Interaction forces between carbon nanospheres: A molecular dynamics simulation study

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HIGHLIGHTS

- Interaction forces between carbon nanospheres are studied using MD simulations.
- The effect of materials is explored, with some common features identified.
- The validity of relevant conventional theories is tested against the MD results.
- Equations are formulated to calculate the interaction forces between carbon nanoparticles.

ARTICLE INFO

ABSTRACT

In this work, the interaction forces between carbon nanospheres are studied using molecular dynamics (MD) simulations. It is shown that the conventional Hamaker approach cannot be directly applied to reliably estimate the van der Waals attraction and Born repulsion forces for nanospheres of different carbon materials. Yet, there are some common features identified, including a finite value of the forces at the surface separation $d \approx 0$ nm, a maximum ratio between the interaction forces obtained from the MD simulation and Hamaker approach at $d \approx 0.4$ nm, a turning point of interaction forces at $d \approx 0.15$ nm. These features can be quantitatively described with a similar mathematical form formulated for silica. Moreover, it is demonstrated that the mechanical contact force between carbon nanospheres at a low compression can be described by the classical Hertz model. Finally, the minimum gap between carbon nanoparticles in collision can be described by the conventional contact mechanics, which is adapted to evaluate the minimum gap.

1. Introduction

Interparticle forces are central to the understanding of many natural phenomena and industrial processes, such as aggregation (Dosta et al., 2013), adsorption (Brzic and Petkovska, 2013), self-assembly (Zhang et al., 2013), dispersions (Tishkova et al., 2013), packing (Dong et al., 2006), and particle flow (Zhu et al., 2007). For nanoparticles, direct measurement of interparticle forces is still challenging, particularly for nanoparticles smaller than 10 nm (Yaminsky and Stewart, 2003). On the other hand, it is known

that the continuum models, developed at the macroscale (Feke et al., 1984; Hamaker, 1937; Johnson, 1985), cannot generally apply to nanoparticles due to the neglect of discrete atomic structure and surface effects (Bishop et al., 2009; Girifalco et al., 2000; Luan and Robbins, 2005). Recently, molecular dynamics (MD) simulation has been developed to calculate the interaction forces between α-quartz silica nanospheres, including the van der Waals (vdW) attraction, Born repulsion and mechanical contact forces during a normal impact (Sun et al., 2013a, 2013b; Zeng et al., 2010). Such MD studies can help clarify a series of fundamental issues from atomic level. In other words, when the size of particles is down to nanoscale of less than 10 nm, the nature of discrete atomic structure cannot be ignored as treated in the continuum models any more, especially for contact force at the interface of two closely interacting nanoparticles. The interaction forces

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between particles at the nanoscale should be material-dependent. Therefore, the effect of nanoparticles of different materials and structures on the forces is worth exploring from the atomic level. In addition, some issues, confined by the properties of silica material itself or the lack of more compelling evidences, have not been clearly unveiled or fully understood, e.g., the factors influencing the minimum gap (or the maximum compression at which the relative velocity between two particle is zero) of particles achieved during a normal impact.

Carbon nanomaterials have attracted continuing research interests because of their great promise in a variety of technological applications derived from their unique properties, (e.g., mechanical, electrical and thermal) and diverse structures, e.g., crystalline diamond (Sandoz-Rosado et al., 2012), amorphous carbon (Suk et al., 2012), graphite (Fu and Yang, 2013), graphene (Lippert et al., 2013), carbon nanotubes (Zhou et al., 2012). While significant worldwide efforts have been devoted to carbon nanotubes and graphene due to their extraordinary properties, carbon nanoparticles have received relatively less attention and the necessity to study their interactions is usually ignored. Nonetheless, carbon nanoparticles have many specific applications. For example, nanodiamond as a new kind of materials, has an extreme hardness, chemical inertness, and inherent biocompatibility. It holds a great promise in the fields of ultrafine polishing, lubricating, composite plating, biomolecular absorbents, and so on (Guan et al., 2006). Therefore, understanding and quantifying the interaction forces between carbon nanoparticles, as one of the important fundamental issues, would be useful in enhancing such applications.

In this work, MD simulations are performed to study the interaction forces between carbon nanospheres (i.e., crystalline diamond and amorphous carbon), aiming to formulate equations to estimate the interactions between carbon nanospheres, including the vdW attraction and Born repulsion. This paper is organized as follows. Section 2 presents the simulation conditions and method. Section 3 details the characterization of discrete atomic structure of diamond and amorphous carbon nanospheres, followed by the evaluation of the interaction forces between crystalline diamond or amorphous carbon nanospheres. In addition, two relevant theories will be evaluated on the basis of their predicted elastic properties for carbon materials and the maximum compression during impact between two nanospheres. The main conclusions are summarized in Section 4.

2. Simulation conditions and method

MD simulations are performed in Materials Studio package using the COMPASS force field, which encompasses a Lennard–Jones n–m potential (LJ^{n-m}, $n=9$ and $m=6$) function between non-bonded atoms and valence interactions between bonded atoms such as bond stretch, angle bending, angle torsion, angle inversion (Rappe et al., 1992). Details can be found in our previous studies. For brevity, the major simulation procedures are as follows (Sun et al., 2013a, 2013b):

- Diamond or amorphous carbon nanospheres with different sizes are carved out of their bulk counterparts by specifying a certain cut-off particle radius (R_o). The diamond nanospheres are created from a faced-centered cubic crystalline structure while amorphous nanospeheres are created from the amorphous structure of a mixture of diamond-like and graphite-like carbon atoms.
- Then, each nanosphere is fully relaxed using the NVT ensemble (i.e., constant number of atoms, constant volume and constant temperature) at 300 K.

- After that, two identical nanospheres are placed at a certain distance, followed by MD simulations using the NVE ensemble (i.e., constant number of atoms, constant volume and constant energy) and velocity Verlet integration algorithm with a time-step of 1 fs (1.0×10^{-15} s). The two nanospheres are allowed to move toward each other at an equal but opposing initial velocity.
- Energies, forces and other atomic information are recorded every 100 steps in an output trajectory file and then correlated to the surface separation (d) between the two nanospheres.

The Hamaker constants for diamond and amorphous carbon are calculated based on the parameters used in COMPASS. The values of potential well depth (ε) and collision diameter of atoms (σ) for diamond-like carbon are 0.062 Kcal/mol and 3.854 Å, respectively (Sun, 1998; Sun and Rigby, 1997). The estimated Hamaker constant ($A = \pi^2 C/v^2$, where $C = 3\varepsilon\sigma^6$ is the vdW attraction interaction parameter, $\upsilon = 4\pi(\sigma/2)^3/3$ is the atom volume of about 29.973 Å^3) is 4.65×10^{-20} J. Similarly, the values of ε and σ for graphite-like carbon are 0.068 Kcal/mol and 3.915 Å, respectively (Sun, 1998; Sun and Rigby, 1997), which results in a Hamaker constant of 5.10×10^{-20} J. In this work, the amorphous carbon consists of almost half diamond-like carbon atoms and half graphite-like carbon ones, therefore an averaged Hamaker constant of 4.875×10^{-20} J is used for amorphous carbon.

The interaction potential energies and their individual potential contributions (e.g., vdW attraction, Born repulsion) can be calculated in a similar way as done before (Sun et al., 2013a, 2013b). Then, the corresponding interaction forces can be obtained by differentiating the interparticle potentials with respect to surface separation (d). This treatment applies to carbon nanospheres before and after their contact, although mechanical contact forces need to be considered after contact.

3. Results and discussion

3.1. Characterization of atomic structures of nanospheres

The thermal vibration may cause surface atoms in nanospheres to fluctuate out of the arbitrary cut-off radius (R_0) and the size of nanospheres becomes vague (Cheng and Robbins, 2010). Therefore, the structure of diamond and amorphous carbon nanospheres will be characterized in a similar way as silica nanospheres (Sun et al., 2013a). All atoms with saturated coordination number are reflected as the "core" of a nanosphere. Atoms with unsaturated coordination are referred to as "surface atoms" while those with saturated coordination are termed as "core atoms", and their individual radial distances from the nanosphere center are denoted as R_i^{surf} or R_j^{core}, respectively. By analyzing the equilibrated structure of nanospheres from the MD simulations, the following structural parameters can be defined: core radius (R^{core}, the maximum value of R_j^{core}), surface roughness (rms), particle radius (R, the average value of R_i^{surf} from all surface atoms), relative surface roughness (rms/R), effective surface thickness (δ), maximum surface thickness (δ_{Max}) and the part of the nanoparticle that is beyond the defined particle radius (Δd).

The results show that rms, δ and δ_{Max} vary to some degree but can be considered as independent of particle size. However, the relative surface roughness (rms/R) decreases sharply with increase in particle size. The core radii R^{core} of diamond nanospheres corresponding to $R_0 = 1.0$, 1.5, 2.0, 2.5 and 3.0 nm are 0.875, 1.343, 1.850, 2.343 and 2.852 nm, respectively; the corresponding defined particle radii R are 0.935, 1.419, 1.931, 2.423 and 2.928 nm, respectively. rms is about 0.42 ± 0.05 Å, δ is about 1.17 ± 0.13 Å, and δ_{Max} is about 1.53 ± 0.18 Å. For diamond nanospheres, there is