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Equilibrium Properties of Hard Sphere Fluid in Confined Geometries: a Density Functional Theory Study *

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One component hard-sphere fluid confined in two planar hard walls is studied by means of density functional theory with Rosenfeld functional and molecular dynamics simulation. The validity of the Rosenfeld functional is examined. Chemical potential, grand potential and free energy as functions of the wall separation are obtained.

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Hard sphere (HS) fluids represent the simplest and yet non-trivial model in describing structure and properties of colloidal suspensions. In the past decades, there are extensive theoretical studies on these systems by means of computer simulations, integral equation theory, density functional theory (DFT) and other methods. These studies have significantly improved our understanding of the structure and equilibrium behaviour of HS fluids,[1−3] especially in the case of confined geometries.[5−7]

Density functional theory was first proposed for the ground state of quantum many particle systems,[8] and it was soon extended to systems at finite temperature.[9] It is now one of the most powerful tools in the theories of liquid physics. In the case of HS fluid, there are many different schemes of DFT available in the literature,[4,13,14] most of them can give accurate predictions of the properties of non-uniform HS fluids. Rosenfeld functional based on weighted density approximation[10] is among a few of the most successful ones. This functional gives exact analytic results in some limiting cases and gives fairly good results in most cases. It is also quite general, valid both for one component and multi-component HS systems.[11,12] It has also been extended successfully to inhomogeneous charge-stabilized colloidal suspensions.[15] In the case of HS fluid confined in walls, comparisons with molecular dynamics simulations show that DFT with Rosenfeld functional can give a good quantitative description of the equilibrium properties of the system.[16]

Studies of fluids in confined geometry are important and interesting, systems in confined geometry usually show different behaviour from the bulk. In this Letter, we present the DFT studies of one component HS fluid confined in two planer hard walls using the Rosenfeld functional. We shall calculate the chemical potential and thermodynamic potentials of the system.

The Rosenfeld functional for the excess (over the ideal gas) free energy of HS fluid is[10]

$$\beta\mathcal{F}_{\rm ex}[\{n_\alpha\}] = \int {\rm d}^3 r\, \Phi(\{n_\alpha(\boldsymbol{r})\}), \tag{1}$$

which is a functional of four scalar weighted densities

$$n_\alpha(\boldsymbol{r}) = \int {\rm d}^3 r' \rho(\boldsymbol{r}')\omega^\alpha(\boldsymbol{r}-\boldsymbol{r}'), \quad \alpha = 0, \cdots, 3, \tag{2}$$

and two vector weighted densities $\boldsymbol{n}_\alpha(\boldsymbol{r})$,

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

where ω^α and $\boldsymbol{\omega}^\alpha$ are the weight functions which depend only on the fundamental geometrical measures of the hard-sphere, namely its volume, surface area, and radius R. They are independent of the density profile of the fluid. The weight functions are given by

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

where Θ is the Heaviside step function and δ is the Dirac delta function. Other scalar weight functions are proportional to $\omega^{(2)}$: $\omega^{(1)} = \omega^{(2)}/(4\pi R)$ and $\omega^{(0)} = \omega^{(2)}/(4\pi R^2)$. The vector weight function $\boldsymbol{\omega}^{(1)}$ is collinear with $\boldsymbol{\omega}^{(2)}$: $\boldsymbol{\omega}^{(1)} = \boldsymbol{\omega}^{(2)}/(4\pi R)$. Equation (1) can be rewritten as

$$\Phi = \Phi_1 + \Phi_2 + \Phi_3, \tag{5}$$

where Φ_1, Φ_2 and Φ_3 are the functions of $n_\alpha(\boldsymbol{r})$, given by

$$\Phi_1 = -\, n_0 \ln(1 - n_3), \tag{6}$$

$$\Phi_2 = \frac{n_1 n_2 - \boldsymbol{n}_1 \cdot \boldsymbol{n}_2}{1 - n_3}, \tag{7}$$

$$\Phi_{3,\rm int} = \frac{\frac{1}{3}n_2^3 - n_2 \boldsymbol{n}_2 \cdot \boldsymbol{n}_2 + \frac{2}{3}|\boldsymbol{n}_2|\boldsymbol{n}_2 \cdot \boldsymbol{n}_2}{8\pi(1 - n_3)^2}$$
$$= \frac{n_2^3}{24\pi(1 - n_3^2)}(1 - 3\xi^2 + 2\xi^3). \tag{8}$$

Here $\xi(\boldsymbol{r}) = |\boldsymbol{n}_2(\boldsymbol{r})|/n_2(\boldsymbol{r})$ is the ratio of the modulus of the vector weighted density $\boldsymbol{n}_2(\boldsymbol{r})$ and the scalar weighted density $n_2(\boldsymbol{r})$.

Giving the chemical potential μ of the system, the equilibrium density profile can be obtained by minimizing the grand potential functional

$$\Omega[\rho(\boldsymbol{r})] = \mathcal{F}(\rho(\boldsymbol{r})] + \int {\rm d}^3 r' \rho(\boldsymbol{r}')(V_{\rm ext}(\boldsymbol{r}') - \mu) \tag{9}$$

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with respect to $\rho(\boldsymbol{r})$. Here $\mathcal{F}[\rho(\boldsymbol{r})]$ is the free energy functional, which can be divided into two parts

$$\mathcal{F}[\rho(\boldsymbol{r})] = \mathcal{F}_{\rm id}[\rho(\boldsymbol{r})] + \mathcal{F}_{\rm ex}[\rho(\boldsymbol{r})]. \tag{10}$$

The part from ideal gas contribution is

$$\beta\mathcal{F}_{\rm id} = \int {\rm d}^3 r' \rho(\boldsymbol{r}')[\ln(\lambda^3\rho(\boldsymbol{r}')) - 1], \tag{11}$$

and the excess part $\mathcal{F}_{\rm ex}[\rho(\boldsymbol{r})]$ is given by Eq. (1), where $\lambda = \left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2}$ is the thermal wavelength. When the equilibrium density profile is obtained and inserted into Eqs. (9) and (10), the functionals $\mathcal{F}$ and Ω reduce to the free energy and the grand potential of the HS fluid.

The two planar hard walls located at $z = 0$ and $z = L$ that confine the HS fluid can be regarded as an external potential $V_{\rm ext}$ in this study,

$$V_{\rm ext}(z) = \begin{cases} \infty, & z < R \quad \text{and} \quad z > L - R \\ 0 & \text{otherwise.} \end{cases} \tag{12}$$

This potential prevent the centres of hard spheres approach the walls closer than R. For simplicity we regard the walls are infinite so that the system studied here is effectively a one-dimensional system, the density profile $\rho(z)$ depends only on the coordinate that perpendicular to the wall, denoted here as z. This enables us to reduce Eqs. (9), (10) and (11) into simpler forms by integrating over x and y. The grand potential functional is simplified to

$$\begin{aligned} \frac{\beta\Omega}{V} =& \frac{1}{L}\Big(\int_0^L {\rm d}z \Phi(\{n_\alpha(z)\}) \\ &+ \int_0^L {\rm d}z' \rho(z')[\ln(\lambda^3\rho(z')) - 1] \\ &+ \int_0^L {\rm d}z' \rho(z')(V_{\rm ext}(z') - \mu)\Big) \\ =& \frac{1}{L}\Big(\int_0^L {\rm d}z \Phi(\{n_\alpha(z)\}) \\ &+ \int_R^{L-R} {\rm d}z' \rho(z')[\ln(\rho(z')) - 1] \\ &- \int_R^{L-R} {\rm d}z' \rho(z')\mu^{\rm eff}\Big), \end{aligned} \tag{13}$$

where $\beta\mu^{\rm eff} = \beta\mu - \ln(\lambda^3)$. The minimization amounts to find the solution of the density profile from the following equation

$$\frac{\delta\left(\frac{\beta\Omega}{V}\right)}{\delta\rho(z)} = 0 \tag{14}$$

for a given chemical potential. In practical calculations, instead of the chemical potential, the mean density of the fluid is usually fixed. In this case we can treat $\mu^{\rm eff}$ as a Lagrange multiplier and its value is determined by the requirement that

$$\int {\rm d}z \rho(z) = L\rho_0. \tag{15}$$

Here ρ_0 is the mean density of the system. In this one-dimensional case, the weighted densities are simplified to

$$n_\alpha(z) = \int_{-R}^{R} {\rm d}z' \rho(z + z')\bar{\omega}^{(\alpha)}(z'), \tag{16}$$

$$\boldsymbol{n}_\alpha(z) = \int_{-R}^{R} {\rm d}z' \rho(z + z')\bar{\boldsymbol{\omega}}^{(\alpha)}(z'). \tag{17}$$

The reduced weighted functions $\bar{\omega}^{(\alpha)}$ are the functions of z only:

$$\bar{\omega}^{(3)} = \pi(R^2 - z^2)\Theta(|z| - R), \tag{18}$$

$$\bar{\omega}^{(2)} = 2\pi R\Theta(|z| - R), \tag{19}$$

$$\bar{\boldsymbol{\omega}}^{(2)} = 2\pi z\boldsymbol{e}_z\Theta(|z| - R). \tag{20}$$

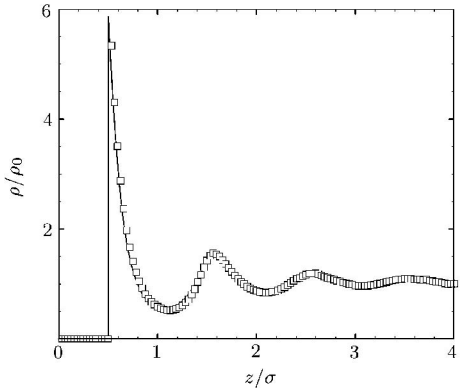

Fig. 1. Density profile of HS fluid confined between two parallel hard walls with the wall separation $L = 8\sigma$ (σ is the diameter of the hard-sphere). The packing fraction is $\eta = 0.35$. The solid line is obtained from density functional theory, and the symbols are from the molecular dynamics simulation.

When the two planar hard walls are far away from each other, the system tends to the bulk system except the parts that close to the two boundaries. If we neglect boundary effects, the density of the system is a constant and equals the mean density ρ_0. In this case the vector-weighted densities $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ and thus ξ vanish. In this limit, we have

$$\Phi_0 = -n_0\ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_2^3}{24\pi(1 - n_3)^2}. \tag{21}$$

Here

$$n_3 = \frac{4\pi}{3}R^3\rho_0 \equiv \eta, \tag{22}$$

$$n_2 = 4\pi R^2\rho_0, \tag{23}$$

$$n_1 = R\rho_0, \tag{24}$$

$$n_0 = \rho_0. \tag{25}$$

The chemical potential can be obtained in this case as

$$\begin{aligned} \beta\mu^{\rm eff} =& \beta\mu - \ln(\lambda^3) \\ =& -\ln(1 - n_3) + \frac{n_2}{1 - n_3}R + \Big[\frac{n_1}{1 - n_3} \\ &+ \frac{n_2^2}{8\pi(1 - n_3)^2}\Big]4\pi R^2 \\ &+ \Big[\frac{n_0}{1 - n_3} + \frac{n_1 n_2}{(1 - n_3)^2} \end{aligned}$$

$$+\frac{n_2^3}{12\pi(1-n_3)^3}\Big]\frac{4}{3}\pi R^3+\ln(\rho_0), \tag{26}$$

which only depends on the mean density $\rho_0 = \eta_0/(\frac{4}{3}R^3)$ or packing fraction η_0.

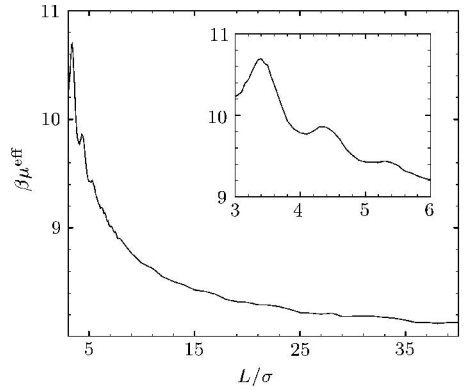

Fig. 2. Effective chemical potentials $\beta\mu^{\rm eff}$ (in units of k_BT) as a function of wall separation. The packing fraction is $\eta = 0.38$. When $L = 40\sigma$, it almost reaches the bulk value 7.96. Insert: a part of small wall separation.

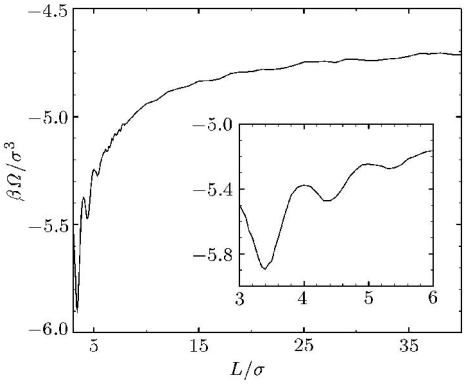

Fig. 3. Excess grand potential density $\frac{\beta\Omega}{V}$ as a function of wall separation. The packing fraction $\eta = 0.38$. The bulk value is 4.64. Insert: a part of small wall separation.

By using the conjugated gradient method, we minimized the functional given in Eq. (9), and thus obtained the profile of the fluid. The procedure to carry out the calculation is the following: we first divide the interval $[0, L]$ into N small intervals, and approximate the integrals of Eqs. (13) and (16) as sums, the densities $\rho(z)$ at each discrete points z_i, i.e., $\rho(z_i)$, are regarded as independent variables. Then we can use the standard conjugate gradient method to minimize the resulting grand potential, which becomes a function of N variables $\rho(z_i)$. The results converge to the continuous case when N is large enough. In our calculation we used different N for different wall separations and packing fractions, typically N is between 2^{10} to 2^{14}. In order to maintain the numerical accuracy, the functional derivative $\delta\Omega/\delta\rho(\boldsymbol{r})$ is also calculated, which is practically zero at the equilibrium density obtained from our numerical calculations. In order to check the exactness of the DFT scheme, we performed *molecular dynamics* simulations to the same system. The agreement of the density profiles obtained from the two methods is excellent when the wall separation L is larger than $6R$, or 3 times of the HS diameter σ. We quantify the agreement by means of the mean square deviation of the density profile, defined as

$$\bar{E} = \frac{1}{N}\sum_{j=1}^{N}\Big(\frac{\rho^{\rm sim}(z_j)-\rho(z_j)}{\rho_0}\Big)^2. \tag{27}$$

Here $\rho^{\rm sim}(z_j)$ is the MD simulated value and $\rho(z_j)$ is from DFT, respectively. We find that $\bar{E}$ becomes larger when L becomes smaller, and reaches 10^{-3} at about $L \geq 3\sigma$. To illustrate the agreement between the Rosenfeld DFT scheme and the MD simulation results, we display the density profiles of a particular HS system in Fig. 1. The packing fraction η of the system is 0.35 and wall separation L is 8σ, its mean square deviation is $\bar{E} = 6 \times 10^{-4}$.

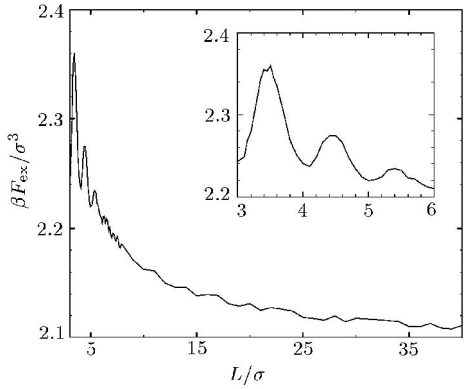

Fig. 4. Excess free energy density $\frac{\beta F_{\rm ex}}{V}$ as a function of wall separation. The packing fraction $\eta = 0.38$. The bulk value is 2.09. Insert: a part of small wall separation.

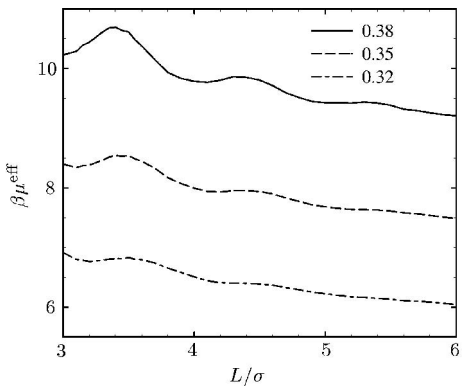

Fig. 5. Effective chemical potentials $\beta\mu^{\rm eff}$ as a function of wall separation. The packing fractions are $\eta = 0.38$ (solid), $\eta = 0.35$ (dashed) and $\eta = 0.32$ (dot-dashed), respectively.

Based on the observation that the DFT scheme can give accurate results of density profiles, we expect that the thermodynamical quantities calculated from it are also in good accuracy. Since quantities such as chemical potential and free energy density are very difficult to be obtained from MD simulations, we calculated

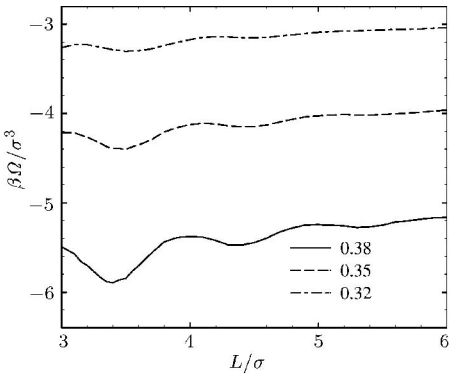

Fig. 6. Excess grand potential densities $\frac{\beta\Omega}{V}$ as a function of wall separation. The packing fractions are $\eta = 0.38$ (solid), $\eta = 0.35$ (dashed) and $\eta = 0.32$ (dot-dashed), respectively.

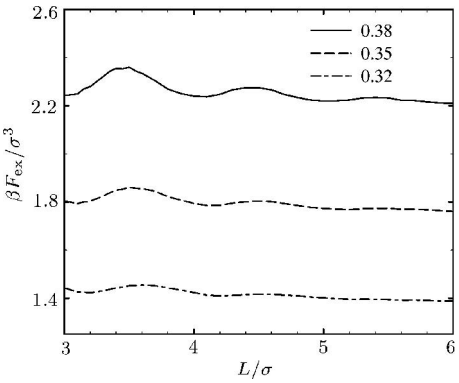

Fig. 7. Excess free energy densities $\frac{\beta F_{ex}}{V}$ as a function of wall separation. The packing fractions are $\eta = 0.38$ (solid), $\eta = 0.35$ (dashed) and $\eta = 0.32$ (dot-dashed), respectively.

these quantities from the DFT. Figure 2 shows the chemical potential as a function of the wall separation. The chemical potential is oscillating decreasing with L, with each minimum at those separations that are the integers of the hard sphere diameter. The excess grand potential density as a function of the wall separation is shown in Fig. 3. It is oscillating increasing to its bulk value and with maximum at integers of the HS diameter. Figure 4 is the plot of excess free energy as a function of the wall separation, it has the same behaviour as the chemical potential. Figures 5–7 show the chemical potentials, excess grand potentials and excess free energies of different packing fractions, all of them show the same oscillating behaviour, and the behaviour is weakened when packing fraction decreases. From the figures we can see that, when the wall separation is larger than about 40 times of the HS diameter, all the quantities reach their respective bulk values. In Fig. 8 we show the chemical potential as functions of packing fractions for different wall separations and the bulk system. The reason that all the thermodynamic quantities are oscillating with wall separations is understandable. When the wall separation is commensurate with the hard sphere diameter, the hard sphere can easily form layered structures with equal layer distance, this then has the effect to increase the entropy density of the system and decrease the free energy density.

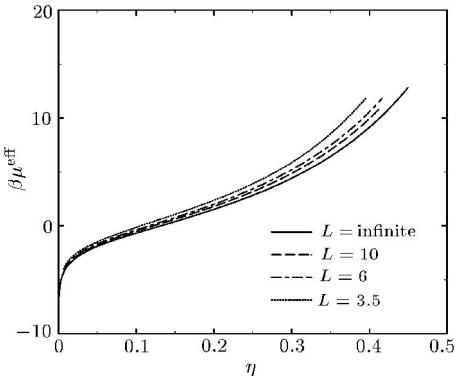

Fig. 8. Chemical potential $\mu^{\rm eff}$ as a function of hard-sphere packing fractions for fixed wall separation. The solid line corresponds to $L = \infty$, i.e., the uniform system, the dashed line corresponds to $L = 10\sigma$, the dot-dashed line corresponds to $L = 6\sigma$, and the dotted line corresponds to $L = 3.5\sigma$.

In summary, we have studied the equilibrium properties of hard-sphere fluid confined in parallel walls by means of DFT and MD simulations. We found that Rosenfeld functional is accurate as long as the wall separation larger than 3 times of hard-sphere diameter, we have observed the oscillation behaviour of chemical potential, excess free energy and excess grand potential. We also conclude from our calculation that the effect of the confinement will become less important when the wall separation larger than about 40 HS diameter.

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