

Thermal conductivity of molecular fluids from molecular dynamics simulations: Application of a new imposed-flux method

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We have applied a new nonequilibrium molecular dynamics (NEMD) method [F. Müller-Plathe, *J. Chem. Phys.* **106**, 6082 (1997)] previously applied to monatomic Lennard-Jones fluids in the determination of the thermal conductivity of molecular fluids. The method was modified in order to be applicable to systems with holonomic constraints. Because the method involves imposing a known heat flux it is particularly attractive for systems involving long-range and many-body interactions where calculation of the microscopic heat flux is difficult. The predicted thermal conductivities of liquid *n*-butane and water using the imposed-flux NEMD method were found to be in a good agreement with previous simulations and experiment. © 2000 American Institute of Physics. [S0021-9606(00)50841-1]

INTRODUCTION

Calculation of thermal conductivity from molecular dynamics (MD) simulations using equilibrium methods suffers significant difficulties due to complications in determining the microscopic heat flux $J(t)$ and the slow convergence of the time integral of the heat flux autocorrelation function.¹ While use of nonequilibrium molecular dynamics (NEMD) methods (e.g., Ref. 2) allows one to circumvent the latter problem, these methods still suffer from the former. This is particularly true for molecular fluids, which often involve long-range interactions (e.g., Coulomb) and/or many-body interactions (e.g., mutual induction effects). While the microscopic definitions of mass flux (self-diffusion) and momentum flux (viscosity) involve only self-particle or self- and interparticle static correlations, respectively, the heat flux involves interparticle dynamic correlations requiring evaluation of pair velocities.^{1,3} Long-range static correlations can be effectively treated using Ewald and related methods; however, no equivalent method exists for handling long-range dynamic correlations. Therefore, in determining thermal conductivity in systems with long-range interactions, one can either ignore these effects by truncating the range of interactions used in calculating the heat flux, include interactions on a sufficient length scale such that correlations vanish, or, preferably, devise a method that does not involve calculation of the microscopic heat flux.

Recently Müller-Plathe suggested an NEMD method for calculation of thermal conductivity.⁴ The idea of the method is to impose an exactly known heat flux on the system and then determine the resulting steady-state temperature gradient in the direction parallel to the heat flux. The thermal conductivity λ is given by the expression

$$\lambda = \frac{\langle J_z(t) \rangle}{2tA \langle dT/dz \rangle}, \quad (1)$$

where $\langle J_z(t) \rangle$ is total heat flux imposed during the simula-

tion on the system in the z direction, $\langle dT/dz \rangle$ is the resultant temperature gradient in this direction, A is the surface area perpendicular to the z -axis, and t is the total simulation time. The heat flux is created by exchanging velocities of particles in “cold” and “hot” slabs located in the middle of the simulation box and adjacent to one of the simulation box boundaries. The cold slab donates its “hottest” particles (particles with the highest kinetic energy) to the hot slab in exchange for the latter’s “coolest” particles (particles with the lowest kinetic energy). Performing this exchange periodically results in the heating up of the hot slab and cooling down of the cold slab. This process eventually yields a steady-state temperature gradient in the z direction due to thermal conduction through slabs separating the cold and hot slabs. The temperature gradient can be easily measured by calculating the local temperature in each slab. The imposed heat flux is given exactly by the relationship

$$\langle J_z(t) \rangle = \sum_{\text{transfers}} \frac{m}{2} (v_c^2 - v_h^2), \quad (2)$$

where v_c and v_h are the velocities of the identical mass particles that participate in the exchange procedure from the cold and hot slabs, respectively.

The imposed-flux NEMD method is compatible with periodic boundary conditions, it satisfies the energy and linear momentum conservation, it is trivial to implement and interpret the results, and it has been shown to yield satisfactory results for a monatomic Lennard-Jones fluid.⁴ Here we discuss modifications to the method that allow it to be applied to molecular systems with holonomic constraints. We then investigate the performance of the method in prediction of the thermal conductivity of real molecular liquids, namely *n*-butane, which does not involve long-range interactions and water, which does.

METHODOLOGY

The imposed-flux NEMD method can be used only in combination with the velocity Verlet algorithm⁵ in which the

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velocities of atoms are among the variables used in the integration of the equation of motion. In order to impose geometric constraints one can use the well-known schemes RATTLE⁶ or SHAKE.⁷ These methods iteratively satisfy bond constraints and additionally remove the component of the relative velocity of the two particles participating in a constraint along the bond connecting them. By exchanging the velocities of atoms participating in different constraints this latter condition is compromised. After velocities are exchanged a call of RATTLE or SHAKE removes any relative velocity along the constrained bonds with irreversible loss of kinetic energy; the total energy of the system is not conserved and the imposed heat flux cannot be measured exactly. In order to overcome this problem we suggest exchanging the translational velocities of two molecules rather than exchanging the velocities of two atoms. By exchanging the molecule center-of-mass velocities for two molecules while keeping the velocities of their atoms unchanged relative to their respective center-of-mass, the velocity constraint condition remains satisfied. It is simple to show that the total kinetic energy and linear momentum are conserved when the center-of-mass velocities of the molecules are exchanged (see Appendix A).

In the originally proposed methodology⁴ the imposed heat-flux NEMD was applied in conjunction with constant T simulations using weak coupling scheme⁸ with a single heat bath. Recently a methodology involving multiple thermostats has been proposed⁹ and applied for various systems.¹⁰ It was found that thermostating of each degree of freedom can significantly improve equilibration and statistics convergence.¹⁰ Since the particles velocities define the “force” for extended degrees of freedom, the direct coupling of imposed heat-flux NEMD with constant T simulations, where each molecule (particle) has its own thermostat, would result in the step function change in the “force” acting on the thermostats assigned to the particles participating in the velocity exchange. Such an instantaneous change in the thermostat force would introduce additional perturbations in the system and can result in the improper temperature control. In order to avoid these complications variables of the thermostats can be exchanged along with particles velocities. In Appendix B it is shown that such exchange procedure will conserve the total Hamiltonian and the thermostats forces.

RESULTS AND DISCUSSIONS

n-Butane. Liquid *n*-butane systems have been widely investigated by MD simulations,^{11–13} including calculation of thermal conductivity via equilibrium MD.^{3,14} Some experimental data for thermal conductivity¹⁵ as well as data obtained from fundamental equation of state (EOS)¹⁶ for *n*-butane are available. In this study the united atom (UA) OPLS (optimized potentials for liquid simulation) force field¹¹ was used for representation of *n*-butane molecules. The interaction between CH_i sites was described by a Lennard-Jones potential. The distance between bonded sites and the bend angles between bonds were constrained, while the dihedral angle was subjected to a torsional potential. Systems with 200 molecules were set up at 150 and 290 K with densities $\rho = 720.36$ and 640.0 kg/m^3 , respectively. The den-

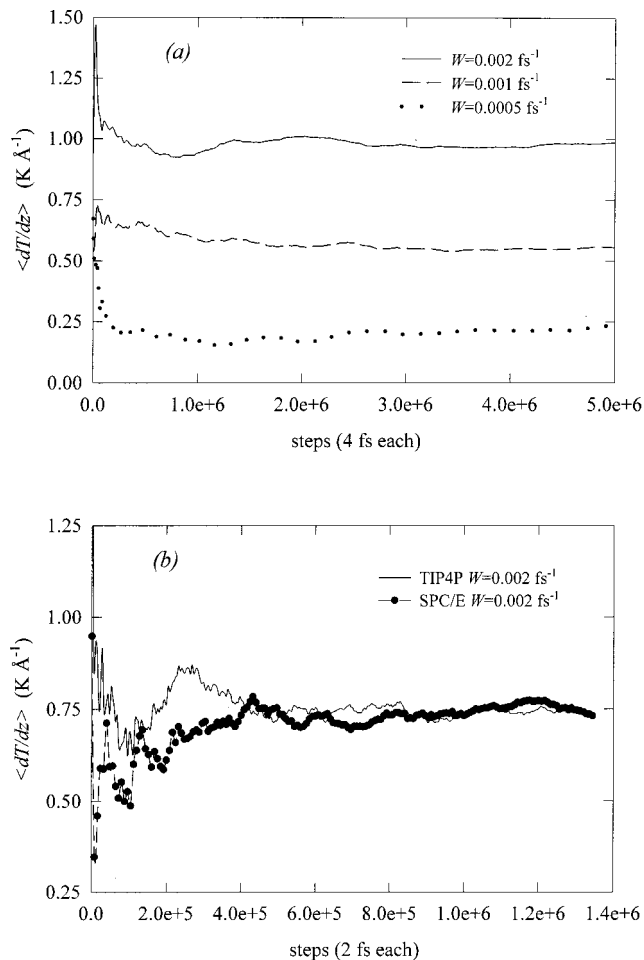


FIG. 1. Average temperature gradient as a function of simulation length for (a) *n*-butane at 150 K and (b) water at 318 K from accumulative statistics.

sities were taken from the simulations of Dysthe *et al.*¹⁴ in order to facilitate comparison of thermal conductivity with their predictions. The orthorhombic simulation box, extended in the z direction, was subdivided into 10 equal slabs of width 6.683 \AA and 400 \AA^2 (for 150 K) or 450.3 \AA^2 (for 290 K) cross-sectional area each. Equilibration runs of 5 ns with a time step of 4 fs in a constant density and temperature (NVT) ensemble using a Nosé–Hoover thermostat and explicit reversible integrator described elsewhere¹⁷ were performed. A nonbonded truncation of 9 \AA was employed. The production runs (in the NVT ensemble) were longer than 20 ns. For both temperatures simulations with three different frequencies (W) of velocity exchange were conducted.

During the simulations the instantaneous temperature in every slab was calculated each time step and an accumulated average temperature for each slab was determined as a function of the length of the run. The temperature profile in the z direction was approximated by a linear function based upon the current (accumulated) average temperature of the slabs, which allowed us to monitor the evolution of $\langle dT/dz \rangle$. The temperature gradient $\langle dT/dz \rangle$ as a function of the number of integration steps is shown in Fig. 1(a) for *n*-butane at 150 K for $W=0.002$, 0.001 , and 0.0005 fs^{-1} . The final average temperature distributions in the z direction together with linear fits are shown in Fig. 2. All distributions are symmetric

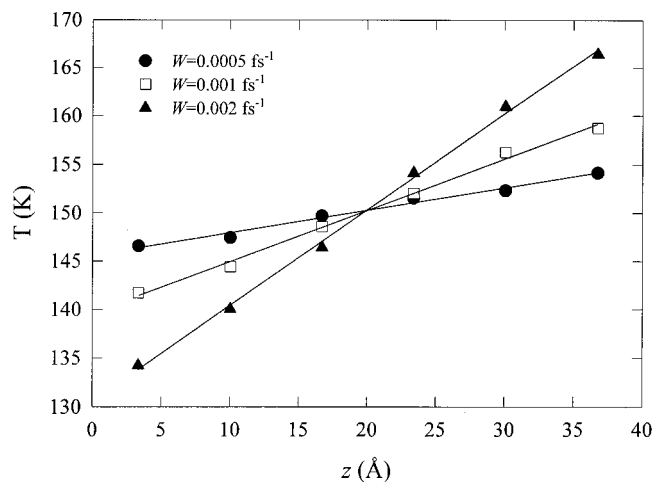


FIG. 2. Final temperature gradient in the z direction for n -butane at 150 K.

and the desired average temperature of 150 K is maintained.

It is important to understand the influence of the exchange frequency W on the calculated thermal conductivity. Figure 3 shows the calculated thermal conductivity (based upon accumulated temperature gradient and flux statistics) of n -butane as a function of the length of the simulation for the three exchange frequencies investigated. It is clear that a larger value of W results in a faster convergence of the thermal conductivity; a larger exchange frequency yields a larger temperature gradient and flux, and hence better statistics for a given length of trajectory. Too large a gradient, however, will result in a non-linear response of the system, thereby setting a maximum for the exchange frequency. As can be seen in Fig. 3, we have chosen a range of W for which the predicted thermal conductivity does not depend on the choice of W beyond its influence on the trajectory length required to obtain good statistics. We believe that an extensive investigation of correlation of W parameter with other simulation parameters (e.g., simulation box geometry, integration time step, temperature, etc.) and influence of those correlations on the statistics convergence should be performed in order to derive the recipe for the optimal choice of

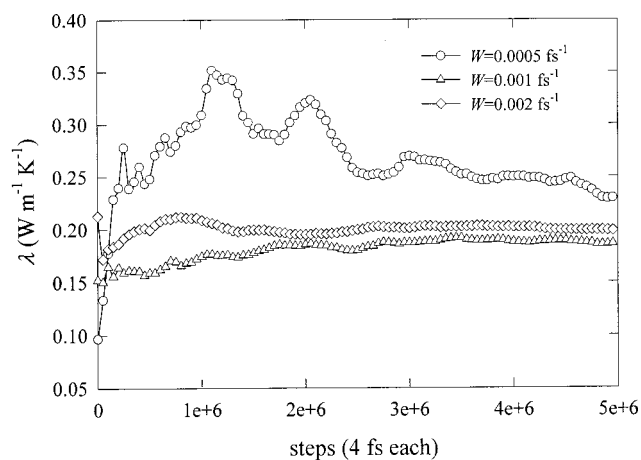


FIG. 3. Thermal conductivity of n -butane at 150 K as a function of simulation length from accumulative temperature gradients and heat fluxes.

TABLE I. Thermal conductivity of n -butane and water.

T (K)	W (fs $^{-1}$)	$\langle dT/dz \rangle$ (K/Å)	λ (W/mK)		
			This work	Previous simulations	Experiment
<i>n</i> -butane					
150	0.0005	0.23	0.228	0.168 ^a	0.192 ^b
	0.001	0.55	0.187		
	0.002	1.01	0.198		
290	0.0005	0.66	0.138	0.123 ^a	0.137 ^b
	0.001	1.19	0.149		
	0.002	2.26	0.147		
TIP4P water					
318	0.002	0.74	0.781		0.64 ^c
	0.004	1.66	0.725		
SPC/E water					
318	0.002	0.73	0.784		0.64 ^c
	0.004	1.55	0.730		

^aReference 14.

^bReference 16.

^cReference 22.

W before the simulation or based on short preliminary simulations. In the meantime, an empirical approach can be taken in order to determine the appropriate velocity exchange frequency. In this approach the most important criteria should be the consistency of the predicted thermal conductivities using different frequencies, which would validate that the simulations with W from the chosen range follow a linear response behavior. Our experience with n -butane, water and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)¹⁸ reveals that when an empirically determined optimal value of W is established for one thermodynamic state, the same value can be reliably used for other states in the wide domain of temperature and pressure.

Thermal conductivities obtained from the imposed-flux NEMD method are compared with equilibrium molecular dynamics simulations¹⁴ and fundamental EOS¹⁶ predictions in Table I. At 290 K we compare our simulation results with the thermal conductivity predicted by EOS at 600 atm, which is the vapor pressure of n -butane at this temperature. Simulation at 150 K using the lowest frequency ($W=0.0005$) was not run long enough to provide the converged value of thermal conductivity (see Fig. 3) and, therefore, has the largest deviation from the EOS prediction. The thermal conductivity of n -butane as well as its temperature dependence predicted by the imposed-flux NEMD method is consistent with EOS values and previous equilibrium MD simulations.

Water. We chose pure water as a model system to test the ability of the imposed-flux NEMD method to yield accurate thermal conductivities for systems with long-range interactions. Despite extensive MD simulation studies of water, it appears that its thermal conductivity has not been calculated. We have performed simulations of pure water employing the widely used TIP4P¹⁹ and SPC/E²⁰ potentials. A nonbonded truncation of 9 Å was employed. Ewald summation⁵ with 152 reciprocal-space vectors and a real-space exponent of $6/L$ ($L=20$ Å) was employed to handle long-range electrostatic interactions. The initial systems of 240 molecules were

equilibrated over 1 ns followed by constant pressure and temperature (NPT) simulations of 1 ns at atmospheric pressure and 318 K in order to determine the equilibrium densities. The predicted densities (992.0 and 985.1 kg/m³ for TIP4P and SPC/E water, respectively) were found to be in good agreement with experiment (990.17 kg/m³). Temperature gradients were then established during 0.5 ns NVT runs, followed by 2.5 ns production runs in the NVT ensemble using a 2 fs integration time step. For both models the simulations were conducted with exchange frequencies $W = 0.002 \text{ fs}^{-1}$ and 0.004 fs^{-1} . The evolution of the temperature gradient for the water systems is shown in Fig. 1(b) for $W = 0.002 \text{ fs}^{-1}$. Despite the fact that the TIP4P and SPC/E models provide noticeably different descriptions of some thermophysical properties (e.g., the self-diffusion coefficient) of pure water,²¹ the steady-state temperature gradients are similar, resulting in similar values of thermal conductivity. The imposed-flux NEMD simulations with $W = 0.004$ have less statistical uncertainty and therefore are believed to provide the most accurate values of the thermal conductivity of water ($\lambda = 0.73 \pm 0.05 \text{ W/mK}$) at 318 K which is in good agreement with experiment.²²

CONCLUSIONS

We have demonstrated that with minor modifications the imposed-flux NEMD method proposed by Müller-Plathe⁴ for calculating thermal conductivity can be used for molecular systems with holonomic constraints. In contrast to equilibrium and other non-equilibrium methods the imposed-flux NEMD method does not involve calculations of the heat flux vector $J(t)$ using the microscopic definition, which is complex and can markedly slow down computations particularly when long-range and/or many-body interactions are involved. Instead, an exactly known heat flux is imposed on the system and the established temperature gradient is measured during the simulation. The rare velocity exchange between two molecules required to establish the temperature gradient causes only small instantaneous perturbations to the system. We have shown that this method can be applied to simulations where multiple thermostats are employed for the temperature control. These advantages as well as simplicity in implementation and interpretation make the method very attractive for practical application in molecular systems. The method was tested on liquid *n*-butane and water. For *n*-butane, simulation results ($\lambda \approx 0.193 \text{ W/mK}$ at 150 K and $\lambda \approx 0.145 \text{ W/mK}$ at 290 K) were in good agreement with EOS and previous equilibrium simulation predictions over a wide temperature range. For water, this work appears to be the first prediction of thermal conductivity from MD simulations and yields values ($\lambda \approx 0.73 \text{ W/mK}$ at 318 K) in good agreement with experiment, demonstrating the applicability of the method to systems with long-range interactions.

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APPENDIX A

The velocity vector of any atom in the system can be expressed as

$$v_i = v_\alpha^{\text{c.m.}} + v_{\alpha_i}^*, \quad (\text{A1})$$

where $v_\alpha^{\text{c.m.}}$ is the center-of-mass velocity of molecule α (to which atom i belongs) and $v_{\alpha_i}^*$ is the velocity of atom i relatively to the center of mass of molecule α . Consider the total kinetic energy (K) of two molecules (α and β) consisting of N atoms and participating in the exchange procedure:

$$\begin{aligned} 2K &= \sum_i^N m_{\alpha_i} (v_\alpha^{\text{c.m.}} + v_{\alpha_i}^*)^2 + \sum_j^N m_{\beta_j} (v_\beta^{\text{c.m.}} + v_{\beta_j}^*)^2 \\ &= v_\alpha^{\text{c.m.}2} \sum_i^N m_{\alpha_i} + 2v_\alpha^{\text{c.m.}} \sum_i^N m_{\alpha_i} v_{\alpha_i}^* + \sum_i^N m_{\alpha_i} v_{\alpha_i}^{*2} \\ &\quad + v_\beta^{\text{c.m.}2} \sum_j^N m_{\beta_j} + 2v_\beta^{\text{c.m.}} \sum_j^N m_{\beta_j} v_{\beta_j}^* + \sum_j^N m_{\beta_j} v_{\beta_j}^{*2}. \end{aligned} \quad (\text{A2})$$

The second and fifth terms in the last expression are equal to zero and therefore

$$2K = v_\alpha^{\text{c.m.}2} M_\alpha + \sum_i^N m_{\alpha_i} v_{\alpha_i}^{*2} + v_\beta^{\text{c.m.}2} M_\beta + \sum_j^N m_{\beta_j} v_{\beta_j}^{*2}, \quad (\text{A3})$$

where M_α and M_β are the total masses of molecules α and β , respectively. The second and fourth terms of the rhs of Eq. (A3) will not be changed after the velocity exchange procedure since these are the contributions of the molecules' rotational motion which we suggest to keep unchanged. If M_α and M_β are equal then exchanging $v_\alpha^{\text{c.m.}}$ and $v_\beta^{\text{c.m.}}$ does not change K and since all positional degrees of freedom in the system are unaffected by the exchange, the total energy of the system will be conserved after the velocity exchange procedure. Similarly it can be shown that the total linear momentum of the system is also conserved.

APPENDIX B

For illustrative purposes let us consider that each particle has its own temperature controller (thermostat). If each of these thermostats are simple Nosé–Hoover type, then equations of motion can be written as

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}, & \dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p}{Q_i} \mathbf{p}_i, \\ \dot{\eta}_i &= \frac{p}{Q_i} \eta_i, & \dot{p} \eta_i &= \frac{\mathbf{p}_i^2}{m_i} - 3kT, \end{aligned} \quad (\text{B1})$$

where each particle ($i = 1, 2, \dots, N$) with position vector \mathbf{r}_i , momentum \mathbf{p}_i and the total acting force \mathbf{F}_i is coupled with

the thermostat η_i which has conjugated mass Q_i and momentum p_{η_i} . The conserved extended Hamiltonian corresponding to equations of motion (B1) is

$$H = \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m_i} + \frac{p_{\eta_i}^2}{2Q_i} + 3kT\eta_i \right] + \phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (\text{B2})$$

where $\phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the potential energy of the N -particle system. If during the exchange procedure between particles i and j the variables $(\mathbf{p}_i, p_{\eta_i})$ and $(\mathbf{p}_j, p_{\eta_j})$ are exchanged, then the extended Hamiltonian (H) and “force” on the thermostats (\dot{p}_{η_i}) would remain unchanged.

In case of molecular fluids at least two thermostats will be required: one is coupled with the molecular center of mass motion, another is coupled with rotational motion of the molecule. Since the molecular rotational motion is not effected by the proposed exchange of the center of mass velocities, therefore only variables of the thermostats coupled with the center of mass motion of molecules i and j should be exchanged simultaneously with velocity exchange.

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