

Derivation of Maxwell's theory of Conductivity

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November 6, 2018

1 For a single sphere

Consider a single spherical particle immersed in an infinite fluid where conduction is the only method of heat transport. A uniform heat flux is imposed upon the system along the z-direction as shown in Fig. ???. The equation for the temperature distribution in the system at steady-state and with no generation or consumption of heat is given by the Laplace equation,

$$\nabla^2 T = 0, \quad (1)$$

where T is the temperature. The Laplace equation can be written in spherical coordinates as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2} = 0, \quad (2)$$

where r is the distance from the point of origin, θ is the polar angle measured from the positive z-axis in the y-z plane, and ϕ is the azimuthal angle measured from the positive x-axis in the x-y plane. Since the heat flux is uniform along the z-direction, the system will be symmetric in the azimuthal direction, $\partial T / \partial \phi = 0$. Therefore, Eq. ?? can be simplified as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) = 0. \quad (3)$$

This equation has multiple solutions such as $T(r, \theta) = 1$, $T(r, \theta) = r \cos \theta$, and $T(r, \theta) = \cos \theta / r^2$ which we confirm by substitution into the equation. Assuming this is all of the relevant solutions, a general solution can be made up of a sum of these terms:

$$T_\alpha = A_\alpha r \cos \theta + B_\alpha \frac{\cos \theta}{r^2} + C_\alpha + \dots \quad (4)$$

For the outer part, we know that as $r \rightarrow \infty$, $T_{out} \rightarrow T_0 + \left(\frac{dT}{dz} \right)_\infty z$. Taking the same limit of the equation we see this functional form arise,

$$\lim_{r \rightarrow \infty} T_{out} = A_{out} r \cos \theta + B_{out} \frac{\cos \theta}{r^2} + C_{out} \quad (5)$$

$$= A_{out} z + C_{out} \quad (6)$$

Therefore $C_{out} = T_0$ and $A_{out} = \left(\frac{dT}{dz}\right)_\infty$. Giving

$$T_{out} = \left(\frac{dT}{dz}\right)_\infty r \cos \theta + B_{out} \frac{\cos \theta}{r^2} + T_0 + \dots \quad (7)$$

where $z = r \cos \theta$. Comparing this to the limiting form we can determine that $C_{out} = T_0$ and $A_{out} = \left(\frac{dT}{dz}\right)_\infty$; however, B_{out} remains undetermined,

$$T_{out} = \left(\frac{dT}{dz}\right)_\infty r \cos \theta + B_{out} \frac{\cos \theta}{r^2} + T_0 \quad (8)$$

Considering the inner section now,

$$T_{in} = A_{in} r \cos \theta + B_{in} \frac{\cos \theta}{r^2} + C_{in} \quad (9)$$

We know that as $r \rightarrow 0$, T must remain finite, therefore $B_{in} = 0$.

$$T_{in} = A_{in} r \cos \theta + C_{in} \quad (10)$$

The remaining boundary conditions of the system are

$$T_{in} = T_{out} \quad \text{for } r = R \quad (11)$$

$$-k_{in} \frac{\partial T_{in}}{\partial r} = -k_{out} \frac{\partial T_{out}}{\partial r}, \quad \text{for } r = R \quad (12)$$

where k_{in} , and k_{out} denote the thermal conductivity of the material inside and outside the sphere respectively. Eq. ?? assumes that there is no interfacial resistance between the sphere and the fluid. Using this first boundary condition and applying it we have the following,

$$\left(\left(\frac{dT}{dz}\right)_\infty R + \frac{B_{out}}{R^2}\right) \cos \theta + T_0 = A_{in} R \cos \theta + C_{in} \quad (13)$$

As θ can vary independently, the equality is only satisfied if $C_{in} = T_0$, and the $\cos \theta$ terms are equal,

$$A_{in} = \left(\frac{dT}{dz}\right)_\infty + \frac{B_{out}}{R^3} \quad (14)$$

Consider the second boundary condition, the radial heat flux is $q_r = -k \partial T / \partial r$ and equating the inner and outer fluxes at $r = R$ yields the following,

$$k_{in} A_{in} \cos \theta = k_{out} \left(\left(\frac{dT}{dz}\right)_\infty \cos \theta - 2 R^{-3} B_{out} \cos \theta \right) \quad (15)$$

$$A_{in} = \frac{k_{out}}{k_{in}} \left(\left(\frac{dT}{dz}\right)_\infty - 2 R^{-3} B_{out} \right) \quad (16)$$

Substituting equating this with Eq. ??,

$$\frac{k_{out}}{k_{in}} \left(\left(\frac{dT}{dz} \right)_{\infty} - 2 R^{-3} B_{out} \right) = \left(\frac{dT}{dz} \right)_{\infty} + \frac{B_{out}}{R^3} \quad (17)$$

$$B_{out} = R^3 \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \left(\frac{dT}{dz} \right)_{\infty} \quad (18)$$

Which implies,

$$A_{in} = \frac{3 \frac{k_{out}}{k_{in}}}{1 + 2 \frac{k_{out}}{k_{in}}} \left(\frac{dT}{dz} \right)_{\infty} \quad (19)$$

Putting this all together,

$$T_{in} = z \frac{3 \frac{k_{out}}{k_{in}}}{1 + 2 \frac{k_{out}}{k_{in}}} \left(\frac{dT}{dz} \right)_{\infty} + T_0 \quad (20)$$

$$T_{out} = z \left(1 + \frac{R^3}{r^3} \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \right) \left(\frac{dT}{dz} \right)_{\infty} + T_0 \quad (21)$$

This is the solution for temperature around a sphere embedded in a linear temperature gradient. We note, that the temperature change caused by a single sphere over the background linear temperature profile is

$$\Delta T_{out} = z \frac{R^3}{r^3} \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \left(\frac{dT}{dz} \right)_{\infty}$$

2 For a mixture

Now consider a mixture of spheres. Assume the spheres are far apart, so that their effect on the temperature profile is just the sum of their changes from the basic linear temperature profile:

$$T_{out}^{(mix)}(r) = z \left(1 + \sum_i^{N_p} \frac{R_{nano}^3}{r_i^3} \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \right) \left(\frac{dT}{dz} \right)_{\infty} + T_0 \quad (22)$$

$$\approx z \left(1 + N_p \frac{R_{nano}^3}{r^3} \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \right) \left(\frac{dT}{dz} \right)_{\infty} + T_0 \quad (23)$$

where in the second line we assume that we are so far away from the nanoparticles, that they are collected near to the origin and so the sum is replaced with a multiplication. Now consider a sphere around the origin and nanoparticles

whose radius is such that it has some particular volume fraction,

$$\phi = \frac{V_{nano}}{V_{sys}} = \frac{N_p 4 \pi R_{nano}^3 / 3}{4 \pi R_{sys}^3 / 3}$$

$$R_{sys}^3 = \frac{N_p R_{nano}^3}{\phi}$$

What is the effective thermal conductivity, k_{eff} of this sphere of radius R_{sys} which gives the same temperature profile as the multi-particle system? I.e., when is the following statement true

$$T_{out}^{(mix)}(r) = z \left(1 + N_p \frac{R_{nano}^3}{r^3} \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \right) \left(\frac{dT}{dz} \right)_{\infty} + T_0$$

$$= z \left(1 + \frac{R_{sys}^3}{r^3} \frac{\frac{k_{out}}{k_{eff}} - 1}{1 + 2 \frac{k_{out}}{k_{eff}}} \right) \left(\frac{dT}{dz} \right)_{\infty} + T_0$$

Eliminating common terms and substituting in the expression for R_{sys}^3 we have,

$$N_p \frac{R_{nano}^3}{r^3} \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} = N_p \frac{R_{nano}^3}{r^3} \frac{1}{\phi} \frac{\frac{k_{out}}{k_{eff}} - 1}{1 + 2 \frac{k_{out}}{k_{eff}}}$$

Cancelling,

$$\phi \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} = \frac{\frac{k_{out}}{k_{eff}} - 1}{1 + 2 \frac{k_{out}}{k_{eff}}}$$

Rearranging for k_{eff} ,

$$\begin{aligned}
\phi \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} &= \frac{k_{out} - k_{eff}}{k_{eff} + 2 k_{out}} \\
(k_{eff} + 2 k_{out}) \phi \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} &= k_{out} - k_{eff} \\
(k_{eff} + 2 k_{out}) \phi \frac{1 - \frac{k_{out}}{k_{in}}}{1 + 2 \frac{k_{out}}{k_{in}}} &= k_{eff} - k_{out} \\
k_{out} \left(2 \phi \frac{1 - \frac{k_{out}}{k_{in}}}{1 + 2 \frac{k_{out}}{k_{in}}} + 1 \right) &= k_{eff} \left(1 - \phi \frac{1 - \frac{k_{out}}{k_{in}}}{1 + 2 \frac{k_{out}}{k_{in}}} \right) \\
k_{out} \left(2 \phi \frac{1 - \frac{k_{out}}{k_{in}}}{1 + 2 \frac{k_{out}}{k_{in}}} + 1 \right) &= k_{eff} \left(1 + \phi \frac{\frac{k_{out}}{k_{in}} - 1}{1 + 2 \frac{k_{out}}{k_{in}}} \right) \\
k_{out} \left(2 \phi \left(1 - \frac{k_{out}}{k_{in}} \right) + 1 + 2 \frac{k_{out}}{k_{in}} \right) &= k_{eff} \left(\phi \frac{k_{out}}{k_{in}} - 1 + 1 + 2 \frac{k_{out}}{k_{in}} \right) \\
k_{out} \left(2 \phi + 1 + 2(1 - \phi) \frac{k_{out}}{k_{in}} \right) &= k_{eff} (\phi + 2) \frac{k_{out}}{k_{in}} \\
\frac{k_{eff}}{k_{out}} &= \frac{\frac{k_{in}}{k_{out}} (2 \phi + 1) + 2(1 - \phi)}{\phi + 2}
\end{aligned}$$