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Liquid correlation across the walls in a slit pore: Effect on the wetting and drying transition

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The liquid structure next to the walls of a slit pore, immersed in a model simple liquid, is studied through a liquid theory and grand canonical Monte Carlo simulations. A liquid correlation across slit walls, of finite width, is found. This correlation modifies the structure and capillary partial wetting and drying transitions of the nonhomogeneous fluid, when close to its liquid-vapor coexistence curve.

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In the study of interfacial phenomena of fluids about membranes or porous materials, little attention has been paid in the literature to the fact that in any real situation the boundary, that separates one side from the other or the interior from the exterior, is of finite thickness. Explicit consideration of this fact reveals important phenomena, such as the violation of the local electroneutrality, in confined electrolyte solutions [1]. It has also been shown that the concentration profiles of a charged fluid, in contact with both sides of a planar charged wall, are correlated [2], and that this effect is relevant to the ion-membrane interaction [3]. There is a strong dependence of these two phenomena on the pore size τ and on the thickness d of the walls, particularly when τ and d approached values of the order of few ionic diameters [1–3]. In the past one of us predicted that fluid-fluid correlation across the walls is also present when nonionic fluids, such as inert gases or alkanes, are confined by a wall of finite thickness [2]. In this work we study a nonionic fluid confined by a slit pore, demonstrate this prediction, and show that such correlation strongly affects the prewetting transitions next to an attractive surface and the drying, or wetting by gas, next to a rigid wall. This is of utmost importance since a fundamental issue in epitaxial film growth, cell membranes biophysics, and colloidal science is the manner in which the adsorbed materials grow from unstructured gas next to a surface to the monolayer coverage and then to thick liquid films. The so-called partial wetting transitions are of particular importance in connection with gas chromatography separations and purification.

For simplicity, the intermolecular potential is taken to be as a hard sphere potential plus a Yukawa tail:

$$u^*(r) \equiv \beta u(r) = \begin{cases} \infty, & r < a \\ -K_F \dfrac{\exp\{-Z_F(r/a-1)\}}{r/a}, & r \geqslant a. \end{cases} \tag{1}$$

This potential has the essential features of real molecules or model potentials, such as the Lennard Jones, and has the advantage of having a simple semianalytical solution in the mean spherical approximation (MSA) [4,5]. In a consistent manner, the particle-wall interaction potential was taken as that of a hard wall with an exponential tail:

$$V_n^*(X_W^n) \equiv \beta V_n(X_W^n) = -K_W^n \exp\left\{ -\frac{Z_W^n X_W^n}{a} \right\}. \tag{2}$$

In Eqs. (1) and (2), r is the particles distance, a is the hard sphere diameter, $X_W^n = |x - x_n|, x$ is the distance from the pore midplane, and x_n is the position of the nth plane of the particles closest approach to the slit walls. That is, for a slit of width τ, having walls of thickness d, for the right wall $x_1 = h$ and $x_2 = h + a + d$, and for the left wall $x_3 = -x_1$ and $x_4 = -x_2$. Here $h = (\tau - a)/2$, Z_F, Z_W^n, and K_F and K_W^n are the *adimensional* range and potential depth parameters, respectively, for the fluid-fluid and fluid-*n*th surface interaction potentials. The wall-fluid potential is infinite within the hard cores. The net particle-slit potential is the sum over the four walls $V^*(x_W) = \Sigma_{n=1}^4 V_n^*(x_W)$.

The liquid concentration profile, as a function of the distance to the slit walls, is given in the three-point extension–hypernetted chain/mean spherical approximation (TPE-HNC/MSA) integral equation theory as [6] $\ln \rho(x_W)/\rho = -\beta V(x_W) + \int_0^\infty [\rho(x_W) - \rho] K(x_W, y) dy$, where $K(x_W, y) = 2\pi \int_{|x_W - y|}^\infty s c_B(s) ds + 2\pi \int_{|x_W + y|}^\infty s c_B(s) ds$, $c_B(s)$ is the bulk direct correlation function in the MSA approximation [4,5]. $\beta = 1/kT$ and T is the temperature, and x_W is the particle distance to the inner or outer surface of the right wall of the slit. $\rho(x_W)$ on the left side of the slit is by symmetry the mirror image of the right side. We solved the TPE-HNC/MSA theory for a variety of conditions close to the vapor-liquid coexistence region and present here only representative results. The TPE-HNC/MSA theory has been shown to be in agreement with grand canonical Monte Carlo (GCMC) results for charged fluids, confined by a charged slit [1] and a charged, single wall [2]. The validity and limitations of a Yukawa fluid have been reported elsewhere [7,8]. Therefore, even though a better description of the bulk fluid, beyond the MSA could be possible and a still better description of the nonhomogeneous fluid can be thought [6–8], the TPE-HNC/MSA theory has the correct physics for this complex system. To ensure this we considered here a low density fluid, $\rho^* \equiv \rho a^3 = 0.1$, and a compromise reduced temperature of $T^* = 1/K_F = 3$, since for high temperatures and low densities the TPE-HNC/MSA is capable of describing all the features predicted by GCMC simulations, as indeed it is shown in Fig. 1.

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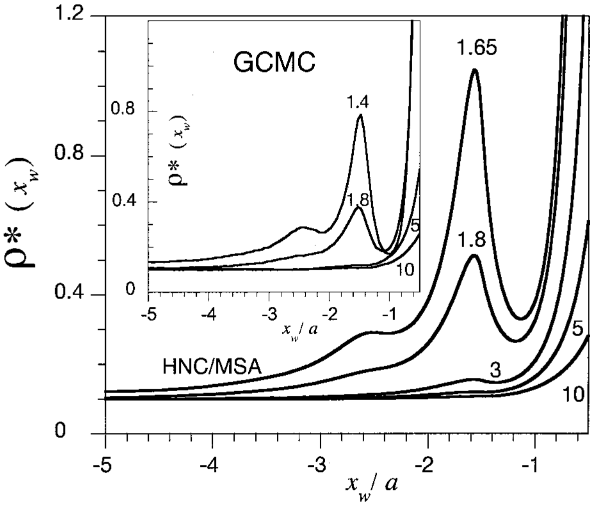

FIG. 1. TPE-HNC/MSA reduced concentration profile, $\rho^*(x_W)$, as a function of the distance to inner and outer wall surfaces, showing the wetting transition of a Yukawa fluid next to a Yukawa attractive, very thick, wall. The bulk density is $\rho^*=0.1$. $Z_F=Z_W=1.8$, $K_W^{in}=10K_F$, $K_F=1/T^*$. Each curve indicates the reduced temperature T^*. The inset shows the corresponding GCMC simulation results.

In Fig. 1 we present the TPE-HNC/MSA results for conditions close to the liquid-vapor coexistence curve of the *homogeneous fluid*, for a large pore, $\tau=10a$, and infinitely thick walls. Results for $\tau=100a$ are identical. For these conditions there is no fluid correlation through the slit walls or between the two walls. Hence, Fig. 1 results are equivalent to those for a fluid next to a single, infinitely thick wall. We show the local concentration profiles $\rho^*(x_W)$ of a dense gas, with a bulk reduced density of $\rho^*=0.1$, for several reduced temperatures, as a function of x_W. Here the range parameters are $Z_F=Z_W=1.8$, $K_W=10K_F$.

As the reduced temperature decreases from 10 to 1.8, the gas wets the surface and molecular layers of liquid form about the solid surface, in a continuous, so called, wetting transition. For a temperature as low as $T^*=1.65$ three layers have already been formed. For lower temperatures, the integral equation has no solution, something which is usually indicative of a first-order transition of the bulk fluid. The inset shows our GCMC results for the same system. The qualitative agreement of the TPE-HNC/MSA theory with the GCMC results is excellent. For high temperatures both results superimpose. For lower temperature the agreement is only qualitative. This is to be expected since, the TPE-HNC/MSA theory is well known to give too large contact values, particularly at low temperatures [2,6,7]. In fact, the vapor to liquid transition in the GCMC occurs at slightly lower temperatures. Though not shown, for still lower T^* the GCMC becomes unstable and the system structure evolves to that of the corresponding equilibrium bulk liquid next to an attractive wall. This general behavior has been reported with Monte Carlo simulations of a Lennard-Jones model potential [9,10] and by direct experimental observations [11–13].

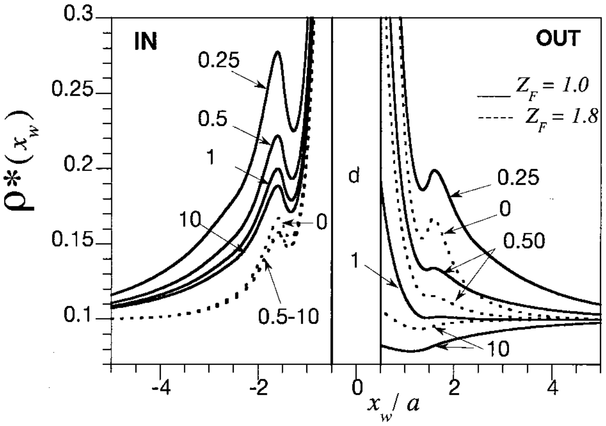

FIG. 2. TPE-HNC/MSA $\rho^*(x_W)$, showing the effect of the walls thickness d and the potential range Z_F on the wetting transition of a Yukawa fluid confined by a pore with Yukawa attractive inner walls. $Z_W^{in}=Z_W^{out}=1.8$, $K_W^{in}=10K_F$, $K_W^{out}=0$, $\rho^*=0.1$, and $T^*=3.0$. The continuous curve (—) is for $Z_F=1.0$ and the dashed curve (– – –) for $Z_F=1.8$. Each curve indicates the wall width d in molecular diameters. We show only the profiles around the right wall.

We now consider a planar slit pore, immersed into a Yukawa fluid at a bulk density $\rho^*=0.1$. The slit is of width τ, and is made of attractive walls, of *finite thickness d*. For simplicity, in all the cases studied we kept the wall-fluid range parameter Z_W fixed at the value 1.8 for all the surfaces. In Fig. 2 we present results for a case where both internal surfaces of the pore have associated a wall-fluid potential depth parameter 10 times that of the fluid-fluid potential, while both external surfaces are rigid, namely, $K_W^{in}=10K_F$ and $K_W^{out}=0$. In this and subsequent figures, the profiles on the left $(x_W<0)$ correspond to the fluid inside the pore. Those to the right $(x_W>0)$ correspond to the fluid outside the pore. The gap in the figures, though fixed, represents the variable distance from the inner to the outer planes of closest approach of the right wall of the pore, $d+a$. That is, x_W, is measured from the left (right) surface of the wall, for the inner (outer) concentration profile. Figure 2 shows the effect on wetting, of the range parameter of the fluid-fluid interaction Z_F and of the thickness of the pore walls, d, for a wide pore, $\tau=10a$. For a wide pore, no correlation with the fluid adsorbed at the left wall is expected. For $Z_F=1.8$ the range of the fluid potential is so short that very little effects are detected for this temperature. The structure inside the pore is independent of the wall thickness from $d=100a$ to $d=0.5a$.

Increasing the potential range by decreasing Z_F to 1.0 shows that the molecular correlation across the walls enhances the wetting layering on the inner attractive wall. This is so because, since $K_W^{out}=0$, reducing d simply brings the outside molecules closer to those inside the pore. For thickness of order $10a$ no correlation is observed, i.e., we recover the expected profiles for attractive (left) and hard (right) walls. For wall thickness less than $0.25a$ no solution is obtained, suggesting that the correlation across the walls could induce the first-order bulk transition from gas to liquid. The profiles on the right hand side of the rigid wall show a cou-

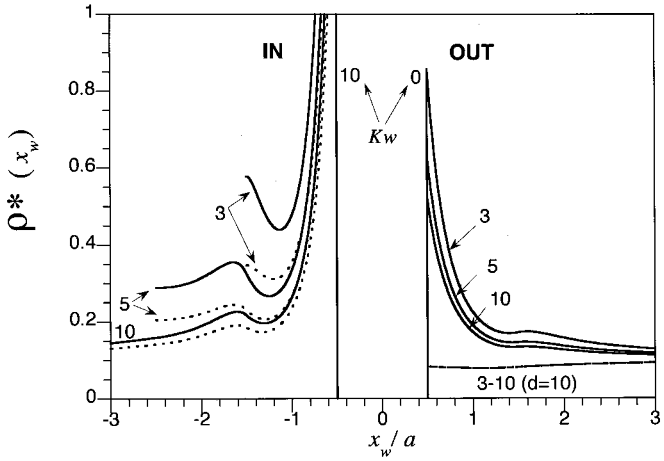

FIG. 3. Effect of the pore size τ on the fluid-fluid correlation across the slit walls. $Z_W^{in}=Z_W^{out}=1.8$, $Z_F=1.0$, $K_W^{in}=10K_F$, $K_W^{out}=0$, $\rho^*=0.1$, and $T^*=3.0$. The continuous curve (—-) is for $d=0.5a$ and the dashed curve (– – –) for $d=10a$. In each curve the wall to wall distance τ is indicated in molecular diameters a.

pling of the interaction of the external fluid with the internal attractive surface and with the fluid wetting it. For $d=10a$ we see the drying of the attractive fluid next to a rigid surface as describe elsewhere [7] , which increases with increasing fluid-fluid potential range. Decreasing d takes the right hand side fluid from a drying to a wetting situation.

The effect of the inner fluid on the fluid outside is further demonstrated in Fig. 3, where we kept the same conditions for the system as in Fig. 2, with $Z_F=1.0$, but decreased the size of the pore. Decreasing the pore size increases the correlation between the adsorbed liquid at both walls of the slit. This correlation produces an increase of the local concentration in the enclosed inner fluid. As we can see, for $d=10a$ no change is observed on the density profiles of the outside fluid, as the pore becomes as narrow as three molecular diameters. However, for a thin wall, $d=0.5a$, the density profiles of the fluid outside are modified as the pore becomes narrower. On the other hand, the structure and, therefore the capillary adsorption, of the fluid inside the pore is influenced by the correlation across the walls described here. For a given pore size, changing from $d=10a$ (dashed curves), where no correlation is possible, to $d=0.5a$ (solid curves) strongly modifies the capillary wetting transition.

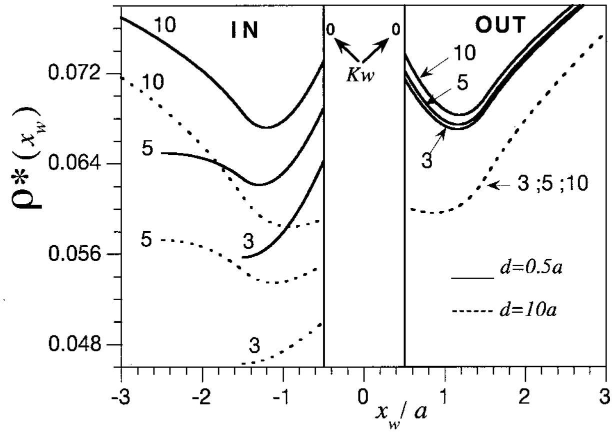

FIG. 4. Effect of the correlation across the walls on the drying transition of a Yukawa fluid confined by two hard walls. $Z_W^{in}=Z_W^{out}=1.8$, $Z_F=0.75$, $K_W^{in}=K_W^{out}=0$, $\rho^*=0.1$, and $T^*=3.0$. The continuous curve (—-) is for $d=0.5a$ and the dashed curve (– – –) for $d=10a$. In each curve the wall to wall distance τ is indicated in molecular diameters a.

Figure 4 shows the results for a Yukawa fluid with an even longer fluid-fluid range, $Z_F=0.75$, enclosed between two hard walls, $K_W^{in}=K_W^{out}=0$. Here the walls simply divide the fluid. For $d=10a$, where no correlation between the inner and outer fluids is present, we see only the effect of the wall-wall correlation. It is interesting that, contrary to the results of Fig. 3, where the inner surfaces are attractive, decreasing the pore size decreases $\rho^*(x_W)$, and the drying is attenuated. In general, the drying observed for a pore of $\tau=10a$ is attenuated when the pore becomes smaller, due to the wall-wall correlation, or for $d=0.5a$, due to the correlation with the outside fluid.

The integral equation results presented here show for the first time, to the best of our knowledge, evidence of fluid-fluid correlation across walls of finite width for a nonionic short-ranged fluid. We show how this correlation can affect the structure and capillary wetting and drying transitions of a non homogeneous fluid close to its liquid-vapor coexistence curve, something which could have interesting consequences in colloidal science, thin films, and biophysical studies.

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