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Evaluation of Interaction Forces between Nanoparticles by Molecular Dynamics Simulation

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Molecular dynamics simulations are used to quantify the interaction forces between nanoparticles, which are critical to nanoparticle systems. It is shown that the fluctuation of surface atomic density and the dynamics of collisions significantly affect the interaction forces. As a result, the Hamaker method cannot accurately estimate the interaction forces for nanoparticles. The proposed approach offers an effective method for determining the interaction forces between nanoparticles.

1. Introduction

The interaction forces between particles are critical to the understanding of various phenomena and behaviors of particle systems such as packing, aggregation, stability, flowability, and adsorption.[1−5] With the recent advances in nanotechnology, nanoparticles (with sizes of 1−100 nm) have attracted considerable attention because of their unique (e.g., electronic, magnetic, and optical) properties, promising potential and existing applications.[6−8] Currently, a wide variety of nanoparticles consisting of either hard materials (e.g., metals, metal oxides) or soft condensed matter (e.g., proteins, lipids, polymer vesicles, dendrimers) can be fabricated. The assembly of these nanoparticles generates many opportunities for a spectrum of structures and functional materials.[9−11] However, the fundamentals underlying such nanoparticle systems have not been well established. One important challenge is to develop a method for accurately determining the interaction forces between nanoparticles and then directing the assembly of nanoparticles into various nanostructures for various functional applications.[1,12−15]

Some efforts have recently been made to understand the interactions between nanoparticles. Experimentally, the surface force apparatus (SFA) and atomic force microscopy (AFM) approaches have been extended to nanoscale systems. These techniques, however, often require atomically smooth and transparent solid surfaces and are applied to microscopic particles and a surface separation of larger than a few nanometers. One promising technique is to combine scanning tunnel microscopy and atomic force microscopy (STM−AFM) for the measurement of the vertical and lateral forces between a single atom and a surface.[16] Theoretically, all kinds of interactions between particles (e.g., atoms, molecules, nanoparticles, and colloidal particles) can be derived from the Schrödinger equation. For example, density functional theory and ab initio methods have been applied to calculate the interactions between the AFM tip and the sample surface.[17,18] Yet, the current computational power does not allow the regular use of such quantum mechanics methods for force calculations between nanoparticles. On the other hand, the Hamaker method can also provide a theoretical starting point for calculating the interaction

forces between nanoparticles. However, its basic formulation fails when it is applied to nanoparticles because it (i) ignores the discrete nature of constituent atoms in a particle[19] and (ii) does not account for surface effects (e.g., atom defects, roughness, and distortion). Both are significant for nanoparticles because of their large specific surface areas. As a compromise between accuracy and computational cost, molecular mechanics becomes a promising approach in calculating the interaction forces between nanoparticles. Recently, one attempt was reported to estimate the interaction forces between two metallic nanospheres by molecular dynamics simulations.[20] Yet, this study was very preliminary and missed some details such as the hysteretic behavior of the interaction forces reported in quantum mechanics calculations[19,20] and experimental observations.[17,21]

In this article, we present an approach for determining the interaction forces between two nanospheres by (i) using the molecular mechanics method to calculate the interaction potential energies between two nanoparticles and (ii) deriving the interaction forces as the gradient of the potential energies. Two situations are considered: One is a static configuration of two interacting nanospheres that have no intraparticle degrees of freedom, and the other is the dynamic configuration of two interacting nanospheres in which atoms are allowed to move around upon collision. We compare our calculated forces with those predicted by the Hamaker method to better understand the deficiency of this conventional method. We also discuss the effects of a few pertinent factors to highlight the difficulty and complexity in quantifying the interaction forces between nanospheres.

2. Methods

To reduce the computational effort, we ignore electronic degrees of freedom and write the interatomic potentials as a function of atomic separation. Specifically, the potentials U_{ij} between two nonbonded atoms are expressed as[22]

$$U_{ij} = \frac{n\varepsilon}{n-m}\left(\frac{n}{m}\right)^{m/n-m}\left[\left(\frac{\sigma}{r_{ij}}\right)^n - \left(\frac{\sigma}{r_{ij}}\right)^m\right] + \frac{z_i z_j}{4\pi\varepsilon_0}\frac{1}{r_{ij}} \quad (1)$$

where r_{ij} is the interatomic separation, σ is the separation at which the van der Waals potential equals the Born potential, ε is the depth of the primary well, and ε_0 is the permittivity of vacuum. z_i and z_j are the charges on atoms i and j, respectively.

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The above interatomic potentials include (i) an attractive part due to the van der Waals forces, which decays according to r_{ij}^{-m}, where m is typically chosen to be 6; (ii) a repulsive contribution known as the Born forces, which decays according to r_{ij}^{-n}, where the value of n ranges from 8 to 20 with a typical value of 12; and (iii) the potential due to electrostatic forces.

Therefore, the interaction potentials between two particles of M and N atoms can be calculated by summing over all pairs of atoms. Under the assumption of pairwise additivity, the potential, U^p, can be written as

$$U^p = \sum_{i=1}^{N} \sum_{j=1}^{M} U_{ij} \tag{2}$$

U_{ij} represents the potential of interactions between the ith atom and the jth atom, including the van der Waals, Born, and electrostatic contributions as determined in eq 1.

Thus, we first calculate the total potentials of isolated particle 1 (U_1^p), isolated particle 2 (U_2^p), and the combined system (U_{12}^p) of particles 1 and 2 at a certain separation. For instance, the total potential of isolated particle 1 is given as

$$U_1^p = U_{bond} + U_{angle} + U_{torsion} + U_{oop} + U_{vdW} + U_{Born} + U_{elec} \tag{3}$$

where the terms on the right represent the contributions of bond, angle, torsion, out-of-plane, van der Waals, Born, and electrostatic interactions, respectively. They have different functional forms depending on the force field used in the calculations. Once the potentials of the isolated particles and the combined two-particle system at a given separation d have been determined, the interaction potentials between particles 1 and 2 can be written as

$$U^p(d) = U_{12}^p - U_1^p - U_2^p \tag{4}$$

With the assumption that no bond is created or broken within and between the nanoparticles, the bonded interaction potential energies (i.e., the first four terms on the right-hand side of eq 3) are canceled in eq 4. The above approach can be applied to determine the interaction potentials of two particles with arbitrary shape, size, and composition. Moreover, the individual contributions (i.e., the van der Waals, Born, and electrostatic interactions) to the total potential can also be obtained.

If the particles are assumed to be rigid, the atomic configurations within each particle will not change with the relative particle separation. Then, the interparticle potentials can be calculated at a series of particle separations, from which the dependence of interparticle potentials on particle separation can be determined. Such molecular-mechanics-based interparticle forces, F_{MM}^p, are derived as the gradients of interparticle potentials with respect to particle surface separation d

$$F_{MM}^p(d) = -\frac{\partial U^p(d)}{\partial d} \tag{5}$$

Accordingly, we can determine the total interparticle force, as well as the individual contributions of the van der Waals, Born, and electrostatic forces.

3. Results and Discussion

3.1. Forces between Static Nanospheres. To implement the above approach, as an example, we calculate the interaction forces of two SiO$_2$ nanospheres. Each nanosphere is initially
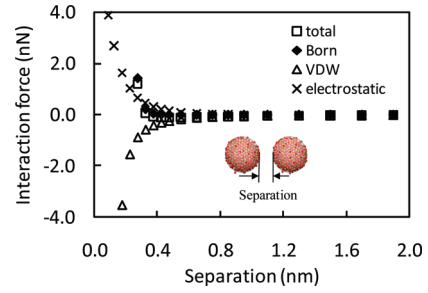

Figure 1. Dependence of the interaction forces on the surface separation of two SiO$_2$ nanospheres (6.84 nm).

created from the crystal supercell and then allowed to undergo a relaxation process under energy minimization to reach an equilibrium configuration. Then, the equilibrated nanosphere is treated as a rigid particle and used for the calculation of the total interaction potentials and forces. Figure 1 shows the calculated interaction forces between two SiO$_2$ nanospheres with a diameter of 6.84 nm and a charge of $-2.4e$. The charge of the nanosphere is the total charge of all atoms in the nanosphere, and the atomic charge is determined by the force field. The charge of the nanosphere will not affect the results of other forces (e.g., vdW, Born). The total interaction force is the sum of three individual contributions in which the van der Waals force and electrostatic force are long-range attractive and repulsive, respectively, and the Born force is short-range repulsive. Moreover, the total interaction force shows a maximum attractive interaction of -0.11 nN between the two nanospheres at a surface separation of about 0.4 nm. Upon contact of the two nanospheres, that is, at a surface separation of less than 0.4 nm, the total force is dominated by the stronger Born repulsive force, which is generated from the overlapping of the electron clouds.

We then assess the applicability of the Hamaker method in the calculation of nanoparticle interaction forces. This is done by comparing the calculated van der Waals and Born interaction forces with those from our molecular mechanics approach. In the Hamaker method, the van der Waals force (F_H^{vdW}) and the Born force (F_H^{Born}) are calculated as the gradients of the corresponding interaction potentials of the formulation[23]

$$U_H^{vdW} = \frac{-A}{6}\left[\frac{2\lambda}{R^2 - (1 + \lambda)^2} + \frac{2\lambda}{R^2 - (1 - \lambda)^2} + \ln\frac{R^2 - (1 + \lambda)^2}{R^2 - (1 - \lambda)^2}\right] \tag{6}$$

$$U_H^{Born} = 4A\left(\frac{\sigma}{r_1}\right)^{n-6}\frac{(n - 8)!}{(n - 2)!}\frac{1}{R} \times$$
$$\left[\frac{-R^2 - (n - 5)(\lambda - 1)R - (n - 6)[\lambda^2 - (n - 5)\lambda + 1]}{(R - 1 + \lambda)^{n-5}} + \right.$$
$$\frac{-R^2 - (n - 5)(\lambda - 1)R - (n - 6)[\lambda^2 - (n - 5)\lambda + 1]}{(R + 1 - \lambda)^{n-5}} +$$
$$\frac{R^2 + (n - 5)(\lambda + 1)R + (n - 6)[\lambda^2 + (n - 5)\lambda + 1]}{(R + 1 + \lambda)^{n-5}} +$$
$$\left.\frac{R^2 - (n - 5)(\lambda + 1)R + (n - 6)[\lambda^2 + (n - 5)\lambda + 1]}{(R - 1 - \lambda)^{n-5}}\right] \tag{7}$$

where $A = \pi^2 q_p \varepsilon \sigma^6$ is the Hamaker constant, q_p is the number density of atoms in a particle, ε is the depth of the potential well in the Lennard-Jones potential equation, and σ is the distance at which the interatomic potential is zero. Parameters ε and σ can be obtained by empirical fitting or from quantum
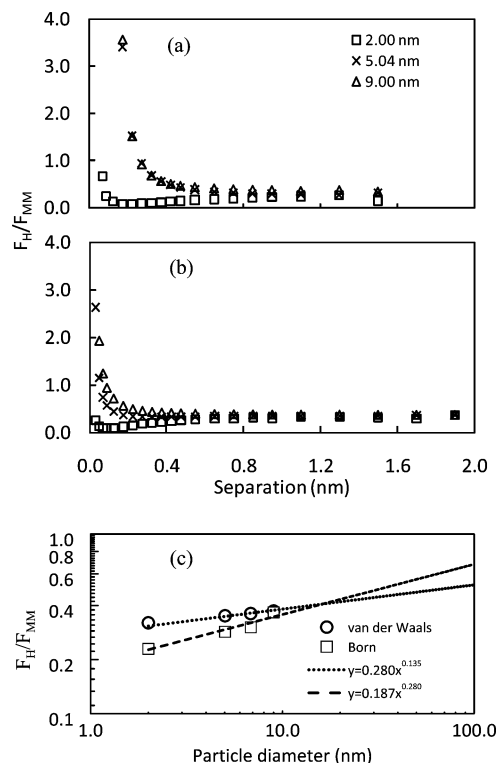
Figure 2. Comparison of the interaction forces calculated by the molecular mechanics (F_{MM}) and Hamaker (F_H) methods: (a) Born repulsive force; (b) van der Waals attractive force; and (c) their dependence on particle size at larger (>0.8 nm) separation, where the lines are drawn according to a power law.

mechanics. $\lambda = r_2/r_1$ is the ratio of the radii of the two spheres, r_1 and r_2. $R = (r_1 + r_2 + d)/r_1$ is the center-to-center separation made dimensionless on r_1, and d is the surface separation between the two spheres. In this calculation, $n = 12$ and $\sigma = 0.33$ are used according to the consistent-valence force field (CVFF), and the Hamaker constant of SiO_2 quartz in vacuum/air (8.86×10^{-20} J) is used.[24]

Note that the starting point of the Hamaker method is the same as the above molecular mechanics method where the additive law applies. However, the Hamaker method goes further, by assuming a uniform atomic density distribution in a particle, which offers numerical convenience in handling eq 2 but induces problems as discussed next. Because the Hamaker method does not consider the electrostatic interaction between the particles, we consider only the van der Waals and Born interaction forces.

The interaction forces of two nanoparticles calculated from the Hamaker method exhibit a significant deviation from those obtained by our molecular mechanics approach, as shown in Figure 2. Upon particle contact (<0.4 nm), the ratio of the forces determined by the two methods (F_H/F_{MM}) increases dramatically with decreasing surface separation. At a certain point, the Hamaker method overestimates the interaction forces. For example, for particle sizes of 5.04 and 9.00 nm, the ratio becomes larger than 1 at a separation of 0.3 nm for the Born forces (Figure 2a) and 0.1 nm for the van der Waals forces (Figure 2b). At a larger surface separation (i.e., >0.8 nm), the force ratio tends to a constant. In other words, the forces calculated by the Hamaker method have a constant deviation from those calculated by the molecular mechanics approach. Moreover, with an increase in particle size, this constant increases (Figure 2c). It is known that, for a given material, when the particle size is greater than a certain value, the
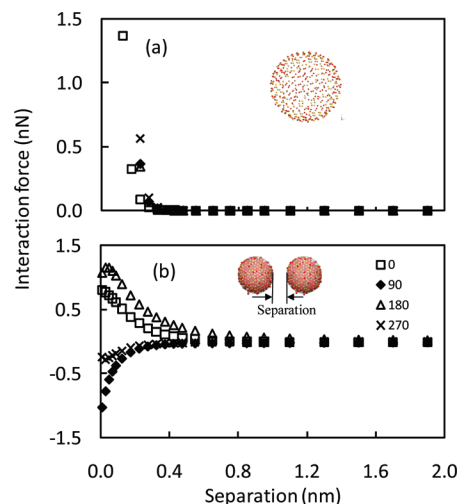

Figure 3. Interaction forces between two SiO_2 nanospheres (5.04 nm) with the right-side nanosphere rotated at a different angle (θ, degree): (a) Born repulsive force, with the inset showing the unsaturated surface atoms (i.e., Si in yellow and O in red) in the nanosphere, and (b) electrostatic force.

Hamaker method is valid, so that the forces obtained should be the same as those from molecular mechanics approach.[22] By extrapolation, the results shown in Figure 2c suggest that the Hamaker method is valid when the particle size is greater than a certain value; specifically, for the SiO_2 nanospheres concerned here, this value is about 400 nm for the Born force and 12.5 μm for the van der Waals force. Further studies are necessary to test the applicability of this extrapolated relationship. This requires a large-scale computation using much larger nanospheres, which might be difficult with the current computational capacity. An alternative method is to introduce certain assumptions to simplify the simulation systems. For example, simulations can be focused on the atoms in the external shell of a nanosphere, which represent the major contribution to the interaction between nanospehres. Such studies are now underway in our laboratory.

3.2. Forces between Dynamic Nanospheres. To examine the effects of the surface on nanoparticle interactions, we used the molecular mechanics approach to calculate the interparticle forces of two nanospheres with different relative orientations. It is known that, with a decrease in particle size, the behavior of the particle properties tends to be affected by the increased relative contribution of the surface atoms. These atoms show a dramatically different bonding state and chemical environment than the bulk atoms of the same materials. Moreover, nanospheres can lose their symmetrical atomic structure and atomic smoothness on the surface. Thus, we calculated the interaction forces between two identical nanospheres but with different orientations by rotating one nanosphere at a given angle. The results indicate that different orientations can give different Born and electrostatic forces at a small surface separation (e.g., around 0.4 nm for Born interaction and 0.8 nm for electrostatic interaction) (Figure 3). The difference is particularly distinct in the electrostatic force, which fluctuates between attraction and repulsion. With an increase in the particle separation, the fluctuation can be ignored. Such behavior can be attributed to the discrete nature of atoms and the surface heterogeneity of nanospheres, which is not considered in the Hamaker method. It is in line with AFM and STM−AFM measurements, which show that minor changes in the nature of the surface (e.g., composition, asperity, defect) can have a large effect on particle−particle interactions[25] and single-atom−surface interactions.[16,17] The heterogeneity of surface atoms is further con-
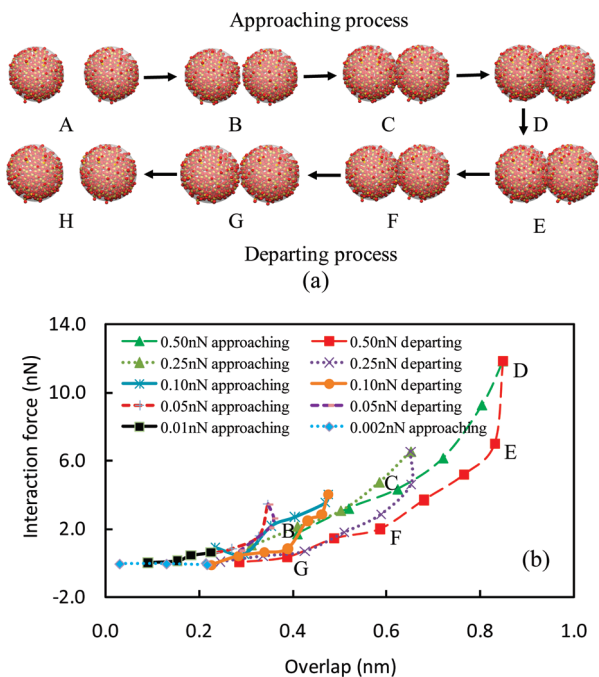
Figure 4. (a) Snapshots of the dynamic approaching and departing processes of two SiO$_2$ nanospheres ($d = 3.00$ nm) under an initial external force of 0.5 nN and (b) the dependence of their total interaction force on the overlap under different initial external forces. The snapshots in a were obtained at the following times (ps): (A) 4.5, (B) 5.5, (C) 5.9, (D) 6.2, (E) 6.4, (F) 6.7, (G) 7.0, and (H) 8.0.

firmed when extracting the unsaturated surface atoms from the nanosphere, shown in the inset of Figure 3a, where neither Si (yellow) nor O (red) atoms are evenly distributed. According to eq 1, the interaction strength between two atoms increases sharply with decreasing separation. Therefore, atoms close to the contact point give the most significant contribution to the overall interaction strength between two nanospheres. The uneven distribution of the unsaturated atoms on the nanopshere surface can lead to fluctuating forces, as observed in Figure 3b. Obviously, it is difficult to formulate a simple equation, such as the one suggested in the literature,[20] to describe such interactions, particularly upon particle contact.

The above calculation is for the interaction between two static nanoparticles. Yet, it does not account for the change in chemical environment of the atoms derived from the interaction process of two nanoparticles. In fact, during a collision, the surface atoms of nanoparticles might change their relative positions. This is because the surface atoms are much more active and have more freedom to move around. This consideration is confirmed from our calculation for two SiO$_2$ nanospheres whose surface atoms are observed to move around upon collision. As an example, here, we show the simulated collision between two colliding nanospheres. In this molecular dynamics simulation, we introduced an initial external force to both nanospheres to force them to move toward each other. After 2 ps, the external force was removed, and the two nanospheres moved toward each other at a certain velocity, collided, and departed. Note that there was an overlap (i.e., deformation) between two nanoparticles upon their collision. The change of the initial force means a change in the relative velocity between particles before the collision. In this study, six different initial external forces (i.e., 0.50, 0.25, 0.10, 0.05, 0.01, and 0.002 nN) were applied, which correspond to relative initial velocities of 520, 455, 285, 155, 70, and 29 m/s, respectively. The force-overlap curve obtained (Figure 4) demonstrates a hysteretic behavior for the

cases with larger initial external forces. That is, upon high-impact collisions, the interaction forces between nanoparticles depend on the interaction history such as approaching or departing. This hysteretic phenomenon reflects the rearrangement of atoms on the interacting surface.

The hysteresis of interaction forces is qualitatively in reasonable agreement with the experimental observations of the dynamic interactions between a single-atom AFM tip and a semiconductor surface[17] and between an AFM tip and a single particle.[21] Moreover, as shown in Figure 4, with the decrease in the initial external force, the maximum interaction force and overlap decrease, indicating a reduced deformation upon nanoparticle collision. Under low initial external forces, the interactions between two nanophseres lead to an equilibrated state at a specific separation distance. Clearly, the interaction forces between colliding nanoparticles are affected by many variables related to particle and material properties, and collision conditions as well. A systematic study is necessary to understand these effects.

4. Conclusions

The interaction forces between two nanoparticles can be determined by molecular mechanics. This approach offers distinct advantages over the traditional Hamaker method because it accounts for the specific contributions from nanoparticle surface atoms. For SiO$_2$ nanospheres, at a large surface separation, the Hamaker method could lead to a constant deviation of Born and van der Waals forces from those obtained by the molecular mechanics approach. The Hamaker method overestimates the interaction forces between nanoparticles. Its calculated forces are equivalent to those from the molecular mechanics approach only when the particle size is large enough.

Moreover, it was found that such factors as the fluctuation of surface atoms can dramatically affect the Born and electrostatic forces, and the dynamics of atoms on the interacting surface results in hysteresis in the interaction force between nanoparticles with high relative collision velocities. It is believed that such complicated force behavior is one of the key factors responsible for the complicated assembly behavior of nanoparticles leading to different functional properties. Quantification of the interparticle forces under different conditions is therefore very important. In fact, it is a priori step for simulation of the dynamics of nanoparticle systems.[26] The molecular mechanics approach proposed could play an important role in this area.

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