

Anomalous heat conduction in a carbon nanowire: Molecular dynamics calculationsGang Wu* and Jinming Dong[†]*Group of Computational Condensed Matter Physics, National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing, 210093, People's Republic of China*

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Heat conduction of a real quasi-one-dimensional material, the finite length carbon nanowire inserted into the single-walled carbon nanotube (SWNT), has been studied by the molecular dynamical method, in which both of the longitudinal as well as transverse motions of the chain atoms in the SWNT have been permitted. It is found that the thermal conductivity κ of the carbon nanowire is very high at room temperature and diverges more likely with the chain length logarithmically.

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I. INTRODUCTION

When a small temperature gradient exists between two boundaries of a material, it is expected that heat will be transported through the material, which usually obeys Fourier's law of conduction ($\vec{j} = -\kappa \nabla T$), a well-known fact in three-dimensional systems, where \vec{j} is the heat amount flowing through a unit surface per unit time, ∇T is the gradient of the temperature field over the material, and κ is defined as the thermal conductivity. It is not clear, however, whether Fourier's law is still correct in the lower (one- or two-) dimensional systems, which stimulated a great interest in the past several years. It has been shown¹⁻¹⁴ that heat conduction exhibits anomalous behavior in some one-dimensional systems. For example, in the one-dimensional (1D) integrable systems, such as the harmonic chain and the monoatomic Toda model, no temperature gradient can be set up. In some 1D nonintegrable systems, such as the Frenkel-Kontorova (FK) model,² the discrete ϕ^4 model⁴ and the Lorentz model,⁵ the temperature gradient is uniform, and the heat conductivity κ is a constant, being independent of system size, which means these 1D systems still obey Fourier's law. However, in some other anharmonic 1D systems, like the Fermi-Pasta-Ulam (FPU) β model,^{6,2} the diatomic Toda chain,⁷ or in 1D hard-particle gases with alternating masses,⁷⁻⁹ the temperature gradient can be formed as $dT/dx \sim L^{-1}$, and their κ scales as $\kappa \sim L^\alpha$, where L is the system size and $\alpha > 0$. Recently Wang and Li¹⁴ studied the anomalous thermal conduction in 1D polymer chains with a modeled Hamiltonian and found three types of divergent exponent α in them that are caused by different couplings between longitudinal and transverse motions. Although a great deal of theoretical research on the problem had been done in the past several years, there exists right now still a lot of controversy about the divergence behavior of the thermal conductance in low dimensional systems, and many important and fundamental questions in this field remain unsolved.

All these systems mentioned above seem to be far from real physical materials. What will happen to the thermal conduction in a real low dimensional material? Will it follow Fourier's law or not? All of these problems not only stimulate fundamental research interests, but also have great potential applications in the thermal conduction of nanomateri-

als. When the dimensions of electronic devices shrink to nanoscale due to the fast progress in the present microelectronic technology, the thermal conduction problem becomes more and more important because a significant energy should be dissipated in a much smaller, compact space. And the divergence of the thermal conductance with the length in the low dimensional materials promises the possibility of making more outstanding heat dissipation nanomaterials, solving the thermal dissipation problem coming from the miniaturization of electronic and optical devices. So, it is very interesting to study the heat conduction in a real 1D or quasi-1D physical system.

Recently, carbon nanotubes (CNTs) have attracted much attention due to their remarkable electronic, thermal, and mechanical properties.¹⁵ The diameter of a typical nanotube ranges from several to several tens angstroms, and that of the smallest one is only 3 Å (Ref. 16), while their lengths can be several μm , and even reach to several mm, being much larger than their diameters. Thus a carbon nanotube can be thought of as a very good 1D system. In fact, many experiments and numerical simulations have found that the thermal conductivity κ of SWNTs is extremely high although there exists a distribution of the obtained κ values. For example, the observed room temperature thermal conductivity of SWNT rope is about 1750–5800 W/mK (Ref. 17), and for individual multiwalled carbon nanotubes (MWNTs), this value is larger than 3000 W/mK.¹⁸ Using equilibrium and nonequilibrium molecular dynamics simulations, recent numerical simulations also give similar results. Berber *et al.*¹⁹ found that, for an isolated (10, 10) nanotube at room temperature, $\kappa \approx 6600$ W/mK. Maruyama²⁰ claimed that κ of (5, 5) nanotube diverges as a power law relation with the tube length and got a rather smaller κ value of about 150–500 W/mK for the (5, 5) tube. Zhang and Li²¹ studied three armchair SWNTs, i.e., (5, 5), (10, 10), and (15, 15), and found that their κ 's diverge as a power law, too, with their κ values of about 700–2200 W/mK higher than that in Ref. 20. Yao *et al.*²² also studied the same three armchair tubes and found their κ 's could diverge with their lengths and have the same higher κ value of about 400–2500 W/mK.

At the same time, a new type of carbon structure, carbon nanowires (CNWs)²³ have been discovered in the cathode deposits prepared by hydrogen arc discharge evaporation of carbon rods. The CNWs are made of extraordinarily long 1D

linear carbon chains consisting of more than 100 carbon atoms inserted into the innermost tube (7 Å diameter) of MWNTs. The CNW can be considered as another good example of the real 1D physical system. In this paper, we will investigate in detail the heat conduction in the CNWs and pay much of our attention to the divergence behavior of their thermal conductivity.

In what follows we first introduce the model Hamiltonian and calculation method. Then in Sec. III we give the main numerical results and discuss the divergence of thermal conductivity in the CNWs. The paper ends with some concluding remarks in Sec. IV.

II. MODEL

As is well known, a bare long carbon chain cannot be stable, and so we suppose a chain of N carbon atoms with the same mass m_c is inserted into a single-walled carbon nanotube. The interaction between chain atoms is simulated by the Tersoff-Brenner bond order potential,²⁴ and the interaction between carbon chain and outside nanotube is described by the Lennard-Jones (LJ) potential,

$$u(x) = 4\varepsilon \left[- \left(\frac{\sigma}{x} \right)^6 + \left(\frac{\sigma}{x} \right)^{12} \right]. \quad (1)$$

In our simulation, ε and σ are taken as 2.41 meV and 3.4 Å (Ref. 25), respectively. Then the Hamiltonian of the chain system can be written as

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i,j=1}^N V_{ij} + U_i, \quad (2)$$

where

$$V_{ij} = f_c(\vec{r}_{ij}) [a_{ij} f_R(\vec{r}_{ij}) + b_{ij} f_A(\vec{r}_{ij})]. \quad (3)$$

Here, $f_c(\vec{r}_{ij})$ is a cutoff function, $f_R(\vec{r}_{ij})$ and $f_A(\vec{r}_{ij})$ are two Morse type functions which represent the attractive and repulsive effects of the potential, respectively, and a_{ij} and b_{ij} are two parameters describing bond order and bond angular effects. Full details of the model potential are available in the original paper of Tersoff and Brenner.²⁴ U_i is external potential exerted by the outside nanotube. m_i is the mass of chain atoms, i.e., the carbon atom mass. For simplicity, we assume the carbon atoms on the outside nanotube are distributed *continuously*, which is well known as the continuum model and is used in a lot of systems.^{26–37} For example, based upon the same idea, Girifalco *et al.* developed a simple universal graphitic potential in their paper.³⁷ Now, following them, we take the external potential as

$$U(r) = n_\sigma \int u(x) d\Sigma, \quad (4)$$

where r and x represent the time-dependent distances of the wire atom to tube axis and surface element $d\Sigma$, respectively. n_σ is the mean surface density of tube atoms. In the cylindrical coordinates, $U(r)$ can be expressed as

$$U(r) = n_\sigma \int u(x) \rho d\theta dz, \quad (5)$$

where

$$x = \sqrt{(\rho \cos \theta - r)^2 + \rho^2 \sin^2 \theta + z^2}, \quad (6)$$

ρ is the radius of the outside tube, and θ and z are two other cylinder coordinates of $d\Sigma$.

Thus, when $r \neq 0$, the surface integral can be simplified to give

$$U(r) = 3\pi\rho n_\sigma \varepsilon \left[- \frac{\sigma^6}{(4\rho r)^{\frac{5}{2}}} I_5 + \frac{21}{32} \frac{\sigma^{12}}{(4\rho r)^{\frac{11}{2}}} I_{11} \right], \quad (7)$$

where

$$I_n = \int_0^{\pi/2} \frac{dt}{(a^2 + \sin^2 t)^{n/2}},$$

$$a^2 = \frac{(\rho - r)^2}{4\rho r}. \quad (8)$$

Here, I_n is an integral related to the hypergeometric function, which can be made exactly in an expanded series, and the obtained result is expressed as

$$I_n = \frac{\pi}{2} b^{-n} \left[1 + \sum_{m=1}^{\infty} \frac{(2m-1)!!(2m+n-2)!!}{(n-2)!![(2m)!!]^2 b^{2m}} \right],$$

$$b^2 = a^2 + 1 = \frac{(\rho + r)^2}{4\rho r}. \quad (9)$$

But when $b \rightarrow 1$, i.e., $r \sim \rho$, the summation in the I_n will converge very slowly. So, in that case, after using some algebra techniques, a more efficient expression can be finally obtained,

$$I_{2k+1} \approx \left\{ \frac{1}{(2k-1)!!} \left(\frac{2}{a^2} \right)^{k-1} \sum_{m=0}^{k-1} \frac{[(2m)!!]^2 (k-m-1)!}{[m!]^3 2} \left(\frac{a}{4} \right)^{2m} + \frac{(2k-1)!!}{(2k)!!} \right\}. \quad (10)$$

This expression is an approximate one, but when a is small enough, it can give the very accurate result of I_n , and needs only to take a few terms in its summation. Thus combining Eqs. (7)–(9) with Eq. (10), we obtain an efficient external potential, representing in high precision the interaction between the chain atoms and the outside tube.

In this work, we consider only armchair SWNT (5, 5) as the outside tube because its radius is about 3.4 Å, which is the closest to that of the innermost tube observed experimentally.²³ The average equilibrium distance between the chain atoms is set to be $a = 1.84$ Å, which means there are four carbon atoms in three periods of the outside armchair nanotube. We should mention that at present there are *no experimental data* about the distance between carbon atoms in the nanowire, which is so selected from the *commensurability* between both periods of nanowire and outside SWNT.

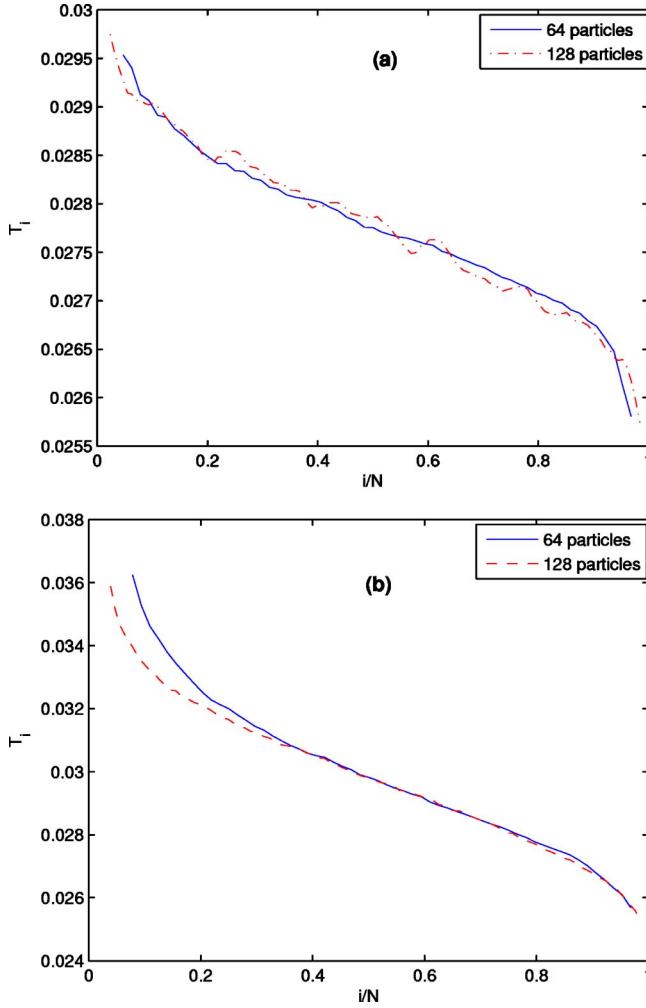


FIG. 1. The temperature profiles on the chain at $T_L=0.03$ and $T_R=0.025$, with $N=64$ (solid line) and 128 (dash-dot lines). The averages are carried over a time interval of 10^4 – 10^5 . The distance between CNW atoms is 1.844 \AA . (a) Eighth-order Runge-Kutta algorithm. (b) Velocity Verlet algorithm.

In fact, we can choose different a values to study their effects on the thermal conduction of the CNW, which is beyond the scope of the present investigation and will be left for future study.

We determine the heat current in a temperature gradient by the nonequilibrium molecular dynamics method. Two atoms at each end of the CNW are subject to heat baths at T_L and T_H , respectively, which usually can be simulated by Nosé-Hoover thermostats.³⁸ The equations of motion for these four atoms are written as

$$\begin{aligned}\ddot{\vec{r}}_i &= -\zeta_L \dot{\vec{r}}_i + \vec{f}_i, \\ \ddot{\vec{r}}_j &= -\zeta_R \dot{\vec{r}}_j + \vec{f}_j,\end{aligned}\quad (11)$$

where f_i is the force applied on the i^{th} carbon atom. The thermal variables ζ_L and ζ_R evolve according to the equations

$$\dot{\zeta}_{L,R} = \frac{1}{Q} \left(\sum_i \frac{\vec{p}_i^2}{m_i} - g k_B T \right),$$

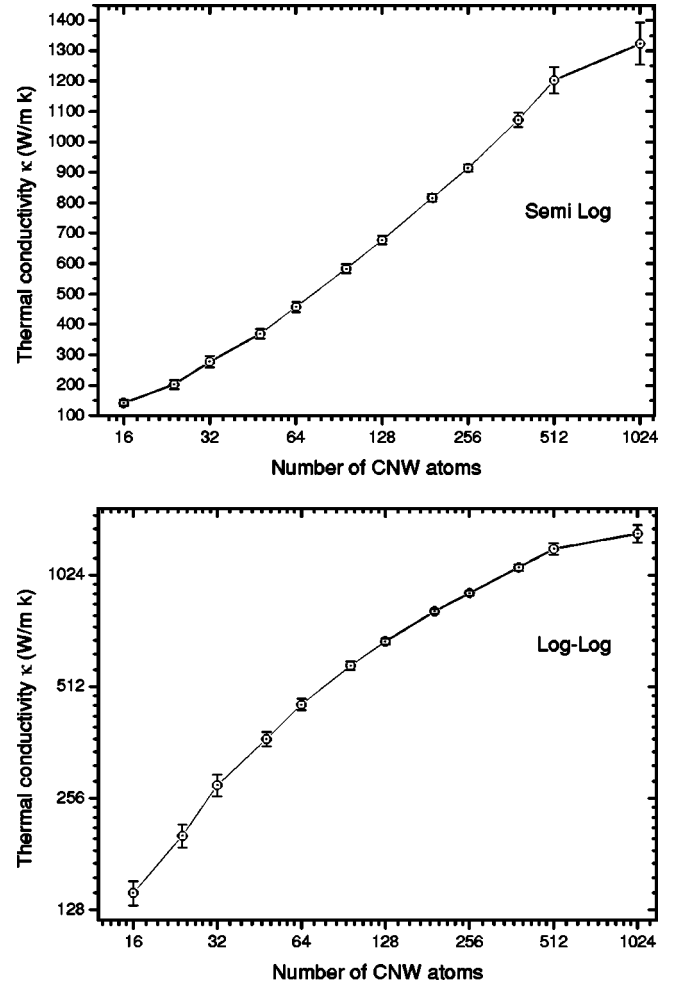


FIG. 2. Thermal conductivity of the CNW as a function of its length. $a_0=1.844 \text{ \AA}$. (a) Linear-logarithm plot. (b) Log-log plot. The solid lines in (a) and (b) are used for guiding eyes.

$$Q = g k_B T \tau^2. \quad (12)$$

The number of degrees of freedom for particles in thermostats is given by $g=6$, and τ is the relaxation time of the heat bath. The rest of the atoms follow the equations of motion

$$\ddot{\vec{r}}_i = \vec{f}_i, \quad i = 3, \dots, N-2, \quad (13)$$

and fixed boundary conditions are assumed for the zeroth and $(N+1)$ th atoms $\{\vec{r}_0 \equiv (0, 0, 0), \vec{r}_{N+1} \equiv [0, 0, (N+1)a]\}$.

We first use an eighth-order Runge-Kutta algorithm to solve the ordinary differential equations, which provides more accurate results than those of the usual fourth-order Runge-Kutta algorithm. The time step is chosen from $h=0.01$ to 0.05 in the unit of 0.035 267 ps . Typical total MD steps are taken as 10^7 to 10^8 , and, for comparison, we also use the velocity Verlet algorithm³⁹ in the same evolution.

The total heat flux can be expressed as follows:

$$\vec{J}(t) = \frac{d}{dt} \sum_i \vec{r}_i(t) \varepsilon_i(t), \quad (14)$$

where $\vec{r}_i(t)$ is the time-dependent coordinate of the wire atom i , and $\varepsilon_i(t)$ is its total energy, which contains both of the

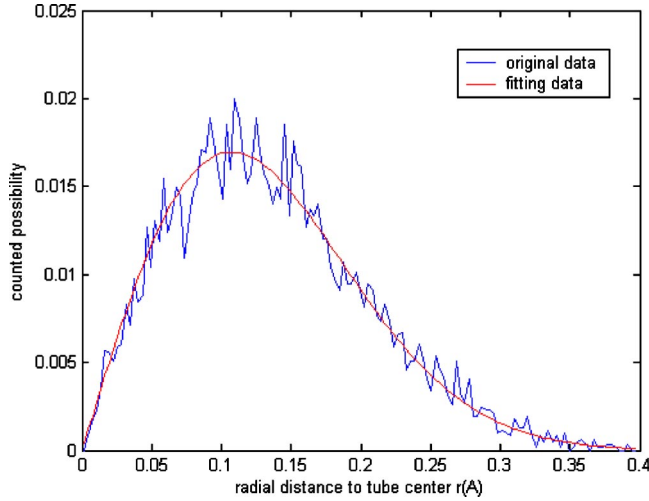


FIG. 3. Statistical radial distribution for the motion of wire atoms perpendicular to the tube axis.

kinetic and the potential energies. After introducing the force on the atom i from atom j , i.e., $\vec{F}_{ij} = \partial \varepsilon_i / \partial \vec{r}_j$, the instantaneous local heat current per particle can be expressed as

$$\vec{J}(t) = \sum_i \dot{\vec{r}}_i \varepsilon_i + \sum_{i,j,i \neq j} \vec{r}_{ij} (\vec{F}_{ij} \cdot \dot{\vec{r}}_i), \quad (15)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the relative distance between atoms i and j .

Because of the linear temperature distribution, the classical definition on the heat conductivity can be used, leading to

$$\kappa = JN / (T_L - T_R). \quad (16)$$

When $N \rightarrow \infty$, the above expression corresponds to the coefficient of heat conductivity of the chain under temperature $T = (T_L + T_R) / 2$. In our MD process, T_L and T_R are kept as 0.03 and 0.025, which correspond to real 348 K and 290 K in practice, respectively.

The alternative way to calculate the heat conductivity of the chain is based on the Green-Kubo formula,⁴⁰

$$\kappa_s = \frac{1}{k_B T^2 N} \int_0^t \langle J(\tau) J(0) \rangle d\tau, \quad (17)$$

where $J(t)$ is defined in Eq. (14). In our calculations, we found that these two definitions always give almost equal results. (The difference between them never exceeds a few percent.)

III. NUMERICAL RESULTS AND DISCUSSION

In Fig. 1 we show the temperature distribution on the chain, calculated by both the eighth-order Runge-Kutta algorithm [Fig. 1(a)] and the velocity Verlet algorithm [Fig. 1(b)]. It is seen from Figs. 1(a) and 1(b) that the linear temperature distribution can be obtained with both algorithms, but there are still some small differences between them. The velocity Verlet algorithm is a very efficient one, by which a very smooth temperature distribution is obtained, but in this case,

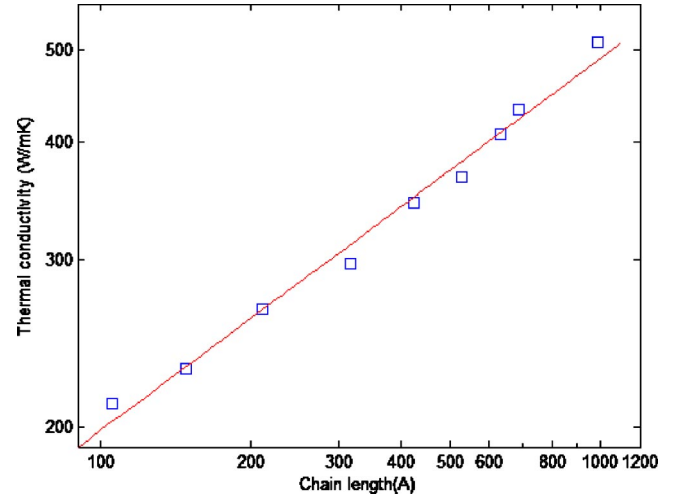


FIG. 4. The length dependence of thermal conductivity of the perfect 1D carbon chain model.

the Nosé-Hoover boundary condition on the left end of the chain with the higher temperature could not be well treated unless the chain is long enough, which may result from the sensitivity of this algorithm to the thermostat boundary condition. So, we will mainly use the Runge-Kutta algorithm in this work, and the velocity Verlet algorithm is used only as a reference.

The calculated thermal conductivities of CNWs with different lengths are shown in Fig. 2, in which two types of scales are shown, i.e., linear-logarithm and log-log scale. Here we should explain our definition of the cross section of CNW. The statistical radial distribution for the motion of wire atoms along the direction perpendicular to the tube axis is calculated, and the obtained result is given in Fig. 3, which can be fitted by $f(r) = A \cdot r \cdot \exp[-(r/b)^2]$, with r the radial distance to the tube axis. It is found that the parameter b is equal to 0.151 Å, so the final cross section area for the heat transport can be expressed as $4\pi b^2$.

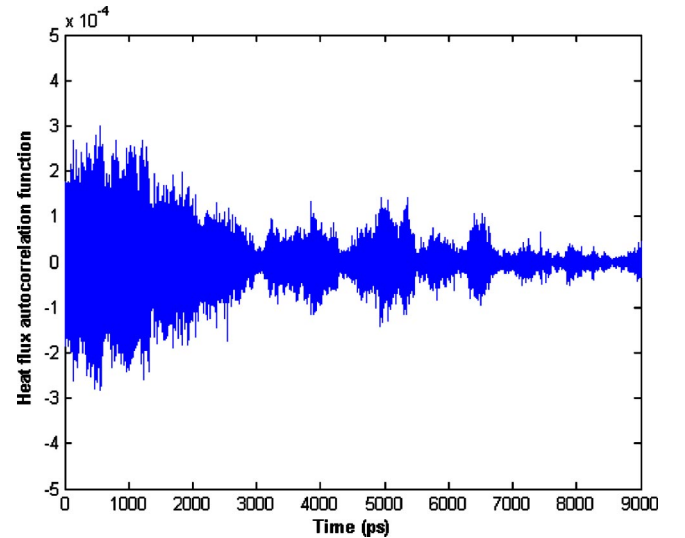


FIG. 5. Heat flux autocorrelation function of CNW with 64 particles.

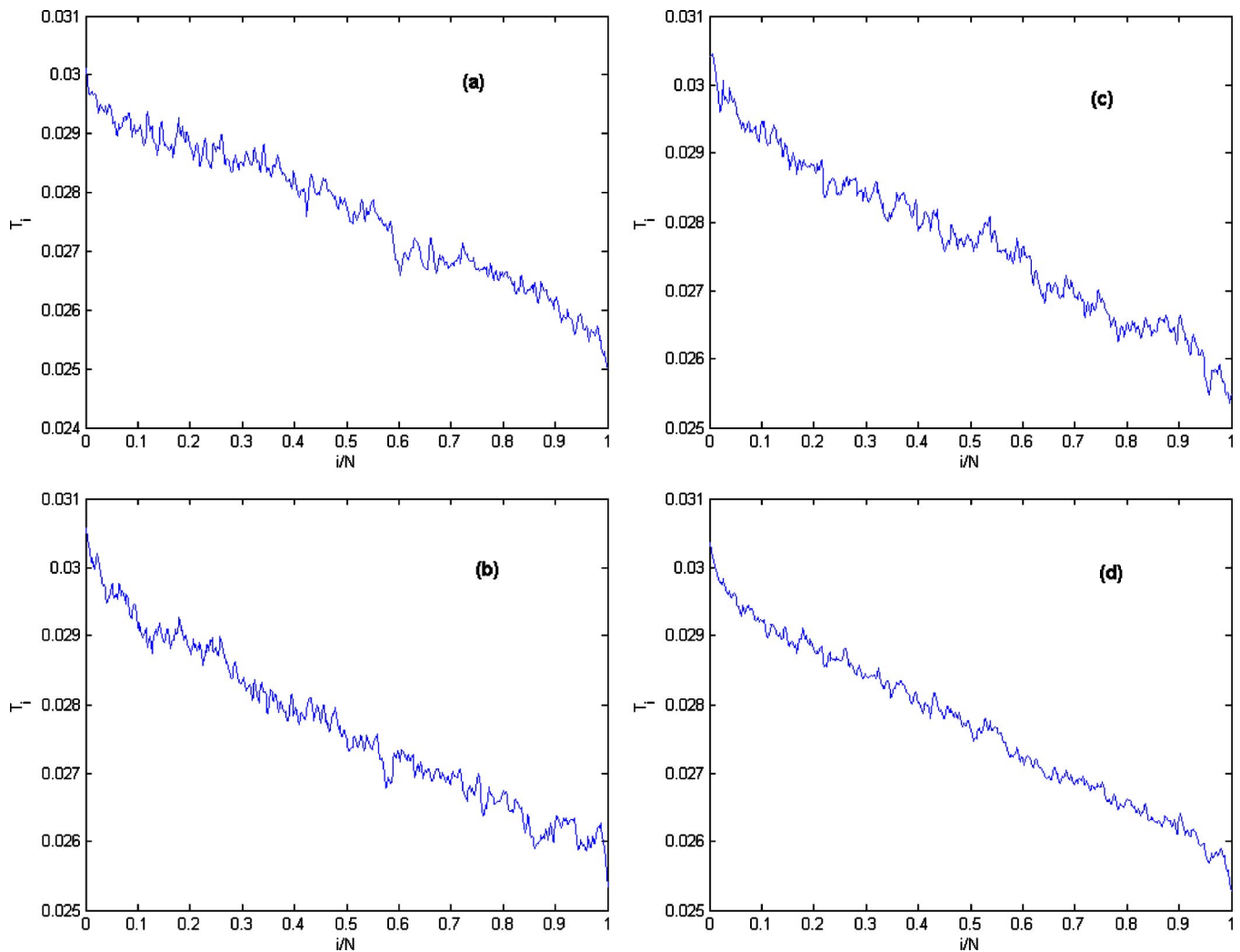


FIG. 6. The final temperature distributions of 512 particles evolved from different initial temperature profiles. (a) Low initial temperature. (b) Linear initial temperature. (c) High initial temperature. (d) Average of (a), (b), and (c).

Thus in this case, the thermal conductivity κ is obtained to be $142 \text{ W/mK} \sim 1323 \text{ W/mK}$, for the chain length L from 3 nm to 188 nm, which is very high. For comparison, it is interesting to list the κ value of the SWNTs with their lengths in the same range, which is about 10^2 W/mK (Ref. 20), or about $10^2\text{--}10^3 \text{ W/mK}$.^{21,22} So, the thermal conductivity of CNW is at least comparable to that of the SWNTs, not much smaller than that of the SWNT. For example, our calculated thermal conductivity of the CNW with 512 atoms is $1.2 \times 10^3 \text{ W/mK}$. But Zhang and Li²¹ got the corresponding thermal conductivity of nearly $1.6 \times 10^3 \text{ W/mK}$ for the (5, 5) SWNT having 384 layers with a length that is the same as that of the CNW, which is on the same order as our CNW result.

Now we would like to ask a question. Which type of divergence behavior does our CNW system follow? Power law or logarithmic law? From Fig. 2 it is clearly seen that when the system length is increased, the κ does *not* show completely a linear behavior in both of the linear-log and log-log scales, making it difficult to justify which type of divergent behavior, power or logarithmic law is suitable to the CNW. But, comparing Fig. 2(a) with Fig. 2(b), we could

conclude that the κ of the CNW prefers more the logarithmic divergence than the power law, at least for the middle part of the data from about 32 to 512 atoms. This demonstrates that the divergence behavior of the CNW is different from that of the SWNT, following the power law. Why logarithmic for the CNW? We think it is just the transverse motions of the carbon atoms on the CNW to relax its thermal conductance divergence and lead it to deviate from the 1D power law divergence.

In order to see more clearly the influence of the transverse motion of the CNW, we have also studied the thermal conductivity of perfect 1D carbon chains connected by the Tersoff-Brenner bond order potential, in which their transverse motions are not permitted. The initial equilibrium distance between their neighboring atoms is set to be 1.65 \AA , and their cross sections are determined as follows. As is well known, the cutoff distance in the Tersoff-Brenner bond order potential is about 2.0 \AA , which can be approximately considered as an interaction range between two nearby carbon chains. So, the cross section of a perfect 1D carbon chain can be roughly estimated to be about 3.14 \AA^2 . The length dependence of the thermal conductivity is shown in Fig. 4. It is

seen from Fig. 4 that the κ diverges with chain length, as $\kappa \propto L^\beta$, with $\beta \approx 0.39 \pm 0.02$, and its κ is about 212 W/m K–511 W/m K, which is comparable with the result of CNW.

A comparison between the thermal conductivities of both a 1D carbon chain and the quasi-1D CNW clearly show that it is indeed the transverse motions of the carbon atoms on the CNW that cause its logarithmic thermal conductance divergence. We should emphasize that in real systems, the divergence of thermal conductivity will not be as simple as that found in the theoretical models such as the FPU model, which probably rests with the aspect ratio of the system.

The heat flux autocorrelation function in the case of $N=64$ is also calculated and shown in Fig. 5, from which it is seen that after a very slow decay in about 9000 ps, the heat flux autocorrelation function decreases to a small value. A similar phenomenon has been observed by Yao *et al.*,²² which can be understood by the fact that after a long enough evolution, the final state has no relationship with the initial state.

Finally, we will check the validity of the ensemble average in this low dimensional system. First, we compare those evolutions starting from the different initial conditions. The obtained results are shown in Fig. 6. Here the low or high initial temperature means the initial temperature of every atom on the chain is set to the lower or higher boundary temperature, respectively. And the linear initial temperature means the initial temperature of every atom is chosen based upon a linear temperature distribution between the two boundaries. All the distributions are calculated after a time interval $\approx 2 \times 10^5$.

At first sight, the four figures in Fig. 6 seem to be the same. In fact there are only small differences between them, which means our numerical results are reasonable, being independent of the initial conditions. However, it is seen from Fig. 6 that Fig. 6(d) is the smoothest one, which means an average over the other three can give a more reliable result, just like averaging over a longer time interval. Thus, we can improve our calculation efficiency by the following method. Very different initial states are chosen first, from which the system evolves, and after a period of evolution time, an average over the different system evolutions starting from the different initial conditions can be made. This method can be considered as a high efficient parallel algorithm, by which the highest acceleration coefficient can be gained.

IV. CONCLUSION

In this paper, the heat conduction of a finite length carbon chain inserted into a (5, 5) SWNT has been studied by using the nonequilibrium molecular dynamics method, in which both longitudinal and transverse motions of the chain atoms are permitted. The interaction between chain atoms and nanotubes has been simulated by a continuous model for the nanotube. It is found that the heat conduction of CNW does not obey Fourier's law, and its thermal conductivity κ logarithmically diverges with CNW length L as $\kappa \sim \log(L)$.

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