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Hard discs in circular cavities: density functional theory versus simulation

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Three different density functional approaches, namely the Rickayzen, Takamiya–Nakanishi and Rosenfeld approximations, have been employed to study the equilibrium particle density distributions of hard-disc fluids in hard circular cavities. Also, Monte Carlo simulations have been performed to test the theoretical results. The comparison with the simulation data shows that the Rosenfeld approximation, which is based on the fundamental geometrical measures of the particles, is better than the Takamiya–Nakanishi and Rickayzen approximations and yields good agreement with the computer simulation data even for higher densities.

1. Introduction

The thermodynamic, structural and dynamical properties of fluids confined to cavities have been the subject of long-standing theoretical, experimental and practical interest, for recent investigations [1–3]. One important application concerns the behaviour of fluids in porous media or single cavities which leads to significant changes due to confinement effects and shifts of the static and dynamic correlations relative to the bulk behaviour. Most of the theoretical studies for structural properties are based on density functional theory of strongly inhomogeneous fluids [4, 5]. Different approximations for the free energy functional have been proposed to describe the structural properties of a hard-sphere fluid confined to different kinds of cavities; for example, the weighted-density approximation of Tarazona and co-workers [6], the density functional approximation of Rickayzen and co-workers [7, 8] based on the density functional expansion, and the geometrically based fundamental-measure free-energy model of Rosenfeld [9, 10]. The crux of the density functional approximation lies in the fact that the exact form of the free energy functional $F[\rho]$ is not known. To find a reliable approximation for $F[\rho]$ is now a major activity in the density functional research realm. A comparison with 'exact' computer simulation data shows that density functional approximations generally describe the thermodynamic and structural properties of confined three-dimensional hard-sphere fluids well, even if each density functional approximation has its own advantages and disadvantages in the actual application. However, almost every application has been restricted to the three-dimensional hard-sphere fluid, not on the two-dimensional system such as the hard-disc fluid [11]. Therefore, the thermodynamic and structural properties of the confined hard-disc fluid have been studied little compared with those of the confined hard-sphere fluid. Moreover, the density functional approximations proposed for the hard-disc fluid have not been tested in the study of structural properties of a confined hard-disc fluid in detail. Such a study is also of great importance for investigating the physical properties of an emulsion interacting strongly in two dimensions [12] or for recent experiments of paramagnetic colloids confined to two dimensions in a circular-shaped cavity [13–16].

The purpose of this work is to examine three different density functional approximations to study the structural properties of the confined hard-disc fluid. In § 2, we will briefly review three different density functional approximations, which are the two-dimensional weighted-density approximation proposed by Takamiya and Nakanishi [17], the two-dimensional version of the density functional approximation of Rickayzen and co-workers [7, 8], and the two-dimensional 'fundamental measures' free-energy model proposed by Rosenfeld [9, 10], for the hard-disc fluid. In § 3, we use these approximations to study the equilibrium particle density distribution of a hard-disc fluid in a hard circular cavity and compare it with computer simulation

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data. The structural stability limit for the confined hard-disc fluid has also been investigated. Finally, our conclusions are presented in § 4.

2. Theory

In the density functional theory, the grand-canonical potential $\Omega[\rho]$ and the intrinsic (Helmholtz) free energy functional $F[\rho]$ are both a unique functional of the one-particle density $\rho(\mathbf{r})$ and they are related as

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r}\rho(\mathbf{r})\{u_{ext}(\mathbf{r}) - \mu\}, \quad (1)$$

where μ is the equilibrium chemical potential of the system and $u_{ext}(\mathbf{r})$ is an external potential. In two spatial dimensions, the free energy functional $F[\rho]$ can be generally written as the ideal contribution $F_{id}[\rho]$ plus the excess free energy functional $F_{ex}[\rho]$ originating from the particle interaction

$$\begin{aligned} F[\rho] &= F_{id}[\rho] + F_{ex}[\rho] \\ &= \beta^{-1}\int d\mathbf{r}\rho(\mathbf{r})\{\ln[\Lambda^2\rho(\mathbf{r})] - 1\} + F_{ex}[\rho], \end{aligned} \quad (2)$$

where $\beta = 1/k_BT$ is the inverse temperature and $\Lambda = h/(2\pi m k_B T)^{1/2}$ is the thermal de Broglie wavelength.

The equilibrium particle density distribution of the inhomogeneous fluid corresponds to the minimum of the grand-canonical potential satisfying the Euler–Lagrange relation [4]

$$\frac{\delta\beta\Omega[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta\beta F[\rho]}{\delta\rho(\mathbf{r})} + \beta\{u_{ext}(\mathbf{r}) - \mu\} = 0. \quad (3)$$

If the inhomogeneous fluid is in contact with the homogeneous bulk fluid, its chemical potential μ is equal to that of the homogeneous bulk fluid. The equilibrium particle density distribution (or density profile) is then given by the equation

$$\rho(\mathbf{r}) = \rho_b \exp\left\{-\beta u_{ext}(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho]) - c^{(1)}(\rho_b)\right\}, \quad (4)$$

where ρ_b is the homogeneous bulk density, $c^{(1)}(\mathbf{r};[\rho])$ is the one-particle direct correlation function (DCF) of the inhomogeneous fluid and $c^{(1)}(\rho_b)$ is the one-particle DCF of the homogeneous fluid

$$c^{(1)}(\mathbf{r};[\rho]) = -\frac{\delta\beta F_{ex}[\rho]}{\delta\rho(\mathbf{r})}. \quad (5)$$

Since the exact form of the excess free energy (or the one-particle DCF) for the hard-disc fluid is unknown, some kind of approximation must inevitably be introduced to calculate the equilibrium particle density distributions of a hard-disc fluid in a confined system.

2.1. *Takamiya–Nakanishi approximation*

Takamiya and Nakanishi [17] have proposed a density functional approximation, which is based on a weighted-density approximation, to calculate the radial distribution function of hard-disc fluids and the static structure of hard-disc fluids around a central hard triatomic molecule. In doing so, the density-dependent weighting function in the density functional method proposed by Tarazona [6] for 3D hard-sphere fluids has been applied to 2D hard-disc fluids. In the Takamiya–Nakanishi approximation, the excess free energy functional $F_{ex}[\rho]$ is assumed to be

$$F_{ex}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})f[\bar{\rho}(\mathbf{r})], \quad (6)$$

where $f(\rho)$ is the excess free energy per particle and the weighted density $\bar{\rho}(\mathbf{r})$ is defined as

$$\bar{\rho}(\mathbf{r}) = \frac{2\bar{\rho}_0(\mathbf{r})}{[1-\bar{\rho}_1(\mathbf{r})] + \left\{[1-\bar{\rho}_1(\mathbf{r})]^2 - 4\bar{\rho}_0(\mathbf{r})\bar{\rho}_2(\mathbf{r})\right\}^{1/2}}, \quad (7)$$

with

$$\bar{\rho}_i(\mathbf{r}) = \int d\mathbf{s}\rho(\mathbf{s})\omega_i(|\mathbf{r}-\mathbf{s}|), \quad i = 0, 1, 2. \quad (8)$$

In equation (8), the weighting functions, $\omega_i(r)$, are given as

$$\omega_0(r) = \frac{1}{\pi}\sigma^2, \quad r < \sigma, \quad (9)$$

$$\begin{aligned} \omega_1(r) &= 0.390 - 0.552\left(\frac{r}{\sigma}\right) + 0.080\left(\frac{r}{\sigma}\right)^2, \quad r < \sigma, \\ &= 0.282\left(\frac{\sigma}{r}\right) - 0.966 + 0.791\left(\frac{r}{\sigma}\right) \\ &\quad - 0.189\left(\frac{r}{\sigma}\right)^2, \quad \sigma < r < 2\sigma, \end{aligned} \quad (10)$$

$$\omega_2(r) = 0.580 - 1.481\left(\frac{r}{\sigma}\right) + 0.815\left(\frac{r}{\sigma}\right)^2, \quad r < \sigma, \quad (11)$$

where σ is the diameter of the hard discs. Equations (6)–(11) constitute the Takamiya–Nakanishi approximation for the hard-disc fluid [17].

In this case, the one-particle DCF, $c^{(1)}(\mathbf{r};[\rho])$, appearing in the density profile equation is simply given as

$$c^{(1)}(\mathbf{r};[\rho]) = -\beta f[\bar{\rho}(\mathbf{r})] - \int d\mathbf{s}\rho(\mathbf{s})\beta f'[\bar{\rho}(\mathbf{s})]\frac{\delta\bar{\rho}(\mathbf{s})}{\delta\rho(\mathbf{r})}, \quad (12)$$

where the prime of $f(\rho)$ denotes the derivative with respect to the density. In the homogeneous state, equation (12) becomes

$$c^{(1)}(\rho_b) = -\beta f(\rho_b) - \rho_b\beta f'(\rho_b), \quad (13)$$

since $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r}) = \rho_b$ and $\int d\mathbf{r}\omega_0(r) = 1$ for the homogeneous state. Therefore, the Takamiya–Nakanishi approximation requires the excess free energy $f(\rho)$ for hard-disc fluids as input. For numerical calculations a suitable choice of the excess free energy $f(\rho)$ of the hard-disc fluid is the empirical free energy of Santos *et al.* [18]

$$\beta f(\eta) = \frac{(2\eta_0 - 1)\ln[1 - \eta(2\eta_0 - 1)/\eta_0] - \ln(1 - \eta/\eta_0)}{2(1 - \eta_0)}, \tag{14}$$

where $\eta = \pi\rho\sigma^2/4$ is the packing fraction and $\eta_0 = (3^{1/2}/6)\pi$ is the maximum packing fraction corresponding to the closed-packed density.

2.2. *Rickayzen approximation*

In the density functional approximation of Rickayzen and co-workers [7, 8] the excess free energy functional $F_{ex}[\rho]$ is given as

$$\beta F_{ex}[\rho] = -\int d\mathbf{r}\int d\mathbf{s}K(|\mathbf{r} - \mathbf{s}|)\rho(\mathbf{r})\rho(\mathbf{s}) - B\int d\mathbf{r}\int d\mathbf{s}\int d\mathbf{t}L(\mathbf{r},\mathbf{s},\mathbf{t})\rho(\mathbf{r})\rho(\mathbf{s})\rho(\mathbf{t}), \tag{15}$$

where $K(|\mathbf{r} - \mathbf{s}|)$ and $L(\mathbf{r},\mathbf{s},\mathbf{t})$ are the unknown kernels which are symmetric in their arguments. B is an unknown constant, the strength parameter, and determined by the equation of state of the system. Following Rickayzen's argument for three-dimensional hard-sphere fluids, we assume the kernel $L(\mathbf{r},\mathbf{s},\mathbf{t})$ for the two-dimensional hard-disc system to be

$$L(\mathbf{r},\mathbf{s},\mathbf{t}) = \int d\mathbf{u}a(|\mathbf{r} - \mathbf{u}|)a(|\mathbf{s} - \mathbf{u}|)a(|\mathbf{t} - \mathbf{u}|), \tag{16}$$

with

$$a(r) = \frac{1}{\pi\sigma^2}\theta(r - \sigma), \tag{17}$$

where $\theta(r)$ is the Heaviside step function which is equal to 1 if $r > \sigma$, and 0 otherwise. The kernel $K(|\mathbf{r} - \mathbf{s}|)$ is chosen to satisfy the two-particle DCF, $c^{(2)}(|\mathbf{r} - \mathbf{s}|, \rho_b)$, of the model system so that

$$c^{(2)}(|\mathbf{r} - \mathbf{s}|, \rho_b) = 2K(|\mathbf{r} - \mathbf{s}|) + 6B\rho_b\int d\mathbf{t}L(\mathbf{r},\mathbf{s},\mathbf{t}). \tag{18}$$

In the Rickayzen approximation, the one-particle DCF, $c^{(1)}(\mathbf{r};[\rho]) - c^{(1)}(\rho_b)$, becomes

$$c^{(1)}(\mathbf{r};[\rho]) - c^{(1)}(\rho_b) = \int d\mathbf{s}c^{(2)}(|\mathbf{r} - \mathbf{s}|, \rho_b)[\rho(\mathbf{s}) - \rho_b] + 3B\int d\mathbf{s}a(|\mathbf{r} - \mathbf{s}|)[\bar{\rho}(\mathbf{s})]^2, \tag{19}$$

with

$$[\bar{\rho}(\mathbf{r})]^2 = \left[\int d\mathbf{s}a(|\mathbf{r} - \mathbf{s}|)[\rho(\mathbf{s}) - \rho_b]\right]^2. \tag{20}$$

The strength parameter B in equation (19) is chosen to satisfy the equation of state for the homogeneous bulk fluid

$$\beta P = -\frac{\beta\Omega[\rho]}{V} = \rho_b - \frac{\rho_b^2}{2}\int d\mathbf{s}c^{(2)}(|\mathbf{r} - \mathbf{s}|, \rho_b) + B\rho_b^3, \tag{21}$$

where P is the pressure of the system and V is the volume [8]. As the input, the two-particle DCF $c^{(2)}(r,\eta)$ and the equation of state for hard-disc fluids which are given by Baus and Colot have been used [19]

$$c^{(2)}(x,\eta) = -\frac{\partial}{\partial\eta}[\eta Z(\eta)]\theta(1 - x) \times \left[1 - a^2\eta + \frac{2}{\pi}a^2\eta\left[\cos^{-1}\left(\frac{x}{a}\right) - \frac{x}{a}\left(1 - \frac{x^2}{a^2}\right)^{1/2}\right]\right], \tag{22}$$

where $x = r/\sigma$ and $Z(\eta)$ is the equation of state for the hard-disc fluid

$$Z(\eta) = \frac{\beta P}{\rho} = \frac{1 + \sum_{n=1}^{6}\alpha_n\eta^n}{(1 - \eta)^2}, \tag{23}$$

with $\alpha_1 = 0$, $\alpha_2 = 0.1280$, $\alpha_3 = 0.0018$, $\alpha_4 = -0.0507$, $\alpha_5 = -0.0533$ and $\alpha_6 = -0.0410$. The constant $a = a(\eta)$ is determined from the following equation [19]

$$\frac{2}{\pi}\left[a^2(a^2 - 4)\sin^{-1}\left(\frac{1}{a}\right) - (a^2 + 2)(a^2 - 1)^{1/2}\right] = \frac{1}{\eta^2}\left[1 - 4\eta - \left(\frac{\partial}{\partial\eta}[\eta Z(\eta)]\right)^{-1}\right]. \tag{24}$$

Equations (4), (19), (21), (22) and (23) constitute the Rickayzen approximation for the confined hard-disc fluid.

2.3. *Rosenfeld approximation*

The 'fundamental measures' free-energy model for inhomogeneous, two-dimensional hard-sphere fluid mixtures, which is based upon the fundamental geometric measures of the particles, was proposed by Rosenfeld [9, 10]. In this approximation, the excess free energy functional for hard-disc fluids is assumed to have the form

$$\beta F_{ex}[rho] = \int d\mathbf{r}\Phi[n_\alpha(\mathbf{r})], \tag{25}$$

where $\Phi[n_\alpha(\mathbf{r})]$ is the excess free energy per volume. It is assumed that the excess free energy density $\Phi[n_\alpha(\mathbf{r})]$

$$\Phi[n_\alpha(\mathbf{r})] = -n_0(\mathbf{r})\ln[1-n_2(\mathbf{r})] + \frac{n_1(\mathbf{r})n_1(\mathbf{r}) - \mathbf{n}_{v1}(\mathbf{r})\cdot\mathbf{n}_{v1}(\mathbf{r})}{4\pi[1-n_2(\mathbf{r})]} \quad (26)$$

is only a function of the system averaged fundamental geometric measure of the particles

$$n_\alpha(\mathbf{r}) = \int \mathrm{d}\mathbf{s}\rho(\mathbf{s})\omega^{(\alpha)}(|\mathbf{r}-\mathbf{s}|), \quad (27)$$

where $\omega^{(\alpha)}(r)$ is the weighting function representing the geometrical properties of the particles and is defined as

$$\omega^{(2)}(r) = \theta(r-\sigma/2), \quad \omega^{(1)}(r) = (\mathbf{r}/r)\delta(r-\sigma/2),$$
$$\omega^{(1)}(r) = \delta(r-\sigma/2), \quad \omega^{(0)}(r) = (1/(\pi\sigma))\delta(r-\sigma/2). \quad (28)$$

Combining equations (5) and (25), the one-particle DCF $c^{(1)}(\mathbf{r};[\rho])$ becomes

$$c^{(1)}(\mathbf{r};[\rho]) = -\int \mathrm{d}\mathbf{s}\sum_\alpha \frac{\partial\Phi[n_\gamma(\mathbf{s})]}{\partial n_\alpha(\mathbf{r})}\omega^{(\alpha)}(|\mathbf{r}-\mathbf{s}|). \quad (29)$$

For the homogeneous state, equation (29) simplifies to

$$c^{(1)}(\rho_b) = \ln(1-\xi_2) - \frac{R^{(2)}\xi_0}{1-\xi_2} - \frac{1}{4\pi}\frac{2R^{(1)}\xi_1}{1-\xi_2} + \frac{1}{4\pi}\frac{R^{(2)}\xi_1^2}{(1-\xi_2)^2} \quad (30)$$

with $\xi_i = R^{(i)}\rho_b$, $R^{(0)} = 1$, $R^{(1)} = \pi\sigma$ and $R^{(2)} = \pi\sigma^2/4$. The advantage of the Rosenfeld approximation compared to the Takamiya–Nakanishi and Rickayzen approximations is that it does not need any information about the equation of state or the two-particle DCF of hard-disc fluids to calculate the density profiles. For the numerical calculation, we have used the two-dimensional Fourier transform method, that is, Hankel transform, to calculate the weighted densities $n_\alpha(r)$ and density profiles $\rho(r)$ because of the special properties of the weighting functions $\omega^{(\alpha)}(r)$ [20]. Taken together, equations (4), (29) and (30) constitute the Rosenfeld approximation for the confined hard-disc fluid.

3. Results and discussion

For the hard-disc fluid in a hard circular cavity, the spatial dependence of quantities like $\bar{\rho}(\mathbf{r}) = \bar{\rho}(r)$, $\rho(\mathbf{r}) = \rho(r)$, and $n_\alpha(\mathbf{r}) = n_\alpha(r)$ is for symmetry reasons on r only. The wall–fluid interaction $\beta u_{ext}(r)$ is given as

$$\beta u_{ext}(r) = 0, \quad r < R$$
$$= \infty, \quad r > R, \quad (31)$$

where R is the radius of the hard circular cavity and r is the distance to the centre of the cavity. Note that the centre of the hard-discs can only access $0 \le r < R - \sigma/2$.

To verify the theoretical results, we have performed grand-canonical and canonical Monte Carlo (MC) simulations for various particle numbers N, also varying the cavity radius R. In a grand-canonical simulation the disc number N is an averaged number since the chemical potential is prescribed. In contrast N is fixed in the canonical ensemble. However, to compare results for a given average number of discs the chemical potential in the grand-canonical simulation is iterative adjusted so that a predefined average number of particles is achieved. In order to find a suitable initial configuration, we started from the corresponding close-packed configuration [21] and scaled the disc diameter to preserve the imposed area fraction. For further details of the grand-canonical MC technique we refer to recent work in three spatial dimensions in [22].

Within density functional theory we obtain the density profiles via solving the equation

$$\rho(\mathbf{r}) = \frac{N\exp[-\beta u_{ext}(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho]) - c^{(1)}(\rho_b)]}{\int \mathrm{d}\mathbf{r}\exp[-\beta u_{ext}(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho]) - c^{(1)}(\rho_b)]}. \quad (32)$$

Note that this ensures the *a priori* correct normalization for a prescribed averaged N corresponding to the prescribed chemical potential μ in the grandcanonical ensemble.

We depict the DFT equilibrium particle density distribution $\rho(r)\sigma^2$ of the hard-disc fluid in a circular cavity with four different radii ($R = 5.0\sigma$, 4.8σ, 4.6σ and 4.22σ) in figures 1–4 together with the computer simulation data. Again for canonical simulations the number of

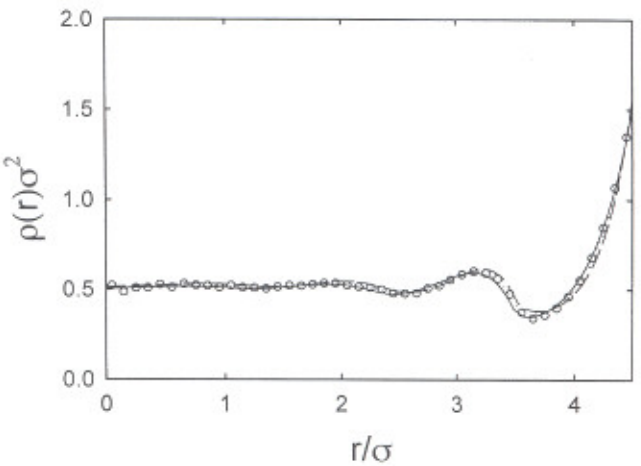

Figure 1. Equilibrium particle density distributions $\rho(r)\sigma^2$ of a hard-disc fluid ($N = 37$) in a hard circular cavity with radius $R = 5.0\sigma$. The solid, dashed, and dotted lines are from the Rosenfeld, Rickayzen and Takamiya–Nakanishi approximations, respectively. The open circles are the data obtained from computer simulations.

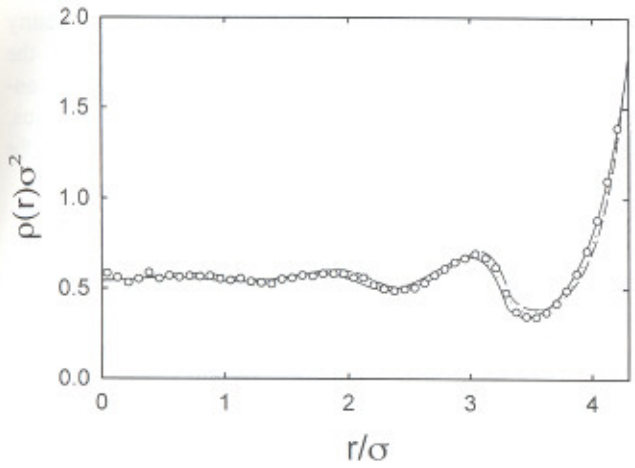

Figure 2. As figure 1, but for $R = 4.8\sigma$.

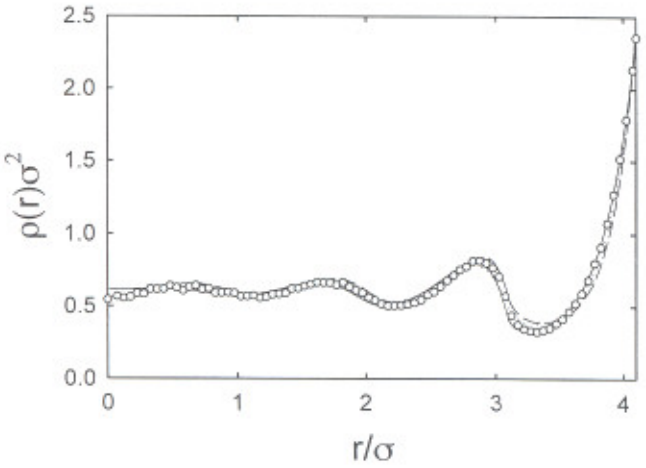

Figure 3. As figure 1, but for $R = 4.6\sigma$.

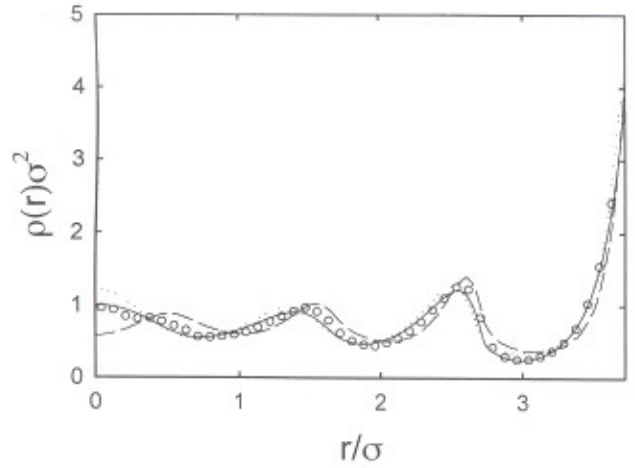

Figure 4. As figure 1, but for $R = 4.22\sigma$.

hard discs is fixed to $N = 37$ and for grand-canonical calculations, the chemical potential is fixed to yield an average number of hard discs of $N = 37$. $N = 37$ corresponds to a *magic* number associated to a closed-packed configuration with the curved hexagonal symmetry [21, 23].

From figure 1 ($R = 5.0\sigma$, $N = 37$) we find excellent agreement of the Rosenfeld and Takamiya–Nakanishi approximations with the computer simulation. However, the Rickayzen approximation exhibits a small discrepancy near the hard cavity wall. No deviations between canonical and grand-canonical computer simulations can be found such that the two ensembles are practically equivalent. The equilibrium particle density distribution exhibits a maximal local density at the cavity boundary followed by an oscillatory behaviour due to layering inside the cavity. The local density at the cavity centre, on the other hand, is governed by global packing constraints, particularly for high densities near close packing. This density is another diagnostic tool to test the capability of density functionals to describe packing properties of discs correctly.

The results of the confined hard-disc fluid for smaller radii ($R = 4.8\sigma$ and $R = 4.6\sigma$) with $N = 37$ are shown in figures 2 and 3. As before, the Rosenfeld approximation exhibits an excellent agreement with the computer simulation. However, by observing small deviations in the first depletion zone near the cavity boundary, it is again confirmed that the Rosenfeld approximation is more precise than the Takamiya–Nakanishi and Rickayzen approximations. For the latter two approximations, the agreement with the computer simulation deteriorates with increasing density.

For even higher density ($R = 4.22\sigma$, $N = 37$), the comparison with simulation data reveals that the Rosenfeld approximation again yields the correct oscillatory behaviour, see figure 4. The Takamiya–Nakanishi approximation, on the other hand, exhibits a discrepancy compared to the computer simulation near the hard circular cavity wall and at the cavity centre. Whereas the Rickayzen approximation shows the worst results compared with the computer simulations. Figure 4 shows that the density of the first peak at the centre of cavity is almost the same as that of the secondary peak which is not reproduced by the Takamiya–Nakanishi approximation. From the close-packed configuration with the curved hexagonal symmetry, we expect that for $N = 37$ the first peak of the density will occur at the centre of the hard cavity and is supposed to become even higher than that of the secondary peak for increasing density (or with decreasing cavity radius). This effect can also be seen from the density profiles of a confined hard-disc fluid with the 'magic' number $N = 7$ associated with a closed-packed config-

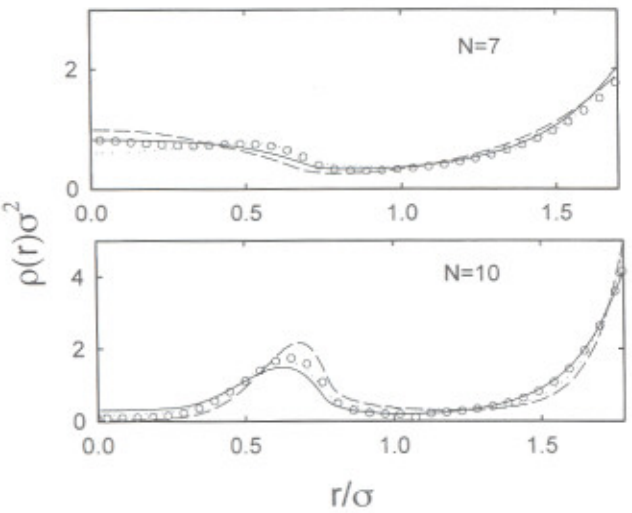

Figure 5. As figure 1, but for $N = 7$ for $R = 2.2\sigma$ and $N = 10$ for $R = 2.28\sigma$.

uration, while for $N = 10$, for instance, the first peak is expected to occur off the cavity centre [21].

We finally calculated density distributions for these two average numbers, close to the freezing packing densities [21] in figure 5: $N = 7$ for $R = 2.2\sigma$ and $N = 10$ for $R = 2.28\sigma$. We note that a bulk phase transition in a finite system depends strongly on the system size and freezing as manifested by slow dynamics occurring for lower density as compared to the bulk density. For these extreme cases, there are deviations at the cavity centre for the Rosenfeld functional as compared to the grand-canonical simulation data. To reproduce the central density is a stringent test for any density functional approximation as this density respects global packing constraints.

We further remark that canonical computer simulations with fixed particle number $N = 7, 10$ yield density profiles which are very close to the canonical ones. The only notable difference occurs at the cavity centre for $N = 10$. This is explained qualitatively as follows. The density profile in the grand-canonical ensemble is a linear superposition of canonical density profiles corresponding to different N. In particular, for an average $N = 10$, the weight of the $N = 9$ contribution is about 30% which has a central disc in its close-packed configuration [21]. This is the reason why the central density is slightly higher in the canonical than in the grand-canonical ensemble.

We finish with two remarks: first, in a complementary sense, one could also use a density functional in the canonical ensemble as recently discussed by White *et al.* [24]. Secondly, as a numerical remark, we note that for increasing density the density functional approximations show a so-called 'structural instability' [25]. Even though the threshold density of this structural stability depends slightly on the numerical iteration method, the stability limit falls close to the freezing density for confined hard-disc fluids in the Rosenfeld approximation. This is similar to the three-dimensional studies in the bulk [25].

4. Conclusions

In summary, we have used three different density functional approximations to study the structural properties of a hard-disc fluid in a hard circular cavity. The calculated results show that the Rosenfeld approximation is a significant improvement upon those of the Takamiya–Nakanishi and Rickayzen approximations and yields good agreement with the computer simulations. For the confined hard-disc fluid, the Rosenfeld approximation shows the 'structural instability' near the freezing density. Qualitatively the physics mostly resembles that of three-dimensional hard-sphere fluids confined in a spherical cage [22, 26].

As far as future research is concerned, it would be very interesting to apply the Rosenfeld approximation to study the structural *correlations* of a two-dimensional hard-disc fluid in a small circular cavity as was done in three dimensions in confinement [24, 27, 28]. There is a further need to study density functionals in extreme cases with only a few discs in cavities in order to highlight differences in the thermodynamic ensembles [22] and to fix problems of symmetry breaking with respect to the angular (orientational) symmetry if a freezing transition is crossed [13]. Also one can think about improving the Rosenfeld functional further in order to get full complete agreement for high densities in small cavities.

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