Adsorption isotherm for flexible molecules in random porous media. Can we regard the system as a binary mixture?

P. Padilla
Chemistry Laboratory III, HC Orsted Institute, Universitetsparken 5, DK-2100, Copenhagen, Denmark

C. Vega
Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

(Received 21 August 1996; accepted 21 October 1996)

The adsorption isotherm for repulsive n-alkanes in a random porous medium has been determined by computer simulation. The porous medium or matrix is obtained by quenching an equilibrium configuration of repulsive spheres. Keeping fixed this configuration of the matrix particles, Grand-Canonical Monte Carlo simulations were used to determine the adsorption isotherm of repulsive n-butane and n-hexane models in the random porous medium. In addition to that, canonical Monte Carlo simulations were performed for the equilibrium binary mixture in which the spherical and n-alkane particles are allowed to move. Chemical potential of the n-alkane molecule in the binary mixture is computed by using the test particle method. We found that, at the same chemical potential, the structure of the n-alkane in the binary mixture and in the quenched medium differs at high densities. However, at the same chemical potential, densities of the n-alkane in the random porous medium and in the binary mixture are quite similar. A consequence of that is that adsorption isotherms can be computed if the properties of the binary mixture are known. We have recently proposed an equation of state for mixtures of hard n-alkane molecules which contains as a particular case the sphere+n-alkane mixture. The chemical potential of the n-alkane in the mixture can be computed analytically and we used this result for determining adsorption isotherms. Excellent agreement with simulation is found. The results of this work suggest that the knowledge of the properties of the binary mixture can be very useful for obtaining adsorption isotherms in random porous media. Finally, the effect of attractive forces on the properties of alkanes in binary mixtures and confined in a random porous medium was also studied. In general, the presence of attractive forces reduces the similarity between the properties of alkanes in these two systems. © *1997 American Institute of Physics.* [S0021-9606(97)50105-X]

I. INTRODUCTION

Adsorption of fluids in pores of well defined geometry (planar wall, slit pore, spherical cavities) have received considerable attention during the last decade.[1] A number of simulation and theoretical studies using integral equation or density functional theory have been presented so that a fairly good understanding of these systems has been achieved. Another interesting problem is the adsorption of fluids in systems with micropores in which the matrix is disordered even on molecular length scale. For these systems the pores do not present a fixed geometry and the structure of the matrix presents a certain degree of randomness or disorder. For instance silica gels, which are usually used in adsorption experiments, cannot be modeled by pores of well defined geometry since the gels present a more or less random structure. An important step towards the understanding of the adsorption on these systems was made by Madden and Glandt who consider the fluid-solid system as a binary mixture with one component quenched. Madden and Glandt[2] were able to write a set of Ornstein-Zernicke like equations for the fluid-quenched matrix problem which are commonly denoted as the Madden and Glandt equations (MG). Given and Stell[3] showed that certain graphs were missing in the original derivation and proposed the correct version of the Madden and Glandt equations, although they showed that the exact version reduces to the former one when the Percus-Yevick closure is used.

It was soon clear that the determination of adsorption isotherms from the structural results obtained from the MG equations would be of great interest. After some unsuccessful attempts,[4,5] Vega *et al.*[6] proposed a compressibility route for determining the chemical potential of the fluid in the porous material. Vega *et al.* thought this route to be approximate but later on Ford and Glandt[7] and Rosinberg *et al.*[8] independently showed that this route is exact when the Percus-Yevick closure is used in the MG equations. Ford and Glandt and Rosinberg *et al.* obtained the exact expression for obtaining the chemical potential of the fluid from the structural information arising from the MG equations.[7,8] Therefore the exact set of equations governing the structure of the fluid in the random medium, and the exact expression to obtain the chemical potential of the fluid from this structure are now known exactly. For binary mixtures, the OZ equations and the routes to determine the chemical potential from the structural information are well known since long ago. At least now we know what to do although not so much about how to do it.

In this paper we focus on a different issue. It was found in Ref. 6 that the chemical potentials of the fluid in the porous material and in the binary mixture are quite similar when the matrix particles are much bigger than the fluid ones. Recently Ford, Thompson and Glandt[9] have also found the same result for the case in which the matrix particles are of the same or smaller size than the fluid particles. These two works show that the chemical potential of the fluid in the binary mixture and in the porous medium are quite similar regardless of the size ratio between fluid and matrix particles. Can we understand these results? For the case in which the matrix particles are bigger than the fluid ones the similarity in the chemical potential follows directly from the similarity in the structure. In Ref. 6 it was found that when matrix particles are bigger than fluid ones then the structure of the fluid in the binary mixture is almost identical to that of the fluid in the porous medium. This similarity in the structure is a direct consequence of the fact that certain graphs appearing in the density expansion of the structural functions of the mixture do not contribute much when the size ratio between matrix and fluid particles is large. For the case in which the matrix particles are smaller than the fluid ones the origin of the similarity between the chemical potentials is not clear, since in this case the structure of the fluid in the binary mixture and in the porous medium are probably different. In any case, although further work is still needed to understand the origin of this similarity, the important result arising from Refs. 6, 9 is that the chemical potential of the fluid in a binary mixture and in a porous medium are quite similar regardless of the size ratio between fluid and matrix particles. The importance of this result should not be overlooked. It means that approximate (but reliable) adsorption isotherms can be obtained if the chemical potential of the fluid in the binary mixture is known. Much is known about equilibrium binary mixtures. The point we want to make here is that this information can be used for obtaining interesting results on an apparently unrelated problem: the determination of adsorption isotherms in random porous media. This idea has recently been used within a mean field treatment.[10]

In particular, we shall focus in this paper on the adsorption of n-alkanes particles in a random porous medium of spherical particles. The reason for choosing this system is threefold. First we want to test whether the similarity in the chemical potential of the fluid in the quenched medium and in the equilibrium mixture holds also for a fluid composed of nonspherical particles. Second we want to analyze the problem of the conformational equilibrium within the pore. Certainly the confinement may induce changes in the population of the different conformers of the n-alkane.[11] Finally since a good equation of state (EOS) is now available for mixtures of hard n-alkane models[12–14] (the spherical + n-alkane mixture being a particular case) we want to apply it for obtaining the adsorption isotherm of the n-alkane in the random porous medium. That will illustrate how the determination of adsorption of complex particles can be faced with quite simple tools.

The scheme of the paper is as follows. In Section II we discuss the evaluation of the total chemical potential for flexible models. In Section III a theoretical equation of state for mixtures of hard n-alkane models will be presented. Details concerning the simulations performed in this work will be given in Section IV. Results will be presented in Section V and in Section VI the conclusions will be discussed.

II. THE CHEMICAL POTENTIAL OF FLEXIBLE MODELS

In this section an expression for the total chemical potential of flexible molecules will be derived. Let us assume that the Rotational Isomeric State approximation (RIS) is valid, and we regard a fluid composed of flexible molecules as a multicomponent mixture.[15] For instance, fluid n-butane is regarded as a tri-component mixture of trans, $gauche^+$ and $gauche^-$. For simplicity let us assume that for the flexible model in consideration there are only two conformers (the extension to the case of more conformers is trivial). The two possible conformers (components of the mixture) are denote as A and B. The free energy of the system, A, is given by[16]

$$A=-kT\,\ln\left(\frac{q_A^{N_A}q_B^{N_B}}{N_A!N_B!}\,\frac{\int\,\exp(-\beta U(N_A,N_B))dN_A dN_B}{V^{N_A+N_B}}\right),\tag{1}$$

where N_A and N_B are the number of A and B molecules respectively, $\beta=1/kT$, V is the volume, dN_A and dN_B denote integration over the coordinates of the N_A and N_B particles, U is the potential energy of the system and q_A is the ideal gas partition function of molecule A which is given by:

$$q_A=(\Lambda_A^{-3}V)(q_A^v q_A^{\rm rot})\exp(-D_A^*)=f(T)V\,\exp(-D_A^*),\tag{2}$$

where Λ_A is the de Broglie thermal wavelength of molecule A, q_A^v is the vibrational partition function, $q_A^{\rm rot}$ the rotational partition function, and D_A^* is the electronic energy of molecule A in the ground state in kT units. A similar expression can be written for q_B. For simplicity let us assume that Λ_A, q_A^v and $q_A^{\rm rot}$ have the same values for molecules A and B, so that the product of all these functions is denoted as $f(T)$ or simply f. Then Eq. (1) can be rewritten after some algebra as:

$$\begin{aligned}\frac{A}{NkT}=&-\ln(f(T))+(\ln(\rho)-1)+x_A D_A^*+x_B D_B^*\\&+x_A\,\ln(x_A)+x_B\,\ln(x_B)\\&-\frac{1}{N}\,\ln\left(\frac{\int\,\exp(-\beta U)dN_A dN_B}{V^{N_A+N_B}}\right),\end{aligned}\tag{3}$$

where x_A is the molar fraction of component A and $\rho=(N_A+N_B)/V$ is the total number density of the system. Then by using the standard thermodynamic relation:

$$\frac{\mu_A}{kT}=\left(\frac{\partial A/kT}{\partial N_A}\right)_{T,V,N_B}\tag{4}$$

one obtains for the chemical potential of component A μ_A

$$\frac{\mu_A}{kT}=\frac{\mu_A^{\mathrm{id}}}{kT}+\frac{\mu_A^{\mathrm{conf}}}{kT}=(-\ln(f)+D_A^{*}+\ln(\rho x_A)) -\ln\langle\exp(-\beta U_A^{\mathrm{test}}(N_A,N_B))\rangle, \tag{5}$$

where $U_A^{\mathrm{test}}(N_A,N_B)$ is the intermolecular interaction energy of a test particle of type A when inserted into a fluid with N_A particles of type A and N_B particles of type B. The brackets in Eq. (5) denote canonical average. The ideal part is defined by the sum of the first three terms on the right hand side of Eq. (5), and the configurational part by the last term. We define the configurational part of a given property as the difference of this property in the real system and in a system of non-interacting particles when both are at the same temperature, density and *composition*. This is different from a residual property. Residual properties are the difference between the thermodynamic properties of the real system and that of an ideal gas at the same temperature and density. Note that the composition of the ideal gas may differ from that of the real system so that configurational and residual properties are not the same. The formulas presented so far are valid for any kind of binary mixture. However, in the case that molecules A and B are in chemical equilibrium (interconversion between molecules or conformers A and B is possible) then it must also holds that:

$$\mu_A=\mu_B. \tag{6}$$

The mass law arising from Eqs. (5)–(6) can be written as:

$$\frac{x_B}{x_A}=\frac{x_B^0}{x_A^0}\ \exp(-\beta(\mu_B^{\mathrm{conf}}-\mu_A^{\mathrm{conf}})), \tag{7}$$

where x_A^0 is the molar fraction of component B at zero density which is proportional to $\exp(-D_A^{*})$ (we assume that the rest of the ideal gas partition function is identical for both conformers). If components A and B are in chemical equilibrium then the Gibbs energy of the system, G, can be written as:

$$G=N_A\mu_A+N_B\mu_B=N\mu. \tag{8}$$

The importance of Eq. (8) is as follows. If one wishes to compute the chemical potential of the flexible molecule, then it is sufficient to compute the chemical potential of one selected conformer, say A (after all, the chemical potential of all the conformers is the same since they are in chemical equilibrium).

Before finishing this discussion let us evaluate the derivative of A/NkT with respect to the molar fraction of component A (i.e x_A). Starting from Eq. (3) and taking into account that $x_B=1-x_A$ one obtains:

$$\left(\frac{\partial A/NkT}{\partial x_A}\right)_{T,V,N}=\mu_A/kT-\mu_B/kT. \tag{9}$$

What Eq. (9) says is that the derivative of the free energy with respect to the molar fraction of component A is just the difference in the chemical potential between components A and B. If the system is in chemical equilibrium then Eq. (6) must hold, and that means that the derivative in Eq. (9) must be zero, or in other words that the free energy must by a minimum with respect to variation in composition at a given temperature, volume and total number of particles.

Eqs. (1-9) can easily be extended to the multicomponent case. In the case of λ different conformers, the condition of chemical equilibrium given by Eq. (6) is replaced by $\lambda-1$ equations (Eq. (6) with the conformers 1 and λ, 2 and $\lambda,\ldots,\lambda-1$ and λ). Also Eq. (9) is now replaced by a system of $\lambda-1$ equations, implying on the right hand side, conformers 1 and λ, conformers 2 and λ, 3 and λ and so on. Finally the presented formalism can also be extended to the case in which one cannot enumerate the different conformers, since they form a continuum depending on a given variable or set of variables. For instance, we can think that n-butane is a system where the different configurations (values of the torsional angle) form a continuum defined by the variable ϕ_1' which can take values from 0 to 2π. In the case of n-pentane the different configurations form a continuum defined by the value of the two torsional angles (ϕ_1',ϕ_2'). Let us denote as ϕ the set of torsional angles defining the configuration of the molecule (we assume bond lengths and angles are fixed), so that the integral of $d\phi$ is one:

$$d\phi=\frac{d\phi_1' d\phi_2' \ldots d\phi_s'}{(2\pi)^s}, \tag{10}$$

$$\int_0^1\cdots\int_0^1 d\phi=\frac{\int_0^{2\pi}\cdots\int_0^{2\pi} d\phi_1' d\phi_2'\cdots d\phi_s'}{(2\pi)^s}=1, \tag{11}$$

where s is the number of torsional degrees of freedom of the molecule. Let us now define $p(\phi)$ as the probability distribution function (normalized to one) of the torsional angles. In particular, $p(\phi)d\phi$, is the probability of finding a molecule with the torsional angles between ϕ and $\phi+d\phi$. The function $p(\phi)$ must satisfy:

$$\int_0^1\cdots\int_0^1 p(\phi)d\phi=1. \tag{12}$$

The function $p(\phi)$ is a probability density. For a system with a continuous distribution of the torsional angles Eq. (5) must be rewritten as:

$$\frac{\mu_\phi}{kT}=-\ln(f)+D_\phi^{*}+\ln(\rho p(\phi))-\ln\langle\exp(-\beta U_\phi^{\mathrm{test}})\rangle \tag{13}$$

and Eq. (8) is replaced by an integration over ϕ of the product of N $p(\phi)\mu_\phi$. The continuous version of Eq. (9) for a system in chemical equilibrium is:

$$\frac{\delta(A/NkT+\tau(\int p(\phi)d\phi-1))}{\delta p(\phi)}=0, \tag{14}$$

where we now use functional derivation. τ is a Lagrange multiplier which guarantees that the function $p(\phi)$ is normalized to one. Eq. (14) is a well known result within density functional theory.[17–19]

III. THEORETICAL EOS FOR HARD N-ALKANE MIXTURES

Wertheim[20] and Chapman *et al.*[21] have recently proposed an EOS for chains of m tangent hard spheres. The compressibility factor Z as given by Wertheim's EOS is:

$$Z=\frac{p}{\rho kT}=(m)\frac{1+y+y^2-y^3}{(1-y)^3}-(m-1)\frac{1+y-y^2/2}{(1-y)(1-y/2)}, \tag{15}$$

where the packing fraction, y, is given by the product of the number density of the chains times the molecular volume. In principle, Wertheim EOS is only valid for tangent hard spheres. We have recently shown[12–14] how to extend Wertheim EOS for chains with overlapping between contiguous sites so that hard n-alkane models can be described. In addition, an extension to hard n-alkane mixtures has also been proposed.[14] Our extension of Wertheim EOS to multicomponent hard bodies mixtures is given by:

$$Z=\frac{p}{\rho kT}=(2\alpha_{\mathrm{mixture}}-1)\frac{1+y+y^2-y^3}{(1-y)^3}-(2\alpha_{\mathrm{mixture}}-2)\frac{1+y-y^2/2}{(1-y)(1-y/2)}, \tag{16}$$

where the non-sphericity parameter $\alpha_{\mathrm{mixture}}$, the volume V_{mixture} and the packing fraction of the mixture y are given by:

$$\alpha_{\mathrm{mixture}}=\sum x_\omega \alpha_\omega, \tag{17}$$

$$V_{\mathrm{mixture}}=\sum x_\omega V_\omega, \tag{18}$$

$$y=\rho V_{\mathrm{mixture}}. \tag{19}$$

The sums in Eqs. (17) and (18) run over the different components of the mixture. V_ω, α_ω and x_ω are the volume, non-sphericity parameter and molar fraction respectively of component ω and ρ is the total number density. The non-sphericity parameter α_ω of component ω is defined through the second virial coefficient of this component (see Refs. 12, 13, 22 for details):

$$\alpha_\omega=\frac{1}{3}\left(\frac{B_{\omega\omega}}{V_\omega}-1\right), \tag{20}$$

where $B_{\omega\omega}$ is the second virial coefficient of the hard ω particles. Basically we can say that we are using Wertheim EOS with the parameter m of the original theory replaced by $2\alpha_{\mathrm{mixture}}-1$. This replacement ensures that the second virial coefficient of the mixture, as obtained from Wertheim EOS, is very close to the exact value. Let us now apply the previous equations to the particular case of a hard sphere + n-alkane mixture. We shall use the RIS approximation for the n-alkane. Let us assume that there are ν possible conformers. Then the sphere+n-alkane mixture has $1+\nu$ different components (the sphere is the component 1 and the conformers are the components 2 to $1+\nu$). In this work we shall consider equimolar sphere-n-alkane mixtures. Therefore Eq. (17) now reads (taking into account that the value of the non-sphericity parameter of a spherical particle is one):

$$\alpha_{\mathrm{mixture}}=\frac{1}{2}+\sum_{\omega=2}^{1+\nu} x_\omega \alpha_\omega, \tag{21}$$

$$\sum_{\omega=2}^{1+\nu} x_\omega=\frac{1}{2}. \tag{22}$$

A similar expression can be written for V_{mixture}. Note that since we are studying equimolar sphere+n-alkane mixtures the sum of the molar fractions of the different n-alkane conformers must be 0.5 as stated in Eq. (22). The ν components of the n-alkane are in chemical equilibrium and therefore, we have $\nu-1$ equations as Eq. (6) (see previous section). Thus, the values of x_ω in Eqs. (21) and (22) are not arbitrary. In fact they must guarantee that the chemical potential of the different conformers is the same. As it was shown in the previous section this is equivalent to minimize the free energy of the system with respect to variations of the molar fraction of the different conformers of the n-alkane. Consequently, the values of x_ω are obtained by solving the following set of equations:

$$\left(\frac{\partial A/NkT}{\partial x_\omega}\right)_{T,V,N}=0 \qquad \omega=2,3,\ldots, \tag{23}$$

along with the normalization condition given by Eq. (22). The free energy, A, is the sum of the ideal, A^{id} and configurational, A^{conf} free energies. These are given by:

$$\frac{A^{\mathrm{id}}}{NkT}=\frac{1}{2}\ln\left(\frac{1}{2}\right)+\sum_{\omega=2}^{1+\nu} x_\omega \ln(x_\omega/\Omega_\omega)+\sum_{\omega=2}^{\omega=1+\nu} x_\omega D_\omega^*, \tag{24}$$

$$\frac{A^{\mathrm{conf}}}{NkT}=2(\alpha_{\mathrm{mixture}}-1)\ln\left(\frac{2(1-y)^2}{(2-y)}\right)-\frac{(2\alpha_{\mathrm{mixture}}-1)(2y-3)}{(1-y)^2}-3(2\alpha_{\mathrm{mixture}}-1). \tag{25}$$

In Eq. (24) Ω_ω is the degeneracy of conformer ω. For instance, the *trans-gauche* conformer of n-pentane (tg) has $\Omega_{tg}=4$ since tg^+,tg^-,g^+t,g^-t are equivalent conformers. D_ω^* is the intramolecular energy of conformer ω (in kT units) with respect to the all trans conformer (which is taken as the zero of energies). The configurational free energy was obtained from integration of Eq. (16). Solution of Eqs. (21)–(25) allow the determination of x_ω and hence of the total free energy for a given density and temperature. The pressure is then obtained from Eq. (16). Values of α_ω and V_ω for the different conformers of n-alkanes from n-butane up to n-octane have been reported in Ref. 12. The configurational chemical potential of conformer η, μ_η^{conf}, is obtained from the thermodynamic relation:

$$\left(\frac{\partial A^{\mathrm{conf}}/kT}{\partial N_\eta}\right)_{T,V,N_\omega\neq N_\eta}=\mu_\eta^{\mathrm{conf}}/kT \tag{26}$$

which when Eq. (25) is used yields:

$$\mu_{\eta}^{\mathrm{conf}}/kT=\frac{A^{\mathrm{conf}}}{NkT}+\frac{(Z-1)}{y}\rho V_{\eta}+\frac{\partial A^{\mathrm{conf}}/NkT}{\partial \alpha_{\mathrm{mixture}}}\times\left(\alpha_{\eta}(1-x_{\eta})-\sum_{\omega=1,\omega\neq\eta}^{1+\nu}\alpha_{\omega}x_{\omega}\right). \tag{27}$$

Note that although the total chemical potential of all the conformers must be the same, this is not necessarily true for the configurational part. Eq. (27) can also be used to determine the configurational chemical potential of the spherical particle.

The procedure presented so far can be considered as a discrete version of density functional theory. After all we are writing the total free energy as a function of the molar fractions (the singlet correlation function) and minimizing the total free energy with respect to variations in composition (the functional must be stationary). This methodology was already presented in Refs. 12 and 13. We applied it to n-alkane models to obtain the changes in conformational equilibrium with density at a given temperature. Nevertheless, for n-alkanes changes in conformational equilibrium with density at a given temperature were found to be small, and for that reason, good results for the equation of state and configurational properties can be obtained by using the ideal gas population of conformers. That avoids the somewhat cumbersome procedure of solving Eq. (23) at each temperature and density. In summary, instead of solving Eq. (23) one can simply use the ideal gas population of conformers, using it for determining the EOS, configurational free energy and configurational chemical potential of conformer η by using Eq. (16), Eq. (25) and Eq. (27) respectively, with the set of x_{ω}^{0} instead of x_{ω}. The values of x_{ω}^{0} are obtained from:

$$x_{\omega}^{0}=\frac{\Omega_{\omega}\exp(-D_{\omega}^{*})}{\sum_{\omega=2}^{1+\nu}\Omega_{\omega}\exp(-D_{\omega}^{*})}\quad \omega=2,3,\ldots,1+\nu. \tag{28}$$

For the equimolar sphere-n-alkane mixture, a factor of 0.5 must be included on the right hand side of Eq. (28) (the sum of the molar fraction of the different conformers of the n-alkane must be 0.5). D_{ω}^{*} will be obtained from Eq. (13) and Eq. (7) of Ref. 13. In our theoretical calculations we will not consider conformers including $g^{+}g^{-}$ or $g^{-}g^{+}$ sequences since their probability of occurrence is very small[15] (this is usually denoted as the pentane effect).

IV. SIMULATION DETAILS

In the present section the potential models used in this work as well as the details of the simulations will be described. The united atom model will be used for describing the n-alkane, so that for instance n-butane is described by four interaction sites located on the position of the carbon atoms. The bond length and bond angle are fixed. The C-C bond length is set to $l=1.53$ Å, and the C-C-C bond angle to $\theta=109.5°$. We shall use the torsional potential proposed by Ryckaert and Bellemans.[23] Two kinds of pair potentials will be simulated, the full Lennard-Jones potential (LJ), and the Weeks Chandler-Andersen (WCA) reference system[24] corresponding to the LJ model. We would like to stress that in the present work we do not want to make any attempt of comparing our results with experiment, hence, the model chosen for representing alkane chains is not an optimized one.

We shall first describe the LJ model. The expressions for the sphere-sphere interaction u_{mm}, sphere-n-alkane u_{mf} and n-alkane-n-alkane u_{ff} are given by:

$$u_{mm}^{\mathrm{LJ}}=4\epsilon_{mm}\left(\left(\frac{\sigma_{mm}}{r}\right)^{12}-\left(\frac{\sigma_{mm}}{r}\right)^{6}\right), \tag{29}$$

$$u_{ff}^{\mathrm{LJ}}=\sum_{i=1}^{i=n}\sum_{j=1}^{j=n}4\epsilon_{ff}\left(\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{6}\right), \tag{30}$$

$$u_{mf}^{\mathrm{LJ}}=\sum_{i=1}^{i=n}4\epsilon_{mf}\left(\left(\frac{\sigma_{mf}}{r_{mi}}\right)^{12}-\left(\frac{\sigma_{mf}}{r_{mi}}\right)^{6}\right). \tag{31}$$

In this work, $\sigma_{mm}=5.4804$ Å, $\sigma_{ff}=3.923$ Å, $\sigma_{fm}=4.7017$ Å (applying Lorentz-Berthelot mixing rule) and $\epsilon_{mm}/k=\epsilon_{ff}/k=\epsilon_{fm}/k=72$ K. The value of sigma for the spherical molecules, σ_{mm}, is chosen so that the spherical particle has a volume very close to that of the n-butane chain. Eq. (30) describes the interaction energy between two different n-alkane molecules. In this equation, r_{ij} is the distance between interaction site i in molecule 1 and interaction site j in molecule 2. The number of carbon atoms in the n-alkane is denoted as n. In addition to that, we shall also use an intramolecular LJ interaction between interaction sites separated by at least four C-C bonds. In Eq. (31) r_{mi} denotes the distance between the sphere and the site i of the n-alkane.

The WCA system can be easily obtained from the expressions of the LJ potential given by Eqs. (29)–(31) by applying the general expression:

$$u^{\mathrm{WCA}}=u^{\mathrm{LJ}}+\epsilon \quad r<2^{1/6}\sigma, \tag{32}$$

$$u^{WCA}=0 \quad r>2^{1/6}\sigma \tag{33}$$

to the mm, fm and ff interactions. For the WCA model the simulations were performed at $T=366.88$ K. At this temperature the Barker-Henderson prescription[25] applied to the WCA n-alkane-n-alkane potential yields for the diameter of the equivalent hard spheres (d) $d=3.7109$ Å, so that the reduced bond length is $L^{*}=l/d=0.4123$. Virial coefficients of hard n-alkane models for this elongation have been recently determined.[12] These second virial coefficients will be used in the application of the theory described in the previous section to the present model.

In summary, in this work two type of pair potential functions have been used, a LJ type and WCA type. Additionally, two types of systems will be considered. The first system is an equilibrium equimolar binary mixture sphere+n-alkane (the molar fraction of the spherical component and of the n-alkane are 0.5), and the second is a quenched matrix made up of spherical molecules in which the n-alkane chains are adsorbed.

Let us first discuss the way in which the computer simulations of the binary mixture were performed. The equilibrium binary mixture was studied by NVT Monte Carlo (MC) simulation. During the simulation, conformer populations, intermolecular structure and the chemical potential of the n-alkane were evaluated. The total chemical potential of the n-alkane in the mixture will be obtained as follows. From the discussion of Section II, we know that the condition of chemical equilibrium implies that the chemical potential of all the different conformers be the same. The general expression for the chemical potential of a given conformer within the mixture is given by (according to the discussion of Section II and Eq. (13)):

$$\frac{\mu_\phi}{kT} = -\ln(f\sigma_{ff}^3) + D_{\boldsymbol{\phi}}^* + \ln(\rho_f^*) + \ln(p(\boldsymbol{\phi})) - \ln\langle \exp(-\beta U_{\boldsymbol{\phi}}^{\text{test}})\rangle, \tag{34}$$

where we have defined the reduced number density as:

$$\rho_f^* = \frac{N_f}{V}\sigma_{ff}^3 \tag{35}$$

and N_f is the number of n-alkane molecules in the system. We shall set the value of $f\sigma_{ff}^3$ to one so that the first term on the right hand side of Eq. (34) is zero. Eq. (34) is valid for any conformer. When applied to the all trans conformer (the conformer with all torsional angles set to zero) one obtains:

$$\frac{\mu_{tt\cdots t}}{kT} = D_{tt\cdots t}^* + \ln(\rho_f^*) + \ln(p(tt\cdots t)) - \ln\langle \exp(-\beta U_{tt\cdots t}^{\text{test}})\rangle, \tag{36}$$

where $D_{tt\cdots t}^*$ is the intramolecular energy (in kT units) of the all *trans* conformer, and $p(tt\cdots t)$ is the probability density of finding the all *trans* conformer in the simulated mixture. The intramolecular energy $D_{tt\cdots t}^*$ is given by the summation of the torsional energy, and the site-site intramolecular energy. In the particular case of the all trans conformer the torsional energy is zero, thus, only the site-site intramolecular energy must be evaluated. Eq. (36) can easily be implemented. During the NVT MC simulation, an all *trans* test particle is randomly inserted in the mixture from time to time. The interaction energy of this test particle with the rest of the particles of the system is computed. In this way $\langle \exp(-\beta U_{tt\cdots t}^{\text{test}})\rangle$ is computed. Also, during the simulation the probability of finding an all trans conformer is estimated. We evaluated $p(tt\cdots t)$ as:

$$p(tt\cdots t) = \left\langle \frac{N_f(t\pm\Delta, t\pm\Delta, .., t\pm\Delta)}{N_f(\Delta/\pi)^{n-3}} \right\rangle, \tag{37}$$

where the numerator in Eq. (37) is the number of molecules with all the bonds located within $\pm\Delta$ radians of the perfect *trans* state (this with all the torsional angles set to zero). In this work we set the value of Δ in radians so that it corresponds to 5 degrees. The power $(n-3)$ appears in the denominator of Eq. (37) due to the fact that for an n-alkane with n interaction sites there are $(n-3)$ torsional degrees of freedom.

Equation (36) can also be applied to other conformers different from the all *trans.* That constitutes a cross-check of the calculations since the chemical potential of the different conformers should be identical (they are in chemical equilibrium). It is interesting to stress that with Eq. (36) we are computing the total chemical potential.

In the NVT simulations we typically used 80 alkane chains and 80 spherical particles. We performed 200000-250000 MC steps for equilibration and 1000000-1250000 MC steps for obtaining averages in the case of the WCA system, and 400000 MC steps for equilibration and 2000000 MC steps for obtaining ensemble averages in the case of the LJ model. Each MC step consists of an attempt to displace the center of mass of a molecule (chain or sphere), an attempt to rotate a chain, and an attempt to partially or totally regrow a chain using the configurational bias method.[26] The matrix-carbon and intermolecular carbon-carbon correlation functions were obtained during the run. Every 400 MC steps we perform 1000 attempts of inserting a test particle for the computation of the configurational part of the chemical potential.

Now let us describe the second kind of simulations carried out in this work for an alkane confined in a matrix of quenched spheres. This system will be studied by Grand Canonical MC (GCMC) simulations. First, a MC NVT simulation of a system made up of spherical particles only is performed. One of the equilibrium configurations is quenched and, after that, spherical particles will remain fixed in their positions during the rest of the calculations. The system composed of quenched spherical particles will form the matrix (random porous medium) in which the n-alkane fluid will be confined. GCMC simulations are now performed so that the adsorption isotherm can be computed. The adsorption isotherm gives for a given temperature, densities of the n-alkane molecules in the random medium for different values of the chemical potential. The input data in GCMC simulations are temperature, volume and chemical potential, and in our case the configuration of the matrix particles. General details concerning GCMC simulations can be found in Ref. 27. Here we only describe special aspects concerning our system. Smit and Siepmann,[28,29] have recently introduced a quite useful methodology for performing GCMC simulations of chain molecules. They introduce a new concept which is denoted as an ideal chain. In our case the ideal chain is made up of n-alkane particles which (i) do not present intermolecular interactions; (ii) present intramolecular interactions of torsional type described in this work by the Ryckaert and Bellemans torsional potential; (iii) do not present intramolecular site-site interactions.

Note that an ideal chain *is not* an ideal gas. An ideal gas satisfies (i) and (ii) but not requirement (iii).

Let us assume that we create an experimental set up like the one shown in Fig. 1. System I is a binary equilibrium mixture, system II is a gas made up of ideal n-alkane chains, and system III is the n-alkane fluid confined in the random porous medium. Note that there is not spherical particles in system II. The three phases are in thermal (but not in mechanical) equilibrium. Let us assume that the n-alkane particles are in chemical equilibrium, and therefore present the same chemical potential in the three phases. When the equilibrium is established the number density of the n-alkane in

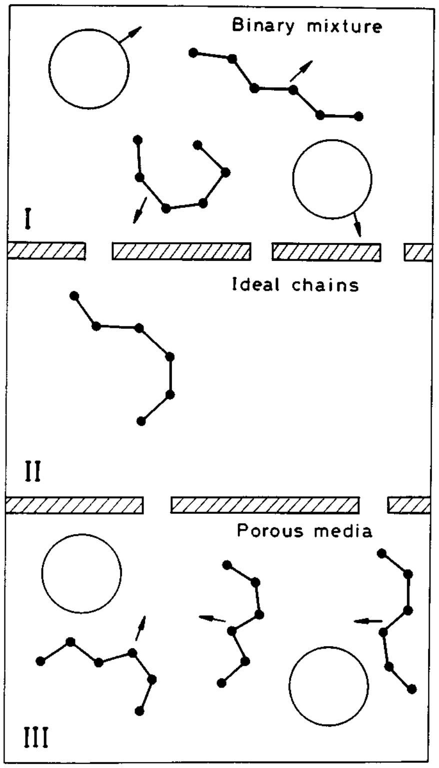

FIG. 1. Imaginary set-up in which an equilibrium binary mixture (spherical + n-alkane particles) denoted as phase I is in equilibrium with a gas made up of ideal chains (see main text for the definition of an ideal chain) denoted as phase II, and this phase II is in equilibrium with a quenched matrix of spherical particles which is denoted as phase III. Equilibrium between phases I, II, and III is thermal but not mechanical. In addition to that the n-alkane molecules in the three phases are in chemical equilibrium. The number densities of spherical particles in phases I and III are the same. However, the number density of n-alkane particles in phases I, II, and III are in general different.

the binary mixture, ideal chain, and the confined fluid are $\rho^*_{f,\mathrm{mixture}}$ $\rho^*_{f,\mathrm{IC}}$ and $\rho^*_{f,\mathrm{quenched}}$ respectively.

Using the general formalism developed in Section II, the chemical potential of an ideal chain can be obtained if the chemical potential of the ideal chain in the all *trans* conformation (or in any other conformation) is known. By using Eq. (36) and taking into account that for the ideal chain the last term in Eq. (36) is zero, and the first term is zero for the all *trans* conformer one obtains:

$$\frac{\mu^{\mathrm{IC}}_{tt\cdots t}}{kT}=\ln(\rho^*_{f,\mathrm{IC}})+\ln(p^{\mathrm{IC}}(tt\cdots t)), \tag{38}$$

where the superscript IC denotes properties of the ideal chain. For an ideal chain, $p(tt\cdots t)$ is a function of temperature only and is given by:

$$p^{\mathrm{IC}}(tt\cdots t)=\left(\frac{\pi\int_{-\Delta}^{\Delta}\exp(-\beta u_{\mathrm{tor}}(\phi_1'))d\phi_1'}{\Delta\int_0^{2\pi}\exp(-\beta u_{\mathrm{tor}}(\phi_1'))d\phi_1'}\right)^{n-3}, \tag{39}$$

where u_{tor} stands for the torsional potential. The limits of integration in the numerator of Eq. (39) arise from the fact that the *trans* conformer has been defined as this within the interval $\pm\Delta$.

If the phases I and II are in chemical equilibrium with respect to the n-alkane molecules, we can equate the chemical potential of both systems given by Eqs. (36) and (38) to obtain:

$$\frac{\mu_{tt\cdots t}}{kT}=\ln(\rho^*_{f,\mathrm{IC}})+\ln(p^{\mathrm{IC}}(tt\cdots t)) \tag{40}$$

which can be rearranged to:

$$\rho^*_{f,\mathrm{IC}}=\frac{\exp(\mu_{tt\cdots t}/kT)}{p^{\mathrm{IC}}(tt\cdots t)}=\frac{\exp(\mu/kT)}{p^{\mathrm{IC}}(tt\cdots t)}, \tag{41}$$

where in the last term of Eq. (41) we have dropped the subindex $tt\cdots t$, since all the conformers present the same chemical potential at equilibrium which is simply denoted as μ/kT. Therefore, for any equilibrium binary mixture for which we know the chemical potential from Eq. (36), one can obtain the density of the ideal chain in equilibrium $\rho^*_{f,\mathrm{IC}}$ from Eq. (41). What we shall do now is a GCMC simulation between a bath of ideal chains, with chemical potential μ and density $\rho_{f,\mathrm{IC}}$ and the porous medium (where n-alkane chains will be confined). We start from Eq. (4) of Smit's paper[29] which gives the probability of accepting a new n-alkane particle in the porous medium. This equation is written as:

$$P(N_f\rightarrow N_f+1)=\frac{V}{N_f+1}\rho_{f,\mathrm{IC}}\exp(-\beta(U(N_f+1)-U(N_f))), \tag{42}$$

where N_f is the current number of n-alkane molecules (already confined in the porous medium). By using the value of $\rho_{f,\mathrm{IC}}$ obtained from Eq. (41) one obtains:

$$P(N_f\rightarrow N_f+1)=\frac{V/\sigma_{ff}^3}{(N_f+1)p^{\mathrm{IC}}(tt\cdots t)}\exp(\beta(\mu-U(N_f+1)+U(N_f))) \tag{43}$$

and a similar formula can be written for the probability of removing an n-alkane particle from the confined fluid. Since our confined n-alkane fluid is in equilibrium with an ideal chain gas, the conformations of the particles that we are trying to insert into the quenched medium must obey the ideal chain distribution function of torsional angles. There is not any problem with that except that the probability of inserting chains becomes very low at high densities, so that equilibration is difficult. To improve that, we shall use configurational bias as described by Smit.[29] The final working expressions used in our GCMC calculations for the probability of either accepting the creation of a particle acc($N_f\rightarrow N_f+1$) or accepting the removal of a particle acc($N_f\rightarrow N_f-1$) are:

$$\mathrm{acc}(N_f\rightarrow N_f+1)=\min\left[1,\frac{V/\sigma_{ff}^3}{(N_f+1)p^{\mathrm{IC}}(tt\cdots t)}\exp(\beta\mu)W^n\right], \tag{44}$$

$$\mathrm{acc}(N_f\rightarrow N_f-1)=\min\left[1,\frac{N_f}{V/\sigma_{ff}^3p^{\mathrm{IC}}(tt\cdots t)\exp(\beta\mu)W^o}\right], \tag{45}$$

TABLE I. MC results for equimolar sphere+n-alkane WCA mixtures. The temperature is 366.88 K in all the cases. Densities are reduced by using σ_{ff}^3. Results for the compressibility factor Z are given. Ideal, configurational and total chemical potentials of the all *trans* conformer are shown. In parentheses the ideal, configurational and total chemical potentials of the g^+ conformer for n-butane and of the ttg^+ conformer for n-hexane are also presented. In the last column the estimate of the chemical potential of the n-alkane as given by the average of the total chemical potentials of the two considered conformers is presented.

n	ρ^*	Z	$\mu_{tt\ldots}^{\mathrm{id}}/kT$	$\mu_{tt\cdots t}^{\mathrm{conf}}/kT$	μ/kT	$\overline{\mu}$/kT
4	0.082763	1.58	−1.32(−0.94)	1.15(1.13)	−0.17(−0.19)	−0.18
4	0.206909	3.36	−0.43(−0.37)	4.23(4.16)	3.80(3.79)	3.795
4	0.331055	7.59	0.01(0.16)	10.77(10.62)	10.78(10.78)	10.78
6	0.068397	1.62	2.47(2.43)	1.39(1.37)	3.86(3.80)	3.83
6	0.170992	3.60	3.35(3.42)	5.22(5.13)	8.57(8.54)	8.555
6	0.273588	8.40	3.80(3.86)	13.68(13.62)	13.68(13.62)	13.65

where W^n and W^o are the Rosenbluth factors of the new (incoming) or the old (leaving) n-alkane chain as defined by Eqs. (14) and Eq. (17) of Ref. 29. In short, we use the same procedure described by Smit in Section 2.3 of his paper,[29] but replacing $\exp(\beta\mu^B)$ by $\exp(\beta\mu)/p^{\mathrm{IC}}(tt\cdots t)$. For growing the chains with the configurational bias method (step 2 in Section 2.3.2 of Smit's paper), we generated q trial torsional angles according to the Boltzmann distribution of the Ryckaert and Bellemans torsional potential. We use q=5 for n-butane chains and q=7 for n-hexane chains. The torsional angles were generated with the procedure introduced by Almarza *et al.*[30] We performed 250000 MC steps for equilibration and 1250000 MC steps for the collection of ensemble averages for the WCA model, and 400000 MC steps for equilibration and 2000000 MC steps for obtaining averages for the LJ model. In these simulations a MC step consist of an attempt to displace a chain, an attempt to rotate a chain, an attempt to partially or totally regrow a chain, and an attempt to insert or delete a chain (see page 160 of Ref. 29 for details). During the simulations, the average density of the confined fluid, the carbon-matrix and intermolecular carbon-carbon correlation functions, and the conformer population were evaluated.

In summary, we have performed NVT MC of an equilibrium binary mixture. The chemical potential of the all *trans* conformer is computed using Eq. (36). This is also the chemical potential of the n-alkane in the mixture denoted as μ, since all the conformers must present the same chemical potential. Then, the density of the ideal chain in equilibrium with the mixture is computed from Eq. (41). Finally, the ideal chain system is put into contact with the porous medium, at the wished chemical potential μ and a GCMC simulation is performed. To improve the efficiency of insertion we used configurational bias as described in Ref. 29. The kind of questions we want to ask by this long procedure are three. The first is: are densities of the n-alkane in the binary mixture and in the porous medium similar when both systems present the same chemical potential for the n-alkane? The second is: are the structures of the n-alkane in the binary mixture and in the porous medium similar when the chemical potential of the n-alkane is the same in both systems? The third is: is the conformational equilibrium of the n-alkane similar in the binary mixture and in the porous medium? In the next section we present the results of this work.

V. RESULTS

In this section we will show the results obtained for the model systems described in the previous section. We shall start with the results for the WCA systems. In Table I, the computer simulation results for WCA equimolar equilibrium mixtures composed of sphere+n-butane and sphere+n-hexane are presented. For each type of mixture, the three densities were chosen so that the total volume fractions correspond approximately to 0.10, 0.25 and 0.40. Results for the compressibility factor are shown in the third column. For a given volume fraction the compressibility factor of the sphere+n-hexane mixture is larger than that of the sphere +n-butane mixture. This is a consequence of the higher non-sphericity as given by Eq. (21) of the n-hexane mixture. In Ref. 14 it was shown that the non-sphericity increases with the length of the chain and that provokes an increase in the compressibility factor for a given volume fraction. The ideal, configurational, and total value of the chemical potential for the all *trans* conformers are also presented in Table I. The ideal, configurational, and total value of the chemical potential for the g^+ (n-butane) and ttg^+ (n-hexane) conformers are also included in parentheses. As it can be seen the total chemical potential of the all *trans* conformer is equal (within the uncertainty of the simulations) to that of the g^+ for n-butane and to that of the ttg^+ for n-hexane. That constitutes a cross-check of our calculations since the condition of chemical equilibrium implies that the chemical potential must be the same for all the conformers. The configurational chemical potential of the ttg^+ conformer is slightly lower than this of the all *trans* conformer. In other words the insertion of the ttg^+ conformer into the mixture is easier than the insertion of the all *trans* conformer. This can be understood from the fact that the non-sphericity of the ttg^+ conformer is lower[12] than this of the ttt. In the last column of Table I our estimate for the chemical potential of the n-alkane at the studied conditions is given. This estimate is simply the average of the total chemical potential of the all *trans* conformer and of the conformer with the gauche defect.

TABLE II. Comparison between theory and MC results for the equimolar sphere+n-alkane WCA mixtures.

n	ρ^*	Z^{MC}	Z^{theory}	$\mu_{tt\cdots t}^{\mathrm{conf,MC}}/kT$	$\mu_{tt\cdots t}^{\mathrm{conf,theory}}/kT$
4	0.082763	1.58	1.57	1.15	1.12
4	0.206909	3.36	3.32	4.23	4.11
4	0.331055	7.59	7.76	10.77	10.78
6	0.068397	1.63	1.61	1.39	1.34
6	0.170992	3.60	3.54	5.22	5.04
6	0.273588	8.44	8.53	13.68	13.51

We shall now compare the simulation results obtained in this work for the WCA systems to those from the theory described in Section III of this work. The problem is that the theory of Section III applies to a system of hard body particles and our simulations correspond to WCA systems. To overcome that, we assign a hard body diameter to the spheres and to the n-alkane sites by using Barker-Henderson prescription,[25] and we assume that properties of the WCA system are the same as those of an equivalent hard body system. In Table II, the simulations results presented in Table I are compared to the results obtained from the theory. The theoretical results correspond to those obtained from Eqs. (16) and (27), assuming that conformational changes with density are small so that the conformational population can be evaluated with Eq. (28). It should be noticed that the effect of the approximation given by Eq. (28) on the equation of state and configurational chemical potential of the different conformers is small and therefore, Eq. (28) can be safely used if one is simply interested in the determination of the thermodynamic properties of the mixture. As it can be seen in Table II, the agreement between theory and simulation is remarkably good for the EOS as well as for the configurational chemical potential of the all *trans* conformers. Moreover, the agreement does not deteriorate significantly when increasing the length of the n-alkane. Thus, we can conclude that Wertheim EOS gives a good description of the EOS and chemical potential of sphere+n-alkane mixtures. This is important since it means that it may be useful for analyzing the behavior of polymers in spherical solvents.

In Table III, the conformational population of the n-alkane in the mixture as obtained from simulation and theory is presented. Since we are now interested in analyzing conformational changes with density, when implementing the theory, Eq. (23) was solved at each temperature and density. The main effect of an increase in density is to reduce the population of the all *trans* conformer, which is quite elongated, and to increase the population of the *gtg* conformer which is by far more spherical. The same behavior was found[13] in a WCA model of pure n-hexane. The theory is again quite efficient in predicting the conformational changes with density of the mixture. In passing, we should mention that the conformational equilibrium obtained from MC simulations with fixed bond angles is identical to that obtained from Molecular Dynamics (MD) simulations where bending is allowed but with a very large value of the bending constant. The use of constraints over bond angles in MD simulations changes the conformational equilibrium so that a MC simulation and a MD simulation with fixed bond angles yield different conformational equilibrium (see Ref. 13).

TABLE III. Conformational equilibrium in sphere+n-alkane WCA mixtures. The lowest and highest densities presented in Table I for each n-alkane are denoted as ρ_1^* and ρ_2^* respectively. Results obtained from the theoretical treatment of Section III are also presented.

	ρ_1^*		ρ_2^*	
Conformer	MC	Theory	MC	Theory
t	0.597(1)	0.595	0.566(1)	0.551
g	0.403(1)	0.405	0.434(1)	0.449
ttt	0.272(4)	0.279	0.247(5)	0.241
ttg	0.364(2)	0.375	0.365(3)	0.378
tgt	0.178(2)	0.187	0.180(3)	0.188
tgg	0.060(7)	0.030	0.064(2)	0.037
gtg	0.120(1)	0.128	0.136(2)	0.154
ggg	0.006(1)	0.001	0.008(5)	0.002

TABLE IV. Average density of the n-alkane particles in the quenched medium, $\rho_{f,\mathrm{quenched}}^*$, as obtained from GCMC simulations at $T=366.88$ K for the WCA sphere-n-alkane model. Results for two independent configurations of the matrix particles are shown. Values of $\overline{\mu}$ used in the GCMC simulations are those presented in the last column of Table I. The number density of the spherical particles constituting the matrix ρ_m^* are just the half of those presented in the second column of Table I. In the last column the number density of the n-alkane, $\rho_{f,\mathrm{mixture}}$, in an equimolar binary mixture with the same chemical potential of the n-alkane is presented.

n	$\overline{\mu}/kT$	ρ_m^*	$\rho_{f,\mathrm{quenched}}^*$	$\rho_{f,\mathrm{mixture}}^*$
4	−0.18	0.0414	0.0411,(0.0415)	0.0414
4	3.795	0.1035	0.1011,(0.1019)	0.1035
4	10.78	0.1655	0.1576,(0.1571)	0.1655
6	3.83	0.0342	0.0341,(0.0341)	0.0342
6	8.555	0.0855	0.0843,(0.0847)	0.0855
6	13.65	0.1368	0.1334,(0.1341)	0.1368

Once the properties of the binary mixture have been presented, let us now present the properties of n-alkane fluids in random porous media, which were obtained from GCMC simulations. As the input value of the chemical potential in the GCMC simulations we used the values of $\overline{\mu}$ presented in the last column of Table I. Now, the output of the simulation is the average density of the n-alkane in the random porous medium. These averages are shown in Table IV. We present results for two independent configurations of matrix particles. The first thing to be noted is that there are not significant differences between the results obtained with two independent configurations of matrix particles. That guarantees that the use of only one configuration of the matrix particles yields a good estimate of the result that would be obtained by averaging over all possible configurations of the matrix particles. As the difference between the n-alkane densities for two independent configurations of the matrix is of about 0.001 (see Table IV) the use of only one configuration of the matrix particles makes the third decimal digit of the n-alkane density uncertain. This error is small, and therefore a comparison between the quenched media and the binary mixture can be performed on a solid ground. Certainly in more precise work one should consider as many configurations of the

TABLE V. Conformational equilibrium in a quenched system made up of spheres (matrix) and fluid (n-alkane particles) interacting through a WCA potential as obtained from GCMC simulations. The lowest and highest chemical potentials presented in the last column of Table I for each n-alkane are denoted as μ_1/kT and μ_2/kT respectively.

Conformer	μ_1/kT	μ_2/kT
t	0.595(5)	0.576(5)
g	0.405(5)	0.424(5)
ttt	0.272(1)	0.243(5)
ttg	0.363(2)	0.368(4)
tgt	0.178(1)	0.178(4)
tgg	0.061(1)	0.065(2)
gtg	0.120(1)	0.137(1)
ggg	0.006(1)	0.007(1)

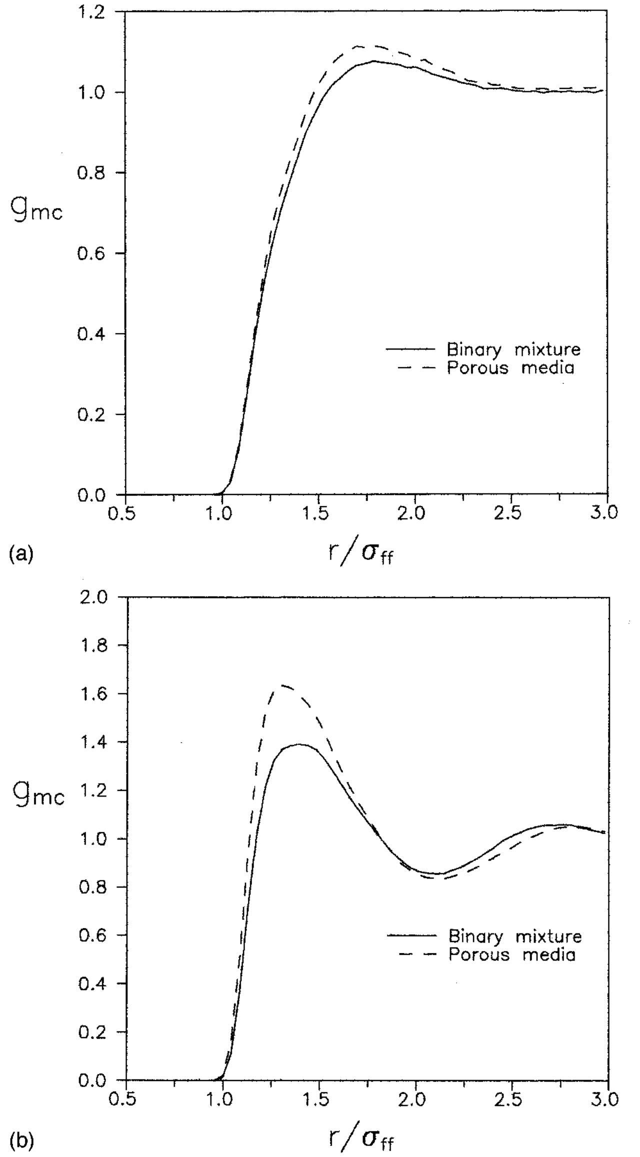

FIG. 2. Sphere-carbon correlation functions for the sphere+n-butane WCA system. Solid lines are results for the binary mixture and dashed line for the quenched medium. (a) Results for the lowest chemical potential of the n-butane particles presented in Table I. (b) Results for the highest chemical potential of the n-butane particles presented in Table I.

matrix particles as possible. In the last column of Table IV the number density of an equimolar mixture at the same chemical potential is also presented. By comparing the last two columns of Table IV we learn that at the same chemical potential, the number densities of n-alkane particles in the binary mixture and in the porous medium are quite similar (the number density of spherical particles is the same in both systems). For the binary mixture, the density of the n-alkane molecules is slightly larger than in the porous medium but the difference is never larger than 5 percent. The likeness between the densities of the n-alkane in the porous medium and in the mixture, at the same chemical potential, is probably the most important result of this work. It shows that adsorption isotherms of n-alkane in random porous media can be obtained from theoretical treatments of binary equilibrium mixtures. The results of Table IV give further evidence of the fact that, for certain properties, the confined alkane in the quenched medium and the binary mixture are not too different. The first indication of that was obtained in Ref. 6 for mixtures of spherical hard particles, further evidence was obtained in Ref. 9 again for mixtures of spherical hard particles. Now, in this work, we show that this is again true for the somewhat more complicated system of the sphere+n-alkane mixture. The message of Table IV is: at the same number density of the matrix particles and chemical potential of the n-alkane, the number densities of the n-alkane in the mixture and in the porous medium are quite similar. In Table V, the conformational equilibrium of the n-alkane confined in the porous medium at the lowest chemical potential (i.e. lowest density of n-alkane molecules) and at the highest chemical potential considered in this work are presented. As it can be seen, there is a decrease in the population of the all *trans* conformer and an increase in the population of the more spherical conformers as the *gtg* when increasing the density. By comparing the results of Tables III and V we conclude that the conformational equilibrium of the n-alkane in the mixture and in the quenched medium are rather similar.

The results presented so far emphasize the similarities between the binary mixture and the quenched medium. Does this similarity extend also to structural properties? To analyze this point in Figs. 2–5 we present results for site-site correlations functions. We have defined two site-site correlation functions, the sphere-carbon, g_{mc}, and the carbon-carbon, g_{cc}, correlation functions:

$$g_{mc}(r)=\frac{1}{n}\sum_{i=1}^{i=n} g_{m,i}(r), \tag{46}$$

$$g_{cc}(r)=\frac{1}{n^2}\sum_{i=1}^{i=n}\sum_{j=1}^{j=n} g_{i,j}(r), \tag{47}$$

where the indexes i and j run over the carbon atoms of the n-alkane and $g_{m,i}$ and $g_{i,j}$ are the site-site correlation functions between the spheres and carbon i, and between carbons

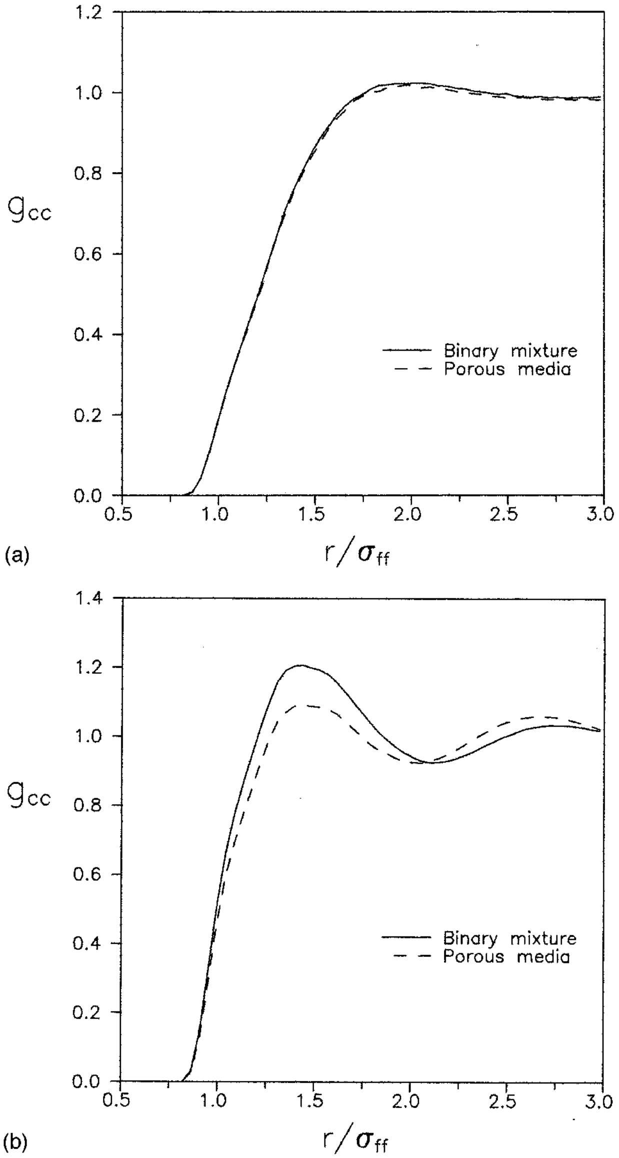

FIG. 3. As in Fig. 2 for the carbon-carbon correlation function of the sphere +n-butane WCA system. (a) Results for the lowest chemical potential of the n-butane particles presented in Table I. (b) Results for the highest chemical potential of the n-butane particles presented in Table I.

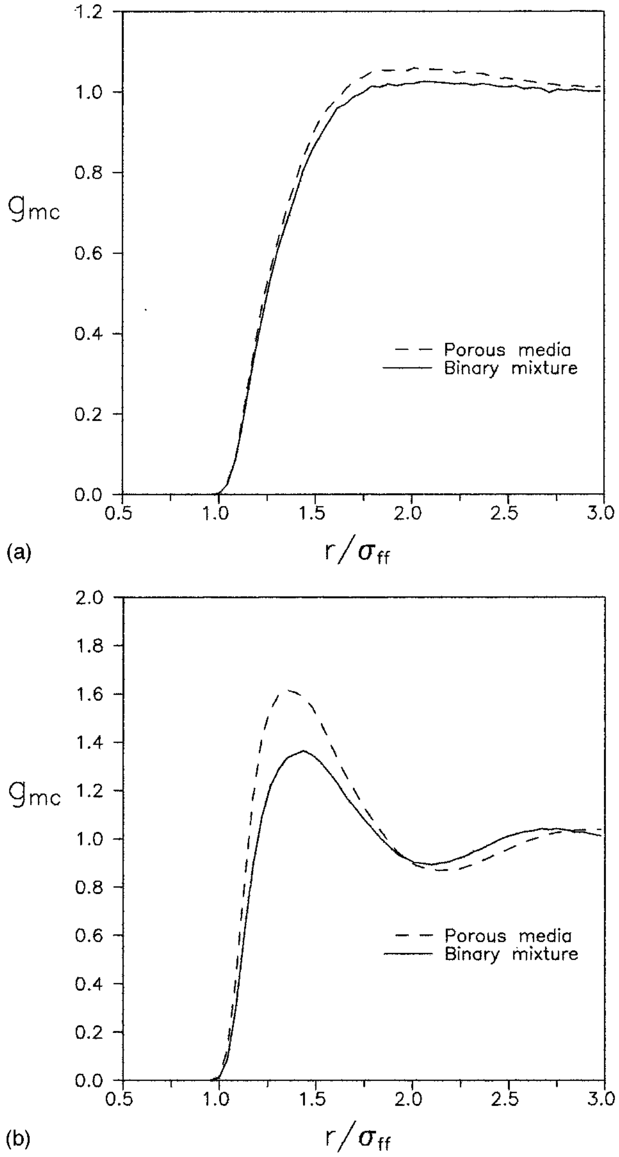

FIG. 4. Sphere-carbon correlation functions for the sphere+n-hexane WCA system. Solid lines are results for the binary mixture and dashed line for the quenched medium. (a) Results for the lowest chemical potential of the n-hexane particles presented in Table I. (b) Results for the highest chemical potential of the n-hexane particles presented in Table I.

i and *j* respectively. Note that the function g_{cc} as defined by Eq. (47) contains correlations between carbons in different molecules only.

In Fig. 2 results for the carbon-sphere correlation function in the binary mixture and in the porous medium are presented. Results correspond to the sphere+n-butane mixture. As it can be seen in Fig. 2a at the lowest chemical potential considered (i.e. lowest density of n-alkane particles) the two correlation functions are quite similar. This can be understood from the fact that the structure of an infinitely diluted fluid in a matrix is identical to that of an infinitely diluted fluid in the binary mixture. In Fig. 2b, results are presented for the highest chemical potential considered. Differences in the structure of the n-alkane in the mixture and in the porous medium are clearly visible. In Fig. 3, results for the carbon-carbon correlation functions of the sphere+n-butane system are presented. It is clear that at low densities the structure of the n-alkane in the mixture and in the porous medium are quite similar. However, at large densities differences are significant. In Fig. 4, results for the sphere-carbon correlation function of the sphere+n-hexane WCA system are displayed. Again at the lowest chemical potential, the alkane fluid in the mixture and confined present alike structures, but at the highest chemical potential they are quite different. In Fig. 5, results for the carbon-carbon correlation function in the system sphere+n-hexane are presented. Similar conclusions to those previously described for n-butane can be drawn.

The results of Figs. 2–5 illustrate that the structures of

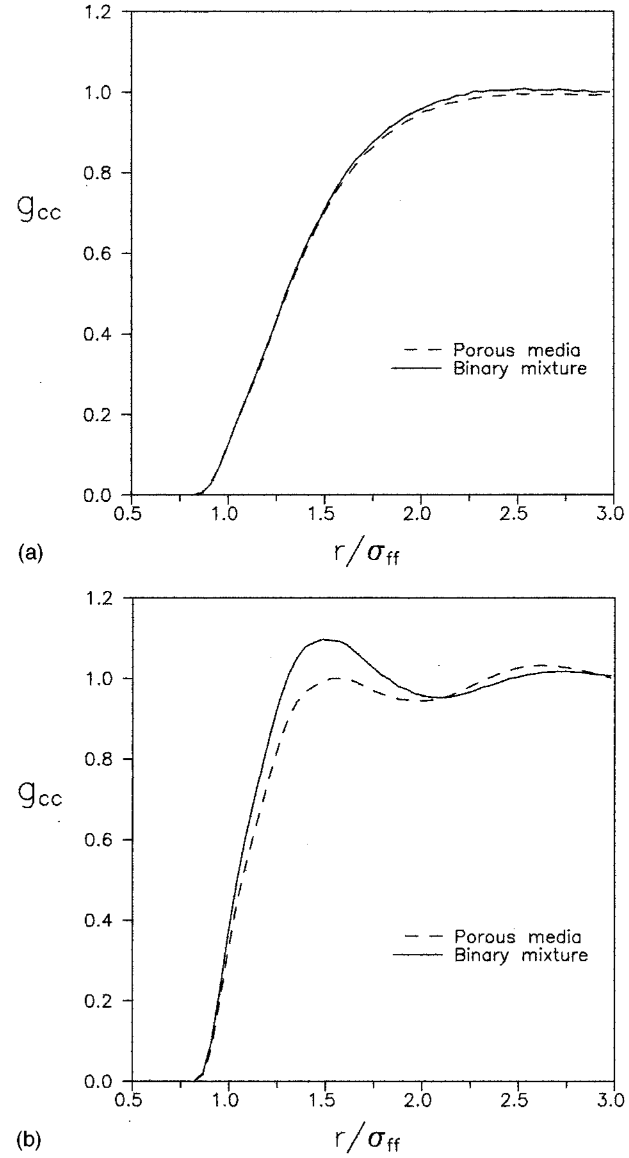

FIG. 5. As in Fig. 4 for the carbon-carbon correlation function of the sphere +n-hexane WCA system. (a) Results for the lowest chemical potential of the n-hexane particles presented in Table I. (b) Results for the highest chemical potential of the n-hexane particles presented in Table I.

the fluid (as described by site-site correlation functions) in the binary mixture and in the porous medium are alike at low densities and quite different at high densities. From the results presented in Tables III and V, we know that the conformational equilibria of the n-alkane in the mixture and in the porous medium are very similar. Therefore, the differences appearing in Figs. 2–5 are not due to differences in conformational population between these two systems. Rather, the origin of the discrepancy is a different packing of the chains in the two systems. Recently, Chandler[31] has proposed a set of integral equations for obtaining the structure of a polymer confined into a disordered porous material. The equations proposed by Chandler combine the polymer reference interaction site model theory (PRISM) of Schweizer and Curro[32] with the formalism of Madden and Glandt. These equations were recently solved by Glandt *et al.*[9,33,34] for tangent hard spheres in several porous media. It would be interesting if this theory could be implemented for models like those presented in this work. Site-site correlation functions obtained from simulation in this work may be obtained from the authors upon request.[35]

The results presented so far support the following statement: for sphere+n-alkane systems of a given composition, the thermodynamic properties and specially the chemical potential of the n-alkane in the mixture and in the porous medium are quite similar (note that this sentence is equivalent to that stated previously concerning the similarity of the n-alkane densities for a given chemical potential, and number density of matrix particles). This is true at low and high densities. Structural properties of both systems are similar when the density of both the spheres and the n-alkanes particles is low, but they differ significantly when the density of spheres and n-alkane particles is high. Further theoretical work is clearly needed in order to understand why at high densities of matrix and fluid particles, the chemical potential of the n-alkane is similar in both systems in spite of the fact that the fluid structure is rather different.

All the results presented so far correspond to a WCA sphere+n-alkane system. To see if the conclusions stated above hold also when attractive forces are included we have performed simulations of truncated LJ systems. We used the potential given by Eqs. (29)–(31) but truncated (and shifted) at 2.5σ. Matrix-matrix interactions are truncated (and shifted) at $2.5\sigma_{mm}$, fluid-matrix interactions are truncated (and shifted) at $2.5\sigma_{mf}$, and fluid-fluid interactions are truncated (and shifted) at $2.5\sigma_{ff}$. The simulations are now performed at T=550 K. This is done to avoid the two phases coexistence region. In Table VI we present the results from the NVT MC calculations. For a given volume fraction, the n-hexane mixture presents a lower compressibility factor than the mixture with n-butane. This is the opposite of what was found for the WCA systems. The chemical potential of the all *trans* conformer is identical (within the uncertainty of the simulations) with that of the other considered conformers which again constitutes a cross-check of our calculations. The results presented in Table VI indicate that, for n-butane, the configurational contribution to the chemical potential of the *gauche* conformer is lower than this of the *trans* conformer. However, for n-hexane, the configurational chemical potential of the all *trans* conformer is lower than this of the ttg^+ one. It seems that attractive forces favor the all *trans* conformer. That was already anticipated in Ref. 13.

In Table VII, results from our GCMC for the LJ systems are presented. The chemical potentials used in the GCMC simulations are those of the n-alkane molecule in the binary mixtures presented in Table VI (see last column of this table). Again, it is clear that for a given chemical potential, the density of the n-alkane in the binary mixture and in the quenched medium is similar. Nevertheless, the quantitative agreement in the value of the densities is now poorer than for the WCA model and we found that in the binary mixture the density of n-alkane molecules is higher than in the porous medium although the difference is never larger than about 10

TABLE VI. As in Table I for sphere+n-alkane LJ equimolar mixtures. The pair interactions are truncated and shifted as described in the text. The temperature is $T=550$ K. Results for the g^+ and ttg^+ conformers are shown in parentheses. In the last column the estimate of the chemical potential taken as the average of the chemical potentials of the two considered conformers is presented.

n	ρ^*	Z	$\mu^{\mathrm{id}}_{tt\cdots}/kT$	$\mu^{\mathrm{conf}}_{tt\cdots t}/kT$	μ/kT	$\overline{\mu}/kT$
4	0.082763	1.110(5)	−1.42(−1.35)	−0.35(−0.41)	−1.77(−1.76)	−1.765
4	0.206909	1.796(8)	−0.82(−0.78)	0.61(0.58)	−0.21(−0.20)	−0.205
4	0.331055	4.20(1)	−0.37(−0.28)	3.47(3.42)	3.10(3.14)	3.12
6	0.068397	1.00(1)	1.07(1.06)	−0.43(−0.41)	0.64(0.65)	0.645
6	0.170992	1.53(1)	1.98(2.02)	−0.19(−0.16)	1.79(1.86)	1.825
6	0.273588	3.87(2)	2.4(2.4)	2.7(2.9)	5.2(5.3)	5.25

percent. It should be remembered that for the WCA potential we also found a larger value of the density of n-alkane molecules in the mixture than in the porous medium although the difference in this case was never larger than 5 percent. Therefore, we conclude that although the similarity between the binary mixture and the porous medium holds also for the LJ system (a system with attractive forces) the differences are now larger than in the WCA case.

Before finishing we would like to show how the similarity between the binary mixture and the quenched medium can be used for the determination of adsorption isotherms. We shall assume that the chemical potential of the n-alkane in the binary mixture and in the quenched medium are the same for a given number density of spheres and n-alkane particles. In Fig. 6, theoretical adsorption isotherms for WCA n-butane and WCA n-hexane in a matrix of WCA spheres (the volume fraction of the spheres is approximately 0.20) are presented. Results correspond to T=366.88 K and to the WCA models described in Section IV. The adsorption isotherms were obtained from the theory for hard body mixtures described in Section II. We used the BH prescription[25] to map the WCA model into an equivalent model of hard bodies. We assumed for this simple calculation that the conformational population of the n-alkane in the bulk and in the binary mixture is given by the ideal gas distribution (see Eq. (28)). Therefore, for a given temperature, we shall simply assume that the *relative population* of the different conformers is fixed and given by Eq. (28). In Fig. 6, the adsorption of the n-alkane (i.e. the number density of n-alkane molecules in the porous medium) is plotted as a function of the pressure of the n-alkane molecules in the bulk. Fig. 6 shows the amount of n-alkane adsorbed when the porous medium is brought into contact with a pure fluid of n-alkane molecules (bulk) and the system reaches the equilibrium at a given pressure. As it can be seen, for a given pressure the adsorption of n-butane is larger than that of n-hexane. This is expected since the smaller size of the n-butane molecule makes its adsorption easier. In Fig. 7, the adsorption data of Fig. 6 are presented in a different way. Now partition coefficients of the n-alkane molecules are plotted as a function of the volume fraction of the n-alkanes in the bulk. The partition coefficient is defined as:

$$K=\frac{\rho^*_{f,\mathrm{quenched}}}{\rho^*_{f,\mathrm{bulk}}}, \tag{48}$$

TABLE VII. Average density of the n-alkane particles in the quenched medium, $\rho^*_{f,\mathrm{quenched}}$ as obtained from GCMC simulations at T=550 K for sphere-n-alkane LJ models. Values of $\overline{\mu}$ used in the GCMC simulations are those presented in the last column of Table VI. The number density of the spherical particles constituting the matrix ρ^*_m are just the half of those presented in the second column of Table VI. In the last column the number density of the n-alkane, $\rho_{f,\mathrm{mixture}}$, in an equimolar binary mixture with the same chemical potential is presented.

n	$\overline{\mu}/kT$	ρ^*_m	$\rho^*_{f,\mathrm{quenched}}$	$\rho^*_{f,\mathrm{mixture}}$
4	−1.765	0.0414	0.0407	0.0414
4	−0.205	0.1035	0.0972	0.1035
4	3.12	0.1655	0.1470	0.1655
6	0.645	0.0342	0.0336	0.0342
6	1.825	0.0855	0.0788	0.0855
6	5.25	0.1368	0.1258	0.1368

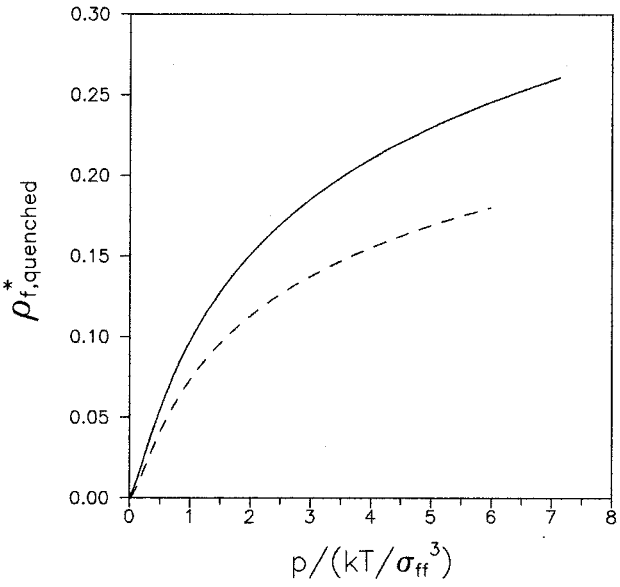

FIG. 6. Adsorption isotherms of the WCA models of n-butane and n-hexane in a matrix of WCA spheres. The model is that described in Section IV. Temperature is $T=366.88$ K. The number density of the matrix particles is fixed and corresponds to $\rho^*_m=0.1655$. Results were obtained by using the theory described in Section III and assuming that population of conformers is given by the ideal gas distribution. The reduced number density of the n-alkane molecules in the porous medium is shown as a function of the pressure of the bulk n-alkane fluid. Solid line corresponds to n-butane and dashed line to n-hexane.

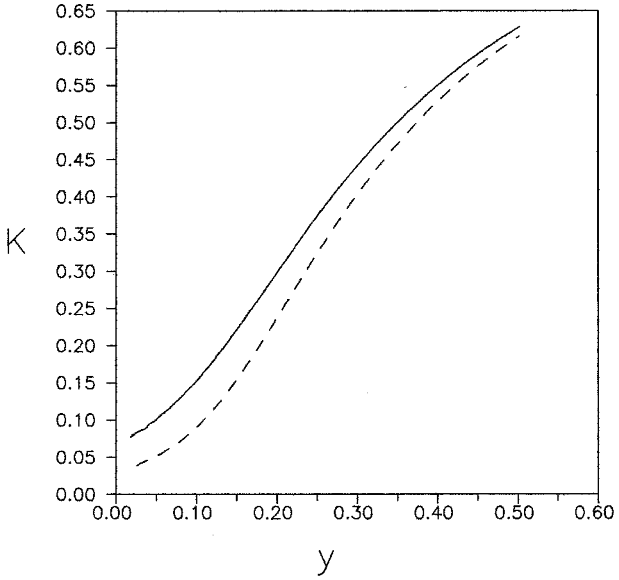

FIG. 7. Partition coefficient, K, (see Eq. (48) of the main text) of the WCA n-alkane molecules as a function of the volume fraction of the bulk n-alkane fluid. Results and conditions are those presented in Fig. 6. Solid line corresponds to n-butane and dashed line to n-hexane.

where $\rho^*_{f,\mathrm{bulk}}$ is the reduced number density of the n-alkane molecules in the bulk. As it can be seen the partition coefficient increases with the density of the bulk fluid. This is in agreement with the results of Ref. 34. The value of K for $y=0$ is just the Henry constant of the n-alkane molecule in the porous medium. As it can be seen in Fig. 7 the Henry constant for n-butane is larger than for n-hexane. This is again due to the smaller volume of the n-butane molecule.

The results shown in Figs. 6 and 7 illustrate how adsorption isotherms can be computed from the theoretical treatment described in Section III of this work.

VI. CONCLUSIONS

In this work we have performed computer simulations of WCA models of sphere+n-alkane. We considered two n-alkane models, one describing n-butane and the other describing n-hexane. In particular, NVT simulations were performed for the equilibrium equimolar mixtures of spheres and n-alkanes. By using the Widom test particle method, the chemical potential of the n-alkane in the mixture was computed. Then, by using this value of the chemical potential GCMC simulations were performed in a medium where the spheres are quenched and the average density of the n-alkane was obtained.

We found that structural properties of the fluid (site-site correlation functions) differ significantly in the mixture and in the porous medium. However, it is found that for a given chemical potential of the n-alkane the density of the n-alkane in the mixture and in the porous medium are practically the same. This can be stated in a slightly different way. One can say that for a given fixed density and composition, the chemical potential of the n-alkane in the mixture and in the quenched medium do not differ much. Similar results were previously found for spherical systems.[6,9] This work shows that this also holds for non spherical flexible molecules. Conformational changes with density in the mixture and in the quenched medium are analogous. There is a decrease in the population of the all *trans* conformer, and an increase in the population of those conformer presenting *gauche* bonds. Since conformational equilibrium in both systems is similar the differences in the site-site correlation functions found in the binary and quenched medium cannot be attributed to changes in conformational population. They are due to the different way the n-alkane chains pack in both media. These conclusions hold for n-butane and n-hexane, so that for the chains considered here there is not length dependence. We also performed simulations in LJ systems. The conclusions obtained for WCA systems hold also for the LJ potential although the presence of attractive forces makes the discrepancies in thermodynamic properties between the mixture and the porous medium slightly larger. Further theoretical work is needed to understand why the strong difference between the structure of the fluid particles (n-alkane) in the binary mixture and in the porous medium is not reflected in the chemical potential of the n-alkane which remains quite close for both types of systems.

The EOS for mixtures of hard n-alkanes proposed recently by us, can be applied to the description of mixtures of sphere+n-alkane particles. In fact, quite good agreement with simulation is found for the EOS and chemical potential in these kinds of systems. That will be quite useful in the future for considering the behavior of polymers solved in solution of spherical particles. Moreover, our finding concerning the similarity in the thermodynamic properties of the mixture and quenched medium allow us to go one step further. We simply assume that the chemical potential of the n-alkane in the quenched medium is the same as that in the binary mixture. In this way, adsorption isotherms for hard models of n-butane and n-hexane in a matrix of hard spheres have been computed.

ACKNOWLEDGMENTS

This work has been financially supported by project PB94-0285 of the Spanish DGICYT (Direccion General de Investigacion Cientifica y Tecnica). The Grant No. 11-0065-1 from the Danish Natural Science Research Council is gratefully acknowledged. P.P. acknowledges the University of Copenhagen for a Curie postdoctoral grant. The authors want to thank B. Smit for helpful discussions.

[1] R. Evans, Course of Lectures at Les Houches School on Liquids at Interfaces, 1988.
[2] W.G. Madden and E.D. Glandt, J. Stat. Phys. **51**, 537 (1988).
[3] J.A. Given and G. Stell, J. Chem. Phys. **97**, 4573 (1992).
[4] L.A. Fanti and E.D. Glandt, AIChE J. **35**, 1883 (1989).
[5] L.A. Fanti, E.D. Glandt, and W.G. Madden, J. Chem. Phys. **93**, 5945 (1990).
[6] C. Vega, R.D. Kaminsky, and P.A. Monson, J. Chem. Phys. **99**, 3003 (1993).
[7] D.M. Ford and E.D. Glandt, J. Chem. Phys. **100**, 2391 (1994).
[8] M.L. Rosinberg, G. Tarjus, and G. Stell, J. Chem. Phys. **100**, 5172 (1994).
[9] D.M. Ford, A.P. Thompson, and E.D. Glandt, J. Chem. Phys. **103**, 1099 (1995).

[10] R.D. Kaminsky and P.A. Monson, Chem. Eng. Sci. **49**, 2967 (1995).
[11] B. Smit and T.L.M. Maesen, Nature **374**, 42 (1995).
[12] C. Vega, S. Lago, and B. Garzon, J. Chem. Phys. **100**, 2182 (1994).
[13] P. Padilla and C. Vega, Mol. Phys. **84**, 435 (1995).
[14] C. Vega, L.G. MacDowell, and P. Padilla, J. Chem. Phys. **104**, 701 (1996).
[15] P.J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1968).
[16] T.L. Hill, *Statistical Mechanics* (McGraw–Hill, New York, 1956).
[17] E. Enciso, J. Alonso, N.G. Almarza, and F.J. Bermejo, J. Chem. Phys. **90**, 413 (1989).
[18] S. Tang and G.T. Evans, J. Chem. Phys. **99**, 5336 (1993).
[19] G.J. Vroege and H.N. Lekkerkerker, Rep. Prog. Phys. **55**, 1241 (1992).
[20] M.S. Wertheim, J. Chem. Phys. **87**, 7323 (1987).
[21] W.G. Chapman, G. Jackson, and K.E. Gubbins, Mol. Phys. **65**, 1057 (1988).
[22] M. Rigby, Mol. Phys. **32**, 575 (1976).
[23] J.P. Ryckaert and A. Bellemans, J. Chem. Soc. Faraday Discuss. **66**, 95 (1978).
[24] J.D. Weeks, D. Chandler, and H.C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
[25] J.A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[26] D. Frenkel, G. Mooij, and B. Smit, J. Phys. Condensed Matter, **4**, 3053 (1992); J.J. de Pablo, M. Laso, and U. W. Suter, J. Chem. Phys. **96**, 2395 (1992).
[27] See, for example, G.E. Norman, and V.S. Filinov, High Temp. Res. USSR **7**, 216 (1969); W. van Meegen and I. Snook, J. Chem. Phys. **73**, 4656 (1980).
[28] B. Smit and J.I. Siepmann, J. Phys. Chem. **98**, 8442 (1994).
[29] B. Smit, Mol. Phys. **85**, 153 (1995).
[30] N.G. Almarza, E. Enciso, J. Alonso, F.J. Bermejo, and M. Alvarez, Mol. Phys. **70**, 485 (1990).
[31] D. Chandler, J. Phys. Condensed Matter **42**, F1 (1991).
[32] K.S. Schweizer and J.G. Curro, Phys. Rev. Lett. **58**, 246 (1987).
[33] A.P. Thompson and E.D. Glandt, J. Chem. Phys. **99**, 8325 (1993).
[34] A.P. Thompson and E.D. Glandt, Macromolecules **29**, 4314 (1996).
[35] paz@st.ki.ku.dk and cvega@eucmos.sim.ucm.es