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Molecular dynamics simulations of structural features and diffusion properties of fullerene-in-water suspensions

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Abstract

This study performs molecular dynamics (MD) simulations to investigate the structural features and diffusion properties of fullerene-in-water suspensions. The numerical results reveal that an organized structure of liquid water is formed close to the surface of the fullerene molecule, thereby changing the solid/liquid interfacial structure. The organized structure formation becomes more pronounced as the fullerene size is reduced. This observation implies that a transition zone exists between the organized liquid water layers and the random distribution region. Furthermore, the results indicate that the structural stability of fullerene-in-water suspensions improves as the fullerene volume fraction increases, but is insensitive to changes in the fullerene size. Finally, the simulation results reveal that the diffusion coefficient of the water molecules varies as a linear function of the fullerene loading, but is independent of the fullerene size.

Keywords: Structural feature; Diffusion coefficient; Fullerene-in-water suspensions; Molecular dynamics (MD) simulation

1. Introduction

Suspensions of solids in fluids have widespread applications in a number of fields, including transportation, energy supply and production, electronics, and so forth [1–3]. Solid–fluid suspensions have many favorable transport properties, many of them related to solid/liquid systems. Furthermore, the structural features and diffusion properties determine the dispersion and stability of nanoparticle suspensions. To further the development of future nanoparticle suspensions applications, it is necessary that the structural features and diffusion properties of nanoparticles suspensions be well understood. However, it is difficult to explore these properties using direct experimental approaches. Fortunately, molecular dynamics (MD) simulations provide valuable insights into the physics of suspensions and enable the solid/liquid interfacial characteristics of their transport properties to be clarified. The MD simulation method describes the atomic motions of the constituent particles of a system by making the assumption that the particles satisfy the laws of classical mechanics at the atomic scale [4]. The power of the MD approach becomes increasingly apparent as the characteristic size of the system decreases. MD simulation results enable the transport property data and phenomenological mechanisms of a system to be determined. In a previous study, the current authors performed a series of MD simulations to examine the structural features and thermal conductivity of silicon nanoparticles and the numerical results were in good agreement with the experimental data [5].

The structural characteristics and diffusion properties of nanoparticle suspensions are an important index in micro-electro-mechanical system (MEMS) and nano-electro-mechanical system (NEMS) applications, and are dependent on the temperature, pressure, and environmental conditions. For the investigation of water structure around fullerene particles as well as influence of this structure on interaction between fullerenes, Pettitt and co-workers [6] employed molecular dynamics simulations to calculate enthalpy–entropy contributions

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to the hydrophobic interaction between nanoscopic hydrophobic solutes, modeled as graphene plates in water. The results showed that contact configurations are entropically stabilized and solvent-separated configurations are enthalpically stabilized or show entropy–enthalpy compensation or cancellation. However, their study did not consider the effect of solute surface curvature for the solute–solvent interaction. The strength of the solute–solvent interaction may depend on surface curvature. Smith et al. [7–9] also adopted the MD method to investigate the nature of water-induced interactions between carbon nanoparticles such as C_{60} fullerenes, carbon nanotubes, and grapheme sheets in aqueous solution. Their result showed that the hydration of these nonpolar carbon nanoparticles does not exhibit classical hydrophobic characteristics and promotes the formation of a high-density hydration shell of water around nanoparticles. Hence, the water liquid phase between carbon nanoparticles remains stable with decreasing particle separation, resulting in a repulsive solvent-induced contribution to the potential of mean force between carbon nanoparticles. However, their study did not consider the size effect of fullerene molecules for fullerene–water interactions. Hence, several recent studies have investigated the diffusion coefficient of water molecules in different environments, e.g., constrained within carbon nanotubes [10], between parallel plates [11], and in sodium chloride solutions [12]. However, the structural features and diffusion characteristics of nanoparticle suspensions are less well understood. Accordingly, this study performs MD simulations to investigate the structural features and diffusion properties of a suspension comprising fullerenes dispersed in liquid water. The structural characteristics and diffusion properties of nanoparticle suspensions are then investigated as a function of the fullerene size and the fullerene volume fraction.

2. MD simulations

The fullerene-in-water system is modeled using classical molecular dynamics simulations with periodic boundary conditions imposed in three spatial directions. Since fullerene molecules consisted of carbon atoms held together by covalent bonds without any chemical reactions in the simulation process, the original Brenner potential model could be used to describe the behavior of fullerene molecules and this model has been widely applied in previous studies of fullerenes [13]. In the original Brenner potential, the total potential energy is expressed as

$$V=\sum_{i}\sum_{j(i<j)} f_c(r_{ij})\left\{V_R(\vec{r}_{ij})-b^*_{ij}V_A(\vec{r}_{ij})\right\}, \tag{1}$$

where the summation is performed for every chemical bond; $\vec{r}_{ij}$ is the vector pointing from atom i to atom j, with $r_{ij}=|\vec{r}_{ij}|$; and $V_R(r)$ and $V_A(r)$ are the repulsive and attractive components of the Morse type potential, respectively, and are given by

$$V_R(r)=f_c(r)\frac{D_e}{S-1}\exp\left\{-\beta\sqrt{2S}(r-R_e)\right\}, \tag{2}$$

$$V_A(r)=f_c(r)\frac{D_eS}{S-1}\exp\left\{-\beta\sqrt{2/S}(r-R_e)\right\}, \tag{3}$$

where the cutoff function, $f_c(r)$, is a simply decaying function centered at $r=R$ with a half-width of D; i.e.,

$$f_c(r)=\begin{cases}1, & (r-R-D),\\ \frac{1}{2}-\frac{1}{2}\sin[\frac{\pi}{2}(r-R)/D], & (R-D\leqslant r\leqslant R+D),\\ 0, & (r>R+D).\end{cases} \tag{4}$$

Table 1
Parameters used in the original Brenner potential

Parameters	C–C
D_e (eV)	6.325
R_e (nm)	0.1315
S	1.29
β (nm^{-1})	1.5
a	1.1304×10^{-2}
n	1
δ	0.80469
c	19
d	2.5
h	−1
R (nm)	0.185
D (nm)	0.015

Finally, b^*_{ij} in Eq. (1) expresses the modification of the attractive force, $V_A(r)$, in accordance with θ_{ijk}, the bond angle between bonds i–j and j–k; i.e.,

$$b^*_{ij}=\frac{b_{ij}+b_{ji}}{2},$$

$$b_{ij}=\left\{1+a^n\left[\sum_{k(\neq i,j)} f_c(r_{ik})g(\theta_{ijk})\right]^n\right\}^{-\delta}, \tag{5}$$

$$g(\theta_{ijk})=1+\frac{c^2}{d^2}-\frac{c^2}{d^2+(h-\cos\theta_{ijk})^2}. \tag{6}$$

The parameters used in the present study for the original Brenner potential model are summarized in Table 1.

Both flexible [14,15] and rigid models [16,17] have been widely proposed to describe the intramolecular interactions. However, it has been demonstrated that the flexible models provide a more accurate prediction of the thermal properties and diffusion behaviors [18,19]. The current study adopts the flexible F3C water model [19] to describe the interactions of the water molecules. This model accurately predicted the structural and dynamic properties of water, which are in good agreement with those determined from experimental data [19]. A further advantage of the F3C water model is that it employs a short-range truncation distance. This reduces the computational load and hence permits the MD simulations to consider a greater number of water molecules or to employ time steps of longer duration. The F3C water model has the following form:

$$V=V_{\mathrm{bond}}+V_{\mathrm{bend}}+V_{\mathrm{vdw}}+V_{\mathrm{els}}, \tag{7}$$

where the intermolecular potentials V_{bond} and V_{bend} represent the bond strength energy and the bending energy of a water molecule, respectively. V_{bond} and V_{bend} are given by

$$V_{\mathrm{bond}}(b_i)=\sum_{N=1}^{N_b}K_b^{\mathrm{OH}}\left(b_i-b_0^{\mathrm{OH}}\right)^2, \tag{8}$$