Structure of a hard sphere fluid in ultrathin films between corrugated walls. A grand canonical Monte Carlo study

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Recibido el 6 de mayo de 1998; aceptado el 18 de enero de 1999

We have investigated a local structure of a hard sphere fluid adsorbed in a slit-like pore with corrugated walls using grand canonical Monte Carlo simulations. The pore walls are modelled as an infinite set of regularly spaced rectilinear grooves of a few hard sphere diameter wide; the grooves are of stepwise shape along one of the axes of the pore plane and infinite in another direction. The interactions between fluid particles and pore walls are assumed to be of a hard sphere type. We discuss the density profiles of fluid particles in a wide and narrow region of the pore and analyze the density distribution in the step region. We have obtained that the maximum fluid density is observed in the corner of a groove. It is shown that the pore walls corrugation may yield a periodic variation of a fluid density parallel to the walls in the center of the pore. This effect depends on the width of the pore and on the depth of the grooves.

Keywords: Pores; fluid structure; adsorption; computer simulation

Mediante el método de simulación Monte Carlo Gran Canónico, estudiamos propiedades estructurales locales de un fluido de esferas duras absorbido en un poro tipo ranura con paredes corrugadas. Las paredes del poro están separadas por unos cuantos diámetros de esferas duras en una dirección de los ejes cartesianos, y de forma de escalón (con esquinas tipo 'saliente' y tipo 'hoquedad'). En las otras direcciones las paredes tienen distancia infinita. Entre las especies del fluido se suponen interacciones de tipo esfera dura. Discutimos los perfiles de densidad de las partículas del fluido para las regiones ancha y angosta. Analizamos la distribución de densidad en la región de transición. Encontramos que el máximo de la densidad del fluido se observa en las esquinas-hoquedad de la estría. Mostramos que las paredes corrugadas del poro pueden dar lugar a variaciones periódicas a lo largo del eje del poro, determinadas por el ancho del propio poro.

Descriptores: Poros; estructura de fluido; adsorción; simulación por computadora

PACS: 61.20.Ja

1. Introduction

The structural and thermodynamic properties of fluids confined in pores and in porous media are of much interest for basic research and several applications. Adsorption of fluids in pores of idealized geometry, such as slit-like, cylindrical and spherical, for example, have been the subject of much research, see *e.g.* Refs. 1–10. Integral equations, a density functional approach and computer simulations have complemented each other in the microscopic description of phenomena occuring under confinement. In the majority of theoretical studies, the pore walls have been modelled by the potentials which vary only in the direction normal to the substrate surface. In some cases the walls have been considered as almost flat substrates made of atoms explicitly, that interact with particles of adjacent fluid.

Most tribologically relevant surfaces are rough on the nanoscale and on higher scales as well. Previously, there were very few studies of fluids adsorbed in pores with corrugated walls, see *e.g.* Refs. 11–13, mostly by computer simulations. However, understanding of the local microscopic structure of fluids in pores with corrugated walls, its manifestation in quasimacroscopic effects and in thermodynamics, is far from being complete.

In this preliminary communication we present our first results concerning the behavior of a hard sphere fluid in slit-like pores with corrugated walls. We choose the walls to have a stepwise shape. The reason is that in some natural and synthetic materials one can find pores and planar surfaces that contain steps of a height of several atomic layers [14]. We have investigated the system by using grand canonical Monte Carlo simulations. At present, the application of theoretical methodological tools, that has been used previously for pores with idealized noncorrugated walls, seems difficult. The simulation results presented in this study, besides of interest on their own, are necessary as a helpful benchmark for the development of relevant theoretical approaches.

2. A model for a fluid in a slit-like pore with corrugated walls and grand canonical Monte Carlo procedure

In the present work we are considering a hard sphere fluid (f) with simple interparticle interaction,

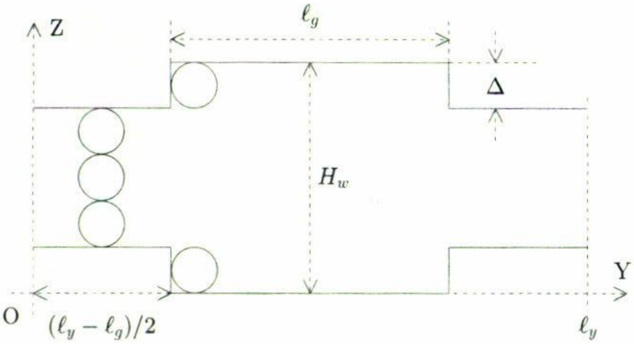


FIGURE 1. Sketch of the unit cell used in the GCMC simulations.

$$U_{ff}(r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma_f \\ 0, & r_{ij} > \sigma_f \end{cases} , \qquad (1)$$

where σ_f is the diameter of fluid species and r_{ij} denotes distance between particles i and j, in a slit-like pore. The system is studied by using GCMC simulation. Without loss of generality, we choose σ_f as a lenght unit, $\sigma_f = 1$. A pore represents a slit of a periodically variable width. The walls of the pore are stepwise. In a wider region the pore width is H_w, in the narrower part its width is $H_w - 2\Delta$, such that Δ is the depth of the groove. We choose z axis to be normal to the pore walls, each of the corrugated walls is parallel to xy plane. The width of the groove along y axis is taken to be l_g. The system is infinite along x direction. For better understanding by the reader, in Fig. 1, we present the sketch of the zy projection of the simulational cell with sizes H_w, l_y and l_x along x axis. The confining surfaces are assumed to be impermeable, hard walls for fluid species, such that the distance of the closest approach of fluid particles to any point of the pore walls is 0.5.

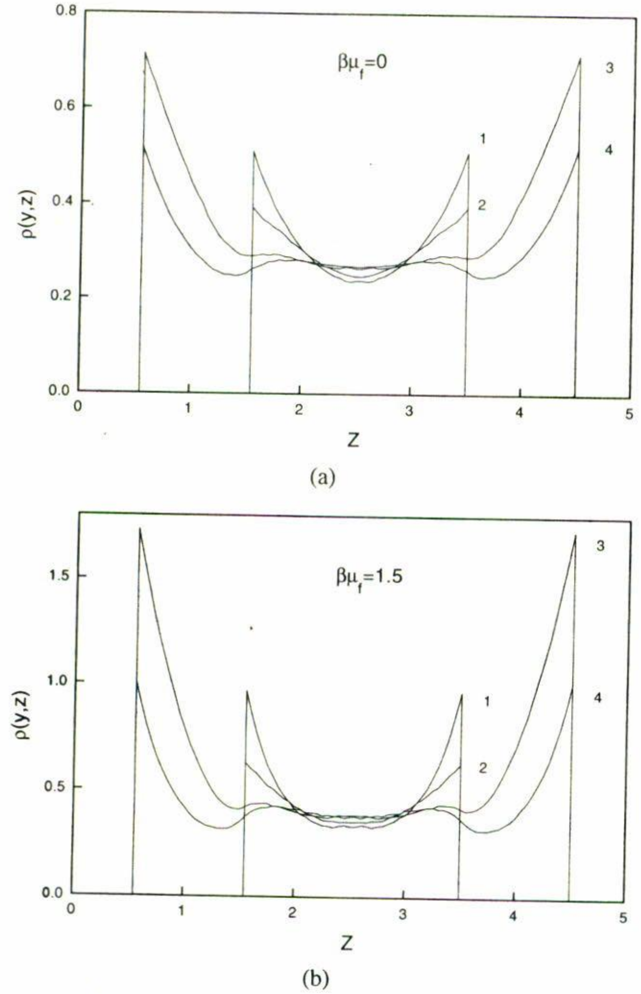
The Monte Carlo simulations in the GCMC ensemble has been performed according to a standard algorythm [15]. The external parameters of the simulations are the chemical potential, the volume and temperature. However, for a system of hard spheres in question the temperature is irrelevant. The periodic boundary conditions were imposed along x and y axes. To generate an initial configuration we have inserted randomly hard spheres into a pore under the restriction that they do not overlap with pore walls and with each other. Each simulational step have consisted of attempts to displace a particle, as in common Metropolis MC algorythm in the canonical ensemble, to delete a randomly chosen particle and to create a particle at a random position in the pore. Attempts to displace, to create and annihilate particles have been performed with equal probability 1/3. The parameter of maximal displacement of particles has been chosen equal to $0.5\sigma_f$. The total acceptance can be tuned by choosing differently this parameter. However, in all our runs the total acceptance of particles displacements, of creation and of annihilation, has remained reasonable, it equals approximately 20%. Usually, the individual acceptances of creation and annihilation of particles comprise 1/5 and less of the acceptance of displacements. The length of each of the runs was of the order of 10^6 steps. Each Monte Carlo step includes cycles over all the particles of the system, such that one attempts to displace a randomly chosen particle, to create and annihilate it and then proceeds to another randomly chosen particle. However, each of the particles of the system is attempted to move, to create and annihilate, more than once. Stable value for the total acceptance, as well as the equality of acceptances for creation and annihilation, *i.e.*, the stability of the value for average number of particles at a chosen value of the chemical potential, serve as criteria to perform collecting of statistical averages.

We have chosen the following sets of parameters of a pore in our study. The pore width H_w was taken to be 7 and 5, $\Delta = 1$, $l_g = 7.5$, $l_y = 15$. Two grooves are separated by the distance $(l_y - l_g)/2 = 7.5$, along y axis. According to the choice of the pore our simulational parallelepiped was with the edges H_w, $l_y = 15$, l_x; the values for l_x were chosen of the order $40 \div 80$, such that a sufficiently large number of particles to collect averages can accomodate in the box. All the values for the chemical potential of fluid species chosen in the present study have provided a number of fluid particles of the order $(2 \div 3) \times 10^2$.

3. Results and discussion

Let us proceed with the description of the results obtained. We consider first the model in which a pore is wide, both in the narrower region and in the groove region, $H_w = 7$, $\Delta = 1$; $l_y = 15$; $l_g = 7.5$. The density profiles of fluid particles, $\rho(z, y)$ at $\beta\mu_f = 0$ and 1.5, from GCMC simulations, are shown in Figs. 2a and 2b. The density profiles of fluid particles in the pore have been obtained, as usual in simulations, by calculating the number of particles in small volume elements, the edge of the cubic volume element was 0.05. Moreover, we have used the symmetry properties of the simulation box along different directions, to improve statistics for the density profiles.

We present the density profile in a wider region of the pore of the width $H_w = 7$, along the normal passing through the centers of opposite grooves, $\rho(z, y = 0.5l_y = 7.5)$, label 4 in Fig. 2; in the narrow region of the pore of the width $H_w - 2\Delta = 5$, along the normal passing through the centers of opposite steps, $\rho(z, y = 0) = \rho(z, y = 15)$, label 1; and the density profile of fluid particles along the normal with respect to pore walls, however close to the step edge inside the groove, $\rho(z, y = 4.35)$, label 3. Actually, a particle can be found in contact with a groove wall, *i.e.*, at $y = 4.25$. However, any contact value of the density profile must be obtained by extrapolation, therefore we have decided to show the profile at $y = 4.35$. In addition to these three profiles, we have shown in Fig. 2, the density distribution of fluid particles, $\rho(z, y = 3.55)$, label 2 in Fig. 2, *i.e.*, in the narrower part of the slit-like pore in question, but very close to the groove edge.



(a)

(b)

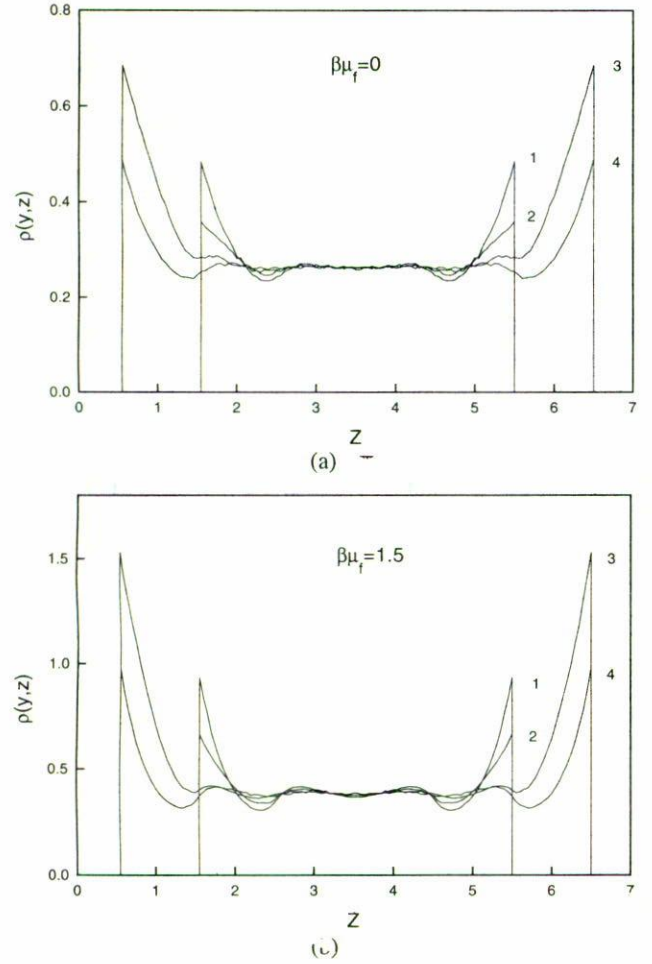
FIGURE 2. The density profiles of particles in a slit-like pore with stepwise corrugation of walls with $H_w = 7$, $\Delta = 1$, at $\beta\mu_f = 0$ (part a) and $\beta\mu_f = 1.5$ (part b). The density profiles, $\rho(z, y = 0)$, $\rho(z, y = 3.55)$, $\rho(z, y = 4.35)$, $\rho(z, y = 7.5)$, *i.e.*, in the center of a narrow part, close to the edge in the narrow part, in the corner of the groove and finally in the center of a wide part are shown with labels 1, 2, 3 and 4, respectively.

We observe that at $\beta\mu_f = 0$ (Fig. 2a) in the case of a pore with $H_w = 7$ and $\Delta = 1$, the effects of two pore walls in the wider and in the narrower part do not overlap mutually. In the central part of the pore the fluid is uniform, its density is constant up to fluctuations, and therefore the fluid is almost in its bulk state. Due to the presence of this bulk state, we have been able to check our computational algorythm, *i.e.* to check, if the contact value of the density profile on a wall corresponds to the bulk fluid pressure. The contact theorem for a hard sphere fluid in contact with a hard wall [16], relates the bulk fluid pressure with the contact value of the density profile, $\beta P = \rho(z = 0)$, where P is the bulk pressure. It appeared that at $\beta\mu_f = 0$, the contact values of the profile in the characteristic points of the pore along y axis (but far from the step discontinuity of the pore walls) are equal, *i.e.*, $\rho(z = 0.5\Delta, y = 0) = \rho(z = H_w - 0.5\Delta, y = 0) = \rho(z = 0.5\Delta, y = 0.5l_y) = \rho(z = H_w - 0.5\Delta, y = 0.5l_y)$, and coincide with the value of the bulk pressure, if a highly accurate equation of state for hard spheres of Carnahan-Starling was used [17]. In addition, we have verified that the bulk density agrees with the chosen value of $\beta\mu_f$ in the simulations and by using the expression for the chemical potential for hard spheres that follows from the Carnahan-Starling equation of state.

The density profiles in a wide and narrow region of the pore with labels 1 and 4 are almost of equal shape, they are just shifted with respect to each other along z axis. Most interesting is that the fluid density profile close to the edge (with the label 3), inside the groove, is very different from aforementioned two profiles. First of all, the contact value of the density profile, *i.e.*, the fluid density in the inner corner of the edge is very high. This density profile practically does not exhibit oscillations that usually characterize layering of a fluid inside a pore. We observe that the density close to the edge, but in the narrower part of the pore (with the label 2), is much lower than in the internal narrower part of the pore. Therefore, it becomes evident that stepwise grooves generate lateral inhomogeneity of adsorbed fluid density. However, in the central part of the pore the fluid inhomogeneity is not seen.

At a higher value of the chemical potential of adsorbed fluid, $\beta\mu_f = 1.5$, Fig. 2b, we observe very similar trends. Evidently, the contact values of all the profiles are much higher than for the case $\beta\mu_f = 0$. The fluid density in the pore becomes higher. In the central part of the slit small inhomogeneities of density become to develop. Weak trends for layering of adsorbed fluid in a narrower part of the pore, that correspond to the distribution between two opposite steps, can be observed at $\beta\mu_f = 1.5$, in contrast to the case of a lower chemical potential $\beta\mu_f = 0$. The difference in the contact values of the profiles labeled by the numbers 1 and 4 (in the narrower and in the wider part of the pore, respectively) is negligibly small, in the case $\beta\mu_f = 0$ and for $\beta\mu_f = 1.5$. The reason is that both values of the chemical potential are not too high. Even for a higher value of the chemical potential, that corresponds to the bulk fluid density $\rho_f = 0.5$, the contact values of the density profiles of hard spheres in the pores with widths $H_w = 7$ and $H_w - 2\Delta = 5$ are practically equal, see *e.g.* Fig. 3 of Ref. 4. Observed trends of behavior of the density profiles are physically correct and understandable.

Let us now proceed to the case of a narrower pore. In Fig. 3, we consider the results for a pore which is characterized by the width, $H_w = 5$, and by the depth of a groove $\Delta = 1$. The other parameters of the box are as before: $l_y = 15$, $l_g = 7.5$. Majority of trends discussed above in the description of Fig. 2, remain valid for the case of a narrower pore. Most important is that the fluid density in the central part of the slit becomes inhomogeneous, as seen in both parts (a and b) of Fig. 3. It is worth mentioning that the difference between the density in a wide part and in the corner, seems to be dependent mostly on the value of the chemical potential



(a)

(b)

FIGURE 3. The same as in Fig. 2 but for the pore with $H_w = 5$, $\Delta = 1$, at $\beta\mu_f = 0$ (part a) and $\beta\mu_f = 1.5$ (part b). The nomenclature of labels is like in Fig. 2.

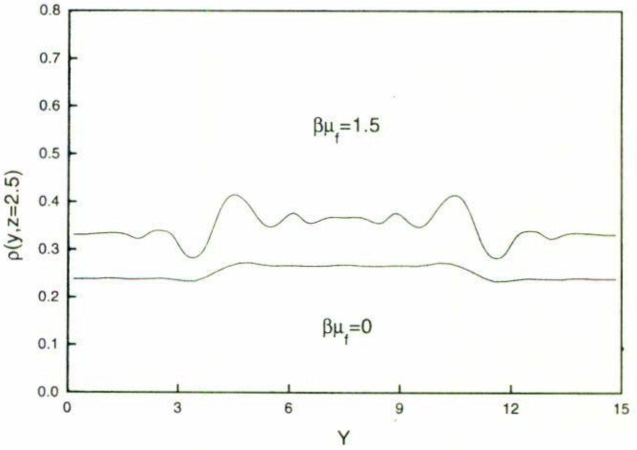


FIGURE 4. The density profiles of particles along y axis of the slit like pore at its center $z = 2.5$ ($H_w = 5$, $\Delta = 1$). The lower curve corresponds to the chemical potential $\beta\mu_f = 0$ whereas the upper curve is for $\beta\mu_f = 1.5$.

(*cf.* Figs. 2 and 3), rather then the pore width for both sets of parameters in question. The contact values of the profiles 1 and 4 in Fig. 3 are equal up to statistical inaccuracy in close agreement with the results presented in Fig. 3 of Ref. 4 for pores of the width 5 and 3. For higher values of the chemical potential and narrower pores, the contact values would be certainly different.

The final issue which we would like to discuss is the following. One may expect that with increasing chemical potential of fluid species, *i.e.*, with increasing fluid density, trends for layering of adsorbed fluid would increase. Stronger layering then can yield stronger inhomogeneity in the central part of the slit-like pore. In order to investigate the lateral ordering of fluid particles in the pore we have calculated the density profile along y axis in the center of the pore with $H_w = 5$, $\Delta = 1$, *i.e.*, at $z = 2.5$, at two values of the chemical potential, $\beta\mu_f = 0$ and $\beta\mu_f = 1.5$, Fig. 4. At a higher value of the chemical potential, the fluid density in the pore is higher than at $\beta\mu_f = 0$. The effect of corrugation due to the stepwise discontinuities is more pronounced at a higher adsorbed density; we observe developing lateral layering of adsorbed fluid in the narrower part of the pore, as well as in the wider part of the pore close to the steps, with increasing chemical potential. However, a more extensive simulational study is necessary to relate the augmenting density in the corners of the grooves of each of the pore walls with lateral ordering of adsorbed fluid.

To conclude, this work considers an important problem of the structure of fluids in slit-like pores with stepwise corrugated walls. At this initial stage of investigation of pores with rough walls we have restricted ourselves to the model with solely repulsive interparticle interactions. The model has been studied by using GCMC simulations. The development of theoretical approaches for slit-like pores with different corrugation of walls is difficult at present, and anyway would require computer simulation data. In this study we have observed the effect of augmenting density in the corner of a groove for different pore widths. Another interesting observation concerns the development of the inhomegeneity of adsorbed fluid density in the central part of the pore. These trends have been considered dependent on the fluid chemical potential. Even simple model in question, would require further studies involving larger set of values for the geometry of corrugation. In general, the influence of pore walls roughness at a molecular scale and energetic heterogeneity on adsorption, structure and the phase diagram of fluids in pores is the intriguing issue which we hope to address in our future work. At present computer simulations are the only reliable tools to study these systems of basic and practical importance. Nevertheless, we hope that the results obtained would stimulate the development of density functional approaches for pores of this and other symmetries restricted by corrugated walls.

This project has been supported in parts by DGAPA of the UNAM under the grant IN111597, by the National Council for Science and Technology (CONACyT) under grant No. 25301E.

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