



Solvation force in hard ellipsoid molecular liquids with rod-sphere and rod- surface interactions

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ARTICLE INFO

Article history:

Received 19 April 2019

Revised 9 August 2019

Accepted 28 August 2019

Available online 29 Aug 2019

Keywords:

Solvation force

Colloid

Hard ellipsoid fluid

Rod - sphere potential,

Rod surface - potential,

Density functional theory

ABSTRACT

In a previous study, one of the authors of this work calculated the solvation force of a hard ellipsoid fluid with hard Gaussian overlap potential using hard needle wall interaction and non-linear equation proposed by Grimson-Rickyzen. In the present study, using density functional theory and extended restricted orientation model, the solvation force of hard ellipsoid fluid in the presence of more realistic rod-sphere and rod-surface interactions is calculated. We investigate weak and strong molecule-surface coupling strengths. The colloids distance effects on density profiles are calculated. We could not find the exact or simulation results for comparison. The results in the case $k = 3.0$ are compared with the solvation force of hard Gaussian overlap fluid and hard needle-wall interaction. The results corresponded, qualitatively.

1 Introduction

Structure of fluids, are altered near colloidal particles. The force between two colloids is called solvation force. In this paper the solvation force in fluids of hard ellipsoidal molecules with the new particle- wall interactions is calculated. This force has applications in industries, biological fluids, foods, chemical and medical products [1]. Immersed particles with the scale of $10 \mu\text{m}$ to 10nm create solvation force.

There are different methods to calculate the solvation force. It was calculated for confined polar and nonpolar fluids [2-9] by experimental and Monte Carlo simulation [10] methods. Because of the simplicity it was studied extensively in simple spherical molecular fluids [11-15]. Furthermore it

was obtained by Monte Carlo simulations for thin layer of Gay-Berne fluid [16, 17] between two solid walls [18, 19]. In confined hard ellipsoidal molecular fluids with soft particle-wall interactions it has not been much studied theoretically [20].

In one of our previous studies [21], immersed colloidal particles in a fluid of hard ellipsoidal molecules with hard Gaussian overlap (HGO) potential and hard needle-wall (HNW) interaction [22] was studied. In this paper, immersed colloidal particles in a fluid of hard ellipsoidal molecules with more realistic rod-sphere (RSP) and rod-surface potentials (RSUP) [23] are considered. The RSP describes the interaction between a Gaussian ellipsoid and a sphere located in the surface plane. In RSUP each particle effectively interacts with infinity spheres located in the surface plane [23]. The hard ellipsoid (HE) particles do not

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DOI: 10.22051/jitl.2019.25598.1027

interact directly with the substrates, rather another hard ellipsoid is inserted in each particle. As shown in Fig 1, in both models, HE molecules absorb into the walls.

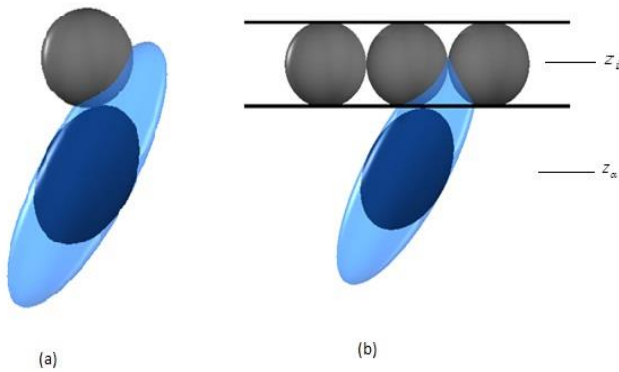


Figure 1. The two particle-wall configurations, (a) RSP and (b) RSUP interactions [23].

We use the density functional theory (DFT) to study the surface influence on liquid crystalline systems. The density functional theories [24, 25] are capable of predicting the phase diagram of liquid crystals [26,27], and also capable of describing the structure near a solid surface and phase transition [25]. Allen [28] showed even the simplest density functional theory namely, the Onsager [29] theory can describe the structure of the surface layer under the influence of external perturbations. This theory has been used to study the thermodynamics of homogeneous and structural properties of inhomogeneous molecular fluids, such as hard ellipsoidal fluids (HE) [30, 31], hard circular cylinders and hard rectangular rods [32,33] and HGO [22] fluids confined between planar walls. Teixeira [31] used the Onsager approximation of density-functional theory with a simple Parsons–Lee re-scaling to study a hybrid-aligned liquid crystal under a very strong confinement. Also, Gurin et al. [34] studied positional ordering of hard cylinders in tubular nanopores and compared the results with classical DFT.

Here we use the hyper-netted chain (HNC) density function proposed by Rickayzen and co-workers [35]. The grand potential of a confined liquid crystal can be written as a functional of the

number density of molecules in any direction. After minimizing the grand potential we can obtain the equilibrium number densities, then we obtain the density profile, the average number density [33, 36], and order parameter of a liquid crystal confined between walls before calculating the solvation force.

The extended restricted orientation model (EROM) [37] based on the density functional theory (DFT) and the new direct correlation function (DCF) of Ref. [38] are used to calculate the number density. The RSP and RSUP [23, 39] are used for interaction of colloids and hard ellipsoids with HGO type potential [40] which have also considered for interaction between ellipsoid molecules. The exact contact distance of hard ellipsoid (HE) molecules is considered instead of the approximate shape parameter of Ref. [39]. For calculation of solvation force the equations which have been proposed by Grimson and Rickayzen, [15, 41] are used. Solvation forces are calculated by using the obtained number densities. Numerical calculations are done by the Fortran software and iteration method [42].

In Section 2, the formalism of solvation force is introduced. In Section 3 the solvation force of a hard ellipsoid fluid with RSP and RSUP interactions is calculated. Finally in Section 4 we obtain the results and present the discussion and conclusions deduced from this work and propose some directions for future studies.

2 Formalism of solvation force

We consider the immersed colloids as rough walls. For confined fluid between these two separated walls by a distance h perpendicular to z direction, following the work of Grimson and Rickayzen, [15] the grand potential difference is;

$$\begin{aligned}
 & \beta(\Omega[\rho] - \Omega[\rho_0]) \\
 &= \beta \int d\vec{r} V_{ext}(z)(\rho(z) - \rho_0) \\
 &+ \int d\vec{r} \rho(z) \ln\left(\frac{\rho(z)}{\rho_0}\right) \\
 &- \int d\vec{r} (\rho(z) - \rho_0) \\
 &- \frac{1}{2} \int d\vec{r} d\vec{r}' [(\rho(z) - \rho_0)] c(\vec{r} \\
 &- \vec{r}') [\rho(z') - \rho_0], \quad (1)
 \end{aligned}$$

where $\rho(z)$, ρ_0 and $V_{ext}(z)$ are the inhomogeneous one particle density, the homogeneous one particle density, and the external potential respectively. Also $\beta = (1/k_B T)$ and $c(\vec{r} - \vec{r}')$ are inverse temperature and direct correlation function. The pressure $P(h)$ that acts upon planar surfaces is defined by [15]

$$\beta P(h) = -\frac{\partial(\Delta\Omega)}{\partial h}, \quad (2)$$

where h is the distance of two colloids. Hence, for studying the interaction of two colloids, we need the pressure which arises from the fluid outside the colloids. This pressure will be the same as for two colloids separated by an infinite distance. Thus the total force per unit area which acts to separate the colloids will be

$$f(h) = P(h) - P(\infty). \quad (3)$$

With this definition, positive $f(h)$ corresponds to a repulsive interaction and negative $f(h)$ corresponds to an attractive interaction. Stable equilibrium separations, therefore, are those at which $f(h)$ passes through zero with a negative spatial gradient.

When minimizing Eq. (1), using the Hyper-Netted-Chain (HNC) approximation [35, 43], and differentiating Eq. (1) with respect to the distance h in a confined liquid, the solvation force can be obtained as follows [15]:

$$f(h) = \frac{\rho(h) - \rho(\infty)}{\beta}, \quad (4)$$

where $\rho(h)$ is one particle density at the position of colloids. By using the Percus-Yevick approximation of density profile, the solvation force is given by:

$$f(h) = \frac{\rho(h)^2 - \rho(\infty)^2}{2\beta\rho_0} \quad (5)$$

Equations (4) and (5) are called non-linear and linear solvation forces in the literature [15, 41].

3 Calculation of solvation force in ellipsoidal molecular fluid

In real confined ellipsoid fluids, particles can penetrate into the walls, so it can be a soft wall model [19, 22, 23]. For the ellipsoidal molecular liquid as a solvent, the particle-wall interaction has been modeled using RSP and RSUP interactions, where the particles-surface interaction is represented by an ellipsoid, a reduced length, k_s , located at the center of the particle. k_s is the determined degree of substrate penetrability [22]. These potentials are convenient interactions for the study of substrate effects on the alignment of liquid crystal molecules. The degree of surface penetrability is increased by decreasing k_s .

The reduced length, k_s , varies between the limits $[0:k]$. The elongation k is the ratio of the length $2a$ and the breath $2b$ of particles, $k = 2a/2b$. $2b$, the length of the minor axis of the molecules, is assumed to be unit length. As Fig 1 and Refs. [22, 23] show, the molecule-wall interaction potential is written as

$$V(z_i, \theta_\alpha) = \begin{cases} 0 & IF \quad |z_\alpha - z_i| \geq \sigma_w(k_s, \theta_\alpha) \\ \infty & IF \quad |z_\alpha - z_i| < \sigma_w(k_s, \theta_\alpha) \end{cases} \quad (6)$$

where z_i , is position of the wall, σ_w is the normal distance between center of the reduced ellipsoid and

sphere in planar substrate or surface walls. The coordinates $(z_\alpha, \theta_\alpha)$ refer to the position and orientation of the molecules. For RSP and RSUP interactions, the contact distances are given by [23]:

$$\sigma_w^{HGO-Sphere} = \sigma_0 \left[\left(1 - \chi_s \cos^2(\theta_\alpha) \right)^{-1/2} - \frac{1}{2} \right], \quad (7)$$

and

$$\sigma_w^{HGO-Surface} = \sigma_0 \left[\left(\frac{1 - \chi_s \sin^2(\theta_\alpha)}{1 - \chi_s} \right)^{1/2} - \frac{1}{2} \right], \quad (8)$$

where $\chi_s = (k_s^2 - 1)/(k_s^2 + 1)$ is anisotropy of the reduced ellipsoids. These contact functions have been used as the basis for the particle-substrate interactions. In RSP, the surface, as viewed by any particle, was taken to be represented by a sphere located in the surface plane but with the same x - and y -coordinates as those of the particles in ref [23]. With RSUP, each HE particle effectively interacts with a planar continuum rather than a single sphere [23].

The interaction between two ellipsoidal particles by means of the HGO potential is given by [40]

$$V(\vec{r}_{ij}, \hat{\omega}_i, \hat{\omega}_j) = \begin{cases} \infty & \text{IF } r_{ij} \leq \sigma(\vec{r}_{ij}, \hat{\omega}_i, \hat{\omega}_j) \\ 0 & \text{IF } r_{ij} > \sigma(\vec{r}_{ij}, \hat{\omega}_i, \hat{\omega}_j) \end{cases} \quad (9)$$

where $\hat{\omega}_i = (\theta_i, \varphi_i)$ describes the orientation of the major axis of particle i and $\hat{r}_{12} = \vec{r}_{12}/r_{12}$ is a unit vector along the line connecting the centers of the two particles, and $\sigma(\vec{r}_{ij}, \hat{\omega}_i, \hat{\omega}_j)$ is given by [35]

$$\sigma(\vec{r}_{12}, \omega_1, \omega_2) = 2b \left[\frac{1 - \chi[(\hat{r}_{12} \cdot \hat{\omega}_1)^2 + (\hat{r}_{12} \cdot \hat{\omega}_2)^2]}{1 - \chi^2(\hat{\omega}_1 \cdot \hat{\omega}_2)} - \frac{2\chi^2(\hat{r}_{12} \cdot \hat{\omega}_1)(\hat{r}_{12} \cdot \hat{\omega}_2)(\hat{\omega}_1 \cdot \hat{\omega}_2)}{1 - \chi^2(\hat{\omega}_1 \cdot \hat{\omega}_2)} + \frac{\lambda[(\hat{r}_{12} \cdot \hat{\omega}_1)^2 + (\hat{r}_{12} \cdot \hat{\omega}_2)^2]}{1 - \chi^2(\hat{\omega}_1 \cdot \hat{\omega}_2)} \right]^{-1/2}, \quad (10)$$

Where χ is anisotropy of the molecule versus k :

$$\chi = \frac{k^2 + 1}{k^2 - 1}, \quad (11)$$

and λ is obtained by

$$\lambda = 1 - \chi - \frac{4b^2}{(a+b)^2}. \quad (12)$$

Equation (10) predicts the exact contact distance of HE molecules and Eq. (13) of Ref. [39] is the approximate contact distance of HGO molecules. From references [36, 37] each molecule can be aligned in $N = 2m^2$ different directions, $\hat{\omega}_{\alpha\beta} = (\theta_\alpha, \varphi_\beta)$ where

$$\alpha = 0, 1, \dots, m-1, \quad \cos \theta_\alpha = -1 + \frac{2\alpha + 1}{m}, \quad (13)$$

and

$$\varphi_\beta = \beta \frac{\pi}{m}, \quad \beta = 0, 1, \dots, 2m-1. \quad (14)$$

These allowed directions are uniformly distributed over the surface of a sphere, so equal weighting can be assigned to them. Using the EROM model [37] for molecular liquids, the grand potential, Eq. (1), changes to

$$\begin{aligned} & \frac{\beta \Omega [\rho_{\alpha\beta}(z)]}{A} \\ &= \sum \int_{-h_\alpha/2}^{h_\alpha/2} dz \rho_{\alpha\beta}(z) \left[\ln \left(\frac{N \rho_{\alpha\beta}(z)}{\rho_B} \right) - 1 \right] \\ &+ \beta \sum_{\alpha\beta} \int_{-h_\alpha/2}^{h_\alpha/2} dz \rho_{\alpha\beta}(z) V_e(z, \omega_{\alpha\beta}) \\ &- \frac{1}{2} \sum_{\alpha\beta} \sum_{\gamma\delta} \int_{-h_\alpha/2}^{h_\alpha/2} dz_1 \int_{-h_\alpha/2}^{h_\alpha/2} dz_2 C_{\alpha\beta\gamma\delta}(z_1 - z_2) \\ &\times \left(\rho_{\alpha\beta}(z_1) - \frac{\rho_B}{N} \right) \left(\rho_{\alpha\beta}(z_2) - \frac{\rho_B}{N} \right), \end{aligned} \quad (15)$$

where A is the area of the walls and

$$C_{\alpha\beta\gamma\delta}(z_1 - z_2) = \frac{1}{A} \int dx_1 dx_2 dy_1 dy_2 C(\vec{r}_1, \hat{\omega}_1, \vec{r}_2, \hat{\omega}_2, \rho_B), \quad (16)$$

where $C(\vec{r}_1, \hat{\omega}_1, \vec{r}_2, \hat{\omega}_2, \rho_B)$ is the DCF of a homogeneous fluid.

Minimizing Eq. (15) with respect to the density with no external potential other than the hard ellipsoid-wall, gives a coupled integral equation [36,37]:

$$\rho_{\alpha 0}(z) = \frac{\rho_B}{N} \exp \left[\sum_{\gamma=0}^{m-1} \int_{-h_{\alpha}/2}^{h_{\alpha}/2} dz_1 (\rho_{\gamma 0}(z_1) - \frac{\rho_B}{N}) \sum_{\delta=0}^{2m-1} c_{\alpha 0 \gamma \delta}(z_1 - z) \right], \quad (17)$$

Where $\rho_{\alpha 0}$ is the number density of molecules for any given value of φ and θ_{α} where

$$h_{\alpha} / 2 = h / 2 - \sigma_W. \quad (18)$$

For calculating $C_{\alpha 0 \gamma \delta}(z_1 - z)$ of hard ellipsoids, we use the proposed DCF of Refs [38, 44] as follows

$$C(\vec{r}_{12}, \hat{\omega}_1, \hat{\omega}_2) = C_{PY-Roth} \left(\frac{|\vec{r}_1 - \vec{r}_2|}{\sigma(\vec{r}_{12}, \hat{\omega}_1, \hat{\omega}_2)} \right) [1 + \alpha' P_2(\hat{\omega}_1 \cdot \hat{\omega}_2)], \quad (19)$$

where α' is a parameter and $P_2(\hat{\omega}_1, \hat{\omega}_2)$ is the second Legendre polynomial.

$C_{PY-Roth} \left(\frac{|\vec{r}_1 - \vec{r}_2|}{\sigma(\vec{r}_{12}, \hat{\omega}_1, \hat{\omega}_2)} \right)$ was introduced in Ref.

[38]. The total needed density for calculation of solvation force is given:

$$\rho_{tot}(z) = 2m \sum_{\alpha=0}^{m-1} \rho_{\alpha 0}(z) \quad (20)$$

In our calculations, we choose $k=3.0$ as it was used in the simulations of refs [22, 23]. For the most commonly used elongation of $k=3.0$ HGO fluid, the transition occurs for $\rho \approx 0.30$ with slight system size dependence [23]. Hence, we chose $\rho_B = 0.24$ and 0.32 as the bulk isotropic and nematic densities of confined HE liquid, respectively.

We solve integral Eq. (17) for $N = 512$ by using an iterative method and use Eq. (20) for the total one particle densities. As mentioned in the literature [18, 22, 33, 36, 39], the density profiles, $\rho_{tot}(z)$, provide information about the layering in

the confined fluid through the location number and height of its peaks. The tendency of confined liquids to orient in a particular direction when in contact with the container walls is called the anchoring phenomenon. The anchoring induced by an interface with interactions, is known as homeotropic, tilt or planar. In homeotropic and planar arrangements, the particles are perpendicular and parallel to the surfaces respectively [18, 22]. Between the two arrangements, lies the possibility of substrate-induced tilt. As mentioned in Refs. [33, 36, 39] and confirmed in the present calculations, the cases, $k_s = 0.0$ and $k_s = 3.0$, result homeotropic, tilt or planar arrangements. For the limited case, $k_s = 0.0$, the number density profiles for HE confined fluid with $h \gtrsim 0.0$ up to 6 times of molecular elongation, are calculated. For the case $k_s = 0.0$ of RSP and RSUP, in region $h \approx 0.3$, there is one monolayer between the two separated walls. For the two cases, in region $h < 0.3$, $\rho(h) \rightarrow 0.0$. Also for case, $k_s = 3.0$, $h = 1.0$ up to six times of molecular elongation, density profiles are calculated. The case RSUP with $k_s = 3.0$, corresponds to the hard particle-hard wall interaction. Hence, for $h < 1.0$ the layer is squeezed out, $\rho(h) \rightarrow 0.0$ and from Eq. (4), $\beta f(h) \rightarrow -\rho(\infty)$ is attractive. For $1.0 \lesssim h < 1.3$, there is one monolayer between the two separated walls. For all h values, the case RSP with $k_s = 3.0$, corresponds to tilt anchoring. Hence, for $h < 1.4$ the layer is squeezed out, $\rho(h) \rightarrow 0.0$ and $\beta f(h) \rightarrow -\rho(\infty)$ is attractive. For $1.4 \lesssim h < 1.78$, there is one monolayer between the two separated walls. All mentioned results in layering of molecules are confirmed in solvation force profiles, see Figs 2- 5.

From Eq. (4), by using the calculated results of number densities, $\rho(h)$, the solvation force with RSP and RSUP interactions are obtained. The solvation forces for HE confined model with RSP and RSUP

interactions are shown in Figs 2 and 3 for limited cases, $k_s = 0.0$, $k_s = 3.0$ and the constant bulk densities. The effects of two contact functions in isotropic and nematic bulk densities are shown.

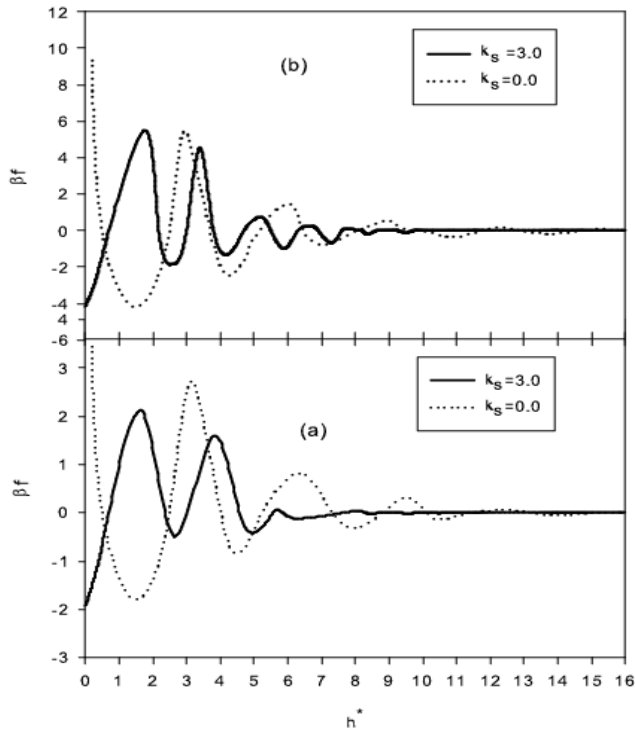


Figure 2. Solvation force for confined systems of HE particles as a function of $h^* = h/2b$ for $k = 3.0$, (a) $\rho_B = 0.24$ and (b) $\rho_B = 0.32$ using the RSP interaction. The solid and dotted curves are $k_s = 3.0$ and $k_s = 0.0$ (our calculations), respectively. The effect of RSP interaction variation for solvation force of isotropic and nematic HE fluid are shown.

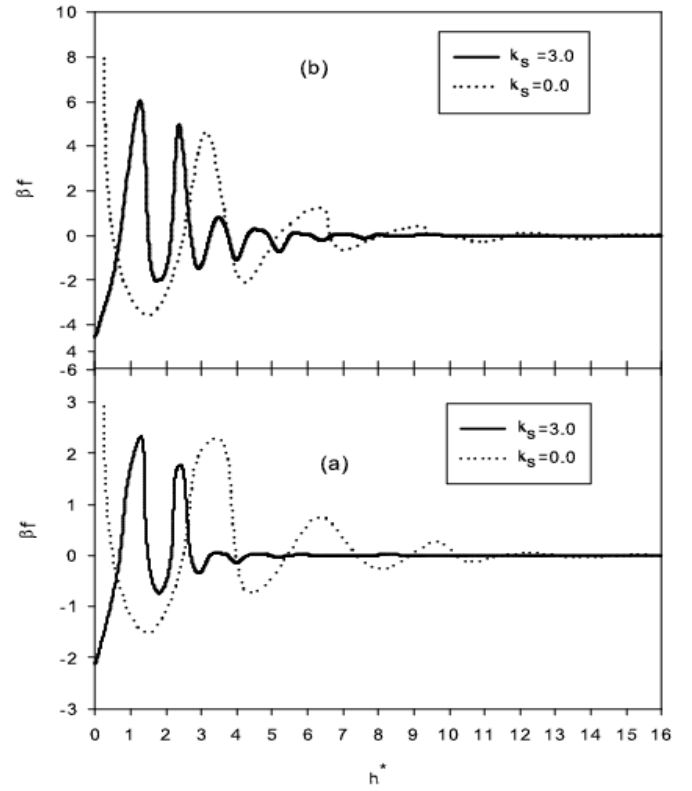


Figure 3. Solvation force for confined systems of HE particles as a function of h^* for $k = 3.0$ and $k_s = 3.0$, (a) $\rho_B = 0.24$ and (b) $\rho_B = 0.32$ using RSP and RSUP interactions. The solid and dashed curves are RSP and RSUP (our calculations), respectively. For RSP and RSUP interactions the effect of bulk density variation for solvation force of planar and tilted arrangements at $k_s = 3.0$ are shown.

In Figs 4 and 5 the effects of number densities on solvation forces due to different interactions with $k_s = 0.0$ and $k_s = 3.0$ are shown.

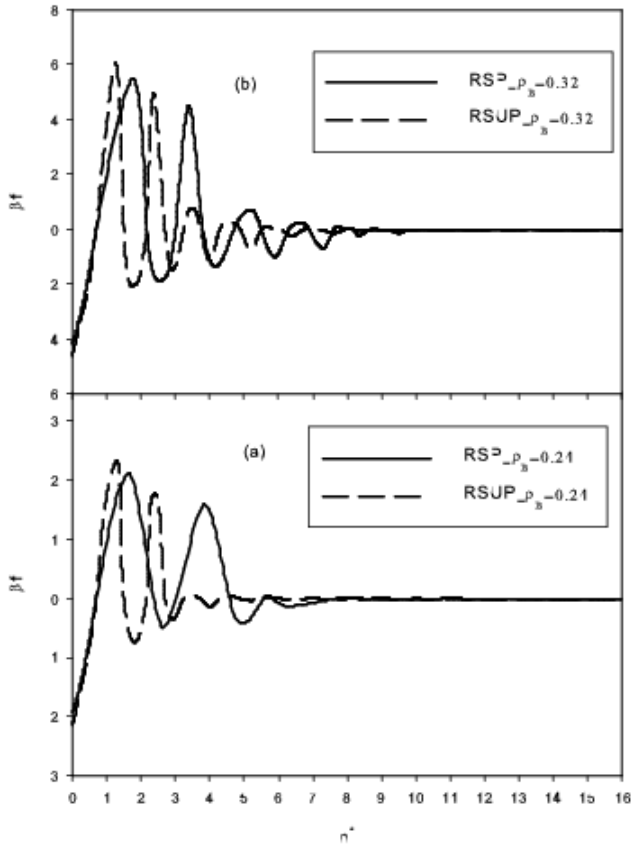


Figure 4. Solvation force for confined systems of HE particles as a function of h^* for $k = 3.0$ and $k_s = 0.0$, using RSP and RSUP interactions in different bulk densities. The solvation forces for these two models are shown for $k_s = 0.0$ and different bulk densities.

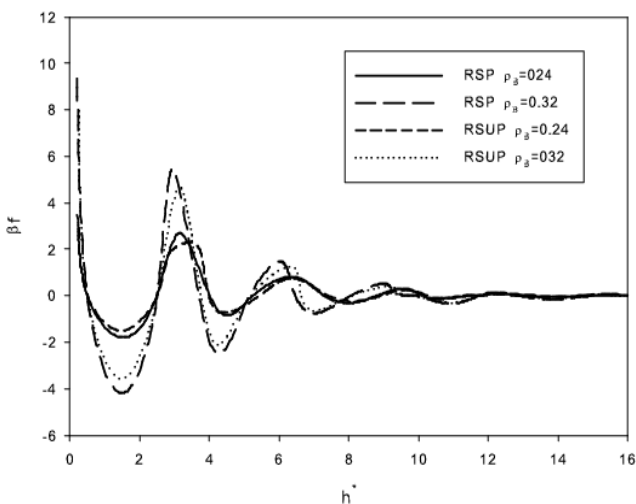


Figure 5. Solvation force for confined systems of HE particles as a function of h^* for $k = 3.0$, $k_s = 3.0$, $\rho_B = 0.32$ using RSUP and HNW potentials. The solid, and dashed curves are RSUP (our calculations) and HNW given in [21], respectively.

We could not find the experimental or theoretical data for solvation force of hard ellipsoidal molecular fluids with these two interactions. Hence, in Fig 6 the solvation force profile in $k_s = k$ as a case of RSUP interaction, is compared with the results of HNW interaction of Ref. [21]. The results are in qualitative agreement.

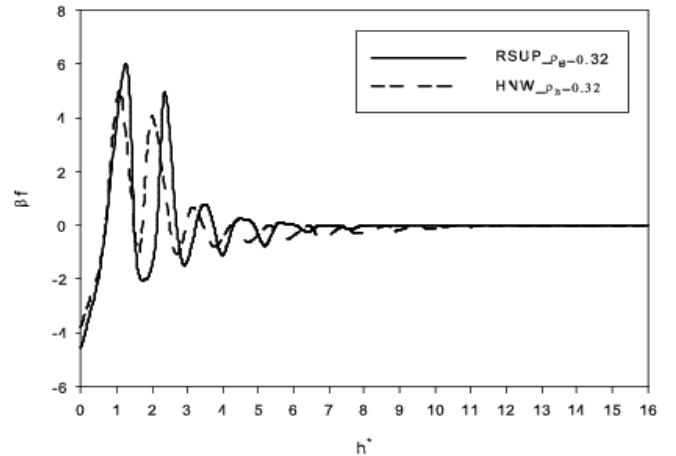


Figure 6. Solvation force for confined systems of HE particles as a function of h^* for $k = 3.0$, $k_s = 3.0$, $\rho_B = 0.32$ using RSUP and HNW potentials. The solid, and dashed curves are RSUP (our calculations) and HNW given in [21], respectively.

4 Results and discussion

The solvation force of confined HE fluid between colloids has been studied using the density functional theory presented in Section 3. The RSP and RSUP interactions between colloids and ellipsoid molecules are considered. In our calculations we have used the EROM model and nonlinear Grimson– Rickayzen formalism of the solvation force. In all solvation force figures, the forces are oscillatory functions. These decaying oscillatory forces vary between attraction and repulsion forces.

As the bulk density increases, heights and depth of oscillations are increased for all reduced molecule lengths. Also as the distance of colloids increases, oscillations decay away from each colloid. In particular, the figures show oscillatory behavior with periodicity correlating with size of the molecules and magnitude, which decays within a few molecular layers. In the cases

$k_s = 0.0$ and $k_s = k$ of RSUP the peak to peak separation of force oscillations corresponds to $\approx k$ and $\approx 2b$ respectively. These results agree with homeotropic and planar arrangements [23] of a confined HE fluid with RSUP interaction. The maximas (repulsive parts) correspond to the well-formed layer configurations while the minimas (attractive parts) occur when wall separation is not enough for well-formed layering of HE fluids. Stable separations correspond to the h values where $f(h)$ switches from positive (repulsive) to negative (attractive). In the two interactions, for elongation, $k = 3.0$, the cases for which $k_s = 0.0$ correspond to the homeotropic arrangement [23]. Thus solvation force oscillations of RSP and RSUP in the case, $k_s = 0.0$, corresponds to homeotropic arrangement. Conversely in the case $k_s = k$ for RSUP, planar alignment develops, so the number of oscillations increases and their spatial period decreases.

In Figs 2(a) and 2(b) the effect of RSP interaction variation for solvation force of isotropic and nematic HE fluid are shown, respectively. Also in Figs 3(a) and 3(b) the RSUP interaction variation are shown. For RSP and RSUP cases, the first maximum shifts away from the walls as the anchoring changes from homeotropic ($k_s = 0.0$) to tilt or planar ($k_s = k$). The observed peak-peak separation distance of RSP at $k_s = k$ is not appropriate for either homeotropic or planar anchoring states. The peak-peak separations correspond to tilted arrangement of confined HE molecules. In planar and homeotropic arrangements, the main peaks are located at distances $\approx 2b$ and $\approx 0.2\sim 0.3$ from the walls and correspond to the first molecules layering. The amplitude of maxima to adjacent minima in bulk nematic is longer than for the isotropic case. For the planar case, oscillations in $f(h)$ of period ~ 1.1 in the nematic phase indicate stratification which corresponds to integer numbers of planar layers in the h interval. For the homogeneous case of RSUP, the oscillations are of longer period and weaker amplitude, indicating weaker orientational coupling in this geometry.

In Figs 4(a) and 4(b) the effect of bulk density variation for solvation force of planar and tilted arrangements at $k_s = 3.0$ are shown. The increase in bulk density from isotropic to nematic, increases the height of maxima and depth of minima in planar and tilted arrangements. The heights and depths of oscillations of RSUP in isotropic and nematic densities are higher than for the RSP case. Also peak to peak separations of force oscillations increase from RSUP to RSP. This increment corresponds to tilted alinement of RSP.

The amplitude of oscillations tends to zero in $h \gtrsim 4.0$ and $h \gtrsim 7.0$ for planar isotropic and nematic cases of RSUP, respectively. For tilted isotropic and nematic cases of RSP, zero amplitude occurs in $h \gtrsim 8.0$ and $h \gtrsim 10.0$, respectively.

The solvation forces for these two models are shown in Fig 5 for $k_s = 0.0$ and different bulk densities. For homeotropically isotropic and nematic cases of the two interactions, the amplitudes tend to zero in $h \gtrsim 3k$ and $h \gtrsim 4k$, respectively. These behaviors correspond to layering and orientational ordering of confined HE molecules. Peaks of isotropic cases shifted away from the wall and broadened.

To some extent, it is reasonable to compare our results with the results of Ref. [21], because simulation or experimental results of solvation force for hard ellipsoid fluids with RSP or RSUP interaction were not available. For the case $k = 3.0$, $k_s = 3.0$, as a RSUP interaction, our results are compared with results of confined HGO fluids with HNW interaction in Fig 6. The main reasons for the discrepancy in Fig 6 may be due to molecule-surface interaction strength difference and molecule- molecule interaction difference.

5 Conclusions

The conclusions are summarized as follows:

(a) In real confined ellipsoid fluids, particles can absorb into the walls. k_s is determined as the degree of substrate penetrability [22, 23]. The RSP and RSUP models are alternative interactions for studying these confined fluids.

(b) In homeotropically anchored cases ($k_s = 0.0$), the formation of layering requires more space than in planar and tilt anchored cases. The distance Δh between the first and second maxima or minima in solvation force corresponds roughly to the large 'diameter' of a HE molecule.

(c) In RSP tilt anchored cases ($k_s = k$), for isotropic and nematic bulk densities, the formation of layering requires more space than in RSUP planar anchored cases. The distance Δh between two consecutive maxima or minima in solvation force of RSP is $1.4 < \Delta h < k$.

(d) In RSUP nematic planar cases, the periods of force oscillations close to the walls are approximately smaller than those farther from the walls. This effect depends on influence of the layers near the walls on adjacent molecules in these cases.

(e) The results show that factors such as particle-wall interactions and bulk number density of HE fluids can have significant effect on solvation forces of the confined fluids.

(f) The present calculations showed that the extended restricted orientational model of HNC density functional theory, by using Eq. (10) instead of Eq. (13) of Ref. [39], can be usefully applied to confined liquids comprised of HE particles with RSP and RSUP particle-wall potentials. Finally, EROM could qualitatively predict the solvation forces corresponding to the behavior of homeotropic, tilt, and planar arrangements of the HE confined liquid.

We can calculate the solvation force of confined Gay-Berne fluids with realistic particle-substrate interactions; using this theoretical model and simulation methods. Also we can calculate the solvation force of confined HE using simulation methods. We will do these in future works.

Acknowledgments

The authors would like to thank the Yasouj University Research Council for financial support for this work [grant number Gryu-89131110].

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