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Controlling the composition of a confined fluid by an electric field

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Starting from a generic model of a pore/bulk mixture equilibrium, we propose a novel method for modulating the composition of the confined fluid without having to modify the bulk state. To achieve this, two basic mechanisms—sensitivity of the pore filling to the bulk thermodynamic state and electric field effect—are combined. We show by Monte Carlo simulation that the composition can be controlled both in a continuous and in a jumpwise way. Near the bulk demixing instability, we demonstrate a field induced population inversion in the pore. The conditions for the realization of this method should be best met with colloids, but being based on robust and generic mechanisms, it should also be applicable to some molecular fluids. © 2009 American Institute of Physics.

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I. INTRODUCTION

The question of how the adsorption of foreign particles affects the properties of materials and the means to control this is of central importance in domains ranging from separation processes to nanotechnology. This motivates the continuing investigation on the factors determining the adsorption process and the search of conditions most favorable for its control (composition of the adsorbing fluid, adsorption geometry, etc.).¹ The purpose of this communication is to propose a novel method that allows this, on the basis of Monte Carlo simulations of a fluid-slit pore equilibrium. To avoid having to consider specific interactions as in molecular adsorption, we choose to point out the basic mechanisms on a simple model with only hard-sphere and dipolar interactions. The situation closest to this model is then the adsorption of macroparticles. Another reason is the recent development of studies of colloidal adsorption.² Indeed, while numerous studies exist on molecular adsorption (see, for example, Refs. 3 and 4, and Ref. 5 for more recent work), one practical advantage of using colloids is the possibility to tune their effective interaction (e.g., by adding polymeric depletants) and their coupling with external fields, possibly in confined geometry.⁶ The actual behavior may, however, be complicated by the interplay of different effects (see, for example, the role of static and hydrodynamic forces in microfluidics devices).⁷ We thus propose here a method that allows a fine control of the composition of the adsorbed fluid, while remaining very simple.

II. METHOD

We start with the simplest confinement geometry: an open slit pore with parallel walls in equilibrium with a bulk fluid. It has been used in several theoretical studies to determine the parameters affecting the behavior of the confined fluid (see, for example, Refs. 3 and 8–14 and references therein). Since we seek a method in which the pore geom-

etry, the interactions (between the particles and the particles and the confining medium) as well as the bulk thermodynamic state are fixed, one alternative is the coupling with an external field. This should always be possible since besides particles having a permanent dipole such as magnetic colloids, colloidal particles are always polarizable to some extent. We thus took a uniform electric field $E = Eu_z$ normal to the walls. As in Ref. 15, we considered a mixture in which one species bears a dipole moment μ , taken permanent for simplicity. The field is then not applied in the bulk. We thus have pure hard-spheres (species 1) and dipolar hard-spheres (species 2), possibly with a nonadditive diameter σ_{12} in the potential u_{12}^{HS} (see also the discussion of Fig. 5). Both species have a hard-sphere interactions with the walls. This makes the model more appropriate¹¹ to a mixture of hard-sphere-like colloidal particles, than to a molecular mixture (see, however, the final remarks). The effect of an external field (and temperature) on the filling of a cylindrical pore was also studied in Ref. 16 (see also Ref. 17 for a slit pore), but not from a bulk mixture. Previous studies considered the role of the pressure in one-component fluids (e.g., Ref. 8), or the total density and the mole fractions^{9,13,14} in bulk mixtures but without field. As shown below, the combination of both will play here a crucial role. An inhomogeneous multicomponent mixture with anisotropic interactions being difficult to study by analytical methods (we are aware of one study by density functional theory of the adsorption from a mixture of polar molecules),¹⁸ we used Monte Carlo simulation (see also, for example, Refs. 15, 16, and 19–21). We already pointed out how the structure can be modulated by the combination of various interactions^{10,11} and by the action of the field.¹⁵ However, only the density profile of the particles through the pore could be modulated in Ref. 15 since the total number of particles was kept fixed (simulations in the canonical ensemble). An important difference here is that we consider an open pore which exchanges particles with a reservoir. One may then achieve much stronger variations in the density of each component in the pore. The physical pore is assumed large enough that the interfacial region in which it is in con-

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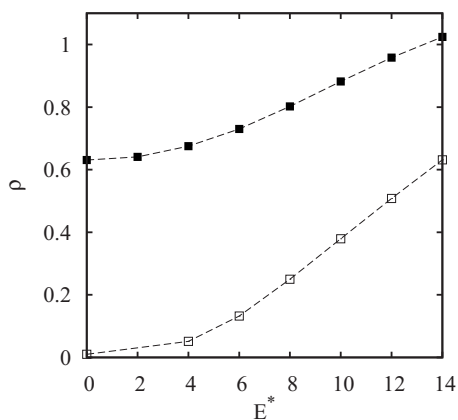


FIG. 1. Effect of the applied field on the filling of the pore by a one-component dipolar fluid. ρ is the total density in the pore and E^* the field strength in reduced units. The bulk density is $\rho_b=0.51$ (filled squares) and $\rho_b=0.0102$ (empty squares) $\mu^*=1$. The lines are a guide to the eye.

tact with the reservoir plays a negligible role.²² For this reason we will refer to the fluid in the reservoir far from this region as the “bulk.” The pore/fluid equilibrium is determined by the equality of the chemical potentials μ_1 and μ_2 of both species in the bulk and in the pore. But since the practical control variables are the total density ρ_b and mole fraction x_2 of the dipolar species, in the bulk, the latter is studied in the canonical ensemble. By considering only homogeneous states or metastable states very close to the coexistence boundary, μ_1 and μ_2 in the bulk are determined with sufficient accuracy from Widom’s insertion method (see, for example, Ref. 23 for this point). μ_1 and μ_2 are then used to study the fluid in the pore in the grand canonical ensemble. We can then compute the average density of each species in the pore as a function of ρ_b and x_2 . Hereafter, reduced variables $E^*=E(\sigma^3/kT)^{1/2}$ and $\mu^*=\mu/(kT\sigma^3)^{1/2}$ will be used and the results will be given for $\mu^*=1$. The reduced density in the pore is $\rho=\bar{N}\sigma^3/V$, with \bar{N} the average number of particles for a lateral surface S with periodic boundary conditions in the x and y directions and $V=S(H-\sigma)$ the accessible volume in the pore. We took a pore width $H=3\sigma$. In the bulk, $N=N_1+N_2$ is fixed.

III. RESULTS

We show in Fig. 1 the first basic mechanism: a field induced filling of the pore by a one-component dipolar fluid. At increasing field strength E^* , the pore is progressively filled by the dipoles with a rate that depends on ρ_b . For the value of the E^* and μ^* used here, the explanation seems that the field-dipole interaction energy $-\sum_i \mu_i \cdot E$ offsets the entropy loss due to their orientation in the direction of the field. This is more visible at low ρ_b , in which case the slope is nearly constant beyond $E^*=8$. For a particle diameter of $1\text{ }\mu\text{m}$ and $T=300\text{ K}$, for example, this corresponds to $E=49\times 10^{-3}\text{ V}/\mu\text{m}$ and $\mu=2\times 10^5\text{ D}$. Thanks to the scaling factor $\sigma^{-3/2}$ in its definition, the same value of μ^* is also appropriate for the dipolar interaction between molecular species. The dipole moment being then of the order of 1 D , a field strength of the order 10 V/nm is needed to obtain the same reduced energy $-\mu^*E^*$. Such field strengths are not

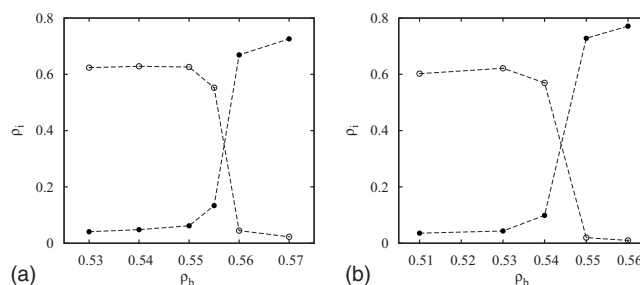


FIG. 2. Population inversion in a pore in equilibrium with a bulk mixture close to demixing. (a) Mixture of symmetric nonadditive hard-spheres. Filled circles: adsorption; open circles: desorption; the bulk concentration of the adsorbing species is $x_2=0.02$. The nonadditivity parameter is $\delta=0.2$. (b) Mixture of hard-spheres and dipolar hard-spheres with $\delta=0.2$, $\mu^*=1$, and $x_2=0.02$; filled circles: adsorption of the dipolar hard-spheres.

unusual for confinement at the molecular scale (for water in nanopores see, for example, Refs. 16 and 17; in particular Fig. 1 in the last one). Note that the equilibrium state in presence of the field may not always be the filled one at other parameters or if more complex interactions are considered (see Ref. 16, for example), due to the competition between energetic and entropic contributions.

Figure 2 illustrates the second mechanism: the relative population of a pore in equilibrium with a mixture having a natural tendency to demix. The simplest one is the mixture of nonadditive hard-spheres,²⁴ in which the cross diameter is $\sigma_{ij}=1/2(\sigma_i+\sigma_j)(1+\delta)$. Previous studies^{9,13,14} have shown that when the pore is in equilibrium with a mixture in which one species is in the minority (say, $x_2=0.02$ for a nonadditivity parameter $\delta=0.2$) a population inversion occurs in the pore when the total bulk density is varied. This occurs here for ρ_b between 0.55 and 0.56 for a pure nonadditive HS mixture and between 0.54 and 0.55 for the hard-sphere dipole mixture.

Having the basic ingredients, we may now combine them to produce the desired effect: by choosing the composition of the bulk fluid so as to be close to the population inversion in the pore, we anticipate that the closer we are from the threshold density the weaker will be the external field E_{tr}^* required to trigger it. This is shown in Fig. 3. In the

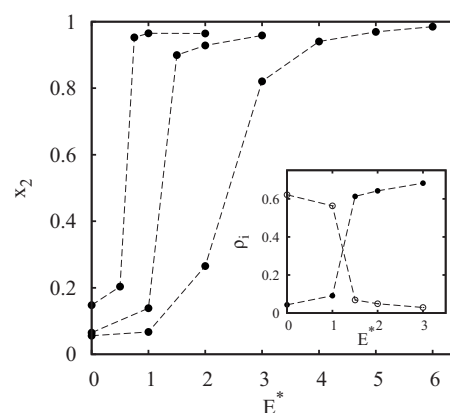


FIG. 3. Field induced dipolar selective adsorption. The curves show the dipoles mole fraction in the pore as a function of the reduced applied field strength. The curves are for a bulk mole fraction $x_2=0.02$ and bulk densities (from right to left) $\rho_b=0.51, 0.53, 0.54$. The inset shows the corresponding dipoles and hard-spheres density in the pore for $\rho_b=0.53$.

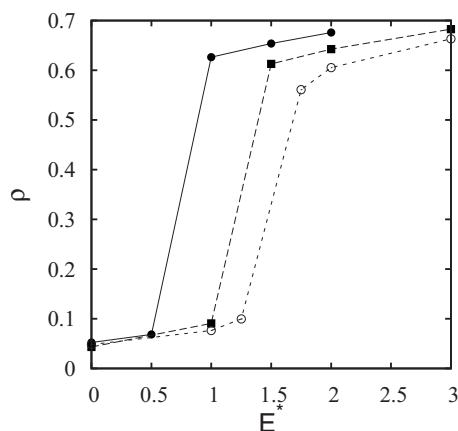


FIG. 4. Adsorption-field strength curves at different temperatures. The curves show the dipoles mean density in the pore as a function of the applied field strength at $T=285$, 300, and 325 K from left to right. The curves are for a bulk mole fraction $x_2=0.02$ and bulk densities $\rho_b=0.53$. Here $E^*(T)=E^*(300)(T/300)^{1/2}$.

most favorable case shown, the actual value of E_{tr} is about 3×10^{-3} V/ μm .

A small variation in the applied field produces the inversion: the dipolar particles are selectively absorbed by a weak change about E_{tr} , the converse being possible, perhaps with some hysteresis.¹³ Near the adsorption jump ($\rho_b=0.53$, $E^*=0.5$ for $\mu^*=1$) a slight change in temperature ($\delta T=25$ °C in Fig. 4) produces a detectable change in adsorption. This observation may be important for some applications (since the reduced variables combine E and μ with T , while $E=0$ in the bulk, one has to rescale E^* by the factor $T^{1/2}$ to compare two temperatures at a given values of E).

Finally, in order to check the effect of a different interaction u_{12} between species 1 and 2, we also show in Fig. 5 the result for a Yukawa repulsive potential. We observe that the phenomenon is quite general. The requirement for observing a sensitive field effect is that the self-coordination

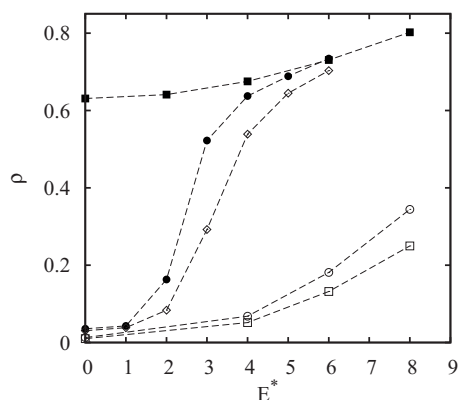


FIG. 5. Effect of the applied field on the filling of the pore by different model fluids. ρ is the density of the dipolar species, in the pore. Empty squares: one-component dipolar fluid (for $\rho_b=0.0102$ as in Fig. 1); open circles: additive mixture of hard-spheres and dipoles (with $x_2=0.02$ and $\rho_b=0.51$ in the bulk). Diamonds: same for a Yukawa repulsion between the dipoles and the hard-spheres; filled circles: same for the nonadditive hard-spheres-dipolar hard-spheres mixture. The range of the Yukawa potential (with $\epsilon^*=8$) gives the same contribution to the second virial coefficient as the nonadditive hard-spheres potential with $\delta=0.2$. Filled squares: one-component dipolar fluid with $\rho_b=0.51$ (as in Fig. 1).

should be more favored in the mixture. The poor miscibility can be favored by suitable chemical composition of the particles surface layers.^{25,26} Weak specific interaction with the pore walls can be achieved similarly.

As our main goal was to demonstrate the phenomenon of a field activated adsorption from an unstable mixture, we used a simple simulation strategy. Accordingly, we did not conduct a detailed study of the behavior of the confined fluid. For instance, phase equilibrium in the pore may take place before the spontaneous condensation (adsorption jump) predicted in the grand canonical simulation.²⁷ According to Duda *et al.*,¹³ the inversion line for nonadditive hard-spheres is close to the bulk fluid coexistence line but the two phenomena are different. We actually observed that the inversion corresponds to a bulk fluid close to demixing or slightly in the two-phase region. Regardless of this, the essential point is that the density in the liquidlike phase should be close to the value after the adsorption jump, as in one-component systems.²⁷ The precise relation between these observations and other phenomena such as capillary condensation, wetting, hysteresis, etc. (see, e.g., Refs. 27–29) will be discussed in future work.

IV. CONCLUSION

In conclusion, these results show that the combination of two generic mechanisms allows a quite sensitive control of the pore filling. Although this method has been demonstrated for particles that are closest to the optimum conditions (i.e., hard-sphere-like colloids), none of them is exclusive; and since the basic mechanisms (demixing instability and coupling with an external field) are quite generic, this prediction should concern a broader class of systems (including molecular ones). In order to benefit from the field effect, one species should be either polar (e.g., ferrocolloid in magnetic fields) or much more polarizable than the other (the results given here being relative to permanent dipoles³⁰). The solution should also not contain free charges to avoid particle motion due to the action of the field (electrohydrodynamic flows), not considered in this simple model. Polar molecules being on the other hand rather common, one should consider in this case also the role of specific interactions. We believe that further experimental studies and simulations on this method are worthwhile given the diversity of possible applications of this field controlled composition of the confined fluid and hence flexible control of the physical properties that depend on the composition of the confined fluid. Just as an example, one may consider to modulate in this way the dielectric response of the confined fluid for optical applications.

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