Short Communication

Rachid Chebbi*

Formulation of heat conduction and thermal conductivity of metals

https://doi.org/10.1515/phys-2019-0028
Received Nov 12, 2018; accepted Apr 24, 2019

Abstract: The well-known low-pressure monatomic gas thermal conductivity expression is based on the Maxwell-Boltzmann velocity distribution and involves the mean particle velocity, the gas heat capacity at constant volume and the particle mean free path. The extension of the formula to a free electron Fermi gas, using the Fermi velocity along with the Sommerfeld electronic heat capacity, was demonstrated in the literature using the Boltzmann transport equation. A different formulation of heat conduction in sufficiently pure metals, yielding the same formula for the thermal conductivity, is provided in the present investigation using the free electron Fermi gas energy distribution with the thermal conductivity determined from the net heat transfer occurring due to random motions of the free electrons in the presence of temperature gradient. Potential applications of this approach include extension of the present kinetic model incorporating quantum effects to cases in which electron scattering occurs such as in nanowires and hollow nanowires.

Keywords: thermal conductivity; metals; formulation; free electron model; Drude-Sommerfeld model

PACS: 44.10.+i, 67.80.-s,72.10.-d, 72.15.Eb, 72.15.-v

1 Introduction

Heat conduction in sufficiently pure metals is predominantly by conduction electrons [1, 2] as compared with heat conduction by phonons [3]. The different types of scattering are discussed in [2, 4, 5]. According to the Wiedemann-Franz law [1, 2, 4–6], the ratio of the thermal conductivity k to the electrical conductivity σ is proportional to temperature T. The proportionality constant, $k/(\sigma \times T)$, is independent of the solid metal. A derivation using the transport equation and requiring elastic scattering is given in Lifshitz and Pitaevskii [2]. Landau theory of Fermi liquids [4–6] accounts for electron-electron collisions by introducing quasiparticles of effective mass larger than the particle mass [5]. Inelastic collisions cause deviations from the Wiedemann-Franz law [2, 4, 5].

The kinetic theory of monatomic gases at low pressure provides the following expression for the thermal conductivity [1]:

$$k_g = \frac{1}{3} v_g C_{v,g} \lambda_g \tag{1}$$

where v_g is the average molecular speed, $C_{v,g}$ is the heat capacity per unit volume and λ_g is the gas particle mean free path. The above formula was extended to solids while including two contributions to the thermal conductivity, one denoted as k_{ph} due to lattice vibrations (predominant in the case of nonconductors) conveyed by phonons at the speed of sound and the other k_e due to the motion of free electrons (predominant in the case of sufficiently pure metals) [6]. This yields the following expression for k_e [3, 5, 6]:

$$k_e = \frac{1}{3} v_e C_e \lambda \tag{2}$$

where the subscript e refers to electrons, C_e is the electron heat capacity per unit volume and λ denotes the free electron mean free path.

The assumptions and limitations of the Drude free electron theory for metals are discussed in Ashcroft and Mermin [5]. Drude theory provides an expression for the thermal conductivity of metals similar to the one obtained for monatomic ideal gases with the Maxwell-Boltzmann velocity distribution. Drude theory successfully predicts the Wiedemann-Franz law despite the fact that the electronic heat capacity of metals is in disagreement with experimental findings. The Sommerfeld theory extends the Drude theory, and instead uses quantum Fermi-Dirac statistics [5, 6] leading to a linear dependency of the electronic heat capacity on temperature in agreement with experiments, and to satisfy the Wiedemann-Franz law, v_e is taken as the Fermi velocity v_F [5, 6]. A rigorous approach using the transport equation along with the concept of quasiparticles yields $v_e = v_F$ for a free electron gas [4].

Metals have high thermal conductivities. The effective thermal conductivity of composite solids can be estimated

***Corresponding Author: Rachid Chebbi:** Chemical Engineering Department, American University of Sharjah, Sharjah, United Arab Emirates; Email: rchebbi@aus.edu

using the classical formula of Maxwell [1] involving the thermal conductivities of the two solid materials and the volume fraction of the dispersed phase. Nanofluids consist of nanoparticles dispersed in a fluid. The enhancement of the thermal conductivity of the fluid has been subject to numerous studies. Recent reviews are provided in [7, 8] and in the references therein. Most formulas for the effective thermal conductivities involve the thermal conductivity of the nanoparticles material. A theoretical model for the effective thermal conductivity of the nanomaterial involving other physical properties of the nanomaterial than the thermal conductivity, while not requiring any empirical fitting parameter, is provided in [8]. Possible mechanisms for thermal conductivity enhancement are discussed in [9], and in [10] based on molecular dynamics simulation. The impact of Brownian motion on the thermal conductivity enhancement factor is discussed in [9, 11]. Other new materials having high thermal conductivities include metal foams, materials combining nanomaterials and nanofoams [7], and metallic nanoporous materials [12].

In the present investigation, we provide a formulation of the thermal conductivity of metals using the free electron Fermi gas energy distribution and considering the net heat flux driven by temperature gradient and resulting from random motions of the energy carriers in a free electron Fermi gas. The derivation is different from the one given in the literature based on the Boltzmann transport equation. A brief theoretical background is provided for the quantum Fermi-Dirac distribution used in the Sommerfeld model for the electronic heat capacity. Next comes a theoretical formulation of heat conduction, deriving Equation (2) for the thermal conductivity of metals with v_e equal to the Fermi velocity v_F and C_e equal to the Sommerfeld electron heat capacity using the quantum Fermi-Dirac energy distribution. Potential applications of the model are presented in the last section.

2 Theoretical Background

The free electrons are constrained to move in a cubic volume of volume V with side length $L = V^{1/3}$. Applying the Schrödinger equation while restricting the free electrons to remain in the volume yields quantized energy levels [6]

$$\varepsilon_{\vec{k}} = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) \tag{3}$$

where m_e is the electron mass and the wave vector ($\vec{k}$) components are quantized as

$$k_x = n_x\frac{2\pi}{L}; \quad k_y = n_y\frac{2\pi}{L}; \quad k_z = n_z\frac{2\pi}{L} \tag{4}$$

where n_x, n_y and n_z are integers. Each state occupies a volume of $(2\pi)^3/V$ in the $\vec{k}$ space allowing for a maximum of two electrons as limited by the Pauli Exclusion Principle.

The Fermi-Dirac probability of occupancy is given in Kittel [6] as

$$f(\varepsilon, T) = \frac{1}{\exp\left[(\varepsilon - \mu)/k_B T\right] + 1} \tag{5}$$

where μ is the chemical potential at temperature T and k_B is Boltzmann constant.

At $T = 0$ K, the maximum energy level is the Fermi energy ϵ_F, with all states of energy levels less than or equal to ϵ_F fully occupied by free electrons, leading to [6]

$$\varepsilon_F = \frac{\hbar^2}{2m_e}\left(3\pi^2\frac{N}{V}\right)^{2/3} \tag{6}$$

where N is the number of free electrons which is equal to the number of atoms for monovalent metals. Equating the kinetic energy to the Fermi energy ϵ_F provides the Fermi velocity

$$v_F = \left(2\varepsilon_F/m_e\right)^{1/2} \tag{7}$$

The number of states of energy less than or equal to ϵ is provided by a similar equation to Equation (6), with N_ϵ equal to the number of states of energy equal to or lower than ϵ, leading after differentiation to a state density of [6]

$$D(\varepsilon) = \frac{dN_\varepsilon}{d\varepsilon} = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\varepsilon^{1/2} \tag{8}$$

Using

$$N = \int_0^\infty D(\varepsilon) f(\varepsilon, T)\, d\varepsilon \tag{9}$$

leads to μ as a function of ϵ_F and T [5], showing μ nearly equal to ϵ_F for T/T_F small, which is typically the case as the lowest Fermi temperature $T_F = \epsilon_F/k_B$ for Cs, among the monovalent metals considered, is 1.83×10^4 K [6].

The heat capacity per unit volume [6]

$$C_e = \frac{1}{V}\frac{d}{dT}\int_0^\infty D(\varepsilon) f(\varepsilon, T)\ \varepsilon\, d\varepsilon \tag{10}$$

is shown to be given, for $T << T_F$, in [6]:

$$C_e \cong \frac{D(\varepsilon_F)}{V}\int_0^\infty (\varepsilon - \varepsilon_F)\ \frac{\partial f}{\partial T} d\varepsilon \tag{11}$$

$$\cong k_B^2 T \frac{D(\varepsilon_F)}{V} \int_{-T_F/T}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx$$

$$\cong k_B^2 T \frac{D(\varepsilon_F)}{V} \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx = \frac{1}{2}\pi^2 n k_B \frac{T}{T_F}$$

using the change of variable $x = (\varepsilon - \varepsilon_F)/k_B T$, with n denoting the concentration of free electrons.

3 Theoretical Formulation of Heat Conduction and Thermal Conductivity

Heat transfer is by conduction. The heat flux q_y in the y-direction is related to the temperature gradient by Fourier's law

$$q_y = -k\frac{\partial T}{\partial y} \tag{12}$$

where k denotes the thermal conductivity, with heat considered to be transferred predominantly by free electrons in the case of sufficiently pure metals [2, 6]. In the metal, energy carriers (free electrons) may reach plane y from the top or bottom (Figure 1). The numbers of free electrons of energy in the range $\epsilon - \epsilon + d\epsilon$ (velocity in the range $v - v + dv$) are shown in Figure 1 for the top and bottom layers.

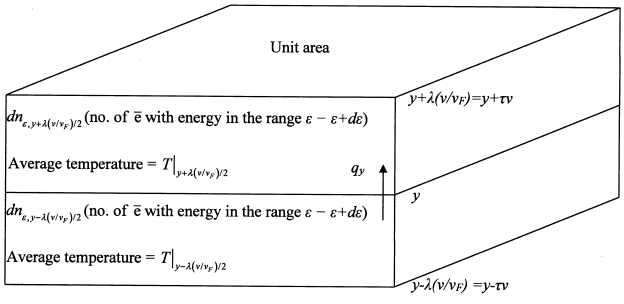

Figure 1: Schematic of the volumes enclosing free electrons of energy ranging between ε and $\varepsilon + d\varepsilon$, with one sixth of them crossing the central plane y from both the lower side and upper side during time τ. q_y is the net heat flux in the y-direction.

The temperatures needed to determine f are taken at mid distances $y + \tau v/2 = y + \lambda(v/v_F)/2$ and $y - \tau v/2 = y - \lambda(v/v_F)/2$, where time τ is λ/v_F. One sixth of the electrons cross plane y in both directions, assuming the x, y and z directions are similar, considering the case of a spherical or nearly spherical Fermi surface. During time τ, the net energy crossing the unit area plane y is given by

$$-k\frac{\partial T}{\partial y}\tau = \int_0^{\infty} \frac{1}{6}\left(\frac{dn_{\varepsilon,y-\lambda(v/v_F)/2}}{d\varepsilon} - \frac{dn_{\varepsilon,y+\lambda(v/v_F)/2}}{d\varepsilon}\right)\varepsilon d\varepsilon \tag{13}$$

where

$$\frac{dn_{\varepsilon,y-\lambda(v/v_F)/2}}{d\varepsilon} = \lambda(v/v_F)\frac{D(\varepsilon)}{V} f\left(\varepsilon,\ T|_{y-\lambda(v/v_F)/2}\right); \tag{14}$$

$$\frac{dn_{\varepsilon,y+\lambda(v/v_F)/2}}{d\varepsilon} = \lambda(v/v_F)\frac{D(\varepsilon)}{V} f\left(\varepsilon,\ T|_{y+\lambda(v/v_F)/2}\right)$$

Using the chain rule,

$$f(\varepsilon)\big|_{T|y-\lambda(v/v_F)/2} - f(\varepsilon)\big|_{T|y+\lambda(v/v_F)/2} = -\frac{\partial f}{\partial T}\frac{\partial T}{\partial y}\lambda(v/v_F) \tag{15}$$

and then substituting into Equation (13) yields

$$-k\frac{\partial T}{\partial y}\tau = \frac{\partial T}{\partial y}\int_0^{\infty} -\frac{1}{6}\frac{D(\varepsilon)}{V}\frac{\partial f}{\partial T}\lambda^2(v/v_F)^2\,\varepsilon d\varepsilon \tag{16}$$

Substituting for v from $\varepsilon = m_e v^2/2$ and v_F from Equation (7) into Equation (16) yields

$$k = \frac{\lambda^2}{6\tau\varepsilon_F}\int_0^{\infty}\frac{\partial f}{\partial T}\frac{D(\varepsilon)}{V}\varepsilon^2 d\varepsilon \cong \frac{\lambda^2}{6\tau\varepsilon_F}\frac{D(\varepsilon_F)}{V}\int_0^{\infty}\frac{\partial f}{\partial T}\varepsilon^2 d\varepsilon \tag{17}$$

Differentiating f with respect to temperature provides

$$\frac{\partial f}{\partial T} = \frac{1}{T}\frac{xe^x}{(e^x+1)^2};\quad x = \frac{\varepsilon-\mu}{k_B T}. \tag{18}$$

Substituting into Equation (17) and using the assumption $T << T_F$ (for which $\mu \cong \varepsilon_F$) gives

$$k \cong \frac{\lambda^2}{6\tau\varepsilon_F} \cdot k_B\frac{D(\varepsilon_F)}{V}\int_{-T_F/T}^{\infty}\frac{xe^x}{(e^x+1)^2}\left[x^2(k_B T)^2 + 2x\varepsilon_F k_B T + \varepsilon_F^2\right]dx \tag{19}$$

$$\cong \frac{\lambda^2}{6\tau\varepsilon_F}k_B\frac{D(\varepsilon_F)}{V}\left[(k_B T)^2\int_{-\infty}^{\infty}\frac{x^3e^x}{(e^x+1)^2}dx + 2\varepsilon_F k_B T\int_{-\infty}^{\infty}\frac{x^2e^x}{(e^x+1)^2}dx + \varepsilon_F^2\int_{-\infty}^{\infty}\frac{xe^x}{(e^x+1)^2}dx\right]$$

Given that

$$\frac{e^{-x}}{(e^{-x}+1)^2} = \frac{e^{-x}\times e^{2x}}{(e^{-x}+1)^2\times e^{2x}} = \frac{e^x}{(e^x+1)^2} \tag{20}$$

Table 1: Physical properties and comparison of mean free paths with numerical simulation results at room temperature for Na, K, Cu, Ag and Au in [14]. Electron valence = 1 [6].

Element	Electron valency	k, W/m·K at 300 K [13]	$v_F \times 10^{-6}$, m/s [6]	Density, g/cm^3 at 298K [13]	λ, nm (free electron theory)	λ, nm [14] (numerical)	Percent deviation
Sodium	1	141	1.07	0.97	28.5	30.9	7.6
Potassium	1	102	0.86	0.89	31.2	31.5	0.8
Copper	1	401	1.57	8.96	35.9	39.9	10.1
Silver	1	429	1.39	10.5	49.1	53.3	7.8
Gold	1	317	1.39	19.3	36.2	37.7	3.9

Table 2: Physical properties and comparison of mean free paths with numerical simulation results at room temperature for other metals in [14].

Element	Electron valency	k, W/m·K at 300 K [13]	$v_F \times 10^{-6}$, m/s [6]	Density, g/cm^3 at 298K [13]	λ, nm (free electron theory)	λ, nm [14] (numerical)	Percent deviation
Magnesium	2	156	1.37	1.74	16.0	20	19.8
Calcium	2	200	1.28	1.54	26.9	35.4	24.0
Zinc	2	116	1.82	7.14	7.8	13.7	43.4
Cadmium	2	96.6	1.62	8.65	8.2	15.1	45.9
Aluminium	3	237	2.03	2.7	12.8	18.9	32.3

only the second integral term in Equation (19) can be kept as the other two functions in the integration signs are odd, reducing Equation (19) to

$$k \cong \frac{\lambda^2}{6\tau\varepsilon_F} k_B \frac{D(\varepsilon_F)}{V} \left[2\varepsilon_F k_B T \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx \right] \qquad (21)$$

Using $\lambda/\tau = v_F$, and substituting for C_e from Equation (11) gives after rearrangement

$$k \cong \frac{1}{3}\lambda v_F k_B^2 T \frac{D(\varepsilon_F)}{V} \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx = \frac{1}{3}\lambda v_F C_e \qquad (22)$$

which is consistent with Equation (2) with v_e equal to v_F and C_e equal to the Sommerfeld electronic heat capacity per unit volume.

4 Potential Applications of the Present Approach

The results using Equation (22) (or Equation (2) with $v_e = v_F$) are compared with the numerical results [14] for Na, K, Cu, Ag and Au in Table 1. The free electron mean free paths were obtained from Equation (22). Calculation of the electron heat capacity per unit volume C_e, using Equation (11), requires the free electron concentration n, determined using the metal molar mass and density from [6]. The deviations from the published numerical free electron mean free paths are found to be in the range 0.8%-10.1% with an average deviation of 6.0%. The results support the applicability of the free electron theory to transport properties in the case of nearly spherical Fermi surfaces [5].

For Mg, Ca, Zn, Cd (electron valence = 2 [6]) and Al (electron valence = 3 [6]), deviations in the range 19.1%-45.9% can be observed in Table 2. For aluminium, the deviation is 32.3%.

As mentioned in the first section, new materials having large thermal conductivity and involving metals include metallic nanoporous materials, nanofluids containing metallic nanoparticles, metal foams and materials including both nanomaterials and nanofoams. Optimizing laser-based processing also requires the thermal conductivity of metals [15]. Main applications of the abovementioned materials and laser-based processing are listed in [7, 15, 16]. The thermal conductivity formula, Equation (22) (Equation (2) with $v_e = v_F$), can be used for metals of electron valence equal to one like copper as a very good approximation as mentioned above, and for metals of higher electron valence like aluminium as a fairly good approximation. Modeling of the thermal conductivity of nanowires and hollow nanowires involves electrons trans-

fer modeling. On the other hand, the model presented in this paper shows a kinetic approach including quantum effects that could be extended to treat problems involving electron scattering such as those occurring in hollow nanowires [16], and nanowires [12, 17].

5 Conclusion

Energy carriers (mainly free electrons in the case of sufficiently pure metals) reaching a plane from opposite sides with different levels of energy permit a net flux yielding heat transfer by conduction. The different directions are considered equivalent (isotropic model). The validity of Equation (2), with v_e equal to the Fermi velocity v_F and C_e equal to the Sommerfeld electron heat capacity, was demonstrated in the present investigation for a free electron Fermi gas using the free electron Fermi gas energy distribution. The derivation is different from the one presented in the literature based on the Boltzmann transport equation. Applications include the use of the metal thermal conductivity formula in expressions estimating the thermal conductivity of high conductivity materials, and extension of the present kinetic approach including quantum effects to cases involving electron scattering such as those occurring in nanowires and hollow nanowires.

References

[1] Bird R.B., Stewart W.E., Lightfoot E.N., Transport Phenomena, Wiley, New York, 2007
[2] Lifshitz E.M., Pitaevskii, L.P., Course of Theoretical Physics, Physical Kinetics. Vol. 10, Elsevier, Amsterdam, 2008
[3] Incropera F.P., Dewitt D.P., Bergman T.L., Lavine A.S., Fundamentals of Heat and Mass Transfer, Wiley, New York, 2007
[4] Abrikosov A.A., Fundamentals of the theory of metals, Dover, New York, 2017
[5] Ashcroft N.W., Mermin, N.D., Solid State Physics, Thomson Learning, Singapore, 1976
[6] Kittel C., Introduction to Solid State Physics, Wiley, New York, 1996
[7] Xu H.J., Xing Z.B., Wang, F.Q., Cheng, Z.M., Review on heat conduction, heat convection, thermal radiation and phase change heat transfer of nanofluids in porous media: Fundamentals and applications, Chemical Engineering Science, 2019, 195, 462-483
[8] Chebbi, R., A theoretical model for thermal conductivity of nanofluids, Materials Express, 2017, 7, 51-58
[9] Keblinski P., Phillpot S.R., Choi S.U., Eastman J.A., Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids), Int. J. Heat Mass Transfer, 2002, 45, 855-863
[10] Abou-Tayoun N., Chebbi R., Thermal conductivity of liquid water and water–copper nanofluid from equilibrium molecular dynamics simulation, Journal of Computational and Theoretical Nanoscience, 2017, 14, 3237–3245
[11] Chebbi R., Thermal conductivity of nanofluids: Effect of Brownian motion of nanoparticles, AIChE Journal, 2015, 61, 2368-2369
[12] Huang C., Lin Z., Feng Y., Zhang X., Wang G., Thermal conductivity prediction of 2- dimensional square-pore metallic nanoporous materials with kinetic method approach, International Journal of Thermal Sciences, 2017, 112, 263-269
[13] CRC Handbook of Chemistry and Physics, 95th ed., W.M. Haynes, Ed. (CRC Press, Boca Raton, FL, 2014).
[14] Gall D., Electron mean free path in elemental metals, J. Appl. Physics, 2016, 119, 085101
[15] Li C.H., Luan D.C., Zhu Q.H., Zheng W.G., A universal theoretical model for thermal integration in materials during repetitive pulsed laser-based processing, Optik-International Journal for Light and Electron Optics, 2018, 171, 728-736
[16] Huang C., Wang Q., Rao Z., Thermal conductivity prediction of copper hollow nanowire, International Journal of Thermal Sciences, 2015, 94, 90-95
[17] Huang C., Feng Y., Zhang X., Lee J., Wang G., Electron mean free path model for rectangular nanowire, nanofilm and nanoparticle, Physica B, 2014, 438, 17–21