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Development of a picture of the van der Waals interaction energy between clusters of nanometer-range particles

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The importance of the long-range Lifshitz–van der Waals interaction energy between condensed bodies is well known. However, its implementation for interacting bodies that are highly irregular and separated by distances varying from contact to micrometers has received little attention. As part of a study of collisions of irregular aerosol particles, an approach based on the Lifshitz theory of van der Waals interaction has been developed to compute the interaction energy between a sphere and an aggregate of spheres at all separations. In the first part of this study, the iterated sum-over-dipole interactions between pairs of approximately spherical molecular clusters are compared with the Lifshitz and Lifshitz-Hamaker interaction energies for continuum spheres of radii equal to those of the clusters' circumscribed spheres and of the same masses as the clusters. The Lifshitz energy is shown to converge to the iterated dipolar energy for quasispherical molecular clusters for sufficiently large separations, while the energy calculated by using the Lifshitz-Hamaker approach does not. Next, the interaction energies between a contacting pair of these molecular clusters and a third cluster in different relative positions are calculated first by coupling all molecules in the three-cluster system and second by ignoring the interactions between the molecules of the adhering clusters. The error calculated by this omission is shown to be very small, and is an indication of the error in computing the long-range interaction energy between a pair of interacting spheres and a third sphere as a simple sum over the Lifshitz energies between individual, condensed-matter spheres. This Lifshitz energy calculation is then combined with the short-separation, nonsingular van der Waals energy calculation of Lu, Marlow, and Arunachalam, to provide an integrated picture of the van der Waals energy from large separations to contact. [S1063-651X(98)14309-X]

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I. INTRODUCTION

The van der Waals (VDW) forces are universal, in the sense that they act between all atoms and molecules as well as condensed bodies [1]. The origins of these forces are the instantaneous charge fluctuations in individual atoms and molecules as well as in condensed media. They play roles in numerous important physical, chemical, and biological phenomena. Examples include, but are not limited to, particle aggregation in the gas phase, adhesion, physical adsorption, wetting, and flocculation of particles in liquids.

Calculations of the VDW energy between condensed bodies have been made by Bradley [2], Hamaker [3], Lifshitz [4], Langbein [5], and others (see Ref. [6] for a list of other authors). The approaches can be broadly classified as being two body and many body. The two-body approaches [2,3] obtain the interaction energy by a pairwise summation of the direct intermolecular interactions [7–9]. The many-body approaches [4,5,10], on the other hand, include both the direct interactions and the induction correlations of molecules within each condensed body and between the two interacting condensed bodies. All calculations based on many-body approaches thus far have been made for geometrically simple systems. However, many realistic bodies, such as aggregated particles formed in colloidal and in gas-phase processes, are geometrically asymmetrical and highly irregular [11,12]. Calculations of the many-body VDW energy between bodies having irregular geometry, from large separations to contact, to our knowledge, have never been made. The purpose of this study is to develop a method for the calculation of this VDW energy between a nanometer-range spherical particle and an aggregate comprised of similarly sized primary particles from distant initial separation to contact. Such calculations are useful in molecular dynamic trajectory simulations of particle aggregation, in which the force derived from the interaction energy and the initial conditions play an important role.

This paper is structured as follows: In Sec. II, we present the interaction energy calculations for two spherical particles for large and near-contact separations and develop an analysis of the dependences at different distances, which permits a parametrization of the interaction energy over all separations. In Sec. III, we extend the above calculations to complex particles comprised of several spherical particles and find a simple means of calculating the many-body VDW energy, which is readily applicable to clustered particles of arbitrary shapes. Finally, in Sec. IV we present the conclusions.

II. INTERACTION ENERGY CALCULATIONS: SPHERICAL PARTICLES

A. Continuum matter

Several approaches are available in the literature for the calculation of the VDW energy between spherical particles.

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The Hamaker approach calculates the VDW interaction energy between two spherical particles assuming simple pairwise addition of corresponding intermolecular energies. For the case of two spherical particles of radii *a*, *b* and molecular number densities n_A, n_B whose center-of-mass separation is *R*, the result of the summation is

$$E_{AB}=-\frac{A_{AB}^{H}}{6}\left[\frac{2ab}{R^2-(a+b)^2}+\frac{2ab}{R^2-(a-b)^2}+\ln\left\{\frac{R^2-(a+b)^2}{R^2-(a-b)^2}\right\}\right], \tag{1}$$

where the constant A_{AB}^{H} is called the Hamaker constant and is defined as

$$A_{AB}^{H}=\pi^2 n_A n_B C_6. \tag{2}$$

In Eq. (2), C_6 is given by

$$C_6=\frac{3\hbar}{2\pi}\int_{-\infty}^{+\infty}\alpha_A(i\xi)\alpha_B(i\xi)d\xi, \tag{3}$$

where $\alpha(i\xi)$ denotes the (scalar) frequency-dependent molecular polarizability taken on the imaginary axis for computational convenience and $\hbar$ is Planck's constant. While the Hamaker potential is mathematically simple, it suffers from two general defects: (1) it does not take into account the collective effects that are operative in condensed matter, and (2) the interaction energy diverges upon contact rather than converging to a finite value.

The Lifshitz theory of the van der Waals interaction, on the other hand, is based on a continuum approach in that it calculates the interaction energy without direct reference to the molecular structure of the particles. The interaction energy is due to the perturbation of the free electromagnetic field caused by the introduction of the two bodies into free space [4,13]. This approach has full generality, is applicable to any body at any temperature, and has the correct behavior in the limiting case of rarefied media (i.e., giving the intermolecular energy). However, analytical expressions for the interaction energies can be obtained from Lifshitz theory only for certain regular interactant geometries. Solutions are available for interacting half-spaces [4], spheres [14], films, layers, and planes [15], and a sphere with a plane [16]. Moreover, being a continuum approach, it can only be used for distance scales greater than the molecular dimensions.

The Lifshitz-Hamaker approach [1,5,17] is a hybrid in that it assumes the *geometrical* dependence of pairwise addition of the intermolecular interaction similar to the Hamaker approach, while incorporating the collective effects through an alternative form of the Hamaker constant. For interacting half-spaces *A* and *B* separated by a vacuum, the Lifshitz-Hamaker (LH) constant is expressed as

$$A_{AB}^{\mathrm{LH}}\approx\frac{3}{4}kT\left[\frac{\varepsilon_A(0)-1}{\varepsilon_A(0)+1}\right]\left[\frac{\varepsilon_B(0)-1}{\varepsilon_B(0)+1}\right]+\frac{3\hbar}{8\pi}\int_{2\pi kT/\hbar}^{\infty}\left[\frac{\varepsilon_A(i\xi)-1}{\varepsilon_A(i\xi)+1}\right]\left[\frac{\varepsilon_B(i\xi)-1}{\varepsilon_B(i\xi)+1}\right]d\xi, \tag{4}$$

where *T* is the temperature, $\varepsilon_A(i\xi)$ and $\varepsilon_B(i\xi)$ are the dielectric constants of bodies *A* and *B* on the imaginary frequency axis, and *k* is Boltzmann's constant. For interacting half-spaces, replacement of A_{AB}^{H} by A_{AB}^{LH} exactly expresses the nonretarded Lifshitz theory results while for spheres, A_{AB}^{LH} provides a lower bound of the magnitude of the VDW energy [14] when used in Eq. (1). Although the replacement of Eq. (2) by Eq. (4) is helpful in accounting for the collective intermolecular interactions characterizing condensed matter in the continuum limit, it does not indicate the manner in which the summed discrete interactions approach the condensed matter interaction energy with increasing numbers of molecules. Nevertheless, the Lifshitz-Hamaker approach has often been used in the literature. The assumption that it provides an adequate approximation for spheres has not been adequately quantified and will be examined as part of this study.

Langbein [15] developed an alternative, ''molecular'' approach to describe the interaction energy of continuous bodies by adapting Bade's [18] perturbation theory computation of the collective dispersion energy among discrete molecules. By regrouping terms and using the standard Clausius-Mossotti relation to express the dielectric constant in terms of the molecular density and polarizability, Langbein [5] ''derived'' the nonretarded version of the Lifshitz interaction energy between half-spaces. This same approach was then utilized by Langbein [14] to derive a slowly convergent series solution for the interaction energy of two continuum spheres. This slow-convergence difficulty can be overcome by using an accurate mathematical approximation to Langbein's exact expression for the Lifshitz energy. The approximation was developed by Keifer, Parsegian, and Weiss (KPW) [16], who showed it to have better than 2% accuracy. Their nonretarded interaction energy for continuum bodies can be expressed as

$$E(z)=\frac{\hbar}{2\pi}\int_{2\pi kT/\hbar}^{\infty}g(\xi,z)d\xi-\frac{kT}{2}g(0,z), \tag{5}$$

where *z* is the distance between the centers of the interacting spheres, and ξ is the frequency. The function $g(\xi,z)$ [16] is an infinite sum over terms involving ξ and *z*, some of which are themselves infinite sums. The calculation of $g(\xi,z)$ can be accelerated by using a rapid summation technique that uses a nonlinear transformation developed by Aitken [19].

B. Discrete clusters

The work of Langbein summarized above suggests [20] an approach to the calculation of the VDW energy between molecular clusters that is consistent [17] with all levels of molecular aggregation from London–van der Waals interaction of a pair of molecules to the continuum Lifshitz theory. Considering each molecule as a discrete oscillator, the total energy may be shown [16,15] to be expressed as

$$(\Delta E_{AB})_{\mathrm{total}}=\frac{h}{8\pi^2}\int_{-\infty}^{\infty}d\xi\ \ln\{\det[\mathbf{I}-\boldsymbol{\alpha}(i\xi)\mathbf{T}]\}, \tag{6}$$

where

$$\boldsymbol{\alpha}(i\xi)=\begin{pmatrix}\boldsymbol{\alpha}^{(A)} & 0\\ 0 & \boldsymbol{\alpha}^{(B)}\end{pmatrix} \tag{7}$$

is the polarizability matrix for the system and $\mathbf{I}$ is the $3N_A \times 3N_B$ identity matrix with N_X the number of molecules in cluster X. Each major submatrix $\boldsymbol{\alpha}^{(X)}$ is diagonal in the 3×3 polarizability tensors, each of which corresponds to a distinct molecule in cluster X. The dipolar coupling tensor $\mathbf{T}$ for the system is comprised of elements $\mathbf{T}_{ij}=-\boldsymbol{\nabla}_i\boldsymbol{\nabla}_j[1/(r_i-r_j)]$ and

$$\mathbf{T}=\begin{pmatrix}\mathbf{T}^{(A)} & \mathbf{T}^{(C)}\\ \mathbf{T}^{(C)} & \mathbf{T}^{(B)}\end{pmatrix}, \tag{8}$$

where the indices are such that $\mathbf{T}^{(A)}$ couples only molecules within A, $\mathbf{T}^{(B)}$ couples only molecules within B, and $\mathbf{T}^{(C)}$ couples the molecules in the separate clusters. The cluster interaction energy ΔE_{AB} is given as the difference between the energy of the fully coupled clusters and the sum of the individual cluster self-energies in isolation of each other [i.e., Eq. (6) with $\mathbf{T}^{(C)}$ set to 0],

$$\Delta E_{AB}=(\Delta E_{AB})_{\text{total}}-(\Delta E_A+\Delta E_B). \tag{9}$$

The energy as represented by Eq. (9) is the basis for computing the ‘‘discrete’’ long-range cluster interaction energies in this paper. While it is a relatively crude representation for general intracluster properties, for intercluster attraction it should be realistic, provided no collective states such as conduction bands form within the clusters. Amadon and Marlow [17] calculated the VDW interaction energy between molecular clusters using this formulation of the iterated van der Waals interaction energy over discrete molecules. The prototype clusters used in their calculations were carbon tetrachloride (CCl_4) molecular clusters comprised of 13 and 55 molecules in icosahedral and 33 molecules in dodecahedral configurations. Through the use of a repulsive component to the VDW energy that varied as r^{-24}, where r is the separation between the molecules, they define a molecular ‘‘diameter’’ (σ). The ‘‘contact energy’’ in their calculation therefore corresponds to a separation σ between ‘‘point molecules.’’ The interaction energy calculations require large amounts of computer time even for calculations involving small molecular clusters.

C. Comparison

First, the interaction energy is computed using the discrete approach [Eq. (9)] and is labeled E_D. The molecular clusters are then replaced by spherical particles of the same mass, corresponding radii, and dielectric properties as the molecular clusters cited above (see [17]), and then the interaction energies using the Lifshitz-Hamaker approach (E_{LH}), Eqs. (1)–(4), and the KPW approximation for the Lifshitz energy (E_{Lif}), Eq. (5), are determined. Figures 1(a)–1(c) are graphs of the relative difference of E_{Lif} or E_{LH} and E_D versus scaled separation for pairs of 13-, 33-, and 55-molecule CCl_4 clusters, respectively. The solid lines correspond to $(E_{\text{Lif}}-E_D)/E_D$ versus $d_{\text{c.m.}}/d_{\text{av}}$ and the dashed lines correspond to $(E_{\text{LH}}-E_D)/E_D$ versus $d_{\text{c.m.}}/d_{\text{av}}$, where $d_{\text{c.m.}}$ is the center-of-mass separation of the particles and d_{av} is the average diameter for the discrete cluster [17]. The graphs indicate that for large surface-to-surface separations of the particles, E_{Lif} converges to E_D within the accuracy of the approximation used to compute E_{Lif}, while E_{LH} underestimates the exact energy E_D by 10–15%. For small separations, both approximations overestimate the attractive inter-

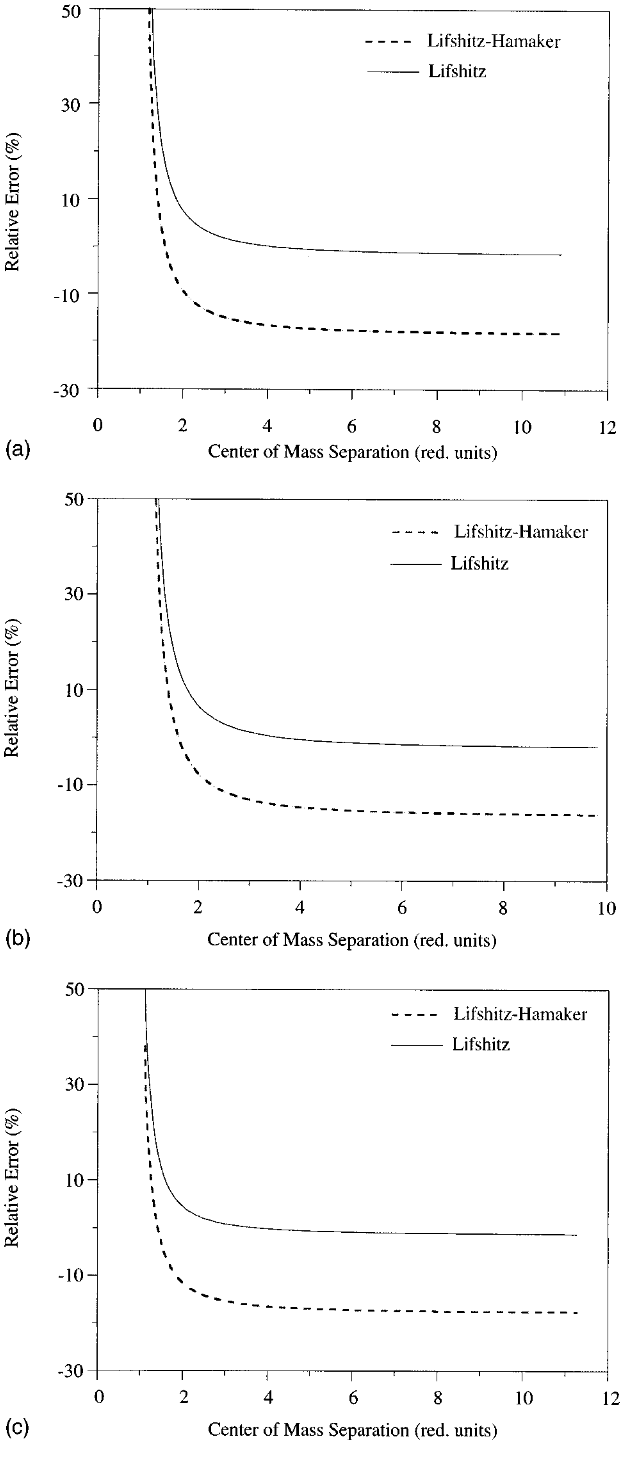

FIG. 1. The errors in Lifshitz-Hamaker and Lifshitz energies relative to the discrete energy for a pair of (a) 13-molecule icosahedral CCl_4 clusters, (b) 33-molecule dodecahedral CCl_4 clusters, and (c) 55-molecule icosahedral CCl_4 clusters. The center-of-mass separation ($d_{\text{c.m.}}$) is in units of the average cluster diameter (d_{av}), which is 1.558 nm, 2.259 nm, and 2.544 nm for (a), (b), and (c), respectively.

action energy, a typical result for the macroscopic interaction. Although the Amadon and Marlow approach avoids the problem of singularity of the interaction energy upon contact through the use of a repulsive component to the VDW energy between the molecules, it still assumes that the molecules are point particles. Another disadvantage of this approach is that the interaction energy calculations are computationally intensive and are, therefore, impractical for determining interactions between larger particles.

A new and computationally feasible calculation of the interaction energy for ultrafine particles at short-range separation to contact (where the above calculations fail) has been developed by Lu, Marlow, and Arunachalam [21], hereafter referred to as the LMA approach. The calculations show that at, or near, contact, the molecular size effects are important and must be taken into consideration. The contact energies calculated using this method are finite as opposed to the infinite values obtained with methods that consider the molecules to be point particles. As the surface-to-surface separation between the particles increases, molecular size effects become decreasingly important, and the short-range energy converges smoothly to the continuum energy calculated using the Lifshitz approach. Let us now examine the domains within which each of the above approaches are valid, as well as the convergence criterion. We will then present a parametrized representation of the interaction energy over all separations. This simple, yet accurate, representation is easily programmable and will be particularly beneficial to dynamic simulations of particle aggregation where considerable time is spent on the evaluation of interparticle forces.

The rationale behind the LMA approach is based on Langbein's observation [15] that the two-body potential between condensed bodies has the same dependence on the surface-to-surface separation as the many-body potential, provided that this separation is small compared to the sizes of the condensed bodies involved. In other words, at small separations, the many-body effects modify only the interaction constant, while leaving the functional dependence of the interaction potential on the separation distance unchanged. It follows, therefore, that if a two-body potential is obtained, the corresponding nonretarded many-body potential at small separation can be obtained by simply replacing the two-body interaction constant (Hamaker constant) by the many-body interaction constant (Hamaker-Lifshitz constant), which is defined, to a first approximation, by

$$C=\frac{kT}{4}\sum_{n=0}^{\infty}{}'\left[\frac{\varepsilon(i\xi_n)-\varepsilon_0(i\xi_n)}{\varepsilon(i\xi_n)+\varepsilon_0(i\xi_n)}\right]^2, \tag{10}$$

where $\xi_n=2n\pi kT/\hbar$ $(n=0,1,...)$, $\varepsilon(i\xi)$, and $\varepsilon_0(i\xi)$ are frequency-dependent dielectric constants evaluated at imaginary frequencies for the condensed body and the surrounding medium, respectively. The prime on the sum indicates that the $n=0$ term is weighted by $\frac{1}{2}$. The k represents Boltzmann's constant, and T is the ambient temperature. In addition to the small separation requirement, Langbein also specified [15] that the change in dielectric constant with respect to distance should be small near the surface. This second proviso is unnecessary for our calculations because we have incorporated the effects of molecular size into our considerations to give a finite contact energy. In contrast, Langbein assumed the dielectric constant to be a function of separation such that a finite contact energy can be obtained with the singular potential; consequently, the dielectric constant must be a smooth function of separation near the surface for his energy calculations.

Based upon the above argument and taking into account the finite molecular size, Lu *et al.* [21] derived the small-separation dispersion energy between two spheres of equal radii r as

$$\begin{aligned}E_{\mathrm{SR}}=-\frac{Cr}{2d}\Bigg\{&\frac{4rd}{(d+2r)^2}+\frac{2rd}{(d+2r)(d+4r)}+\frac{2r}{d+2r}[1-G(d)]-\frac{d}{d+2r}G(d)+\frac{2d}{r}\left[2E_1\left(\frac{d}{a}\right)-E_1\left(\frac{2d}{a}\right)+\ln\frac{d(d+4r)}{(d+2r)^2}\right]\\&-\frac{2r}{3(d+2r)}\left(\frac{d}{a}\right)^4\left[E_1\left(\frac{d}{a}\right)-E_1\left(\frac{2d}{a}\right)\right]+\frac{r}{d+2r}\left(\frac{d}{a}\right)\left[\frac{7}{6}F_2\left(\frac{2d}{a}\right)-\frac{27}{16}F_1\left(\frac{2d}{a}\right)+\frac{39}{16}F_0\left(\frac{2d}{a}\right)\right]\Bigg\},\end{aligned} \tag{11}$$

where d is the surface-to-surface separation distance between the spheres. This formula is applicable whenever the interaction between two spheres, made of the same material, is almost entirely due to the dispersion interactions. For two spheres made of different materials, the surfaces involved must be low-energy ones, as discussed in detail in [21]. The molecular size (in atomic units) a is determined by

$$\frac{1}{a}=1.25\left(\frac{I}{I_H}\right)^{1/2}, \tag{12}$$

where I and I_H are the first ionization potentials of the atom or molecule considered and a hydrogen atom, respectively. In the case of condensed bodies, I can be represented well by [21]

$$I=\hbar\omega_{UV}, \tag{13}$$

where $\omega_{\mathrm{UV}}=1.7\times10^{-16}$ rad s^{-1} for CCl$_4$. In Eq. (11),

$$\begin{aligned}G(d)=&F_3\left(\frac{2d}{a}\right)-\frac{4}{3}F_2\left(\frac{2d}{a}\right)+\frac{2}{3}F_1\left(\frac{2d}{a}\right)-\frac{4}{3}F_0\left(\frac{2d}{a}\right)\\&-2\left[F_3\left(\frac{d}{a}\right)-\frac{4}{3}F_2\left(\frac{d}{a}\right)+\frac{2}{3}F_1\left(\frac{d}{a}\right)-\frac{4}{3}F_0\left(\frac{d}{a}\right)\right],\end{aligned} \tag{14}$$

$$F_n(x)=e^{-x}\sum_{i=0}^{n}\frac{1}{i!}x^i, \tag{15}$$

$$E_1(x)=\int_x^\infty \frac{e^{-y}}{y}\,dy. \tag{16}$$

At $d=0$, Eq. (11) can be shown to reduce to a form that gives a finite value for the contact energy. When $d \gg a$, i.e., the interacting surfaces are farther apart than the molecular dimensions, but the separation is still small in comparison to the size of the spheres, i.e., $d \ll r$, the equation for the short-range energy reduces to

$$E_{\mathrm{SR}}=-\frac{Cr}{2d}\left[\frac{4rd}{(d+2r)^2}+\frac{2rd}{(d+2r)(d+4r)}+\frac{2r}{d+2r}+\frac{2d}{r}\ln\frac{d(d+4r)}{(d+2r)^2}\right]. \tag{17}$$

Comparing the above equation for E_{SR} with the equation for the Lifshitz energy [14] at comparable separations,

$$E_{\mathrm{Lif}}=-\frac{Cr}{2d}. \tag{18}$$

We can see that, for $d \ll r$, $E_{\mathrm{SR}} \rightarrow E_{\mathrm{Lif}}$ when

$$\left[\frac{4rd}{(d+2r)^2}+\frac{2rd}{(d+2r)(d+4r)}+\frac{2r}{d+2r}+\frac{2d}{r}\ln\frac{(d+4r)}{(d+2r)^2}\right]=1. \tag{19}$$

Solving for d from the above equation, we obtain the distance $d_{c1}=0.01r$. For surface-to-surface separations greater than d_{c1}, because E_{SR} converges to E_{Lif}, we can now say that the molecular size effect is small. Whereas, for $d<d_{c1}$, the molecular size effect must be considered, and the LMA approach that incorporates this effect should be used to calculate the interaction energy. See [21] for a determination of separation distance at which Lifshitz theory should fail.

In the present calculation, the short-range component of the van der Waals energy, from contact to a surface-to-surface separation, d_{c1}, is computed using Eqs. (11)–(16). KPW's approach is then used to obtain the interaction energy from d_{c2}, the smallest distance for which the Lifshitz energy and the energy calculated using the LMA approach converge [21], to initial separation d_0 in a collision simulation. Using these energy values as input, we parametrized the interaction energy for all interparticle separations. The aim in developing this set of parameters is to provide a smooth, continuous function for the interaction energy that is easily differentiable and programmable. In dynamic simulations where a considerable fraction of the total CPU time is spent in the force calculation, such a parametrization will allow the forces to be calculated simply and efficiently by a call to a subroutine containing the equation for the force. The parametrization for the nonretarded VDW interaction energy is given below as

$$E(d)=\frac{1+a_1 d+\cdots+a_{n-1}d^{n-1}}{b_1+b_2 d+\cdots+b_{n+6}d^{n+5}}. \tag{20}$$

In the limiting cases corresponding to $d=0$ and $d\rightarrow\infty$, by proper choice of parameters, the above equation reduces to the correct functional forms and gives the correct limiting interaction energy values. By setting $1/b_1=$contact energy, Eq. (21) can be made to give the contact energy at $d=0$. As $d\rightarrow\infty$, $E(r)\rightarrow(a_{n-1}/b_{n+6})d^{-6}$. Thus, by setting $a_{n-1}/b_{n+6}=C_{\mathrm{Lif}}$, where C_{Lif} is the Lifshitz constant, at large separations Eq. (21) can be made to reduce to the form of the nonretarded Lifshitz energy. The parameters used to fit the interaction energy for $\mathrm{CCl_4}$ are presented in Table I. The parametrized interaction energy and the corresponding force from a center-of-mass separation of $10d_0$, where d_0 is the contact separation between the two clusters, through contact are presented in Figs. 2 and 3, respectively.

III. INTERACTION ENERGY CALCULATIONS: COMPLEX PARTICLES

At the basis of the calculations of E_{Lif} and of E_D for two molecular clusters and their close correspondence with each other is the fact that all molecules comprising the clusters are collectively coupled to each other. For small clusters, the ''iterated-dipole'' interaction energies of the clusters, i.e., E_D, can be calculated as described above. However, in aggregation studies involving typically ultrafine particles with diameters of the order of several nanometers, such calculations are clearly computer time-intensive and, therefore, not practical. Conversely, E_{Lif} provides an adequate accounting of the energy between spherical particles, but in general analytical solutions to the Lifshitz theory of van der Waals interaction exist only for a limited number of idealized geometries and, hence, cannot *a priori* be expected to portray accurately the interaction energies involving aggregates of particles. However, we can ask how important the many-body interactions that represent intermolecular coupling in the aggregate are if the coupling between constituent particles in the aggregate is carried out to a sufficiently high order. Specifically, if the interaction energy between a particle and an aggregate could be expressed as a simple sum over the Lifshitz energy (E_{Lif}) values between each constituent particle of the aggregate and the single particle, then a computationally tractable long-range energy would be available for aggregation calculations. Such a calculation is a primary goal of this study.

To determine if the above interaction picture is useful, three 55-molecule $\mathrm{CCl_4}$ clusters (circumscribed sphere diameter of 2.82 nm [17]) were arranged so that two were in contact and the third was some distance away from them. The completely coupled, iterated-dipole energies among the three clusters were computed over a range of separation distances. Next, only the energy resulting from coupling the single cluster separately to each of the contacting clusters (referred to as the discrete-pairwise sum) was calculated. In this manner, the effect of the coupling between the molecules of the contacting clusters (coupling energy) on the total interaction energy was computed. These calculations were performed for two extreme relative orientations of the contacting clusters and the isolated cluster. In the first instance, the centers of the three clusters lie on a line (linear orientation), whereas in the second instance, the contacting pair of clusters were rotated by 90° about their contact point

TABLE I. The parameters used to fit the van der Waals energy from contact to large separations for a pair of CCl_4 continuum spherical particles of diameter 2.544 nm.

Parameters	Values
a_1	−57.8460
a_2	954.8547
a_3	−3093.6990
b_1	−9.5677
b_2	4.1931
b_3	−18.9670
b_4	−724.6654
b_5	1113.7198
b_6	6055.6064
b_7	7423.4565
b_8	2613.6556
b_9	505.7056
b_{10}	32.6514

relative to the first orientation so the three clusters were in the T orientation. The results of these calculations, along with the energy between a sphere and set of paired spheres calculated according to the Lifshitz theory, are shown in Figs. 4(a) and 4(b). It is evident that for both orientations, the difference between the discrete energies due to complete coupling and partial coupling of the molecules (referred to as the coupling energy) is orders of magnitude smaller than either one of the discrete energies. This result, combined with the observation that the Lifshitz and discrete energy have a close correspondence, indicates that, regardless of the orientations of the interacting clusters, the difference made by calculating the total interaction energy as a sum over the individual Lifshitz energy (E_{Lif}) values, as suggested above, is small. Comparison of the coupling energies in Figs. 4(a) and 4(b) shows that for the same center-of-mass separations the coupling energy for the linear orientation is greater than that for the T orientation. This observation further corroborates the results of Vold [22], who demonstrated, based on the Hamaker theory, that for a given center-of-mass separation, the interaction energy for ellipsoidal particles is largest for end-to-end orientation of particles.

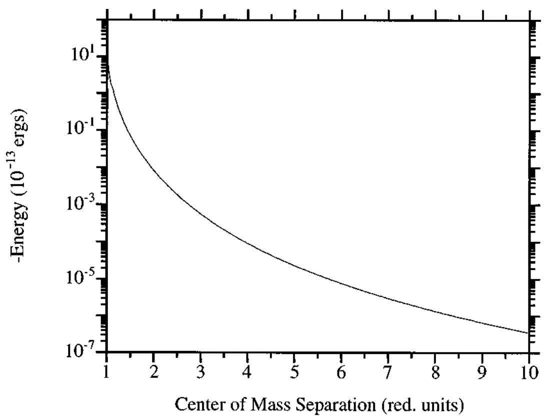

FIG. 2. The parametrized van der Waals energy as a function of the scaled center-of-mass separation for a pair of CCl_4 continuum particles of diameter 2.544 nm.

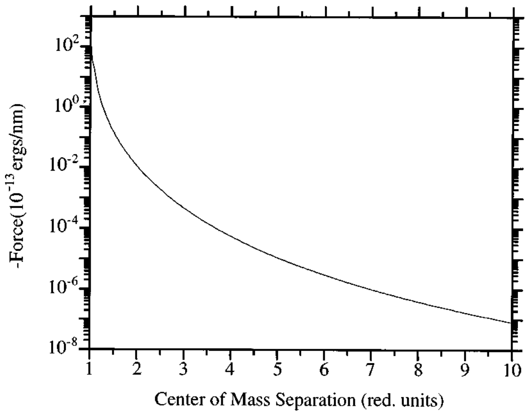

FIG. 3. The parametrized van der Waals force as a function of the scaled center of mass separation for a pair of CCl_4 continuum particles of diameter 2.544 nm.

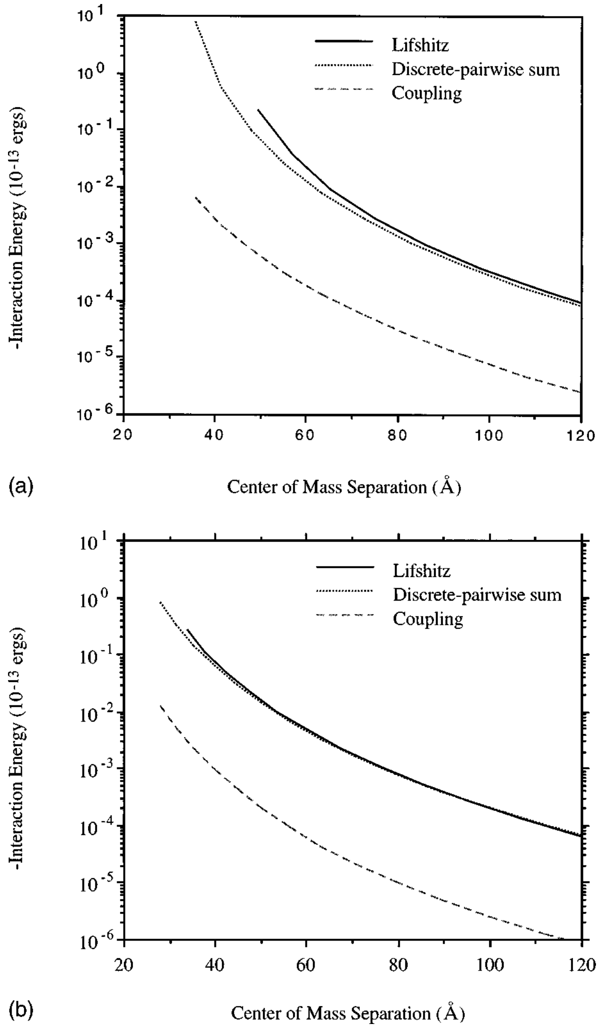

FIG. 4. The interaction energies and coupling energy between a contacting pair of CCl_4 clusters and a third cluster in: (a) the linear orientation, and (b) the T orientation. The coupling energy is the difference between the interaction energy obtained by coupling all molecules in the three-cluster system and the energy obtained by ignoring the interactions between the molecules in the adhering clusters.

IV. CONCLUSIONS

To summarize, we have formulated a method for calculating the van der Waals energy between complex particles, aggregates of spherical particles, from large separations through contact. The method has several advantages. (1) It presents an integrated and internally consistent picture of the van der Waals energy from the large separations, where the collective effects characteristic of condensed matter are important, to near contact separations, where the molecular effects become increasingly important. (2) It provides a parametrization of the interaction energy over all separations, which can significantly reduce computation time, while retaining all of the physics of the interactions. Such a parametrization is especially beneficial for molecular dynamics simulation calculations [23], where the largest part of the computational time is spent in the calculations of the interparticle energies and forces. (3) It enables the calculation of the Lifshitz–van der Waals interaction energy between irregularly shaped aggregates of particles.

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