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Heat flow choking in carbon nanotubes

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ABSTRACT

Based on Einstein's mass–energy relation, the equivalent mass of thermal energy or heat is identified and referred to as thermomass. Hence, heat conduction in carbon nanotubes (CNTs) can be regarded as the motion of the weighty phonon gas governed by its mass and momentum conservation equations. The momentum conservation equation of phonon gas is a damped wave equation, which is essentially the general heat conduction law since it reduces to Fourier's heat conduction law as the heat flux is not very high and the consequent inertial force of phonon gas is negligible. The ratio of the phonon gas velocity to the thermal sound speed (the propagation speed of thermal wave) can be defined as the thermal Mach number. For a CNT electrically heated by high-bias current flows, the phonon gas velocity increases along the heat flow direction, just like the gas flow in a converging nozzle. The heat flow in the CNT is governed by the electrode temperature until the thermal Mach numbers of phonon gas at the tube ends reach unity, and the further reduction of the electrode temperature has no effect on the heat flow in the CNT. Under this condition, the heat flow is said to be choked and temperature jumps will be observed at the tube ends. In this case the predicted temperature profile of the CNT based on Fourier's law is much lower than that based on the general heat conduction law. The thermal conductivity which is determined by the measured heat flux over the temperature gradient of the CNT will be underestimated, and this thermal conductivity is actually the apparent thermal conductivity. In addition, the heat flow choking should be avoided in engineering situations to prevent the thermal failure of materials.

1. Introduction

Fourier's law of heat conduction, describing the heat transfer behavior in materials subjected to a temperature difference has been proved valid by numerous experiments and widely used in a variety of engineering areas related to heat transfer, although it is only a phenomenological model. Because of the essence of heat diffusion, Fourier's law contradicts the principle of the microscopic reversibility in thermodynamics. Onsager once pointed out that [1] "We recognize that Fourier's law is only an approximate description of the process of conduction, neglecting the time needed for acceleration of the heat flow." In fact this time needed for acceleration of the heat flow is induced by thermal "inertia", which is understood as the lag effect of the gradually increased heat flux after the establishment of the temperature gradient like the other ubiquitous generalized fluxes and forces [2].

The effects of the thermal inertia should exist no matter whether the heat transfer state is unsteady or steady. For unsteady states, ignoring the thermal inertia leads to the unphysical conclusion of the infinite heat propagation speed in Fourier's law. In order to eliminate this anomaly, many theoretical models were developed. In 1958, Cattaneo [3], and subsequently Vernotte [4], Morse and Feshbach [5] proposed a damped wave model for heat conduction which is referred to as C–V model. In 1965, Kaliski [6] obtained a telegraph wave equation of temperature based on the dynamical generalization of Onsager's theory with the thermal inertia postulated. Tzou [7,8] proposed a dual-phase-lag model to cover the fundamental behaviors of diffusion, wave, phonon–electron interactions and pure phonon scattering. The phase lag of the heat flux captures the small-scale response in time, and the phase lag of the temperature gradient captures the small-scale response in space. Tang and Araki [9,10] obtained the analytical solutions of the C–V model and the dual-phase-lag model to investigate the non-Fourier heat conduction behaviors under the ultra-high heating speed conditions, and then gave the detailed discussions about the wave, wavelike and diffusive thermal responses of the metallic films subjected to the ultra-short pulsed lasers. Besides the theoretical models, some experimental results [11–13] have also indicated that the thermal wave phenomena with a finite propagation speed existed in cryogenic liquids or solids heated by ultra-short pulsed lasers.

Cao and Guo [14] proposed the equivalent mass of phonon gas based on Einstein's mass–energy relation which is referred to as thermomass. The momentum conservation equation of the phonon gas/thermomass, which actually is the general heat conduction

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Nomenclature

A	cross-sectional area (m^2)
c	light speed in vacuum (3.0×10^8 m/s)
C	specific heat (J/kg K)
C_h	thermal sound speed (m/s)
d	wall thickness (m)
D	diameter (m)
E_{D0}	thermal vibration energy (J)
f_h	resistant force (N)
K_D	apparent thermal conductivity (W/mK)
K_I	intrinsic thermal conductivity (W/mK)
L	length (m)
M_h	thermomass (kg)
Ma_h	thermal Mach number
P_h	thermomass pressure (Pa)
q	heat flux (W/m^2)
q_c	critical heat flux (W/m^2)
S	internal heat source (W/m^3)
t	time (s)
T	temperature (K)
T_0	electrode temperature (K)
u_h	drift velocity of phonon gas (m/s)
u_s	moving speed of internal heat source (m/s)
x	coordinate in axial direction (m)

Greek symbols

γ	Grüneisen constant
ρ	density (kg/m^3)
ρ_h	thermomass density (kg/m^3)
τ	characteristic time (s)

Subscript

h	thermomass

law, was established based on the Newtonian mechanics. When the inertial force can be ignored, the general heat conduction law will reduce to Fourier's law. Some existing experimental results can be well explained by the general heat conduction law. Pop et al. [15] measured the thermal conductivity of a single-walled carbon nanotube using an electrical self-heating method under high-bias current flows. The results showed that the average temperature over the nanotube deviated from that predicted by Fourier's law with a constant thermal conductivity. Deshpande et al. [16] measured the temperature profile along an electrically heated individual suspended carbon nanotube (CNT) using a spatially resolved Raman spectra method. The significant temperature jumps at the ends of the CNT were observed. These experimental results provide us some evidences for the existence of the thermal inertia in the steady heat conduction. This article intends to reveal the heat flow choking phenomena in CNTs under the ultra-high heat flux conditions based on the general heat conduction law.

2. Motion equations for phonon gas

Phonon is the energy quantum of the quantized lattice vibration energy, and the state of the thermal vibration energy of lattice can be characterized as a phonon gas consisting of a large number of randomly moving phonons [17]. Hence, as the smallest transfer unit of the lattice thermal energy, phonon is the main energy carrier in the heat conduction of dielectrics. The equivalent mass of phonon gas which is referred to as the thermomass, was derived from Einstein's mass–energy relation by Guo et al. [18] as

$$M_h = \frac{E_{D0}}{C^2}, \tag{1}$$

where M_h is the equivalent mass of phonon gas, $c = 3.0 \times 10^8$ m/s is the speed of light in vacuum and E_{D0} is the thermal vibration energy.

In addition, Guo et al. [18] established a state equation of the phonon gas in the dielectrics as

$$P_h = \gamma \rho_h C T = \frac{\gamma \rho}{c^2}(CT)^2, \tag{2}$$

where γ, C, T, ρ, P_h and ρ_h represent the Grüneisen constant, specific heat, temperature, density of the dielectrics, pressure and density of the phonon gas, respectively. Here, the density of the phonon gas is $\rho_h = \frac{\rho C T}{c^2}$. It is noted that Eq. (2) is very similar to the state equation of an ideal gas.

In fluid mechanics, one can obtain the mass and momentum conservation equations of the phonon gas as

$$\frac{\partial \rho_h}{\partial t} + \rho_h \frac{\partial u_h}{\partial x} + u_h \frac{\partial \rho_h}{\partial x} = \frac{S}{c^2}, \tag{3a}$$

$$\rho_h\left(\frac{\partial u_h}{\partial t} + u_h \frac{\partial u_h}{\partial x}\right) + u_h \frac{S}{c^2} + \frac{\partial P_h}{\partial x} + f_h = 0, \tag{3b}$$

where S is the internal heat source, $u_h = \frac{q}{\rho C T}$ is the drift velocity of the phonon gas. In one-dimensional steady states without internal heat sources, the momentum conservation equation (3b) can be simplified as [14]

$$\rho_h u_h \frac{du_h}{dx} + \frac{dP_h}{dx} + f_h = 0. \tag{4}$$

The three terms on the left-hand side of Eq. (4) are the inertia force, driving force and resistant force of the phonon gas, respectively. Furthermore, one can rewrite Eq. (4) as

$$K_I\left(1 - \frac{q^2}{2\gamma \rho^2 C^3 T^3}\right)\frac{dT}{dx} + q = 0, \tag{5a}$$

$$K_D \frac{dT}{dx} + q = 0, \tag{5b}$$

where K_I and K_D are the intrinsic and apparent thermal conductivities, and $K_D = K_I\left(1 - \frac{q^2}{2\gamma \rho^2 C^3 T^3}\right)$. The term $\frac{q^2}{2\gamma \rho^2 C^3 T^3}$ represents the dimensionless thermal inertia. Due to the effect of thermal inertia, the heat flux is no longer proportional to the temperature gradient. When the heat flux is not extremely high and the inertia force term can be ignored, Eq. (5a) will reduce to Fourier's law as

$$K_I \frac{dT}{dx} + q = 0, \tag{6}$$

where K_I is the intrinsic thermal conductivity.

3. Thermal wave

The following equation can be derived from Eqs. (3a) and (3b) for unsteady heat conduction without internal heat sources:

$$\tau\left(\frac{\partial q}{\partial t} + 2u_h \frac{\partial q}{\partial x} - u_h^2 \rho C \frac{\partial T}{\partial x}\right) + K_I \frac{\partial T}{\partial x} + q = 0, \tag{7}$$

where $\tau = \frac{K_I}{2\gamma \rho C^2 T}$ has a unit of time, corresponding to the relaxation time in C–V model. τ is called the characteristic time of thermomass which is usually in order of magnitude of 10^{-10} s. One can get the following damped wave equation with a constant τ as:

$$\rho\tau C\frac{\partial^2 T}{\partial t^2}+\rho C\frac{\partial T}{\partial t}=K_{\mathrm{I}}\left(1-\frac{\rho C\tau u_{\mathrm{h}}^2}{K_{\mathrm{I}}}\right)\frac{\partial^2 T}{\partial x^2}-\frac{K_{\mathrm{I}}u_{\mathrm{h}}}{\gamma CT}\frac{\partial^2 T}{\partial t\,\partial x}. \tag{8}$$

When $\frac{\rho C\tau u_{\mathrm{h}}^2}{K_{\mathrm{I}}} \ll 0031$, the thermal sound speed (propagation speed of the thermal disturbance) in the phonon gas can be expressed as

$$C_{\mathrm{h}}=\sqrt{\frac{K_{\mathrm{I}}}{\rho C\tau}}=\sqrt{2\gamma CT}. \tag{9}$$

It is noted that Eq. (9) is similar to the formula of the sound speed in ideal gas.

Tzou [19] investigated the thermal shock phenomena caused by an ultra-fast moving heat source in solids as the speed of the heat source exceeds the thermal sound speed. Experimental evidence has been found by studying the temperature distribution around a rapidly propagating crack tip [20]. Based on the thermal wave theory, a thermal Mach number has been brought forward as

$$Ma=\frac{u_{\mathrm{s}}}{C_{\mathrm{h}}}, \tag{10}$$

where u_{s} is the speed of the internal heat source, and C_{h} is the thermal sound speed.

Likewise, we may define the ratio of the drift velocity of the phonon gas to the thermal sound speed as the thermal Mach number

$$Ma_{\mathrm{h}}=\frac{u_{\mathrm{h}}}{C_{\mathrm{h}}}. \tag{11}$$

Then Eq. (6) can be rewritten as

$$K_{\mathrm{I}}(1-Ma_{\mathrm{h}}^2)\frac{dT}{dx}+q=0. \tag{12}$$

4. Heat flow choking in CNT

Fig. 1 shows an experimental schematic diagram of a single CNT suspended between the two electrodes with the same temperature T_0. The CNT is electrically heated by high-bias current flows. Assuming the CNT is evenly heated by the internal Joule heat, a parabolic temperature profile will exist along the CNT. The heat flows from the middle to the two ends of the CNT. The drift velocity of the phonon gas increases in the tube as the phonon gas density ρ_{h} decreases along the heat flow direction, just like the gas flow in a converging nozzle. The heat flux is governed by the electrode temperature until Ma_{h} reaches unity at the tube ends. In this case, the temperature and heat flux at the tube ends are called critical temperature and critical heat flux. According to Eq. (5a), the critical heat flux is $q_{\mathrm{c}}=\sqrt{2\gamma\rho^2C^3T_0^3}$. Further reduction of the electrode temperature will have no effect on the heat flow in CNT, and then the heat flow is said to be choked. Meanwhile the temperature jumps $\Delta T=\sqrt[3]{q^2/\left(2\gamma\rho^2C^3\right)}-T_0$ will be observed at the tube ends.

In order to investigate the heat flow choking phenomena quantitatively, we calculated the phonon gas drift velocity, the thermal Mach number and the temperature profiles of CNT with the following parameters: density $\rho = 1400\ \mathrm{kg/m^3}$ [21], specific heat $C = 500$ J/kg K [22], intrinsic thermal conductivity $K_{\mathrm{I}} = 3000$, 5000 W/mK, diameter $D = 1.8$ nm, length $L = 10\ \mu$m, Grüneisen constant $\gamma = 1$, electrode temperature $T_0 = 300$ K and heating power $S = 1.0\ \mu$W (the critical heat flux is $1.15 \times 10^{11}\ \mathrm{W/m^2}$, which corresponds to the heating power $S = 0.44\ \mu$W). The cross-sectional area is calculated as $A = \pi Dd$, in which the tube wall thickness $d = 0.34$ nm. A finite difference scheme is used to solve the governing equation (5a), and the nonlinear thermal inertia coefficient is updated every calculation step until the maximum relative error of the temperatures of the two steps is less than 10^{-6}.

The inset in Fig. 2 shows that the thermal Mach number increases with the rising heat flux and the falling local temperature along the heat flow direction. The drift velocity of the phonon gas increases from zero ($x = 0\ \mu$m) to more than 700 m/s which equals to the local thermal sound speed at the tube end ($x = 5\ \mu$m), i.e. $Ma_{\mathrm{h}}=\frac{u_{\mathrm{h}}}{C_{\mathrm{h}}}=1$, as shown in Fig. 2. The drift velocity and thermal Mach number are calculated with different intrinsic thermal conductivities. The higher K_{I} will result in higher drift velocity and lower thermal sound speed, but the temperature jumps at the tube ends remain the same.

Since the maximum heat flux of $2.60 \times 10^{11}\ \mathrm{W/m^2}$ under the simulation condition is much higher than the critical heat flux of $1.15 \times 10^{11}\ \mathrm{W/m^2}$, a significant temperature jump about 200 K occurs at the tube end as shown in Fig. 3. For comparison, the calculated temperature profile based on Fourier's law is also given in Fig. 3, which is much lower than that based on the general heat conduction law. The maximum temperatures of the general law and Fourier's law decrease as the intrinsic thermal conductivity increases, but the temperature difference from the two laws is slightly affected by the intrinsic thermal conductivity.

It can be seen in Fig. 4 that the calculated average temperature of the CNT based on Fourier's law is proportional to the heating power. However, there is a "turning point" in the average temperature curve predicted by the general heat conduction law, where the heat fluxes at the tube ends reach the critical ones and the heat flow begins to be choked. The average temperature is calculated as the integral of the CNT temperature divided by its length. The turn-

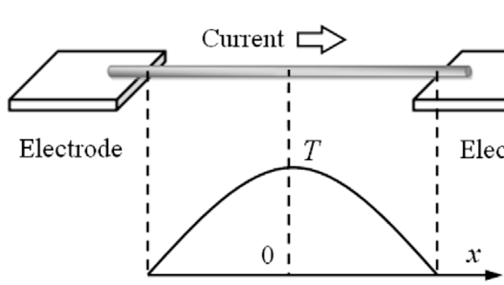

Fig. 1. An electrically heated CNT suspended between the two electrodes with a typical parabolic temperature profile.

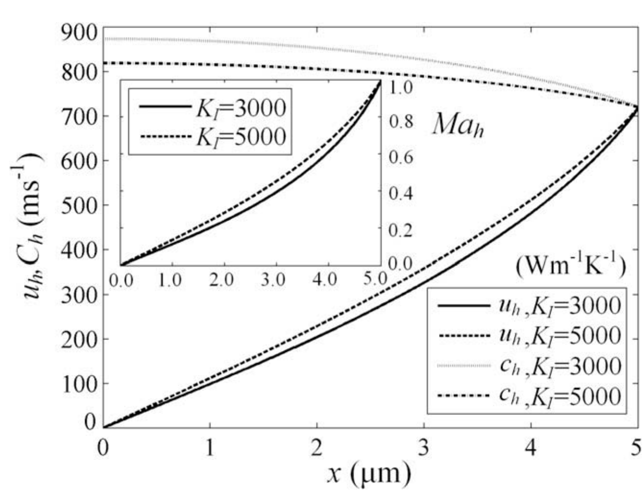

Fig. 2. The drift velocity and thermal sound speed in the CNT with different intrinsic thermal conductivities.

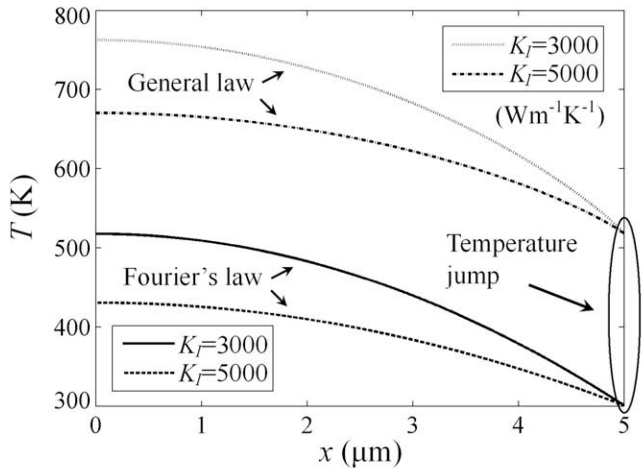

Fig. 3. Temperature profiles calculated based on the general law and Fourier's law.

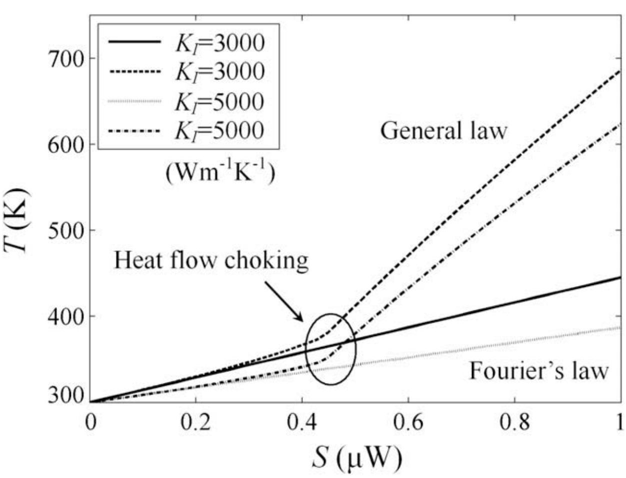

Fig. 4. Variation of the average temperatures of the nanotube versus the heating power.

ing point stays the same as the intrinsic thermal conductivity varies. Before this turning point, the difference between the tube average temperatures predicted by the general law and Fourier's law is quite small. Nevertheless, after the turning point, the heat flow choking induced temperature jumps at the tube ends lead to a much larger difference in the average temperatures predicted by the two different conduction laws. The heat flow choking should be taken into account under the ultra-high heat flux conditions, otherwise the temperature jumps at the tube ends could lead to the thermal failure of CNTs in practical applications.

The average temperatures over the nanotube at different ambient temperatures are calculated with the current–voltage experimental data from Ref. [13] using the Landauer–Büttiker approach [23,24] as shown in Fig. 5. It is seen that the temperature curves predicted by the general law (solid line in Fig. 5) agree with the experimental results well, while the temperature curves (dash dot line in Fig. 5) predicted by Fourier's law deviate from the experimental results. There are some differences between the predicted temperatures by the general law and the experimental data, which may come from the temperature dependence of the intrinsic thermal conductivity of the CNT. The general heat conduction law can be used to investigate the movement of phonon gas quantitatively which actually results in the heat flow in CNTs. The future nanodevices based on CNTs or other dielectric materials may benefit from the general heat conduction law.

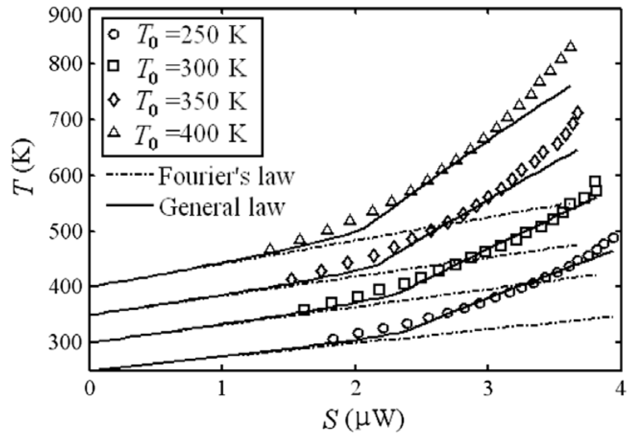

Fig. 5. Average temperatures based on the general law and Fourier's law using the existing experimental data from Ref. [13].

5. Conclusion remarks

1. Heat conduction in solid is due to the motion of phonon gas, whose equivalent mass is referred to as the thermomass. The momentum conservation equation for the phonon gas can be regarded as the general heat conduction law, which reduces to Fourier's heat conduction law if the heat flux is not very high and the consequent inertial force of the phonon gas is negligible.
2. The general heat conduction law is a damped wave equation with a wave speed which is referred to as the thermal sound speed in solid. Hence, the thermal Mach number $Ma_{\rm h}$ can be defined as the ratio of the drift velocity of the phonon gas to the thermal sound speed.
3. The phonon gas flow in a CNT resembles the gas flow in a converging nozzle. The heat flow is choked as the temperatures at the tube ends exceed the critical ones or the heat fluxes at the tube ends exceed the critical ones, since the thermal Mach numbers at the tube ends cannot be greater than unity. Meanwhile, the temperature jumps will occur at the tube ends under this situation.
4. In the case of the heat flow choking, if we set the intrinsic thermal conductivity $K_{\rm I}$ as a constant, the CNT temperature will be underestimated according to Fourier's law. Consequently, the thermal conductivity is also underestimated according to Fourier's law which is actually the apparent thermal conductivity $K_{\rm D}$. In addition, the heat flow choking should be avoided in practical applications, since it will give rise to the temperature jumps and the resulting large thermal stresses at the ends of CNTs may cause the thermal failure of materials.

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