

Molecular dynamics study of thermal diffusion in a binary mixture of alkanes trapped in a slit pore

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Abstract

We have used direct nonequilibrium molecular dynamics computer simulations to study the influence of an alumino-silicate slit pore on thermal diffusion in equimolar methane/*n*-decane. We have computed the Soret coefficient S_T as a function of the pore width. The S_T values deviate from the ones in a pore-free situation only for pores narrower than 35 Å. We have then investigated the possible causes for this deviation. We have noticed that the solid behaves as a thermal short-circuit for the liquid but this has no consequence on the thermal and solutal profiles in the mixture. The main influence of the confinement of the liquid lies in the 'freezing' of the layer of molecules in contact with the pore walls. Outside this layer, the thermal diffusive behaviour of the mixture does not depart from the one in bulk fluid. This finding has enabled us to compute a 'corrected' Soret coefficient where the influence of the porous medium is eliminated.

1 INTRODUCTION

It is quite difficult to determine reliable values for Soret coefficients S_T experimentally. This has motivated the search for theoretical and numerical techniques to alleviate these difficulties [Köhler and Wiegand 2002]. Among them, direct nonequilibrium molecular dynamics (DNEMD) computer simulations have been

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shown to mimic experimental setups closely enough to allow the direct computation of S_T without assumptions on other thermodynamic parameters. Furthermore, they provide insight into the microscopic mechanisms leading to the thermal diffusion process. Thus, in our case, DNEMD yields direct insight into the distortions of the concentration fields induced by the porous medium we are interested in, whereas alternate methods such as equilibrium MD or synthetic non-equilibrium MD do not offer this advantage.

Several problems currently impede a fuller understanding of thermal diffusion and make reliable predictions of S_T near impossible. DNEMD simulations can be used to shed light in particular areas that are relevant to these problems, for instance concerning the identification and the disentanglement of the microscopic effects governing this phenomenon:

- Recently, optical measurements have enabled to split the Soret coefficient of the benzene-cyclohexane mixture into two additive contributions [Debuschewitz and Köhler 2001]. The first one is an isotope effect and is independent of concentration. It depends on the differences of mass and moments of inertia of the two components. The second one is a chemical effect and depends on the concentration. DNEMD studies could contribute to quantifying the relative contribution of these two effects.
- Concerning the above-mentioned chemical effect, progress is underway [Bordat et al. 2001]. However, even basic features such as the influence of the interaction potential between molecules on S_T remain unclear.
- The influence of a porous medium on the Soret effect has been little studied and still remains an open question.

The last point is of foremost importance for industrial applications, particularly in oil recovery, where thermal diffusion seems to play a non-negligible role in the fluid flows of petroleum reservoirs [Faissat and Montel 1996]. Keeping in mind this industrial concern, we have addressed the problem by performing DNEMD simulations of an equimolar liquid methane/*n*-decane mixture subject to a thermal gradient in porous media. Among possible porous geometries, the role of atomic-scale randomly-placed crystallites has been studied elsewhere [Colombani et al. 2002]. We intend to focus here on another limiting case, a simple slit pore geometry.

In this paper, we will briefly recall the simulation method used and then study the characteristics of thermal diffusion of alkanes in a slit pore, first at a phenomenological level and then at an atomic scale. Finally, we will draw conclusion about the possibility of predicting Soret coefficients in porous media.

2 SIMULATIONS

We have used a modified HEX algorithm [Hafskjold et al. 1993, Ikeshoji and Hafskjold 1994] where the periodic simulation box is divided into 24 layers (in our case) and the periodicity of space is recovered by imposing two adverse thermal gradients across the box (one in the first twelve layers and the other in the following twelve), see figure 1. The liquid in layers 1 and 24 is maintained by thermostats at a high temperature and in layers 12 and 13 at a low temperature. In exact analogy to the experiment, the Soret coefficient is computed via the Soret steady

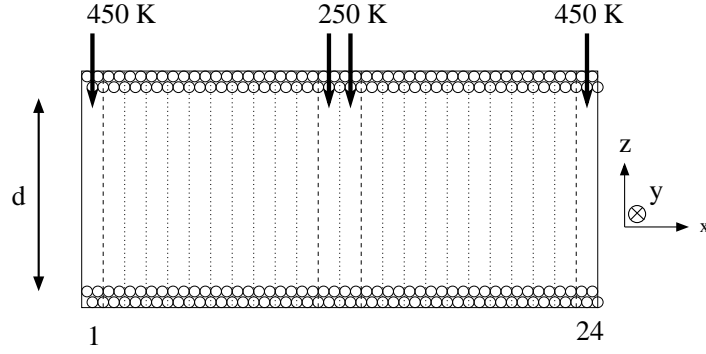


Figure 1: General setup of the simulation box.

state relation $S_T = \Delta x/[x(1-x)\Delta T]$ from the differences in temperature and concentration, ΔT and Δx , between a hot and a cold end of the box; x is the overall mole fraction of methane (here $x=0.5$).

The interactions between particles in the liquid and the solid walls are often modelled by so-called 'integrated potentials', which represent the pore walls as structureless interfaces [Steele 1974]. To advance toward a more realistic representation of adsorption phenomena, which seems of importance in our case, we have preferred to use a fully atomistic representation of the porous medium. This improved level of approximation is in particular expected to bring a better representation of the 'freezing' of molecules near the walls, avoiding artefacts like thermal creep (microscopic Marangoni effect) in the box [Galliéro et al. 2002]. Indeed, it has been shown that the dynamic behaviour of confined liquids can be drastically modified when changing a flat wall into a slightly corrugated one, while this change has no influence on the static properties [Bocquet and Barrat 1994].

The two crystallites limiting the pore have been modelled by harmonic face-centered cubic crystals. The potential parameters were chosen to mimic the structural and dynamical properties of alumino-silicates with a reasonable degree of accuracy [Demontis et al. 1988].

It is the purpose of the present work to focus mainly on the solid-liquid interactions. Thus, we eliminated all specificities from the alkanes models (flexibility, ...) and choose to represent them, within the united atom approximation, by Lennard-Jones (LJ) 12-6 potentials with the parameters derived by Simon *et al.* [Simon et al. 1999]. The relative sizes of the particles can be characterized by their σ_{LJ} parameters, which are 3.88 Å for methane, 6.80 Å for decane and 3.37 Å for the alumino-silicate oxygens. LJ potential with cut-off radii are used rather than LJ spline potential, the latter disturbing the medium-range interactions in a way detrimental to the S_T computations [Bordat et al. 2001]. The interactions between the pore walls and the molecules in the liquid are thus also represented by LJ potentials, with parameters obtained with the Lorentz-Berthelot mixing rules from the ones of the alkanes [Simon et al. 1999] and alumino-silicate [Pohl et al. 1996]. The resulting interaction potentials and the list of potential parameters for methane, *n*-decane, and the wall particles have been given elsewhere [Colombani et al. 2002].

The temperature difference between the ends of the box was $\Delta T=200$ K (250 K at one end and 450 K at the other) creating a thermal gradient parallel to the walls. The resulting $\Delta T/T_{mean}$ ratio is large (~ 0.6) compared to usual

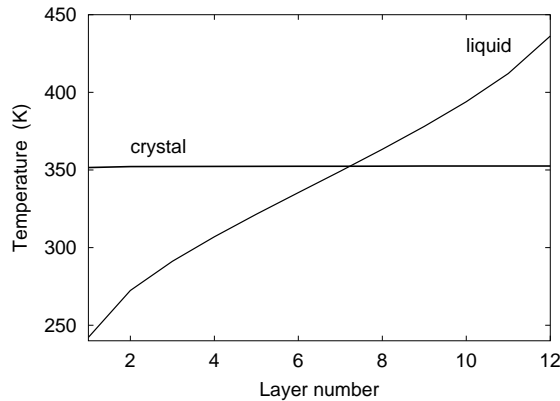


Figure 2: Temperature profile in the liquid and in the solid crystal in half a simulation box of a 30 Å wide slit pore. The layers numbered 1 and 12 are the thermostated ones.

experimental and numerical ones (<0.1) in order to remain within a reasonable range of temperatures and at the same time maximize the concentration gradient in the adsorbed liquid. In this way, the influence of the slit pore on the thermal diffusion should be brought out clearly.

The density of the mixture was about $600 \text{ kg}\cdot\text{m}^{-3}$. The pressure always exceeded the critical pressure ($P_c=20 \text{ MPa}$ for $T=350 \text{ K}$) so the mixture was in a supercritical regime. However the high density led to a structure very similar to normal liquids (see radial distribution functions in [Colombani et al. 2002]).

3 PHENOMENOLOGICAL BEHAVIOUR

As a first step, we have investigated the thermal behaviour of the system to identify eventual distortions of the thermal field compared to the pore-free case. Figure 2 displays the thermal profiles along the box in the liquid and in the solid in the stationary state for a 30 Å wide slit pore. As mentioned, only the liquid in the two extreme layers is kept at constant temperatures by thermostats; a linear thermal profile builds up between these two layers. No thermostat is applied to the solid. From figure 2 we see that heat conduction is fast enough in the solid to maintain a uniform temperature; the non-transient nature of this feature has already been demonstrated [Colombani et al. 2002]. Thus, no noticeable thermal gradient exists in the solid. This 'short-circuiting' effect seems, however, not to have any influence on the liquid, which shows a linear thermal profile.

We have then looked at the concentration distribution. Figure 3 shows a typical Soret induced mole fraction gradient inside the pore. Like the ones in pore-free geometries, it is linear within our error margins, indicating an apparently weak influence of the pore walls on the concentration field. Furthermore, we verified that despite the large applied temperature gradient the system does not depart from the linear regime of the diffusion laws, similarly to what has been found experimentally in other systems [Bert and Dupuy-Philon 1997].

Since the shapes of the temperature and concentration fields are not disturbed by the porous medium, the Soret coefficient can be computed, like in the bulk, through the relation mentioned in Section 2. Particular care has, however,

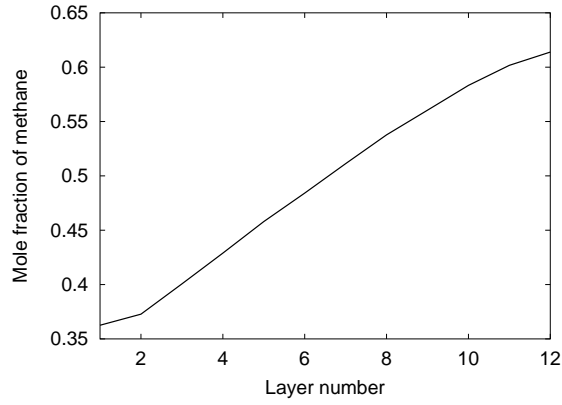


Figure 3: Mole fraction of methane in the liquid mixture confined by a 30 Å wide slit pore. The layers numbered 1 and 12 are the thermostated ones.

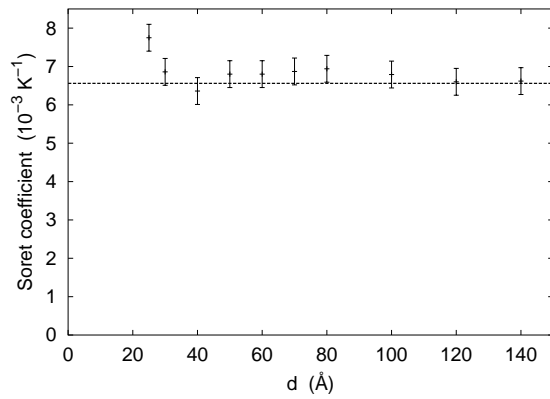


Figure 4: Evolution of the Soret coefficient with the slit pore width. The line is the value of S_T in a pore-free system.

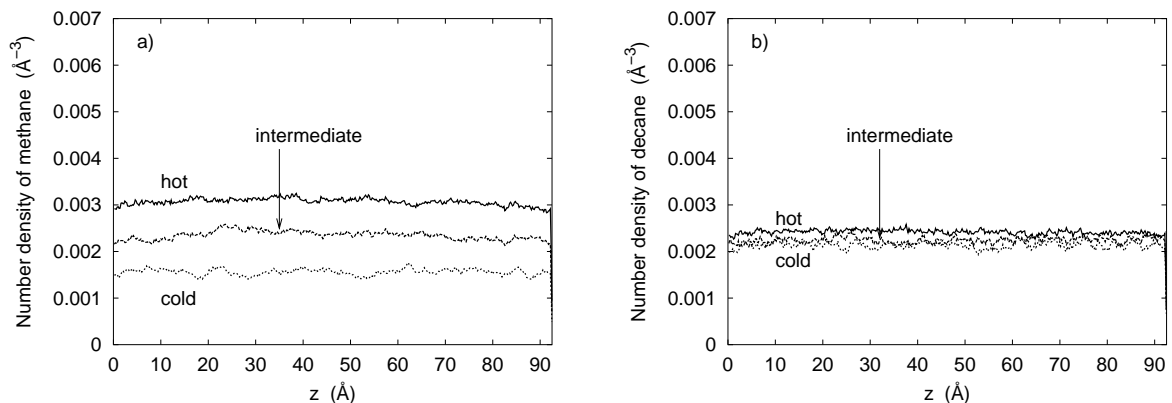


Figure 5: Number density a) of methane and b) of *n*-decane in a hot, intermediate, and cold layer in the pore-free geometry.

been taken to establish the validity of the computed results:

- The values of the mole fraction of methane are calculated in 24 slabs of liquid perpendicular to the gradients, see figure 1. The width of these layers has been chosen in all simulations to be larger than the diameter of the methane LJ sphere ($\sigma_{LJ}=3.88$ Å). This choice has led to large simulated systems with up to 3600 molecules in the liquid and 3456 atoms in the solid for the 140 Å wide pore. In comparison, the smallest system (the 25 Å wide pore) contains 1000 particles, which, according to Bordat *et al.* [Bordat et al. 2001], is sufficient to avoid finite size effects.
- The ΔT and Δx values used in the computation of S_T are average values over entire nonequilibrium simulations (with up to 53 ns simulated time) to guarantee a good statistical accuracy. The simulations were stopped after the calculated S_T value changed by less than 0.05×10^{-3} K $^{-1}$ during the last ten simulated ns.

We have plotted in figure 4 the values of S_T for various pore widths. The main feature of this curve is the negligible influence of the porous medium for pore widths down to 35 Å. The slight modulation of S_T above this value is probably insignificant. To elucidate the origin of this evolution, it is necessary to go beyond phenomenological quantities and to look into the microscopic mechanisms. For example, in pores as narrow as a few molecular diameters, the behaviour of the liquid, both in terms of structure and dynamics, could very well be quite different from the one seen in the bulk fluid, which should in turn influence the Soret effect.

4 MICROSCOPIC MECHANISMS

First, we have searched for hydrodynamic patterns in the box. Indeed, for pores with smooth walls, the change of interface energy with temperature can lead to nonrealistic convection loops in the pore (see Section 2). In order to check this, we have subdivided the box in $100 \times 100 \times 100$ parallelepipeds in the three dimensions of space and computed the local momenta in these subdivisions.

They are always zero if averaged over sufficiently long simulation times, showing the absence of structured flows. Thus the corrugation of our walls is sufficient to provide realistic boundary conditions for the diffusion of the molecules in the liquid.

Next, to study adsorption phenomena, we have computed the local number density of methane and decane in three layers perpendicular to the x axis of the box (see figure 1) for three systems:

- Figure 5 displays the local number densities in a bulk system (pore-free). The number density of methane is larger in the hot region while the one of n -decane is quite uniform along the box, whatever the temperature. We thus see clearly that the concentration gradient is mainly a consequence of methane migration. The fact that methane molecules are responsible for the settlement of the solutal gradient has also been verified in the slit pore geometry. Accordingly, we will focus below exclusively on the methane distribution. The larger density of methane in the hot region is what leads to the positive Soret coefficient (lighter component migrates toward the hot end).
- Then, we have studied a slit pore case without temperature gradient. As can be seen in figure 6a, a layered structure builds up near the walls—due to the solid-liquid interaction—and progressively vanishes into the bulk liquid when thermal stirring prevails.
- Finally, we have considered the slit pore case with a thermal gradient. Figure 6b shows that a layered structure is built up in the z direction while in the x direction (hot, intermediate, and cold layers) the number density of methane decreases. We observe that the 'bulk' liquid (molecules which are not in the first adsorption layers) behaves like in the pore-free geometry (methane density larger in the hot region). On the other hand, in the first adsorption layers, i.e. in the range of the high peaks in figure 6b, we find no concentration gradient and the mixture behaves as if in thermal equilibrium. This remains true for all pore widths studied (between 25 and 140 Å).

We have then checked whether the absence of concentration gradient in the adsorbed layers results from an eventual local decrease of the thermal gradient in these layers due to the neighbouring presence of the crystal. Figure 7 displays the local temperature in the 50 Å wide slit pore in the same three layers as in figure 6b. The temperatures across the pore, including the adsorbed layers, are found to be uniform. Thus, there is no damping of the thermal gradient by the solid, and the absence of concentration gradient is purely a consequence of the physisorption of the alkanes on the pore walls.

Therefore, for the chosen interaction strengths, characteristic of alkane-alkane and aluminosilicate-alkane interactions, the wall influence on the Soret concentration field seems limited to the first adsorbed layer, where the increased spatial correlation of the liquid molecules with the solid hinders the thermal diffusion.

To test the validity of this picture, we have carried out the following modification in our Soret coefficient computations: Instead of evaluating the methane mole fraction in the entire liquid slabs, we limited our computation to the 'free' molecules, i.e. molecules outside of the two (bottom and top) adsorbed layers. Figure 8 shows the evolution of this corrected S_T (S_T^{cor}) with the pore width.

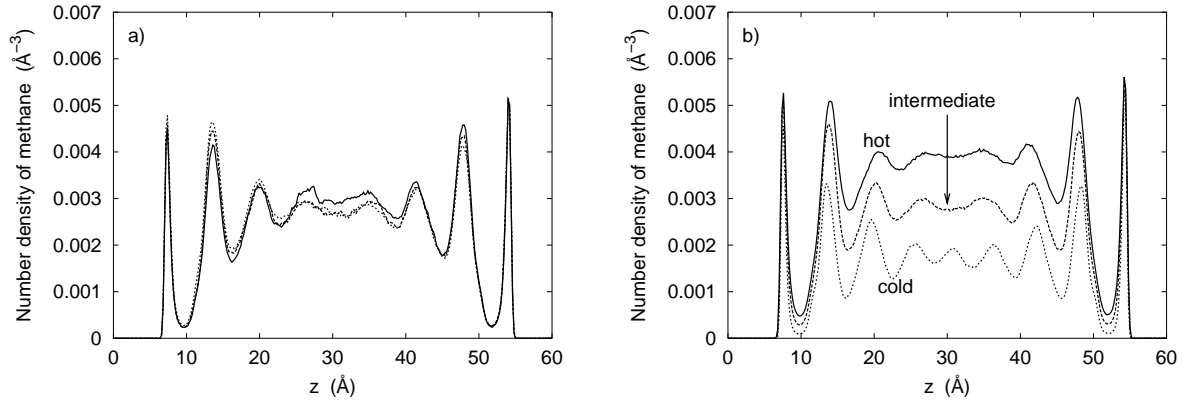


Figure 6: Number density of methane in three layers perpendicular to the walls in a 50 \AA wide slit pore a) in thermal equilibrium and b) with a thermal gradient parallel to the walls. The figures are not symmetrized, the deviations between the heights of the two first adsorption peaks ($z \approx 7$ and 54 \AA) provide a rough estimate of the uncertainties in the statistical averages.

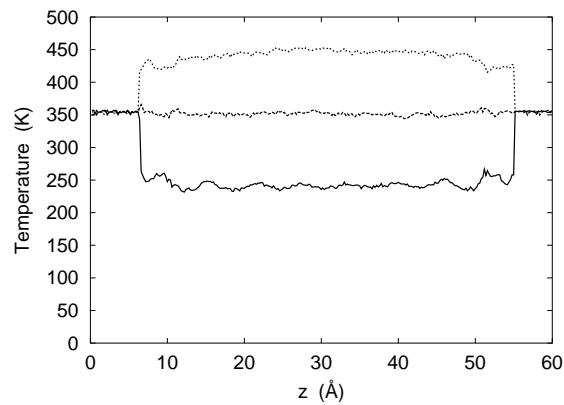


Figure 7: Local temperature in a 50 \AA wide slit pore in the same three layers perpendicular to the walls as in figure 6b.

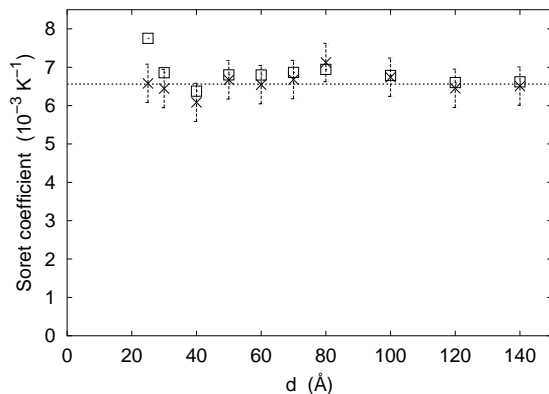


Figure 8: Evolution of the Soret coefficient S_T (squares) and of the corrected Soret coefficient S_T^{cor} (crosses) with the slit pore width. The line is the value of S_T in a pore-free system. Error bars have been drawn only for the S_T^{cor} values.

This coefficient remains constant, within our error bars, whatever the pore geometry. The increase at very low pore widths (figure 4) has disappeared. This confirms our conclusion that the slit pore influence is limited to some sort of 'freezing' of molecules in the first adsorbed layers.

Comparing these slit pore results with the ones in simulation box with random atomic-scaled porosity [Colombani et al. 2002], we argue that adsorption phenomena are, at a microscopic scale, the leading cause of deviations between Soret coefficients in homogeneous and porous media. As a first order correction, the adsorbed layers can simply be excluded from the computation. Subsequently, the inclusion of adsorption equilibria and their temperature dependence can be envisaged in order to take selective adsorption into account. We note, however, that the above assertions concern systems where the liquid-solid interactions are close to our silicate-alkane case, excluding for example specific situations like non-wetting liquids.

5 CONCLUSION

We have investigated in this work the influence of a microscopic alumino-silicate slit pore on the Soret coefficient by direct nonequilibrium molecular dynamics computer simulations. We have determined that in this case the solid has no measurable influence on the shapes of the thermal and solutal gradients in the liquid. Its main role is limited to the 'freezing' of a (or in other cases possibly several) layer(s) of liquid. Even in the second adsorption layer, the molecules behave like the bulk liquid with respect to the Soret coefficient. So the Soret coefficient can be estimated by excluding the molecules in these adsorbed layers from the computation of the concentration gradient.

A more detailed evaluation will need the knowledge of the selective adsorption behaviour of methane and *n*-decane. For pore with widths larger than several molecular diameters this correction should remain small. Chain-models of decane (in contrast to the spherically averaged ones used here) could bring in additional effects, e.g entropic effects, partial phase separation etc. The in-

fluence of these effects on the transport coefficients cannot be gauged from the present study. One might expect at least a modification of the depth of the layer in which the pore influences the liquid structure and dynamics. In the mixture, it could also add to the well-known concentration dependence of the Soret effect [Köhler and Wiegand 2002], which is not addressed here either. Another improvement could also consist in taking into account the pressure gradient—caused by the thermal gradient—through the evaluation of a possible barodiffusion contribution to the concentration gradient. Finally, the implementation of the Soret flux in the numerical simulations of the macroscopic flows in petroleum fields should also include convective phenomena, which were not present in our study at a microscopic scale.

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