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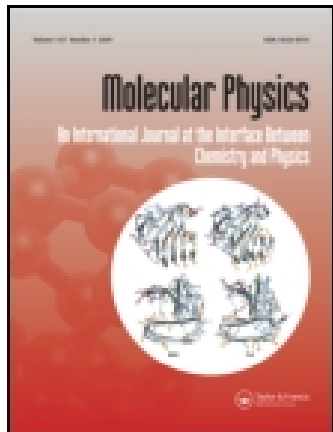
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Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tmph20>

A grand canonical Monte Carlo study of Lennard-Jones mixtures in slit shaped pores

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Published online: 23 Aug 2006.

To cite this article: Roger F. Cracknell, David Nicholson & Nicholas Quirke (1993) A grand canonical Monte Carlo study of Lennard-Jones mixtures in slit shaped pores, *Molecular Physics: An International Journal at the Interface Between Chemistry and Physics*, 80:4, 885-897, DOI: [10.1080/00268979300102741](https://doi.org/10.1080/00268979300102741)

To link to this article: <http://dx.doi.org/10.1080/00268979300102741>

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A grand canonical Monte Carlo study of Lennard-Jones mixtures in slit shaped pores

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(Received 30 March 1993; accepted 10 May 1993)

The grand-canonical Monte Carlo (GCMC) technique has been used for simulating the adsorption of mixtures in slit pores with graphite properties. Spherical Lennard-Jones models were used to model methane and ethane at super critical temperatures. A GCMC algorithm for mixtures which included attempts to change identities of particles was found to be more effective than conventional GCMC. Results were compared with density functional theory (DFT) calculations of Tan and Gubbins (1992; *J. phys. Chem.*, **96**, 845) and with ideal adsorbed solution theory (IAST) isotherms derived from single component data. Our simulation results were found to agree qualitatively rather than quantitatively with the DFT mixture results, the IAST was found to work well for the system studied. Adsorption selectivity was found to depend on packing considerations as well as the relative potential well depths of the adsorbate wall interactions.

1. Introduction

The ability to separate mixtures of gases or liquids is fundamental to a large number of industrial processes. One method of effecting a separation is to selectively adsorb one component of the mixture in a porous material. While issues such as the relative permeabilities of the mixture components in the porous material are important, the viability of many separation processes involving adsorption in a microporous material depends primarily on whether one component is sufficiently strongly adsorbed relative to another.

Multicomponent adsorption data over a wide range of state conditions are required to design the equipment for separating mixtures, and it is of considerable practical importance to have a reliable method for predicting mixed-gas adsorption isotherms. One approach to this problem is to start with adsorption data for each component in the mixture in the same way that one might start with equations of state for each component in a liquid mixture [1]. By considering the adsorbed mixture as an ideal solution at constant spreading pressure and temperature, it is possible to predict a mixed component isotherm. This is the ideal adsorbed solution theory (IAST) [2]. An alternative approach is to start with models for the intermolecular forces between the fluid particles and between the fluid and the pore and by solving the statistical mechanics of the problem, to predict the multicomponent isotherms corresponding to the model used. An exact solution of the

statistical mechanics can be obtained by computer simulation. Recently, a number of simulations of mixtures have appeared in the literature. Mixtures in slit-like pores have been investigated by Sokolowski and Fischer [3] using the molecular dynamics technique. Karavias and Myers [4], and Razmus and Hall [5] have simulated mixture adsorption in zeolites using the grand canonical ensemble Monte Carlo (GCMC) technique, while Finn and Monson [6] and Kierlik *et al.* [7] have presented results for mixture adsorption on a single solid surface using the Monte Carlo technique in the isothermal–isobaric (NPT) ensemble. As an alternative to molecular simulation, density functional theory (DFT) has also been used to study fluid–solid interfacial phenomena [8]. Versions of the DFT due to Meister, Kroll and Groot (MKG) [9, 10] and Kierlik and Rosinberg (KR) [11, 12] have been applied to the study of adsorbed Lennard-Jones mixtures. DFTs have the advantage of being less computationally intensive than full molecular simulations; it is important however to determine the accuracy of such theories in comparison with molecular simulation. The MKG theory has been compared with the Sokolowski–Fischer simulation [3] for model Ar–Kr mixtures in slit pores, while the KR theory has been compared with the Finn–Monson simulation for Ar–CH₄ on a graphite surface [6]. Broadly speaking, the density functional theories are found to be in qualitative rather than quantitative agreement with simulation for the systems on which the comparison was made; the discrepancy has been attributed to the mean field treatment of the attractive part of the sorbate–sorbate interactions.

Tan and Gubbins have modified a DFT of Tarazona [13] in order to study mixtures [14]; they have presented results for model methane–ethane mixtures in slit shaped graphitic pores over a wide range of pore sizes and physical conditions [15]. They presented a number of plots of selectivity against bulk pressure at constant temperature and constant bulk mole fraction, and have devised a classification scheme for the types of selectivity isotherm they obtain. The results they obtain for near ambient temperatures (296.2 K) for different pore sizes are of considerable significance for putative industrial methane ethane separation processes. To what extent the Tan–Gubbins results can be seen as quantitatively accurate depends firstly on the accuracy of the DFT they use (in view of other comparisons of simulation and DFT) and secondly on the extent to which a spherical Lennard-Jones model can be regarded as an accurate representation of ethane.

In this work, we present GCMC results for model methane–ethane mixtures in graphitic slit pores at near ambient temperatures. We have used the spherical models for methane and ethane used previously by Tan and Gubbins in order to facilitate comparison with their work. In addition, by simulating single component isotherms, we are also able to make a self consistent test of the ability of the IAST to predict mixture selectivity isotherms.

2. Model

The model used in this work was the same as that used by Tan and Gubbins [15]. Both ethane and methane were modelled by cut and shifted Lennard-Jones potentials:

$$u_{ij}^{\text{cs}}(r) = \begin{cases} u_{ij}^{\text{FULL}}(r) - u_{ij}^{\text{FULL}}(r_{\text{cut}}), & r < r_{\text{cut}}, \\ 0, & r > r_{\text{cut}}, \end{cases} \quad (1)$$

where r_{cut} is the cut-off (in this work $2.5\sigma_{ij}$) and u_{ij}^{FULL} is the full Lennard-Jones potential, given by

$$u_{ij}^{\text{FULL}} = -4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} \right]. \quad (2)$$

The Lennard-Jones parameters used in the simulation are summarized in table 1. Mixed parameters were calculated from the Lorentz–Berthelot rules.

The graphitic surface was treated as stacked planes of Lennard-Jones atoms. The interaction energy between a fluid particle and a single graphitic surface is given by the ‘10–4–3’ potential of Steele [16]

$$u_{\text{sf}}(z) = 2\pi\rho_s\epsilon_{\text{sf}}\sigma_{\text{sf}}^2\Delta \left[\frac{2}{5} \left(\frac{\sigma_{\text{sf}}}{z} \right)^{10} - \left(\frac{\sigma_{\text{sf}}}{z} \right)^4 - \frac{\sigma_{\text{sf}}^4}{3\Delta(0.61\Delta + z)^3} \right], \quad (3)$$

where Δ is the separation between graphite layers and ρ_s is the number of carbon atoms per unit area in a graphite layer. The values used for Δ and ρ_s were 0.335 nm and 114 nm^{-2} respectively. σ_{sf} and ϵ_{sf} are the solid–fluid Lennard-Jones parameters which were calculated by combining the graphite parameters in table 1 with the appropriate fluid parameters according to the Lorentz–Berthelot rules. The external field, $u^{(1)}$, in a slit pore of width H is the sum of the interaction with both graphitic surfaces and can be expressed mathematically as

$$u^{(1)} = u_{\text{sf}}(z) + u_{\text{sf}}(H - z). \quad (4)$$

It is important to stress that it is unlikely that ethane can adequately be represented by a one centre Lennard-Jones model. However, by using spherical models for the mixture components, comparison can be made with results from DFT and ideal adsorbed solution theory.

3. Simulation model

The technique of GCMC computer simulation is well suited to adsorption problems since it allows the chemical potential of each component in the bulk phase to be specified at the start of the simulation [17]. A drawback of the method is that the acceptance rate for creating particles in dense phases can be low, so that many configurations are required to obtain good statistics; to avoid this problem, Monson and coworkers have chosen to study adsorption phenomena in the NPT ensemble [6, 7]. For adsorption on a single surface (which is what they have studied), this method is very convenient; however, for adsorption in a slit shaped micropore, a problem arises because the pressure tensor normal to the pore walls, \mathbf{p}_{zz} , (which is an input to the simulation) is not equal to the bulk pressure, unlike the case of adsorption on a single surface.

Table 1.

Pair	σ/nm	ϵ/k_{B}
$\text{CH}_4\text{--CH}_4$	0.381	148.1
$\text{C}_2\text{H}_6\text{--C}_2\text{H}_6$	0.395	243.0
$\text{C}(\text{graphite})\text{--C}(\text{graphite})$	0.340	28.0

For a mixture of components a and b , the probability of a particular configuration in the grand ensemble is given by

$$P = \frac{V^{(N_a+N_b)} z_a^{N_a} z_b^{N_b} \exp[-\beta E_c(r)]}{\Xi N_a! N_b!}, \quad (5)$$

where $z_a = \exp(\beta\mu_a)/\Lambda_a^3$ and $z_b = \exp(\beta\mu_b)/\Lambda_b^3$ are absolute activities. $E_c(r)$ is the configurational energy and Λ_a and Λ_b are the thermal de Broglie wavelengths of each component. A standard GCMC algorithm consists of three types of trial; moving a particle, attempting to create a particle and attempting to delete a particle. In a Metropolis sampling scheme, the probability of a move being accepted is

$$P_{\text{MOVE}}^{\text{ACC}} = \min\{1, \exp[-\beta\Delta E_c(r)]\}, \quad (6)$$

where ΔE_c is the change in configurational energy resulting from the move. The probability of a creation being accepted is

$$P_{\text{CR}}^{\text{ACC}} = \min\left[1, \frac{V z_i}{N_i + 1} \exp[-\beta\Delta E_c(r)]\right], \quad (7)$$

and the probability of a deletion being accepted is

$$P_{\text{DEL}}^{\text{ACC}} = \min\left[1, \frac{N_i}{Z_i V} \exp[-\beta\Delta E_c(r)]\right], \quad (8)$$

where subscript i refers to either components a or b . For a two-component system, it is possible to use an additional type of trial, i.e. changing the identities of adsorbed particles.

Consider a trial in which a methane molecule is changed into an ethane molecule. The ratio of probabilities of the new and old states is given by

$$\frac{P(N_e + 1, N_m - 1)}{P(N_e, N_m)} = \frac{N_m z_e}{(N_e + 1) z_m} \exp[-\beta\Delta E_c(r)]. \quad (9)$$

In a Metropolis algorithm, particle swaps are accepted with probability

$$P_{\text{SWAP}}^{\text{ACC}} = \min\left[1, \frac{N_m z_e}{(N_e + 1) z_m} \exp[-\beta\Delta E_c(r)]\right]. \quad (10)$$

The number of ethane to methane and methane to ethane attempted swaps were kept the same to maintain microscopic reversibility. The acceptance probability of an ethane to methane swap is given by equation (10) with the subscripts m and e interchanged.

We tested to see whether it was advantageous to use the particle swap move by running two simulations at the same state point but using different algorithms. The results are summarized in table 2. The ratio of mole fractions in the pore was chosen

Table 2. GCMC. $z_m \sigma_{mm}^3 = 0.03$. $z_e \sigma_{mm}^3 = 0.03$. $kT/\epsilon_{mm} = 2.0$. $H = 2.5\sigma_{mm}$. 1×10^7 configurations.

Algorithm	$\langle x_e/x_m \rangle$	$\text{Var}(x_e/x_m)$
GCMC without swaps	9.53	7.488
GCMC with swaps	9.56	7.66

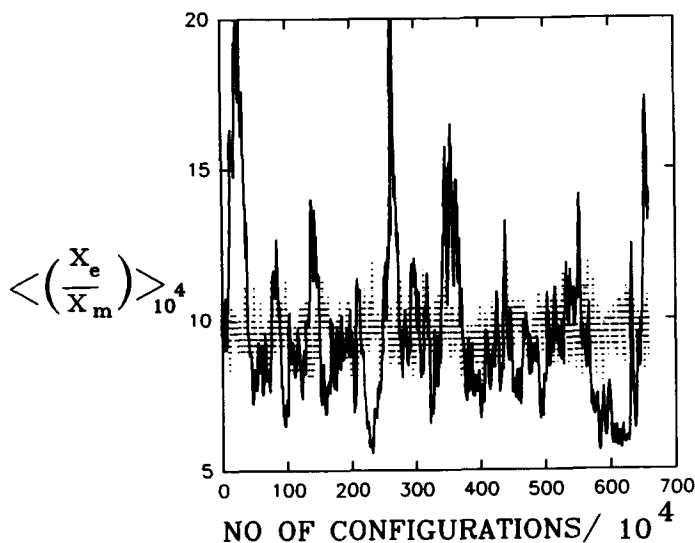


Figure 1. Successive averages over 10^4 configurations, without particle swaps (solid line) and with particle swaps (dotted line).

as the bench mark quantity because it is closely related to the adsorption selectivity. It can be seen from the results in table 2 that both methods yield an ensemble average value for the ratio of mole fractions differing by less than statistical error. Likewise the variance of the ratio of mole fractions agree within statistical error. Figure 1 is a 'control chart' showing averages taken over successive blocks of 10 000 configurations for GCMC algorithms with and without swaps. The average over 10 000 configurations is much more stable for the algorithm with swaps than for the algorithm without. It is important to stress that consideration of the fluctuation of averages over 10 000 configurations is a very different matter from the fluctuation in (x_e/x_m) *per se*, the variance of this quantity being the same within statistical error for both algorithms.

It is clear therefore while both algorithms lead to the same results, the algorithm incorporating particle swaps is far less prone to statistical error than the algorithm without. In the rest of the paper, the results are calculated from a GCMC algorithm using particle swaps. Simulations were run for 10^7 configurations on an Intel i860 processor. A simulation containing 300 particles took approximately 3 h.

4. The ideal adsorbed solution theory (IAST)

The IAST [2] is essentially an application of Raoult's law to adsorbed phases. For a given component i , we can write

$$Py_i = P_i^0(\pi)x_i, \quad (11)$$

where y_i and x_i are the bulk and pore mole fractions of i respectively, P is the total bulk pressure and $P_i^0(\pi)$ is the bulk pressure corresponding to spreading pressure π in the single-component isotherm of component i . GCMC was used to generate single-component isotherms for methane and ethane for which P_i^0 and π are related

according to

$$\pi(P_i^0) = \frac{RT}{A} \int_0^{P_i^0} n_i^0(p) d \ln p. \quad (12)$$

It is possible for example to calculate x_i for a given P and y_i by first solving for $P_i^0(\pi)$ in the equation

$$\sum_i \frac{P y_i}{P_i^0(\pi)} - 1 = 0. \quad (13)$$

This equation follows from (11) since the sum of the mole fractions in the pore must equal unity.

To implement the IAST, we first simulated single-component isotherms. The adsorption uptake was fitted over three separate low, moderate and high pressure regions to a smooth tenth-order polynomial in pressure. We found that accurate fitting in the low-pressure region is particularly important because of the nature of the integral in (12). The latter was evaluated for various values of P_i^0 , using Simpson's rule, and a smooth tenth-order polynomial was used to fit π to P_i^0 . Equation (13) was solved using a Newton–Raphson method.

5. Comparison of IAST, GCMC and DFT

Simulated single-component isotherms (GCMC) for methane and ethane in slit pores of width $H/\sigma_{mm} = 2.5$ and width $H/\sigma_{mm} = 8.0$ are shown in figures 2 and 3. Here H is the ‘carbon to carbon’ or physical width of the slit, the inner or chemical width, H' , is equated to $H - \Delta$, where Δ is the width of the graphite planes. The results are for a reduced temperature of $kT/\epsilon_{mm} = 2.0$ (296.2 K). In the reduced units of pressure used, $P\sigma_{mm}^3/\epsilon_{mm} = 0.1$ corresponds to approximately 37 bar. The pressure was calculated from the absolute activity (which is the input to the simulation) by also running a GCMC program for bulk fluid. Figures 4–6 show ‘selectivity isotherms’ for a methane–ethane mixture in a slit pore of width

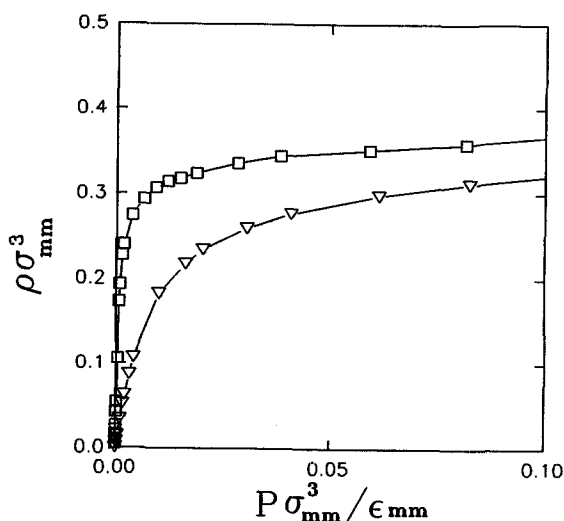


Figure 2. Single-component isotherms for ethane (\square) and methane (∇), in a graphitic slit pore of width $H/\sigma_{mm} = 2.5$, $kT/\epsilon_{mm} = 2.0$ (296.2 K).

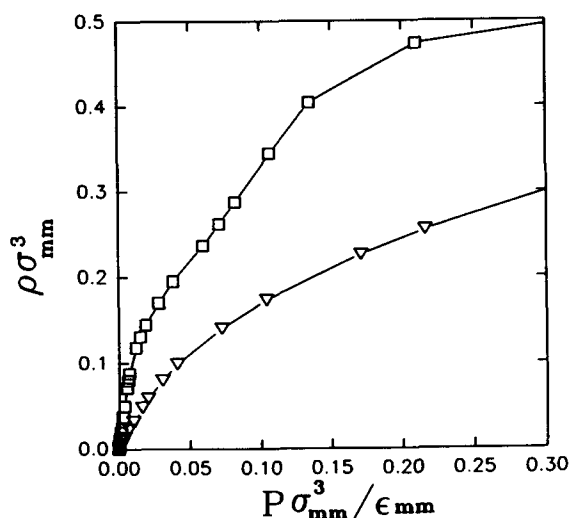


Figure 3. Single-component isotherms for ethane (\square), and methane (∇), in a graphitic slit pore of width $H/\sigma_{mm} = 8.0$, $kT/\epsilon_{mm} = 2.0$ (296.2 K).

$H/\sigma_{mm} = 2.5$ for various bulk composition. Figure 7 shows 'selectivity isotherms' for a pore of width $H/\sigma_{mm} = 8.0$ for equimolar bulk concentrations. We have defined selectivity in the usual way as the ratio of the mole fractions in the pore divided by the ratio of the mole fractions in the bulk, namely

$$S = \frac{y_e/y_m}{x_e/x_m} \quad (14)$$

Strictly speaking, the isotherms (from GCMC) were generated at a fixed ratio of activities, rather than bulk mole fraction; in practice this means that in figure 4 the GCMC results refer to $y_m = 0.5$ at the low-pressure end and $y_m = 0.47$ at

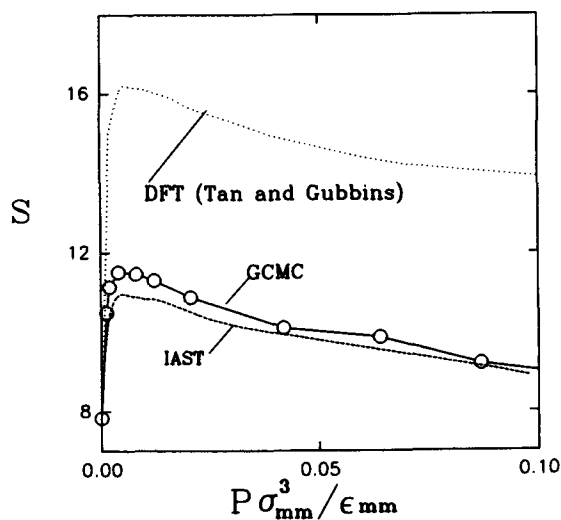


Figure 4. Comparison of GCMC, IAST and DFT results (from [15]). Methane-ethane mixture adsorbed in a graphitic slit pore. $H/\sigma_{mm} = 2.5$, $kT/\epsilon_{mm} = 2.0$ (296.2 K). $y_m = 0.5$.

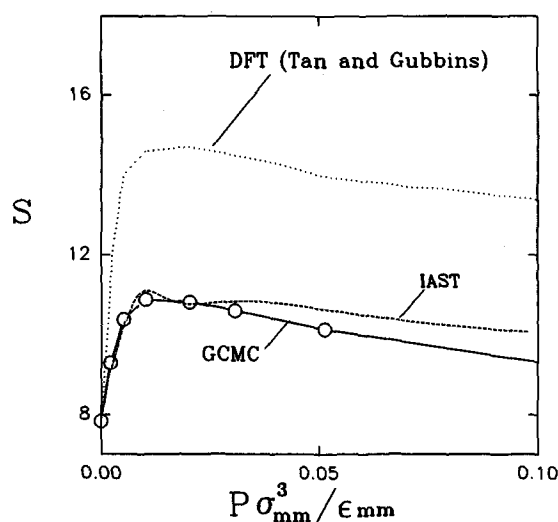


Figure 5. Comparison of GCMC, IAST and DFT results (from [15]). Methane–ethane mixture in a graphitic slit pore of width $H/\sigma_{mm} = 2.5$, $kT/\epsilon_{mm} = 2.0$ (296.2 K). $y_m = 0.9$.

$P\sigma_{mm}/\epsilon_{mm} = 0.1$. Bulk non-ideality was accounted for in calculating the selectivities.

The most striking feature of figures 4–7 is that the density functional theory results from [15] predict universally higher selectivities than GCMC. Because the selectivity is the ratio of mole fractions, it is likely to be particularly sensitive to any shortcomings in the theory. There is however quite good qualitative agreement in the shapes of the selectivity isotherms between GCMC and DFT. One possible explanation for the discrepancy is that in the particular form of the density function theory used, the weighting function for the density expansion contained only zeroth and first-order terms [13]. Another explanation which is pertinent to all versions of

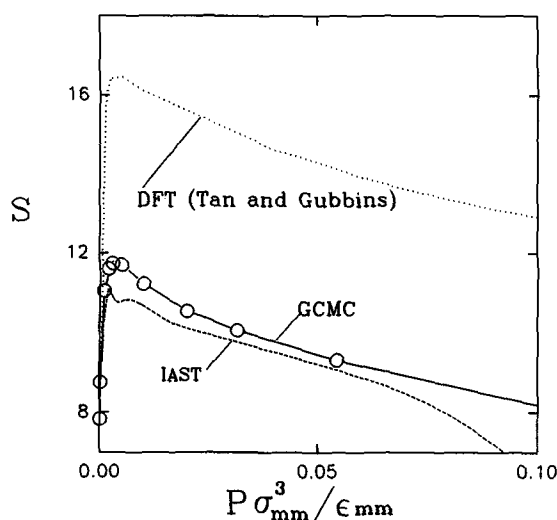


Figure 6. Comparison of GCMC, IAST and DFT results (from [15]). Methane–ethane mixture in a graphitic slit pore of width $H/\sigma_{mm} = 2.5$, $kT/\epsilon_{mm} = 2.0$ (296.2 K). $y_m = 0.1$.

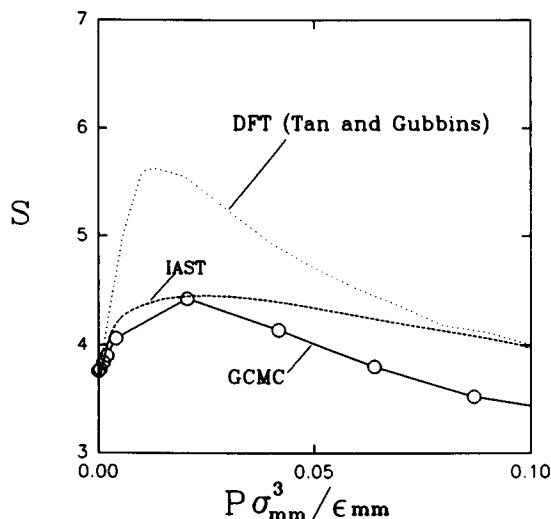


Figure 7. Comparison of GCMC, IAST and DFT results (from [15]). Methane-ethane mixture adsorbed in a graphitic slit pore. $H/\sigma_{mm} = 8.0$, $kT/\epsilon_{mm} = 2.0$ (296.2 K). $y_m = 0.5$.

the DFT is the inadequacy of the mean field assumption for the attractive forces; for bulk systems it is well known that this leads to an overestimate of the critical temperature [18], however Kierlik *et al.* [7] suggest that the mean field approximation may also lead to errors in the essentially two-dimensional submonolayer adsorption regime. Recently, several papers have appeared in which modifications to density functional theories are suggested to compensate for this problem [19, 20] although none of these modified theories have been as yet applied to mixtures.

The ideal adsorbed solution theory works quite well over a range of pressures and bulk mole fractions. This is consistent with previous comparisons of IAST with simulation for spherical Lennard-Jones particles of a not too dissimilar size [4, 6]. The larger deviation between IAST and simulation for the pore of width $y_m = 0.1$ at high pressure can be attributed to non-ideality of the bulk phase. The selectivity isotherms calculated using the IAST show a small kink at reduced pressures ($P\sigma_{mm}^3/\epsilon_{mm}$) ranging from 0.005 for $y_m = 0.1$ to 0.03 for $y_m = 0.9$. Thus the IAST predicts a selectivity isotherm which is type II in Tan and Gubbins' classification of selectivity isotherms [15], whereas the GCMC (and the DFT) would predict a type I isotherm in that classification. Type I selectivity isotherms occur when the temperature is well above the capillary critical temperature, type II isotherms occur when the temperature is marginally above the capillary critical temperature. The kink may be due to the fact that the IAST was calculated in part from single-component ethane which has a higher capillary critical temperature than a methane-ethane mixture. The absence of the kink in the GCMC results is due to pore fluid non-ideality.

6. Influence of pore size on adsorption selectivity

Tan and Gubbins [15] have shown that selectivity in the Henry's law limit, S_0 goes through a maximum with respect to pore width, H , the position of the maximum depending on the relative sizes of the components. At very low pore sizes, the larger component is excluded from the pore by geometric considerations,

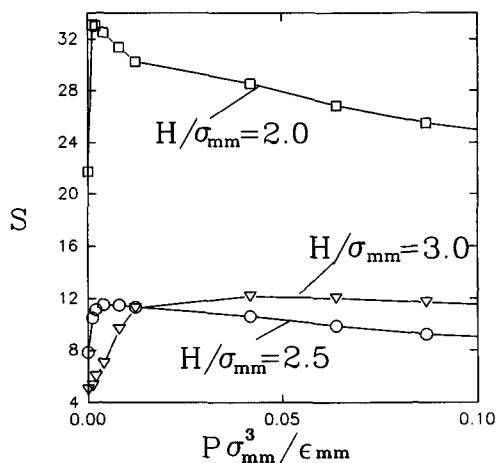


Figure 8. Ethane/methane selectivities (from GCMC) for graphitic slit pores of widths $H/\sigma_{mm} = 2.0, 2.5$ and 3.0 against pressure. $kT/\epsilon_{mm} = 2.0$. $y_m = 0.5$.

thus for the potential model used in this work, a pore width of $H/\sigma_{mm} = 1.6$ would have a selectivity close to zero since the carbon atoms that comprise the wall of the pore have a hard sphere diameter of $0.895\sigma_{mm}$ and ethane would be excluded from the pore. At pore sizes around $H/\sigma_{mm} = 2.0$, both components can enter the pore, the potential between ethane and the pore wall is stronger than for methane, and

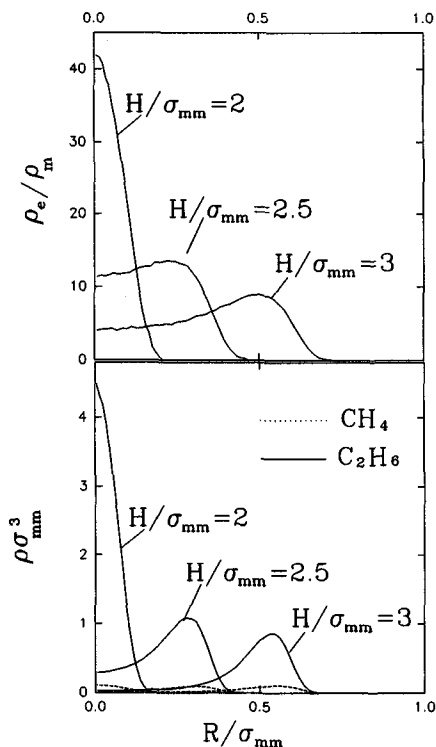


Figure 9. Density profiles of each component and mole ratio profiles in pores of various sizes for bulk pressure $P\sigma_{mm}/\epsilon_{mm} = 0.002$. $kT/\epsilon_{mm} = 2.0$.

ethane is selectively adsorbed. At larger pore sizes, the ethane/pore wall potential well remains deeper than the methane/pore potential well. However, as the pore size increases, the magnitude of the potential well depth for each component decreases and so does the magnitude of the difference between the well depths of methane and ethane; thus S_0 decreases with pore size, although it always remains greater than unity since $\epsilon_{ee} > \epsilon_{mm}$.

Figure 8 shows GCMC results for selectivity isotherms for pore widths $H/\sigma_{mm} = 2.0, 2.5$ and 3.0 for $y_m = 0.5$. At low pressures, selectivity decreases monotonically with pore size because of the reasons discussed above. For reduced pressures ($P\sigma_{mm}^3/\epsilon_{mm}$) above 0.014 , however, the selectivity for the pore of width $H/\sigma_{mm} = 3.0$ is higher than for the pore of width $H/\sigma_{mm} = 2.5$ for $y_m = 0.5$. Figures 9 and 10 show density profiles and density ratio profiles (i.e. the ratio of local densities plotted against position in the pore) for the three pore sizes. Figure 9 is at a reduced pressure of 0.002 and figure 10 at a reduced pressure of 0.042 . In figure 10, there is an appreciable density of ethane in the centre of the pore of width $H/\sigma_{mm} = 2.5$ but negligible density in the centre of the larger pore, this indicates that the ethane cannot form two neatly packed layers in the pore of width $H/\sigma_{mm} = 2.5$, but is able to for the larger pore. Methane, being smaller, is better able to form two layers in the pore of width $H/\sigma_{mm} = 2.5$. Thus selectivity is strongly influenced by adsorbate packing constraints as well as by the adsorbate-wall potential.

7. Conclusions

We have shown that a GCMC algorithm for mixtures which incorporates particle exchanges samples phase space more efficiently than a conventional GCMC

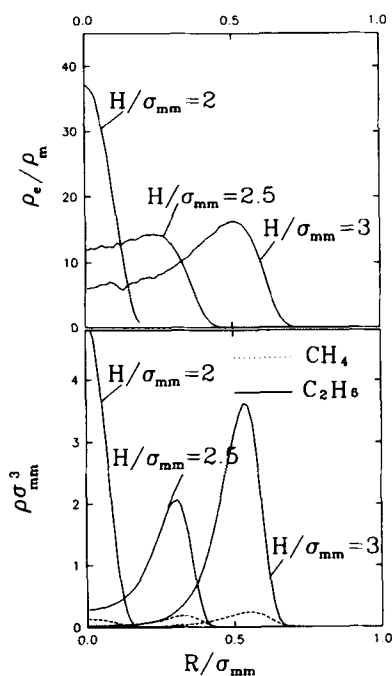


Figure 10. Density profiles of each component and mole ratio profiles in pores of various sizes for bulk pressure $P\sigma_{mm}^3/\epsilon_{mm} = 0.042$. $kT/\epsilon_{mm} = 2.0$.

algorithm. Using this algorithm, we have simulated single-component isotherms and mixture isotherms for spherical Lennard-Jones models of methane and ethane in a model graphitic pore. The simulations predict generally lower values of selectivity than is suggested by the DFT calculations from [15], although qualitative agreement is obtained in the shapes of selectivity isotherms. For the system studied, the IAST is in reasonable quantitative agreement with our GCMC results. We have also shown that adsorption selectivity depends on pore packing constraints as well as the relative depths of the adsorbate-wall potentials.

The applicability of these results to experimental methane-ethane systems is uncertain since the model of ethane used is unrealistic; also we have ignored the atomic structure of the graphite comprising the pore walls, this may become important for small pores; nevertheless the comparison between GCMC, DFT and IAST is valid. We note that the choice of cut-off has some effect on the results, in our results for the $H/\sigma_{mm} = 2.5$ pore, we found that selectivities were enhanced by about 7% if unshifted Lennard-Jones potentials, cut at 5σ were used instead of potentials cut and shifted at 2.5σ .

This work is part of a larger programme of study of separation in carbon membranes. We plan in future papers to investigate more realistic models of hydrocarbons, rather than the spherical models adopted here, in particular the effect of 'non-sphericity' of ethane on methane/ethane selectivity and IAST predictions is worthy of study since it has been found that IAST predictions deteriorate for adsorbed molecules differing greatly in size or polarity [4].

This work was funded by BRITE EURAM CONTRACT BREU-CT92-0568. The authors wish to acknowledge Mr R. J.-M. Pellencq of Imperial College, Dr M. Mustapha and Mr R. Gurr of BP Engineering, and Mr S. Tennison of BP Research for their informative comments and encouragement. It is a pleasure also to thank Dr S. J. Zara of Imperial College and the staff of Transtech Ltd for their helpful assistance with computer hardware.

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