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Non-Fourier heat conductions in nanomaterials

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We study the non-Fourier heat conductions in nanomaterials based on the thermomass theory. For the transient heat conduction in a one-dimensional nanomaterial with a low-temperature step at both ends, the temperature response predicted by the present model is consistent with those by the existing theoretical models for small temperature steps. However, if the step is large, the unphysical temperature distribution under zero predicted by the other models, when two low-temperature cooling waves meet, does not appear in the predictions by the present model. The steady-state non-Fourier heat conduction equation derived by the present model has been applied to predict the effective thermal conductivities of nanomaterials. The temperature and size dependences of effective thermal conductivities of nanofilms, nanotubes, and nanowires from the present predictions agree well with the available data from experiments in the literature and our molecular dynamics simulation results, which again proves the validity of the proposed heat conduction equations. The present analysis suggests that the inertial effect of high-rate heat and the interactions between heat and surface in confined nanostructures dominate the non-Fourier heat conduction in nanomaterials. © *2011 American Institute of Physics*. [doi:10.1063/1.3634078]

I. INTRODUCTION

The famous Fourier's law of heat conduction presents a linear relationship between the heat flux ($\mathbf{q}$) through a material and the gradient of temperature (T),[1] whose differential form is $\mathbf{q} = -k\nabla T$, where k is the material thermal conductivity. The Fourier's law is simple in mathematics and has been widely used even though it is only an empirical relationship. In principle, however, the Fourier's law leads to an unphysical infinite heat propagation speed within a continuum field for transient heat conduction processes because of its parabolic characteristics, which is in contradiction with the theory of relativity. To overcome this contradiction, a hyperbolic model with a time (t) dependent term has been proposed, which is named as the Cattaneo-Vernotte (CV) model,[2,3] to modify the Fourier's law for the transient heat conduction process, $\mathbf{q} + \tau_{CV}\partial\mathbf{q}/\partial t = -k\nabla T$, where τ_{CV} denotes the relaxation time. The introduced time-derivative term in the CV model describes a wave nature of heat propagation at a finite speed, which has been proved in both theory and experiments.[4–6] However, such Fourier-type or CV-type models still suffer from insufficiency of physical bases[7] and possible violation of thermodynamics laws.[8,9] Considering the non-equilibrium thermodynamics and the micro-macro interactions of heat carriers, a phenomenological hyperbolic two-step (HTS) model[5,10] and, consequently, an alternative dual-phase-lag (DPL) model[6,11–13] have been developed for the ultrafast heating process.

In fact, the Fourier's law has met great challenges in heat conductions at ultra-small scales, both temporal and spatial scales, where energy transport plays a very important role for material designs[14–17] and new power resources.[18,19] Several theoretical and experimental studies have reported that nanoscale heat conduction violates Fourier's law[20–27] and, therefore, the effective thermal properties derive significantly from those at normal scale.[23,25,28–33] The mechanisms for such violations and deviations can be divided into three distinguished levels: the quantum level, the particle level, and the continuum level. The violation and reconstruction of Fourier's law in a quantum system have been recently studied.[20,34,35] When the characteristic length of heat conduction is comparable to the mean free path of heat carriers, the particle effect leads heat conduction to a ballistic transport. The ballistic heat-conduction equations have been derived from the Boltzmann equation[36] and applied frequently to explain the deviations of nanoscale energy transport from the Fourier's law.[28,32,37,38] Meanwhile, most theories prove Fourier's law valid for the diffusive heat conductions.[34] However, recent experimental and numerical studies have reported breakdown of Fourier's law in nanomaterials, even if the phonon mean free path is much shorter than the characteristic length.[24,25] The mechanism may lie in the ultrahigh-rate heat flux from the extremely high temperature gradient or the super-low cross-section area. In these cases, the continuum assumption may be still valid, even if the characteristic length falls into nanoscale. Such phenomena are of great interests because of much more potential technical and engineering applications, but still lack fundamental understandings. Several theories have been developed to describe the heat transport in nanomaterials, including phonon dynamics,[36,39–41] phonon hydrodynamics,[42–45] thermomass theory,[46–48] and extended nonlocal theories.[49,50] Most recently, Jou's group even obtained predictions of effective

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thermal conductivities of nanomaterials comparable with the experimental data based on the phonon theories.[51,52]

In this article, we focus on the non-Fourier heat conduction in nanomaterials based on the thermomass theory under the continuum assumption. We aim at establishing general equations of heat conduction in continuum media that can fully describe the non-Fourier conduction in nanomaterials. We will demonstrate predictions of non-Fourier conduction behaviors and effective thermal conductivities of nanomaterials that agree well with available numerical and experimental data.

II. HEAT CONDUCTION EQUATIONS BASED ON THERMOMASS THEORY

A. Thermomass concept

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.[53] However, theoretical and experimental studies since the early 20th century[6,54,55] have shown that heat owns "inertia". Tolman[56] first found that heat has a weight, which was consequently supported by other researchers.[57,58] Recently Guo[46,59] has 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,[60] 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, the thermomass treats heat as a flux of substance with mass.

We assume that heat conductions can be treated as thermomass gas flows in media driven by a temperature gradient. The thermomass gas is a gas-like collection of massive thermons. Thermon is defined as a unit quasi-particle carrying thermal energy. For fluids, the thermons are supposed to be attached on the fundamental particles of the medium. For solids, the thermomass gas is the phonon gas for crystals, attached on the electron gas for pure metals, or just between both for most other solids. In the heat conduction process in solid, the thermomass gas flows through the vibrating lattices or molecules, just as a real gas flows through a porous medium. To concern the heat transfer behavior in medium, we focus on the macroscopic flow characteristics of the thermomass gas rather than the details of each single thermon, and therefore, we suppose the thermomass gas as a continuum, and its transport process can be described by the classical Newton's mechanics.

B. Governing equations

Similar to the real gas, the equation of state (EOS) is rather complicated for the thermomass gas, especially for the liquids. A general form of the EOS of the thermomass gas can be simply written as a function of $F(p_{\mathrm{T}}, \rho_{\mathrm{T}}, T, \xi) = 0$, where p_{T} is the thermomass pressure, ρ_{T} is the density of thermomass gas, T is the local temperature, and ξ denotes the effects of interaction between thermons. When the interaction between thermons is negligible, the EOS may have an explicit form. Guo has given the EOS for the thermomass gas in the ideal gas,[46] $p_{\mathrm{T}} = \kappa\rho_{\mathrm{T}}CT$, where κ denotes the ratio of specific heats of the ideal gas and C is the specific heat of solid. Guo *et al.*[59,61] also deduced the EOS of phonon gas in dielectric solid based on the Debye state equation, $p_{\mathrm{T}} = \gamma\rho_{\mathrm{T}}CT$, where γ is the Grüneisen constant. The density of thermomass gas is related to the medium density by[59,61] $\rho_{\mathrm{T}} = \rho CT/c^2$, where c is the speed of light ($\sim 3 \times 10^8$ m/s) and ρ is the density of medium. It is very interesting to find that the EOS of the phonon gas in crystal is in a very similar form as that for the ideal gas, except for the proportional parameter (κ or γ). Therefore, we propose here a general form of EOS for the ideal thermomass gas as

$$p_{\mathrm{T}} = \alpha\rho_{\mathrm{T}}CT, \tag{1}$$

with α as a proportional parameter, whose value differs for different states of media. For metals, when the static electric interaction effect between free electrons is negligible for the thermon transport, the EOS of Eq. (1) is also available. Eq. (1) indicates that a higher temperature may lead to a higher thermomass pressure, so that the thermomass gas will be driven to flow by a thermomass pressure difference.

To derive the governing equations of the thermomass gas flow, we need to define the macroscopic velocity of thermomass gas flow first. Based on the thermomass concept, the mass flow rate of the thermomass gas can be calculated by $\dot{m}_T = \mathbf{q}/c^2 = \rho_T \mathbf{u}_T$, which yields the determination of the macroscopic drift velocity as

$$\mathbf{u}_T = \frac{\mathbf{q}}{\rho CT} \tag{2}$$

Eq. (2) indicates that the macroscopic velocity of thermomass gas is identical to the transport velocity of heat flow, which is calculated by the heat flux divided by the thermal energy per volume. The value of this velocity is usually very small in our normal life.

Consider a heat conduction process under a temperature difference in a continuum material without internal heat sources. The physical picture in the thermomass theory is that the thermomass gas flows, driven by a thermomass pressure difference in a porous medium. The governing equations for the thermomass gas transport can be derived very similarly as the classical fluid mechanics if the local equilibrium and continuity are assumed. The continuity equation is

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

The momentum equation is

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

where D/Dt denotes the total derivative and $\mathbf{f}_T$ is the effective resistance force per unit volume. Here, we introduce an effective resistance term ($\mathbf{f}_T$) instead of the viscous term

($\mu_T \nabla^2 \mathbf{u}_T$) to avoid two troubles: (i) viscosity (μ_T) determination for complex materials; (ii) interaction effects between the thermomass gas and the lattice/solid molecules. Therefore, we only concern the overall velocity of the thermomass gas instead of the flow details inside, such as how the thermomass gas passes by the lattice/solid molecules.

C. General heat conduction equations in continuum

Equations (3) and (4) describe the transport of thermomass gas in continuum materials with no other artificial assumptions. Substitutions of Eqs. (1) and (2) into (3) and (4) yield a set of heat conduction equations:

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

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

The first four terms of Eq. (6) are derived from the total derivative of velocity of the thermomass gas, which reflects the inertial effects. The fifth term is from the thermomass pressure driving effect, and the last term represents the resistance effect. Each parameter of the equations has a clear physical meaning and can be determined by measurement or analysis. Such governing equations of heat conduction can also be derived from the phonon-Boltzmann equation, which will appear in our coming publications.

Comparing the present heat conduction equations with Fourier's law and assuming Eq. (6) is consistent with the Fourier's law once the inertial terms are negligible, one can determine the resistant force in the Fourier's law by

$$\mathbf{f}_T = \frac{2\alpha \rho C^2 T}{c^2 k}\mathbf{q}. \tag{7}$$

This process indicates that the new equations of heat conduction will degrade to the Fourier's law when all of the inertial effects are negligible or fall to a form similar to but not exactly the same as the CV model if only the special inertial effects are negligible. The Fourier's law essentially means the balance between the driving force and the resistant force in the thermomass fluid dynamics.

III. ONE-DIMENSIONAL HEAT CONDUCTION EQUATIONS IN NANOMATERIALS

The one-dimensional form of the present heat conduction equation, Eq. (6), is

$$\frac{\partial \mathbf{q}}{\partial t} - \frac{\mathbf{q}}{T}\frac{\partial T}{\partial t} + \frac{\mathbf{q}}{\rho C T}\frac{\partial \mathbf{q}}{\partial x} - \frac{q^2}{\rho C T^2}\frac{\partial T}{\partial x} + 2\alpha \rho C^2 T \frac{\partial T}{\partial x} + \mathbf{f}_T c^2 = 0. \tag{8}$$

Therefore, the one-dimensional general heat conduction equation under the linear resistance assumption is

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

where

$$\tau_T = \frac{k}{2\alpha \rho C^2 T} \tag{10}$$

is a characteristic time,

$$l = \frac{qk}{2\alpha C(\rho C T)^2} = u_T \tau_T \tag{11}$$

is a characteristic length for non-Fourier heat conduction, which differs from the thermon mean free path and characterizes the strength of non-Fourier effect, and

$$b = \frac{q^2}{2\alpha \rho^2 C^3 T^3} \tag{12}$$

is a dimensionless parameter. The non-Fourier effects must be considered when the time scale is comparable to the characteristic time (τ_T) or the spatial scale is comparable to the characteristic length (l).

It is noticed that Eq. (9) has an analogous form to the phonon gas hydrodynamics equation,[62] except for the resistance term. We use an effective resistance force instead of the viscous term in the phonon hydrodynamics equation. This simplification treatment avoids troubles from thermomass gas viscosity determination for complex materials and from exact description of interaction effects between the thermomass gas and the lattice/solid molecules of materials. Therefore, simple models can be incorporated to reflect geometric effects on the resistance of thermomass gas flows. For bulk materials or where the characteristic length (D) of nanostructure vertical to the heat flux direction is much greater than the characteristic length of heat conduction (l), Eq. (7) stands, which means the resistance is not relevant to the geometry of materials. However, when D of nanomaterials is comparable to l, the thermomass flow resistance is enhanced by interactions between thermomass gas and confined surfaces. Similar to the rarefied gas flow in microchannels,[63] an exponential function has been proposed based on the Boltzmann equation to reflect such an enhancement[64] by

$$\mathbf{f}_T = \frac{2\alpha \rho C^2 T}{c^2 k(1 - e^{-D/l})}\mathbf{q}, \tag{13}$$

where D could be the diameter or relevant length of the nanowires or nanotubes. Hence, the governing equations for the heat conduction in one-dimensional materials are

$$\frac{\partial \mathbf{q}}{\partial x} = 0, \tag{14}$$

$$\frac{\mathbf{q}}{\rho C T}\frac{\partial \mathbf{q}}{\partial x} - \frac{q^2}{\rho C T^2}\frac{\partial T}{\partial x} + 2\alpha \rho C^2 T \frac{\partial T}{\partial x} + \frac{2\alpha \rho C^2 T}{k(1 - e^{-D/l})}\mathbf{q} = 0, \tag{15}$$

which lead to

$$\left(1 - \frac{q^2}{2\alpha \rho^2 C^3 T^3}\right)k\frac{\partial T}{\partial x} + \frac{\mathbf{q}}{(1 - e^{-D/l})} = 0. \tag{16}$$

Eq. (16) governs the steady non-Fourier heat conduction, with k representing the intrinsic thermal conductivity. The apparent thermal conductivity is calculated by

$$k_{eff} = \frac{qL}{\Delta T}, \tag{17}$$

where L is the length/thickness of the material and ΔT is the temperature difference.

IV. NON-FOURIER HEAT CONDUCTIONS AND DISCUSSION

The present heat conduction equations have been applied to model non-Fourier conductions in one-dimensional nanomaterials. The one-dimensional form of the general heat conduction equations can be found in the Appendix. For the transient cases, we compare the present predictions with the CV model. For the steady-state non-Fourier heat conductions, we predict effective thermal conductivities of various nanomaterials by solving the equations and compare with the available data from experiments and molecular simulations.

A. Transient non-Fourier heat conductions

The ultrafast heating process has many important applications and has been studied by various models, as mentioned in the Introduction. The present heat conduction equation, Eq. (6) or its one-dimensional form Eq. (9), degrades to the very similar form as the CV model when the spatial inertial effects of heat are negligible. However, the physical significances of the characteristic times are different. The characteristic time in the CV model represents the relaxation time for approaching the thermodynamic equilibrium, while that in the thermomass model describes the lagging response from temperature gradient to heat flux. Their values may be very close for high conductivity media, such as metals, or deviate significantly (orders of magnitudes) for dielectrics. Thanks to their quite different physical significances, the two models have different predictions for the transient heat conduction behavior in nanomaterials.

Consider the heat conduction response to a temperature step at both ends for a one-dimensional metal material. The schematic diagram is shown in Fig. 1(a). The material is L in length and at an initial temperature, T_0. When time starts ($t > 0$), the temperature at the two ends switches to $T_w = T_1$ and then keeps constant. We solve the present general heat conduction equation, Eq. (9), and compare the results with the existing popular theoretical models, including the CV model,[2,3] the HTS model,[5,10] and the DPL model.[6,11–13] The equations can be consistently non-dimensionalized when $L = k/\rho C\sqrt{2CT}$. Figures 1(b)–1(e) compares the temperature distributions at different time points ($t^* = t/\tau = 0.3$ or 0.9) for different boundary conditions ($T_1{}^* = T_1/T_0 = 0.9$ or 0.3). Figures 1(b) and 1(c) show the results when the boundary temperature step is small ($\Delta T^* = 1 - T_1{}^* = 0.1$), and Figs. 1(d) and 1(e) show the comparisons for a high one ($\Delta T^* = 0.7$). The results indicate that, when the ΔT^* is small, the temperature distributions from the present model agree well with those from the other models, except for the fluctuating temperature distribution from the present model; otherwise, when the ΔT^* is high, the results from the present model deviate significantly from the other models. Especially, Fig. 1(e) shows that, when the two thermal waves from the boundaries meet, the previous models lead to an unphysical temperature distribution under zero, similarly reported in Refs. 9 and 65, whereas the present model results in a reasonable temperature distribution with the inertial effects of heat considered.

B. Steady-state non-Fourier conductions and effective thermal conductivity

The present heat conduction equation, Eq. (6), indicates that the inertial effect of heat is not negligible, even for steady-state cases when the heat flux is extremely high. Experiments and atomistic simulations have reported anomalous size (thickness[30] or length[25,32]) or temperature[16,28,29,31,33] dependence of effective thermal conductivity of nanomaterials, including nanofilms,[30,33] nanotubes,[17,29,31] and nanowires,[25,28] even if the characteristic size of the nanomaterial is larger than the mean free path of heat-carrier particles. The mechanism in such anomalous heat conductions has never been revealed, due to insufficiency of corresponding continuum theories. The present heat conduction equations provide a way to model the steady-state non-Fourier conduction behavior in nanomaterials and to predict the effective thermal conductivities. For heat conductions in one-dimensional nanomaterials, the governing equation, Eq. (16), suggests that the non-Fourier effect in steady-state heat conductions mainly results from the inertial effect of high-rate heat and the heat-surface interactions in nanostructures.

Figure 2 shows the predicted effective thermal conductivities of nanomaterials, including nanofilms, nanotubes, and nanowires, compared with the available data from experiments and molecular simulations. The predicted thermal conductivities of a gold thin film varying with temperature are compared with the experimental data by Zink *et al.*[33] in Fig. 2(a). The thickness of the film is 16.3 nm,[33] and the other properties of gold are from Refs. 66 and 67. We only compare data when the temperature is above the Debye temperature of gold, because the electrical interaction between electrons may not be negligible below the Debye temperature for metals that influence the equation of state of thermomass gas. The present predictions agree well with the experimental data. Figure 2(b) demonstrates the temperature dependences of effective thermal conductivities for two carbon nanotubes. For nanotubes, 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. The two carbon nanotubes have the same intrusive material properties ($\rho = 2000$ kg/m^3, $C = 600$ J/kg K, $k = 2000$ W/m K, and $\alpha = 1$[66]), but different lengths and diameters, which are $L = 3.02$ μm and $D = 1.65$ nm for case 1 and $L = 1.95$ μm and $D = 1.55$ nm for case 2.[17] The experimental data is from Ref. 17, which suggests ΔT at around 20 K. The predictions from the new heat conduction equation basically agree with the measurements, which again proves the validity of

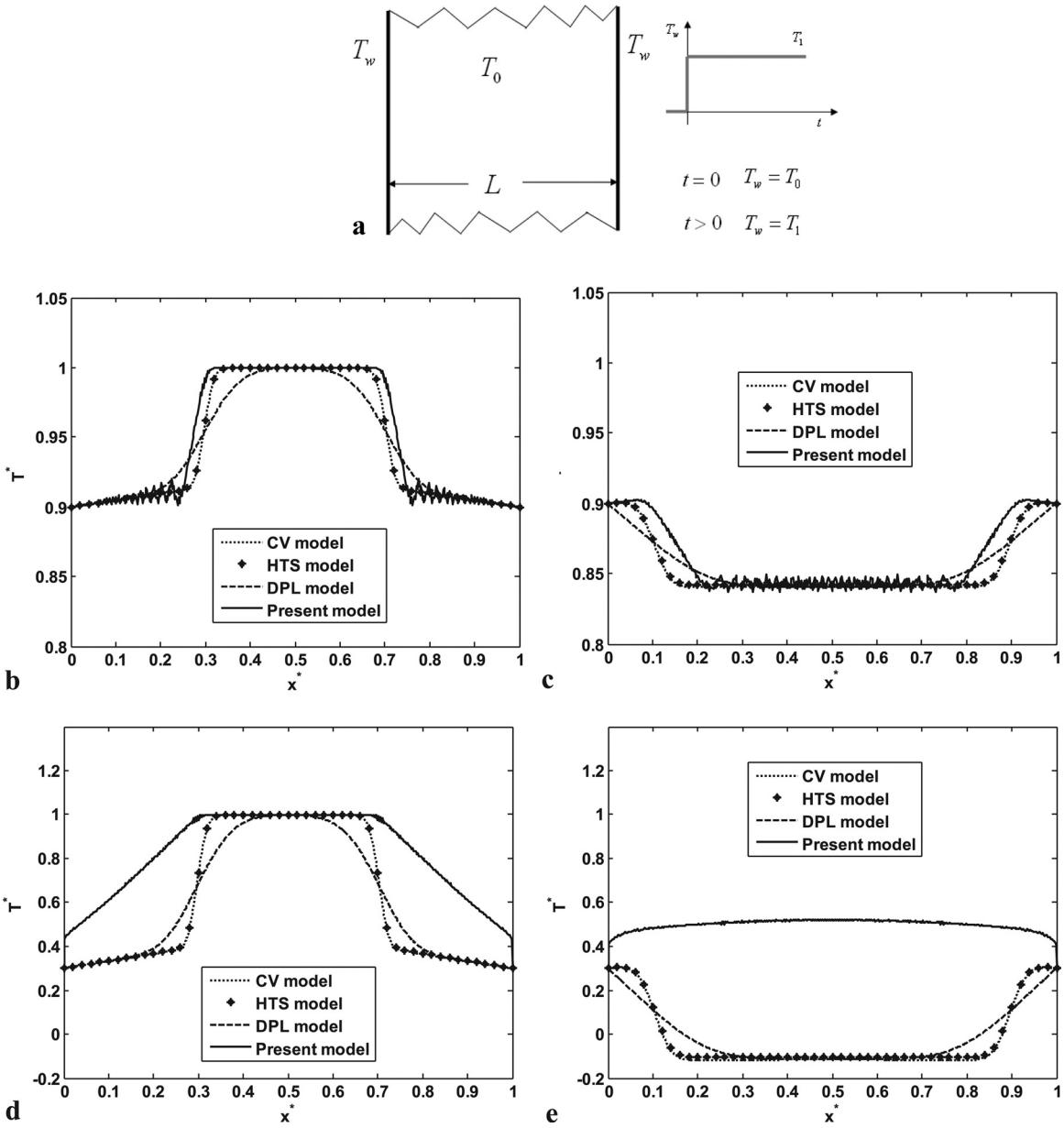
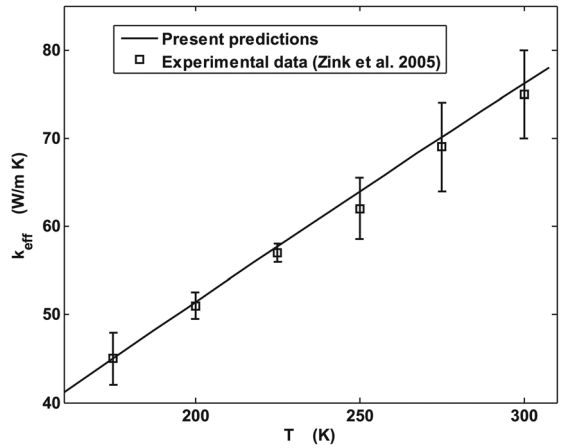


FIG. 1. Thermal wave propagation behavior for different boundary conditions. The non-dimensional parameters are defined as $x^* = x/L$, $T^* = T/T_0$, and $t^* = t/\tau$. (a) Schematic of temperature response to two-side temperature step; (b) $T_w^* = 0.9$, $t^* = 0.3$; (c) $T_w^* = 0.9$, $t^* = 0.9$; (d) $T_w^* = 0.3$, $t^* = 0.3$; (e) $T_w^* = 0.3$, $t^* = 0.9$.

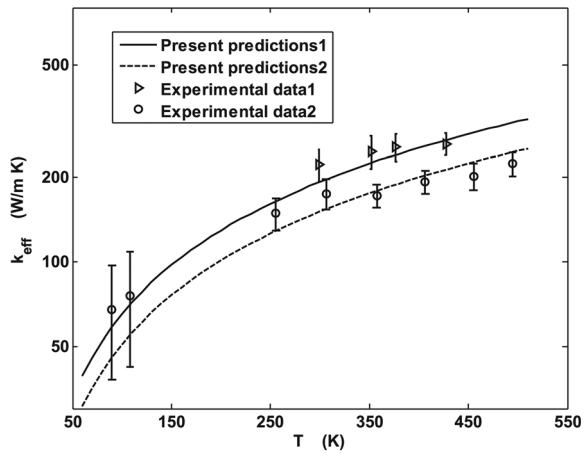
our model. Since the length dependence of effective thermal conductivities of nanowires has never been measured by experiments, we compare our predictions with the available data from molecular dynamics (MD) simulations in the literature. Figure 2(c) shows the effective thermal conductivity as a function of length for a nanowire with a characteristic width of $D = 1.22$ nm of the cross section, where the symbols are from the MD simulations by Yang *et al.*[25] The silicon properties used in the present model are $\rho = 2330$ kg/m^3, $k = 163$ W/m K, $C = 700$ J/kg K, and $\alpha = 1$.[66] The present predictions agree very well with the MD simulations when the aspect ratio (L/D) is high. For a low aspect ratio, the heat resistance may be enhanced, due to the end effect, and the predicted effective thermal conductivity should be reduced as a result. The relevant work will be studied in the future, which may lead to a better agreement in the entire range of aspect ratios.

V. CONCLUSIONS

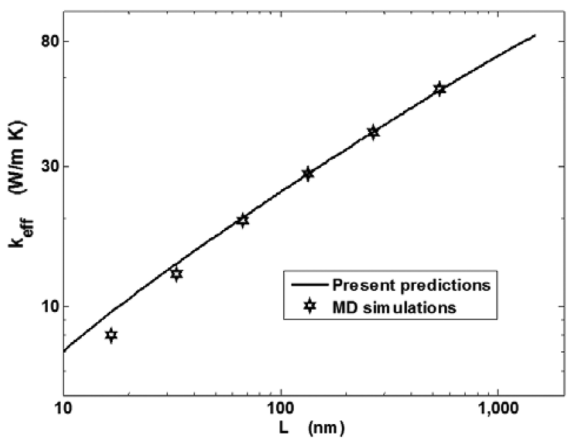
The non-Fourier heat conductions in nanomaterials have been studied using the proposed heat conduction equations based on the thermomass theory. We establish the general heat conduction equations, which treat heat as a substance with mass that can flow in materials driven by a temperature difference. The governing equations of thermomass gas flow therefore lead to a new relationship between heat flux and temperature field. The present heat conduction equation degrades to the Fourier's law, in case all the inertial effects of heat are negligible, and is compatible with the previous laws of thermodynamics. For the transient heat conduction in a one-dimensional nanomaterial with a step temperature at both ends, the temperature responses predicted by the present model are compared with those by popular existing theoretical models. Especially, the unphysical temperature



(a) Temperature dependence for gold thin film



(b) Temperature dependence for carbon nanotubes



(c) Length dependence for silicon nanowires

FIG. 2. The effective thermal conductivities of nanomaterials. (a) Temperature dependence of thermal conductivity for gold thin film. The thickness of film L = 16.3 nm [Ref. 33], the given temperature difference $\Delta T = 50$ K, and the properties of gold are: $\rho = 19.3 \times 10^3$ kg/m^3, k = 138 W/m K, C = 128 J/K [Ref. 66], $\gamma = 2.8$ [Ref. 67]. The symbols are the experimental data from Zink *et al*. [Ref. 33]. (b) Temperature dependence of thermal conductivity for 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 [Ref. 17]. The intrinsic properties of carbon are $\rho = 2000$ kg/m^3, C = 600 J/kg K, k = 2000 W/m K, and $\gamma = 1$ [Ref. 66]. The symbols are experimental data from Pettes and Shi [Ref. 17]. (c) Length dependence of thermal conductivity for silicon nanowires. The nanowires have a square cross-section of 1.22×1.22 nm^2. The given temperatures at the two ends are 330 K and 270 K. The symbols are data from MD simulations by Yang *et al*. [Ref. 25]. The material properties used in the present predictions are $\rho = 2330$ kg/m^3, k = 163 W/m K, C = 700 J/kg K, and $\alpha = 1$ [Ref. 66].

distribution under zero predicted by the other models, when two low-temperature cooling waves meet, does not appear in the predictions by the present model. The steady-state non-Fourier heat conduction has been modeled by the present general heat conduction equations, which have never been studied elsewhere, and the effective thermal conductivities of nanomaterials have therefore been predicted. The temperature and length dependences of effective thermal conductivities of nanofilms, nanotubes, and nanowires that resulted from the present predictions agree well with the available data from experiments in the literature and our MD simulation results, which prove the validity of the proposed heat conduction equations. The present analysis suggests that the inertial effect of high-rate heat and the heat-surface interactions in confined nanostructures dominate the non-Fourier heat conduction in nanomaterials.

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APPENDIX: COMPATIBILITY WITH PREVIOUS LAWS OF THERMODYNAMICS

The new heat conduction equations have to be compatible with the previous laws of thermodynamics. There are four well-recognized principles of thermodynamics up to now in the world. As follows, we will show that the present heat conduction equations based on the thermomass concept have good compatibility with the four laws of thermodynamics.

The *zeroth law of thermodynamics* states that, if two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other. In the thermomass gas model, the thermomass gas is driven by the thermomass pressure, as shown in Eq. (1), which is proportional to the square of temperature. Based on the fluid mechanics, if two gases can be statically equilibrium with a third, their pressure should be equilibrium. This means that their temperature should be identical for thermomass gases.

The first law of thermodynamics can be written as

$$\rho C \frac{\partial T}{\partial t} + \nabla \cdot \vec{q} = 0, \tag{A1}$$

which is exactly consistent with the continuity equation of the thermomass gas if each term is divided by c^2.

The *second law of thermodynamics* has a mathematical form as[68]

$$\nabla \cdot \left(\frac{\vec{q}}{T} \right) + \rho \frac{\partial s}{\partial t} = \sigma, \tag{A2}$$

where s is the specific entropy and σ denotes the entropy production. Alternatively, it can be written as[69]

$$\sigma = -\frac{1}{T^2} \cdot \nabla T, \tag{A3}$$

which needs to be proved always positive for isolated systems required by the second law. For the thermomass gas model, Eq. (A3) can be rewritten as

$$\sigma = \frac{c^4}{2\alpha\rho C^2 T^3} (\rho_T \vec{u}_T) \cdot (-\nabla p_T). \tag{A4}$$

For an isolated system, the thermomass gas can only be driven by the thermomass pressure gradient so that the momentum and the pressure gradient of fluid are always in opposite directions. Therefore, the entropy production in thermomass gas flow is always positive, which is consistent with the second law of thermodynamics.

An alternative statement of the *third law of thermodynamics* is that the absolute zero temperature can never be reached. Based on the special relativity, the speed of light can never be reached, i.e.,

$$u_T < c. \tag{A5}$$

Substitution of Eq. (2) into Eq. (A5) yields

$$T > \frac{q}{\rho C c} \geq 0, \tag{A6}$$

which proves the thermomass gas model compatible to the third law of thermodynamics.

[1]J. Fourier, Analytical Theory of Heat (Dover, New York, 1955).
[2]P. Vernotte, C. R. Acad. Sci. Hebd Seances Acad. Sci. D **246**(22), 3154 (1958).
[3]C. Cattaneo, C. R. Acad. Sci. Hebd Seances Acad. Sci. D **247**(4), 431 (1958).
[4]S. D. Brorson, J. G. Fujimoto, and E. P. Ippen, Phys. Rev. Lett. **59**(17), 1962 (1987).
[5]T. Q. Qiu and C.L. Tien, Int. J. Heat Mass Transfer **37**(17), 2789 (1994).
[6]D. Y. Tzou, J. Thermophys. Heat Transfer **9**(4), 686 (1995).
[7]D. D. Joseph and L. Preziosi, Rev. Mod. Phys. **61**(1), 41 (1989).
[8]M. B. Rubin, Int. J. Eng. Sci. **30**(11), 1665 (1992).
[9]C. Bai and A. S. Lavine, ASME Trans. J. Heat Transfer **117**(2), 256 (1995).
[10]T. Q. Qiu and C. L. Tien, ASME Trans. J. Heat Transfer **115**(4), 835 (1993).
[11]D. Y. Tzou, Int. J. Heat Mass Transfer **38**(17), 3231 (1995).
[12]D. Y. Tzou and K. S. Chiu, Int. J. Heat Mass Transfer **44**(9), 1725 (2001).
[13]D. Y. Tzou and Y. S. Zhang, Int. J. Eng. Sci. **33**(10), 1449 (1995).
[14]K. Schwab, E. A. Henriksen, J. M. Worlock, and M. L. Roukes, Nature **404**(6781), 974 (2000).
[15]S. K. Bux, R. G. Blair, P. K. Gogna, H. Lee, G. Chen, M. S. Dresselhaus, R. B. Kaner, and J. P. Fleurial, Adv. Funct. Mater. **19**(15), 2445 (2009).
[16]A. I. Hochbaum, R. K. Chen, R. D. Delgado, W. J. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. D. Yang, Nature **451**(7175), 163-U5 (2008).
[17]M. T. Pettes and L. Shi, Adv. Funct. Mater. **19**(24), 3918 (2009).
[18]A. Barreiro, R. Rurali, E. R. Hernandez, J. Moser, T. Pichler, L. Forro, and A. Bachtold, Science **320**(5877), 775 (2008).
[19]W. Choi, S. Hong, J. T. Abrahamson, J. H. Han, C. Song, N. Nair, S. Baik, and M. S. Strano, Nature Mater. **9**, 423 (2010).
[20]Y. Dubi and M. Di Ventra, Phys. Rev. B **79**(11), 115415 (2009).
[21]B. Li and J. Wang, Phys. Rev. Lett. **91**(4), 044301 (2003).
[22]M. Rashidi-Huyeh, S. Volz, and B. Palpant, Phys. Rev. B **78**(12), 125408 (2008).
[23]X.-P. Zhang and J.-D. Bao, Phys. Rev. E **73**(6), 061103 (2006).
[24]C. W. Chang, D. Okawa, H. Garcia, A. Majumdar, and A. Zettl, Phys. Rev. Lett. **101**(7), 075903 (2008).
[25]N. Yang, G. Zhang, and B. W. Li, Nanotoday **5**, 85 (2010).
[26]K. Hippalgaonkar, B. Huang, R. Chen, K. Sawyer, P. Ercius, and A. Majumdar, Nano Lett. **10**(11), 4341 (2010).
[27]J. W. Roh, K. Hippalgaonkar, J. H. Ham, R. Chen, M. Z. Li, P. Ercius, A. Majumdar, W. Kim, and W. Lee, ACS Nano **5**(5), 3954 (2011).
[28]R. Chen, A. I. Hochbaum, P. Murphy, J. Moore, P. D. Yang, and A. Majumdar, Phys. Rev. Lett. **101**(10), 105501 (2008).
[29]C. W. Chang, A. M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Y. Li, A. Majumdar, and A. Zettl, Phys. Rev. Lett. **97**(8), 085901 (2006).
[30]S. R. Choi, D. Kim, S. H. Choa, S. H. Lee, and J. K. Kim, Int. J. Thermophys. **27**(3), 896 (2006).
[31]M. Fujii, X. Zhang, H. Q. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe, and T. Shimizu, Phys. Rev. Lett. **95**(6), 065502 (2005).
[32]N. Mingo and D. A. Broido, Nano Lett. **5**(7), 1221 (2005).
[33]B. L. Zink, B. Revaz, J. J. Cherry, and F. Hellman, Rev. Sci. Instrum. **76**(2), 055902 (2005).
[34]Y. Dubi and M. Di Ventra, Phys. Rev. E **79**(4), 042101 (2009).
[35]L.-A. Wu and D. Segal, Phys. Rev. E **77**(6), 060101 (2008).
[36]G. Chen, Phys. Rev. Lett. **86**(11), 2297 (2001).
[37]M. E. Siemens, Q. Li, R. G. Yang, K. A. Nelson, E. H. Anderson, M. M. Murnane, and H. C. Kapteyn, Nature Mater. **9**(1), 26 (2010).
[38]H. Y. Chiu, V. V. Deshpande, H. W. C. Postma, C. N. Lau, C. Miko, L. Forro, and M. Bockrath, Phys. Rev. Lett. **95**(22), 226101 (2005).
[39]N. B. Li, P.Q. Tong, and B.W. Li, EPL **75**(1), 49 (2006).
[40]L. H. Liang and B. W. Li, Phys. Rev. B **73**(15), 153303 (2006).
[41]X. X. Ni, M. L. Leek, J. S. Wang, Y. P. Feng, and B. W. Li, Phys. Rev. B **83**(4), 045408 (2011).
[42]F. X. Alvarez, J. Alvarez-Quintana, D. Jou, and J. R. Viejo, J. Appl. Phys. **107**(8), 084303 (2010).
[43]F. X. Alvarez and D. Jou, Appl. Phys. Lett. **90**(8), 083109 (2007).
[44]F. X. Alvarez and D. Jou, J. Appl. Phys. **103**(9), 094321 (2008).
[45]F. X. Alvarez, D. Jou, and A. Sellitto, J. Appl. Phys. **105**(1), 014317 (2009).
[46]Z. Y. Guo, J. Eng. Thermophys. **27**(4), 631 (2006).
[47]Z. Y. Guo and B. Y. Cao, Acta Phys. Sin. **57**(7), 4273 (2008) (in Chinese).
[48]M. Wang, B. Y. Cao, and Z. Y. Guo, Fron. Heat Mass Transfer **1**, 013005 (2010).
[49]D. Y. Tzou, Int. J. Heat Mass Transfer 54(1-3), 475 (2011).
[50]D. Y. Tzou and Z. Y. Guo, Int. J. Therm. Sci. **49**(7), 1133 (2010).
[51]F. X. Alvarez, D. Jou, and A. Sellitto, ASME Trans. J. Heat Transfer **133**(2), 022402 (2011).
[52]J. Alvarez-Quintana, *et al.*, Int. J. Heat Mass Transfer **54**(9-10), 1959 (2011).
[53]E. Mendoza, Phys. Today, **14**(2), 32 (1961).
[54]W. Nernst, "Die theoretischen grundlagen des neuen wärmesatzes," Thermodynamical Papers of the Physico-Chemical Institute of the University of Berlin, edited by Halle W. Knapp (1918).
[55]L. Onsager, Phys. Rev. **37**(4), 405 (1931).
[56]R. C. Tolman, Phys. Rev. **35**(8), 0904 (1930).
[57]C. Eckart, Phys. Rev. **58**(10), 919 (1940).
[58]L. D. Landau and E. M. Lifshitz, Fluid Mechanics (Pergamon, London, 1959).
[59]Z. Y. Guo and Q. W. Hou, ASME Trans. J. Heat Transfer **132**(7), 072403 (2010).
[60]A. Einstein, H. A. Lorentz, H. Minkowski, and H. Weyl, The Principle of Relativity (Dover, New York, 1952).
[61]Z. Y. Guo, B. Y. Cao, H. Y. Zhu, and Q. G. Zhang, Acta Phys. Sin. **56**(6), 3306 (2007).
[62]V. A. Cimmelli, A. Sellitto, and D. Jou, Phys. Rev. B **82**(18), 184302 (2010).
[63]M. R. Wang and Z. X. Li, J. Eng. Thermophys. **25**(5), 840 (2004).
[64]M. Wang and Z.Y. Guo, Phys. Lett. A **374**(42), 4312 (2010).
[65]C. Korner and H. W. Bergmann, Appl. Phys. A **67**(4), 397 (1998).
[66]See http://en.wikipedia.org/wiki/ for information about the material properties.
[67]D. S. Sanditov, A. A. Mashanov, and M. D. Darmaev, Tech. Phys. **54**(9), 1398 (2009).
[68]E. R. G. Eckert and R. M. Drake, Analysis of Heat and Mass Transfer (McGraw-Hill, New York, 1972).
[69]A. Barletta and E. Zanchini, Int. J. Heat Mass Transfer **40**(5), 1007 (1997).