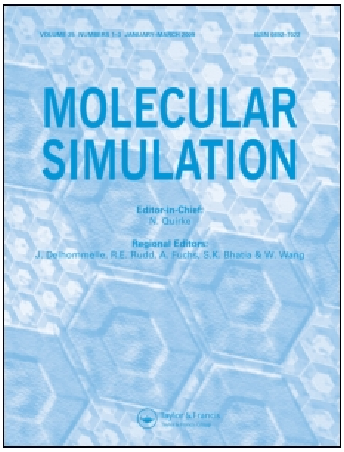
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Thermal Conductivity of Mixtures of Polyatomic Fluids Using Nonequilibrium Molecular Dynamics

P. Ravi[a]; S. Murad[a]
[a] Chemical Engineering Department, University of Illinois at Chicago, Chicago, IL, USA

To cite this Article Ravi, P. and Murad, S.(1992) 'Thermal Conductivity of Mixtures of Polyatomic Fluids Using Nonequilibrium Molecular Dynamics', Molecular Simulation, 9: 3, 239 — 245

To link to this Article: DOI: 10.1080/08927029208047430

URL: http://dx.doi.org/10.1080/08927029208047430

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1992, Vol. 9, pp. 239–245
Reprints available directly from the publisher
Photocopying permitted by license only

THERMAL CONDUCTIVITY OF MIXTURES OF POLYATOMIC FLUIDS USING NONEQUILIBRIUM MOLECULAR DYNAMICS

P. RAVI and S. MURAD

Chemical Engineering Department, University of Illinois at Chicago, Chicago, IL 60680-4348, USA

(*Received February 1992; accepted April 1992*)

The thermal conductivity of dense polyatomic fluid mixtures has been studied using the method of nonequilibrium molecular dynamics. Molecular mixtures of the type spherical–nonspherical and nonspherical–nonspherical, have been investigated. In addition, we have examined the contribution to thermal conductivity from internal rotational modes. Internal rotational contributions are needed for predicting thermal conductivity of polyatomics. Our results combined with those we obtained for pure polyatomics, have shown that the usual approximation made in theories, that these contributions are density independent is incorrect. Finally, we have also developed an approximate method for predicting internal contributions to thermal conductivity, that includes density dependence.

KEY WORDS: Polyatomic fluids, thermal conductivity, nonequilibrium molecular dynamics, internal degrees of freedom.

INTRODUCTION

Computer simulation methods have been widely used during the past two decades to study the thermal conductivity of pure fluids and mixtures. Both equilibrium (Green–Kubo) and nonequilibrium molecular dynamics algorithms have been extensively used [1–3]. More recently the nonequilibrium algorithm developed by Evans [4] has been extended for nonspherical systems [5], and has been used to study the thermal conductivity of several nonspherical fluids [5–8]. In this paper we have used this nonequilibrium molecular dynamics method to study the thermal conductivity of mixtures of the types spherical–nonspherical and nonspherical–nonspherical. The contribution from internal rotational degrees of freedom have been given special attention, since a satisfactory theory for predicting the thermal conductivity of polyatomics has to include these internal contributions. Since no satisfactory theory is currently available for obtaining such contributions, most predictive techniques assume out of necessity, that these contributions are density independent and equal to the dilute gas value, which can be estimated from kinetic theory. We have also developed a simple approximation for estimating these internal contributions, that accounts for the density dependence of these contributions, as the simulation results strongly indicate.

THEORY AND METHOD

In our work we have used the non-canonical linear response theory method for polyatomics [5]. In this method an external field is used to increase the energy of all particles in the system with more than the average energy, and decrease it for those with less than the average energy. This leads to a heat flux in the system, whose magnitude is used to estimate the thermal conductivity. The equations of motion given below show how such an external field can be incorporated in an NEMD study,

$$\dot{\boldsymbol{r}}_i = \boldsymbol{p}_i/m, \tag{1}$$

$$\dot{\boldsymbol{p}}_i = \sum_j \boldsymbol{f}_{ij} + (E_i - \bar{E})\boldsymbol{F}(t) + \tfrac{1}{2}\sum_j \boldsymbol{f}_{ij}\cdot[\boldsymbol{r}_{ij}\boldsymbol{F}(t)] - \frac{1}{2N}\sum_{jk} \boldsymbol{f}_{jk}[\boldsymbol{r}_{jk}\cdot\boldsymbol{F}(t)] - \alpha p_i, \tag{2}$$

$$I^p_{xx}\frac{d\omega^p_{ix}}{dt} = \Gamma^p_{ix} + \omega^p_{iy}\omega^p_{iz}(I^p_{yy} - I^p_{zz}) + \tfrac{1}{2}\sum_j \Gamma^p_{ijx}[r_{ij}F(t)]. \tag{3}$$

In Equations (1–3), $\boldsymbol{r}_i$ is the center of mass position of molecule i, m, the mass, $\boldsymbol{p}_i$, the linear momentum, $\boldsymbol{f}_{ij} = -\partial\phi_{ij}/\partial\boldsymbol{r}_i$, where ϕ_{ij} is the intermolecular potential (see below), and $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. N is the number of particles in the system. $\bar{E}$ is the average energy per particle, while E_i is for particle i. $\boldsymbol{F}(t)$ is the external field, which for simplicity, usually kept fixed at a constant value, and with only one non-zero component (e.g., z). α, the thermostatting multiplier, ensures constant translational kinetic energy. $\boldsymbol{\omega}^p$ is the principal angular velocity and $\boldsymbol{\Gamma}^p_{ij}$ is the principal torque on i due to j only, while Γ^p_i is that on i due to all other molecules. $\boldsymbol{I}^p$ is the principal moment of inertia. Equation (3) represents the expression for ω^p_x, the x component of ω^p. Similar equations can be written for the y and z components.

The thermal conductivity, λ can then be estimated from the equation,

$$\lambda^{\text{total}} = \frac{1}{T}\frac{\langle J_Q(t\to\infty)\rangle}{F(t)}, \tag{4}$$

where T is the temperature and the heat flux vector is

$$\boldsymbol{J}_Q = \frac{1}{V}\left[\sum_i E_i\frac{\boldsymbol{p}_i}{m} + \frac{1}{2}\sum_{ij} \boldsymbol{r}_{ij}\left(\frac{\boldsymbol{p}_i}{m}\cdot\boldsymbol{f}_{ij} + \omega^p_i\cdot\boldsymbol{\Gamma}^p_{ij}\right)\right]. \tag{5}$$

In Equation (5), V is the volume of the simulation cube. The method can be extended to mixtures by replacing p with π in Equation (5), to account for diffusive heat flux in the system [9]:

$$\boldsymbol{\pi}_i = \boldsymbol{p}_i - \frac{1}{N_v}\sum^{v}\boldsymbol{p}_i, \tag{6}$$

where N_v is the number of particles of species v and the summation in Equation (6) is only over species v.

For studying the contributions to thermal conductivity from various modes, J_Q, can be broken up into a rotational part given by,

$$\boldsymbol{J}^{\text{rot}}_Q = \frac{1}{2V}\left[\sum_j (\boldsymbol{\omega}^p_i\cdot\boldsymbol{I}^p\cdot\boldsymbol{\omega}^p_i)\frac{\boldsymbol{p}_i}{m} + \frac{1}{2}\sum_{ij}\boldsymbol{r}_{ij}(\boldsymbol{\omega}^p_i\cdot\boldsymbol{\Gamma}^p_{ij})\right], \tag{7}$$

while the remaining part is usually referred to as the translational contribution. The rotational contribution to thermal conductivity can then be estimated from,

$$\lambda^{\text{rot}} = \frac{1}{T}\frac{\langle J^{\text{rot}}_Q(t\to\infty)\rangle}{F(t)}. \tag{8}$$

Table 1 Intermolecular potential models.

Benzene	
$\sigma_{SS} = 0.35\,\text{nm}$	$\varepsilon_{SS}/K = 77.0\,\text{K}$
Bond length $= 0.1756\,\text{nm}$	
Methane I (nonspherical model)	
$\sigma_{CC} = 0.3350\,\text{nm}$	$\varepsilon_{CC}/K = 51.198\,\text{K}$
$\sigma_{CH} = 0.2995\,\text{nm}$	$\varepsilon_{CH}/K = 23.798\,\text{K}$
$\sigma_{HH} = 0.2813\,\text{nm}$	$\varepsilon_{HH}/K = 8.631\,\text{K}$
C–H Bond length $= 0.1094\,\text{nm}$	
Methane II (spherical model)	
$\sigma = 0.3733\,\text{nm}$	$\varepsilon/K = 149.92\,\text{K}$

In addition it is also possible to break up the rotational contributions into that from the inertieal term, and the torque term, identified by the first and second terms in Equations (7), respectively.

RESULTS

The method outlined above was used to study model mixtures of benzene and methane, to represent both spherical–nonspherical and nonspherical–nonspherical mixtures (see below). Details of the simulation technique are given in the Appendix. For benzene, a six center site–site Lennard–Jones potential has been used [10]. For methane, we have used two potential models. The first is a five center site–site Lennard–Jones potential (methane I) [11], while the second is an effective central Lennard–Jones potential (methane II) [12]. All the potential models used here have been found to give reasonable thermodynamic and transport properties for both benzene and methane. Details of the intermolecular potential models are given in Table 1. For the mixtures, we have used the usual Lorentz–Berthelot rules for cross interactions [13]. Results for mixtures of the type spherical–spherical, including multi-component mixtures, have been previously reported [2, 3, 14].

All results have been reported in dimensionless units based on the site–site benzene parameters (see Table 1). For ease of comparison, we have attempted to study mixtures at approximately equivalent "reduced" densities and temperatures. These reduced densities and temperatures have been based on the pseudo-critical densities and temperatures of the mixtures. For mixtures of the type benzene–methane (non-polar) the Lee–Kesler mixing rules [15] are known to work well and have been used here for obtaining the pseudo-critical densities and temperatures of these mixtures. This however does result in the "dimensionless' density and temperature of the mixtures (defined on the basis of the site–site benzene parameters) not remaining constant.

Results for benzene–methane I mixtures (nonspherical–nonspherical) are given in Table 2. The thermal conductivity is further divided into contributions from the rotational modes, as well as the torque contributions (see Equation (7)). Other contributions can be obtained easily since,

$$\lambda^{\text{total}} = \lambda^{\text{rot}} + \lambda^{\text{tr}}, \qquad (9)$$

Table 2 Thermal conductivity of model benzene–methane I mixtures.

x^a	T^*	ρ^*	λ^{total}	λ^{rot}	$\lambda^{rot\text{-}torque}$
100.0	5.50	0.24	8.95 ± 0.13	3.02 ± 0.08	2.78 ± 0.07
75.0	4.73	0.29	9.21 ± 0.06	3.27 ± 0.06	3.03 ± 0.05
50.0	3.88	0.36	9.93 ± 0.14	3.48 ± 0.07	3.28 ± 0.06
25.0	2.94	0.46	11.27 ± 0.09	3.69 ± 0.11	3.54 ± 0.10
0.00	1.86	0.62	15.60 ± 0.24	4.81 ± 0.08	4.67 ± 0.07

[a] Mole precent of benzene

$$\lambda^{\mathrm{rot}} = \lambda^{\mathrm{rot\text{-}inertial}} + \lambda^{\mathrm{rot\text{-}torque}}.$$

For mixtures of the type nonspherical–nonspherical (Table 2), at the roughly constant reduced densities and temperatures studied, it is apparent that the contributions from both the total internal and torque terms are approximately a constant percentage of the total thermal conductivity. In this case all the overall internal contribution are 33% ± 3%. In addition, it is clear that most of the contribution from the internal part, is in fact from the torque term (see Equation (9)). The translational part is however the dominant term of the thermal conductivity of these mixtures. This observation, perhaps, also explains why theories that have used the incorrect approximation, that the internal contribution is equal to the density independent kinetic theory result, have been reasonably successful for the nonpolar type mixtures studied here. By using empirical corrections (which such theories use), it is reasonably simple to rescale the translational term to account for errors associated with using the dilute gas values for internal contributions for dense fluids. However, such behavior may not be observed in other mixtures that are more complex in nature (e.g., polar–nonpolar mixtures). Many theories for thermal conductivity are known to fail for such mixtures.

Table 3 gives results for benzene–methane II (spherical–nonspherical type) mixtures. Since the potential used for methane, here, is an effective overall potential, it should be expected to account for both the translational and rotational modes, via the translational modes only. Up to benzene mole fractions of 50%, the internal contributions for mixtures with either methane I or methane II are identical within the statistical accuracy of the simulations. It appears that benzene by virtue of its larger size, and stronger molecular interactions (see Table 1), almost completely dominates the behaviour of the mixture. For smaller benzene concentrations, the effect of methane being modelled as a spherical molecule can be seen. For example at 25% benzene, the internal contributions are 33% in the case of nonspherical methane

Table 3 Thermal conductivity of model benzene–methane II mixtures.

x^a	T^*	ρ^*	λ^{total}	λ^{rot}	$\lambda^{rot\text{-}torque}$
100.0	5.50	0.24	8.95 ± 0.13	3.02 ± 0.08	2.78 ± 0.07
75.0	4.73	0.29	9.28 ± 0.20	3.23 ± 0.13	3.05 ± 0.12
75.0[b]	4.73	0.31	11.78 ± 0.11	4.04 ± 0.11	3.90 ± 0.10
50.0	3.88	0.36	10.02 ± 0.07	3.33 ± 0.06	3.20 ± 0.05
50.0[b]	3.88	0.43	15.79 ± 0.14	4.96 ± 0.09	4.93 ± 0.08
25.0	2.94	0.46	10.44 ± 0.05	2.61 ± 0.08	2.53 ± 0.07
0.00	1.86	0.62	13.01 ± 0.06	0	0

[a] Mole precent of benzene.
[b] These show the effect of density at constant temperature (see text).

Table 4 Comparison of internal contributions for benzene–methane mixtures.

A. Model I for methane

x^a	T^*	ρ^*	*Internal (rotational) contributions*		
			NEMD	*Eucken*[c]	*Equation (10)*[d]
100.0	5.50	0.24	3.02 ± 0.08	0.208	3.13
75.0	4.73	0.29	3.27 ± 0.06	0.439	4.02
50.0	3.88	0.36	3.48 ± 0.07	0.626	4.63
25.0	2.94	0.46	3.69 ± 0.11	0.658	4.77
0.00	1.86	0.62	4.81 ± 0.08	0.571	5.70

B. Model II for methane

x^a	T^*	ρ^*	*Internal (rotational) contributions*		
			NEMD	*Eucken*[c]	*Equation (10)*[d]
100.0	5.50	0.24	3.02 ± 0.08	0.208	3.13
75.0	4.73	0.29	3.23 ± 0.13	0.439	2.74
75.0[b]	4.73	0.31	4.04 ± 0.11	0.439	3.51
50.0	3.88	0.36	3.33 ± 0.06	0.626	2.88
50.0[b]	3.88	0.43	4.96 ± 0.09	0.626	4.66
25.0	2.94	0.46	2.61 ± 0.08	0.658	3.04
0.00	1.86	0.62	0	–	–

[a] Mole percent of benzene.
[b] See Table 3.
[c] Estimated error is 5% [16, 17].
[d] Estimated error is 15%.

mixtures, and 25% in the case of spherical methane mixtures; a significant difference that cannot be attributed to statistical error. In addition the two models for methane do not, as could be expected, give identical results for the total thermal conductivity of methane. At $T^* = 1.86$, and $\rho^* = 0.62$, the thermal conductivities are 15.60, and 13.01, for methane I and methane II respectively, a difference of about 17%. The nonsphercial model gives results closer to the experimental value for this state condition (the experimental value is 15.50). However, it is possible that for a different state condition, the spherical model could do as well or even better than the non-spherical model. The marked entries (*b*) in Table 3, are provided to clearly show the inadequacy of the approximation, that the internal contributions are independent of density changes, as had been shown previously for pure fluids [7, 8].

Our results also indicate that for pure fluids, and mixtures of the types investigated here, the internal contributions can be represented reasonably well by a simple approximation,

$$\lambda^{\mathrm{int}}(\rho, T) = \lambda^{\mathrm{int}}(0, T)\frac{\lambda^{\mathrm{tr}}(\rho, T)}{\lambda^{\mathrm{tr}}(0, T)}, \tag{10}$$

$\lambda^{\mathrm{int}}(0, T)$ and $\lambda^{\mathrm{tr}}(0, T)$, the zero density (dilute gas) rotational–internal and translations contributions, respectively, can be obtained from kinetic theory. We have used the modified Eucken method, as used in TRAPP and other semi-empirical methods [16, 17]. In our calculations we have used NEMD results for $\lambda^{\mathrm{tr}}(\rho, T)$, although there are several methods available for estimating these contributions, such as TRAPP [17]. Table 4 compares the NEMD results, the kinetic theory results, and those from Equation (10) for mixtures. Figure 1 shows results for the critical isotherm of pure

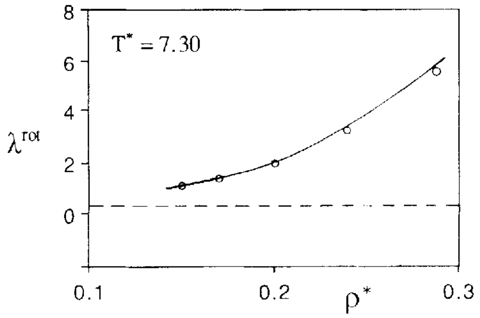


Figure 1 Comparison of internal contributions for pure benzene along the critical isotherm. - - Equation (10); ○ ○, NEMD; — —, Eucken correlation [16, 17].

benzene. Similar results were obtained for other state conditions of benzene as well [8]. These results show that Equation (10), although perhaps not very accurate, gives significantly better values for $\lambda^{int}(\rho, T)$, compared to the presently used kinetic theory-density independent approximation, and is just as simple to use.

CONCLUSIONS

We have presented thermal conductivity results based on the NEMD method, for mixtures of the type spherical–nonspherical and nonspherical–nonspherical. In addition contributions from the rotational modes have also been investigated. These contributions are important in prediction techniques for thermal conductivity. A simple approximation has been suggested for the internal rotational thermal conductivity, which is significantly better than the approximation currently used in most theories.

Acknowledgements

This work is funded by the Division of Chemical Sciences, Office of Basic Energy Research, Department of Energy, through Grant No. DE-FG02-87ER13769. The computations were performed on IBM 3090 at University of Illinois Computer Center and on Cray Y-MP at Supercomputer Computations Research Institute, Florida State University.

APPENDIX: DETAILS OF THE NEMD SIMULATION

Here we outline the details of the simulation technique employed. The simulations were carried out on 108 molecules (648 LJ sites for pure benzene) using a spherical cutoff of 3.0. The initial configuration was that of an FCC. Configurations from a previous simulation were used when possible. Equilibration took 20 000–30 000 time steps and an additional 100 000–150 000 time steps were needed for the thermal conductivity to converge. We used a reduced time step of 0.0005. The translational and rotational equations of motion were solved using Gear's fifth order predictor–corrector scheme (see Reference [11] for more details on the method used for solving the rotational equations of motion). The range of external fields used in this work were $F(t)^* = 0.1, 0.2, 0.3$ in reduced units. We found that within statistical uncertainties there was no observable dependence of the conductivity with respect to the magnitude of the external field. Calculations were also carried out for a 256 particle system (up to 1536 sites), and we verified that there was no size dependence. The gaussian thermostat (α in Equation (2)) was used to control the translational temperature. With the thermostat on and translational velocity rescaling done every time step the temperature was maintained within 1% of the desired value. No thermostat was used in the rotational equations of motion. Linear and angular momenta were conserved. As a further check, we tested the program with the thermostat turned off and $F(t)^* = 0$ (conventional EMD) to ensure that the total energy is conserved. The thermodynamic properties obtained from these EMD simulations agreed with previously published results [10–12]. In addition, the thermal conductivities obtained were found to agree, reasonably, with experimental values for both benzene and methane [18]. Although, this is not a direct test of the NEMD algorithm, in view of the previous success of these potential models for a wide range of thermodynamic and transport properties, such agreement should have been expected.

References

[1] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987).

[2] C. Hoheisel and R. Vogelsang, "Thermal transport coefficients for one- and two-component liquids from time correlation functions computed by molecular dynamics," *Comp. Phys. Rep.*, **8**, 1 (1988).

[3] D.J. Evans and G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London (1990).

[4] D.J. Evans, "Homogeneous NEMD algorithm for thermal conductivity – Application of non-canonical linear response theory," *Phys. Lett.*, **91A**, 457 (1982).

[5] D.J. Evans and S. Murad, "Thermal conductivity in molecular fluids," *Mol. Phys.*, **68**, 1219 (1989).

[6] B.Y. Wang and P.T. Cummings, "Nonequilibrium molecular dynamics calculation of the transport properties of carbon dioxide," *Fluid Phase Equilibria*, **53**, 191 (1989).

[7] S. Murad, D.P. Singh, H.J.M. Hanley and D.J. Evans, "Thermal conductivity of a model diatomic fluid," *Mol. Phys.*, **72**, 487 (1991).

[8] P. Ravi, S. Murad, H.J.M. Hanley and D.J. Evans, "The thermal conductivity coefficient of polyatomic molecules: Benzene," *Fluid Phase Equilibria*, in press (1992).

[9] D. McGowan and D.J. Evans, "Heat and matter transport in binary liquid mixtures", *Phys. Rev. A*, **34**, 2133 (1986); "Addendum," *Phys. Rev. A*, **36**, 948 (1987).

[10] D.J. Evans and R.O. Watts, "On the structures of liquid benzene," *Mol. Phys.*, **32**, 93 (1976).

[11] S. Murad and K.E. Gubbins, "Molecular dynamics simulation of methane using a singularity-free algorithm," *Computer Modeling of Matter*, P. Lykos, Editor, ACS Symposium Series **86**, 62 (1978).

[12] B. Saager and J. Fischer, "Predictive power of effective intermolecular pair potentials: MD simulation results for methane up to 1000 MPa," *Fluid Phase Equilibria*, **57**, 35 (1990).

[13] T.M. Reed and K.E. Gubbins, *Applied Statistical Mechanics*, McGraw-Hill, New York (1973), pp. 131.

[14] P. Ravi and S. Murad, "Thermal conductivity of continuous, semi-continuous and discrete mixtures using nonequilibrium molecular dynamics," *Molec. Sim.*, **7**, 325 (1991).

[15] J.M. Prausnitz, R.N. Lichtenthaler and E.G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, New Jersey (1986), pp. 472.

[16] R.C. Reid, J.M. Prausnitz and B.E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1987), Ch. 10.

[17] J.F. Ely and H.J.M. Hanley, "Prediction of transport properties. 2. Thermal conductivity of pure fluids and mixtures," *Ind. Eng. Chem. Fundam.*, **22**, 90, 1983; STRAPP, the latest version of TRAPP, is available from NIST.

[18] P.E. Liley, T. Makita and Y. Tanaka, *Properties of Inorganic and Organic Fluids*, C.Y. Ho, Editor, CINDAS Data Series on Material Properties, Volume V-1, Hemisphere, New York (1988).