Solvation Force of Ellipse-Shaped Molecules Moving in One Dimension and Confined between Two Parallel Planar Walls

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(Received 20 May 2014, Accepted 5 December 2014)

The model fluids containing hard ellipses (HEs) and Gay-Berne (GB) particles where their center is moving in one dimension and confined between two parallel walls with different interactions are investigated using Monte Carlo simulation, NVT ensemble. The dependency of fluid pressure with respect to the wall distances is studied. The oscillatory behaviors are seen in this quantity against wall separations. The total average number density profile of particles is calculated using the angular number density. For both HE and GB particles confined between hard walls the total average number density at the wall shows a similar oscillatory behavior. We also related the pressure of these systems to the relevant solvation force between two colloidal particles. We have investigated the dependency of this quantity to the packing fraction, temperature, structure of the walls confining the particles and the interaction between ellipses of the fluid. Finally it is possible to reach the required solvation forces by changing the thermodynamic or structural properties.

INTRODUCTION

Understanding the properties of a molecular fluid confined between solid surfaces has been one of the important interests for many researchers from practical and theoretical points of view. An essential property of liquids confined between solid boundaries which are smooth on the molecular scale is their tendency to show layered structures. This property leads to oscillatory solvation forces between confining surfaces, which have been observed and simulated for simple models of liquids such as spheres [1,2] and non-polar globular molecules [3-5] as well as for complex liquids such as straight-chain alkanes [6,7]. These properties have been studied [8,9] experimentally by using the surface force apparatus (SFA), atomic force microscopy (AFM), and friction force microscopy (FFM). Many computer simulations [1,2,10-12] and other theoretical approaches [13,14] have been also used to study these kinds

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of systems.

Molecular simulation techniques have been widely used to investigate the thermodynamics of confined fluids [15,16], and in particular have led to understand the relationship between fluid structure and solvation force at the molecular level.

Bordarier *et al*. [15] have used grand canonical Monte Carlo and molecular dynamics to simulate and study the properties of thin films confined between two surfaces. In their model the fluid and wall species consist of two different Lennard-Jones rare gas atoms. They have reported that, the solvation force is exponentially damped as wall separation is increased. The existing of periodic curve and all peaks of maximum amplitude in the solvation force depend on the wall structures.

Configurational bias grand canonical Monte Carlo simulations have been used by Porcheron *et al*. [17] to model butane confined between planar and non-planar walls. In order to model surface roughness effects on the nanometer scale, they have used furrowed walls. They have

reported that the fluid confined between planar walls exhibits a damped oscillatory solvation force or pressure profile. A transition from an oscillatory to a non-oscillatory behavior is observed when the characteristic length of the furrow reaches the typical dimensions of a butane molecule. Using a newly developed grand canonical ensemble molecular dynamics method for simulations of confined liquids Gao et al. [18] investigated equilibrium structures, solvation forces, and conformational dynamics of thin confined films of spherical molecules, straight-chain alkanes and a branched alkane. The solvation force oscillates as a function of the gap width for the spherical and straight-chain alkane liquids and exhibit attractive and repulsive regions, while for the branched alkane the solvation forces are mostly repulsive, with the development of attractive shallow local regions for small values of the gap width. In another article [19] they investigate the internal energy and entropic origins of density layering and solvation force oscillations.

In order to study the binding of the defects to the particles, the adsorption of a particle at a solid surface for a system consisting of spherical particles suspended in a nematic liquid crystal, Grollau and his coworkers performed Monte Carlo simulations and dynamic field theory [20]. They reported an effective repulsive force acting between the particle and the wall.

Pizio et al. [21] studied the solvation force between two plates modified with a tethered layer of chain and showed that the grafting density and the structure of chains change the solvation force whereas the concentration of the solution plays a minor role.

In this paper, we extend our previous study [22] to a comparative investigation of structure and solvation force oscillations in confined fluid. This system includes confined molecules of ellipse shape between two walls in 1D. These walls can also be estimated to be two nano circular particles suspended in an ellipse shape fluid. This assumption is reasonable because of the great size of these particles similar to colloidal particles, as proposed by Moradi et al. by using density functional theory [23]. So we calculate the solvation force between these nano circle-shaped particles. We choose two different types of particle interactions, hard ellipse and GB potential and also we choose the confining surface solid as hard and soft walls.

COMPUTATIONAL METHODS

According to the directional and spatial configuration of ellipses confined between two walls due to the change of wall separation, here we calculate density profiles, pressures and solvation forces of the systems of ellipses with various distances of walls and we show how the configuration of ellipses and solvation forces change by changing the wall separations.

We perform the Monte Carlo simulation in NVT ensembles, for a system of confined ellipses and choose a 1D simulation line (x direction) such that the length of the line is exactly equal to the distance between walls. The number of the particles in the simulation line is chosen such that the average number density of particles in the box is equal to the bulk number density of a given system of ellipses. The particles can rotate freely in x-y plane, while their centers can only move in x direction. We have chosen 6 to 32 particles in the simulation line in order to reach the desired value of packing fraction.

To start the simulation, we insert the particles on the line systematically with a specific configuration. We choose the positions and directions of the ellipses such that there are not any overlaps between them. Our calculations consist of about 10-20 $\times$ 10^6 steps for equilibration and about 10-25 $\times$ 10^6 steps for calculating and obtaining the averaged quantities.

The interaction between the particles is GB potential which is defined as:

$$v^{GB} = 4\varepsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij})\{R^{12} - R^6\}$$

(1)

where R is given by

$$R = \frac{\sigma_0}{r_{ij} - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) + \sigma_0}$$

(2)

in this relation, σ_0 is side-by-side distance, r_{ij} is the distance between center of particles i and j, σ is the intermolecular separation at which the potential vanishes, and thus represents the shape of the molecules. We have calculated σ quantity using the procedure explained in Ref. [24]. The well depth $\varepsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij})$, representing the anisotropy of the attractive interactions is written as,

$$\varepsilon\left(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}\right) = \varepsilon_0 \varepsilon^\nu\left(\hat{u}_i, \hat{u}_j\right) \varepsilon'^\mu\left(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}\right) \tag{3}$$

where,

$$\varepsilon\left(\hat{u}_i, \hat{u}_j\right) = \left\{1 - \chi^2\left(\hat{u}_i, \hat{u}_j\right)^2\right\}^{-1/2} \tag{4}$$

and

$$\varepsilon\left(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}\right) = 1 - \frac{1}{2}\chi' \times \left\{ \frac{\left(\hat{r}_{ij}\cdot\hat{u}_i + \hat{r}_{ij}\cdot\hat{u}_j\right)^2}{1 + \chi'\left(\hat{u}_i\cdot\hat{u}_j\right)} + \frac{\left(\hat{r}_{ij}\cdot\hat{u}_i - r_{ij}\cdot\hat{u}_j\right)^2}{1 - \chi'\left(\hat{u}_i\cdot\hat{u}_j\right)} \right\}. \tag{5}$$

where, χ' is defined in terms of ε_e and ε_s, the end-to-end and side-by-side well depths, respectively, as

$$\chi' = \left\{1 - \left(\varepsilon_e/\varepsilon_s\right)^{1/\mu}\right\} / \left\{1 + \left(\varepsilon_e/\varepsilon_s\right)^{1/\mu}\right\} \tag{6}$$

The overall energy scale is set by the value of energy parameter ε_0. In our calculations, the parameters μ and ν are chosen with the values 2 and 1, respectively. Also we assume $\sigma_0 = 0.5$.

We have examined three kinds of wall-particle potential such as:

- Hard wall
- Wall with inserted soft ellipses at different angles, which can interact with the GB particles of the system.
- Wall with inserted hard ellipses at different angles, which can interact with the GB particles of the system.

For more information you can see Ref. [25]. We change the position and direction of molecules and accept the configuration conditionally, using the Metropolis algorithm [26-28]. In order to find the distance between the particles and the hard wall, we have used the procedure described in reference [29] and repeat this procedure for many times until the system reaches the equilibrium. After that, we are able to calculate the average value of desired quantities. For hard ellipse system, as mentioned in reference [25], the pressure is estimated by counting the overlaps that result from a small isotropic volume scaling, but for the GB system we have used the usual virial theorem as reported in reference [22]. We can relate the pressure of the system to the solvation force between two nano circular particles suspended in a hard-ellipse or GB fluid. The solvation force, $f(d)$, is defined as the total force per unit length which acts

to separate the plates and is written as,

$$\beta f(d) = \beta\left(p(d) - p(\infty)\right) \tag{7}$$

where $p(d)$ and $p(\infty)$ are the fluid pressures when the separation of the walls are d and infinit, respectively, and $\beta = 1/k_B T$.

RESULTS AND DISCUSSIONS

Here, we have performed some simulations on the systems with different distances of walls, d, different packing fractions and aspect ratios of k = a/b = 4.0, where a and b are semi-major and semi-minor axes of ellipse. Now we are interested to discover how the density profile and pressure of these systems depend on the separation of the walls. The semi- major diameter of ellipse, a, is chosen as the unit length for all simulations. As in our previous article, [22] we start to obtain the average of quantities when the systems reach to their minimum energy; we also check the thermal and mechanical equilibrium of these systems.

Figure 1 shows the average number density, ρ_{av}, which defines the sum of the particle densities in all directions over the bulk density for the systems of hard ellipses, with the same value of packing fraction (as is defined by $\eta = 2b\rho$), $\eta = 0.5$ and three different values of d. The height of the density profiles for these three values of wall distances show an oscillation behavior near the walls. However, far from the walls they have almost the same values. In order to see the effect of the intermolecular interactions, we perform the MC simulation for systems with the same parameters as shown in Fig. 1, except those being composed of GB ellipses. The average number density profile for these systems at $T^* = 1.0$, where the reduced temperature $T^* = k_B/\varepsilon_e$, are presented in Fig. 2. The similar oscillatory behavior can be seen for different values of wall separation near walls for both kinds of interactions between ellipses. As mentioned in the previous article, [22] for hard ellipses the total density near the hard wall is proportional to the pressure of the system, $\beta_P = <\rho_w>$.

So, we have found that the ellipse-shape particles show an oscillation behavior in their average density profile, which is independent of their interactions.
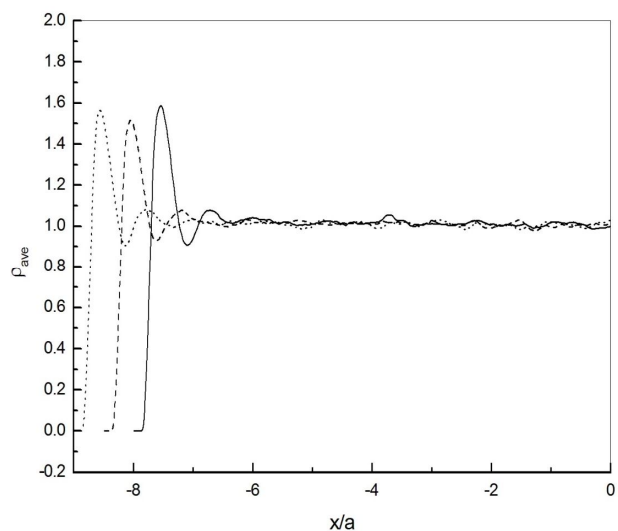
Figure 3 shows a comparison between the pressure of a

Fig. 1. Average number density profile *vs.* distance from wall for systems of hard ellipses with $\eta = 0.5$ and $k = 4.0$, solid curve is for a system with d = 16, dashed curve is for a system with d = 17 and dotted curve is for a system with d = 18.
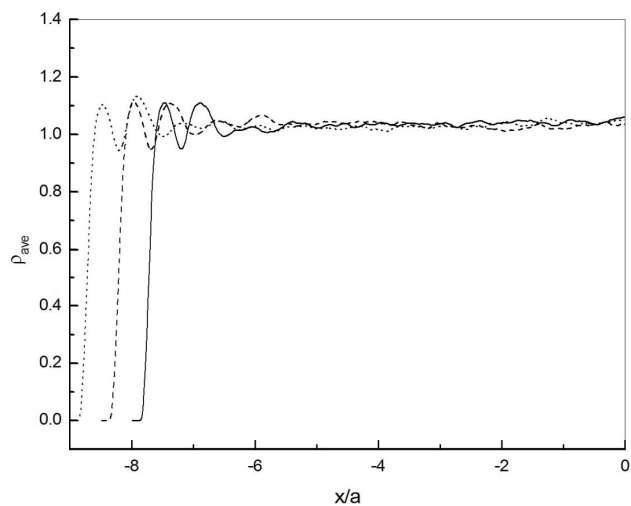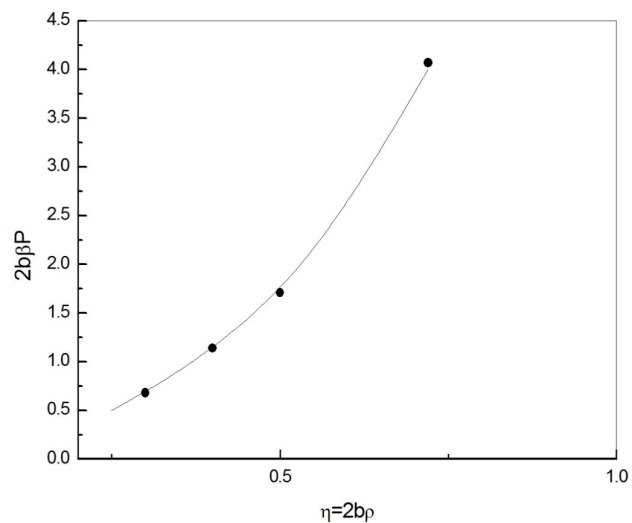

Fig. 3. Pressure *vs.* η for a system of hard ellipses and k = 4.0, solid curve is for NpT ensemble and dots are for NVT ensemble.
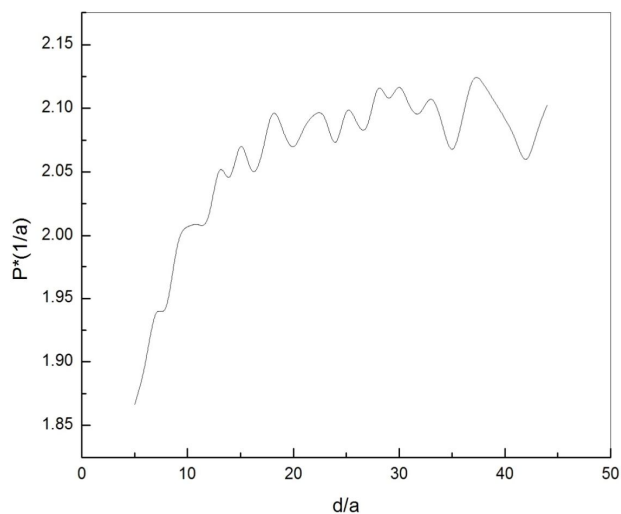

Fig. 2. Average number density profile *vs.* distance from wall for systems of GB ellipses with $\eta = 0.5$ and $k = 4.0$, solid curve is for a system with d = 16, dashed curve is for a system with d = 17 and dotted curve is for a system with d = 18.

Fig. 4. Reduced pressure of a system of GB particles *vs.* distances between walls.

system of hard ellipses for different values of η using NPT and NVT ensembles, which show similar results; the NPT results have been calculated by Ferrero *et al*. [30].

Now, we are interested to consider how the pressure of system depends on the separation of walls, d, and see if there is any oscillatory behavior in this quantity. So, we perform the MC simulation for the systems with different wall distances and the same packing fraction and aspect ratio. Figure 4 shows the reduced pressure, $P^* = P/K_BT$, versus the distance of the walls for systems composed of GB particles for k = 4.0, η = 0.5 and T^* = 1.0. Also, the pressures of a system composed of GB particles against the wall separation for k = 4.0 and η = 0.8, at two different temperatures, are presented in Fig. 5. These figures again show an oscillation behavior in the pressures of such systems, which will be discussed later. It is interesting to see in Fig. 5, the similar oscillations happen at almost the same amount of wall separations, so the location of these fluctuations do not depend on the temperature of the systems. As mentioned before, we can relate the pressure of the systems to the solvation force of two colloidal particles. Using Eq. (1), we have calculated the solvation force for systems with different packing fractions and temperatures, the results are shown in Fig. 6. This figure shows the oscillatory behavior of the solvation force between two nano particles for two different interactions of HE and GB. As seen in Fig. 6, for small separations of walls and for the case of hard ellipses the solvation force is positive which means that the interaction between nano particles is repulsive whereas for the case of GB ellipses the interaction is attractive. But for greater values of wall distance the force goes to zero value as expected. In the case of HE, since there is only repulsive force between the particles, they tend to be near the walls more than the case of GB particles, because their interacting force is attractive as well as repulsive part, which made them to be closer to each other. These properties give the positive and negative values for the solvation force of HE and GB systems, respectively, for small wall separations. For more investigations, the solvation force for a GB system at a given packing fraction and two different temperatures are plotted in Fig. 7. For small wall separations the solvation force is positive and shows a repulsive force between colloidal particles and for large wall distances it goes to zero. The similar behavior of
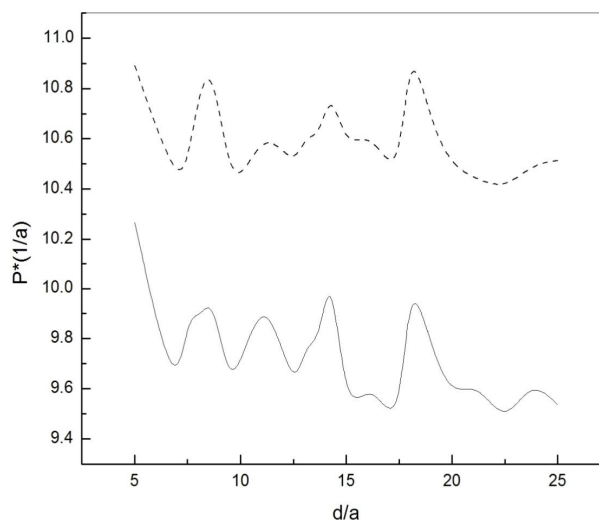

Fig. 5. Reduced pressure of the systems *vs*. wall separation For η = 0.8, solid curve is for T^* = 1.0 and dashed curve is for T^* = 2.0.
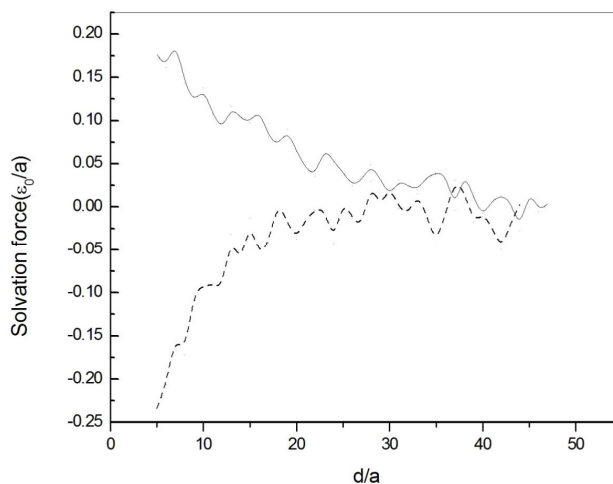

Fig. 6. Solvation force *vs*. distance of walls, for η = 0.5, solid curve is for a system of HE and dashed curve is for a system of GB interaction.

solvation forces for two temperatures can be seen. By increasing the packing fraction, the solvation force shows repulsive characteristic near the walls compared to the case of η = 0.5, this can be explained as follows, the particles
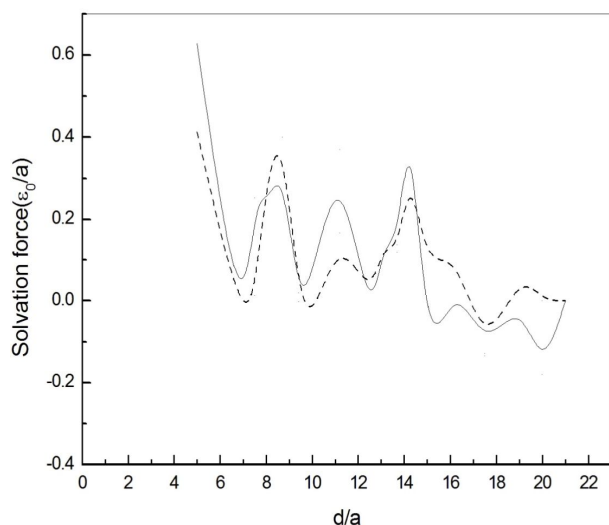
Fig. 7. Solvation force for system of GB ellipses *vs.* distance of walls, for $\eta = 0.8$, solid curve is for $T^* = 1.0$ and dashed curve is for $T^* = 2.0$.
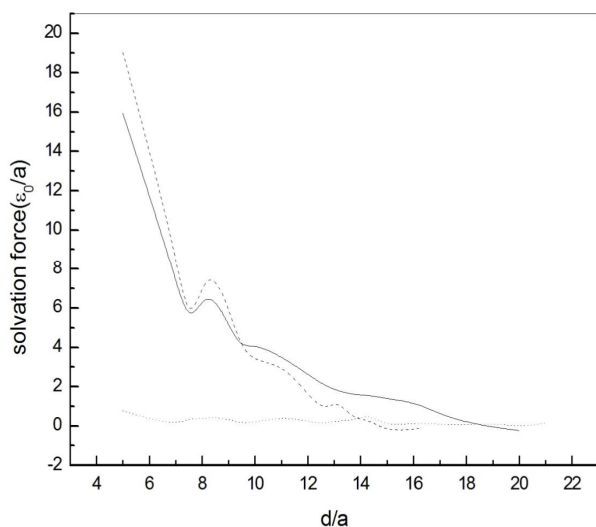

Fig. 8. Solvation force for system of GB ellipses *vs.* distance of walls, dotted curve is for hard wall, solid curve is for soft wall at $T^* = 1.0$ and dashed curve is for soft wall at $T^* = 2.0$, $\eta = 0.8$.

have less space to rotate or move and get closer to the walls, so they show more repulsion, but at large wall separations we can see small attraction between the walls.

In this part of our research we change the structure of the wall and switch from hard wall to the case where one soft ellipse is sunk into the wall at various angles with respect to the x axis. In this case, the confined particles interact with the sunk particles instead of the hard wall and this situation can affect the solvation force. Figure 8 shows the solvation force for systems with $\eta = 0.8$ and a comparison is made for hard and soft walls (one parallel ellipse inserted in the hard wall at 90°). As seen in this figure, the magnitude of the solvation force between soft walls is more than that of the hard walls, indicating the stronger repulsive interaction between them. The reason is, there exists attractive force between the ellipses and walls, as shown in our previous article. Figure 8 also shows that the behavior of solvation forces for soft wall at both temperatures $T^* = 1.0$ and $T^* = 2.0$ are almost similar. The solvation force for soft wall-GB systems with $\eta = 0.5$ and different temperatures are presented in Fig. 9. Figure 10 presents the solvation forces for hard walls and different kinds of soft walls which can be obtained by changing the angle of the inserted ellipses in the walls. First of all, we can see that in the case of hard wall the solvation force shows attraction in small wall distances because the particles are less willing to be near the walls due to the attractive interaction between themselves, but in the case of soft walls they can feel the attraction to the walls too, so the solvation force will become more repulsive in this case. This figure also shows that by changing the angle of the ellipses, inserted in walls from 90 degree to 0 degree, their repulsive character is increased, which may be explained as follows. By decreasing the angle, the structure of the wall is changed more in comparison with the hard wall, so the particles can be attracted to the walls more and the solvation force will show more repulsion. These figures also show that by increasing the wall distances their solvation forces become smooth and show small oscillations around 0 values. Finally, we change the inserted soft ellipse in the wall by hard one. In this case, the solvation force for perpendicular inserted ellipse is represented in Fig. 11. As expected, for hard ellipse inserted to the wall the solvation force for small d is more attractive than the case of soft ellipse inserted, but for large wall distances both of them oscillate around zero value. Also we can see that for the system with inserted hard ellipse the solvation force reaches to zero more quickly. The FFT of solvation force shows a
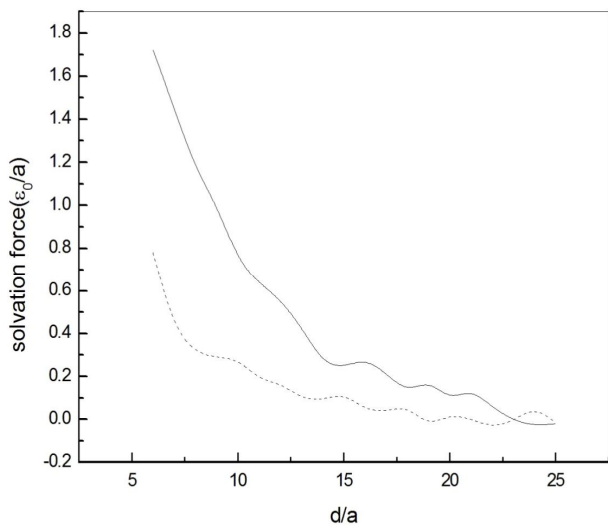
Fig. 9. Solvation force for system of GB ellipses *vs.* distance of soft walls, for $\eta = 0.5$, solid curve if for soft wall with 0 degree ellipses inserted and $T^* = 2$ and dashed curve is for soft wall with 0 degree ellipses inserted and $T^* = 1$.
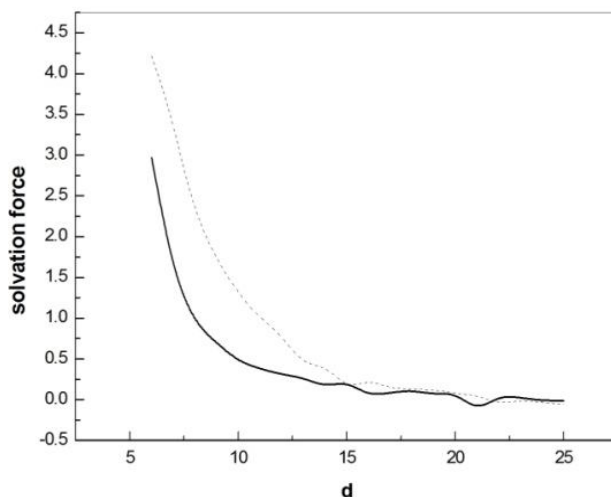

Fig. 11. Solvation force for system of GB ellipses *vs.* distance of walls, for $\eta = 0.5$, and two different kinds of ellipses inserted in the walls, solid line is hard ellipse and dashed line is for GB particle inserted in the walls both at the angle of 90°.
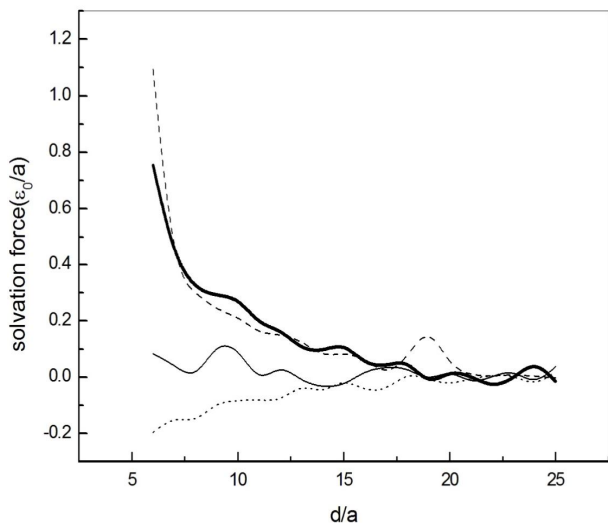

Fig. 10. Solvation force for system of GB ellipses *vs.* distance of soft walls, solid curve is for soft wall with 90 degree ellipse inserted, dashed curve is for soft wall with 30 degree ellipse inserted, thick solid curve is for soft wall with 0 degree ellipse inserted and dotted curve is for hard wall, $\eta = 0.5$.
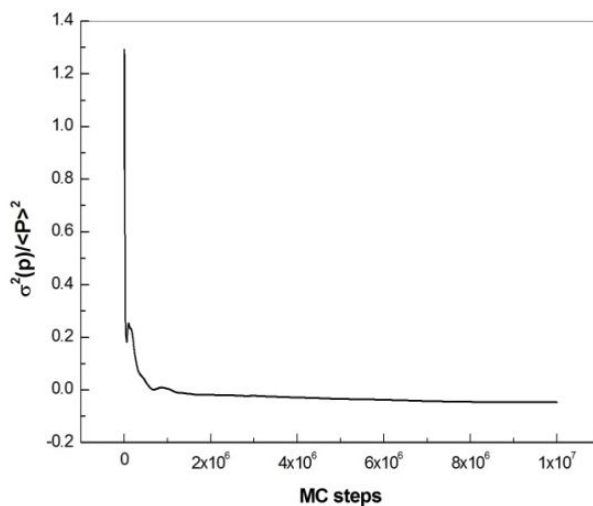

Fig. 12. The relative variance in pressure of a confined system of GB particles.
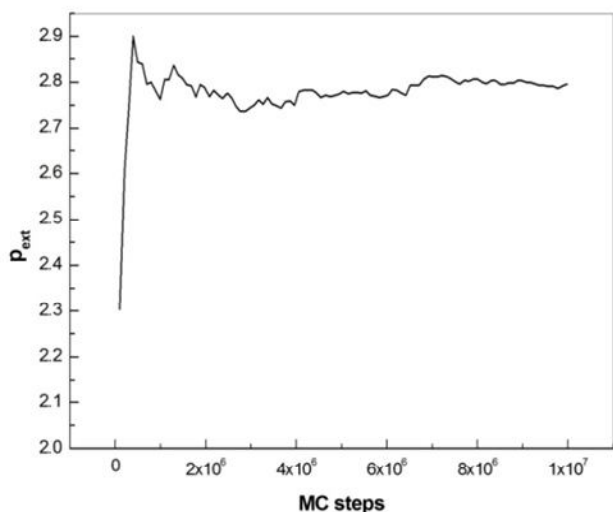
Fig. 13. The external pressure of a system of confined GB particles, *vs*. steps of MC simulation.

periodicity in solvation force at almost with a period of integer × semi-minor or integer × semi-major or integer × (semi-minor + semi- major) diameters.

In order to show the reliability of our results, we have reported as an example the relative variance in pressure for a system of GB particles confined between hard walls at T^* = 1.0, η = 0.5 and d = 1, as shown in Fig. 12. As seen, this quantity has reached to the final value of 0.05% tolerance after 5×10^6 steps. Also, Fig. 13 shows how the external pressure converges to its final value for a system of confined GB particle at T^* = 1.0, η = 0.5, for soft walls and when the wall separation is 7. After about 5×10^6 steps it has reached to its final value. So, we can conclude that our results have the desired accuracy.

CONCLUSIONS

We conclude that, there is an oscillation force between two nano particles separated at d distance which depends on the structure of the fluid in which they are suspended. This oscillatory behavior is due to the formation of the layers of the molecules in the fluid near the wall of colloidal particles and can change by changing packing fraction, temperature, the interaction between ellipses of the fluid, and wall-

particle interaction. Therefore, it is possible to reach the required solvation forces by changing the thermodynamic or structural parameters within bounds of thermodynamic stability.

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