Thermal Diffusion in alkane binary mixtures. A molecular dynamics approach[1].

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ABSTRACT

We have employed *Direct* Non-Equilibrium Molecular Dynamics (NEMD) simulations to compute the thermal conductivity and the thermal diffusion coefficient α_T in a methane–*n*-decane binary mixture in the liquid state. We discuss the choice of a non-equilibrium molecular dynamic method rather than the equilibrium method using Green-Kubo integrals. We emphasise the fact that using *direct*-NEMD, there is no need for additional calculation of any thermodynamic property of the mixture. The *n*-decane molecules are realistically modelled as flexible bodies and using the Anisotropic United Atoms (AUA) interaction scheme of Toxvaerd. The statistical uncertainty for the thermal conductivity is less than 1% and that for the thermal diffusion factor is about 5%. We show that the thermal conductivity results agree with predictions from Assael. The thermal diffusion data are in accordance with the empirical relationships of Kramers and Broeder and experimental results, where available.

KEY WORDS: alkane mixture; molecular simulation; non-equilibrium molecular dynamics; Soret effect; thermal conductivity; thermal diffusion factor.

Introduction

When a fluid mixture is placed in a thermal gradient, one observes a separation of the components in the mixture. This separation leads to a mole fraction gradient parallel to the thermal gradient. This effect is known as the Soret effect or the thermal diffusion effect. Its amplitude is described by a phenomenological coefficient, α_T, the thermal diffusion factor. The separation by thermal diffusion is usually small, but its effect can be quite important under special conditions such as in oil reservoirs [1]. In this case, it is of considerable importance to get reliable data for α_T.

Since its discovery in 1850 by Ludwig and the first systematic studies in liquid mixtures by Soret, thermal diffusion has been the subject of both experimental and theoretical work. However, both microscopic theories based on kinetic theory of gases applied to dense fluids [2], and macrocopic theories based on irreversible thermodynamics are unable to give accurate data for the thermal diffusion factor in dense fluid systems [1]. From an experimental point of view, thermal diffusion is very difficult to measure [3, 4]. Only recently, independent groups have obtained consistents results on toluene–*n*-hexane [5, 6, 7] and water–methanol [5, 6, 8] mixtures.

During the 80's, several authors have attempted to compute transport coefficients using molecular dynamics (MD) methods in multi-component systems [9, 10, 11, 12, 13]. Transport coefficients can be obtained using the Green–Kubo (GK) formulae and equilibrium MD or *synthetic* non-equilibrium molecular dynamics (NEMD) [14, 15]. One can also mimic the real experiment by modifying the conditions at the boundaries of the simulation box. This method is called *boundary driven* NEMD or *direct* NEMD. In the next section, we explain why *direct* NEMD must be used to compute the thermal diffusion factor in organic binary mixtures in order to give "experimental-like" data for the thermal diffusion factor. Then we briefly describe the model and the potential used in our computations along with some computational details. We finally give some data for thermal conductivity and thermal

diffusion factor obtained for the methane–n-decane binary mixture.

Methodology

Using the GK-MD approach, one computes the phenomenological coefficients L_{ij} related to the thermal diffusion factor α_T. For a binary mixture, we have:

$$\alpha_T = \frac{1}{\mu_{11}^w w_1} \frac{L_{1q}}{L_{11}} \tag{1}$$

where w_1 is the mass fraction of the heavy component (component 1). The sign of α_T is arbitrarily chosen so that α_T is positive when the lighter component concentrates in the hot region. μ_{11}^w is the partial derivative of the chemical potential of component 1, μ_1 with respect to w_1 at constant pressure P, and temperature, T:

$$\mu_{11}^w = \left(\frac{\partial \mu_1}{\partial w_1}\right)_{P,T} \tag{2}$$

A direct comparison of GK-MD results of the mutual diffusion, D, and α_T with experimental data requires values of μ_{11}^w. Many authors use the ideal value, but Jolly and Bearman [9] and Schoen and Hoheisel [10] derived μ_{11}^w by integration of the partial pair correlation functions. However, Stoker [16] mentions that it is difficult to obtain good statistics by this method and used UNIFAC [17] to predict μ_{11}^w.

According to the GK relationships [12] L_{11} is given by the infinite time integral of the autocorrelation function of the mass flux $\mathbf{J_1}$ and L_{1q} is defined in terms of the cross correlation of the mass flux and the heat flux $\mathbf{J_q}$. L_{11} is related to the mutual diffusion coefficient D and L_{1q} is directly connected to the thermal diffusion coefficient D_T. $\mathbf{J_1}$ is the instantaneous mass flux of component 1 and can be readily computed during an equilibrium MD run whereas $\mathbf{J_q}$ is not directly accessible from a single simulation. The instantaneous heat flux, $\mathbf{J_q}$ is given by the expression $\mathbf{J_q} = \mathbf{J_U} - (\mathbf{h_1} - \mathbf{h_2})\mathbf{J_1}$, where $\mathbf{J_U}$ is the internal energy flux and h_i is the specific partial enthalpy of component i. Recently, Daivis and Evans [18] have given microscopic expression for $\mathbf{J_U}$ for flexible molecular models. There exists no microscopic

expression for h_i for constant N ensembles. Most of the authors use macroscopic data from experimental work or the ideal mixture expressions. Vogelsang *et al.* [19] report that even the sign of α_T may change when using ideal values of h_i instead of calculated ones. Some authors have attempted to compute h_i using MD techniques [20] but these simulations give poor statistics.

In order to avoid these problems, we have computed α_T using the Heat EXchange algorithm (HEX) proposed by Hafskjold *et al.* [21]. A heat flux is created in the simulation box by exchanging kinetic energy between a *hot* and a *cold* region so that the total energy of the system is conserved. The simulation box is replicated in a direction perpendicular to the heat flux to enable periodic boundary conditions in three dimensions. The system develops a temperature gradient and an internal energy flux. At the stationary state, the thermal diffusion factor is given by :

$$\alpha_T = \left(-\frac{T}{w_1 w_2}\frac{\nabla w_1}{\nabla T}\right)_{\mathbf{J_1=0}} \tag{3}$$

This method gives a direct "measure" of the thermal diffusion factor in a single NEMD run.

Model and computational details

We have used the anisotropic united atoms (AUA) model proposed by Toxvaerd [22] to model *n*-decane. In the AUA model, the positions of the interaction sites are shifted from the center of mass of the carbon atoms to the geometrical center of the methyl (CH_3) and methylene (CH_2) groups [23]. In this way, the site-site interactions depend on the relative orientations of the interacting chains, as in real molecules. The magnitude of the shift is noted d_1 for CH_3 and d_2 for CH_2. This model gives simulation results for the diffusion coefficient, as well as the pressure and the trans-gauche configuration in excellent agreement with experimental data in *n*-pentane and *n*-decane in the liquid phase [23]. Methane was modelled using a 1-center Lennard-Jones potential given by Möller *et al.* [24]. All the potential

parameters can be found in Table 1.

The site-site intermolecular interaction is given by the Lennard-Jones potential :

$$V_{LJ}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{4}$$

where r_{ij} is the distance between sites i and j and σ_{ij} and ϵ_{ij} are the potential parameters. We use the Lorentz–Berthelot mixing rules $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ where ϵ_{ii} and σ_{ii} are the potential parameters for like site interactions.

In addition to the intermolecular site-site interactions, the atomic units (CH_2 and CH_3) are affected by intramolecular constraints and forces. The carbon–carbon bond lengths d_{cc} are constrained to their mean value using the RATTLE algorithm by Andersen [25]. The angle bending potential is

$$V_B(\beta) = \frac{1}{2}k_\beta\left(\cos\beta - \cos\beta_0\right)^2 \tag{5}$$

k_β is the bending force constant, β_0 is the equilibrium bond angle and β is the instantaneous bond angle. The torsion potential is a fifth order polynomial in $\cos\phi$, where ϕ is the dihedral angle :

$$V_T(\phi) = \sum_{i=0}^{5} a_i(\cos\phi)^i \tag{6}$$

The intramolecular potential also includes Lennard-Jones interactions between sites separated by three or more centers.

The equations of motion are solved using the *Verlet velocity* algorithm with a timestep of 0.005 ps. The cut-off radius r_c is 2.5 $\sigma_{methane}$. We have used a neighbour list with a list radius, $r_l = 1.1\ r_c$. In order to obtain small statistical uncertainty, runs have been carried out for 7 to 10 ns (1 – 2 million timesteps) on a simulation box containing 1600 molecules. This system contains 10240 centers of force and requires a large amount of computational time. A parallel version of the code has been implemented on Cray T3D and T3E. The CPU time for one timestep is about 0.025 s on the Cray T3E with 64 processors. Under these conditions, each run required 12 hours and the statistical uncertainty on α_T was less than 5%.

Results

The methane–*n*-decane binary mixture can be considered as a model for gas-oil mixture and has non-negligeable excess thermodynamic properties. It has been studied for many years by several groups. Sage and Berry have reported thermodynamic data [26], Knapstad *et al.* [27] have made systematic studies of viscosity and Hafskjold and coll. [28] have done measurements of inter- and intra- diffusion coefficients, all at elevated temperature and pressure. However, there exists only one data point for thermal diffusion in this mixture, from Lindeberg [29].

We have studied a methane–*n*-decane binary mixture with a methane mole fraction $x_1 = 0.4$ at six different state points in the dense liquid region, far from the critical point. The temperature and density data used for the different runs are given in Table 2.

The HEX algorithm can be used to compute the thermal conductivity of the mixture. At the stationary state, when the mass flux $\mathbf{J_1} = \mathbf{0}$, the thermal conduction κ is given by the expression [30]:

$$\kappa = -\frac{\langle \mathbf{J_q} \rangle}{\nabla T} = \lambda - \frac{D_T^2}{D}\, \mu_{11}^w\, \rho\, w_1^2\, w_2\, T \tag{7}$$

where $\langle \mathbf{J_q} \rangle$ is the average of the instantaneous heat flux, λ is the thermal conductivity and ρ is the density of the system. The difference between λ and κ is due to the thermal diffusion effect and is a second order term. Quantitatively, it turns out that the difference between λ and κ is at the most a few percent [30]. Figure 1 shows the thermal conduction κ computed at 307 K at four different densities. The statistical uncertainty is less than 1%. To our knowledge, there is no experimental data on thermal conductivity in methane–*n*-decane mixtures. In order to check the validity of the method, we have compared the simulated data with a prediction given by Assael [31] which is reported to have an accuracy of 5%.

One observes that the two sets of data are in excellent agreement, the uncertainties are small and the error bars overlap. The difference between simulated and

predicted data never exceed 6%. The predicted and computed data both increase with density, but one observes a systematic deviation from the Assael correlation. The systematic deviation cannot be explained by the difference between κ and λ which can be estimated using experimental diffusion coefficients, the simulated α_T and ideal μ_{11}^{w}. For this system the difference is four orders of magnitude smaller than the absolute values of λ and κ.

Finally, we present the results obtained for the thermal diffusion factor α_T for the six different runs. The data are plotted in Figure 2 and reported in Table 2. First of all, we note that for the six different runs, α_T is positive. This result is in qualitative agreement with the empirical laws of Kramers and Broeder [32] which states that for homologous series, the component enriching at the cold side is the one having the greatest number of carbon atoms. The experimental result obtained by Lindeberg at 307 K and 0.67 g·cm^{-3} is 0.82 $\pm$ 0.08. Under identical conditions, we found a value of 1.21 $\pm$ 0.06, about 30% higher than the experimental value. However, this difference is not very large compared to the general discrepancies often observed between experimental thermal diffusion data from different authors.

There is a very small number of systematic studies of the thermal diffusion factor with temperature, pressure or composition. It is therefore very difficult to predict the correct trend for the methane–*n*-decane in the liquid state. Zhang *et al.* [6], have observed a decrease of the Soret coefficient S_T ($S_T = \alpha_T/T$) with increasing temperature in toluene–*n*-hexane liquid mixtures. We observed the same trend in our system. We also observed a decrease of α_T with increasing density at constant temperature. Although this behaviour is different from what is observed in gas mixtures [33], it is in qualitative agreement with Dougherty and Drickamer results in CS_2–*n*-octane mixture in the liquid state [34]. Hence, we note that the general trends of α_T from our simulations in the methane–*n*-decane system with temperature and density are in qualitative agreement with experimental results on binary mixtures in liquid state.

Conclusion

We have presented a general methodology to compute thermal conductivity and thermal diffusion factor in a "realistic" binary n-alkane mixture. Using the HEX algorithm, we avoid the computation of quantities difficult to obtain using molecular dynamics, namely the partial derivatives μ_{11}^{w} and the partial enthalpies h_i. Parallelising the NEMD code has enabled us to obtain κ and α_T with a statistical uncertainty less than respectively 1% and 5%.

The thermal conduction data computed from *direct* NEMD are in excellent agreement with predictions from Assael. The thermal diffusion factor data are in good agreement with previous experimental results and the general behaviour with temperature and density is consistent with experimental results on binary mixtures in liquid state. These results show that *direct* NEMD can be a powerfull tool for the study of thermal diffusion in molecular liquid mixtures.

LIST OF SYMBOLS

a_i	Parameters for the intramolecular torsion potential
d_1	AUA distance for CH_2
d_2	AUA distance for CH_3
d_{cc}	Carbon-carbon bond length
D	Mutual diffusion coefficient
D_T	Thermal diffusion coefficient
h	Integration time step
h_i	Specific partial enthalpy of component i
$\mathbf{J_i}$	Instantaneous mass flux of component i
$\mathbf{J_q}$	Instantaneous heat flux
$\mathbf{J_U}$	Instantaneous internal energy flux
k_β	Bending force constant

L_{ij}	Phenomelogical coefficient
P	Pressure
r_c	Intermolecular potential cut-off distance
r_{ij}	Distance between sites i and j
r_l	Neighbour list radius
S_T	Soret coefficient
T	Temperature
V_{LJ}	Lennard-Jones potential
V_B	Intramolecular bending potential
V_T	Intramolecular torsion potential
w_i	Mass fraction of component i
x_i	Mole fraction of component i

Greek symbols:

α_T	Thermal diffusion factor
β	Instantaneous bond angle
β_0	Equilibrium bond angle
ϵ_{ij}	Lennard-Jones potential parameter for type i – type j interaction
κ	Thermal conduction
λ	Thermal conductivity
μ_i	Chemical potential of component i
μ_{11}^w	Partial derivative of the chemical potential of component 1 with the mass fraction of component 1
ϕ	Dihedral angle
ρ	Mass density
σ_{ij}	Lennard-Jones potential parameter for type i – type j interaction

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Table 1: Model and potential data

Bond length and AUA distances:		
d_{cc} = 1.54 Å	d_1 = 0.275 Å	d_2 = 0.370 Å
Mass of the interacting sites (kg·mol^{-1}) :		
$m_{CH_2} = 0.014$	$m_{CH_3} = 0.015$	$m_{CH_4} = 0.016$
Lennard-Jones potential:		
CH_2	$\epsilon/k_B = 80$ K	$\sigma = 3.527$ Å
CH_3	$\epsilon/k_B = 120$ K	$\sigma = 3.527$ Å
CH_4	$\epsilon/k_B = 150$ K	$\sigma = 3.7327$ Å
Bending potential :		
$\beta_0 = 114.6°$	k_β = 520 kJ mol^{-1}	
Torsion potential (kJ mol^{-1}):		
$a_0 = 8.6279$	$a_1 = 20.170$	$a_2 = 0.67875$
a_3 = -26.018	a_4 = -1.3575	a_5 = -2.1012

Table 2: Thermal diffusion factor α_T, thermal conduction κ and pressure P computed at different temperature T and density ρ. The methane mole fraction is 0.4.

Run	T (K)	ρ (g·cm^{-3})	P ±2% (MPa)	κ ±1% (W· m^{-1} · K $^{-1}$)	α_T ± 5%
1	307	0.66	16.1	0.133	1.34
2	307	0.67	27.1	0.138	1.21
3	307	0.68	38.5	0.144	1.26
4	307	0.703	69.8	0.158	1.05
5	350	0.66	49.7	-	1.12
6	350	0.67	62.3	-	1.08

FIGURE CAPTIONS

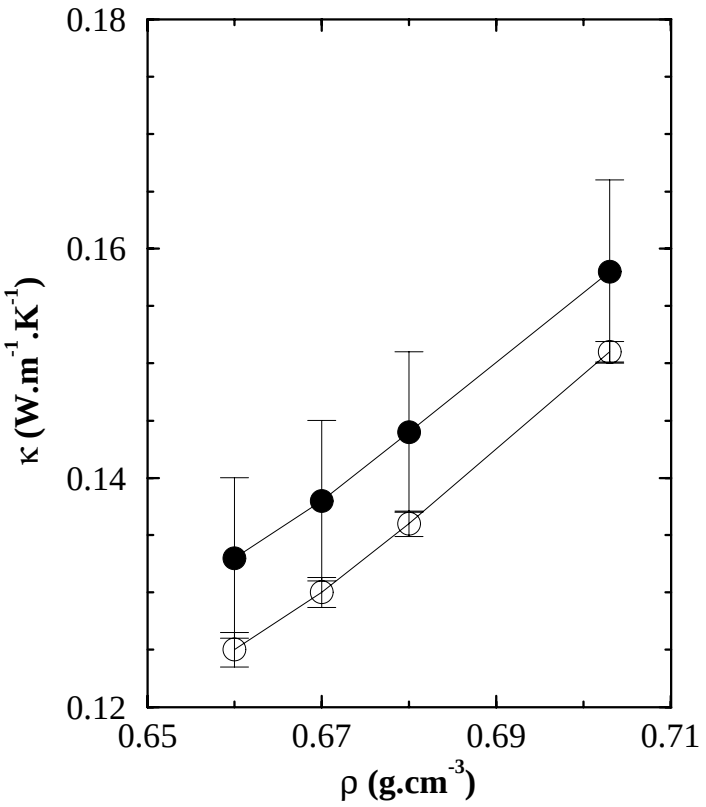

Figure 1: Thermal conduction κ versus density obtained by NEMD (○) and thermal conductivity λ predicted from the Assael correlation (●).

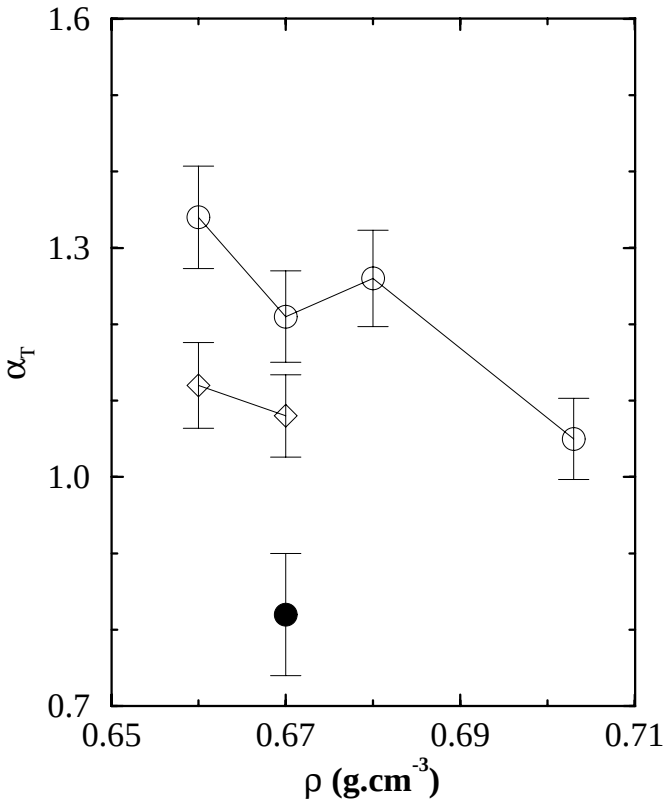

Figure 2: Thermal diffusion factor α_T versus density obtained by NEMD at 307 K (○) and 350 K (◇); Experimental point from Lindeberg (●) at 307 K.