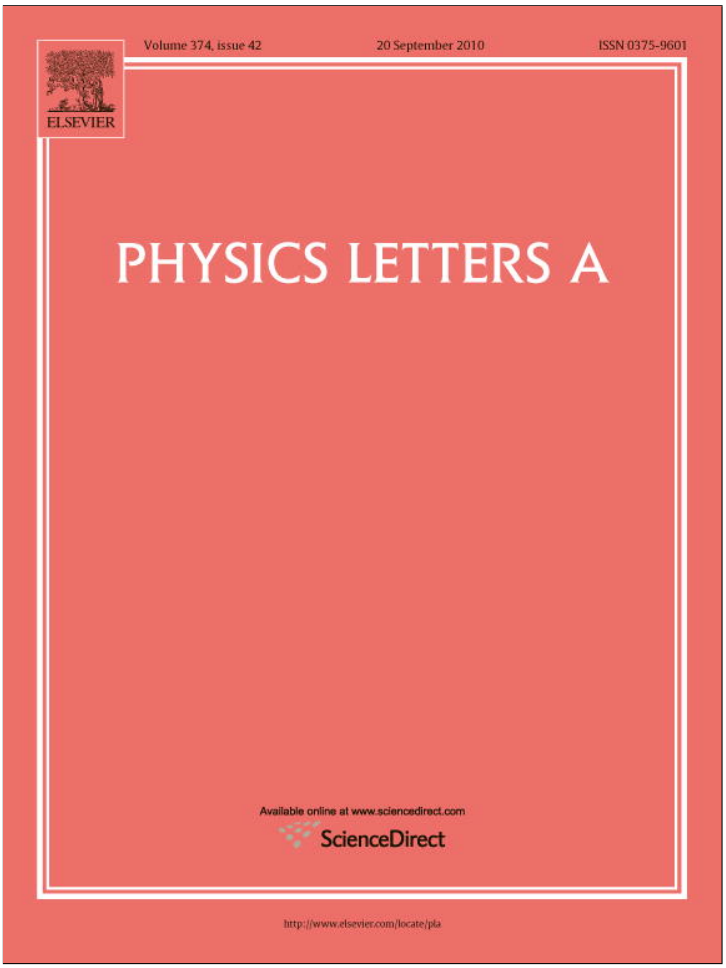

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Understanding of temperature and size dependences of effective thermal conductivity of nanotubes

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ABSTRACT

The anomalous thermal transport properties of nanotubes may lead to many important applications, but the mechanisms are still unclear. In this work, we present new governing equations for non-Fourier heat conduction in nanomaterials based on the concept of thermomass. The effective thermal conductivities of nanotubes are therefore predicted which agree very well with the available experimental data. Analysis suggests that the inertial effect of heat and the confined heat flux by nanostructured surfaces are two key mechanisms causing the anomalous temperature and size dependences of effective thermal conductivity of nanotubes.

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Nanotubes, as a typical one-dimensional nanostructured material, have received significant attention since discovery [1] because of their quite different effective properties from bulk materials [2,3], and various potential applications in electronic, optical and energy conversion devices [4]. In particular, a better understanding of thermal transport in nanotubes is crucial for new design and optimization of thermoelectric power generation [5–7] and thermal management of microelectronics [8]. Numerous experiments have reported that the effective thermal conductivity of nanotubes strongly depends on temperature and size (length and diameters) [9–13]. The Fourier's law has been proved violated in nanomaterials even when the phonon mean free path is much shorter than the characteristic length [14,15]. Therefore mesoscopic models based on the Boltzmann equation [16,17] and atomistic simulations [18–21] have been employed to analyze such anomalous varieties of thermal transport in nanotubes, which are often ascribed to the contribution of ballistic conduction. Unfortunately there is still no prediction with reasonable agreements with experimental data up to now based on these *first-principle* analyses [22]. In principle, the effective thermal properties need to be determined through the governing equations of thermal transport in nanostructures, which is one of typical non-Fourier conductions. We develop in this Letter a set of heat-conduction equations for the thermal transport in nanostructures based on the concept of thermomass, and demonstrate that the equation has good estimations of effective thermal conductivity of nanotubes compared with available experimental data. The analysis from this theory reveals the physical essence of the non-Fourier appearance of heat conduction in nanostructures.

Heat has been generally regarded as a process of energy transfer, instead of substance transport, since the famous Caloric-Dynamic argument in the 19th century [23]. However, theoretical and experimental studies since the early of the 20th century [24–26] have shown that heat owns "inertia". Recently Guo et al. [27–29] have proposed a thermomass concept, stating that heat owns a mass–energy duality, exhibiting energy-like features in conversion processes and mass-like characteristics in transfer processes. The mass of heat is determined by the mass–energy equivalence of Einstein, which therefore leads to the "inertia" and "weight" of heat in heat transfer. Because the mass of heat is extremely small (10^{-16} kg for 1 J heat), it has been seldom measured but may show its significance in ultrafast heating or ultrahigh-rate heat transfer processes. Distinguished from the traditional Caloric theory [23], the thermomass theory treats heat as a flux of substance with mass.

We assume that heat conduction can be treated as a thermomass gas flow in media driven by a thermal potential gradient. The thermomass gas is a gas-like collection of massive thermons, which is defined as quasi-particles of heat carriers. To concern the

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heat transfer behavior in a medium, we only focus on the macroscopic flow behavior of thermomass gas rather than the details of each single thermon, so that the thermomass gas is assumed as a continuum and its transport process can be described by the classical fluid mechanics and gas dynamics.

Similar to the real gas, the thermomass gas may have a complicated equation of state (EOS) if the thermon interactions are not negligible. However for most dielectric solids, the EOS of thermomass gas (phonon gas) falls into a simple form based on the Debye state equation [28–30]:

$$p_T = \gamma \rho_T C T, \tag{1}$$

where p_T is the thermomass gas pressure, γ the Grüneisen constant, ρ_T the density of thermomass gas defined as $\rho_T = \rho C T/c^2$ with ρ representing the solid density and c the speed of light, C is the solid specific heat capacity and T is the local thermodynamic equilibrium temperature.

The mass flow rate ($\dot{m}_T$) of the thermomass gas can be calculated by $\dot{m}_T = \mathbf{q}/c^2 = \rho_T \mathbf{u}_T$, which leads to the determination of the macroscopic drift velocity of thermomass gas

$$\mathbf{u}_T = \frac{\mathbf{q}}{\rho C T}. \tag{2}$$

Eq. (2) indicates that the macroscopic velocity of thermomass gas is identical to the transport velocity of heat flow, which is defined as the heat flux divided by the thermal energy per volume. Consider the thermomass gas flowing in a continuum medium driven by a thermomass pressure difference without internal heat sources. The governing equations for the thermomass gas transport can be derived very similarly to the classical gas dynamic theories,

$$\frac{\partial \rho_T}{\partial t} + \nabla \cdot (\rho_T \mathbf{u}_T) = 0, \tag{3}$$

$$\rho_T \frac{D\mathbf{u}_T}{Dt} + \nabla p_T + \mathbf{f}_T = 0, \tag{4}$$

where D/Dt denotes the total derivative, and $\mathbf{f}_T$ is the resistance force per unit volume when the thermomass gas flows through the material porous lattices. Eqs. (3) and (4) describe the transport of thermomass gas in continuum media with no other artificial assumptions. Substitutions of Eqs. (1) and (2) into Eqs. (3) and (4) yield the heat conduction equations in dielectric solids:

$$\frac{\partial(\rho C T)}{\partial t} + \nabla \cdot \mathbf{q} = 0, \tag{5}$$

$$\frac{\partial \mathbf{q}}{\partial t} - \frac{\mathbf{q}}{T}\frac{\partial T}{\partial t} + \frac{1}{\rho C T^2}\mathbf{q}(T \otimes \nabla \mathbf{q} - \mathbf{q} \otimes \nabla T) + 2\gamma \rho C^2 T \nabla T + \mathbf{f}_T c^2 = 0. \tag{6}$$

The first four terms of Eq. (6) are derived from the total derivative of velocity of the thermomass gas, which reflect the thermomass inertial effects, i.e. the inertia of heat. The fifth term is from the thermomass pressure driving effect, and the last term represents the resistance effect. Eqs. (5) and (6) govern the heat conduction process in solid. This set of partial differential equations (PDE) can get solved by available PDE solvers or by incorporated into the computational fluid dynamics software. The one-dimensional form of Eq. (6) is:

$$\frac{\partial \mathbf{q}}{\partial t} - \frac{\mathbf{q}}{T}\frac{\partial T}{\partial t} + \frac{\mathbf{q}}{\rho C T}\frac{\partial \mathbf{q}}{\partial x} - \frac{q^2}{\rho C T^2}\frac{\partial T}{\partial x} + 2\gamma \rho C^2 T \frac{\partial T}{\partial x} + \mathbf{f}_T c^2 = 0. \tag{7}$$

When the velocity of thermomass gas flow is not high, the resistance term, $\mathbf{f}_T$, can be determined by assuming a linear relationship between resistance and velocity,

$$\mathbf{f}_T = \frac{2\gamma \rho C^2 T}{c^2 k}\mathbf{q}, \tag{8}$$

where k is the local thermal conductivity. The one-dimensional general heat conduction equation under the linear resistance assumption is further expressed as

$$\tau_T \frac{\partial \mathbf{q}}{\partial t} - l\rho C \frac{\partial T}{\partial t} + l\frac{\partial \mathbf{q}}{\partial x} - bk\frac{\partial T}{\partial x} + k\frac{\partial T}{\partial x} + \mathbf{q} = 0, \tag{9}$$

where $\tau_T = k/2\gamma\rho C^2 T$ is the characteristic time, $l = qk/2\gamma \times C(\rho C T)^2 = u_T \tau_T$, is the characteristic length for heat propagation, and $b = q^2/2\gamma\rho^2 C^3 T^3$ is a dimensionless parameter charactering the compressibility of thermomass flow. Eq. (9) indicates clearly the wave nature of heat propagation even in conduction. It degenerates to the Fourier's law if all the thermomass inertial effects (the first four terms) are negligible, or to the same form as the Cattaneo equation [31] for transient heat conductions. However the physical significances of the characteristic time in Eq. (9) are different from the relaxation time in the Cattaneo equation. The characteristic time in Eq. (9) means the lagging time from the temperature gradient to the corresponding heat flux, while that in the Cattaneo equation is the relaxation time from the thermal non-equilibrium to the equilibrium state [31].

Based on the fluid dynamics of gas flow, Eq. (8) is only valid when the characteristic length of nanostructure, D, is much greater than the characteristic length of heat conduction, l. If D of the nanotube is comparable to l, the thermomass flow resistance will be enhanced by the gas–surface interaction. An exponential function is therefore presented based on the Boltzmann equation to reflect such an enhancement, similar to the high-Kn gas flows in three-dimensional microchannels [32], by

$$\mathbf{f}_T = \frac{2\gamma \rho C^2 T}{c^2 k}\frac{\mathbf{q}}{(1 - e^{-D/l})}. \tag{10}$$

Eq. (10) indicates that the resistance enhancement of thermomass by the gas–surface interaction actually leads to weakened heat flux in nanotubes. Hence the governing equation for the steady non-Fourier heat conduction in one-dimensional nanostructured dielectric materials is

$$\left(1 - \frac{q^2}{2\gamma\rho^2 C^3 T^3}\right)k\frac{\partial T}{\partial x} + \frac{\mathbf{q}}{(1 - e^{-D/l})} = 0, \tag{11}$$

where k is the intrinsic thermal conductivity. After solving Eq. (11) numerically at given boundary conditions, the effective thermal conductivity are therefore calculated by $k_{\text{eff}} = qL/\Delta T$, with L representing the length of nanotubes and ΔT the temperature difference between ends.

To validate the present heat conduction equations, we first applied Eq. (11) to predict the temperature dependences of effective thermal conductivity for two types of nanotubes, carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs), and compared the predictions with the experimental data. For simplification, we use constants for the intrusive properties of materials which are from the database elsewhere [33]. The wall thickness is used as the characteristic size calculated by $D = (d_o - d_i)/2$ with d_o representing the outer diameter and d_i the inner diameter of the nanotubes. Fig. 1a shows the effective thermal conductivities for two CNTs, with same material properties but different lengths and diameters, $L = 3.02$ μm and $D = 1.65$ nm for case 1, and $L = 1.95$ μm and $D = 1.55$ nm for case 2 [12]. The experimental data is from Ref. [12], which suggests ΔT at around 20 K. Fig. 1b compares the

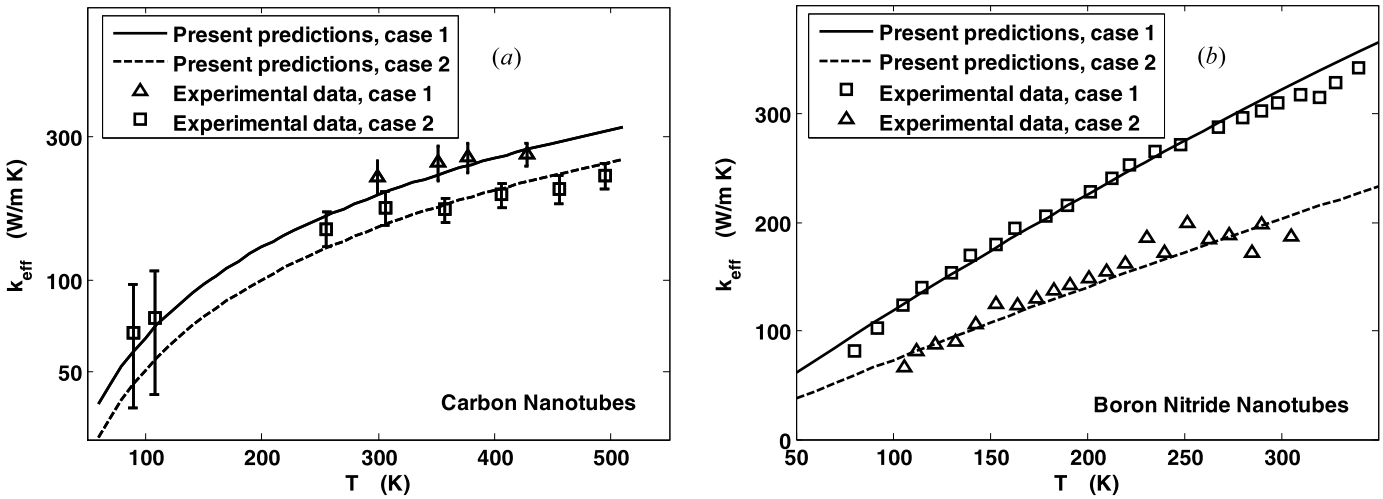

Fig. 1. Temperature dependences of effective thermal conductivities predicted by Eq. (11) compared with the experimental data. (a) Carbon nanotubes with $L = 3.02$ μm and $D = 1.65$ nm for case 1, and $L = 1.95$ μm and $D = 1.55$ nm for case 2 [12]. The intrinsic properties of carbon are $\rho = 2000$ kg/m^3, $C = 600$ J/kg K, $k = 2000$ W/m K, and $\gamma = 1$ [33]. (b) Boron nitride nanotubes with estimated $L = 5$ μm and $D = 10$ nm for both cases [10]. The properties of natural-abundance boron nitride are $k = 600$ J/kg K and $\rho = 2100$ kg/m^3, and those for isotopically pure boron nitride are $k = 740$ W/m K and $\rho = 3450$ kg/m^3 [33]. The other properties are $C = 108$ J/kg and $\gamma = 2$ [33].

thermal conductivities of two BNNTs, with same sizes ($L = 5$ μm and $D = 10$ nm) but different material properties. We employed the properties of cubic boron nitride (c-BN), $k = 740$ W/m K and $\rho = 3450$ kg/m^3, for case 1, and those of hexagonal boron nitride (h-BN), $k = 600$ W/m K and $\rho = 2100$ kg/m^3, for case 2 [33]. The experimental set suggests the BNNT testing length about 5 μm and ΔT around 2 K [10]. Both figures in Fig. 1 illustrate good agreements between the predictions and the experimental data. The results also indicate that the effective thermal conductivity of nanotubes is much smaller than the bulk property and decreases with decreasing temperature significantly. It needs to be mentioned that we use constant intrinsic properties, including density and thermal conductivities, etc., of bulk materials in this work. The present theoretical model reveals that the inertial effect of heat and the confined heat flux by nanostructured surfaces are two key mechanisms dominating the non-Fourier conduction and the effective thermal conductivity of nanotubes at low and moderate temperature. At high temperature, the temperature dependence of intrinsic thermal conductivity of bulk material may play an important role, which will be studied in our future work.

There are basically two viewpoints of size effects on the effective thermal conductivity of nanotubes. One is the effective thermal conductivity may increase infinitely with length for ideal one-dimensional nanomaterials [15], and the other one is it will converge to the bulk property as the length is large enough [5]. In our theory, Eq. (11) suggests that the thermomass inertial effect depends on L and the resistance enhancement effect is mainly related to D. Therefore we can study the size dependence of effective thermal conductivity of nanotubes by solving this equation. Fig. 2 shows the results for carbon nanotubes at $T = 300$ K and $\Delta T = 10$ K. Both L and D of CNT influence the effective thermal conductivity (k_{eff}) significantly. For a given D, a smaller L leads to high heat flux and thermomass inertial effect, and as a result k_{eff} decreases with a decreasing L. When the nanotube is long enough, the k_{eff} will approach to the intrinsic thermal conductivity (k). The effective thermal conductivity k_{eff} also decreases significantly as D gets smaller when L is fixed. However, k_{eff} may not approach to k despite a very large D if L is very small. For the current modeling parameters, the effective thermal conductivity of the nanotube is only 0.06 of the intrusive one when $L = 1$ μm and $D = 1$ nm.

In summary, we have established a new set of heat conduction equations by introducing the concept of thermomass. Heat is

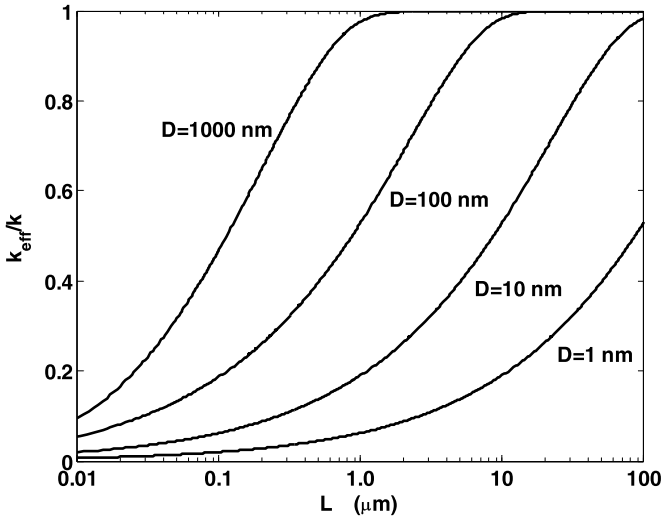

Fig. 2. Size dependence (D and L) of effective thermal conductivity of carbon nanotubes at $T = 300$ K and $\Delta T = 10$ K.

treated as flow of substance with mass, named as thermomass, when conducting in solid. We therefore can describe the heat conduction behavior by a set of PDEs through similar methodologies as the classical fluid mechanics. The simplified one-dimensional formula of these equations is a much better alternative to predict the effective thermal conductivity of nanomaterials. Computational results show good agreements with experimental data, and therefore suggest that the inertial effect of heat and the confined heat flux by nanostructured surfaces are two of dominant mechanisms to the anomalous temperature and size dependences of effective thermal conductivity of nanotubes. The present governing equations for heat conduction are readily incorporated into available PDE solvers and engineering software to deal with ultrafast or ultrahigh-rate heat conduction processes in complicated nanostructures.

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