# Lennard-Jones triple-point conductivity via weak external fields

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We have performed a nonequilibrium molecular-dynamics (NEMD) computation of thermal conductivity for a simple dense fluid near the triple point using the differential NEMD method and a translationally invariant algorithm recently proposed by Evans. We have simulated a set of thermal gradients in the range 75.8 K/cm to $2.54\times10^8$ K/cm. Our main conclusion concerns the response of the energy current at $\vec{K}=\vec{0}$, which is linear in the range indicated. To check the efficiency of the present NEMD technique we have compared the nonequilibrium results with our own and Levesque's equilibrium Green-Kubo results. The agreement found is remarkable.

## I. INTRODUCTION

The hydrodynamic transport coefficients can be obtained from simulations in two ways, either by equilibrium molecular-dynamics experiments by using the standard Green-Kubo relations or by nonequilibrium molecular-dynamics (NEMD) simulation. The success of the NEMD approach rests on the possibility it offers to study directly the response induced by a suitable perturbation and the validity of the linear phenomenological laws.

Moreover, it is generally agreed that NEMD techniques are more efficient in terms of computer time. For the particular case of thermal conductivity the design of a thermal perturbation has proved to be more difficult, and up to now three techniques have been used.

The first two[1,2] consist of models in which suitable boundary conditions allow the simulation of stationary nonequilibrium states. A thermal gradient is realized in the first by setting up two "fluid walls" at different temperatures at opposite boundaries of the molecular-dynamics (MD) box in the direction of the heat flux. In the second the contact between the fluid and two heat reservoirs at different temperatures is obtained through stochastic boundary conditions on the velocity distribution.

In the differential method[3] the response induced by the perturbing field is computed as the difference between the energy current measured in two separate phase-space trajectories, namely the perturbed (external field switched on) and unperturbed (no external field) trajectories.

Each of these techniques has disadvantages. In the first two the thermal gradients simulated are much larger than the experimental gradients. This is necessary in order to obtain a satisfactory signal-to-noise ratio. Moreover, wall effects are unavoidable. On the other hand, in the realization of the differential method as stated in Ref. 3, it appears to be impossible to take the required zero-wave-vector limit in the observable of interest.

Recently, Evans[4] has proposed a translationally invariant NEMD algorithm which allows the calculation of the thermal conductivity for a system with periodic boundary conditions. The method has been tested on a dense Lennard-Jones fluid subjected to non-Hamiltonian perturbations equivalent to very large "nonphysical" thermal gradients. The system is maintained in a steady state by removing heat thanks to an appropriate rescaling of the second moment of the velocity. Evans finds a reasonable extrapolation to zero perturbation of the observed thermal conductivity while the last increases with the "thermal gradient": a phenomenon without any obvious physical explanation. Similar ideas have been independently developed by Dixon and Gillan,[5] who proposed the use of similar non-Hamiltonian perturbation in conjunction with the differential technique. However, they did not study the dependence of the calculated thermal conductivity on the strength of perturbation and, for the single perturbation studied, they found a disappointing lack of agreement with their own Green-Kubo result.

In this work we present a NEMD computation of the thermal conductivity for the same thermodynamic state considered in Ref. 4. We simulate a set of "small" thermal gradients by using the algorithm proposed by Evans but adopting the differential method. The main result of our computer experiment is that we find statistical linearity for gradients in the range 75.8 K/cm to $2.54\times10^8$ K/cm. We did not use larger perturbations to avoid any detectable heating of the system. Indeed, for the largest gradient studied, the difference between the total energy of the perturbed and unperturbed system was less than one part over $10^4$. Our range includes the lower part of the range studied by Evans. Our results do not support Evans's finding that "thermal conductivity" increases with increasing field. We have no simple explanation for this discrepancy because the most relevant difference in the two methods is the presence in Evans's procedure of the "velocity rescaling," a seemingly irrelevant detail. However, both extrapolations at zero field are in good agreement with published experimental results; the difference between the two results could well come from the fact that our system has $N=256$ particles and a cutoff radius $r_c=3.5\sigma$ while Evans's system has $N=108$ particles and $r_c=2.5\sigma$.

In Sec. II we recall Evans's extension of linear-response theory to describe noncanonical systems where the motion

 

is not derivable from a Hamiltonian. In Sec. III we give details of the calculations and we describe how to implement the differential technique in the computer experiment. Section IV contains our results and an assessment of the efficiency of the NEMD method through comparison of the calculated thermal conductivity with that obtained in the generated equilibrium run. Some concluding remarks are collected in Sec. V.

## II. NONCANONICAL LINEAR-RESPONSE THEORY

Consider an equilibrium system characterized by a Hamiltonian $H_0=H_0(\{\vec{q}_i,\vec{p}_i\}_{i=1,N})$. Then, for $i=1,N$,

$$\dot{\vec{q}}_{i0}=\frac{\partial H_0}{\partial \vec{p}_i}=\frac{\vec{p}_i}{m}\ , \tag{2.1}$$

$$\dot{\vec{p}}_{i0}=-\frac{\partial H_0}{\partial \vec{q}_i}=\vec{F}_i\ . \tag{2.2}$$

This system is subject to an external time-dependent perturbation $\vec{F}(t)$, with

$$\dot{\vec{q}}_i=\frac{\vec{p}_i}{m}+\vec{F}(t)\cdot\overleftrightarrow{C}_i\ , \tag{2.3}$$

$$\dot{\vec{p}}_i=\vec{F}_i+\vec{F}(t)\cdot\overleftrightarrow{D}_i\ , \tag{2.4}$$

where $\overleftrightarrow{C}_i=\overleftrightarrow{C}_i(\{\vec{q}_i,\vec{p}_i\}_{i=1,N})$ and $\overleftrightarrow{D}_i=\overleftrightarrow{D}_i(\{\vec{q}_i,\vec{p}_i\}_{i=1,N})$ are phase-space functions of suitable tensorial nature.

Let us assume the general case in which

$$\sum_{i=1}^{N}\left[\frac{\partial}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right]=\vec{F}(t)\cdot\left[\sum_{i=1}^{N}\left[\frac{\partial}{\partial \vec{q}_i}\cdot\overleftrightarrow{C}_i+\frac{\partial}{\partial \vec{p}_i}\cdot\overleftrightarrow{D}_i\right]\right]\neq 0\ . \tag{2.5}$$

If $\rho^N(t)=\rho^N(t\mid\{\vec{q}_i,\vec{p}_i\}_{i=1,N})$ is the $N$-particle phase-space distribution function, we have the following Liouville equation:

$$\frac{\partial\rho^N(t)}{\partial t}=-\sum_{i=1}^{N}\left[\frac{\partial\rho^N(t)}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial\rho^N(t)}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right]-\rho^N\sum_{i=1}^{N}\left[\frac{\partial}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right]. \tag{2.6}$$

Now we define the "perturbed" and "unperturbed" Liouville operators through their action on a dynamic variable $B=B(\{\vec{q}_i,\vec{p}_i\}_{i=1,N})$:

$$iL(t)B=\sum_{i=1}^{N}\left[\frac{\partial B}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial B}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right]+B\sum_{i=1}^{N}\left[\frac{\partial}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right], \tag{2.7}$$

$$iL_0B=\sum_{i=1}^{N}\left[\frac{\partial B}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_{i0}+\frac{\partial B}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_{i0}\right]. \tag{2.8}$$

The linearized Liouville equation is

$$\frac{\partial\Delta\rho^N}{\partial t}=-iL_0\Delta\rho^N(t)-i\Delta L(t)\rho_0^N\ , \tag{2.9}$$

where $i\Delta L=i(L-L_0)$, and we assume

$$\vec{F}(t)=0,\quad t\le 0 \tag{2.10}$$

and $\rho_0^N=e^{-\beta H_0}/\int dq^N dp^N e^{-\beta H_0}$ is the canonical equilibrium distribution function. The formal solution of (2.9) is

$$\Delta\rho^N(t)=-\int_0^t e^{-iL_0(t-t')}i\Delta L(t')\rho_0^N dt'\ , \tag{2.11}$$

where

$$i\Delta L(t)\rho_0^N=\sum_{i=1}^{N}\frac{\partial\rho_0^N}{\partial \vec{q}_i}\cdot(\dot{\vec{q}}_i-\dot{\vec{q}}_{i0})+\sum_{i=1}^{N}\frac{\partial\rho_0^N}{\partial \vec{p}_i}\cdot(\dot{\vec{p}}_i-\dot{\vec{p}}_{i0})+\rho_0^N\sum_{i=1}^{N}\left[\frac{\partial}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right]. \tag{2.12}$$

Hence,

$$\Delta\rho^N(t)=\int_0^t e^{-iL_0(t-t')}\beta\rho_0^N\sum_{i=1}^{N}\left[\frac{\partial H_0}{\partial \vec{q}_i}\cdot\overleftrightarrow{C}_i\cdot\vec{F}(t)+\frac{\partial H_0}{\partial \vec{p}_i}\cdot\overleftrightarrow{D}_i\cdot\vec{F}(t)\right]-\int_0^t e^{-iL_0(t-t')}\rho_0^N\sum_{i=1}^{N}\left[\frac{\partial}{\partial \vec{q}_i}\cdot\dot{\vec{q}}_i+\frac{\partial}{\partial \vec{p}_i}\cdot\dot{\vec{p}}_i\right]. \tag{2.13}$$

Therefore, in the general noncanonical case, there is an extra term contributing to $\Delta\rho^N(t)$ which is not proportional to $\beta$. In the thermal case the "*ad hoc*" forms for (2.3) and (2.4) are

$$\dot{\vec{q}}_i=\frac{\vec{p}_i}{m}\ , \tag{2.14}$$

$$\dot{\vec{p}}_i=\sum_{\substack{j=1\\ j\neq i}}^{N}\vec{F}_{ij}+\left[E_i-\sum_{l=1}^{N}E_l/N\right]\overleftrightarrow{I}\cdot\vec{F}(t)+\tfrac{1}{2}\sum_{\substack{j=1\\ j\neq i}}^{N}\vec{F}_{ij}\vec{q}_{ij}\cdot F(t)-\frac{1}{2N}\sum_{k=1}^{N}\sum_{\substack{j=1\\ j\neq k}}^{N}\vec{F}_{jk}\vec{q}_{jk}\cdot\vec{F}(t)\ , \tag{2.15}$$

where $\overleftrightarrow{I}$ is the unit tensor of rank two and

$$E_i=\frac{p_i^2}{2m}+\tfrac{1}{2}\sum_{\substack{j=1\\ j\neq i}}^{N}\phi_{ij}(\mid\vec{q}_{ij}\mid),\quad \vec{q}_{ij}=\vec{q}_j-\vec{q}_i\ .$$

Notice that if the unperturbed system is translationally invariant and $\vec{P}(t=0)=\sum_i\vec{p}_i(t=0)=\vec{0}$, then the total momentum is conserved and equal to zero. Substituting (2.15) and (2.14) in (2.13) we finally get

$$\Delta\rho^N(t)=\int_0^t e^{-iL_0(t-t')}\beta\rho_0^N\left[\sum_{i=1}^N\left[\frac{\vec{p}_i}{m}\cdot\overleftrightarrow{I}\cdot\vec{F}(t)\right]\left[E_i-\sum_{l=1}^N E_l/N\right]\right.$$
$$\left.+\tfrac{1}{2}\sum_{i=1}^N\sum_{\substack{j=1\\j\neq i}}^N\left[\frac{\vec{p}_i}{m}\cdot\vec{F}_{ij}\right]\cdot[\vec{q}_{ij}\cdot\vec{F}(t)]-\frac{1}{2N}\sum_{i=1}^N\sum_{j=1}^N\sum_{\substack{k=1\\k\neq j}}^N\left[\frac{\vec{p}_i}{m}\cdot\vec{F}_{jk}\right]\cdot[\vec{q}_{jk}\cdot\vec{F}(t)]\right]$$
$$-\int_0^t e^{-iL_0(t-t')}\rho_0^N\sum_{i=1}^N\frac{\partial}{\partial\vec{p}_i}\left[E_i-\sum_{l=1}^N E_l/N\right]\cdot\vec{F}(t)\ . \tag{2.16}$$

In the center-of-mass reference frame, for which $\vec{P}(t)=\sum_i\vec{p}_i(t)=\vec{0}$, Eq. (2.16) becomes

$$\Delta\rho^N(t)=\int_0^t e^{-iL_0(t-t')}\beta\rho_0^N\left[\sum_{i=1}^N\left[\frac{\vec{p}_i}{m}\cdot\overleftrightarrow{I}\cdot\vec{F}(t)\right]E_i+\tfrac{1}{2}\sum_{i=1}^N\sum_{\substack{j=1\\j\neq i}}^N\left[\frac{\vec{p}_i}{m}\cdot\vec{F}_{ij}\right]\cdot[\vec{q}_{ij}\cdot\vec{F}(t)]\right]\ . \tag{2.17}$$

The linear response of the energy current can now be calculated in the usual way by averaging over $\Delta\rho^N(t)$. We find

$$\langle\vec{J}^E(\vec{K}=\vec{0})\rangle_t=\beta\int_0^t\langle\vec{J}^E(\vec{K}=\vec{0},0)\vec{J}^E(\vec{K}=0,t-t')\rangle_0\cdot\vec{F}(t')dt'\ . \tag{2.18}$$

Choosing $\vec{F}(t)=(0,0,\bar{F}_z)\Theta(t)$, where

$$\Theta(t)=\begin{cases}0, & t<0\\ 1, & t>0\end{cases} \tag{2.19}$$

as is done in Ref. (4), we find for the thermal conductivity

$$\lambda=\lim_{t\to\infty}\frac{\langle J_z^E(\vec{K}=\vec{0})\rangle_t}{\bar{F}_z TV}\ , \tag{2.20}$$

where $V$ and $T$ are respectively the volume and the equilibrium temperature of the system. However, in the linear region other choices of $\vec{F}(t)$ are possible. A particularly simple choice is to set $\vec{F}(t)=(0,0,\bar{F}_z)\delta(t)$ [$\delta(t)$ is the Dirac $\delta$ function]; this is the one adopted and discussed in the following sections.

## III. MODEL AND COMPUTER EXPERIMENT

We consider a system of 256 particles enclosed in a cube $\Lambda$ interacting through a two-body potential of Lennard-Jones type. We cut the potential at a distance $R_c=3.35\sigma$; our units are $\sigma$ for length, $\epsilon$ for energy, and $\tau=(m\sigma^2/48\epsilon)^{1/2}$ for time ($\sigma=3.405$ Å, $\epsilon=119.8k_B$, $\tau=3.112\times10^{-13}$ sec for argon). Throughout the numerical experiment we maintain periodic boundary conditions in all directions. We studied the thermal response of the fluid near its triple point: $\rho\sigma^3=0.8442$, $k_BT/\epsilon=0.721$ as a function of the perturbation. To implement the differential method the paths of the particles in perturbed and unperturbed trajectories are followed simultaneously and the time variation of the response is calculated as the difference in the relevant dynamical variable. This yields the mechanical response. The statistical response is obtained by averaging the mechanical response over a certain number of such pairs of trajectories. Therefore, in addition to carrying out a normal molecular-dynamics run, we also perturb the system at regular intervals in time. Below we describe the prescription to be used for the case at hand.

The form of $\vec{F}(t)$ chosen to generate the perturbed trajectories is

$$\vec{F}(t)=\vec{\bar{F}}\delta(t)\ . \tag{3.1}$$

Inserting (3.1) in (2.14) and (2.15) we have

$$\dot{\vec{q}}_i=\frac{\vec{p}_i}{m}\ , \tag{3.2}$$

$$\dot{\vec{p}}_i=\sum_{\substack{j=1\\j\neq i}}^N\vec{F}_{ij}+\left[E_i-\sum_{l=1}^N E_l/N\right]\overleftrightarrow{I}\cdot\vec{\bar{F}}\delta(t)$$
$$+\tfrac{1}{2}\sum_{\substack{j=1\\j\neq i}}^N\vec{F}_{ij}\vec{q}_{ij}\cdot\vec{\bar{F}}\delta(t)-\frac{1}{2N}\sum_{k=1}^N\sum_{\substack{j=1\\j\neq k}}^N\vec{F}_{jk}\vec{q}_{jk}\cdot\vec{\bar{F}}\delta(t)\ . \tag{3.3}$$

In solving Eq. (3.3) we use the central-difference algorithm of Verlet.[6] At $t=0$, however, the perturbation appears as an impulsive force; to take into account the presence of a $\delta$ function, some modification of the algorithm is needed. Following the general procedure described in Ref. 3 the initial velocity value is changed as follows:

$$\vec{v}_i(0_+)=\vec{v}_i(0_-)+\left[E_i-\sum_{l=1}^N E_l/N\right]\overleftrightarrow{I}\cdot\frac{\vec{\bar{F}}}{m}$$
$$+\tfrac{1}{2}\sum_{\substack{j=1\\j\neq i}}^N\vec{F}_{ij}\vec{q}_{ij}\cdot\frac{\vec{\bar{F}}}{m}-\frac{1}{2N}\sum_{k=1}^N\sum_{\substack{j=1\\j\neq k}}^N\vec{F}_{jk}\vec{q}_{jk}\cdot\frac{\vec{\bar{F}}}{m}\ , \tag{3.4}$$

while the coordinates are unchanged.

For the applied field $\vec{F}(t)=(0,0,\tilde{F}_z)\delta(t)$ the relation between the energy current $\langle J_z^F(\vec{K}=\vec{0})\rangle_t$ and the autocorrelation $\langle J_z^E(\vec{K}=\vec{0})J_z^E(\vec{K}=\vec{0},t)\rangle_0$ is

$$\langle J_z^E(\vec{K}=\vec{0})\rangle_t=\beta\tilde{F}_z\langle J_z^E(\vec{K}=\vec{0})J_z^E(\vec{K}=\vec{0},t)\rangle_0 . \quad (3.5)$$

Thus the decay of the autocorrelation function $C_E(t)$ is given by

$$C_E(t)=\langle J_z^E(\vec{K}=\vec{0})\rangle_t/\langle J_z^E(\vec{K}=\vec{0})\rangle_{t=0} \quad (3.6)$$

and the thermal conductivity by

$$\lambda=K\int_0^\infty C_E(t)dt=K\int_0^{t_p} C_E(t)dt , \quad (3.7)$$

where $K=\langle J_z^E(\vec{K}=\vec{0})\rangle_{t=0}/\tilde{F}_zTV$ and $t_p$ is the time corresponding to the plateau value of the integral. This value is easily found for this particular autocorrelation function. In Table I we list the perturbations we studied together with the thermal gradients to which they are equivalent. The equivalence is obtained via Fourier's law identifying $\nabla_z T/T$ and $\bar{F}_z=\tilde{F}_z/h$, where $h$ is the time step used ($h=0.032$).

TABLE I. Strengths of external perturbation $\tilde{F}$ and equivalent thermal gradients used in this work and/or in Ref. 4. To obtain $\tilde{F}$ in cgs from $\tilde{F}$ in Verlet's units multiply by the factor $9.14\times10^{-6}$. Temperature $T=0.721$.

| $\tilde{F}$ $[(m/48\epsilon)^{1/2}]$ | $\nabla T$ $(\epsilon/k_B\sigma)$ | $\nabla T$ (K/cm) |
|---|---|---|
| $9.57\times10^{-10}$ [a] | $2.155\times10^{-8}$ | 75.8 |
| $9.57\times10^{-9}$ [a] | $2.155\times10^{-7}$ | $7.58\times10^{2}$ |
| $9.57\times10^{-7}$ [a] | $2.155\times10^{-5}$ | $7.58\times10^{4}$ |
| $9.57\times10^{-5}$ [a] | $2.155\times10^{-3}$ | $7.58\times10^{6}$ |
| $9.57\times10^{-4}$ [a] | $2.155\times10^{-2}$ | $7.58\times10^{7}$ |
| $1.6\times10^{-3}$ [b] | 0.036 | $1.27\times10^{8}$ |
| $3.2\times10^{-3}$ [b] | 0.072 | $2.54\times10^{8}$ |
| $6.4\times10^{-3}$ [c] | 0.144 | $5.08\times10^{8}$ |
| $9.6\times10^{-3}$ [c] | 0.216 | $7.62\times10^{8}$ |
| $12.8\times10^{-3}$ [c] | 0.288 | $1.02\times10^{9}$ |
| $1.6\times10^{-2}$ [c] | 0.36 | $1.27\times10^{9}$ |
| $1.92\times10^{-2}$ [c] | 0.433 | $1.52\times10^{9}$ |

[a]Our values.
[b]Common values.
[c]Values of Ref. 4.

## IV. RESULTS

### A. Thermal conductivity

Some results obtained after averaging the dynamical response over 84 pairs of trajectories are shown in Fig. 1(a) for a perturbation value $\tilde{F}=9.57\times10^{-5}$. In Fig. 1(b) we plot the normalized integrals of the response $I(t)=\int_0^t C_E(t')dt'$ used to evaluate the thermal conductivity via Eq. (3.7). The decay of $C_E(t)$ to zero is almost monotonical and its negative values are an indication of the statistical noise. This has been confirmed by computing, for the same value $\tilde{F}$, a second group of 84 segments. The dynamical response of the second group was computed for a longer time to estimate the level of the noise with increasing time. For all perturbations listed in Table I the statistical linearity of the response is verified up to the fourth figure. The values of thermal conductivity obtained in our computations are affected by an error given by the combined error on $K$ and $I=\int_0^{t_p} C_E(t)dt$:

$$\frac{\Delta\lambda}{\lambda}=\frac{\Delta K}{K}+\frac{\Delta I}{I} . \quad (4.1)$$

Neglecting the contribution of the standard deviation on temperature we have

$$\Delta K=\sigma_J/\sqrt{N_s} , \quad (4.2)$$

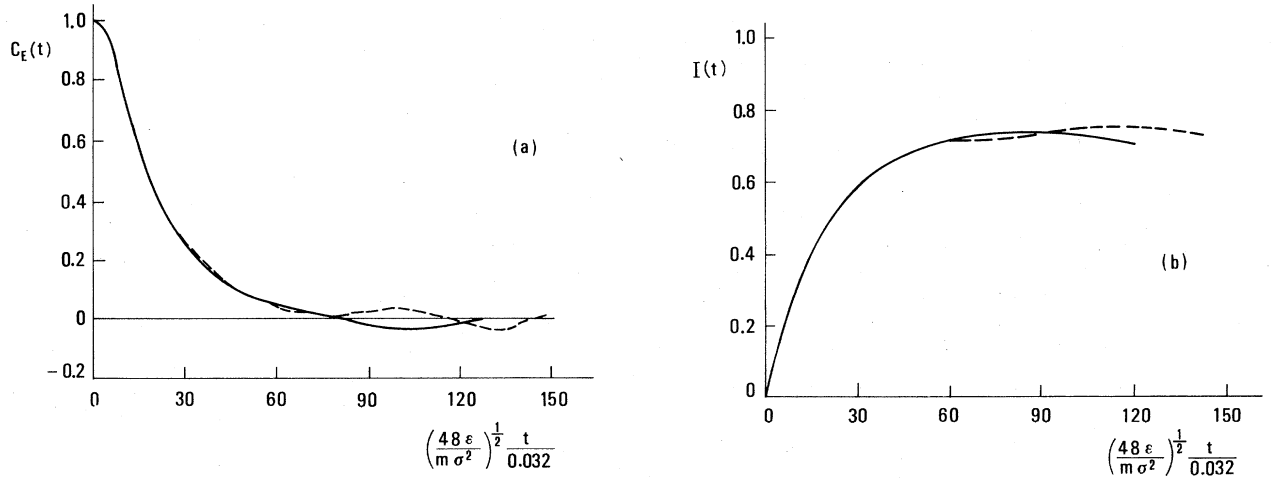


FIG. 1. (a) $C_E(t)$. Normalized dynamical response of the energy current. $\tilde{F}=9.57\times10^{-5}$. Solid curve: average of the first 84 segments. Dashed curve: average of the second 84 segments. (b) $I(t)$. Integral of the normalized dynamical response of the energy current. $\tilde{F}=9.57\times10^{-5}$. Solid curve: average of the first 84 segments. Dashed curve: average of the second 84 segments. $T=0.721$, $\rho=0.8442$.

where $\sigma_J$ is the standard deviation of the heat current and $N_s$ the number of segments. To estimate $\Delta I$ we computed the standard error of the integral of the relaxation profile to time $t_p$:

$$I' = \int_0^{t_p} \frac{J_z^E(\vec{K}=\vec{0},t)}{J_z^E(\vec{K}=\vec{0},0)}dt \ . \tag{4.3}$$

The upper time limit $t_p$ is the value corresponding to the maximum of $I(t)$. Due to the strict linearity of our results the errors on the values of $\lambda$ obtained for different perturbations are identical. For the perturbation $\tilde{F}=9.57\times10^{-5}$ we obtained the best precision by computing two independent sets of 84 segments each. This gives a reduction of $\sqrt{2}$ of the combined error. Therefore, we can assign to our $\lambda$'s the error computed for this value of $\tilde{F}$. The resulting error is of the order of 2.6%.

In Fig. 2 we compare our data with those of Evans. It can be easily seen that they do not support any dependence of $\lambda$ on $\tilde{F}$. Finally, in Table II for completeness we list our numerical results for $\lambda$ together with all other previously obtained by equilibrium and nonequilibrium MD. Some experimental data[7,8] are also collected. It is apparent that the agreement is remarkable.

### B. Green-Kubo formula: equilibrium results

To compare NEMD results with equilibrium results we have computed, starting from our equilibrium trajectory, the thermal conductivity via the Green-Kubo formula:

$$\lambda = K^{GK} I^{GK} \ , \tag{4.4}$$

where

$$K^{GK} = \langle [\vec{J}^{\,E}(\vec{K}=\vec{0})]^2 \rangle_0 / 3T^2V \ , \tag{4.5}$$

$$I^{GK} = \int_0^{t_p} \frac{\langle \vec{J}^{\,E}(\vec{K}=\vec{0})\cdot\vec{J}^{\,E}(\vec{K}=\vec{0},t)\rangle_0}{\langle [\vec{J}^{\,E}(\vec{K}=\vec{0})]^2\rangle_0}dt$$

$$= \int_0^{t_p} C_E^{GK}(t)dt \ . \tag{4.6}$$

From Fig. 3 it is clear that the comparison between $C_E(t)$, $C_E^{GK}(t)$ and $I(t)$, $I^{GK}(t)$ is quite satisfactory. $\Delta K^{GK}$ is given by $\sigma_{J^2}/\sqrt{N_I}$, where $N_I$ is the number of the independent equilibrium configurations. As can be observed in Fig. 3(a) the autocorrelation of the energy current approaches zero after about 100 time steps; therefore it appears reasonable to assume that it is the decorrelation time. $I^{GK}$ is obtained by integrating the average of $C_E^{GK}(t)$ over two independent runs, each one lasting 16 384 time steps. $\Delta I^{GK}$ is the related standard error. The plateau value $t_p$ is the maximum of $I^{GK}(t)$ to 300 time steps. We found $\lambda=0.993\pm0.07$ to be compared with the values of Levesque,[9] $\lambda=1.02\pm0.06$ and $1.03\pm0.04$. The equilibrium result is practically identical to the NEMD result and both are in better agreement with the values found by Levesque than the extrapolated data of Evans (see Table II).

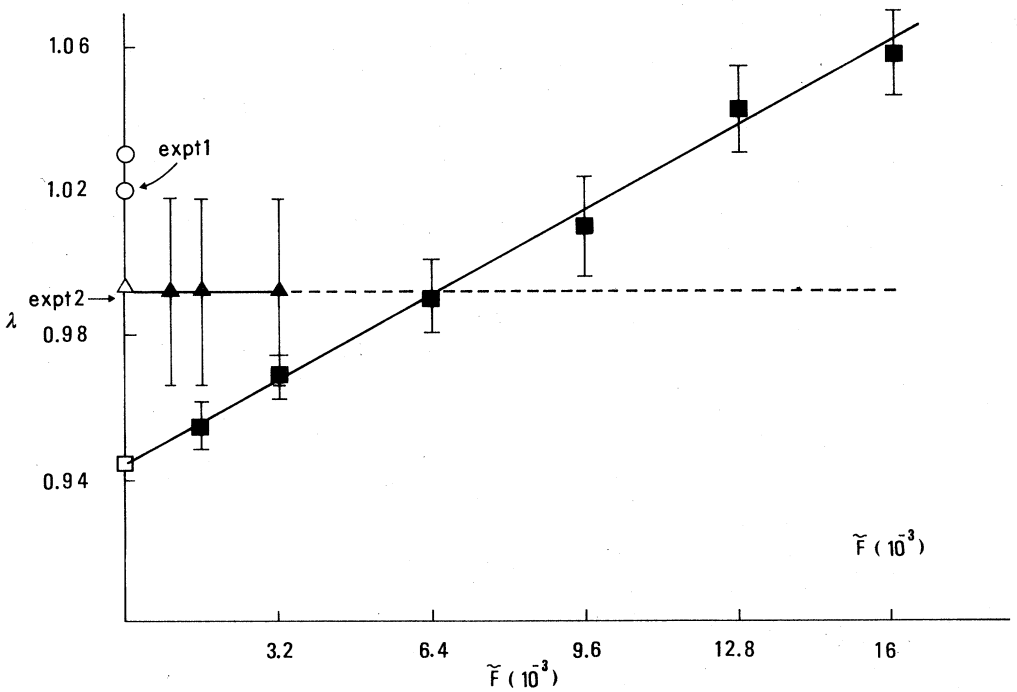


FIG. 2. Thermal conductivity $\lambda$ as a function of the strength of perturbation. (△) Equilibrium result; (▲) NEMD results ($N=256$ particles, $r_c=3.5\sigma$); (■) Data from Ref. 4 ($N=108$ particles, $r_c=2.5\sigma$); (□) Extrapolated datum from Ref. 4; (○) Data from Ref. 9; expt1 and expt2 are experimental results from Refs. 7 and 8, respectively; the dashed line extrapolates our NEMD results.

TABLE II. Results for thermal conductivity. Comparison between present results and results from equilibrium and nonequilibrium molecular-dynamics method. The experimental results are also reported. $T$, temperature; $N_p$, number of particles; $\tilde{F}$, strength of perturbation; $N$, number of time steps; $K$, $K^{GK}$, $t_p$ are defined in Eqs. (3.7) and (4.5); $\lambda$, thermal conductivity; DM, nonequilibrium results by differential method; EV, Evans's results (Ref. 4); FWM, fluid-wall method (Ref. 1); EQ, our equilibrium result; LEQ, Levesque equilibrium results (Ref. 9); expt, experimental data (Refs. 7 and 8). $\rho=0.8442$.

| $T$ $(\epsilon/k_B)$ | $N_p$ | $\tilde{F}$ $[(m/48\epsilon)^{1/2}]$ | $N$ | $K\pm\Delta K$ $(48\epsilon k_B/m\sigma^3)$ | $t_p$ | $\lambda\pm\Delta\lambda$ $[(k_B/\sigma)(48\epsilon/m\sigma^2)^{1/2}]$ | Source |
|---|---|---|---|---|---|---|---|
| 0.721 | 256 | $9.57\times10^{-10}$ | 10080 (84×120)[a] | 1.373±0.02 | 83 | 0.992±0.033 | DM |
| 0.721 | 256 | $9.57\times10^{-9}$ | 10080 (84×120) | 1.373±0.2 | 83 | 0.992±0.033 | DM |
| 0.721 | 256 | $9.57\times10^{-7}$ | 10080 (84×120) | 1.373±0.02 | 83 | 0.992±0.933 | DM |
| 0.721 | 256 | $9.57\times10^{-5}$ | 10080 (84×120) | 1.373±0.02 | 83 | 0.992±0.033 | DM |
| 0.721 | 256 | $9.57\times10^{-5}$ | 12600 (84×150) | 1.385±0.02 | 117 | 1.028±0.04 | DM |
| 0.721 | 256 | $9.57\times10^{-5}$ | (b) | 1.379±0.014 | 101 | 0.994±0.026 | DM |
| 0.721 | 256 | $9.57\times10^{-4}$ | 10080 (84×120) | 1.373±0.02 | 83 | 0.992±0.033 | DM |
| 0.721 | 256 | $1.6\times10^{-3}$ | 10080 (84×120) | 1.373±0.02 | 83 | 0.992±0.033 | DM |
| 0.721 | 256 | $3.2\times10^{-3}$ | 10080 (84×120) | 1.373±0.02 | 83 | 0.992±0.033 | DM |
| 0.722 | 108 | $1.6\times10^{-3}$ | 100000 | | | 0.955±0.07 | EV |
| 0.722 | 108 | $3.2\times10^{-3}$ | 48000 | | | 0.969±0.006 | EV |
| 0.723 | 108 | $6.4\times10^{-3}$ | 26000 | | | 0.99 ±0.01 | EV |
| 0.725 | 108 | $9.6\times10^{-3}$ | 35000 | | | 1.010±0.014 | EV |
| 0.727 | 108 | $12.8\times10^{-3}$ | 48000 | | | 1.042±0.012 | EV |
| 0.729 | 108 | $1.6\times10^{-2}$ | 39000 | | | 1.058±0.012 | EV |
| | 108 | $1.92\times10^{-2}$ | | | | 1.088±0.022 | EV |
| 0.722 | 216 | $6.4\times10^{-4}$ | 32000 | | | 0.95 ±0.06 | FWM |
| | | | | $K^{GK}\pm\Delta K^{GK}$ | | | |
| 0.721 | 256 | | 32768 | 1.337±0.062 | 105 | 0.993±0.07 | EQ |
| 0.715 | 256 | | 64000 | | 280 | 1.02 ±0.06 | LEQ |
| 0.722 | 864 | | 139000 | | 280 | 1.03 ±0.04 | LEQ |
| 0.722 | 108 | | Extrapolated | | | 0.944 | EV |
| 0.7095[c] | | | | | | 1.02 | expt |
| 0.720[d] | | | | | | 0.99 | expt |

[a]The first number in parentheses is the number of segments, the second the length of the segment.
[b]Average of the two preceding.
[c]$\rho=0.8443$.
[d]$\rho=0.841$.

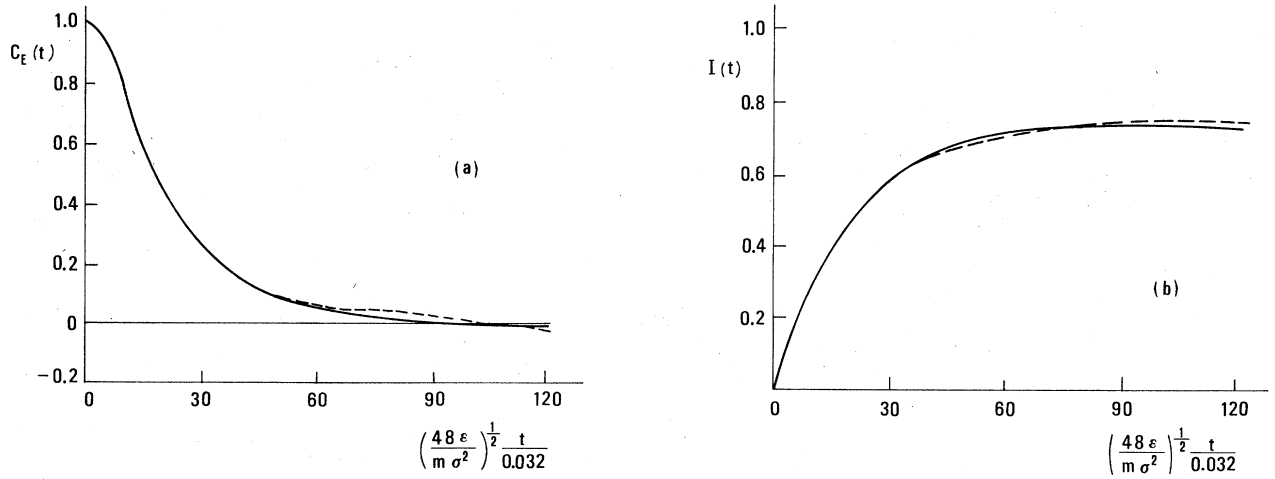


FIG. 3. (a) $C_e(t)$ (solid curve). Normalized dynamical response of the energy current. We show the average of the two results for $\tilde{F}=9.57\times10^{-5}$, Fig. 1(a). $C_E^{GK}(t)$ (dashed curve). Normalized equilibrium autocorrelation function of the energy current. (b) $I(t)$ (solid curve). Integral of the normalized dynamical response of the energy current. We show the average of the two results for $\tilde{F}=9.57\times10^{-5}$, Fig. 1(b). $I^{GK}(t)$ (dashed curve). Integral of the normalized equilibrium autocorrelation function of the energy current. $T=0.721$, $\rho=0.8442$.

## V. CONCLUSIONS

We have implemented a NEMD computation of thermal conductivity in the framework of the differential method[3] for a dense fluid near the triple point. By adopting the translationally invariant algorithm proposed by Evans[4] we simulated a set of thermal gradients ranging from 75.8 K/cm to $2.54\times10^{8}$ K/cm for a Lennard-Jones system subjected to periodic boundary conditions. The aim of our work was to investigate the linearity of the response and, consequently, to test the nonlinearity found by Evans. Our results do not evidence any dependence of thermal conductivity on the external perturbation over all the range studied and do not support the findings of Evans which indicate an increasing value of "thermal conductivity" with increasing external field.

There are two differences between our simulation and that of Evans. First of all, due to the use of small perturbations we do not have to rescale the velocities at each time step. This is surely a safer procedure because recently Nosé[10] has shown that the rescaling is not consistent with a dynamical canonical ensemble. Second, we studied the dynamical response of the system to a $\delta$-like perturbation (not to a $\Theta$-like perturbation). Mathematically the two forms are equivalent only in the linear regime. In the nonlinear region the former can be used in the investigation of the nonlinear relaxation, while only the latter permits studying the dependence of $\lambda$ on the applied thermal gradient. This difference is, however, unimportant because the translationally invariant algorithm proposed by Evans gives the thermal conductivity only in the linear regime while the nonlinear response is not tied to the thermal transport.

Evans's method works remarkably well and we found a very good agreement between NEMD, equilibrium Green-Kubo, and experimental results. We believe the method can have a variety of useful applications. We hope in particular to study the coupling of concentration fluctuations with thermal currents in liquid mixtures.

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