Controlling the composition of a confined fluid by an electric field

C. Brunet, J. G. Malherbe and S. Amokrane

Physique des Liquides et Milieux Complexes,
Faculté des Sciences et de Technologie, Université Paris Est,
61 av. du Général de Gaulle, 94010 Créteil Cedex, France

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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.

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 e.g.\[3, 4\] and refs\[5\] for more recent work), one practical advantage of using colloids is
the possibility to tune their effective interaction (eg. 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 [3, 8, 9, 10, 11, 12, 13, 14] and references therein). Since we seek a method in which the pore geometry, 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 $E = E \mathbf{u}_z$ normal to the walls. As in [15], we considered a mixture in which one species bears a dipole moment $\mu$, 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 non-additive diameter $\sigma_{12}$ in the potential $u_{12}^{HS}$ (see also the discussion of figure 5). Both species have a hard-sphere interactions with the walls. This makes the model more appropriate 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 [16] (see also and [17] for a slit pore), but not from a bulk mixture. Previous studies considered the role of the pressure in one-component fluids (eg. [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 e.g. [15, 16, 19, 20, 21]). We already pointed out how
the structure can be modulated by the combination of various interactions \cite{10,11} and by
the action of the field \cite{15}. However, only the density profile of the particles through the pore
could be modulated in \cite{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
of the density of each component in the pore. The physical pore is assumed large enough that
the interfacial region in which it is in contact with the reservoir plays a negligible role \cite{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 $\mu_1$ and $\mu_2$ of both species in the bulk and in the pore. But since the practical control variables are the total density $\rho_b$ 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, $\mu_1$ and $\mu_2$ in the bulk are determined with sufficient accuracy from Widom’s insertion method (see for eg \cite{23} for this point). $\mu_1$ and $\mu_2$ 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 $\rho_b$ and $x_2$. Hereafter, reduced variables $E^* = E(\sigma^3/kT)^{1/2}$ and $\mu^* = \mu/(kT\sigma^3)^{1/2}$ will be used. 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 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 figure 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 $\rho_b$. For the value of the $E^*$ and $\mu^*$ used here, the explanation seems that the field-dipole interaction energy $-\sum_i \mu_i E$ offsets the entropy loss due to their orientation in the direction of the field. This is more visible at low $\rho_b$ in which case the slope is nearly constant beyond $E^* = 8$. For a particle diameter of 1$\mu$m and $T = 300K$, for example, this corresponds to $E = 49 \times 10^{-3}V/\mu m$ and $\mu = 2 \times 10^5D$. Thanks to the scaling factor $\sigma^{-3/2}$ in its definition, the same value of $\mu^*$ is also appropriate for the
dipolar interaction between molecular species.

![Graph](attachment:image.png)

FIG. 1: Effect of the applied field on the filling of the pore by a one-component dipolar fluid.

$\rho$ 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). The lines are a guide to the eye.

The dipole moment being then of the order of one Debye, a field strength of the order $10 \text{V/nm}$ is needed to obtain the same reduced energy $-\mu^*E^*$. Such field strengths are not unusual for confinement at the molecular scale (for water in nanopores see for example [16] and [17], in particular figure 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 non-additive 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 minority (say $x_2 = 0.02$ for a non additivity parameter $\delta = 0.2$) a population inversion occurs in the pore when the total bulk density is varied. This occurs here for $\rho_b$ between 0.55 and 0.56 for a pure non-additive HS mixture and between 0.54 and 0.55 for the hard-sphere dipole mixture.
(a) Mixture of symmetric non-additive hard-spheres. Filled circles: adsorption; Open circles: desorption; the bulk concentration of the adsorbing species is $x_2 = 0.02$. The non-additivity 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.

FIG. 2: Population inversion in a pore in equilibrium with a bulk mixture close to demixing.

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 $E^{tr}_t$ required to trigger it. This is shown in figure 3. In the most favorable case shown the actual value of $E_{tr}$ is about $3 \times 10^{-3} V/\mu m$.

A small variation of 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 adorption jump ($\rho_b = 0.53$, $E^* = 0.5$ for $\mu^* = 1$) a slight change in temperature ($\delta T = 25^\circ C$ in figure 4) produces a detectable change in adsorption. This observation may be important for some applications (since the reduced variables combine $E$ and $\mu$ 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,
FIG. 3: 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. Dipoles mean density in the pore as a function of the applied field strength at $T = 285K$, 300K and 325K from left to right. The bulk mole fraction is $x_2 = 0.02$ and bulk densities are $\rho_b = 0.53$. Here $E^*(T) = E^*(300)(T/300)^{1/2}$. 
we also show in figure 5 the result for a Yukawa repulsive potential.

FIG. 5: Effect of the applied field on the filling of the pore by different model fluids. 
\( \rho \) is the density of the dipolar species, in the pore. *Empty squares*: one-component dipolar fluid (for \( \rho_b = 0.0102 \) as in figure 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 non-additive 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 non-additive hard-spheres potential with \( \delta = 0.2 \). *Filled squares*: one-component dipolar fluid with \( \rho_b = 0.51 \) (as in figure 1).

We observe that the phenomenon is quite general. The requirement for observing a sensitive field effect is that the self coordination should be more favored in the mixture. The poor miscibility can be favored by suitable chemical composition of the particles surface layers \[26, 27\]. 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 \[25\]. According to Duda al.\[13\], the inversion line for non-additive 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 liquid-like phase should be close to the value after the adsorption jump, as
in one-component systems \cite{25}. The precise relation between these observations and other
phenomena such as capillary condensation, wetting, hysteresis, etc. (see e.g. \cite{25,28,29})
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 dipoles). 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.

[1] Fundamentals of adsorption : proceedings of the Fourth International Conference on Funda-
mentals of Adsorption, Kyoto, edited by M. Suzuki, Elsevier Amsterdam (1993).
[2] C. Bechinger, Current Opinion in Colloid and Interface Science 77, 204 (2002).
[3] Z. Tan, Keith E. Gubbins, J. Phys. Chem. 96, 845 (1992)
[4] V. Lachet, A. Boutin, B. Tavitian and A.H. Fuchs, Faraday Discuss., 106, 307 (1997)
[5] F. K. Katsaros, Th. A. Steriotis, G. E. Romanos, M. Konstantakou, A. K. Stubos, and N. K. Kanellopoulos, Microporous and Mesoporous Materials 99, 181 (2007); J. Pires, M. Bestilleiro, M. Pinto, and A. Gil, Separation and Purification Technology 61, 16 (2008); A. Busch, Y. Gensterblum, B. M. Krooss, and N. Siemons, Int. J. of Coal Geology 66, 53 (2006).

[6] A. Yethiraj and A. van Blaaderen, Nature (London) 421, 513 (2003).

[7] H. A. Stone, A. D. Stroock, A. Ajdari Annual Review of Fluid Mechanics 36, 381 (2004).

[8] L. Sarkisov, and P. A. Monson, Langmuir 17, 7600 (2001).

[9] Y. Duda, E. V. Vakarin, J. Alejandre, J. Colloid. Interface. Sci. 258, 10 (2003).

[10] A. Ayadim, J. G. Malherbe and S. Amokrane, J. Chem.Phys. 122, 234908 (2005).

[11] S. Amokrane, A. Ayadim and J. G. Malherbe, J. Phys. Chem. C, 111, 159825 (2007).

[12] A. De Virgiliis, R. L. C. Vink, J. Horbach and K. Binder Phys. Rev. E 78, 041604 (2008).

[13] F. Jiménez-Angeles, Y. Duda, G. Odriozola, and M. Lozada-Cassou, J. Phys. Chem. C, 112, 18028 (2008).

[14] S. Kim, S. Suh and B. Seong, Journal of the Korean Physical Society 54, 60 (2009).

[15] C. Brunet, J. G. Malherbe, and S. Amokrane, J. Chem. Phys. 130, 134908 (2009).

[16] S. Vaitheeswaran, J. C. Rasaiah, and G. Hummer J. Chem. Phys. 121, 7955 (2004).

[17] D. Bratko, C. D. Daub, K. Leung, and A. Luzar, J. Amer. Chem Soc 127, 2504 (2007).

[18] R. R. Kotdawala, N. Kazantzis, and R. W. Thompson, J. Chem. Phys. 123, 244709 (2005).

[19] S. H. Lee, J. C. Rasaiah and J. B. Hubbard, J. Chem. Phys. 85, 5232 (1986).

[20] S. H. L. Klapp and M. Schoen, J. Chem. Phys. 117, 8050 (2002); J. Jordanovic and S. H. L. Klapp, Phys. Rev. Lett. 101, 038302 (2008).

[21] J. Richardi, M. P. Pileni, and J. -J. Weis, J. Chem. Phys. 130, 124515 (2009).

[22] A. Z. Panagiotopoulos, Molec. Phys. 62, 701 (1987).

[23] A. V. Neimark and A. Vishnyakov, J. Chem. Phys. 122, 234108 (2005).

[24] J.G. Amar, Molec. Phys. 67, 739 (1987).

[25] A. V. Neimark and A. Vishnyakov, Phys. Rev. E. 62, 1063 (2000).

[26] P. Bartlett, P., R. H. Ottewill, and P. N. J Pusey, J. Chem. Phys. 93, 1299 (1990).

[27] Y. Hennequin, M. Pollard, and J. S. van Duijneveldt, J. Chem. Phys. 120, 1097 (2004).

[28] R. Evans, U.M.B. Marconi and P. Tarazona, J. Chem. Phys. 84, 2376 (1986).

[29] E. Kierlik, M. L. Rosinberg, G. Tarjus and P. Viot, Phys. Chem. Chem. Phys. 3, 1201 (2001).