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RESEARCH ARTICLE

Properties of a hard-core Yukawa fluid in a uniform gravitational field obtained by a hybrid DFT-Monte Carlo method

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A hybrid self-consistent method using a Density Functional Theory (DFT) and Monte Carlo (MC) simulations has been applied to obtain the density profiles of a hard-core monocomponent Yukawa fluid under the action of a gravitational field. In this method the properties of a N -particles fluid are obtained from a one-particle MC simulation in the presence of a $N - 1$ particles effective field, which is calculated by DFT within a local density approximation. The combined DFT/MC calculation is repeated in a self-consistent way until a desirable degree of accuracy is obtained. Two different approximations are used to feed the DFT approach, the mean spherical approximation (MSA) and the statistical associating fluid theory of variable range (SAFT-VR). Results compare very well with direct N -particles MC simulations in the NVT ensemble, for 3000 particles, with a significant reduction in the computing time.

Keywords: Monte Carlo simulations; density functional theory; Yukawa fluid

1. Introduction

Colloidal suspensions are particles in the mesoscopic scale dispersed in a continuous matrix of another material, which are commonly found in nature and every day life. Colloidal suspensions are important in different research areas for their broad number of applications ranging from material science to drug-delivery processes [1]. Although time and length-scale of colloids are completely different compared to the scales of atoms and molecules, some of their processes are very similar. This analogy between atoms and colloids has improved the comprehension of many interesting phenomenon like crystal nucleation and growth, glass transition, and interparticle interactions, with the advantage that colloids can be observed directly in real space [2–4]. Thus the knowledge of their thermodynamic and structural properties are undoubtedly necessary not only as a test of theoretical approaches but also for technological applications.

One of the main subjects in colloidal science is the control of the assembly of the particles to form ordered structures. In this context, the use of external fields (EF) to control colloidal assembly has become an important topic in the last decades [5,6]. EF may included electric and magnetic fields, temperature

gradients, gravity and even confining walls to manipulate the ordered structures. For example, under suitable conditions of temperature, concentration and ionic-strength, charged-stabilized colloidal particles exhibit spatial inhomogeneities by the presence of gravity, forming ordered structures at the bottom of the sample [7–11]. This phenomenon is explained as a competition between three main factors, namely interparticle interaction, entropy, and gravitational field. The sedimentation phenomenon has been studied extensively by experiments of regular shape colloidal particles having as a starting point the pioneering work of Jean Perrin [12]. Remarkable experiments in sedimentation of spherical particles with very low polydispersity were reported by Takano and Hachisu [13], by Pusey and co-workers [14,15], and by Piazza *et al.* [16], where a test of the hard-sphere (HS) equation of state (EOS) [17–19] was achieved using the equilibrium sedimentation profiles of charged-stabilized colloids, establishing formally the use of HS as a simple and suitable model to study structural properties of sterically-stabilized spherical colloidal particles. Similar results were reported by Biben *et al.* [20] and by Marechal and Dijkstra [11] using Monte Carlo simulation of HS in a gravitational field. An entropic

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lift can be observed for a charged mixture in a gravitational field [21] that can not be modelled by a one-fluid theory [22].

Anisotropy in shape, and polydispersity of colloidal particles lead to richer phase diagrams compared to spherical particles. For example, liquid-crystalline phases have been observed by experiments in both rod-like and disc-like sterically stabilized colloidal particles in the presence of a gravitational field [8,23–32] and by molecular simulation and theory [30,33,34]. The effect of electrostatic forces on the behaviour of charged colloidal particles in a gravitational field has also been reported [9,10].

Classical density functional theory (DFT) [35–37] provides a powerful framework to study the effect of external fields over colloidal particles. Using DFT the sedimentation equilibria of charged-stabilized colloidal particles, modelled as HS, charged hard spheres (CHS), and Yukawa hard spheres (YHS), has been reported by several groups [20,38–43]. These three different cases are often denoted as primitive models, in which the colloidal particles are suspended in a structureless dielectric solvent. Within this group, the Yukawa model has been extensively studied and used as a one-component model for charge-stabilized suspensions as in the very well known DLVO approximation (after Derjaguin, Landau, Verwey and Overbeek) [44]. In the DLVO theory the potential of mean force is consistent with the effective Coulomb-Screened Yukawa pair potential [45,46].

In order to study the behaviour of more complex systems, for example, polymers or arrangements of colloids in the form of cluster aggregates, one can take advantage of classical DFT together with the Statistical Association Fluid Theory (SAFT) [47,48]. SAFT is a physically-based method obtained from the perturbation theory of Wertheim for fluids with highly directional attractive forces [49–52]. SAFT provides powerful equations of state that have been successfully used to model thermodynamic properties of a broad number of systems like alkanes and perfluoroalkanes, electrolytes and ionic liquids, liquid crystals, colloids, and polymeric systems, among others [53–56]. Many versions of SAFT have been reported in the literature, however, the modelling of particles interacting via variable-range pair potentials, like the Yukawa potential, can be easily addressed using the SAFT-VR version by Jackson and co-workers [57,58].

In this work we present a DFT method in order to model a system of YHS particles in the presence of a gravitational field, based on the Mean Spherical Approximation (MSA) solution for this system [59–64]. The fluid model considered here uses the YHS potential as an effective interaction, since we are

not considering charged particles; the repulsive forces are only due to excluded volume effects arising from a hard-sphere potential, and there is not a repulsive interaction due to a real charge-charge repulsion. The Yukawa attractive term describes dispersion forces.

Two different applications of the MSA are studied, the first one using directly the high-temperature expressions derived by Henderson *et al.* [64], and the second one the SAFT-VR model coupled with the MSA theory [58] (DFT-MSA and DFT-SAFT-VR, respectively). The results obtained using DFT-MSA and DFT-SAFT-VR are compared with the density profiles obtained using Monte Carlo (MC) simulations in the NVT ensemble with periodic boundary conditions only in the x and y directions of a system of N -particles interacting via a Yukawa potential in the presence of a gravitational field. Furthermore, the theory allows one to generate a self-consistent model in which one can perform a MC simulation of a one-particle system in the presence of an effective field created by the other $N-1$ particles. This approach cannot reproduce the density profiles close to the wall at the bottom of the simulation box, because of the local character of the DFT approach followed here, but a good agreement is found far away from the wall itself.

2. Homogeneous fluid free energy and DFT

We consider a fluid that consists of N spherical particles of diameter σ . The interaction potential among a pair of particles separated by a distance r is given by a Yukawa potential,

$$u^Y(r) = \begin{cases} \infty, & r < \sigma, \\ -\epsilon \frac{\exp[-\lambda(r-\sigma)]}{r/\sigma}, & r \geq \sigma, \end{cases} \quad (1)$$

where ϵ is the strength of the interaction energy and λ^{-1} is the parameter that characterizes the range of the attractive part of this potential. The N -particles system is under the influence of a homogeneous gravitational field described by

$$u^g(z) = \begin{cases} mgz, & \sigma/2 \leq z \leq Lz - \sigma/2, \\ \infty, & \text{otherwise,} \end{cases} \quad (2)$$

where z is the vertical coordinate of a particle with buoyant mass m , and g is the gravitational acceleration. In order to describe the thermodynamic and structural properties of this system, we define reduced variables for temperature, density and the strength of the gravitational field as $T^* = kT/\epsilon$, $\rho^* = N\sigma^3/V$, and $g^* = mg\sigma/\epsilon$, respectively.

The presence of the external field disrupts the homogeneity of the state of equilibrium, i.e. the equilibrium state for this system is a non-homogeneous one. We shall use the Local Density Approximation (LDA) [35] to get the input profile, $\rho_0(\mathbf{r})$, from which the $c_1(\mathbf{r}, \rho_0(\mathbf{r}))$ effective potential is obtained.

In the density functional theory, the Grand Potential $\Omega[\rho(\mathbf{r})]$ is chosen as the appropriate thermodynamic potential, and is related to the Helmholtz free-energy functional $A[\rho(\mathbf{r})]$ through a Legendre transformation,

$$\Omega[\rho(\mathbf{r})] = A[\rho(\mathbf{r})] + \int d\mathbf{r} \rho(\mathbf{r}) [\phi_{\text{ext}}(\mathbf{r}) - \mu], \quad (3)$$

where $\rho(\mathbf{r})$ is the density distribution, μ is a fixed chemical potential and $\phi_{\text{ext}}(\mathbf{r})$ is an external potential.

The Helmholtz free-energy functional $A[\rho(\mathbf{r})]$ can be divided into two independent parts, an ideal gas contribution $A_{\text{id}}[\rho(\mathbf{r})]$ and an excess part $A_{\text{ex}}[\rho(\mathbf{r})]$,

$$A[\rho(\mathbf{r})] = A_{\text{id}}[\rho(\mathbf{r})] + A_{\text{ex}}[\rho(\mathbf{r})]. \quad (4)$$

The ideal part is known exactly as

$$A_{\text{id}}[\rho(\mathbf{r})] = kT \int d\mathbf{r} \rho(\mathbf{r}) [\ln(\rho(\mathbf{r})\Lambda^3) - 1], \quad (5)$$

with $\Lambda = h/2\pi mkT$ being the thermal de Broglie wavelength. Although there is not an exact expression for the excess part, it is related to the n -order direct correlation functions by

$$c_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; [\rho]) = -\beta \frac{\delta^n A_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \dots \delta \rho(\mathbf{r}_n)}, \quad (6)$$

where $\beta = 1/kT$.

The equilibrium density profile of a uniform system is obtained from the variational principle

$$\frac{\delta \Omega[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = 0, \quad (7)$$

which gives the equilibrium density

$$\rho(\mathbf{r})\Lambda^3 = \exp\left(\beta\mu - \beta\phi_{\text{ext}}(\mathbf{r}) - \beta \frac{\delta A_{\text{ex}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}\right). \quad (8)$$

Using the decomposition $\mu = \mu_{\text{ex}} + kT \ln(\rho_{\text{B}}\Lambda^3)$, with μ_{ex} the excess chemical potential of the bulk fluid and ρ_{B} the density of the bulk fluid (i.e. $\rho(\mathbf{r}) \rightarrow \rho_{\text{B}}$ when $\phi_{\text{ext}} \rightarrow 0$), the density distribution could be rewritten as

$$\rho(\mathbf{r}) = \rho_{\text{B}} \exp(\beta\mu_{\text{ex}} - \beta\phi_{\text{ext}}(\mathbf{r}) + c_1(\mathbf{r})), \quad (9)$$

where

$$c_1(\mathbf{r}) = -\beta \frac{\delta A_{\text{ex}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}, \quad (10)$$

and the external field is given by the gravitational potential $\phi_{\text{ext}}(z) = mgz = (\epsilon/\sigma)g^*z$.

Within LDA we need an excess free energy, $a_{\text{ex}}(\rho)$, obtained from an homogeneous fluid theory. Using $a_{\text{ex}}(\rho)$, the excess free energy functional is given by

$$\beta A_{\text{ex}}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) a_{\text{ex}}(\rho(\mathbf{r})). \quad (11)$$

The excess free energy can be obtained from the high-temperature MSA expansion [64]

$$a_{\text{ex}}^{\text{MSA}}(\rho) = \frac{A}{NkT} = \frac{A_{\text{HS}}}{NkT} + \frac{1}{2} \sum_n \frac{x^n}{n} v_n, \quad (12)$$

where $x = \epsilon/kT$, A_{HS} is the free energy of a hard sphere fluid, and the terms v_n are known to any order as functions of the packing fraction ($\eta = \pi\rho\sigma^3/6$) and the range λ . The first terms v_1 and v_2 are given by [64]

$$v_1 = \frac{2\lambda L(\lambda)}{\exp(-\lambda)L(\lambda) + S(\lambda)}, \quad (13)$$

$$v_2 = -\frac{2w(\alpha_1 - 1 - \alpha_0\psi)}{z\Phi_0}, \quad (14)$$

where

$$L(\lambda) = 12\eta \left[\left(1 + \frac{\eta}{2}\right)\lambda + 1 + 2\eta \right], \quad (15)$$

$$S(\lambda) = (1 - \eta)^2\lambda^3 + 6\eta(1 - \eta)\lambda^2 + 18\eta^2\lambda - 12\eta(1 + 2\eta), \quad (16)$$

$$\Phi_0 = \frac{\exp(-\lambda)L(\lambda) + S(\lambda)}{\lambda^3(1 - \eta)^2}, \quad (17)$$

$$\psi = \lambda^2(1 - \eta)^2 \frac{1 - \exp(-\lambda)}{\exp(-\lambda)L(\lambda) + S(\lambda)} - 12\eta \frac{1 - \lambda/2 - (1 + \lambda/2)\exp(-\lambda)}{\exp(-\lambda)L(\lambda) + S(\lambda)}, \quad (18)$$

$$\alpha_0 = \frac{L(\lambda)}{\lambda^2(1 - \eta)^2}, \quad (19)$$

$$\alpha_1 = \frac{12\eta(1 + \lambda/2)}{\lambda^2(1 - \eta)}. \quad (20)$$

The MSA approximation also can be used within the SAFT-VR approach, in order to model associating chain molecules. The general form of the SAFT free energy for associating chain molecules is given by different contribution terms that depend on the properties of a monomeric fluid [47,48,58]. In the SAFT-VR approach, hard-core monomers interact

via an arbitrary potential of variable range, and in our case we shall only need the monomer contribution to the free energy $a_{\text{ex}}^{\text{SAFT}}$

$$a_{\text{ex}}^{\text{SAFT}}(\rho) = a_{\text{HS}} + \beta a_1 + \beta^2 a_2 + \dots \quad (21)$$

The first-order perturbation term is given by

$$a_1 = -12\eta\epsilon(\lambda^{-1} + \lambda^{-2})g^{\text{HS}}(1; \eta_{\text{eff}}), \quad (22)$$

where $g^{\text{HS}}(1; \eta_{\text{eff}})$ is the contact value of the HS radial distribution function for an effective packing fraction η_{eff} given by

$$\eta_{\text{eff}} = b_1(\lambda)\eta + b_2(\lambda)\eta^2. \quad (23)$$

The b_1 and b_2 coefficients can be obtained as analytical functions of the range parameter λ using the MSA approximation. By expanding both the MSA and SAFT-VR expressions for a_1 in powers of η , we obtain virial coefficients as predicted by both theories. Equating these two expansions, using only the first three virial coefficients, a prediction for these coefficients is obtained [58]

$$b_1 = \frac{\left\{ \begin{array}{l} 24 + 24\lambda - 12\lambda^2 - 4\lambda^3 + 5\lambda^4 \\ -24\exp(-\lambda)(1 + 2\lambda + \lambda^2) \end{array} \right\}}{5\lambda^3(1 + \lambda)}, \quad (24)$$

$$b_2 = \frac{\Delta_0 + \exp(-\lambda)\Delta_1 + \exp(-2\lambda)\Delta_2}{125\lambda^6(1 + \lambda)^2}, \quad (25)$$

where

$$\Delta_0 = -25\lambda^8 - 140\lambda^7 - 364\lambda^6 + 1176\lambda^5 + 672\lambda^4 - 2688\lambda^3 + 4032\lambda + 2016, \quad (26)$$

$$\Delta_1 = -840\lambda^6 - 1008\lambda^5 + 2520\lambda^4 + 672\lambda^3 - 10080\lambda^2 - 12096\lambda - 4032, \quad (27)$$

$$\Delta_2 = 2016\lambda^4 + 8064\lambda^3 + 12096\lambda^2 + 8064\lambda + 2016. \quad (28)$$

The a_2 contribution is given by the local compressibility approximation (LCA)

$$a_2 = \frac{1}{2}K^{\text{HS}}\eta\frac{\partial a_1^*}{\partial \eta}, \quad (29)$$

where a_1^* is determined by [57]

$$a_1^* = -6\eta\lambda^{-1}g^{\text{HS}}(1; \eta^*), \quad (30)$$

with the parameterization

$$\eta^* = d_1(\lambda)\eta + d_2(\lambda)\eta^2. \quad (31)$$

Coefficients d_1 and d_2 are given by

$$\begin{pmatrix} d_1 \\ d_2 \end{pmatrix} = \begin{pmatrix} 0.989601 & -0.872203 & 0.320808 & 0.0 & 0.0 \\ -0.0119152 & -1.24029 & 2.41636 & -2.01922 & 0.647565 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda^{-1} \\ \lambda^{-2} \\ \lambda^{-3} \\ \lambda^{-4} \end{pmatrix}. \quad (32)$$

3. Self-consistent DFT/MC method

A hybrid self-consistent method using Density Functional Theory (DFT) and Monte Carlo (MC) simulations can be applied to study the Yukawa fluid in the presence of an external gravitational field. The properties of a N -particle system are obtained performing a one-particle MC simulation in the presence of an $N-1$ particle effective field, which is calculated by the DFT-LDA method explained in the previous section.

According to the Potential Distribution Theorem for inhomogeneous systems [65,66], the one-body direct correlation function $c_1(\mathbf{r})$ can be expressed in terms of the $N-1$ ensemble average of the total binary interactions of these $N-1$ particles with an extra N th particle, $U(\mathbf{r})$, in the presence of an external field $\phi_{\text{ext}}(\mathbf{r})$:

$$\exp[c_1(\mathbf{r})] = \langle \exp[-\beta U(\mathbf{r})] \rangle_{N-1, \phi_{\text{ext}}}, \quad (33)$$

where

$$U(\mathbf{r}) = \sum_{j=1}^{N-1} u(j, N), \quad (34)$$

and $u(j, N)$ is the pair interaction between particle N and particle j , this last one belonging to the system of $N-1$ particles taken to perform the statistical average in Equation (33). These results allow us to consider the original N particle system as a one-particle interacting with the external field c_1 produced by the $N-1$ remanent particles. Using Equations (10) and (11), this field c_1 is given by the excess chemical potential for the inhomogeneous fluid,

$$c_1(\mathbf{r}) = -\beta\mu_{\text{ex}}[\rho(\mathbf{r})], \quad (35)$$

where μ_{ex} is obtained from the SAFT-VR or MSA expressions for a bulk fluid [58], as explained in the previous section, but evaluated with the density profile for the inhomogeneous fluid, $\rho(\mathbf{r})$. Solving Equation (9) using Equation (35), the density profile $\rho(\mathbf{r})$ can be determined.

In this way, a standard MC simulation for a N -particle system can be carried out using a *single* particle interacting with an effective field $c_1(\mathbf{r})$. In Figure 1 we present a scheme for this type of simulation. Selecting a thermodynamic state (ρ, T^*) for a specified value of the external-field intensity g^* , and starting with an arbitrary initial density-profile $\rho_0(\mathbf{r})$, the effective field $c_1(\mathbf{r})$ is obtained from Equations (6) and (11). One-particle MC simulation is performed in the presence of this field, and once an equilibrated configuration is obtained, the corresponding density profile $\rho(\mathbf{r})$ is calculated. The initial and new profiles are compared within a previously selected tolerance δ . If $|\rho_0(\mathbf{r}) - \rho(\mathbf{r})| < \delta$ then the simulation ends, otherwise the process is repeated obtaining by DFT the new c_1 for the next simulation.

4. Results

The density profiles were obtained using DFT, the hybrid DFT/MC method and standard N -particles MC simulations. Two values of the hard-core Yukawa fluid were selected, $\lambda = 1.8$ and $\lambda = 4.0$. Two isotherms

Figure 1. Flux diagram of the DFT/MC hybrid method implemented in this work. Starting with an initial density profile $\rho_0(\mathbf{r})$, an effective $N-1$ external field $c_1^{(0)}(\mathbf{r}, \rho_0(\mathbf{r}))$ is obtained from a DFT-SAFT-VR approach in the local density approximation. A MC simulation for a single particle interacting with $c_1^{(0)}$ is performed, in order to obtain a new density profile $\rho_{\text{sim}}(\mathbf{r})$ and a new effective field c_1 . The process is repeated until a convergent result is obtained for the simulated density profile with respect to its value in the previous cycle, using an established tolerance δ .

were considered, $T^* = 1.0$ and $T^* = 2.0$, at the same densities $\rho_B^* = 0.1$, $\rho_B^* = 0.5$ and $\rho_B^* = 0.7$. A typical hybrid DFT/MC self-consistent calculation requires of the order of 1×10^8 iterations in order to get a precision of 1×10^{-3} . The complete calculation is performed in 40 s in a Mac Pro with Quad-Core Intel Xeon processors, that runs at 3 GHz. In comparison, a typical N -particles MC calculation requires four days in order to perform 1×10^5 cycles for equilibration and another 1×10^6 cycles for averaging, using 3000 particles in the NVT ensemble, with a box-length in the z -direction (i.e. the gravitational field direction) $L_z^* = L_z/\sigma = 30$, and a potential cut-off radius equal to $0.5L_x$, where L_x denotes the box-length in the x -direction. With respect to the DFT calculations, the local density approximation was applied using the two approaches for the homogeneous free energy that we have described in Section 2, i.e. the MSA and SAFT-VR methods, Equations (12–20) and Equations (21–32), respectively.

A typical N -particles MC density profile is shown in Figure 2, obtained for the system $\lambda = 1.8$ at temperature $T^* = 1.0$ and density $\rho_B^* = 0.5$. The fluid presents a highly-ordered behaviour (see Figure 4(b) below). Due to the wall, strong oscillations are present in the density profile, that can not be reproduced by DFT due to the local density approximation. However, far enough from the wall, once oscillations are not present, the profile decay can be described by the DFT and DFT/MC approaches, as shown in Figures 3, 5 and 7. In Figure 3, the density profile is reported for the system with $\lambda = 1.8$, temperature $T^* = 1$ and

Figure 2. Density profile as a function of the altitude, for a monomeric Yukawa fluid ($\lambda = 1.8$) in the presence of a gravitational field ($g^* = mg\sigma/\epsilon = 1.0$), obtained from a N -particles MC simulation. The corresponding thermodynamic state is given by $T^* = kT/\epsilon = 1.0$ and bulk density $\rho_B^* = \rho\sigma^3 = 0.5$.

Figure 3. Density profiles as a function of the altitude for a monomeric Yukawa fluid ($\lambda = 1.8$) in the presence of a gravitational field ($g^* = mg\sigma/\epsilon = 1.0$), for the thermodynamic states $T^* = 1.0$, $\rho_B^* = 0.1, 0.5, 0.7$, denoted by (a), (b) and (c), respectively. Results correspond to the DFT-SAFT-VR and DFT-MSA predictions, using the LDA approximation (continuous and dashed lines, respectively), compared with N -particles MC and hybrid DFT/MC simulations (circles and squares, respectively).

Figure 4. Snapshots of configurations from MC simulations corresponding to the states reported in Figure 3.

densities $\rho_B^* = 0.1$ (Figure 3(a)), $\rho_B^* = 0.5$ (Figure 3(b)) and $\rho_B^* = 0.7$ (Figure 3(c)). The corresponding snapshots are depicted in Figures 4(a)–(c). Whereas in Figure 3(a) the DFT and DFT/MC methods give very similar results and overestimate the property with

respect to the MC results, however in Figures 3(b) and (c) we can see that for higher densities, the DFT/MC results are superior to DFT. When the temperature is increased up to $T^* = 2.0$, the differences between MC, DFT and DFT/MC are smaller. This behaviour can be

Figure 5. Density profiles as a function of the altitude for a monomeric Yukawa fluid ($\lambda = 1.8$) in the presence of a gravitational field ($g^* = mg\sigma/\epsilon = 1.0$), for the thermodynamic states $T^* = 2.0$, $\rho_B^* = 0.1, 0.5, 0.7$, denoted by (a), (b) and (c), respectively. Results correspond to the DFT-SAFT-VR and DFT-MSA predictions, using the LDA approximation (continuous and dashed lines, respectively), compared with N -particles MC and hybrid DFT/MC simulations (circles and squares, respectively).

Figure 6. Snapshots of configurations from MC simulations corresponding to the states reported in Figure 5.

observed in Figure 5, where the three approaches, for the different values of density, are in good agreement. The corresponding snapshots are given in Figure 6.

The effect of shortening the range is shown in Figures 7 (density profiles) and 8 (corresponding

snapshots), where $\lambda = 4.0$, using the same density values and for temperature $T^* = 2$, which is supercritical, as in the case of the system with range $\lambda = 1.8$. As in the previous case, the differences between methods are small.

Figure 7. Density profiles as a function of the altitude for a monomeric Yukawa fluid ($\lambda=4$) in the presence of a gravitational field ($g^*=mg\sigma/\epsilon=1.0$), for the thermodynamic states $T^*=2.0$, $\rho_B^*=0.1, 0.5, 0.7$, denoted by (a), (b) and (c), respectively. Results correspond to the DFT-SAFT-VR and DFT-MSA predictions, using the LDA approximation (continuous and dashed lines, respectively), compared with N -particles MC and hybrid DFT/MC simulations (circles and squares, respectively).

Figure 8. Snapshots of configurations from MC simulations corresponding to the states reported in Figure 7.

For the three cases it is clear that the DFT/MC approach describes with the same accuracy the density profiles compared with standard MC simulations, with the advantage that the former is a faster methodology. There are no cases where the DFT method alone is significantly better than the

DFT/MC approach, however the reverse case is not true (see Figure 3(b), for example). From the snapshots given, it is also clear that the phases reported in Figures 6 and 8 are typically liquid-like, and the phases from Figure 4 are highly ordered.

5. Conclusions

In this article we have used a self-consistent combined DFT/MC method to study, by a single-particles MC simulation, the density profiles of a hard-core monocomponent Yukawa fluid under the action of a gravitational field. The obtained results compare accurately with respect to standard N -particles MC simulation predictions for the same system. This DFT method is applied within a local approximation, since the gravitational field has a slow variation on the space, and far away from the wall, i.e. once the density oscillations due to the wall (a strong varying field) are not any longer present. The approach can be extended to non-local DFT theories and also can be applied to the simulation of interfacial properties, where a DFT SAFT-VR theory has proved to be very reliable [67,68].

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