

Chapter 2

Thermomass Theory for Non-Fourier Heat Conduction

Abstract With the rapid development of femtosecond laser and micro/nano processing techniques, researchers face great challenges in thermal management and analysis under the extreme conditions. As the theoretical basis of heat transfer, Fourier's law may break down at femtosecond temporal scales and nanometer spatial scales. In 1822, Fourier stated in his book "Analytical theory of heat" that the mechanical principles could not be applied to study the thermal phenomenon, which used concepts that differed from other fields of study [1]. But the heat transport in metals can be analogous to the charge transport according to the Wiedemann–Franz (WF) law [2], it shows internal connection between thermal science and other branches of physics. Guo has developed a novel thermomass theory to analyze the heat conduction using Newtonian mechanics [3], creating a new path for thermal analysis under the extreme conditions.

2.1 Definition of Thermomass and the State Equation of Theron Gas

2.1.1 Definition of Thermomass and Theron Gas

Thermomass (TM) is defined based on Einstein's mass–energy relation [3, 4], it is actually the relativistic mass of thermal energy. The mass–energy relation is given as:

$$E = Mc^2 = \frac{M_0 c^2}{\sqrt{1 - v^2/c^2}} \quad (2.1)$$

where E , M , v , and c are the thermal energy, rest mass, velocity, and speed of light, respectively. M is the relativistic mass. When the velocity is far less than the speed of light, the Eq. (2.1) can be simplified as:

$$E = Mc^2 = \left(M_0 + \frac{1}{2} \frac{M_0 v^2}{c^2} + \dots \right) c^2 \approx (M_0 + M_k) c^2 \quad (2.2)$$

where M_k is the additive mass induced by kinetic energy. The TM M_h is the relativistic mass of internal energy U :

$$M_h = \frac{U}{c^2} \quad (2.3)$$

The total mass M_t can be written as the sum of the rest mass, relativistic mass of kinetic energy and TM:

$$M_t = M_0 + M_k + M_h \quad (2.4)$$

If $v = 0$, the total mass equals the sum of rest mass and TM. The density of TM is given as:

$$\rho_h = \frac{\rho C_v T}{c^2} \quad (2.5)$$

where ρ , C_v and T are the density, specific heat per volume, and temperature, respectively. The drift velocity of TM is given as:

$$u_h = \frac{q}{\rho C_v T} \quad (2.6)$$

where q is the heat flux.

It has to be emphasized that the concept of “thermomass” is different from the concept “caloric” in eighteenth century. Caloric was known as an imaginary, massless fluid that could be neither created nor destroyed. Lavoisier called caloric as the substance of heat, which was even regarded as a new type of “chemical element” [5]. Many thermal phenomena could be explained by the caloric theory, e.g., hot bodies had more caloric while cold ones had less, the flow of caloric from hotter to colder bodies formed heat flux. In the early nineteenth century, Carnot developed his famous principle of the Carnot cycle solely from the caloric viewpoint, and this principle still forms the basis of heat engine theory today [6]. But the caloric theory could not be used to explain the heat generation by friction, since there was nothing but motion communicated to the body that was heated. This problem was successfully resolved by a kinetic theory that explained heat as random movement of particles (atoms, molecules) of the substance. The kinetic theory then became the foundation of modern thermodynamics [7].

The TM is defined as the relativistic mass of thermal energy, unlike the imaginary fluid of caloric. The TM theory reveals a dual nature of heat, i.e., heat behaves like energy during its transformation into other forms of energy; heat behaves like mass during its transfer from hotter to colder bodies [3]. This is much like the wave particle duality of light. Actually, photons exhibit wave properties during their propagation, while they exhibit particle properties during their interaction with other particles, such as electrons and phonons. Einstein’s mass–energy relation demonstrates that mass and energy are two names for the same thing. Neither one can exist without

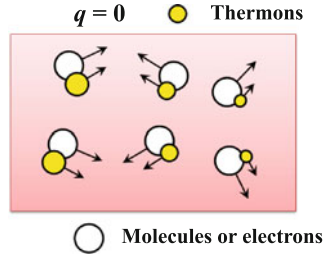


Fig. 2.1 Thermon gas at a uniform temperature

the other, they are two properties connected by a constant. The TM theory is the application example of mass–energy relation in thermal science.

In fact, the mass nature of heat has already been noticed by other researchers in the last century [8]. In 1931, Onsager [9] pointed out in his study of irreversible thermodynamics that Fourier’s law was just an approximation of the heat conduction process, ignoring the time needed for the acceleration of the heat flow. Thus Fourier’s law went against the principle of microreversibility in thermodynamics. The inertia or lagging effect between “force” and “flow” commonly exist in mechanics and electromagnetic. In thermal science, the TM is usually very small and the corresponding inertia effect is negligible, the heat conduction behaves like a diffusion process. In modern physics, the TM inertia may not be negligible under the ultra-fast laser heating and ultra-high heat flux conditions, leading to non-Fourier heat conduction. A Newtonian mechanics is used in the TM theory to establish a general heat conduction law to replace Fourier’s law under these extreme conditions. From a microscopic point of view, the TM of an individual particle (atoms, molecules, etc.) is defined as “Thermon,” all the thermons in a system form thermon gas. The heat conduction of solid is actually the direct flow of thermon gas under its pressure gradient [10].

Figure 2.1 shows a system filled with air molecules or electrons (white circles), the thermons attached to the particles are shown as the yellow circles. At a uniform temperature, all the particles are in the state of thermal equilibrium. The particles and thermons move randomly and the average velocity is zero, the heat flux is also zero.

Figure 2.2 shows a system that is hot on the left side and cold on the right side. Because the system is closed, the average velocity of rest mass particles is still zero. But the thermon gas moves from the hot side to the cold side driven by its pressure gradient, which is proportional to the temperature gradient. A heat flux is established accordingly. The density of thermon gas is $\rho_h = \rho C_v T / c^2$, its drift velocity is $u_h = q / (\rho C_v T)$. In order to analyze the motion of thermon gas theoretically, its state equations of different materials should be given first.

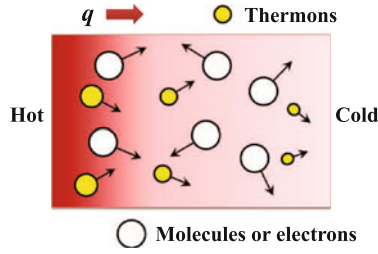


Fig. 2.2 Thermomass flow driven by a temperature gradient

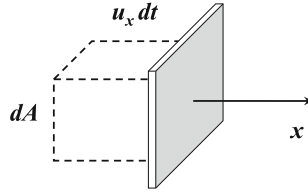


Fig. 2.3 Cube element for calculating the impulse

2.1.2 State Equation of Thermomass Gas in Ideal Gas

There are several assumptions for the thermomass gas in ideal gas: (1) the thermions are attached to the air molecules and satisfy the classical Maxwell–Boltzmann distribution function; (2) Newtonian mechanics is applicable for the thermomass gas. For a system filled with randomly moving particles, the impulse is given as:

$$i = mu_x \quad (2.7)$$

where m , i and u_x are the particle mass, impulse, and velocity in x direction, respectively. A cube at area element dA perpendicular to x direction has a volume of $u_x dt dA$ as shown in Fig. 2.3.

The total impulse of the particles in the cube element is:

$$dI = Ni = inu_x dt dA = nmu_x^2 dt dA \quad (2.8)$$

where $N = nu_x dt dA$ is the number of particles, n is the number density. According to the relation between impulse and pressure $dI = PdAdt$, the pressure can be obtained as:

$$P = nmu_x^2 \quad (2.9)$$

Given a consideration to the spatial symmetry in x , y , and z directions, the square of velocity is given as:

$$u_x^2 = u_y^2 = u_z^2 = \frac{1}{3} \bar{u}^2 \quad (2.10)$$

The pressure is then given as $P = \frac{1}{3}nm\bar{u}^2$ and the pressure of thermon gas is:

$$P_h = \frac{1}{3}nm_h\bar{u}^2 = \frac{1}{3}n\bar{u}^2\left(\frac{1}{2}\frac{m\bar{u}^2}{c^2}\right) = \frac{1}{6}\frac{nm\bar{u}^4}{c^2} \quad (2.11)$$

The classical Maxwell–Boltzmann distribution function is:

$$f_M(u) = 4\pi u^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mu^2}{2k_B T}\right) \quad (2.12)$$

where k_B is the Boltzmann constant.

$$\bar{u}^4 = \int_0^\infty u^4 f_M(u) du = 15 \left(\frac{k_B T}{m}\right)^2 \quad (2.13)$$

Substituting the Eq. (2.13) into the Eq. (2.11), one can get:

$$P_h = \frac{5}{3} \frac{(r-1)}{c^2} \rho C_v T^2 = \frac{5}{3} \frac{\rho C_v R T^2}{c^2} \quad (2.14)$$

where R is the ideal gas constant, r is the ratio of specific heat capacities at constant pressure and constant volume. The Eq. (2.14) shows that the thermon gas pressure is proportional to the square of temperature and the pressure gradient is the driven force of thermon gas.

2.1.3 State Equation of Thermon Gas in Dielectrics

In dielectrics, the phonons are the quantized quasiparticles of the vibration modes of elastic structures, they are the main energy carriers. The direct flow of phonon gas forms heat flux, the phonons can be seen as the thermons for dielectrics. The unit of driven force of thermon gas is Newton, this is quite different from the other generalized forces in irreversible thermodynamics [1, 11]. The Debye state equation for dielectrics is [4, 12]:

$$P = -\frac{\partial E}{\partial V} + \frac{\gamma \partial E_D}{V} \quad (2.15)$$

where E_D is the energy of lattice thermal vibration, γ is the Grüneisen parameter, describes the effect that changing temperature has on the size or dynamics of the lattice. When the temperature is higher than the Debye temperature, the lattice thermal vibration equation is:

$$P_0 V = \gamma E_{D0} = 3\gamma M_0 R T = \gamma M_0 C_v T \quad (2.16)$$

where E_D is the energy of the rest mass of lattices, the TM can be defined as $M_h = E_D/c^2$. Then the total energy of lattice thermal vibration is:

$$E_D = E_{D0} + E_h = (M_0 + M_h) C_v T \quad (2.17)$$

where E_h is the energy of the TM. So the state equation of thermon gas in dielectrics can be given as:

$$P_h V = \gamma M_h C_v T \quad (2.18)$$

$$P_h = \gamma \rho_h C_v T = \gamma \frac{\rho C_v T}{c^2} C_v T = \frac{\gamma \rho}{c^2} (C_v T)^2 \quad (2.19)$$

The pressure of thermon gas P_h is proportional to the square of temperature, the same as in ideal gases. For Si at room temperature, P_h is about 5×10^{-3} Pa.

2.1.4 State Equation of Thermon Gas in Metals

In metals, electrons are the main carriers for charge and heat, some basic assumptions of the classical Drude–Lorentz electron gas model are [13]: (1) the free electron gas in metals behaves like ideal gas; (2) the potential energy between electrons can be neglected and the Maxwell–Boltzmann distribution function is applicable; (3) a thermal equilibrium state is established between the electrons and lattices by collisions, an electron relaxation time τ_e represents the collision time interval.

The Drude–Lorentz model successfully predicts the Wiedemann–Franz (WF) law, but also results in some disagreement with the experimental observation. For example, the specific heat of electron gas can be calculated as: $C_{ve} = \left(\frac{\partial u}{\partial T}\right)_v = 1.5nk_B \approx 10^6 \text{ Jm}^{-3}\text{K}^{-1}$ according to the Drude–Lorentz model, this value is two orders of magnitudes larger than the experimental value. The interactions between electrons and ions should be taken into account to get a satisfied result. Later, Sommerfeld introduced a three-dimensional potential box with an infinite barrier at the surfaces into the classical free electron gas model, the potential energy was taken as a constant within the box. According to the Pauli exclusion principle, a Fermi–Dirac statistics was applied in the Sommerfeld model matching well with the experimental data. Here, the Sommerfeld model is used to establish the state equation of thermon gas.

The thermons in metals are attached to the electrons and the Fermi–Dirac distribution function should be used. The pressure of thermon gas is given as:

$$P_h = \frac{1}{3} n m_h u_h^2 \quad (2.20)$$

where the TM $m_h = \frac{\varepsilon}{c^2}$, ε is the internal energy including contributions of both electrons and lattices. $u_h = \sqrt{\frac{2\varepsilon}{m}}$ is the velocity of randomly moving particles, thus

$P_h = \frac{2}{3} \frac{n\epsilon^2}{c^2 m}$. At a thermal equilibrium state, the electron number between ϵ and $\epsilon + d\epsilon$ is:

$$dn = \sigma(\epsilon, T)d\epsilon = f(\epsilon, T)Z(\epsilon)d\epsilon \quad (2.21)$$

The Fermi–Dirac distribution function is:

$$f(\epsilon, T) = \frac{1}{\exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right) + 1} \quad (2.22)$$

The Sommerfeld electron state density function is:

$$Z(\epsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \quad (2.23)$$

where ϵ_F , k_B and $\hbar$ are the Fermi energy level, Boltzmann constant, and Planck constant, respectively. Further, the pressure of thermon gas is given as:

$$P_h = \frac{2}{3mc^2} \int_0^\infty \epsilon^2 f(\epsilon, T) Z(\epsilon) d\epsilon \quad (2.24)$$

The internal energy of metals is mainly contained in lattices. Due to the strong electron–lattice coupling, the most internal energy is carried by electrons rather than lattice vibration. m in the Eq. (2.24) is responsible for the internal energy, which is mainly decided by the lattices. At the high temperature limit, the energy of lattices is $E = 3k_B T$, thus:

$$nmC_{\max}T = 3nk_B T \quad (2.25)$$

The maximum mass $m_{\max}$ is:

$$m_{\max} = \frac{3k_B}{C_{\max}} \quad (2.26)$$

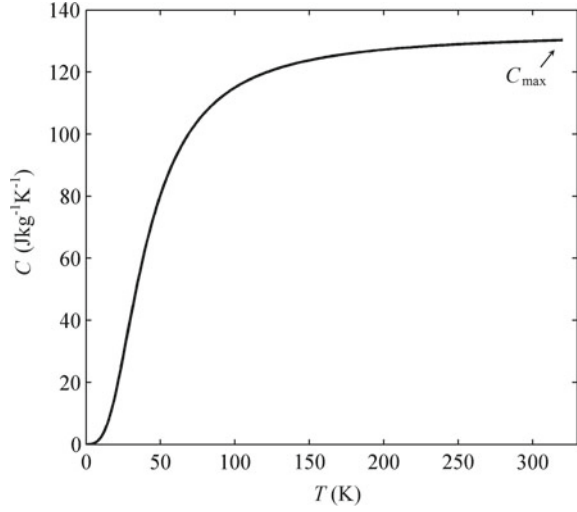
where $C_{\max}$ is the maximum value of specific heat of metals. The temperature-dependent specific heat of gold is given in the Fig. 2.4.

Combining the lattice dynamics theory [14] and existed experimental data [15, 16], an empirical formula of the specific heat of gold is given as:

$$C = \begin{cases} [T < 0.1\theta_D]: & \gamma T + \beta T^3 \\ [0.1\theta_D < T < 280 \text{ K}]: & 9nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \\ [280 \text{ K} < T]: & C_{\max} \end{cases} \quad (2.27)$$

where γ and β are the empirical parameters, θ is the Debye temperature. When the temperature is higher than 300 K, the specific heat C reaches $C_{\max}$. At low temperatures, the mass m is given as:

Fig. 2.4 Cube element for calculating the impulse



$$m = \frac{C m_{\max}}{C_{\max}} = \frac{\rho C_v}{3n k_B} \frac{3\rho k_B}{3n k_B} = \frac{\rho^2 C_v}{3n^2 k_B} \quad (2.28)$$

Substitute the Eq. (2.28) into the Eq. (2.24) and integrate, one can get:

$$\begin{aligned} P_h &\cong \frac{2}{3mc^2} \left[\frac{1}{7\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon_F^{7/2} + \frac{5}{24} (k_B T)^2 \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon_F^{3/2} \right] \\ &= C_{\varepsilon_F} + \frac{5}{36} \frac{k_B^2}{c^2 m} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon_F^{3/2} T^2 \end{aligned} \quad (2.29)$$

where the first term represents the contribution of electron energy to the TM pressure when $T = 0$ K; the second term represents the thermal contribution when $T > 0$ K. Because the temperature gradient makes the driven force for heat flux, the temperature-dependent part is written as P_{hT} :

$$P_{hT} = \frac{5}{36} \frac{k_B^2}{c^2 m} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon_F^{3/2} T^2 \quad (2.30)$$

where m_e is the electron mass. The Fermi energy level is $\varepsilon_F = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{\frac{2}{3}}$ and the Eq. (2.30) can be simplified as:

$$P_{hT} = \frac{5}{12} \frac{\pi^2 n k_B^2}{c^2 m} T^2 \quad (2.31)$$

Substituting the Eq. (2.28) into the Eq. (2.31), one can get:

$$P_{hT} = \frac{5}{12} \frac{\pi^2 n k_B^2}{c^2 m} T^2 = \frac{5}{4} \frac{\pi^2 n^3 k_B^3 T^2}{\rho^2 C_v c^2} \quad (2.32)$$

Compare the Eq. (2.32) with the Eqs. (2.14) and (2.19), one can find that the pressure of thermon gas is proportional to the square of temperature with different coefficients due to the different distribution functions.

2.1.5 Unified State Equation of Thermon Gas

According to the quantum mechanics, the elementary particles include fermions and bosons [17]. Fermions are the particles that have odd half-integer spins; bosons are the ones that have integer spins. Electrons, positrons, neutrons, and protons are all fermions; phonons and photons are bosons. The different elementary classes of phonons and electrons explain the different expressions of thermon gas in dielectrics and metals. But from a macroscopic point of view, these two systems have something in common: (1) thermons have no rest mass in both systems; (2) at a uniform temperature, the thermons are attached to the rest mass particles and its pressure is decided by the different distribution functions of particles; (3) the rest mass of particles keeps constant during collisions, but the TM changes; (4) the motion of thermon gas forms heat flux in both systems, the energy conservation is presented as the mass conservation of thermon gas. These common facts imply that the thermon gas behaves similarly in dielectrics and metals, the difference disappears at high temperature limit and a unified state equation exists.

At high temperatures, the mass m in the Eq. (2.31) is $3k_B/C_v$ and the pressure of thermon gas is:

$$P_{hT} = \frac{5}{36} \frac{\pi^2 n k_B C_v}{c^2} T^2 \quad (2.33)$$

The volume of thermon gas is:

$$V_h = \frac{m_{\max}}{\rho_h} = \frac{3k_B c^2}{\rho C_v^2 T} \quad (2.34)$$

The Grüneisen parameter is:

$$\gamma_h = \frac{P_{hT} V_h}{E} = \frac{P_{hT} V_h}{3k_B T} = \frac{5}{36} \frac{\pi^2 n k_B}{\rho C_v} \quad (2.35)$$

Substituting the Eq. (2.35) into the Eq. (2.33), one can get:

$$P_{hT} = \frac{\gamma_h \rho C_v^2 T^2}{c^2} \quad (2.36)$$

It is noted that the Eq. (2.36) is the same as the Eq. (2.19), it is the unified state equation of thermon gas. At low temperatures, the difference of statistics of different micro-particle systems play an important role and causes a deviation between state equations.

Another question is how to decide the Grüneisen parameter? For metals, the electrons are fermions, the particle number N , internal energy E and pressure P are given as [17]:

$$N = \frac{\sqrt{2}V}{\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{0.5} d\varepsilon}{1 + \exp[(\varepsilon - \mu) / (k_B T)]} \quad (2.37)$$

$$E = \frac{\sqrt{2}V}{\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1.5} d\varepsilon}{1 + \exp[(\varepsilon - \mu) / (k_B T)]} \quad (2.38)$$

$$PV = \frac{2\sqrt{2}V}{3\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1.5} d\varepsilon}{1 + \exp[(\varepsilon - \mu) / (k_B T)]} \quad (2.39)$$

For a fermion system, the relation between pressure and internal energy is $PV = 2/3E$, thus the Grüneisen parameter can be calculated as:

$$\gamma = \frac{PV}{E} = \frac{2}{3} \quad (2.40)$$

But the Eq. (2.40) is only valid under the high temperature, high pressure conditions, normally the Grüneisen parameter will differ from 2/3. Grüneisen parameter expresses the effect that changing temperature has on the pressure. The electrons and phonons are strongly coupled in metals, so the contribution of lattices to the Grüneisen parameter of electron gas should be also taken into consideration.

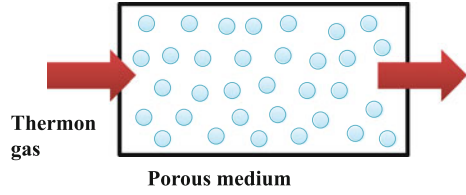
2.2 Non-Fourier Heat Conduction Equation in Unsteady States

2.2.1 Governing Equation of Motion of Thermon Gas

Newtonian mechanics can be applied to analyze the motion of thermon gas. One-dimensional conservation equations of mass and momentum for thermon gas are given as:

$$\frac{\partial \rho_h}{\partial t} + \frac{\partial}{\partial x} (\rho_h u_h) = \frac{S}{c^2} \quad (2.41)$$

Fig. 2.5 Schematic diagram of the flow of thermon gas in solid



$$\frac{\partial}{\partial t} (\rho_h u_h) + \frac{\partial}{\partial x} (u_h \cdot \rho_h u_h) + \frac{\partial P_h}{\partial x} + f_h = 0 \quad (2.42)$$

where S is the internal heat source, f_h is the resistance. The Eq. (2.41) is actually the energy conservation equation. Substituting the Eq. (2.41) into the Eq. (2.42), one can get:

$$\rho_h \left(\frac{\partial u_h}{\partial t} + u_h \frac{\partial u_h}{\partial x} \right) + \frac{u_h S}{c^2} + \frac{\partial P_h}{\partial x} + f_h = 0 \quad (2.43)$$

The flow of thermon gas in solid can be seen as the flow of compressible fluid in porous medium, where the molecules, atoms, or lattices in solid form the framework of the porous medium as shown in the Fig. 2.5.

Darcy's law can be applied to analyze the motion of thermon gas in solid [18]:

$$f_h = \beta u_h \quad (2.44)$$

where β is the coefficient of TM resistance that should be decided by the experiment. The resistance of thermon gas is proportional to its drift velocity.

2.2.2 General Heat Conduction Equation

A general heat conduction law can be established based on the TM theory from the first principles. This general law reveals the inertia effect of TM in heat conduction, just like the fluid inertia in hydrodynamics, vibration inertia in mechanical oscillators, electromagnetic inertia in electrodynamics, etc. The inertia effect roots in the fundamental physical principles that a physical object resists any change in its state of motion. The inertia occurs commonly between any kinds of generalized force and flow. The TM theory reveals that heat has a nature of mass, which is too small to be observed under the common conditions, but under the extreme conditions of ultra-fast heating or ultra-high heat flux, the inertia of TM will represent itself and cause detectable influences to the heat conduction process.

Combining the state equation of thermon gas, the momentum conservation equation of thermon gas 2.43 can be transformed into:

$$\tau_h \left(\frac{\partial q}{\partial t} - \frac{q}{T} \frac{\partial T}{\partial t} + \frac{q}{\rho C_v T} \frac{\partial q}{\partial x} - \frac{q^2}{\rho C_v T^2} \frac{\partial T}{\partial x} + \frac{q}{\rho C_v T} S \right) + \kappa \frac{\partial T}{\partial x} + q = 0 \quad (2.45)$$

where κ , S and τ_h are the thermal conductivity, internal heat source, and characteristic time of thermon gas, respectively. For dielectrics, τ_h can be expressed as:

$$\tau_h = \frac{\kappa}{2\gamma_h \rho C_v^2 T} \quad (2.46)$$

Kinetic theory gives a relaxation time for heat conduction process as [19]:

$$\tau = \frac{3\kappa}{\rho C_v v_s^2} = \frac{\kappa}{\rho C_v v_{tw}^2} \quad (2.47)$$

where v_s is the sound speed and v_{tw} is the propagation speed of thermal wave, $v_{tw} = (v_s/3)^{1/2}$. If one substitutes the classical expression of sound speed $v_s = [r(r-1)C_v T]^{1/2}$ into the Eq. (2.47), it gives:

$$\tau = \frac{3\kappa}{r(r-1)\rho C_v^2 T} \quad (2.48)$$

where r is the ratio of specific heats. Compare the Eqs. (2.48) and (2.46), one can find that the characteristic times of thermon gas and ideal gas have similar expressions, only differing in the constant coefficient. But the physical meanings of τ_h and τ are quite different, τ_h represents the time delay between the flow of thermon gas and its driven force, while τ represents the time needed to return to the equilibrium state from the nonequilibrium state.

Substituting the Eq. (2.41) into the Eq. (2.45), one can get:

$$\tau_h \left(\frac{\partial q}{\partial t} + 2u_h \frac{\partial q}{\partial x} - u_h^2 \rho C_v \frac{\partial T}{\partial x} \right) + \kappa \frac{\partial T}{\partial x} + q = 0 \quad (2.49)$$

The energy conservation equation holds as:

$$\frac{\partial q}{\partial x} = -\rho C_v \frac{\partial T}{\partial t} + S \quad (2.50)$$

To replace q in the Eq. (2.49) with T , the governing equation for temperature can be obtained as:

$$\rho C_v \tau_h \frac{\partial^2 T}{\partial t^2} + \rho C_v \frac{\partial T}{\partial t} = \left(\kappa - \tau_h \frac{q^2}{\rho C_v T^2} \right) \frac{\partial^2 T}{\partial x^2} - \frac{2\tau_h q}{T} \frac{\partial^2 T}{\partial t \partial x} + \tau_h \frac{\partial S}{\partial t} + \frac{2\tau_h q}{\rho C_v T} \frac{\partial S}{\partial x} + S \quad (2.51)$$

The Eq. (2.51) is the general heat conduction equation (law). Obviously, it is a damped wave equation for temperature, the first term on the left side of the equal sign is caused by the temporal inertia of TM, the first two terms on the right side of the

equal sign are caused by the spatial inertia of TM. If $\tau_h = 0$, the general equation 2.51 will reduce to Fourier's heat diffusion equation. In other words, the non-Fourier heat conduction behavior is the consequence of TM inertia. In unsteady states, the general heat conduction equation can be used to predict the propagation of thermal wave, while Fourier's equation results in a paradox of infinite propagation speed of thermal disturbance. Furthermore, the general heat conduction law predicts that the non-Fourier heat conduction phenomenon exists in steady states for the first time.

2.2.3 Two-Step Thermomass Model for Metals

When the metals are heated by ultra-short pulsed lasers, the heat conduction process can be divided into two steps [20]: (1) the electrons absorb the laser energy and then transfer the energy to the lattices by electron–phonon coupling; (2) after reaching the equilibrium temperature of electron–phonon system, the energy of lattices is dissipated by heat diffusion. The first step happens within 10 ps and the thermal equilibrium between electrons and lattices can be established around tens of picoseconds. Take this two-step model into consideration, a two-step TM model (TSTM) has been developed. Several assumptions should be satisfied for TSTM: (1) the state equations of thermon gas in dielectrics and metals are applicable for lattice and electron systems, respectively; (2) ignore the scattering effect at defects and grain boundaries of the metals; (3) the electron–phonon collisions are presented by an electron–phonon coupling factor G .

For electron system, the mass and momentum conservation equations are listed as:

$$\frac{\partial \rho_h}{\partial t} + \rho_h \frac{\partial u_h}{\partial x} + u_h \frac{\partial \rho_h}{\partial x} = \frac{S - G(T_e - T_l)}{c^2} \quad (2.52)$$

$$\rho_h \left(\frac{\partial u_h}{\partial t} + u_h \frac{\partial u_h}{\partial x} \right) + \frac{u_h}{c^2} [S - G(T_e - T_l)] + \frac{\partial P_h}{\partial x} + f_h = 0 \quad (2.53)$$

where T_e, T_l are the electron temperature and lattice temperature, respectively. When the heat flux is not very high, the Eq.(2.53) can be transformed into a governing equation of T_e :

$$\begin{aligned} \tau_e \rho_e C_e \frac{\partial^2 T_e}{\partial t^2} + \rho_e C_e \frac{\partial T_e}{\partial t} = \kappa_e \left(1 - \frac{\rho_e C_e \tau_e u_h^2}{\kappa_e} \right) \frac{\partial^2 T_e}{\partial x^2} - 2\tau_e u_h \rho_e C_e \frac{\partial^2 T_e}{\partial t \partial x} + \\ \left\{ S - G(T_e - T_l) + \tau_e \frac{\partial}{\partial t} [S - G(T_e - T_l)] + 2\tau_e u_h \frac{\partial}{\partial x} [S - G(T_e - T_l)] \right\} \end{aligned} \quad (2.54)$$

where ρ_e, C_e and κ_e are the density, specific heat and thermal conductivity of electrons, $\tau_e = \frac{2\rho_e^2 C_e \kappa_e}{5\pi^2 n^3 k_B^3 T}$ is the characteristic time of electrons.

For lattice system, the mass and momentum conservation equations are listed as:

$$\frac{\partial \rho_h}{\partial t} + \rho_h \frac{\partial u_h}{\partial x} + u_h \frac{\partial \rho_h}{\partial x} = \frac{G(T_e - T_l)}{c^2} \quad (2.55)$$

$$\rho_h \left(\frac{\partial u_h}{\partial t} + u_h \frac{\partial u_h}{\partial x} \right) + \frac{u_h}{c^2} [G(T_e - T_l)] + \frac{\partial P_h}{\partial x} + f_h = 0 \quad (2.56)$$

The governing equation of T_l is given as:

$$\begin{aligned} \tau_l \rho_l C_l \frac{\partial^2 T_l}{\partial t^2} + \rho_l C_l \frac{\partial T_l}{\partial t} = \kappa_l \left(1 - \frac{\rho_l C_l \tau_l u_h^2}{\kappa_l} \right) \frac{\partial^2 T_l}{\partial x^2} - 2\tau_l u_h \rho_l C_l \frac{\partial^2 T_l}{\partial t \partial x} + \\ \left\{ G(T_e - T_l) + \tau_l \frac{\partial}{\partial t} [G(T_e - T_l)] + 2\tau_l u_h \frac{\partial}{\partial x} [G(T_e - T_l)] \right\} \end{aligned} \quad (2.57)$$

where ρ_l , C_l and κ_l are the density, specific heat, and thermal conductivity of lattice, $\tau_l = \frac{\kappa_l}{2\gamma \rho_l C_l^2 T}$ is the characteristic time of lattice.

It is noted that the Eqs. (2.54) and (2.57) are both damped wave equations, where the damping terms are decided by different characteristic times. τ_e is about 10^{-15} s, much shorter than τ_l of 10^{-12} s, thus the thermalization process of electrons happens very fast while T_l is almost a constant. The thermal wave propagation in metals can be quantitatively studied using the Eqs. (2.54) and (2.57), if the characteristic times equal zero, these equations will reduce to heat diffusion equations.

2.2.4 Numerical Simulation Examples

Some numerical simulation examples of TSTM, C-V model, hyperbolic two-step (HTS) model, parabolic two-step (PTS) model, and dual-phase lag (DPL) model are given for comparison. All these models are solved using a finite-difference scheme in double precision. The material properties of Au film used in calculation are: $\kappa = 315 \text{ Wm}^{-1} \text{ K}^{-1}$, $\rho_l C_l = 2.5 \times 10^6 \text{ Jm}^{-3} \text{ K}^{-1}$, $G = 2.6 \times 10^{16} \text{ Wm}^{-3} \text{ K}^{-1}$, $C_e = 70T_e \text{ Jm}^{-3} \text{ K}^{-1}$. The numerical results are shown in the Figs. 2.6 and 2.7.

The PTS model has a parabolic equation, so no temperature fluctuation can be observed in the calculated temperature curve. The other four models have hyperbolic wave equations, which are capable to predict the propagation of thermal waves. A typical expression of damped wave equation is given as:

$$\frac{\partial^2 T}{\partial t^2} + A \frac{\partial T}{\partial t} = B \frac{\partial^2 T}{\partial x^2} + C \quad (2.58)$$

Different A , B , and C coefficients are responsible for different models:

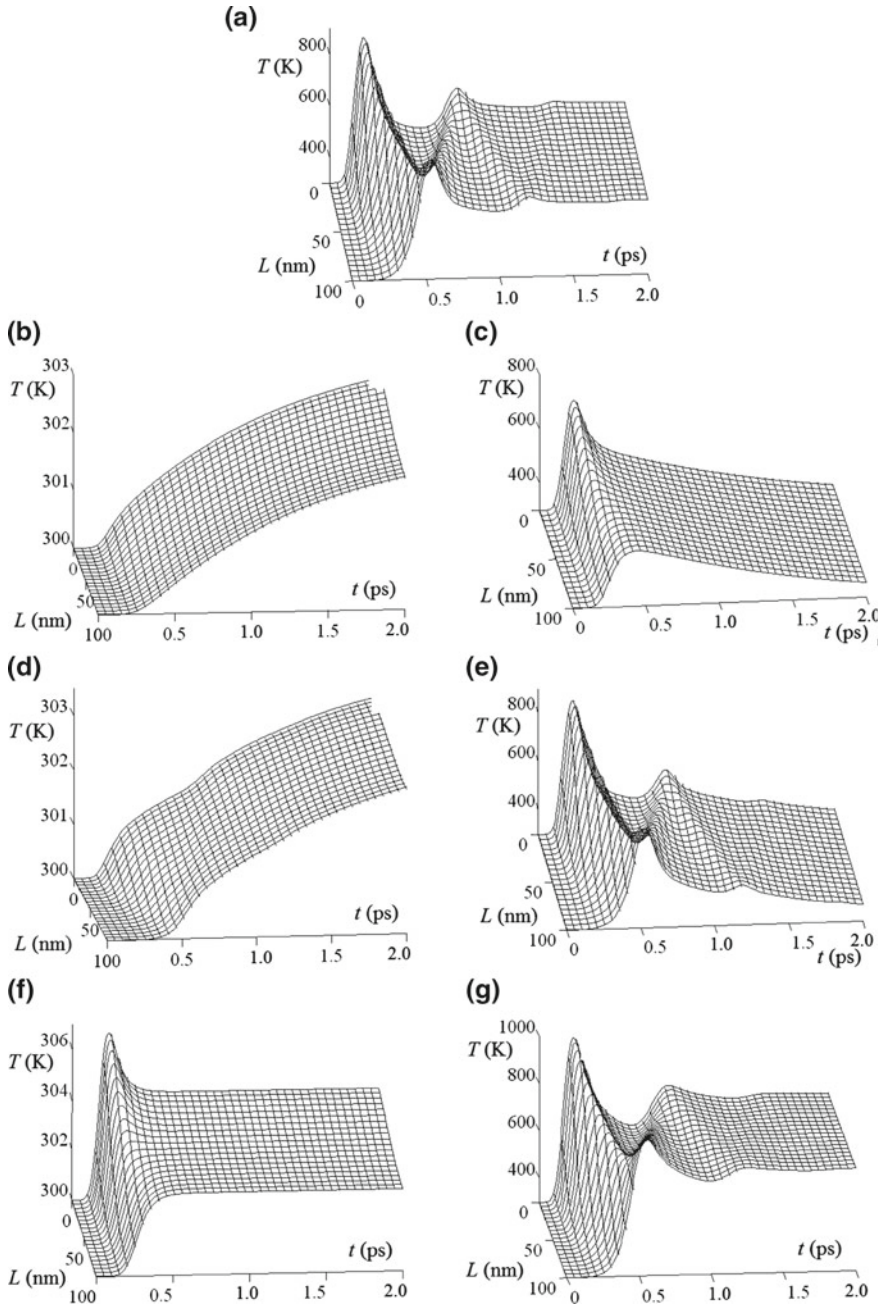


Fig. 2.6 Electron and lattice temperature curves of different models 1. **a** C-V model electron temperature, **b** PTS model lattice temperature, **c** PTS model electron temperature, **d** HTS model lattice temperature, **e** HTS model electron temperature, **f** DPL model lattice temperature, **g** DPL model electron temperature

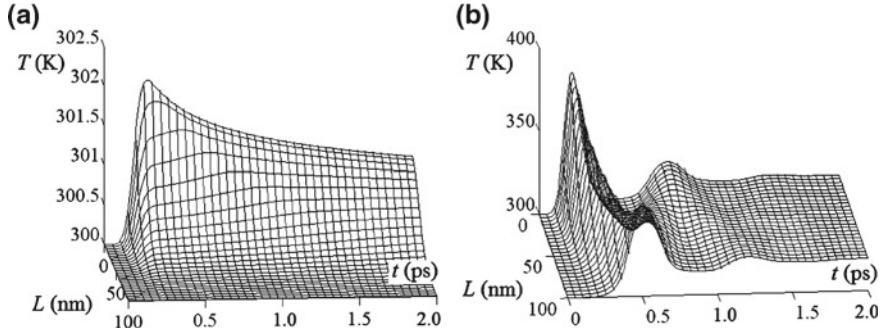


Fig. 2.7 Electron and lattice temperature curves of different models 2. **a** DPL model lattice temperature, **b** DPL model electron temperature

Table 2.1 Coefficient selection for different models

Models	C-V	PTS	HTS
A	$\frac{1}{\tau_0}$	$G \left(\frac{1}{\rho_e C_e} + \frac{1}{\rho_l C_l} \right)$	$\frac{1}{\tau_e} + \frac{G}{\rho_e C_e}$
B	$\frac{\kappa}{\rho C \tau_0}$	$\frac{\kappa_e G}{\rho_e C_e \rho_l C_l}$	$\frac{\kappa_e}{\rho_e C_e \tau_e}$
C	$\frac{1}{\rho C \tau_0} \left(S + \tau_0 \frac{\partial S}{\partial t} \right)$	$\frac{G}{\rho_e C_e \rho_l C_l} \left(S + \frac{\rho_l C_l}{G} \frac{\partial S}{\partial t} \right) + \frac{\kappa_e}{\rho_e C_e} \frac{\partial^3 T_e}{\partial t \partial x^2}$	$\frac{1}{\rho_e C_e \tau_e} \left(S + \tau_e \frac{\partial S}{\partial t} \right) + \frac{G}{\rho_e C_e} \left(\frac{\partial T_l}{\partial t} - \frac{T_e - T_l}{\tau_e} \right)$
Models	DPL	TSTM	
A	$\frac{1}{\tau_q}$	$\frac{1}{\tau_e}$	
B	$\frac{\kappa}{(\rho_e C_e + \rho_l C_l) \tau_q}$	$\frac{\kappa}{\rho C \tau_e} - u_h^2$	
C	$\frac{1}{(\rho_e C_e + \rho_l C_l) \tau_q} \left(S + \tau_q \frac{\partial S}{\partial t} \right) + \frac{\kappa \tau_T}{(\rho_e C_e + \rho_l C_l) \tau_q} \frac{\partial^3 T}{\partial x^2 \partial t}$	$\frac{1}{\rho C \tau_e} \left(S + \tau_e \frac{\partial S}{\partial t} + 2 \tau_e u_h \frac{\partial S}{\partial x} \right) - 2 u_h \frac{\partial^2 T}{\partial t \partial x}$	

From the Table 2.1, one can conclude that:

1. The coefficient of diffusion term A decreases as the relaxation time increases for hyperbolic models, while it increases as the coupling factor G increases in the PTS model;
2. At the same relaxation time, the propagation speed of thermal wave increases as the thermal conductivity increases, decreases as the specific heat increases;

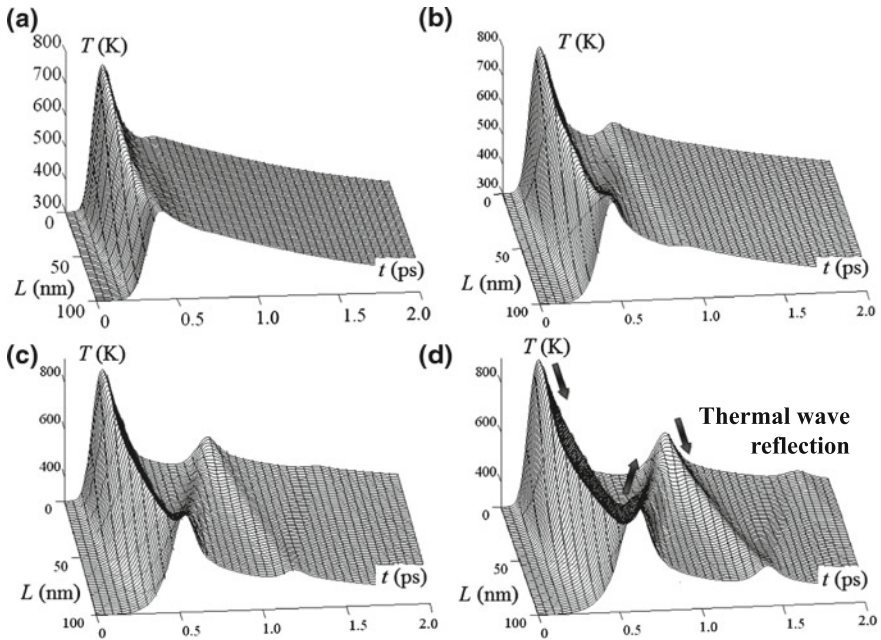


Fig. 2.8 Electron temperature curves predicted by the HTS model at different relaxation times. **a** $\tau_0 = 0.04$ ps, **b** $\tau_0 = 0.08$ ps, **c** $\tau_0 = 0.16$ ps, **d** $\tau_0 = 0.24$ ps

3. Under the same internal heat source condition, the higher specific heat results in smaller temperature responses to the input thermal disturbances, the thermal wave phenomena become less obvious;
4. By giving proper characteristic times, the TSTM model can be reduced to the other kinds of models.

Thermal wave is understood as the result of non-negligible TM inertia. In TM theory, the characteristic time represents the inertia effect of thermal gas. The longer characteristic time, the stronger TM inertia will be. Meanwhile, the higher specific heat of material has more ability to resist the temperature change. So the longer characteristic time and smaller specific heat will cause more obvious thermal wave phenomena. Because the specific heat of lattices is 100 times larger than that of electrons, no temperature wave propagation is observed for lattice temperature. The characteristic time equals zero for the PTS model, thus no thermal wave is observed either.

Different relaxation times 0.04, 0.08, 0.16, and 0.24 ps are used for numerical calculation in the Fig. 2.8.

It is seen in the Fig. 2.8 that a longer relaxation time results in more obvious thermal wave behaviors. The thermal wave can be reflected at the surfaces of the film as shown in the Fig. 2.8d, the arrows show the propagation directions of the thermal wave.

Fig. 2.9 Normalized electron temperature predicted by the C-V model at different specific heats

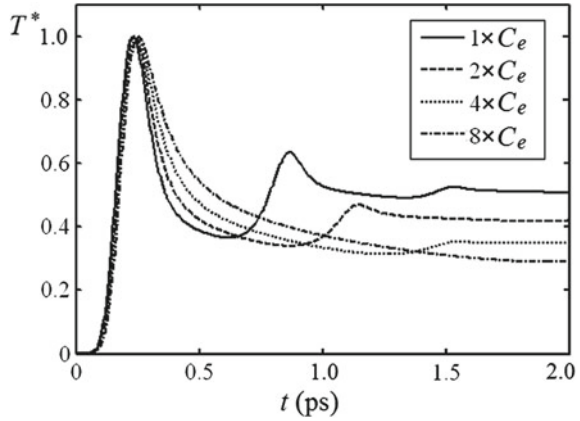
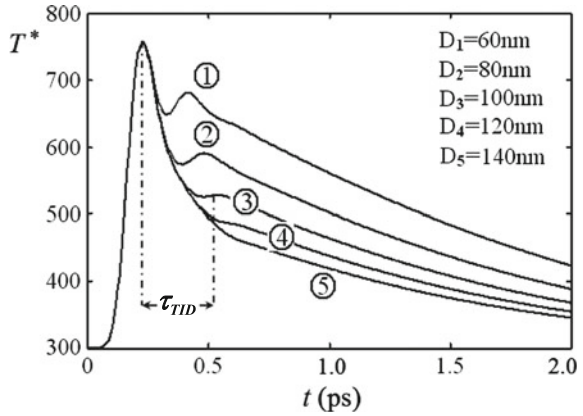


Fig. 2.10 Electron temperature profiles of different film thicknesses when $\tau = 0.4$ ps



It is seen in the Fig. 2.9 that the temperature fluctuation is weakened as the specific heat increases, consistent with the theoretical analysis above. When $8C_e$ is used, the thermal wave disappears and the heat diffusion dominates.

It is also noted that the thermal wave will attenuate during its propagation, similar to the mechanical wave and electromagnetic wave. In order to describe the attenuation of thermal wave quantitatively, a thermal wave time influence domain τ_{TID} has been defined. τ_{TID} is the time needed for the thermal wave to disappear in its direction of propagation, long τ_{TID} means that the attenuation effect is weak and the thermal wave has a larger influence domain. Figures 2.9 and 2.10 show the propagation of thermal wave inside the Au film. For thin films, the thermal wave will be reflected from the rear surface and cause a second temperature peak at the front surface. As the film thickness increases, the thermal wave will be attenuated and the second temperature peak disappears. The time interval between two temperature peaks is defined as τ_{TID} .

Five film thicknesses from 60 to 140 nm are used for calculation as shown in the Fig. 2.10.

Fig. 2.11 Electron temperature profiles of different film thicknesses when $\tau = 0.8$ ps

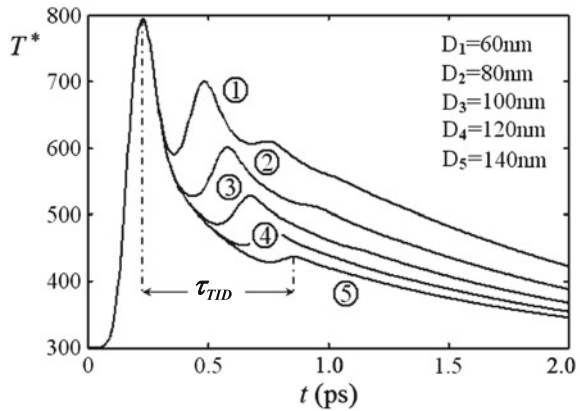
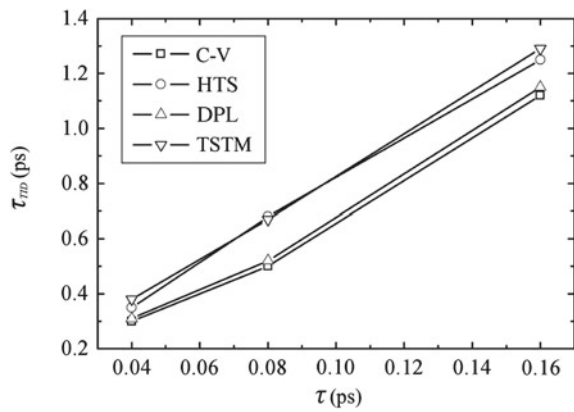


Fig. 2.12 Thermal wave time influence domain plotted with respect to the relaxation time



Based on the calculation results of Figs. 2.10 and 2.11, $\tau_{TID} = 0.55 - 0.20 = 0.35$ ps when $\tau = 0.4$ ps; $\tau_{TID} = 0.88 - 0.20 = 0.68$ ps when $\tau = 0.8$ ps. It is seen that the influence domain of thermal wave increases as the relaxation time increases. The calculation results of different models are summarized in the Fig. 2.12.

Figure 2.12 compares the thermal wave time influence domains of different models. At the same relaxation time, the HTS and TSTM models predict larger τ_{TID} than the DPL and C-V models.

The TSTM model is able to avoid some non-physical problems caused by other thermal wave models. For example, the other thermal wave models will cause negative temperatures during the thermal wave propagation at very low temperatures, while the temperature predicted by the TSTM model keeps positive.

Figure 2.13 shows the physical model of a heat conductor inside which two thermal waves propagates in the opposite directions. At a certain time, these two thermal waves will meet each other in the middle, several thermal wave models are solved numerically to predict the temperature responses. Besides the thermal wave model,

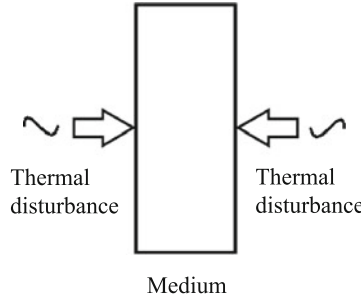
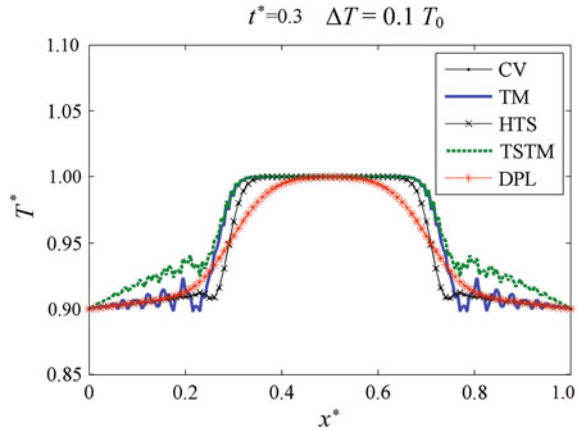


Fig. 2.13 Schematic diagram of two thermal waves propagating in the opposite directions

Fig. 2.14 Temperature distribution under the small thermal disturbance condition when $t^* = 0.3$



the other models will cause negative temperature which is against the third law of thermodynamics [4].

Here, T^* , x^* and t^* are the normalized temperature, length, and time, respectively. T is the environment temperature. When $t^* = 0$, the boundary temperature was suddenly decreased to $0.9T$ and two thermal waves started to propagate in the opposite directions. After a while, these two thermal waves meet each other in the middle position. The Fig. 2.14 gives the predicted temperature responses when $t^* = 0.3$. The TM model is for dielectrics and the TSTM model is for metals. The C–V model is solved using the properties of electron gas and the calculation result is consistent with that of the HTS model.

The Fig. 2.15 gives the calculation result when $t^* = 0.9$. It is seen that temperature in the middle is decreased from the initial temperature T when two thermal waves are superimposed. This can be seen as the interference effect of thermal waves, similar to other kinds of waves, such as light, radio, acoustic, and surface water waves. If the initial temperature T is close to zero and the fluctuated temperature amplitude is large, the negative temperature may occur.

Fig. 2.15 Temperature distribution under the small thermal disturbance condition when $t^* = 0.9$

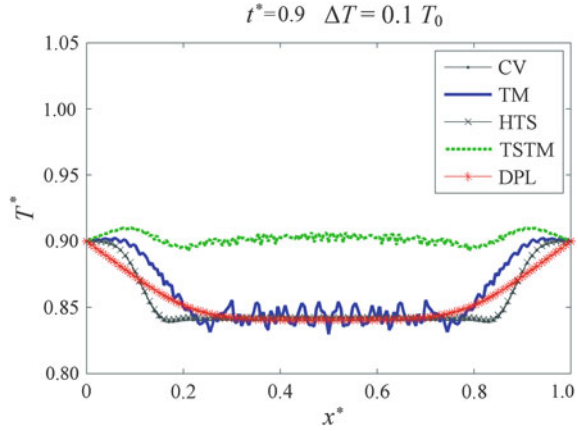
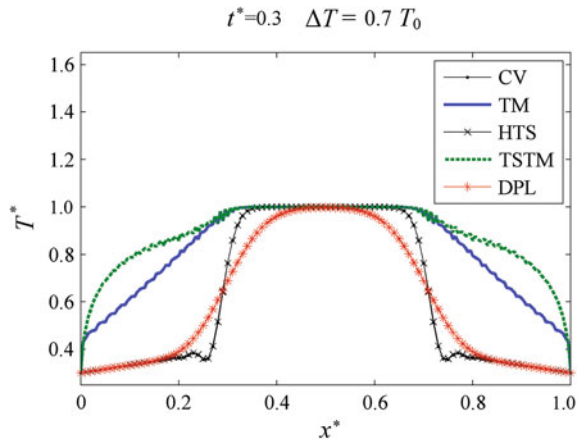


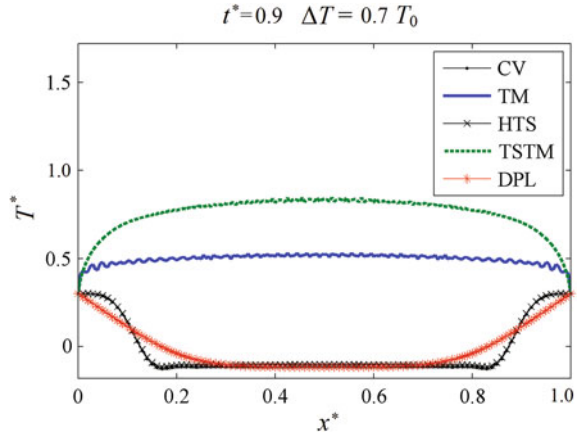
Fig. 2.16 Temperature distribution under the large thermal disturbance condition when $t^* = 0.3$



The Figs. 2.16 and 2.17 show the calculation results when $t^* = 0.3$ and $t^* = 0.9$, where the initial temperature was decreased to $0.3T$. In this case, the initial temperature change ΔT is increased from 0.1 to $0.7T$, the superimposed thermal waves cause negative temperatures in the C-V, HTS, and DPL models, while the TM and TSTM models predict positive temperatures all along. This is because the other models give thermal wave equations by introducing constant relaxation times to the heat diffusion equation, lacking the deep understanding of the physical essence of the relaxation time; in this case, the thermal wave equation has the same expression as the other mechanical wave equations. For mechanical waves, it is correct to observe the negative mechanical wave amplitudes (below the initial equilibrium state); but for thermal waves, the mechanical wave equation is not applicable when T is close to zero.

In the TM model, the thermal wave is known to be caused by the non-negligible inertia effect between the flow of TM and its driven force (temperature gradient).

Fig. 2.17 Temperature distribution under the large thermal disturbance condition when $t^* = 0.9$



Further a general heat conduction equation has been developed based on the first principles, in which the characteristic time is no longer simply a constant, but decided by the material properties, temperature, microscopic distribution function, etc. The general equation is no longer a simple mechanical wave equation, but related with the heat flux, temporal, and spatial partial derivatives of temperature, etc. As a result, the general heat conduction equation is able to predict the thermal wave behavior correctly without any paradoxes.

2.3 Non-Fourier Heat Conduction Equation in Steady States

In steady states, all the other thermal wave models will reduce to Fourier's law, implying no non-Fourier heat conduction existed. But the general heat conduction equation remains different from the Fourier's equation in steady states, giving the first theoretical prediction for the steady non-Fourier heat conduction. One-dimensional steady general heat conduction equation is given as:

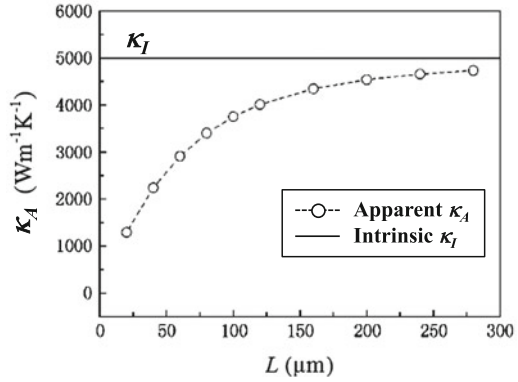
$$\left(\kappa - \tau_h \frac{q^2}{\rho C_v T^2} \right) \frac{\partial^2 T}{\partial x^2} + \frac{2\tau_h q}{\rho C_v T} \frac{\partial S}{\partial x} + S = 0 \quad (2.59)$$

For a constant S , the Eq. (2.59) can be simplified as:

$$\left(\kappa - \tau_h \frac{q^2}{\rho C_v T^2} \right) \frac{\partial^2 T}{\partial x^2} + S = 0 \quad (2.60)$$

Compare with the Fourier's heat diffusion equation, the non-Fourier behavior is mainly caused by the first term in parentheses, which is referred to as the spatial

Fig. 2.18 Thermal conductivity of carbon nanotube plotted with respect to length[12]. Reprinted with the permission from Ref. [12]. Copyright [2007], AIP Publishing LLC



inertia effect of TM. Two kinds of thermal conductivities can be defined from the Eq. (2.60), which are the apparent thermal conductivity κ_A and the intrinsic thermal conductivity κ_I :

$$\kappa_A = \kappa_I - \tau_h \frac{q^2}{\rho C_v T^2} = \kappa_I \left(1 - \frac{q^2}{2\gamma_h \rho^2 C_v^3 T^3} \right) \quad (2.61)$$

The Eq. (2.60) can be also written as:

$$\kappa_A \frac{\partial^2 T}{\partial x^2} + S = 0 \quad (2.62)$$

To avoid confusion, in this thesis, κ_A is referred to as the apparent thermal conductivity, κ_I or κ are referred to as the intrinsic thermal conductivity. The Eq. (2.62) implies that the ratio between heat flux and temperature gradient is the apparent thermal conductivity. κ_A equals κ_I under the common conditions, but under the ultra-high heat flux conditions or at very low temperatures, κ_A will be less than κ_I . Strictly speaking, κ_A is not one of the material properties, because the material property should be decided only by crystal structures, independent with the process properties, such as heat flux, electrical current, size, etc.

The difference between κ_A and κ_I is shown in the Fig. 2.18 in Ref. [12].

The temperature difference between two ends of carbon nanotube (CNT) is controlled to be 20 K in the calculation and the average temperature is 70 K. As the length of CNT increases, the temperature gradient and heat flux decrease. Thus κ_A increases according to the Eq. (2.61). The Fig. 2.18 shows the calculation result that κ_A approaches κ_I as the length increases. The length-dependent thermal conductivity of CNT has been reported in both experiment and molecular simulation [21–24]. The TM theory points out that the spatial inertia effect of TM causes the length-dependent thermal conductivity and gives a prediction from first principles.

2.4 Heat Flow Choking Phenomenon

It is noted from the Eq. (2.60) that a negative thermal conductivity may occur if $\frac{q^2}{2\gamma_h \rho^2 C_v^3 T^3} > 1$. This is against the physical reality. As a matter of fact, a new physical phenomenon “Heat flow choking” is predicted based on this observation. Let us take a look at the choked flow effect: when a subsonic flowing fluid passes through a restriction, the fluid velocity, and therefore the Mach number, increases as the pressure increases for a given environment pressure. The choked flow occurs as the limiting condition when the Mach number equals unity, in this case, the mass flow rate stops to increase with a further increase in the upstream pressure. Similarly, the thermon gas is also compressible and the heat flow choking occurs when the Mach number of the thermon gas equals unity. The propagation speed of thermal disturbance (thermal sound speed) is given from the Eq. (2.51):

$$C_h = \sqrt{\frac{\kappa_I}{\rho C_v \tau_h}} \quad (2.63)$$

For dielectrics, the characteristic time $\tau_h = \frac{\kappa}{2\gamma_h \rho C_v^2 T}$, thus the Eq. (2.63) can be simplified as:

$$C_h = \sqrt{2\gamma_h C_v T} \quad (2.64)$$

It is noted that the Eq. (2.64) is very similar with the expression of sound speed $v_s = [r(r-1)C_v T]^{1/2}$. Further the thermal Mach number Ma_h is defined as the ratio between the drift velocity of thermon gas u_h and the thermal sound speed C_h :

$$\text{Ma}_h = \frac{u_h}{C_h} \quad (2.65)$$

In steady states, the general heat conduction Eq. (2.60) can be simplified as:

$$\kappa_I \left(1 - \text{Ma}_h^2\right) \frac{\partial^2 T}{\partial x^2} + S = 0 \quad (2.66)$$

As mentioned above, $\text{Ma}_h = 1$ is the limiting condition for the heat flow choking. The flows of thermon gas and ideal gas are compared in the Fig. 2.19.

The Fig. 2.19 shows a schematic diagram of thermon gas flow in a heat conductor. Just like the flow of compressible air in a convergent nozzle, the velocity increases and the pressure decreases in the flow direction. The drift velocity of thermon gas increases as it flows in the opposite direction of temperature gradient, meanwhile, the pressure of thermon gas or saying temperature, decreases as well. The pressure change of air flow and temperature change of thermon gas flow are shown in the Fig. 2.20.

As shown in the Fig. 2.20, Mach number equaling unity is the criterion condition for flow choking. In the air flow, a pressure jump occurs at the exit of the nozzle

Fig. 2.19 Comparison between the flows of thermon gas and ideal gas. **a** Flow of gas in a contraction nozzle. **b** Flow of thermon gas in a conductor with equal area. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier

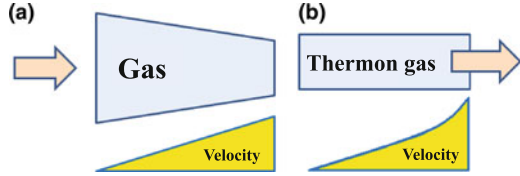
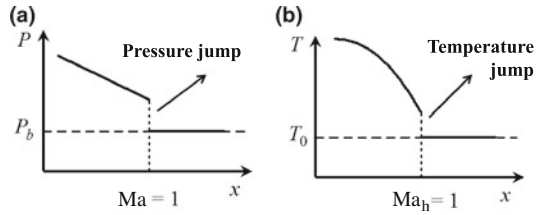


Fig. 2.20 Comparison between the *pressure jump* and *temperature jump* induced by air flow choking and heat flow choking. **a** Pressure profile along the flow direction. **b** Temperature profile along the flow direction. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier



(throat position) when $Ma = 1$; meanwhile in the thermon gas flow, a temperature jump occurs at the cold side of the heat conductor when $Ma_h = 1$. The velocity gradients of air flow and thermon gas flow are given as:

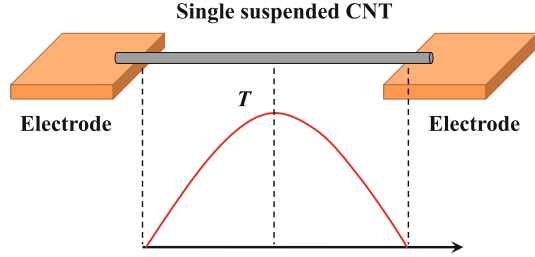
$$\text{Airflow: } \frac{du}{dx} = -\frac{1}{\rho u} \frac{dP}{dx} \quad (2.67)$$

$$\text{Thermongasflow: } \frac{du_h}{dx} = \frac{S}{\rho C_v T} - \frac{q}{\rho C_v T^2} \frac{dT}{dx} \quad (2.68)$$

The first term on the right side of the equal sign in the Eq.(2.68) is caused by the internal heat source. The flows of air and thermon gas are driven by the pressure gradient and temperature gradient with different coefficients, the latter coefficient is proportional to the reciprocal of temperature square. A critical temperature for heat flow choking can be extracted from the equation $Ma_h = 1$ as:

$$T_c = \left(\frac{q^2}{2\gamma_h \rho^2 C_v^3} \right)^{1/3} \quad (2.69)$$

Fig. 2.21 Direct current heating method to measure the thermal conductivity of the CNT



For given material properties, T_c increases as the heat flux q increases, the temperature jump increases as well. Normally, T_c is much smaller than the room temperature and the general heat conduction law can be reduced to Fourier's law. Only for ultra-high heat flux or at very low temperatures, the heat flow choking can be observed in the experiment. The heat flow choking is caused by the spatial TM inertia effect, which was noticed as "thermal inertia" in relativistic thermohydrodynamics [25].

The heat flux in CNT can be ultra-high because of its small cross-sectional area and high burning temperature, making the CNT an ideal material to observe heat flow choking. The Fig. 2.21 gives a schematic diagram of the experiment measuring the thermal conductivity of CNT.

In the Fig. 2.21, an individual CNT is suspended above the substrate with two ends connected with metallic electrodes. In the experiment, a direct current is used to heat the CNT and a reversed parabolic temperature distribution is established along the nanotube. Joule heat generated in the CNT flows from the middle point to the two ends, the heat flux increases as the electrical power increases. When Ma_h equals unity, the heat flow choking can be observed. In this case, the critical heat flux is $q_c = \sqrt{2\gamma\rho^2C^3T_0^3}$ and the temperature jump at the end is $\Delta T = \sqrt[3]{q^2/(2\gamma\rho^2C^3)} - T_0$. The general conduction law can be used to predict the temperature of the CNT. The material properties are chosen as: $\rho = 1,400 \text{ kgm}^{-3}$, $C = 500 \text{ Jkg}^{-1}\text{K}^{-1}$, $D = 1.8 \text{ nm}$, $L = 10 \text{ }\mu\text{m}$, $\gamma = 1$, $T_0 = 300 \text{ K}$, $S = 1 \text{ }\mu\text{W}$ and $q_c = 1.15 \times 10^{11} \text{ Wm}^{-2}$. The cross-sectional area of the CNT is calculated as $A = \pi Dd$, where the shell thickness is $d = 0.34 \text{ nm}$. A finite-difference scheme with double precision is used for numerical calculations.

In the Fig. 2.22, $x = 0$ is the middle position of CNT and the length is $10 \text{ }\mu\text{m}$. The heat flux and drift velocity increase in the x direction, while the thermal sound speed decreases. The heat flow choking occurs at the right end of CNT when $Ma_h = 1$ as shown in the inset of the Fig. 2.22. The drift velocity reaches 700 ms^{-1} at the right end. The calculation results with different intrinsic thermal conductivities are compared in the figure, the higher thermal conductivity results in higher drift velocity, but the temperature jump at the end remains the same.

The maximum heat flux in the calculation is $2.60 \times 10^{11} \text{ Wm}^{-2}$, which is higher than the critical heat flux, thus a temperature jump of 200 K occurs at the end of CNT as shown in the Fig. 2.23. Because of the temperature jump, the temperature predicted by the general heat conduction law is notably higher than that predicted by

Fig. 2.22 Drift velocity and thermal sound speed of CNT with different intrinsic thermal conductivities. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier

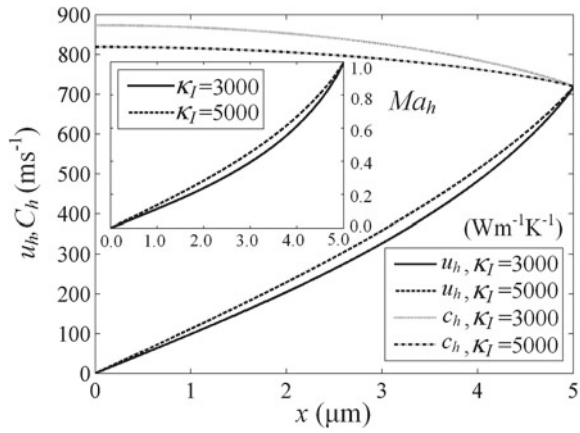


Fig. 2.23 Temperature distributions along the CNT predicted by the general heat conduction law and Fourier’s law. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier

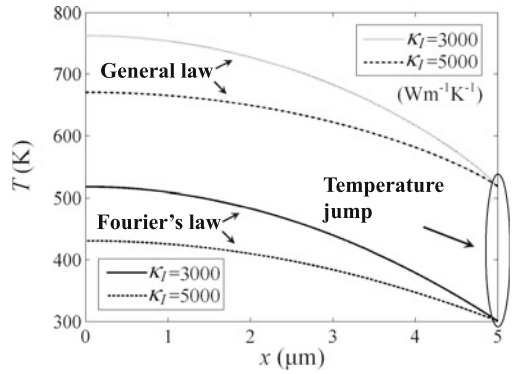
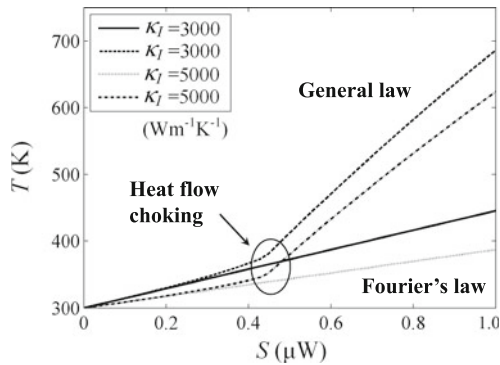


Fig. 2.24 Average temperature of CNT varied with the electrical power. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier



Fourier’s law. Before the proposition of TM theory, the thermal conductivity of CNT is extracted by Fourier’s law only, in this way, the reported thermal conductivities are all apparent ones that are related with the heat flux.

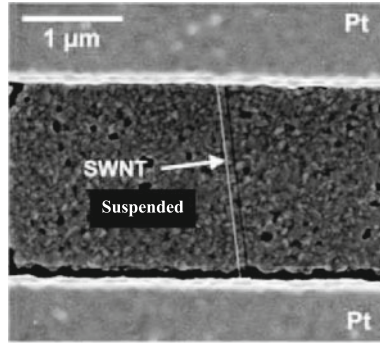


Fig. 2.25 SEM image of the prepared SWCNT sample [26]. Reprinted with the permission from Ref. [26]. Copyright [2006], American Chemical Society

The Fig. 2.24 shows the average temperature of CNT at different electrical powers. Both temperatures predicted by Fourier's law and the general heat conduction law are plotted for comparison. For a constant thermal conductivity, the temperature based on Fourier's law is proportional to the electrical power. Meanwhile, the temperature curve predicted by the general law has a turning point at $0.44 \mu\text{W}$, which is the critical electrical power for appearance of the heat flow choking. Before the turning point, the temperature predicted by the general law is almost the same as that predicted by Fourier's law; after the turning point, the previous temperature increases significantly higher than the latter one because of the increasing temperature jump at the end. Once the heat flow choking occurs, the temperature of CNT could be notably underestimated by Fourier's law, this may cause thermal failure of the CNT-based devices in practical applications.

The experimental result of Pop [26] has been studied to show the effect of heat flow choking on heat conduction process. A single-walled carbon nanotube (SWCNT) with 1.7 nm in diameter and $2.6 \mu\text{m}$ in length has been prepared, and then a direct current heating method was used to measure the thermal conductivity of SWCNT. A scanning electron microscope (SEM) image of the SWCNT is shown in the Fig. 2.25 from the Ref. [26].

As shown in the Fig. 2.25, an individual SWCNT is suspended between two platinum (Pt) electrodes for measurement. The Ref. [26] gives a measured current–voltage curve of SWCNT as shown in the Fig. 2.26.

The average temperature of SWCNT can be extracted from the precisely measured resistance using Landauer–Büttiker model [27, 28]:

$$R(V, T) = R_c + \frac{h}{4q_e^2} \frac{L + \lambda_{\text{eff}}(V, T)}{\lambda_{\text{eff}}(V, T)} \quad (2.70)$$

$$\lambda_{\text{eff}} = \left(\lambda_{AC}^{-1} + \lambda_{OP, \text{ems}}^{-1} + \lambda_{OP, \text{abs}}^{-1} \right)^{-1} \quad (2.71)$$

Fig. 2.26 Current–voltage curve of an individual SWCNT [26]. Reprinted with the permission from Ref. [26]. Copyright [2006], American Chemical Society

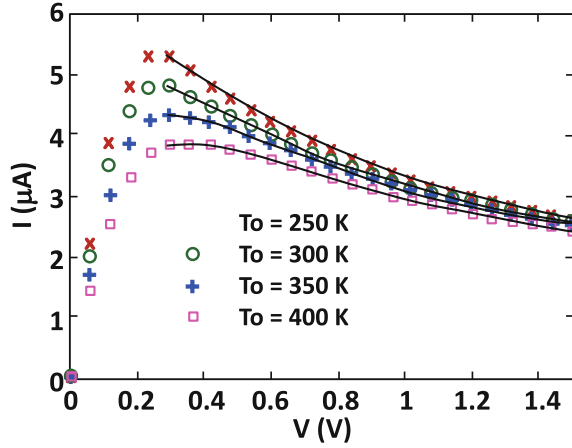
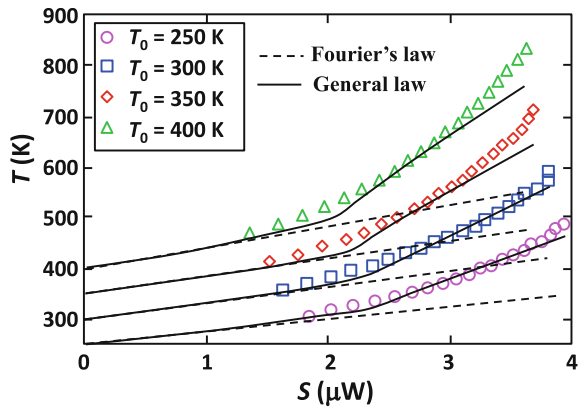


Fig. 2.27 Average temperature of SWCNT plotted with respect to the electric power. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier



where h , q_e and λ_{eff} are the Planck constant, electric charge element and effective electron mean free path, respectively. $h/(4q_e^2) = 6.5 \text{ K}\Omega$ is the quantum contact resistance. Based on the Eqs. (2.70) and (2.71), the temperature–electrical power curve of SWCNT can be plotted in the Fig. 2.27:

The average temperatures predicted by Fourier's law and the general heat conduction law are also plotted in the Fig. 2.27 to compare with the experimental data. Here, a constant thermal conductivity is used for theoretical calculation. It is seen that the general heat conduction law matches well with the experimental data while Fourier's law gives significantly lower predictions. Under the experimental conditions, the drift velocity of thermion gas in the SWCNT is about several hundreds of meters per second, in this case, the assumption that the TM resistance is proportional to the drift velocity is not valid and a second-order correction to the TM resistance is needed.

$$\frac{\partial \rho_h}{\partial t} + \rho_h \frac{\partial u_h}{\partial x} + u_h \frac{\partial \rho_h}{\partial x} = \frac{S}{c^2} \quad (2.72)$$

$$\rho_h \left(\frac{\partial u_h}{\partial t} + u_h \frac{\partial u_h}{\partial x} \right) + u_h \frac{S}{c^2} + \frac{\partial P_h}{\partial x} + f_h = 0 \quad (2.73)$$

The Eqs. (2.72) and (2.73) are the governing equations for the motion of thermon gas, based on which, an one-dimensional steady expression of the general heat conduction equation with internal heat source S can be derived as:

$$\begin{aligned} & \left(\frac{-\kappa_I q S}{\gamma \rho^2 C^3 T^3} \frac{\partial T}{\partial x} + \frac{\kappa_I q^2}{2 \gamma \rho^2 C^3 T^4} \left(\frac{\partial T}{\partial x} \right)^2 \right) + \frac{\kappa_I}{\gamma \rho C^2 T} \left(\frac{S}{\rho C T} - \frac{q}{\rho C T^2} \frac{\partial T}{\partial x} \right) \\ & \times \left(S - \frac{q}{T} \frac{\partial T}{\partial x} \right) + \kappa_I \left(1 - \frac{q^2}{2 \gamma \rho^2 C^3 T^3} \right) \frac{\partial^2 T}{\partial x^2} + S = 0 \end{aligned} \quad (2.74)$$

In order to simplify the Eq. (2.74), an approximate integration equation is given as:

$$q \approx -\kappa_I \frac{\partial T}{\partial x} \approx \frac{1}{2} S L \quad (2.75)$$

Substituting the Eq. (2.75) into the Eq. (2.74), one can get:

$$\kappa_I \left(1 - \frac{q^2}{2 \gamma \rho^2 C^3 T^3} \right) \frac{d^2 T}{dx^2} + \left(1 + \frac{\varepsilon \kappa_I S}{\gamma \rho^2 C^3 T^2} \right) S \approx 0 \quad (2.76)$$

where the parameter ε is:

$$\varepsilon = \frac{\beta_s^*}{4} + \frac{\beta_s^{*2}}{32} + \left(1 + \frac{\beta_s^*}{4} \right)^2 \quad (2.77)$$

where the normalized parameter for the internal heat source is: $\beta_s^* = \frac{S L^2}{T \kappa_I}$, L is the length. A normalized TM resistance is given as:

$$F_h = \beta_1^* U_h + \frac{1}{2} \beta_2^* U_h^2 + \frac{1}{6} \beta_3^* U_h^3 + \dots \quad (2.78)$$

where $F_h = \frac{L}{P_{h0}} f_h$ and $P_{h0} = \frac{\gamma \rho C^2 T_0^2}{c^2}$. Ignoring the high order small quantities, a second TM resistance can be written as:

$$f_h \approx \frac{P_{h0}}{L} \left(\beta_1^* U_h + \frac{1}{2} \beta_2^* U_h^2 \right) = \beta_1 u_h + \beta_2 u_h^2 \quad (2.79)$$

where the first-order coefficient is:

$$\beta_1 = \frac{2 \gamma \rho^2 C^3 T^2}{\kappa_I c^2} \quad \text{and} \quad \beta_1^* = \frac{T^2}{T_0^2} \quad (2.80)$$

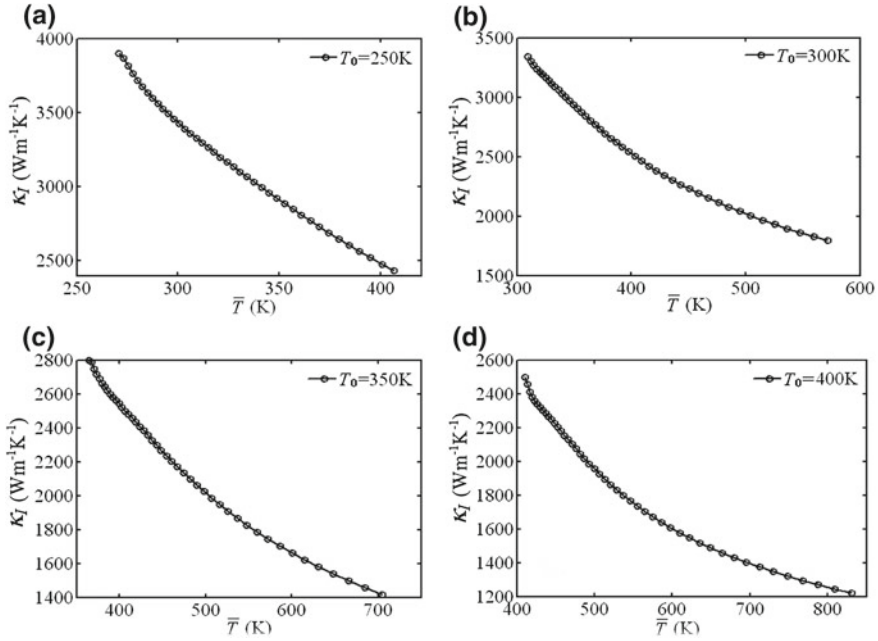


Fig. 2.28 Intrinsic thermal conductivities of SWCNT at different ambient temperatures. **a** Intrinsic thermal conductivity of SWCNT at 250K. **b** Intrinsic thermal conductivity of SWCNT at 300K. **c** Intrinsic thermal conductivity of SWCNT at 350K. **d** Intrinsic thermal conductivity of SWCNT at 400K. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier

and similarly, the second order coefficient is:

$$\beta_2 = \beta_2^* \frac{2\gamma\rho^3 C^4 T_0^2 L}{\kappa_I^2 c^2} \quad \text{and} \quad \beta_2^* = -\beta_{h2}^* \frac{T^2}{T_0^2} \quad (2.81)$$

As a result, a steady general heat conduction equation with a second TM resistance term is obtained as:

$$\kappa_I \left(1 - \frac{q^2}{2\gamma\rho^2 C^3 T^3} \right) \frac{d^2 T}{dx^2} + \left(1 + \frac{\varepsilon \kappa_I S}{\gamma\rho^2 C^3 T^2} - \beta_{h2}^* \frac{L^2 S}{T \kappa_I} \right) S \approx 0 \quad (2.82)$$

If $\beta_h^{**} = -\frac{8\varepsilon(1-\eta)}{\beta_s^{*2}} + \beta_{h2}^*$, where $\eta = \frac{\kappa_A}{\kappa_I} = 1 - \frac{q^2}{2\gamma\rho^2 C^3 T^3}$, ($0 \leq \eta \leq 1$) is the ratio between the apparent and intrinsic thermal conductivities, the Eq.(2.82) can be written as:

$$\kappa_I \eta \frac{d^2 T}{dx^2} + (1 - \beta_h^{**} \beta_s^*) S \approx 0 \quad (2.83)$$

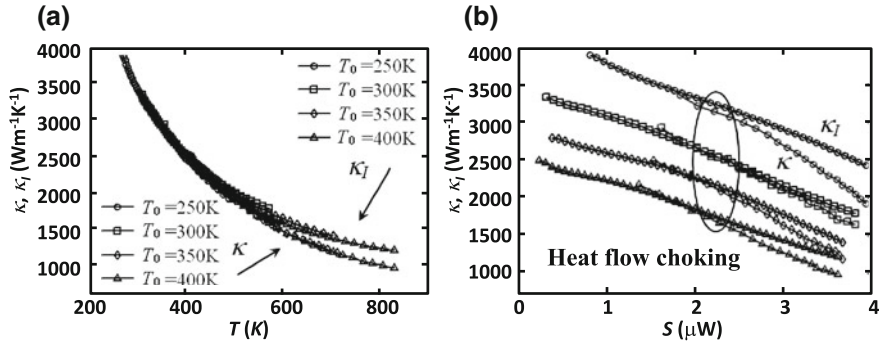


Fig. 2.29 Comparison between κ_I and κ_A of SWCNT. **a** Apparent and intrinsic thermal conductivities varies with temperature. **b** Apparent and intrinsic thermal conductivities varies with heating power. Reprinted from “Heat flow choking in carbon nanotubes, 53, Hai-Dong Wang, Bing-Yang Cao, Zeng-Yuan Guo, 1796–1800”. Copyright [2010], with permission from Elsevier

when $\eta = 1$ and $\beta_{h2}^* = 0$, the Eq. (2.83) will reduce to the heat diffusion equation. Using the modified general heat conduction Eq. (2.83), the intrinsic thermal conductivity κ_I can be extracted from the experimental data from the Ref. [26] as shown in the Fig. 2.28.

The Fig. 2.28 shows that κ_I decreases as the temperature increases from 250 to 800 K. The apparent thermal conductivity κ_A can be extracted from Fourier’s law, κ_I and κ_A are compared in the Fig. 2.29.

The circle in the Fig. 2.29b is drawn to mark the critical electrical power for heat flow choking. Below the critical electrical power, κ_I and κ_A are almost the same; above the critical power, κ_I is notably higher than κ_A and the difference is caused by the TM inertia effect. The comparison result highlights the potential application of the general heat conduction law in thermal analysis of the nanomaterials under the ultra-high heat flux conditions.

2.5 Conclusions

1. The relativistic mass of thermal energy of a single particle (molecule, atom, electron, etc.) is defined as thermon. All the thermons in a system form thermon gas, the heat flux can be understood as the direct flow of thermon gas.
2. Thermon gas is a kind of compressible fluid, whose state equations in ideal gas, dielectrics, and metals are given in this chapter. Similar to the state equation of ideal gas, a unified state equation exists for dielectrics and metals at the high temperature limit. At low temperatures, the difference in several state equations comes from the microscopic distribution functions.
3. Substituting the state equation of thermon gas into the momentum conservation equation, one can get a general heat conduction equation (law). It is a damped

wave equation that can be used to predict the propagation of thermal waves. The thermal wave is caused by the non-negligible temporal TM inertia.

4. A TSTM has been developed for metals heated by ultra-short pulsed lasers. This model is capable of predicting the transient unequilibrium heat conduction between electrons and lattices.
5. Under the ultra-high heat flux conditions, a steady non-Fourier heat conduction behavior is predicted by the TM theory for the first time, i.e., heat flow choking. Similar to the motion of air flow in a convergent nuzzle, when thermal Mach number equals unity, the heat flow choking occurs at the cold side of the heat conductor, causing a temperature jump. In this case, the intrinsic thermal conductivity is notably higher than the apparent one. The theoretical prediction is supported by the experimental result from literature.

References

1. J. Fourier, *Analytical Theory of Heat* (Dover Publications, New York, 1955)
2. G.V. Chester, A. Thellung, The law of Wiedemann and Franz. *Proc. Phys. Soc.* **77**(5), 309 (1961)
3. Z.Y. Guo, Movement and transport of thermomass—thermomass and thermon gas. *J. Eng. Thermophys.* **27**(4), 631–634 (2006). (in Chinese)
4. Z.Y. Guo, B.Y. Cao, H.Y. Zhu, Q.G. Zhang, State equation of phonon gas and its movement conservation equation. *Acta Phys. Sinica* **56**(6), 3306–3312 (2007)
5. A.L. Lavoisier, *Chemical Basis of Theory*. (Peking University Press, Beijing, 2008). (in Chinese)
6. I. Müller, *A History of Thermodynamics: The Doctrine of Energy and Entropy*. (Springer, New York, 2007)
7. W.F. Magie, *A Source Book in Physics* (McGraw-Hill, New York, 1935)
8. H.D. Wang, Z.Y. Guo, Thermon gas—heat carriers in gas and metals. *Chin. Sci. Bull.* **55**(1), 1–7 (2010)
9. L. Onsager, Reciprocal relations in irreversible processes. *Phys. Rev.* **37**, 405–426 (1931)
10. Q.G. Zhang, B.Y. Cao, Z.Y. Guo, Movement and transport of thermomass—state equation of thermon gas. *J. Eng. Thermophys.* **27**, 908–910 (2006). (in Chinese)
11. S.K. Ratkje, P.C. Hemmer, H. Holden, *The Collected Works of Lars Onsager: With Commentary*. (World Scientific, Singapore, 1996)
12. B.Y. Cao, Z.Y. Guo, Equation of motion of a phonon gas and non-Fourier heat conduction. *J. Appl. Phys.* **102**, 053503 (2007)
13. B.X. Cai, *The Basis of the Solid State Physics*. (Higher Education Press, Beijing, 1990). (in Chinese)
14. K. Huang, *Solid State Physics*. (Higher Education Press, Beijing, 1988). (in Chinese)
15. P. Mazur, Low-temperature specific heat of a thin film. *Phys. Rev. B* **23**(12), 6503–6511 (1981)
16. Y. Lu, Q.L. Song, S.H. Xia, Calculation of specific heat for aluminum thin films. *Chin. Phys. Lett.* **22**(9), 2346–2348 (2005)
17. W.H. Tang, R.Q. Zhang, *Equation of State Theory and Calculation Studies* (National University of Defense Technology Press, Beijing, 1999). (in Chinese)
18. M. Chester, Second sound in solids. *Phys. Rev.* **131**(5), 2013–2015 (1963)
19. W.Z. Dai, T.C. Niu, A finite difference scheme for solving a nonlinear hyperbolic two-step model in a double-layered thin film exposed to ultrashort-pulsed lasers with nonlinear interfacial conditions. *Nonlinear Anal.: Hybrid Syst.* **2**, 121–143 (2008)

20. S.I. Anisimov, B.L. Kapeliovich, T.L. Perelman, Electron emission from surface of metals induced by ultrashort laser pulses. *Sov. Phys. JETP* **39**, 375–377 (1974)
21. S. Lepri, R. Livi, A. Politi, Heat conduction in chains of nonlinear oscillators. *Phys. Rev. Lett.* **78**, 1896–1899 (1997)
22. O. Narayan, S. Ramaswamy, Anomalous heat conduction in one dimensional momentum conserving systems. *Phys. Rev. Lett.* **89**, 200601 (2002)
23. S. Maruyama, A molecular dynamics simulation of heat conduction in finite length swnts. *Phys. B: Condens. Matter* **323**, 193–195 (2002)
24. S. Lepri, R. Livi, Heat in one dimension. *Nature* **421**, 327 (2003)
25. S. Sieniutycz, Relativistic thermohydrodynamics and conservation laws in continua with thermal inertia. *Rep. Math. Phys.* **49**(2–3), 361–370 (2002)
26. E. Pop, D. Mann, Q. Wang, K. Goodson, H. Dai, Thermal conductance of an individual single wall carbon nanotube above room temperature. *Nano Lett.* **6**(1), 96–100 (2006)
27. E. Pop, D. Mann, J. Reifenberg, K. Goodson, H.J. Dai, *Electro-Thermal Transport in Metallic Single-wall Carbon Nanotubes for Interconnect Applications* (International Electron Devices Meeting, Washington, DC, 2005)
28. E. Pop, D. Mann, J. Cao, Q. Wang, K. Goodson, H.J. Dai, Negative differential conductance and hot phonons in suspended nanotube molecular wires. *Phys. Rev. Lett.* **95**, 1555051 (2005)

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