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Density Profile of a Hard Disk Liquid System under Gravity *

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The free energy and the density profile of a hard disk liquid system under gravity are calculated by using the dimensional crossover of Rosenfeld hard sphere (3D) functional as well as the functional constructed from the scaled-particle theory which is considered to be very accurate. The two methods give the consistent results for a wide range of packing fractions.

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The density profile of colloid suspensions under gravity is a subject of scientific interest and practical importance. First, there are interesting phenomena of layering, phase transitions, or phase separations related with gravity. Secondly, the study of estuarine sedimentation is very important for environmental improvement. In addition, the equilibrium density distribution of colloid particles under gravity is a competitive result of three main factors, i.e. the direct potential interaction, the entropy, and the gravitation field. Thus it is interesting to see how these competing factors together influence the sedimentation equilibrium of the suspension in confined geometry under gravity.

In recent decades, several groups have made calculations on various aspects of the hard sphere liquid under gravity. For instance, Vrij[1] studied the inhomogeneous density distributions of hard sphere fluids under gravity by using density functional theory (DFT) and the Monte Carlo simulation method. The density profile was also studied by Chen and Ma.[2] Biben *et al.*[3] observed the sudden crystallization on the bottom layer of the simulation box when the gravitational field was strong enough. Jamnik[4] calculated the density distribution of adhesive hard sphere colloids in a planar pore under gravity by means of the Ornstein–Zernike integral equation. Moreover, local density approximation of DFT has been tested in the description of dense colloid suspensions under gravity.[5]

In the theory of inhomogeneous fluids, density functional theory[6,7] is the approach which has been extensively developed and used. DFT has been widely used in recent years for its ability to treat many-electron quantum systems[8,9] as well as many-particle classical systems[7,10] in the same basic framework, but also due to its tremendous computational simplicity and versatility. In this Letter we calculate the density profile for hard disc colloids under gravity by using Rosenfeld DFT after dimensional crossover and functional obtained from the scaled-particle theory.

For an inhomogeneous fluid in an external potential $V_{\rm ext}(\boldsymbol{r})$, the grand potential $\Omega[\rho]$ and the intrinsic Helmholtz free energy $F[\rho]$ are both unique functionals of the density distribution $\rho(\boldsymbol{r})$, and are related as[11]

$$\Omega[\rho]=F[\rho]+\int d\boldsymbol{r}\rho(\boldsymbol{r})(V_{\rm ext}(\boldsymbol{r})-\mu), \tag{1}$$

where μ is the chemical potential of the system. The intrinsic Helmholtz free energy $F[\rho]$ consists of a non-interacting ideal free energy F_{id} and the excess free energy F_{ex} arising due to interparticle interactions

$$F[\rho]=F_{id}[\rho]+F_{ex}[\rho], \tag{2}$$

where $F_{id}[\rho]$ is the contribution of ideal gas which can be evaluated exactly by[12]

$$F_{id}[\rho]=k_BT\int d\boldsymbol{r}\rho(\boldsymbol{r})[\ln(\lambda_0^3\rho(\boldsymbol{r}))-1], \tag{3}$$

where $\lambda_0=\hbar\sqrt{\frac{2\pi}{mk_BT}}$ is the thermal de Broglie wavelength, with k_B as the Boltzmann constant and T the temperature. Rosenfeld proposed that in an inhomogeneous hard sphere fluid system the excess part F_{ex} which comes from the interaction is given by[13]

$$F_{ex}[\rho]=k_BT\int d\boldsymbol{r}\Phi[n_\alpha(\boldsymbol{r})]. \tag{4}$$

We consider the excess free energy density

$$\Phi[n_\alpha(\boldsymbol{r})]=\Phi_1+\Phi_2+\Phi_3,\ \Phi_1=-n_0\ln(1-n_3),$$
$$\Phi_2=\frac{n_1n_2-\boldsymbol{n}_1\cdot\boldsymbol{n}_2}{1-n_3},\ \Phi_3=\frac{\frac{1}{3}n_2^3-n_2(\boldsymbol{n}_2\cdot\boldsymbol{n}_2)}{8\pi(1-n_3)^2}. \tag{5}$$

and

$$n_\alpha(\boldsymbol{r})=\int d\boldsymbol{r}'\rho(\boldsymbol{r}')\omega^{(\alpha)}(\boldsymbol{r}-\boldsymbol{r}'),\quad \alpha=0,1,2,3$$
$$\boldsymbol{n}_\alpha(\boldsymbol{r})=\int d\boldsymbol{r}'\rho(\boldsymbol{r}')\boldsymbol{\omega}^{(\alpha)}(\boldsymbol{r}-\boldsymbol{r}'),\quad \alpha=1,2. \tag{6}$$

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The weight functions $\omega^{(\alpha)}(\boldsymbol{r})$ are characteristic functions for the geometry of particle.

$$\omega^{(3)}(\boldsymbol{r}) = \Theta(|\boldsymbol{r}| - R), \quad \omega^{(2)}(\boldsymbol{r}) = \delta(|\boldsymbol{r}| - R),$$
$$\omega^{(1)}(\boldsymbol{r}) = \frac{\omega^{(2)}(\boldsymbol{r})}{4\pi R}, \quad \omega^{(0)}(\boldsymbol{r}) = \frac{\omega^{(2)}(\boldsymbol{r})}{4\pi R^2},$$
$$\boldsymbol{\omega}^{(2)}(\boldsymbol{r}) = \frac{\boldsymbol{r}}{|\boldsymbol{r}|}\delta(|\boldsymbol{r}| - R), \quad \boldsymbol{\omega}^{(1)}(\boldsymbol{r}) = \frac{\boldsymbol{\omega}^{(2)}(\boldsymbol{r})}{4\pi R}. \tag{7}$$

Then the exact functional relation can be applied and the theory can be used both in a variation procedure or through the exact minimum principle for the equilibrium density,[12] given by the Euler-Lagrange equation

$$\frac{\delta F[\rho]}{\delta \rho(\boldsymbol{r})} + V_{\rm ext}(\boldsymbol{r}) = \mu. \tag{8}$$

The model system we shall investigate here is colloid suspensions of hard disk particles confined between two parallel hard walls with a distance L apart with the external field perpendicular to the walls, where the wall at $z = 0$ is regarded as the bottom of the slit. A schematic representation is given in Fig. 1. Since the disk-like particles follow a relatively common molecular model, such as benzene-hexa-n-alkanoates,[14] CeF_3 [15] and the soluble hexabenzocoronene[16] and so on, therefore the study of them is of practical importance. In addition, the freezing of two-dimensional hard disks[17] and the density distribution of a fluid through a microporous solid[18] were also discussed. Meanwhile, the radial distribution functions of hard disk mixtures as well as the density distributions near the large hard disk and within the hard circular cavity had been studied.[6] However, to our knowledge, as many theoretical studies have been devoted to the understanding of the behavior of elongated hard colloid particles confined in a geometry, suspensions of disc-shaped hard particles confined in a geometry under gravity have not yet been investigated. In the case of extreme confinement, the hard disks are adsorbed on the two-dimensional plane of $y - z$, thus the dimensionality can be reduced to two ($D = 2$). Next, we apply the dimension crossover technique, following Ref. [19], we have

$$\Phi[\{n_\alpha\}; \lambda] = \Phi_1 + \Phi_2 + \lambda\Phi_3, \tag{9}$$

where λ is the variational parameter. The density

$$\rho(\boldsymbol{r}) = \rho(z), \tag{10}$$

the excess free energy density functional takes the form

$$\frac{F_{ex}[\rho(\boldsymbol{r}); \lambda]}{A} = k_B T \int dz \Phi[n_\alpha(z); \lambda], \tag{11}$$

where the weighted densities $n_\alpha(\boldsymbol{r}) = n_\alpha(z)$ are given by[20−22]

$$n_3(z) = \pi \int_{z-R}^{z+R} \rho(z')[R^2 - (z' - z)^2]dz',$$
$$n_2(z) = 2\pi R \int_{z-R}^{z+R} \rho(z')dz',$$
$$\boldsymbol{n}_2(z) = -2\pi \int_{z-R}^{z+R} \rho(z')(z' - z)dz'\hat{\boldsymbol{z}}$$
$$n_0(z) = \frac{n_2(z)}{4\pi R^2}, \quad n_1(z) = \frac{n_2(z)}{4\pi R},$$
$$\boldsymbol{n}_1(z) = \frac{\boldsymbol{n}_2(z)}{4\pi R}. \tag{12}$$

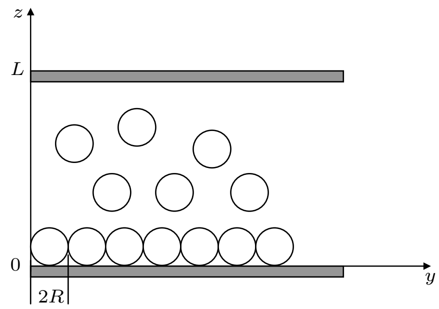

Fig. 1. A schematic diagram of the model system. The normal of thin platelets of radius R is perpendicular to the plane of $y - z$.

In the $2D$ limit,

$$\rho(z) = \rho^{(2D)}\delta(z), \tag{13}$$

where $\rho^{(2D)} = N/A$ is the number of spheres divided by the area of the slab, i.e. the $2D$ density, these weighted densities take the form

$$n_3(z) = \pi\rho^{(2D)}(R^2 - z^2)\Theta(|z| - R),$$
$$n_2(z) = 2\pi\rho^{(2D)}R\Theta(|z| - R),$$
$$\boldsymbol{n}_2(z) = 2\pi\rho^{(2D)}z\Theta(|z| - R)\hat{\boldsymbol{z}}. \tag{14}$$

The $2D$ packing fraction is defined by $\eta = \rho^{(2D)}\pi R^2$. Measuring length in units R, and letting $R = 1$, then the weighted densities are given by

$$n_3(z) = \eta(1 - z^2)\Theta(|z| - 1),$$
$$n_2(z) = 2\eta\Theta(|z| - 1), \quad n_1(z) = \frac{\eta}{2\pi}\Theta(|z| - 1),$$
$$n_0(z) = \frac{\eta}{2\pi}\Theta(|z| - 1), \quad \boldsymbol{n}_2(z) = 2\eta z\Theta(|z| - 1)\hat{\boldsymbol{z}},$$
$$\boldsymbol{n}_1(z) = \frac{\eta}{2\pi}z\Theta(1 - |z|)\hat{\boldsymbol{z}}. \tag{15}$$

The excess free energy per particle can be obtained analytically:

$$f_{ex}^{(2D)}(\lambda, \eta) = \frac{F_{ex}[\rho(\boldsymbol{r})]}{Nk_BT} = \int_{-1}^{1} dz\Phi(z)/\rho^{(2D)}$$
$$= \lambda\eta + \frac{\lambda\eta^2}{3(1 - \eta)} + \left(2 - \lambda + \frac{\lambda\eta}{3(1 - \eta)}\right)$$
$$\times \sqrt{\frac{\eta}{1 - \eta}} \arctan\left(\sqrt{\frac{\eta}{1 - \eta}}\right), \tag{16}$$

and this result is compared with that of the scaled-particle theory (SPT) functional

$$f_{ex}^{(2D)}(\eta) = \eta/(1-\eta) - \ln(1-\eta), \tag{17}$$

which is constructed from the equation of state:[23]

$$P = k_B T\rho/(1-\eta)^2. \tag{18}$$

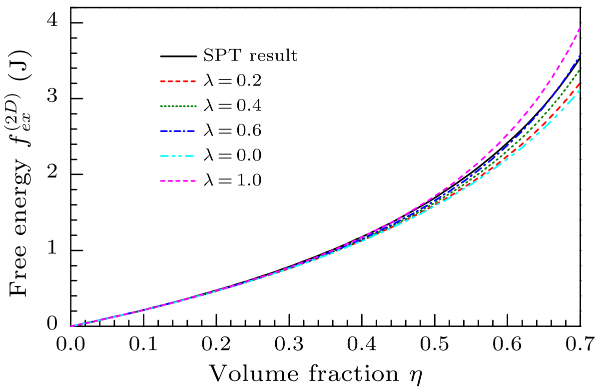

Fig. 2. Excess free energy per particle for hard discs obtained from Eqs. (16) and (17), as a function of the packing fraction η. The lines from top to bottom correspond to $\lambda = 1.0$, 0.6, 0.4, 0.2,0 in Eq. (16). The solid line corresponds to the result of scaled particle theory (Eq. (17)), which is highly accurate.

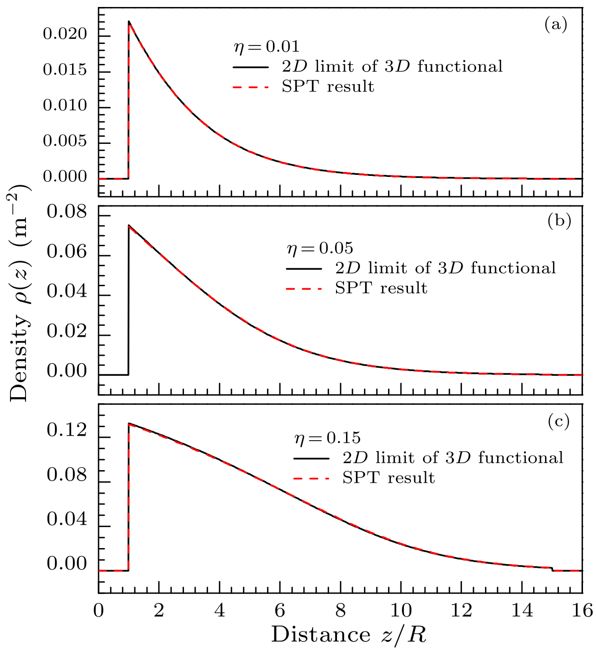

Fig. 3. The density distributions of hard disk liquid under gravity with the gravity length $L_G = \frac{k_BT}{mg} = \sigma$ and the system size is $L = 8\sigma$. From (a) to (c) the packing fractions are $\eta = 0.01, 0.05, 0.15$, respectively.

In Fig. 2, we present the comparative diagrams of excess free energy for several values of λ, from which it is readily seen that the two results are in good agreement when $\lambda = 0.6$. We next apply the functionals to the situation that the system is under gravity and calculate the density distributions of hard disk liquid by means of Rosenfeld functional. The results then are compared with that from the accurate $2D$ SPT density functional.

For a $2D$ liquid system under gravity, the grand potential is given by

$$\begin{aligned}\frac{L\beta\Omega^{\rm disk}[\rho]}{A'} &= \int_R^{L-R} dz\rho(z)[\ln\rho(z)-1] \\ &+ \int_R^{L-R} dz\rho(z)(\beta mgz - \mu^{\rm eff}) \\ &+ \int_R^{L-R} dz\rho(z)\Big[\lambda\eta + \frac{\lambda\eta^2}{3(1-\eta)} \\ &+ \Big(2-\lambda+\frac{\lambda\eta}{3(1-\eta)}\Big) \\ &\times\sqrt{\frac{\eta}{1-\eta}}\arctan\Big(\sqrt{\frac{\eta}{1-\eta}}\Big)\Big],\end{aligned} \tag{19}$$

where $\beta = \frac{1}{k_BT}$, and $\mu^{\rm eff} = \beta\mu - \ln\lambda_0^2$ is an effective chemical potential. In real systems, we usually specify the average density ρ_0 instead of the chemical potential, hence $\mu^{\rm eff}$ can be determined by the relation

$$\int_R^{L-R} dz\rho(z) = L\rho_0. \tag{20}$$

Consequently, the variation of grand potential with respect to ρ can also be obtained by taking $\lambda = 0.6$:

$$\begin{aligned}&\frac{L\beta}{A'}\frac{\delta\Omega^{\rm disk}[\rho]}{\delta\rho} = \ln\rho(z) + \beta mgz - \mu^{\rm eff} + 1.2\pi\rho(z) \\ &+ \frac{0.2\pi^2\rho(z)^2 + 0.7\pi\rho(z)}{1-\pi\rho(z)} + \frac{0.5\pi^2\rho(z)^2 - 0.2\pi^3\rho(z)^3}{[1-\pi\rho(z)]^2} \\ &+ \Big\{\Big[1.4 + \frac{0.2\pi\rho(z)}{1-\pi\rho(z)} + \frac{0.2\pi\rho(z)}{[1-\pi\rho(z)]^2}\Big]\sqrt{\frac{\pi\rho(z)}{1-\pi\rho(z)}} \\ &+ \Big[\frac{0.7\pi\rho(z)}{[1-\pi\rho(z)]^2} + \frac{0.1\pi^2\rho(z)^2}{[1-\pi\rho(z)]^3}\Big]\sqrt{\frac{1-\pi\rho(z)}{\pi\rho(z)}}\Big\} \\ &\times\arctan\sqrt{\frac{\pi\rho(z)}{1-\pi\rho(z)}}.\end{aligned} \tag{21}$$

The equilibrium density profile is obtained by the fact that the functional derivative $\delta\Omega/\delta\rho = 0$. Thus according to Eq. (21) we can obtain the numerical solution of the density profile. We represent the density distributions of hard disc liquid for different values of packing fraction η in Figs. 3 and 4. From the figures, we observe that explicitly, when the particles are very close to the bottom wall the density reaches its maximum, and it decreases gradually as the particles become further and further from the bottom wall because of the influence of gravitational field, which is expected. In addition, it is noted that the whole density distribution extends much further than the gravitation length. This clearly indicates that the interparticle interaction plays a role opposite to the gravity and tends to homogenize the density distribution.

Therefore we have to take account of the potential interaction when studying the real suspensions.

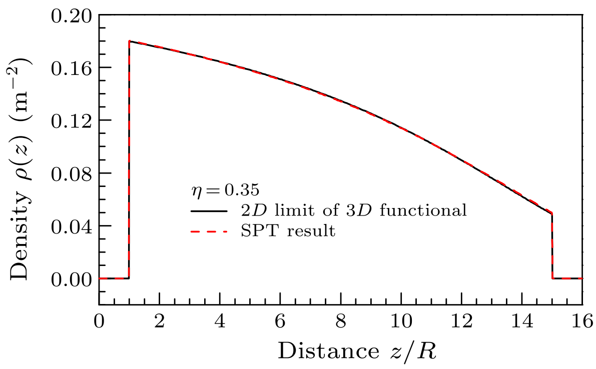

Fig. 4. The density profile of hard disk liquid system under gravity with the same gravity length as Fig. 3. The packing fraction $\eta = 0.35$ and $L = 8\sigma$.

Furthermore, for a given system size and gravity length the density decreases to zero quickly when the packing fraction η is relatively low. However, as η increases the rate of the density tending to zero becomes smaller as is shown in Figs. 3 and 4. From Fig. 4, we can explicitly see that the density near the upper slit wall is much larger than zero when the width of slit maintains at $L = 8\sigma$.

In summary, the density profiles of hard disk liquid under gravity have been calculated by using the dimensional crossover of Rosenfeld functional and then compared with those functional obtained from the SPT. It is found that the two results are in good agreement. Our results are to be compared with computer simulation data and experiment in the future.

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