_im} and Q^X_{j,l_jm} on the two dielectric spheres as (see Appendix B)

$$\langle \beta U_{l_il_jm}\rangle = -\frac{[\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2}{4\tilde{\alpha}_{ij}\tilde{\alpha}_{ji} - [\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2}$$

(37)

where we have dropped the (X) superscript on $\langle \beta U_{l_il_jm}\rangle$, since it is obvious that this quantity is independent of X. Furthermore, the corresponding components $\langle A_{l_il_jm}\rangle$ of the interaction *free* energy are given by

$$\langle \beta A_{l_il_jm}\rangle = -\frac{1}{2}\ln\left[\frac{4\tilde{\alpha}_{ij}\tilde{\alpha}_{ji}}{4\tilde{\alpha}_{ij}\tilde{\alpha}_{ji} - [\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2}\right]$$

(38)

The total interaction free energy between the two spheres is obtained by summing up all the contributions according to

$$\beta A_{\text{int}} = \sum_{l_i=1}^{\infty}\sum_{l_j=1}^{\infty}\sum_{m=0}^{\min(l_i,l_j)} (2 - \delta_{m0})\langle \beta A_{l_il_jm}\rangle$$

(39)

where the factor $(2 - \delta_{m0})$ comes from the independent and equal contributions from the real and imaginary parts for $m > 0$. The total interaction energy βU_{int} can be obtained analogously.

It should be noted that the RHS's of eqs 38 and 37 are (i) independent of β, since $\tilde{\alpha}_{ij} \propto \beta$, and (ii) invariant upon a uniform rescaling of the lengths a_i, a_j, and R, since $\tilde{\alpha}_{ij} \propto a_i^{-(2l_i+1)}$. Furthermore, we find that $\langle A_{l_il_jm}\rangle/\langle U_{l_il_jm}\rangle \neq 1/2$, due to the avoidance of the linear response assumption within the present formalism. However, by expanding the RHS's of eqs 38 and 37 to leading order, the factor $1/2$ is recovered.

Equations 35, 36, 38, and 39 constitute the main results of the present contribution. Equation 36 defines a set of equations that can be solved iteratively for $\hat{\alpha}_1$ and $\hat{\alpha}_2$ after truncation of the infinite sums. The calculated exponents $\hat{\alpha}_1$ and $\hat{\alpha}_2$ can then be inserted into eq 35 to obtain $\tilde{\alpha}_{12}$ and $\tilde{\alpha}_{21}$, which in turn can be inserted into eq 38 to provide the components of the interaction free energy. Further details about the numerical procedure, including truncation error analyses, are given in Appendix C.

**Two Coupled Dielectric Spheres: Perturbation Approach.** The derivation in the previous subsection is exact within the continuum assumption in the sense that no restriction is put upon the strength of the interaction between the dielectric bodies. An approximate solution valid for small interaction energies, approximately corresponding to the first-order perturbation result of Lifshitz theory, can be obtained by assuming that the two dielectric spheres remain in their unperturbed states, corresponding to the vacuum probability distribution (eq 16). This means that the iterative procedure to obtain $\hat{\alpha}$ and $\tilde{\alpha}$ is avoided, and the closed expression for $\langle A_{l_il_jm}\rangle$ becomes

$$\langle \beta A_{l_il_jm}^{(\text{pert})}\rangle = -\frac{1}{2}\ln\left[\frac{4\alpha_i\alpha_j}{4\alpha_i\alpha_j - [\beta R^{-(L+1)}f(l_i,l_j,m,-m)]^2}\right]$$

(40)

A comparison between results obtained from eqs 38 and 40 gives an approximate measure of the range of validity for the perturbation approach of Lifshitz and Langbein theory.

Numerical Results. In Figure 2a we present results describing the quotas $\hat{\alpha}_{l_im}/\alpha_{l_i}$ and $\tilde{\alpha}_{l_il_jm}/\alpha_{l_i}$, where we have dropped the first i and j subscripts on the exponents, as a function of the separation D/a. In particular, we choose to study the exponents with $l_i = l_j = 1$ and $m = 0$, i.e., the ones describing the probability distribution of the axial dipole moment. Furthermore, in Figure 2b, the corresponding quota $\hat{\alpha}_{l0}/\alpha_l$ is presented as a function of l for three different separations. We note that (i) the inequalities $\hat{\alpha} < \alpha$ and $\tilde{\alpha} < \alpha$ are confirmed, meaning that the probability distributions are widened by the presence of the other sphere, and (ii) $\hat{\alpha} < \tilde{\alpha}$, since $\hat{\alpha}$ includes the widening from interactions with *all* moments on the other sphere, whereas the contribution from one of the moments (in this case the dipole) is excluded from $\tilde{\alpha}$, thus leading to a smaller widening of the probability distribution. We furthermore note that (iii) the dipole quota $\hat{\alpha}_{10}/\alpha_1$ deviates more from unity as the separation decreases and (iv) $\hat{\alpha}_{l0}/\alpha_l$ approaches unity at increasing l, the approach being faster for larger separations. The two latter observations naturally reflect the $R^{-2(L+1)}$ distance dependence of the coupling between multipole moments of the two spheres. As a final remark, one may use the present results to assess the accuracy of the perturbative approach described above, using the assignment $\tilde{\alpha} = \alpha$.

Figure 3 shows the effective interaction A_{int} between two spheres of equal radius $a_1 = a_2 = a$ and $\varepsilon = 80$ solved using both the present formalism and the standard Hamaker approach with the Hamaker constant $H = 0.84kT$ obtained from eq 9. A closer study of the results shows that:
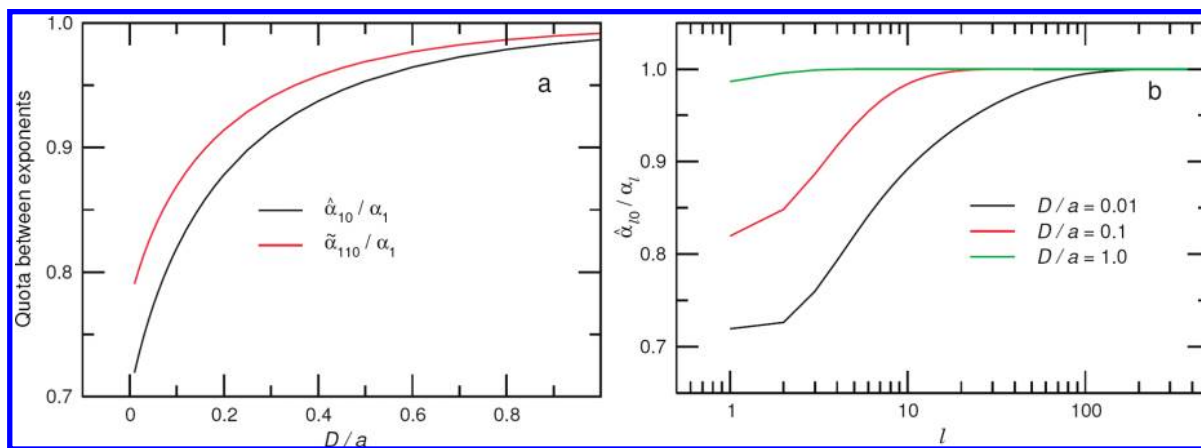
Figure 2. (a) Quota between the exponents α_1, $\hat{\alpha}_{10}$, and $\tilde{\alpha}_{110}$, as a function of the separation D/a and (b) $\hat{\alpha}_{l0}/\alpha_l$ as a function of l for three different separations D/a.
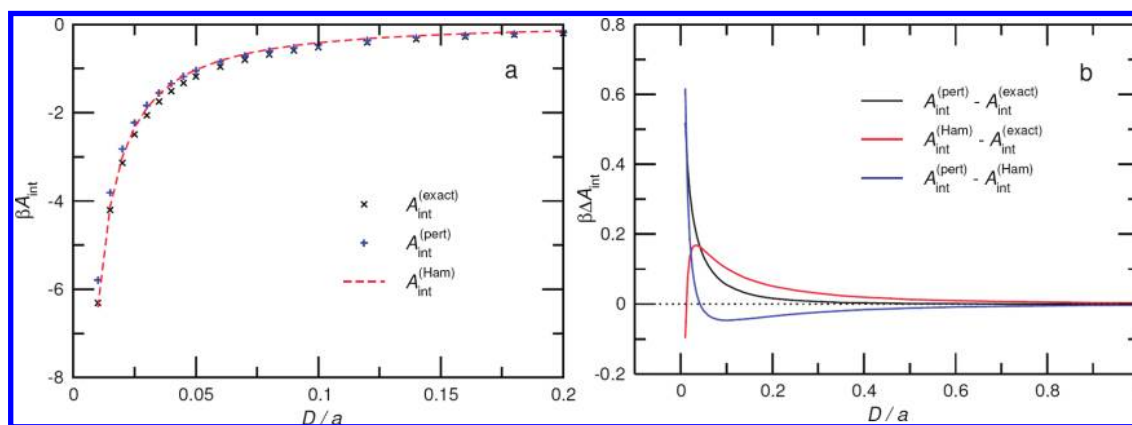
Figure 3. (a) Interaction free energy between two dielectric spheres with $\varepsilon = 80$ calculated using the exact formalism ($A_{int}^{(exact)}$, eq 38), the perturbative approximation ($A_{int}^{(pert)}$, eq 40), and the Hamaker formula ($A_{int}^{(Ham)}$, eq 3) using $H = 0.84kT$ calculated from eq 9. (b) Differences between results obtained using the three different formalisms for a larger range of D/a values. The dotted line corresponds to $\beta\Delta A_{int} = 0$.

1. The perturbative approach is reasonably accurate for $D/a \geq 0.2$, but significantly underestimates the magnitude of the interaction free energy for smaller separations.
2. Compared to the exact solution, the Hamaker expression underestimates $|A_{int}|$ for intermediate separations and slightly overestimates it at short ($D/a \approx 0.01$) separations.
3. The Hamaker equation gives a strong overestimation of $|A_{int}|$ at short separation compared to the perturbative result, whereas the two theories show good correspondence at long and intermediate separations.

The first observation is in accordance with the observed increased deviation from unity of $\tilde{\alpha}_{l_i l_j m}/\alpha_{l_i}$ with decreased separation and gives an approximate range of validity of the present perturbation approximation. It should also be applicable to Lifshitz and Langbein theory, which make use of a perturbative treatment similar to that used to derive eq 40. The discrepancies in observation 2 are due to both the pairwise additivity assumption used to derive the functional form of eq 3 and the perturbative treatment used to calculate H, whereas the difference between $A_{int}^{(pert)}$ and $A_{int}^{(Ham)}$ (observation 3) is due solely to the error in the functional form of the Hamaker expression. A comparison between the different sources of discrepancy shows that the error connected to the perturbation treatment (black curve in Figure 3b) is actually *larger* than that due to the functional form of the Hamaker formula (red curve).

Conclusions

In the present contribution, we have presented an exact derivation of the effective interaction between two spherical bodies of dielectric material based on the coupling between the collective electrostatic fluctuations of the two spheres. The resulting equations are easily numerically solvable for separations $D/a \geq 0.01$ using $\varepsilon = 80$.

The derivation is restricted to the case that all interactions can be described classically, implying that (i) retardation of the interaction can be ignored and (ii) only the zero-frequency dielectric constant $\varepsilon(0)$ needs to be considered. Furthermore, we avoid the linear response approximation inherent in the Lifshitz and Langbein approaches, meaning that our results do not assume that the coupling between the two dielectric bodies is small enough not to perturb their "ground-state" properties. Also, our derivation takes into account the spherical symmetry of the dielectric bodies in an exact but yet simple manner, especially compared to the cumbersome formalism developed by Langbein.

Moreover, our formalism allows for a straightforward perturbative treatment, thus enabling an easy assessment of the accuracy of the linear response approximation, which is inherent in Lifshitz and Langbein theory. Even though the discrepancies between the two approaches are small, it was found that the

error connected with the linear response approximation is of comparable magnitude to that inherent in the Hamaker equation.

Appendix A. Properties of Spherical Multipoles

The spherical multipole moments Q_{lm} defined by eq 21 are in general complex quantities, with the real and imaginary parts acting as independent degrees of freedom. Furthermore, they obey the relationship

$$Q_{l-m} = (-1)^m Q_{lm}^* \qquad (41)$$

which means that the components Q_{lm} and Q_{l-m} are not independent quantities. Because of this, we choose to treat only the multipole moments with $m \geq 0$, and consider separately the real and imaginary components of Q_{lm}. Since the axial component Q_{l0} is real, these quantities ($l + 1$ real and l imaginary components) form the $2l + 1$ independent "fluctuation modes" of Q_l.[23]

One Dielectric Sphere in a Vacuum

The unnormalized probability distribution $P(Q_{l0})$ of the axial multipole moment Q_{l0} of a dielectric sphere in vacuum can be expressed as[17,18]

$$P(Q_{l0}) = \exp(-\alpha_l Q_{l0}^2) \qquad (42)$$

where the exponent α_l is given by eq 18. For the nonaxial components ($m \neq 0$), the probability distribution is instead given by

$$P(Q_{lm}) = \exp(-\alpha_l|Q_{lm}|^2)\exp(-\alpha_l|Q_{l-m}|^2) = \\ \exp[-2\alpha_l(Q_{lm}^R)^2]\exp[-2\alpha_l(Q_{lm}^I)^2] \quad (43)$$

which enables us to write $P(Q_{lm}^X)$ in the form of eq 16.

Interaction between Two Multipoles

We begin by considering the interaction between two aligned axial multipoles $Q_{1,l_1 0}$ and $Q_{2,l_2 0}$. Using the formula for the electrostatic interaction between two multipoles,[21] we obtain the coupling energy according to

$$U_{l_1 0;l_2 0} = (-1)^{l_1} f(l_1,l_2,0,0) R^{-(L+1)} Q_{1,l_1 0} Q_{2,l_2 0} C_{L0}(\Omega) \qquad (44)$$

In the case of nonaxial multipoles $Q_{1,l_1 m_1}$ and $Q_{2,l_2 m_2}$ with $m_1 > 0$ and $m_2 > 0$, we also need to consider the contribution coming from $Q_{1,l_1 -m_1}$ and $Q_{2,l_2 -m_2}$, leading to

$$U_{l_1 m_1;l_2 m_2} = (-1)^{l_1+M}f(l_1,l_2,m_1,m_2)\left[Q_{1,l_1 m_1}Q_{2,l_2 m_2}\frac{C_{LM}^*(\Omega)}{R^{L+1}} + \right.\\ \left. Q_{1,l_1 -m_1}Q_{2,l_2 -m_2}\frac{C_{L-M}^*(\Omega)}{R^{L+1}}\right] + \\ (-1)^{l_1+\mu}f(l_1,l_2,m_1,-m_2)\left[Q_{1,l_1 m_1}Q_{2,l_2 -m_2}\frac{C_{L\mu}^*(\Omega)}{R^{L+1}} + \right.\\ \left. Q_{1,l_1 -m_1}Q_{2,l_2 m_2}\frac{C_{L-\mu}^*(\Omega)}{R^{L+1}}\right] \qquad (45)$$

where $\mu = m_1 - m_2$, and we have used the fact that $f(l_1,l_2,m_1,m_2) = f(l_1,l_2,-m_1,-m_2)$. Now, using eq 41 to relate Q_{lm} and Q_{l-m} and the equivalent formula for C_{lm} leads to the simplification

$$U_{l_1 m_1;l_2 m_2} = 2(-1)^{l_1+M}f(l_1,l_2,m_1,m_2)\mathrm{Re}\left[Q_{1,l_1 m_1}Q_{2,l_2 m_2}\frac{C_{LM}(\Omega)}{R^{L+1}}\right] + \\ 2(-1)^{l_1+m_1}f(l_1,l_2,m_1,-m_2)\mathrm{Re}\left[Q_{1,l_1 m_1}^* Q_{2,l_2 m_2}\frac{C_{L\mu}(\Omega)}{R^{L+1}}\right] \qquad (46)$$

Insertion of the real and imaginary parts of the complex quantities further leads to

$$U_{l_1 m_1;l_2 m_2} = 2(-1)^{l_1+M}f(l_1,l_2,m_1,m_2)\left[(Q_1^R Q_2^R - Q_1^I Q_2^I)\frac{C_{LM}^R(\Omega)}{R^{L+1}} - \right.\\ \left. (Q_1^R Q_2^I + Q_1^I Q_2^R)\frac{C_{LM}^I(\Omega)}{R^{L+1}}\right] + \\ 2(-1)^{l_1+m_1}f(l_1,l_2,m_1,-m_2)\left[(Q_1^R Q_2^R + Q_1^I Q_2^I)\frac{C_{L\mu}^R(\Omega)}{R^{L+1}} - \right.\\ \left. (Q_1^R Q_2^I - Q_1^I Q_2^R)\frac{C_{L\mu}^I(\Omega)}{R^{L+1}}\right] \qquad (47)$$

where $Q_1 = Q_{1,l_1 m_1}$ and $Q_2 = Q_{2,l_2 m_2}$. We now choose, without any loss of generality, a coordinate system such that $\mathbf{R} = (R, \Omega) = (R, \theta, \varphi)$ lies along the z axis, and thus $\theta = \varphi = 0$. This leads to $C_{lm}^I(\Omega) = 0$, $\forall m$, $C_{lm}^R(\Omega) = 0$, $m \neq 0$, and $C_{l0}^R(\Omega) = 1$, implying that a nonzero interaction appears only when $m_2 = \pm m_1$. In this coordinate system, choosing $m_1 = m_2 = m$, eq 47 reduces to

$$U_{l_1 m;l_2 m} = 2(-1)^{l_1+m}f(l_1,l_2,m,-m)R^{-(L+1)}[Q_1^R Q_2^R + Q_1^I Q_2^I] \equiv \\ U_{l_1 m;l_2 m}^{(R)} + U_{l_1 m;l_2 m}^{(I)} \qquad (48)$$

where $U^{(R)}$ and $U^{(I)}$ contain the coupling between the real and imaginary parts of Q_{lm}, respectively. Thus, the real and imaginary parts of $Q_{l_1 m_1}$ and $Q_{l_2 m_2}$ become energetically decoupled from each other using this coordinate system. This fact, together with eq 43, leads to the fact that all probability distributions can be written on the factorized form $P(Q_{lm}) = P(Q_{lm}^R)P(Q_{lm}^I)$. Furthermore, it is clear that the interaction between the real and imaginary parts of Q_{lm} are equal, leading to $P(Q_{lm}^R)$ and $P(Q_{lm}^I)$ having identical functional forms. Now, combining eq 44 (with $C_{L0}(\Omega) = 1$) and eq 48 leads to the following formula:

vdW Interaction between Two Spheres of Dipolar Fluid

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$$U_{l_1m;l_2m} =$$
$$(-1)^{l_1+m}(2 - \delta_{m0})f(l_1,l_2,m,-m)R^{-(L+1)}Q^X_{1,l_1m}Q^X_{2,l_2m} \qquad \forall m \quad (49)$$

Appendix B. Derivation of Interaction Energies and Free Energies

According to basic statistical-mechanical concepts, the electrostatic free energy difference $\langle\beta A\rangle$ between the coupled and uncoupled systems can be expressed as[24]

$$\langle\beta A\rangle = -\ln\frac{Z_c}{Z_u} \qquad (50)$$

where Z_c and Z_u are the configuration integrals of the coupled and uncoupled systems, respectively.

In the case of a dielectric sphere coupled to a permanent charge distribution, the configuration integrals corresponding to the coupling of one multipole component are given by

$$Z^{(X)}_{c,l_im} = \int_{-\infty}^{\infty} P(Q^X_{i,l_im};\rho_j)\,dQ^X_{i,l_im} \qquad (51)$$

and

$$Z^{(X)}_{u,l_im} = \int_{-\infty}^{\infty} P(Q^X_{i,l_im})\,dQ^X_{i,l_im} \qquad (52)$$

where the probability distributions are given by eqs 19 and 16, respectively. Carrying out the integrations and inserting the result into eq 50 readily gives eq 24.

In the case of two coupled dielectric spheres, the corresponding configuration integrals are given by

$$Z^{(X)}_{c,l_il_jm} = \int\int_{-\infty}^{\infty} P(Q^X_{i,l_im},Q^X_{j,l_jm})\,dQ^X_{i,l_im}\,dQ^X_{j,l_jm} =$$
$$\int\int_{-\infty}^{\infty} \exp[-\tilde{\alpha}_{i,l_il_jm}(2 - \delta_{m0})(Q^X_{i,l_im})^2] \times$$
$$\exp[-\tilde{\alpha}_{j,l_il_jm}(2 - \delta_{m0})(Q^X_{j,l_jm})^2] \times$$
$$\exp[-\beta U_{l_im;l_jm}]\,dQ^X_{i,l_im}\,dQ^X_{j,l_jm} \quad (53)$$

where we have used eq 32, and

$$Z^{(X)}_{u,l_il_jm} = \int_{-\infty}^{\infty}\exp[-\tilde{\alpha}_{i,l_il_jm}(2 - \delta_{m0})(Q^X_{i,l_im})^2]\,dQ^X_{i,l_im}$$
$$\times \int_{-\infty}^{\infty}\exp[-\tilde{\alpha}_{j,l_il_jm}(2 - \delta_{m0})(Q^X_{j,l_jm})^2]\,dQ^X_{j,l_jm} \qquad (54)$$

where the subscript u now denotes a system that is uncoupled with respect to Q_{i,l_im} and Q_{j,l_jm}, whereas all other couplings are included implicitly in the exponents $\tilde{\alpha}_{ij}$ and $\tilde{\alpha}_{ji}$. Insertion of the probability distribution from eq 32, followed by integration and insertion of the result into eq 50 gives eq 38 for the free energy components $\langle\beta A_{l_il_jm}\rangle$.

Furthermore, the energetic part $\langle\beta U_{l_il_jm}\rangle$ of the electrostatic interaction can be obtained from the probability distribution of eq 32 through the standard statistical-mechanical expectation value

$$\langle\beta U_{l_il_jm}\rangle = \frac{\int\int_{-\infty}^{\infty}\beta U_{l_im;l_jm}P(Q^X_{i,l_im},Q^X_{j,l_jm})\,dQ^X_{i,l_im}\,dQ^X_{j,l_jm}}{\int\int_{-\infty}^{\infty}P(Q^X_{i,l_im},Q^X_{j,l_jm})\,dQ^X_{i,l_im}\,dQ^X_{j,l_jm}} \qquad (55)$$

where $U_{l_im;l_jm}$ is given by eq 30. A straightforward integration leads to eq 37.

Appendix C. Computational Aspects

Equation 36 was solved iteratively using a Fortran 90 computer code[25] after truncation of the infinite sums at $l = l_{max}$ and $m = \min(l,m_{max})$. The numerical solution is thus subjected to uncertainties arising from (i) the truncation of the multipole expansions and (ii) the iterative solution of eq 36. The far most demanding calculation appeared for the smallest separation considered, for which $D/a = 0.01$.

Figure 4 displays the differences $\beta A_{int}(m_{max}) - \beta A_{int}(m_{max} = 50)$ and $\beta A_{int}(l_{max}) - \beta A_{int}(l_{max} = 500)$, evaluated for $D/a = 0.01$ using $l_{max} = 500$ and $m_{max} = 50$, respectively. This difference gives the best estimation possible of the error in βA_{int}. On an absolute scale, the truncation error in m is $\approx 3 \times 10^{-8}$, and the corresponding error in l is $\approx 6 \times 10^{-4}$. The comparingly fast convergence of the sum over m (i.e., $m_{max} \ll l_{max}$) indicates that the dominant contributions to the interaction free energy come from multipole components of "near-axial" symmetry. For all calculations $m_{max} = 50$ and $l_{max} \leq 500$ were used, keeping an absolute accuracy of at least 6×10^{-4}. Table 1 displays the
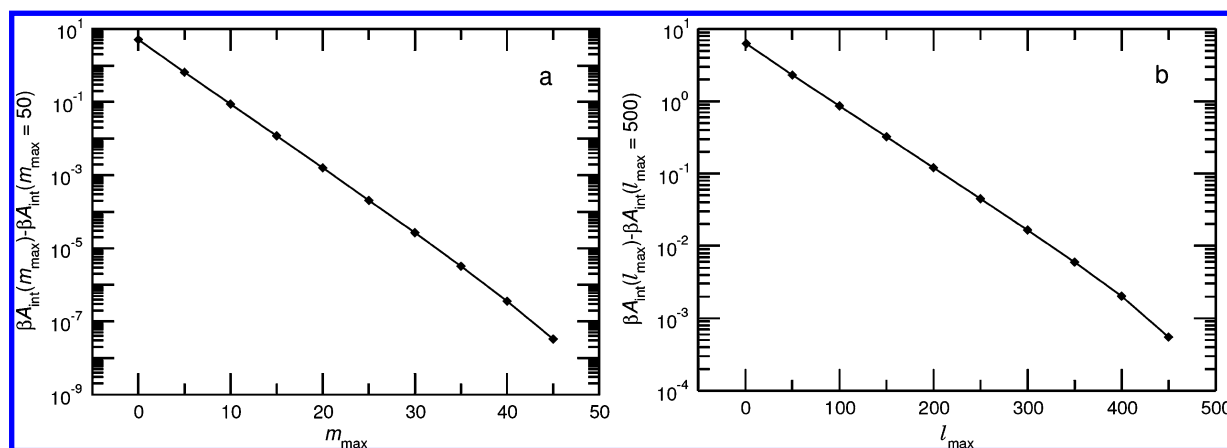
Figure 4. Estimate of the absolute error in βA_{int} as a function of (a) m_{max} with $l_{max} = 500$ and (b) l_{max} with $m_{max} = 50$ for the smallest separation ($D/a = 0.01$) considered, using $\beta A_{int}(l_{max} = 500, m_{max} = 50)$ as an approximation of the exact value. The error due to the iterative solution of eq 36 is negligible compared to the error related to the truncation of the multipole expansions.

TABLE 1: Interaction Free Energy, Truncation Error Analysis, and CPU Time at Different Separations[a]

D/a	βA_{int}	l_{max}	m_{max}	CPU (s)
0.01	−6.308695018	500	50	600
0.1	−0.5157422666	50	13	1
0.5	−0.03911899476	7	3	<0.005

[a] The truncation error in l is $\approx 6 \times 10^{-4}$ and the corresponding error in m is $\approx 3 \times 10^{-8}$.

values of l_{max} and m_{max} needed to maintain this accuracy for three different separations. Also shown is the CPU time needed for the numerical solution. A rough analysis shows that $l_{max} \sim D^{-1}$ and $m_{max} \sim D^{-1}$, whereas CPU $\sim D^{-3}$.

The relative error in $\hat{\alpha}$ due to the iterative solution of eq 36 was always $\lesssim 10^{-10}$, leading to a similar contribution to the relative error in βA_{int}; thus, this error is negligible compared to the error due to the truncation of the multipole expansions. For the shortest separation considered, 20 iterations were required to reach convergence in $\hat{\alpha}$.

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