Interaction forces between nanoparticles in Lennard-Jones (L-J) solvents

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Abstract. Molecular simulations, such as Monte Carlo (MC) and molecular dynamics (MD) have been recently used for understanding the forces between colloidal nanoparticles that determine the dispersion and stability of nanoparticle suspensions. Herein we review the current status of research in the area of nanoparticles immersed in L-J solvents. The first study by Shinto et al. used large smooth spheres to depict nanoparticles in L-J and soft sphere solvents. The nanoparticles were held fixed at a particular interparticle distance and only the solvents were allowed to equilibrate. Both Van-der-waals and solvation forces were computed at different but fixed interparticle separation. Later Qin and Fitchthorn improved on this model by considering the nanoparticles as collection of molecules, thus taking into the account the effect of surface roughness of nanoparticles. Although the inter particle distance was fixed, the rotation of such nanoparticles with respect to each other was also investigated. Recently, in keeping with the experimental situation, we modified this model by allowing the nanoparticles to move and rotate freely. Solvophilic, neutral and solvophobic interactions between the solvent atoms and those that make up the nanoparticles were modelled. While neutral and solvophobic nanoparticles coalesce even at intermediate distances, solvophilic nanoparticles are more stable in solution due to the formation of a solvent shield.

1. Introduction

Nanoparticle surfaces need to be passivated or stabilized to enable the formation of stable nanoparticle dispersions. Such stabilization may be electrostatic or steric or electrosteric or simply the solvent itself or a ligand acts as the stabilizer. Inter nanoparticle forces due to various sources therefore determine the state of dispersion and the stability of nanoparticle suspensions. Properties of such nanofluids depend on the inter-nanostructure forces, as well as the interactions between the nanostructures and the surrounding medium [1, 2]. The focus of the present communication is to review the research in the area of effect of solvent on inter nanoparticle interaction forces.

2. Forces between smooth nanoparticles in L-J Fluids

In the first study by Shinto et al [3] the solvation forces between two large smooth spheres in an L-J fluid was simulated using MD. Interactions between the solvent molecules were given by a dimensionless shifted 12-6 L-J potential expression. In contrast the interaction between solvent particles and nanoparticle were computed using the shifted 10-4-3 L-J potential. Solvophilic or solvophobic particle-solvent molecule interactions were considered. The L-J solvent dimensionless

density was taken to be 0.59 while the dimensionless temperature was chosen to be 1.2. The nanoparticle was assumed to be 10 times the size of the monatomic solvent molecule. The solvation forces were computed at fixed inter-nanoparticle distances which ranged from 0σ to 5.0σ where σ is the diameter of a solvent molecule. For the solvophobic particle-solvent interaction model, the solvation force profile exhibited a strong attractive trend (with decrease in interparticle distance) without display of any oscillatory behaviour (Fig. 1a). The presence of the solvophobic nanoparticles disrupts attractive solvent-solvent interactions and makes difficult the formation of any dense solvent molecule layer near the nanoparticle surface. On the other hand, the solvent density near the solvophilic surface was found to be higher than that near the solvophobic surface. The solvation forces oscillate with a periodicity of about solvent molecule diameter due to the packing effect. This periodicity in oscillatory forces was observed up to three solvent molecular diameters. Solvation forces could be of comparable or greater magnitude to the van der Waals attraction between the nanoparticles.
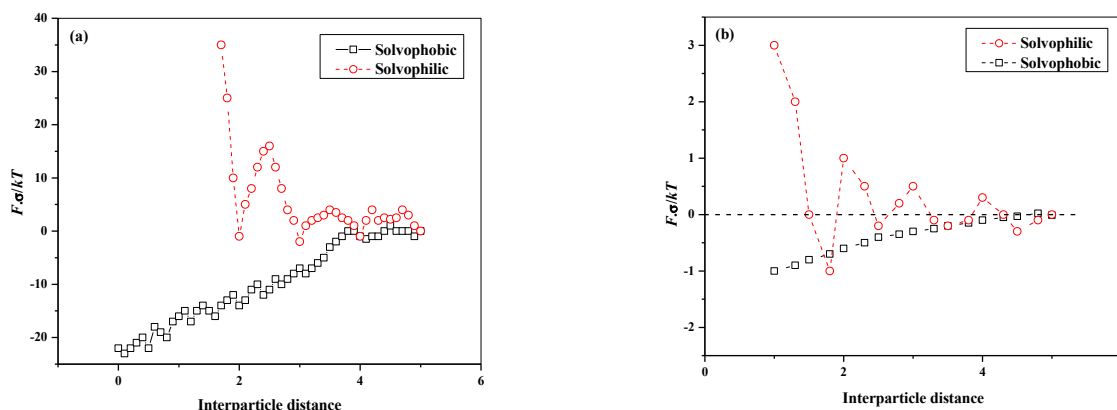

Figure1. A comparison of solvation forces for a) smooth [3] and b) rough [4] nanoparticles.

These solvation force predictions are similar to those to those given by earlier MC and MD simulations for fluids confined between flat and infinite surfaces. The solvent molecules tend to form layers around nanoparticles which prevent the nanoparticles from aggregating. However, when the separation distance between the large particles is smaller than the diameter of the small particles so that no small particles can fit in the gap between the large particles, a net attractive force, the so-called depletion force, between the large particles is expected. The oscillatory nature of the solvation forces is also due to this reason. Properly packed layered solvent molecule structure formation induces a repulsive barrier. Between formation of integral number of packed layers weak attractive depletion forces do occur resulting in observation of oscillatory forces.

3. Effect of surface roughness on solvation forces in L-J Fluids

A very important aspect of inter nanoparticle forces is the balance between solvation and van der Waals forces. For smooth nanoparticles, the above mentioned study by Shinto et al. demonstrated that solvation forces could be of comparable or greater magnitude to the van der Waals attraction between the nanoparticles. On the other hand surface roughness of the nanoparticles can also significantly affect the magnitude of solvation forces influencing the balance between solvation and van der Waals forces. It was with this objective that Qin and Fichthorn [4] simulated nanoparticles

as rigidly fixed L-J clusters. To maintain such nanoparticles in solid state the energy parameter in the LJ expression for solid-solid interactions $\left(\varepsilon^{solid-solid}\right)$ is taken to be 10 times the solvent-solvent $\left(\varepsilon^{solvent-solvent}\right)$ interaction energy parameter. The diameters of solid and solvent molecules are taken to be the same and the typical NVT ensemble molecular dynamics simulations were carried out. Solvophilic or solvophobic nanoparticle-solvent molecule interactions were modelled. Since the solvophilic case is characterized by good attraction between the solvent and solid molecules constituting the nanoparticles, therefore this case is modeled by taking the solid-fluid molecule interaction energy parameter as $\varepsilon_{solvophilic}^{solid-solvent} = 5\varepsilon^{solvent-solvent}$. Weaker interactions between molecules making solvophobic nanoparticles and solvent molecules are modeled by taking $\varepsilon_{solvophobic}^{solid-solvent} = 0.2\varepsilon^{solvent-solvent}$. Figure 1b shows oscillatory solvation forces for solvophilic nanoparticles and monotonic, attractive forces for solvophobic nanoparticles. Similar to results obtained by Shinto et al, here also the solvation forces are found to be comparable or greater than the van der Waals forces. Surface roughness affects van der Waals forces the least and that only for very small interparticle distances. For solvophobic nanoparticles, as the interparticle separation is increased, surface roughness causes fluctuations in the monotonic attractive trend of forces. But in the solvophilic case, surface roughness influences the phase shift of the oscillatory solvation-force profile, as well as the amplitude. This means that the solvation force for a fixed separation can be either attractive or repulsive, depending on the relative orientation of the nanoparticles. Thus in a later work [5] the same authors demonstrated that oscillations diminish or disappear with inter particle distance if the nanoparticles are allowed to rotate although the separation between them is kept fixed.

4. Effect of movement of nanoparticles on solvation forces

In a recent communication [6] our group has modified the model given by Qin and Fichthorn. As in reference [4], here also to include surface roughness we consider the nanoparticles to be clusters of molecules. Solvophilic, neutral and solvophobic interactions between the solvent molecules and those that make up the nanoparticles are considered. Simulations were done using typical NVT ensemble Metropolis algorithm. In this investigation the nanoparticles are free to move as well rotate and thus to find the state of minimum free energy for the given state of the system. This is made possible by considering Monte Carlo (MC) moves for both the molecules making up the nanoparticles and the solvent. The dimensionless temperature is taken to be 1.0. Ensemble average solvation and van der Waal's forces are computed once equilibrium inter nanoparticle distances are achieved.

A simulation is initiated from a state of two nanoparticles at a specified distance. The solvent molecules are added randomly to achieve the L-J solvent dimensionless density 0.64. This study emphasizes finding the interparticle distance at which the two nanoparticles are stable against coalescence. For example, the solvophilic case the configuration starting from initial interparticle distance $\delta_i = 1.5\sigma$ stabilizes at $\delta_{eq} = 1.0\sigma$. A thin solvent shield is found to stabilize the nanoparticle suspension. In contrast to solvophilic case, for the neutral interaction case solvent–solvent molecular interactions and solvent–solid (or nanoparticle) molecule interactions are equal. Therefore, two nanoparticles are effectively solvated or stable against coalescence only at larger δ_i in comparison to solvophilic case. For the solvophobic case the solvent–solvent interactions

are much stronger than solvent–solid interactions. Here the nanoparticles are stable against coalescence at still larger δ_i as compared to solvophilic or the neutral systems. Further, one also observes that solvophilic, neutral and solvophobic systems starting from the same δ_i distance may stabilize to different average δ_{eq} for separate simulation runs. Therefore, stable inter nanoparticle distance configurations seem to represent local minima. In contrast to regular oscillatory behavior found in references 3 and 4, here only weak but irregular oscillatory behaviour of the solvation forces for solvophilic nanoparticles are observed. In the present study force profiles for different nanoparticle orientations and distances are phase shifted relative to one another, so that the solvation forces at a fixed center-of-mass distance can be attractive for some particle configurations and repulsive for others. This suggests that if nanoparticles are allowed to freely rotate and move, they select configurations that minimize the free energy and reduce the solvation forces. For the stable solvophobic nanoparticles case, the solvent–solvent interaction forces stronger than solvent–solid interactions and this is manifested by the slightly positive bias of the solvation forces in the solvophobic system.
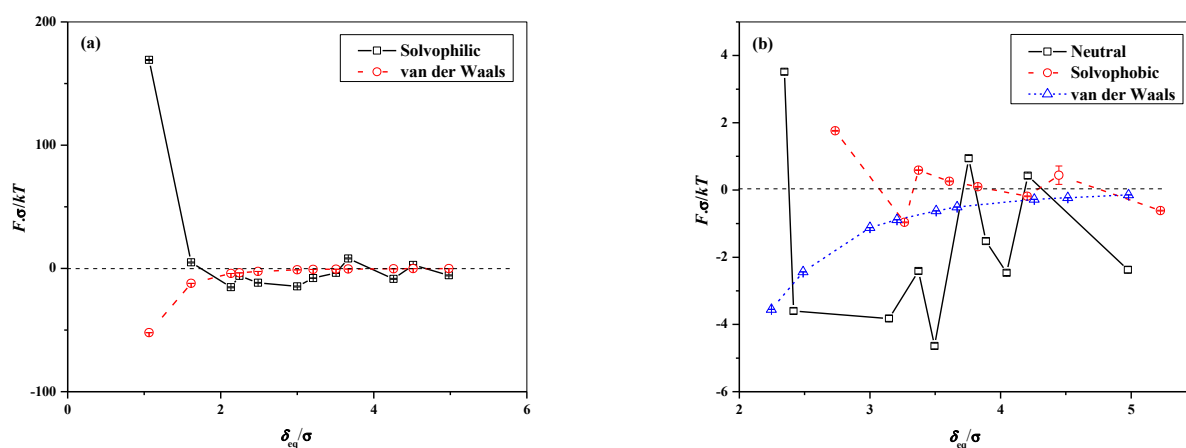

Figure 2. (a) Solvation and van der Waals forces with increasing interparticle distance δ_{eq} for solvophilic system

(b) Solvation forces with increasing interparticle distance (δ_{eq}) for the neutral and solvophobic systems.

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