Lattice thermal conductivity via homogeneous nonequilibrium molecular dynamics

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(Received 16 March 1995)

Thermal conduction in a one-dimensional anharmonic lattice is investigated with the use of homogeneous nonequilibrium molecular dynamics. This approach enables us to obtain thermal conductivity as a function of temperature. Coherent excitations are observed to play an important role in transporting energy, especially when an external "field" becomes large.

PACS number(s): 05.50.+q, 05.20.Gg, 05.60.+w

I. INTRODUCTION

Since the classical work by Fermi, Pasta, and Ulam (FPU) on equipartition of energy among phonon modes [1], much attention has been paid to dynamical properties of a one-dimensional (1D) anharmonic lattice to elucidate the role played by nonlinearity in the interaction among the neighboring particles. The main concern is centered around the fundamental problems such as ergodicity (thermalization) [2,3] and thermal conductivity [4–7]. Recently we observe a new surge of interest in this field due to its close relation to chaos in Hamiltonian or more generally in dynamical systems.

At the time of FPU experiments, it was considered that the presence of nonlinearity in the interaction, which gives rise to energy exchange among phonon modes, would be sufficient to cause thermalization, or an approach to an equilibrium state. Contrary to the expectation, FPU found that equipartition of energy, which is necessary for ergodicity to hold, is not realized and that there exist some recurrence phenomena [1]. This ergodicity problem in a 1D lattice has since been studied intensively with use of various methodologies such as nonlinear wave modulation [8], curvature of a potential surface in differential topology [9], and so on, besides numerical experiments.

Lattice thermal conductivity λ has also been attracting much interest from many researchers. For a harmonic lattice, there is no mechanism for scattering phonons and the conductivity λ is known to diverge [10]. When nonlinearity is plugged in, the phonon mean free path becomes finite and we expect to have finite λ. However, it is by no means clearly understood how much nonlinearity is necessary in order to get finite λ nor how λ depends on temperature.

Numerical experiments based on molecular-dynamics (MD) techniques have been playing a most important role in this field and they may be roughly classified into either an equilibrium (E) or a nonequilibrium (NE) experiments. In the EMD, one calculates the equilibrium time correlation function (TCF) of the heat flux operator J_x and utilizes the Green-Kubo formula, like Eq. (16) below, to obtain thermal conductivity λ [4,5]. This approach is widely used especially in studies on liquids [11], which is, however, known to be much more expensive in terms of computer CPU time than by direct NEMD calculations.

In the NEMD experiments, two heat reservoirs with high and low temperatures T_H and T_L are attached on both sides of the lattice [5–7]. By measuring the average heat flux and the (internal) temperature gradient one can calculate λ as the ratio of the two quantities. We notice, however, some disadvantages inherent in this approach. First, in order to obtain a discernible temperature gradient, one usually imposes (unphysically) a large temperature gradient and consequently one cannot obtain the conductivity extrapolated to zero gradient and moreover one cannot identify the intrinsic temperature T of the system. Thus it is impossible to obtain T dependence of λ. Second, since the system is not spatially homogeneous, one cannot use the periodic boundary condition and one has to simulate a system with many particles ($N \simeq 10\,000$) [7]. Third, the temperature gradient set by an experimenter, $\nabla T \equiv (T_H - T_L)/L$, with L the length of the system, is usually larger than the internal gradient $(\nabla T)_i$, which is realized inside the system [6,7]. Despite these difficulties, it is now observed by EMD and NEMD experiments for many model systems, such as the FPU lattice and the diatomic Toda lattice, that a 1D nonlinear lattice can support the temperature gradient and thus the normal heat conduction or the Fourier heat law holds so long as some conditions on strength of nonlinearity ∇T and the system size N are satisfied [4–7].

In this paper we take quite a different scheme of NEMD, which enables us to employ a periodic boundary condition, thus removing many difficulties encountered in the traditional NEMD explained above. In Sec. II we explain an isothermal linear response theory (LRT) and a new NEMD, due to Evans [12], which is based on the LRT. In Sec. III we formulate heat conductivity in a 1D lattice and finally in Sec. IV numerical results of our homogeneous NEMD and some discussions are presented.

1063-651X/95/52(1)/234(6)/$06.00

II. HOMOGENEOUS NEMD

Following Evans [12] and Evans and Morriss [13], we first summarize briefly the isothermal LRT and its implication on NEMD for transport coefficients to make the paper self-contained. It seems that at the moment this approach is well known only to researchers in liquid physics. We consider the following equation of motion for the set of variables $(\mathbf{q},\mathbf{p})=\{\mathbf{q}_i,\mathbf{p}_i\}$:

$$\begin{aligned}\dot{\mathbf{q}}_i &\equiv d\mathbf{q}_i/dt=\mathbf{p}_i/m+\mathbf{C}_iF_e(t)\ ,\\ \dot{\mathbf{p}}_i &\equiv d\mathbf{p}_i/dt=\mathbf{F}_i+\mathbf{D}_iF_e(t)-\alpha\mathbf{p}_i\ .\end{aligned} \tag{1}$$

If we put $F_e(t)=0$ and $\alpha=0$, Eq. (1) is reduced to the equation of motion derivable from the Hamiltonian

$$H=\sum \mathbf{p}_i^2/(2m)+\Phi\equiv K+\Phi\ , \tag{2}$$

with K and Φ denoting the total kinetic and potential energy, respectively. $F_e(t)$ represents some external effects with $\mathbf{C}_i(\mathbf{q},\mathbf{p})$ and $\mathbf{D}_i(\mathbf{q},\mathbf{p})$ denoting the coupling variables. Along with Evans [12] and Evans and Morriss [13], we will impose an adiabatically incompressible phase-space(AIΓ) condition on $\mathbf{C}_i$ and $\mathbf{D}_i$, which states that under the adiabatic condition $\alpha=0$,

$$\sum[\partial\dot{\mathbf{p}}_i/\partial\mathbf{p}_i+\partial\dot{\mathbf{q}}_i/\partial\mathbf{q}_i]=0\ . \tag{3}$$

With use of the method of least constraint, α in Eq. (1) is determined to be [13,14]

$$\begin{aligned}\alpha&=\sum\{\mathbf{F}_i\cdot\mathbf{p}_i+\mathbf{D}_i\cdot\mathbf{p}_iF_e(t)\}/\sum\mathbf{p}_i^2\\ &\equiv\alpha_0+\alpha_1F_e(t)\ .\end{aligned} \tag{4}$$

It is easily confirmed that if dynamics is governed by Eq. (1) with Eq. (4) the kinetic energy K is kept constant, $K(t)=K_0$.

The LRT is formulated based on the Liouville equation for the distribution function $f(\mathbf{q},\mathbf{p},t)$,

$$\partial f/\partial t=-iL_0f-iL_1(t)f\ , \tag{5}$$

with

$$iL_0f\equiv\sum\{\partial/\partial\mathbf{q}_i\cdot[(\mathbf{p}_i/m)f]+\partial/\partial\mathbf{p}_i[(\mathbf{F}_i-\alpha_0\mathbf{p}_i)f]\}\ , \tag{6}$$

$$iL_1(t)f\equiv\sum\{\partial/\partial\mathbf{q}_i\cdot[\mathbf{C}_if]+\partial/\partial\mathbf{p}_i[(\mathbf{D}_i-\alpha_1\mathbf{p}_i)f]\}F_e(t)\ . \tag{7}$$

The external "force" $F_e(t)$ is operative for $t>0$ and let us first specify the thermodynamic state (ensemble) of our system at $t=0$, which is consistent with $\partial f/\partial t=-iL_0f$ for $t<0$. For this purpose we note that the Liouville equation, for the case $F_e(t)=0$, can be rewritten as

$$df/dt\equiv\partial f/\partial t+\dot{\mathbf{q}}\cdot\partial f/\partial\mathbf{q}+\dot{\mathbf{p}}\cdot\partial f/\partial\mathbf{p}=3N\alpha_0f\ , \tag{8}$$

where contributions of relative order $O(1/N)$ are neglected. Since

$$d\Phi/dt=-\sum\mathbf{F}_i\cdot\mathbf{p}_i/m=-\alpha_0\sum\mathbf{p}_i^2/m=-2\alpha_0K_0\ , \tag{9}$$

we see that $d(\ln f)/dt=-(3N/2K_0)d\Phi/dt$. From this and the fact that $K(t)=K_0=3Nk_BT/2$, we may assume that

$$f(q,p,t=0)=f_{\rm eq}\equiv\exp\{-\Phi/(k_BT)\}\delta(K-K_0)/Z\ , \tag{10}$$

where Z is the normalization. It is seen that the potential energy is canonically and the kinetic energy is microcanonically distributed [13].

For $t>0$ the external force causes $f(\mathbf{q},\mathbf{p},t)$ to deviate from $f_{\rm eq}$. If we are to calculate $\Delta f\equiv f-f_{\rm eq}$ up to linear order in $F_e(t)$, we have an equation for Δf, $\partial\Delta f/\partial t+iL_0\Delta f=-iL_1(t)f_{\rm eq}$, which is easily solved to give

$$\Delta f=-\int_0^t ds\,\exp\{-iL_0(t-s)\}iL_1(s)f_{\rm eq}\ . \tag{11}$$

After some algebra it is seen that

$$iL_1(t)f_{\rm eq}=(k_BT)^{-1}f_{\rm eq}F_e(t)\sum\{\mathbf{C}_i\cdot\mathbf{F}_i-\mathbf{D}_i\cdot\mathbf{p}_i/m\}\ . \tag{12}$$

The important observation to be made is that the right-hand side of Eq. (12) is related to the ratio of adiabatic ($\alpha=0$) change of the internal energy H, Eq. (2),

$$\begin{aligned}(dH/dt)_{\rm ad}&=-F_e(t)\sum\{\mathbf{C}_i\cdot\mathbf{F}_i-\mathbf{D}_i\cdot\mathbf{p}_i/m\}\\ &\equiv-F_e(t)J_{\rm ad}\ .\end{aligned} \tag{13}$$

From Eqs. (11)–(13) we see that

$$\Delta f(\mathbf{q},\mathbf{p},t)=-(k_BT)^{-1}\int_0^t ds\,\exp\{-iL_0(t-s)\}\times f_{\rm eq}J_{\rm ad}F_e(s)\ . \tag{14}$$

If we are interested in a dynamical variable $B(\mathbf{q},\mathbf{p})$ whose equilibrium average vanishes, $\langle B\rangle_{\rm eq}\equiv\int d\mathbf{q}\,d\mathbf{p}Bf_{\rm eq}=0$, we see that $\langle B(t)\rangle\equiv\int d\mathbf{q}\,d\mathbf{p}B\{f_{\rm eq}+\Delta f(\mathbf{q},\mathbf{p},t)\}$ is given by

$$\langle B(t)\rangle=-(k_BT)^{-1}\int_0^t ds\,\langle B(t-s)J_{\rm ad}\rangle_{\rm eq}F_e(s)+O(F_e^2)\ . \tag{15}$$

We note that time evolution of $B(t)$ on the right-hand side of Eq. (15) is governed by Eqs. (1) and (4) with $F_e(t)=0$. The LRT presented in Eq. (15) is called an ergodically consistent LRT in [13] and it has some merits as discussed below.

With use of Eq. (15) one can calculate transport coefficients as follows. First, let us assume that a transport coefficient M is expressed, as usual, as

$$M=C\int_0^\infty dt\,\langle J_m(t)J_m\rangle_{\rm eq}\ , \tag{16}$$

where C is a constant. If one could choose $\mathbf{C}_i$ and $\mathbf{D}_i$ in Eq. (1) so that $J_{\rm ad}$ in Eq. (13) becomes identical to $-J_m$, one could set $B=J_m$ and $F_e(t)=F_e$ to have

$$\lim_{F_e\to0}\lim_{t\to\infty}\langle J_m(t)\rangle=F_eM/(Ck_BT)\ .$$

In NEMD simulation, we solve Eqs. (1) and (4) numerically and calculate $\lim_{t\to\infty}\langle J_m(t)\rangle$ as a time average and M is obtained from

$$M = \lim_{F_e \to 0} \lim_{t \to \infty} (Ck_B T)\langle J_m(t)\rangle / F_e \ . \tag{17}$$

Since our system is thermostated, we can simulate our system with F_e kept finite for long-enough time. If not thermostated, the temperature of the system increases due to the external force and the order of taking the two limiting procedure should be reversed, resulting in some difficulties in numerical calculations of M. In the calculation of the lattice thermal conductivity we precisely follow this procedure presented above.

III. THERMAL CONDUCTIVITY OF A 1D LATTICE

We consider a one-dimensional (1D) lattice with N atoms put along the x axis with a lattice constant a. Each atom is allowed to move in the y direction, perpendicular to the x axis, and we denote by q_i the displacement of the ith atom and by p_i the corresponding momentum. It is noted that the equilibrium position of the ith atom is $x_{i,\mathrm{eq}} = ai$ and $y_{i,\mathrm{eq}} = 0$. The Hamiltonian of the system (FPU β model) is expressed as

$$H = \sum_1^N \{p_i^2/(2m) + \mu(q_{i+1} - q_i)^2/2 + \beta(q_{i+1} - q_i)^4/4\}$$
$$\equiv \sum \{p_i^2/(2m) + \phi(q_i, q_{i+1})\} \ , \tag{18}$$

and we employ a periodic boundary condition $q_{N+1} = q_1$.

Let us now turn to thermal conductivity $M = \lambda$ along the x axis. The Green-Kubo formula for λ is

$$\lambda = (k_B T^2 L)^{-1} \int_0^\infty dt \langle J_x(t) J_x \rangle_{\mathrm{eq}} \ , \tag{19}$$

where L is the length of the system $L = aN$ and the heat flux along the x axis J_x is given, for our particular 1D model, by

$$J_x = (a/2m) \sum p_i \{\partial/\partial q_i [\phi(q_i, q_{i+1}) - \phi(q_{i-1}, q_i)]\}$$
$$\equiv \sum p_i D_i^*(q_{i-1}, q_i, q_{i+1})/m \ . \tag{20}$$

The expression (20) is obtained from a general expressions for the heat flux [11,13]

$$J_x = \sum \{\mathbf{p}_i^2/(2m) + (1/2) \sum_j \phi_{ij}\}(p_{i,x}/m)$$
$$-(1/2) \sum_{ij} r_{ij,x} \mathbf{F}_{ij} \cdot \mathbf{p}_i / m \ , \tag{21}$$

with ϕ_{ij} the interaction between atom i and j, $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$, and $\mathbf{F}_{ij} \equiv -\partial \phi_{ij}/\partial \mathbf{r}_i$ the force on atom i due to atom j. We note in our lattice model that the first term on the right-hand side of Eq. (21) does not contribute to J_x because $p_{i,x} = 0$ and that atoms interact only between nearest neighbors. What we must do next is to find $\{C_i\}$ and $\{D_i\}$ in Eq. (1), which satisfy both Eq. (13) with $J_{\mathrm{ad}} = -J_x$, Eq. (20) and the AIΓ condition (3). As suggested by Evans [12], we take

$$C_i = 0 \quad \text{and} \quad D_i = D_i^* - \sum_j D_j^*/N \tag{22}$$

with D_i^* defined by Eq. (20). Since $\sum D_i = 0$ from Eq. (22), we readily notice from Eq. (2) that $\sum p_i(t) = 0$ for $t > 0$ if $\sum p_i(t = 0) = 0$. Then from Eq. (13),

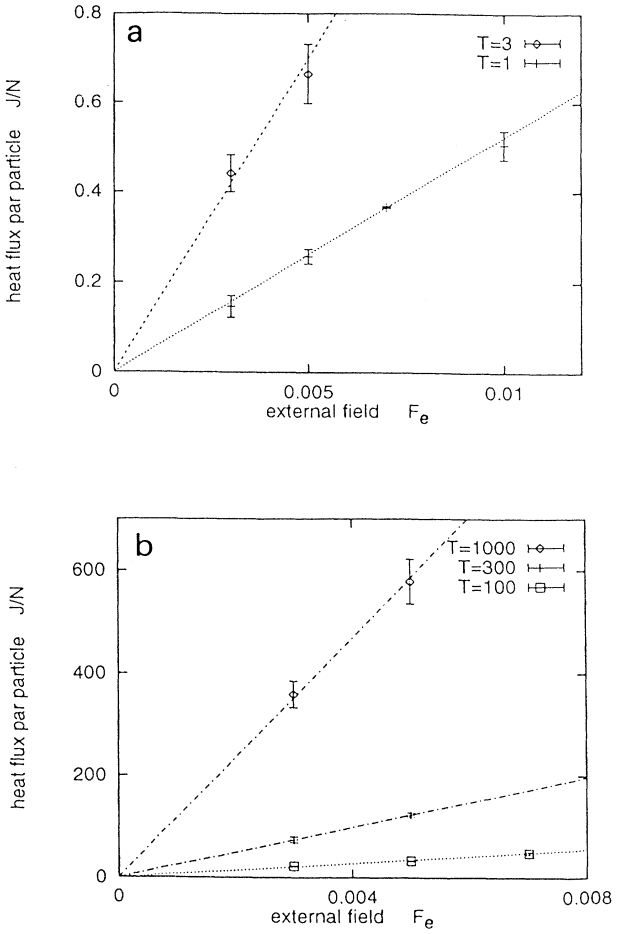

FIG. 1. Heat flux per particle J/N as a function of the external force F_e. (a) for $T = 1,3$ and (b) for $T = 100$, 300, and 1000 ($N = 32$, $\beta = 1.5$).

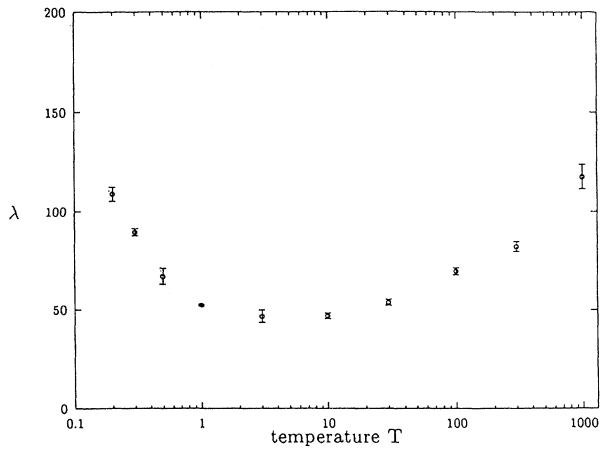

FIG. 2. Thermal conductivity λ as a function of temperature ($N = 32$, $\beta = 1.5$).

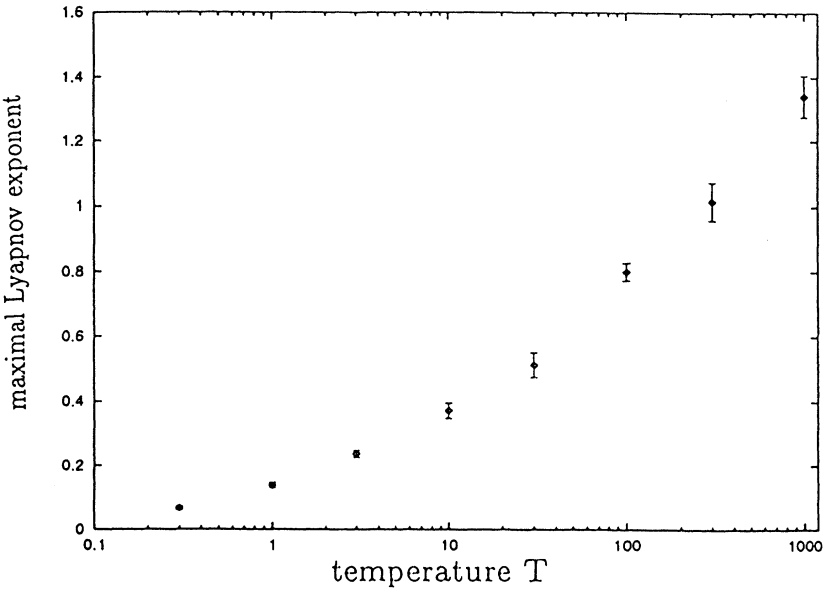

FIG. 3. The maximum Lyapunov exponent as a function of temperature ($N=32$, $\beta=1.5$).

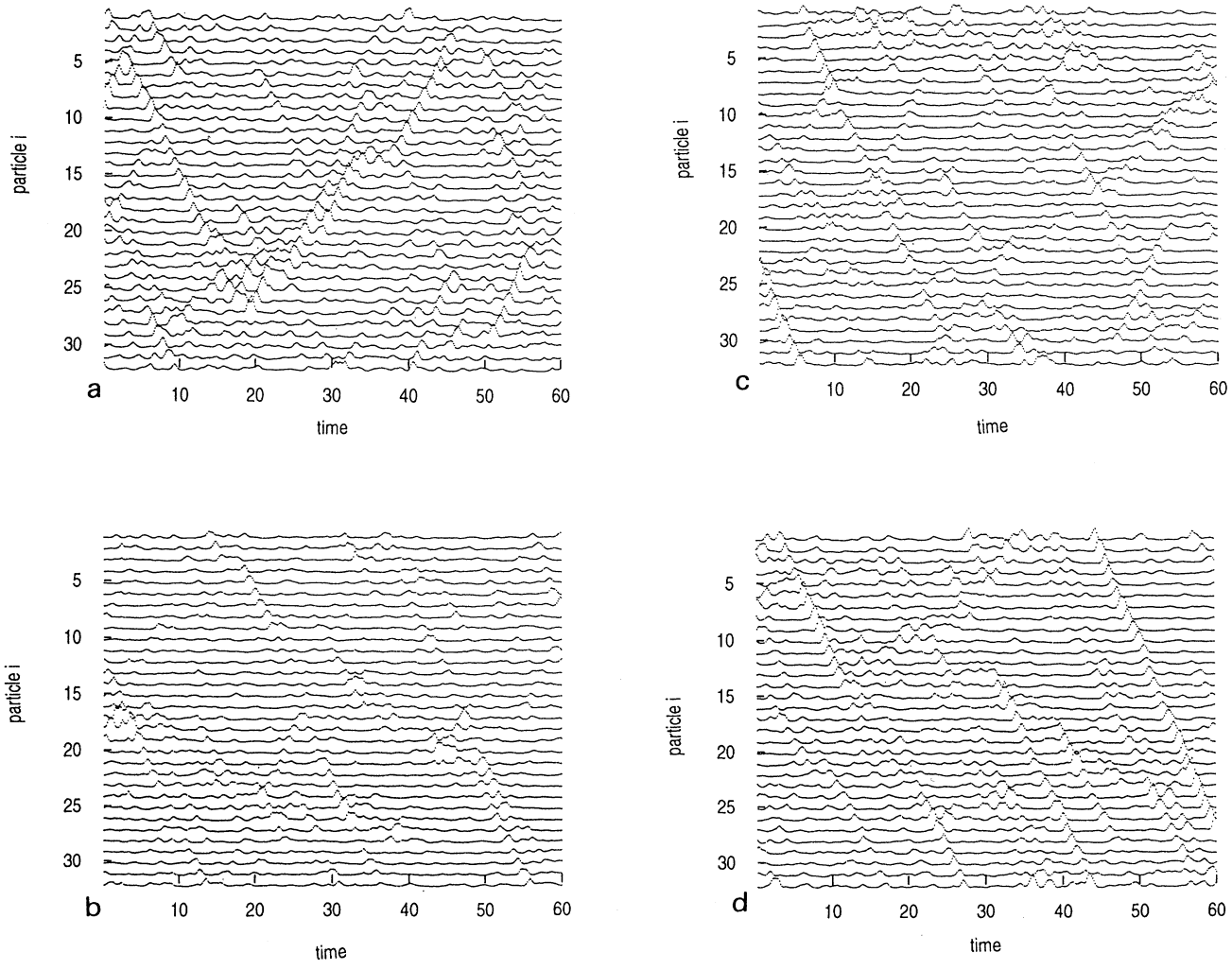

FIG. 4. Time evolution of energy field for $F_e=0$ (a), $F_e=0.003$ (b), $F_e=0.005$ (c), and $F_e=0.007$ (d) ($T=1$, $N=32$, and $\beta=1.5$).

$$(dH/dt)_{\text{ad}} = F_e(t)\sum\{D_i^* - \sum D_j^*/N\}p_i/m$$
$$= F_e(t)\sum D_i^* p_i/m = F_e(t)J_x \ . \quad (23)$$

From the above it turns out that the choice Eq. (22) is the right one. Taking $B = J_x$, we have from Eq. (17) with $C = (k_B T^2 L)^{-1}$,

$$\lambda = \lim_{F_e \to 0} \lim_{t \to \infty} \langle J_x(t) \rangle / (LTF_e) \ . \quad (24)$$

IV. NUMERICAL RESULTS AND DISCUSSIONS

Now we proceed to numerical calculations. As units of length, mass, and time we take a (lattice constant), m (mass of a particle), and $(m/\mu)^{1/2}$ and nondimensional temperature is defined to be $k_B T/(\mu a^2)$ with T denoting temperature and k_B the Boltzmann constant. We will present every physical quantity in a nondimensional form following the prescription above. The important nonlinear parameter β in Eq. (18) becomes, after nondimensionalization above, $\beta' = \beta a^2/\mu$, which we denote β hereafter.

In Fig. 1 we plot $J \equiv \lim_{t \to \infty} \langle J_x(t) \rangle$ for a system with $N=32$ and $\beta=1.5$ [15] as a function of an external field F_e. We observe linear dependence of J on F_e and this makes it possible to calculate λ based on Eq. (24). In passing it is remarked that similar linear dependence is reported also for liquids [16]. In Fig. 2 temperature dependence of $\lambda(T)$ is shown. As is expected from the fact that low temperature corresponds to small nonlinearity or near harmonicity, we observe a sharp increase of $\lambda(T)$ as T becomes small. The data $\lambda(T)$ below $T=1$ are consistent with the behavior $\lambda(T) \propto T^{-1/2}$, which is derivable for a simple kinetic theory [10] $\lambda \sim cvl$ with the specific heat c ($\propto T^0$ at low temperature), velocity of energy carrier $v \propto T^{1/2}$ and a mean free path $l \propto T^{-1}$. As T becomes large $\lambda(T)$ also increases with main cause probably coming from T dependence of c.

We show in Fig. 3 a Lyapunov exponent as a function of T. Since nonlinear effects increase with T, the monotonic increase of Lyapunov exponents is in accord with our intuition. Comparing Fig. 3 with Fig. 2, we note that one cannot simply relate λ to Lyapunov exponents, contrary to the statement in Ref. [7] that large Lyapunov exponents correspond to small λ. However, this is valid in the low-temperature (weak nonlinear) region where as T increases, the Lyapunov exponent increases while λ becomes small. In Fig. 4 we show time variation of the energy field (energy of each particle) for $T=1.0$. In all the figures we observe some energy excitations propagating to the left or right for some duration of time before vanishing in thermal background. As F_e becomes large these excitations live longer and favor moving in the direction of the external force F_e, that is, to the positive x direction. From Fig. 1 we now know that these waves play an important role in heat transport. However, at the present we are not successful in deriving or identifying the excitations based on Eq. (1) with Eqs. (18) and (22).

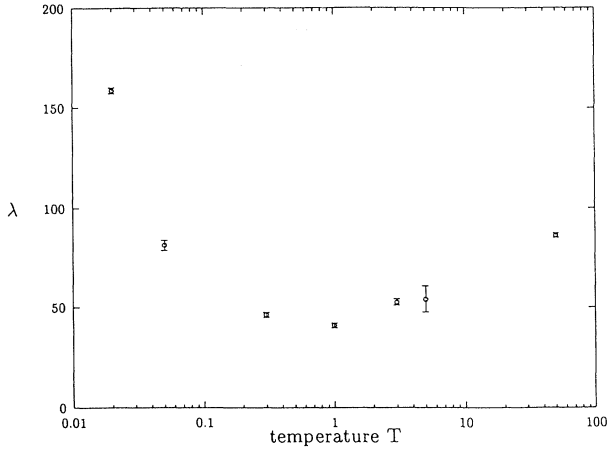

FIG. 5. The same with Fig. 2 except that $\beta=10$.

Finally we comment on the dependence of λ on β, nonlinear parameter in the Hamiltonian Eq. (18), and on N, the system size. In Fig. 5 we plot $\lambda(T)$ for $N=32$ and $\beta=10$. Since β is about seven times larger than the one in Fig. 2, the sharp increase of $\lambda(T)$ as T goes to zero starts at relatively lower temperature in Fig. 5 than in Fig. 2. As to N dependence of our NEMD let us give some general comments. As N increases we observe first that the linear F_e dependence as shown in Fig. 1 is limited to a smaller F_e region and J is not monotonic with F_e for larger F_e. Second, since low-frequency phonons participate in dynamics for larger systems, we need more computation time to obtain J and λ [17]. At the moment we calculated $\lambda(T)$ for $N=64$ and observed only a slight increase of $\lambda(T)$ as compared with the one for $N=32$, Fig. 2. Studies on λ of other systems such as the diatomic Toda lattice [18] and Frenkel-Kontorova system [3] together with the N dependence of λ are in progress and will be reported elsewhere.

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