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Citation: [The Journal of Chemical Physics](#) **106**, 6082 (1997); doi: 10.1063/1.473271

View online: <http://dx.doi.org/10.1063/1.473271>

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A simple nonequilibrium molecular dynamics method for calculating the thermal conductivity

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(Received 1 November 1996; accepted 7 January 1997)

A nonequilibrium molecular dynamics method for calculating the thermal conductivity is presented. It reverses the usual cause and effect picture. The “effect,” the heat flux, is imposed on the system and the “cause,” the temperature gradient is obtained from the simulation. Besides being very simple to implement, the scheme offers several advantages such as compatibility with periodic boundary conditions, conservation of total energy and total linear momentum, and the sampling of a rapidly converging quantity (temperature gradient) rather than a slowly converging one (heat flux). The scheme is tested on the Lennard-Jones fluid. © 1997 American Institute of Physics. [S0021-9606(97)51014-2]

I. INTRODUCTION

“The thermal conductivity has proven to be one of the most difficult transport coefficients to calculate.”¹ The Green–Kubo route suffers from the difficulty of converging the heat flux vector $\mathbf{J}(t)$ and its autocorrelation function. Numerous nonequilibrium molecular dynamics (NEMD) methods have been proposed (see, e.g., Refs. 1–3 and references therein). It is not the purpose of this short note to review them here. Instead, let us look at the features the ideal method should have.

- (i) *Homogeneity.* There should be no artificial “walls” in the simulated system, since these cause a fluid structure different from the bulk.
- (ii) *Boundary conditions.* The method should be compatible with the chosen boundary conditions. In the case of condensed phases, this usually means periodic boundary conditions.
- (iii) *Small temperature gradient.* If the temperature and, consequently, the density vary much over the system then the calculated thermal conductivity will be an average over different temperatures and densities. Moreover, the system may no longer be in the area of linear response.
- (iv) *Conservation of energy and momentum.* If the energy is conserved thermostat problems do not arise and the method is applicable independently of the chosen ensemble.
- (v) *Convergence.* Meaningful statistical averages on intermediate quantities have to be obtained reasonably quickly. Therefore intermediate quantities are to be preferred that do not exhibit overly large fluctuations.
- (vi) *Hamiltonian.* The equations of motion should be derived from a suitable Hamiltonian so that connections with statistical mechanics of the chosen ensemble are easier to make.

The method presented in this article has all of the above features except the last. In addition, it is very simple to derive and to implement.

II. THEORY

Macroscopically, the thermal conductivity λ is defined by

$$\mathbf{J} = -\lambda \nabla T. \quad (1)$$

where ∇T is the gradient of the temperature T , \mathbf{J} is the resulting heat flux vector which is defined as the amount of energy transferred in a given time through a surface of a given area which is perpendicular to the flux direction. It is typically given in units of W m^{-2} . In general, the thermal conductivity is a 3×3 tensor. In this article, we are concerned with isotropic fluids where the temperature gradient and the heat flux are collinear and λ can be taken as scalar. Taking the z direction as the direction of the temperature gradient, we can define the thermal conductivity microscopically in terms of time averages,

$$\lambda = \lim_{\partial T / \partial z \rightarrow 0} \lim_{t \rightarrow \infty} - \frac{\langle J_z(t) \rangle}{\langle \partial T / \partial z \rangle}. \quad (2)$$

The natural simulation experiment, set up in analogy to real experimental measurements, would be to impose a temperature gradient on the simulated system, to calculate the heat flux $J_z(t)$ parallel to the gradient, and to obtain the thermal conductivity through Eq. (2). Such calculations have been done. The problem with this approach, however, is that $J_z(t)$ is a quantity with large fluctuations so its average converges slowly and large temperature gradients are needed to induce a heat flow distinguishable from the noise. Therefore, we proceed in the reverse direction. We impose a heat flux on the system and measure the resulting temperature gradient. This has the advantage that the slowly converging quantity (heat flux) is known exactly and need not be calculated. The temperature and its gradient, on the other hand, are averages calculated over time as well as over many particles so they are better defined and should converge rapidly.

In order to impose a heat flux and to calculate a temperature profile, the simulation box is divided into N slabs perpendicular to the z direction (Fig. 1). In the present work, the

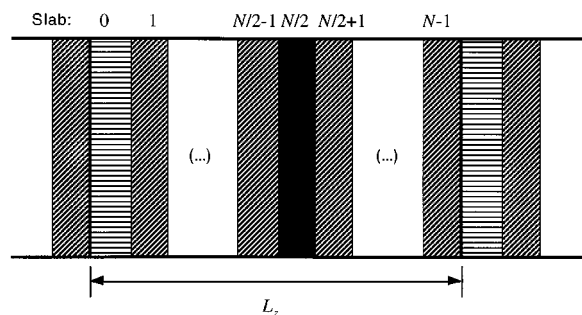


FIG. 1. Subdividing the periodic simulation box into slabs. Slab 0 is the “cool” slab, slab $N/2$ the “hot” slab. Kinetic energy is artificially transferred from the cool to the hot slab and then flows back by thermal conduction. The temperature profile is calculated by determining the temperatures in the intervening slabs (1 to $N/2-1$ and $N/2+1$ to $N-1$).

slabs are chosen to be of identical thickness and, hence, volume. The instantaneous local kinetic temperature T_k in slab k is given by

$$T_k = \frac{1}{3n_k k_B} \sum_{i \in k}^{n_k} m_i v_i^2, \quad (3)$$

where the sum extends over the n_k atoms i in slab k with masses m_i and velocities \mathbf{v}_i ; k_B is Boltzmann’s constant. The temperature profile is then calculated by time averaging.

Slab 0 is defined as the “cool” slab and slab $N/2$ as the “hot” slab. The heat flux is generated by exchanging the velocity vectors of an atom in the cool slab and one in the hot slab in a way that the temperature increases in the hot slab and decreases in the cool slab. We simply take the hottest atom of the cool slab and the coldest atom of the same mass in the hot slab. The distribution of atomic kinetic energies is so wide compared to the temperature difference of the two slabs that we always found the hottest atom in the cool slab to have more kinetic energy than the coolest atom in the hot slab. The above mechanism produces an energy transfer from the cool slab to the hot slab. This leads to a temperature difference between the cool and the hot slab and a temperature gradient in the intervening region. It can be shown that exchanging the velocities of two particles of equal mass leaves the total linear momentum, the total kinetic energy, and the total energy (in a conservative system) unchanged, and that velocity transfer by exchange is the only one which satisfies these conservation laws. The total angular momentum, however, is not conserved. This should normally not be a problem, since, except for vacuum boundary conditions, the angular momentum is anyway not a constant of motion.

After reaching steady state, the energy transfer imposed by the unphysical velocity exchange is exactly balanced by the heat flux in the opposite direction effected by the thermal conductivity of the system. The imposed heat flux, on the other hand, is known exactly, since one only has to sum the “quanta” of energy transported by velocity exchanges. The temperature gradient remaining in the steady state depends directly on the thermal conductivity. The higher λ , the more

efficient the heat transport and the smaller the temperature gradient between slabs 0 and $N/2$. The thermal conductivity is calculated as

$$\lambda = - \frac{\sum_{\text{transfers}} \frac{m}{2} (v_h^2 - v_c^2)}{2t L_x L_y \langle \partial T / \partial z \rangle}. \quad (4)$$

The sum is taken over all transfer events during the simulation time t . The subscripts h and c refer to the hot and the cold particle of identical mass m whose velocities are interchanged. In the orthorhombic periodic geometry of this work, the area through which heat transport takes place is the product of L_x and L_y , the box lengths in x and y , respectively. The factor of 2 in the denominator arises from the periodicity of the arrangement (cf. Fig. 1). Energy can flow from the hot slab to the cold slab in two directions, effectively doubling the area available for the flux. Note that all quantities in Eq. (4) are known exactly, except the temperature gradient which has to be obtained as an ensemble average.

III. COMPUTATIONAL DETAILS

The simulated system consisted of 2592 Lennard-Jones atoms in an orthorhombic periodic cell of size $10.0587 \times 10.0587 \times 30.1762 \sigma^3$ (Lennard-Jones reduced units⁴ are used throughout this paper), leading to a number density ρ^* of 0.849. The cutoff distance was 3σ . A Verlet neighbor list was used and updated every 12 steps. In the update, we take advantage of the elongated geometry of the cell. Particles are first indexed according to their z coordinate. Then the search for neighbors of a particle with index i is only performed over particles j , where j is within a certain range of i , the range given by cell size and cutoff.⁵ A time step Δt^* of 6.965×10^{-3} was used in connection with a multiple-time-step scheme based on the velocity-Verlet algorithm;⁶ long-range forces ($>2.06\sigma$) were evaluated only every 3 time steps, the switching distance was 0.29σ . The average total temperature T^* [defined analogously to Eq. (3), but with a summation over all atoms] is 0.694. In constant- T simulations, T^* is maintained at this value by the weak coupling scheme⁷ with a coupling time of 4.64. In constant-energy (constant- E , microcanonical) simulations no coupling is applied. They are preceded by a short constant- T run during which the system is equilibrated to this temperature. The heat flux is imposed in the z direction and the number of slabs is 20. The magnitude of the heat flux and of the resulting temperature gradient is governed by the interval W (number of time steps) between velocity exchanges. Four different values of W were used. As it is the purpose of this paper to present and verify the new algorithm, rather than to calculate the thermal conductivity of the Lennard-Jones liquid, results for only one state point are reported.

IV. RESULTS AND DISCUSSION

The periodic application of velocity exchanges leads to a temperature gradient. This is shown in Fig. 2 for the simula-

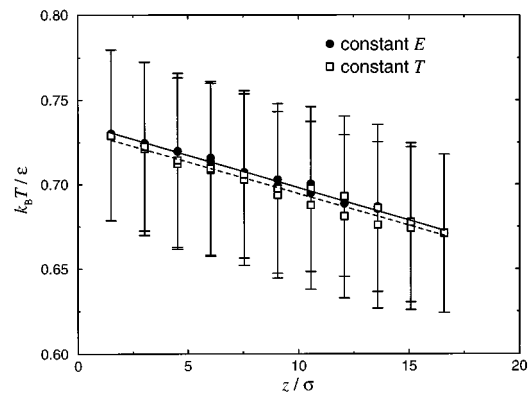


FIG. 2. Temperature profile for a velocity exchange interval W of 120 time steps. Temperatures of the symmetry equivalent slabs are both shown to indicate the convergence. The constant- T data carry error bars which denote the standard deviation of the temperatures in the slabs; the error bars for the constant- E data are very similar and are omitted for clarity. The straight lines indicate least-squares fits to the two data sets.

tions with an interval W of 120 time steps. First, it is noted that the choice of constant energy or constant (total) temperature has no significant effect on the temperature profile. Second, the scatter between the temperatures of slabs which should have the same average temperature by symmetry (like slabs 1 and 18, 2 and 17, etc.) is small, indicating that the

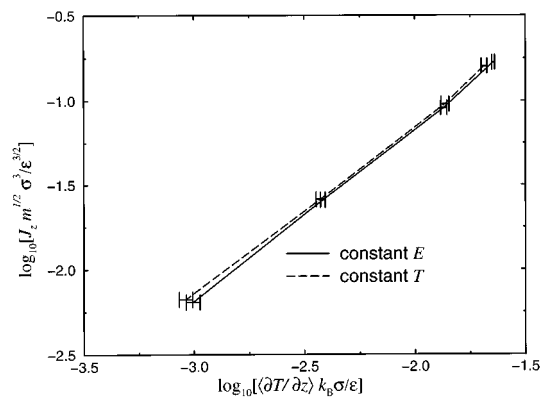


FIG. 4. Relation between the temperature gradient and the heat flux. Note the conventional representation with the temperature gradient being the cause and the heat flux being the effect. Error bars denote the standard error of the slope of the respective temperature profile as obtained by a least-squares fit.

averages of the slab temperatures are converged in spite of their sizable natural fluctuations indicated by error bars. Third, both temperature profiles are linear and can be fitted by straight lines. Their slopes are taken as the temperature gradients, $\langle dT/dz \rangle$. The linear regression also gives the standard error of the slope¹¹ and hence, the gradient. Analysis of the propagation of errors in Eq. (4) allows the calculation of error bars on λ .

The magnitude of the temperature gradient decreases with an increase of W . This is demonstrated in Fig. 3(a). For $W=15$, the temperature spans the range from 0.5 to 0.9, which translates to ~ 60 – 110 K for argon. For $W=480$, on the other hand, the temperature difference between the hot and the cold slab is less than 2 K for Ar, which is to be considered a small perturbation of the system. The temperature profile leads to a concomitant density profile [Fig. 3(b)].

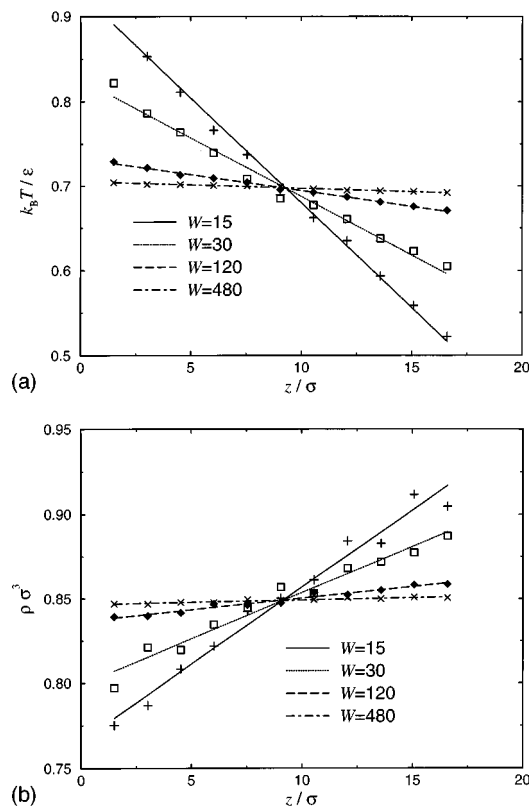


FIG. 3. (a) Temperature profiles and (b) density profiles calculated at constant- T conditions for different velocity exchange intervals W ; symmetry-equivalent data are averaged. The straight lines are least-squares fits to the respective data.

TABLE I. Thermal conductivity λ^* for the Lennard-Jones liquid at $T^*=0.7$ and $\rho^*=0.85$.

Time steps between velocity exchanges W	Simulation length (10^3 time steps)	λ^* , standard error in parentheses
constant- E		
15	2.4	7.43 (0.11)
30	9.6	6.45 (0.21)
120	48	6.70 (0.17)
480	180	6.45 (0.47)
constant- T		
15	2.4	6.51 (0.17)
30	4.8	6.93 (0.56)
120	48	6.92 (0.33)
480	180	7.20 (0.51)
reference values		
MD–Green–Kubo ^a		7.66($T^*=0.745$, $\rho^*=0.85$)
NEMD-weak coupling ^b		7.12($T^*=0.884$, $\rho^*=0.75$)
Experiment ^c		7.02($T^*\approx 0.71$, $\rho^*\approx 0.84$)

^aReference 8.
^bReference 9.
^cData for argon (Ref. 10) reduced using $\epsilon/k_B=119.6$ K, $\sigma=0.3405$ nm, $m=39.95$ amu.

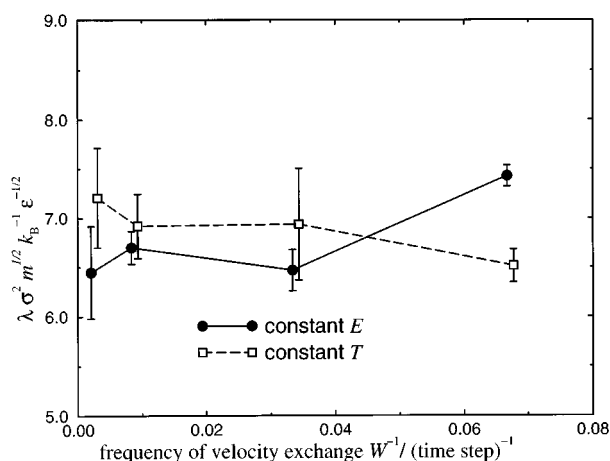


FIG. 5. Dependence of the calculated thermal conductivity on the strength of the applied perturbation given as the reciprocal of the interval between velocity exchanges, W^{-1} . For clarity, the constant- T data are offset in the abscissa.

In the present case, this is also linear to a good approximation, although noisier than the temperature profile. This need not be the case, there could for instance be a liquid–gas boundary with a density jump if the temperature range is so chosen. For $W=480$, the inhomogeneity is small also for the density.

In order to determine if linear response theory [Eq. (2)] is valid, it is useful to plot the flux vs the gradient (Fig. 4). Note, that the figure uses the conventional flux vs force representation, even though in our simulation the flux is imposed and the gradient is the effect. The doubly logarithmic representation of Fig. 4 clearly shows that linear response holds for all but the largest perturbation ($W=15$).

Calculated values for λ are summarized in Table I. All calculated values except one are within 10% of the experimental value at the same state point. Even the $W=15$ calculations yield reasonable conductivities in spite of the huge temperature and density gradients and the breakdown of linear response! The reported simulation lengths, however, indicate that for the weak perturbation ($W=180$) one has to simulate considerably longer to establish a stationary temperature gradient and to accumulate enough statistics. (Having said that, however, one has to keep in mind that even the longest run reported in Table I did not take longer than a night on an entry-level work station.) Simulations with W between 30 and 180 seem to be a good compromise between speed and accuracy. One also notes (Fig. 5) that there is practically no difference between λ values calculated at constant- T or constant- E conditions in relation to their error bars.

V. CONCLUSIONS

A simple method for the calculation of the thermal conductivity has been devised. It has been tested for the

Lennard-Jones fluid and shown to give correct results with reasonable accuracy at modest computational expense. A few features are worth mentioning.

- (i) The method does not alter the boundary conditions. This work uses orthorhombic periodic boundary conditions, but the simulation box is not restricted to be orthorhombic and does not even have to be periodic. The inhomogeneity introduced is limited to the temperature profile and the resulting density profile.
- (ii) Provided the hot particle has the same mass as the cold particle, the method conserves total energy as well as linear momentum. Conservation of total energy means that the method can be applied without a thermostat so it should work with different ensembles.
- (iii) Since only two out of many particles are affected by the velocity exchange, the perturbation has to be considered small for a large enough system. Moreover, in practice velocity exchanges only have to take place every so many time steps. If necessary, one can also think of modifications to the scheme in which particles with smaller energy differences are swapped.
- (iv) Since there are no sources and sinks of energy in the intervening slabs, the steady-state heat flux is the same for all of them. This implies that thermal conductivities for several intermediate temperatures and densities can be calculated from the local temperature gradients, provided there is sufficient sampling. This could be interesting, for example, if the temperature range established in the scheme encompassed a phase transition region with an interface being present in the simulation.¹²
- (v) In contrast to other nonequilibrium schemes, this one is not time-reversal invariant.

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