Intriguing Heat Conduction of a Polymer Chain

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We study heat conduction in a one-dimensional (1D) chain of particles with longitudinal as well as transverse motions. The particles are connected by two-dimensional harmonic springs together with bending angle interactions. Using equilibrium and nonequilibrium molecular dynamics, three types of thermal conducting behaviors are found: a logarithmic divergence with system sizes for large transverse coupling, 1/3 power-law at intermediate coupling, and 2/5 power-law at low temperatures and weak coupling. The results are consistent with a simple mode-coupling analysis of the same model. The 1/3 power-law divergence should be a generic feature for models with transverse motions.

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To understand the microscopic dynamical mechanism of heat conduction is one of the long standing tasks in nonequilibrium statistical mechanics. This problem has attracted increasing attention in recent years [1–13]. The main effort has been focused on the necessary and sufficient conditions of the Fourier law of heat conduction. With strong numerical support, it is argued that chaos (or exponential instability) is the necessary condition [1]. However, recent results show that even linear instability, such as that found in generic polygonal billiards, is sufficient for a normal diffusion and energy transport obeying the Fourier law [2].

In many systems studied so far, the heat conduction violates the Fourier law, namely, the thermal conductivity diverges with system size $N$ as $N^\alpha$, with $\alpha > 0$. It has been proved that for 1D system, the momentum conservation leads to an anomalous heat conduction [3]. However, its specific form of divergence with system size is still of considerable controversy [4, 5, 6, 7, 8]. Based on a renormalization group analysis for a 1D hydrodynamic fluid model, it is argued that in a generic momentum conserving system, the thermal conductivity should be $\kappa \propto N^{1/3}$ [9]. Unfortunately, most existing numerical results do not agree with this prediction because all 1D lattice models considered so far have no transverse degree of freedom that is required in the analysis. However, a mode-coupling theory analysis for the 1D Fermi-Pasta-Ulam (FPU) model gives a divergent exponent 2/5 [10], which is supported by the numerics from different groups [11].

It seems that a universal exponent does not exist. Most recently, it is found that a divergent thermal conductivity is connected with a superdiffusion [11, 12], $\kappa \propto N^{2-2/\beta}$, where $\beta$ is the exponent of the diffusion ($\Delta x^2 \sim t^\beta$, $0 < \beta \leq 2$). The value of $\beta$ changes from model to model. This is justified by all billiard gas models studied.

On the other hand, the understanding of heat conduc-
tion mechanism will allow us to control and manipulate heat current, and eventually to design novel thermal devices with certain function [10]. To this end, more realistic physical models are necessary. Among many others, nanotubes and polymer chains are most promising. Recent molecular dynamics (MD) study of Carbon nanotubes with realistic interaction potential suggested a divergent thermal conductivity for narrow diameter tubes [11]. The strict 1D models may not be applicable to nanotubes. The added transverse motion and the flexibility of the tube at long length scales will certainly scatter phonons, and thus should have a profound effect on thermal transport.

In this Letter, we consider a polymer chain of $N$ point particles with mass $m$ on a 1D lattice. The lattice fixes the connectivity topology such that only the neighboring particles interact. The Hamiltonian is given by

$$H(p, r) = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}K_r \sum_i \left( |r_{i+1} - r_i| - a \right)^2 + K_\phi \sum_i \cos \phi_i, \quad (1)$$

where the position vector $r = (x, y)$ and momentum vector $p = (p_x, p_y)$ are two-dimensional; $a$ is lattice constant. If the system is restricted to $y_i = 0$, it is essentially a 1D gas with harmonic interaction. The coupling $K_r$ is the spring constant; $K_\phi$ signifies bending or flexibility of the chain, while $\phi_i$ is the bond angle formed with two neighbor sites, $\cos \phi_i = -\mathbf{n}_{i-1} \cdot \mathbf{n}_i$, and unit vector $\mathbf{n}_i = \Delta r_i / |\Delta r_i|$, $\Delta r_i = r_{i+1} - r_i$.

We determine the heat current in a temperature gradient by nonequilibrium MD. The system is set up with fixed left most and right most boundary. The average distance between particles is set to $a$, the zero-temperature equilibrium distance. A group of four particles at the two ends are subject to heat baths at temperature $T_L$ and $T_H$, respectively. This is realized by Nosé-Hoover
thermostats. The rest of the particles follow the equations of motion using a velocity Verlet algorithm. We use small time step sizes $h = 0.0005$ to 0.0010. Typical MD steps are $10^8$ to $10^{10}$.

We use the following expression for local heat current per particle:

$$
 m j_i = -\Delta r_i \cdot (p_i + p_{i+1}) \cdot G(i) \\
 -\Delta r_{i-1} \cdot (p_i + p_{i-1}) \cdot G(i-1) \\
 +\Delta r_{i-1} \cdot (p_i \cdot H(i-2, i-1, i-1)) \\
 +\Delta r_i \cdot (p_i \cdot H(i+1, i+1, i)) + p_i h_i,
$$

where $G(i) = \frac{1}{2} K_r ((\Delta r_i - a) n_i$, $H(i, j, k) = K_\phi (n_i + n_k \cos \phi_j)/\Delta r_k|$, and the local energy per particle $h_i = \frac{1}{2} K_r ((\Delta r_{i-1} - a)^2 + (\Delta r_i - a)^2) + K_\phi \cos \phi_i + p_i^2/(2m)$. This is derived from $J = \sum d(r, h_i)/dt$, by regrouping some of the terms using translational invariance. It satisfies the continuity equation in the long-wave limit.

We present our main numerical results in Fig. 1. The data are obtained using 20 1GHz-Pentium PCs over six months of CPU times. We plot the average heat current multiplied by $N$, $jN = (T_H - T_L)\kappa$, in log-log scale (Fig. 1(a)) and linear-log scale (Fig. 1(b)). It is clearly shown that three types of behaviors of the thermal conductivity $\kappa$ are observed, the logarithmic divergence, $\log N$, power-law $\kappa \propto N^\alpha$ with $\alpha = 1/3$, as well as $2/5$, depending on the model parameters. Log-log plot shows linear behavior for data set E, F, H, and J. At the parameters of set E, excellent power-law dependence is found, with an exponent of $\alpha = 0.334 \pm 0.003$ (using an error weighted least-squares fit for $N \geq 128$). Set F is also in good agreement with a slope of 1/3. On the other hand, for set H and J, we have exponent $\alpha$ consistent with 0.4. Set B is consistent with logarithmic divergence, $\kappa \propto \log N$ (see Fig. 1(b)). The model has two key parameters, the temperature $T$, and the transverse coupling $K_\phi$. We should mention that wide range of parameters is scanned, and surprisingly, only the three scalings are found so far in this model.

To understand the simulation results, we consider a simple mode-coupling theory for the present model. The equations of motion in terms of normal-mode coordinates, $Q_k = \sqrt{N} \sum_{j=0}^{N-1} (x_j - ja)e^{2\pi j k/N}$, $Q_k = \sqrt{N} \sum_{j=0}^{N-1} y_j e^{2\pi j k/N}$, for small oscillation near zero-temperature equilibrium position, keeping only leading nonlinearity, are

$$
\frac{d^2 Q_k}{dt^2} = -(\omega_k^\parallel)^2 Q_k^\parallel + \sum_{k'+k''=k} c_{k',k''}^{\parallel} Q_k^\parallel Q_{k'}^\parallel Q_{k''}^\parallel, \quad (3a)
$$

$$
\frac{d^2 Q_k}{dt^2} = -(\omega_k^\perp)^2 Q_k^\perp + \sum_{k'+k''=k} c_{k',k''}^{\perp} Q_k^\perp Q_{k'}^\perp Q_{k''}^\perp, \quad (3b)
$$

where the bare dispersion relations are given by $\omega_k^\parallel = 2\sqrt{\frac{k^2}{m} \sin \frac{\pi k}{N}}$, and $\omega_k^\perp = 4\sqrt{\frac{k^2}{m} \sin \frac{\pi k}{N}}$. The expressions for $c_{k,k'}^{\parallel,\perp}$ are complicated, but can be simplified in the long-wave limit, as $c_{k,k'}^{\parallel,\perp} \propto kk'(k + k')$. Instead of the integer $k$, we can also index the mode by its corresponding lattice momentum $p = 2\pi k/(aN)$.

A central quantity in the mode-coupling theory is the normalized correlation function, $g_p(t) = \langle Q_p(t) Q_p(0) \rangle/\langle Q_p(0)^2 \rangle$. The Fourier-Laplace transform of the correlation function, $g[z] = \int_0^\infty g(t)e^{-int} dt$, is given by

$$
g_p^{\parallel,\perp}[z] = -\frac{i z - p^2 \nu^{\parallel,\perp}[z]}{z^2 - i^2 \nu^{\parallel,\perp}[z]^2 - i z p^2 \nu^{\parallel,\perp}[z]]. \quad (4)
$$

The constants $c_{\parallel,\perp}$ are effective or renormalized sound velocities for the longitudinal and transverse modes. They are defined, e.g., by $(c_{\parallel,\perp})^2 \langle Q_p^{\parallel,\perp}(t)^2 \rangle = k_B T$, as $p \to 0$. The damping functions (memory kernel) are
given by the coupled equations,

\[ \nu^\parallel(t) = \frac{K_\parallel}{2\pi} \int \frac{dp}{\omega} (g^\parallel_p(t))^2, \]
\[ \nu^\perp(t) = \frac{K_\perp}{2\pi} \int \frac{dp}{\omega} g^\parallel_p(t) g^\perp_p(t). \]  

Eqs. (4) and (5) form a closed system of nonlinear integral equations. This is a straightforward generalization of the strict 1D result [6]. The above equations are derived under a number of simplification assumptions, such as long-wave approximation, mean-field type product approximation for the correlation functions, replacing random-force correlation with true force correlation. Some of them can be removed but more complicated equations will result.

In Fourier space, for large \( z \) the solution is found from integration by part, as

\[ \nu^{\parallel\perp}[z] = K^{\parallel\perp}/(iza) + O(z^{-3}). \]

The long-wave asymptotic decay of each mode is controlled by the small \( z \) behavior of the function \( \nu^{\parallel\perp}[z] \). We define \( \delta_\parallel \) and \( \delta_\perp \) by \( \nu^{\parallel\perp}[z] \propto z^{-\delta_\parallel}, z^{-\delta_\perp} \). The dispersion relation is then given by the location of the poles in the correlation function \( g[z] \). The imaginary part of the frequency \( \nu[z] \) gives damping, by \( \gamma_p \propto p^2 \nu[z] \propto p^{-3} \). We note that three types of behaviors can be derived from the above set of equations. If \( K_\parallel \approx K_\perp \) and \( c_\parallel \approx c_\perp \), the two equations reduce to that of strict 1D model, we thus expect the result of Lepri [7], i.e., \( \delta_\parallel = \delta_\perp = 1/3 \). One the other hand, it can be shown rigorously that in the limit of small \( K_\perp \) and small \( c_\perp \), we have \( \delta_\parallel = 0 \) and \( \delta_\perp = 1/2 \). Formally, when \( a \to 0 \), the equation possesses the scaling solution of the form \( \nu[\lambda z] = \lambda^{-\gamma} \nu[z] \); this implies \( \nu[z] \propto 1/z \). These analytic results are supported by numerical solutions of the coupled equations, shown in Fig. 2. They are solved by a brute force numerical integration in Fourier space. Details of the mode-coupling calculation will be presented elsewhere.

In Fig. 2 at parameter set I, we observe very good asymptotic behavior of \( \nu^\parallel[z] \propto z^{-1/2} \) and \( \nu^\perp[z] \propto \text{const}. \) This corresponds to the behavior of MD results for data set E and F in Fig. 1. When \( c_\parallel = c_\perp \) but \( K_\parallel \neq K_\perp \) (set II), we see crossover from \( \delta_\parallel = 1/3 \) to \( 1/2 \). The curve III may be related to the logarithmic divergence. We note that a meaningful, direct mapping from the simulation parameters to mode-coupling parameters is not possible, due to qualitative nature of the theory.

The prediction of \( \delta_\parallel = 1/2 \) and \( \delta_\perp = 0 \) is checked against an equilibrium MD simulation in a microcanonical ensemble with periodic boundary condition. We compute the normal-mode correlation \( \langle Q_\mu(t)Q^*_\nu(0) \rangle \) for each mode specified by the lattice momentum \( p = 2\pi k/(aN) \). The functions are oscillatory with an exponential decay, \( \cos(\omega t)e^{-\gamma_p t} \). The decay constants are obtained by fitting the maximum amplitude as a function of time. The results are presented in Fig. 3. Comparing with results from smaller and larger system sizes, effect of finite sizes appears rather small at \( N = 1024 \). Excellent agreement with mode-coupling theory (\( \gamma \propto k^{2-\delta} \)) is obtained for data set E. However, for data set B and J, the slopes are not consistent with either logarithmic divergence for \( \kappa \) or 2/5 law. This may be interpreted as that we are still not in the asymptotic regime.

To connect the result of damping of the modes with thermal conductivity, it is noted [9, 16] that each mode contributes to the thermal transport independently. Under the linear-response theory, the Green-Kubo formula relates the current-current correlation to the thermal conductivity.

FIG. 2: Real part of \( \nu^\parallel[z] \) and \( \nu^\perp[z] \) vs \( z \) for parameters \( a = 1, K_\parallel = 1, (K_\perp, c_\parallel, c_\perp) \): I: (0.3, 2, 1), II: (1.8, 1, 1), III: (2, 1, 0.5).

FIG. 3: The decay rate \( \gamma^\parallel \) (dots) and \( \gamma^\perp \) (triangles) vs \( k \) for the parameters set B, E, and J at equilibrium temperature \( T = (T_L + T_H)/2 \). The number on the line indicates the slope of the straight line. The system size is \( N = 1024 \).
The Green-Kubo integrand, $\langle J(t)J(0) \rangle /N$, vs time $t$. The parameters are the same as that in Fig. 3. The straight lines have slope $-2/3$ (on E) and $-3/5$ (on J).

The thermal conductivity on a finite lattice is obtained by integrating over $t$ to a time of $O(N)$, Thus $\kappa_N \propto N^{1-1/(2-\delta)} = N^\alpha$. When $\delta_\parallel = 1/2$, we have $\alpha = 1/3$, and when $\delta_\parallel = 1/3$, the exponent $\alpha = 2/5$.

The decay rates for $J$ are assumed to be the same as that for $Q$, thus $\langle J(t)J(0) \rangle \propto \sum_p \exp(-\gamma_p t)$. The amplitude of the exponential decay is approximately independent of $p$. Converting the summation to integral, we have $\langle J(t)J(0) \rangle \propto t^{-1/(2-\delta)}$. The thermal conductivity on a finite lattice is obtained by integrating over $t$ to a time of $O(N)$, Thus $\kappa_N \propto N^{1-1/(2-\delta)} = N^\alpha$. When $\delta_\parallel = 1/2$, we have $\alpha = 1/3$, and when $\delta_\parallel = 1/3$, the exponent $\alpha = 2/5$.

The current-current correlation functions are presented in Fig. 4 for the parameters corresponding to data set B, E, and J in Fig. 3. For data set J, a power-law dependence is in excellent agreement with the theoretical expectation $t^{\alpha-1}$ with $\alpha = 2/5$. For set E, the curve is a bit steeper than expected. This may be due to finite sizes. For set B, where logarithmic divergence is observed, we do not observe good power-law behavior in the correlation.

We need to clarify the relationship between the three types of observed behaviors in the nonequilibrium MD results. From mode-coupling point of view, the 1/3-law is generic and robust, while $\alpha = 2/5$ should be eventually crossover to 1/3 at long length scales. However, such a crossover is not observed in MD data. The crossover effect can be argued for a more general setting. More general mode-coupling equations for a generic interaction potential consistent with the symmetry would have an additional term of $\frac{K_3}{2\pi} \int \frac{dp}{p^2} \langle g_p^\parallel(t) \rangle^2$ for Eq. 5a; Eq. 5b remains the same. Such a term can appear either from cubic or quartic nonlinearity in potential. Contribution from this extra term decays in time $t$ faster than the perpendicular component contribution. Thus, the asymptotic result of $\delta_\parallel = 1/2$ remains true. The same should be also true even if a chain is allowed to move in three dimensions. If the parameter $K_3$ is sufficiently large, we may see exponent close to 0.4. The logarithmic divergence is a bit difficult to interpret. It may require a more refined theory than the present naive mode-coupling theory.

In summary, we have observed three different scalings in a 1D polymer chain. When the transverse motion couples with the longitudinal motion, the thermal conductivity diverges with system size with a 1/3 power-law. This has been demonstrated with a very high precision numerical result and explained in terms of a mode-coupling theory. In the weak coupling regime, a 2/5 power-law is observed which is consistent with the results observed in the FPU model. In the case of strong transverse coupling, a logarithmic divergent law is observed.

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