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Thermal Conductivity of Inhomogeneous Materials

P. G. Klemens[1,2]

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The effective thermal conductivity is calculated from the rate of entropy production per unit volume. Thermal conductivity and the temperature field are expressed in terms of Fourier components and these are related. The rate of entropy production is then obtained in terms of the volume-averaged thermal conductivity and the Fourier components of thermal conductivity. A simple expression for the effective thermal conductivity is found. In the case of striations it leads to well-known results. The formalism is applied to solids with inhomogeneously distributed solutes. It is shown that the thermal conductivity is less than the volume-averaged thermal conductivity and that homogenization by diffusion increases the thermal conductivity. Similar results would apply to the electrical conductivity of inhomogeneous alloys.

KEY WORDS: conductivity; diffusion; entropy; Fourier components; solutes; thermal conductivity.

1. INTRODUCTION

The effective thermal conductivity of an inhomogeneous solid, consisting of a mixture of materials of differing conductivities, is a problem which has not been solved in general, even though there are a variety of partial solutions, each suitable in a particular situation. A brief review of these various methods has been given by Parrott and Stuckes [1]. The present treatment cannot claim to be a general solution but is best suited to cases where the conductivity is a function of position, but the change with position is a smooth one, so that the thermal conductivity can be expressed as a Fourier series.

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[1] Centre of Measurements, Instrumentation and Applied Physics, City University, London EC1V OHB, England.

[2] Permanent address: Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, U.S.A.

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The overall or effective thermal conductivity can be expressed in terms of the rate of entropy production in a temperature gradient. In the case when the thermal conductivity K is constant, the rate of entropy production per unit volume is given by

$$\frac{dS}{dt}=\frac{K}{T^2}|\nabla T|^2 \tag{1}$$

where T is the absolute temperature.

In a material with inhomogeneous thermal conductivity the temperature gradient also varies with position. However, in terms of the average temperature gradient $(\nabla T)_0$ the rate of entropy production, averaged over a large volume, still defines an effective thermal conductivity K_e through the relation

$$T^2\left\langle\frac{dS}{dt}\right\rangle=K_e|\nabla T|^2 \tag{2}$$

It is assumed that the thermal conductivity $K(\mathbf{r})$, a function of position $\mathbf{r}$, can be expressed as a Fourier series about the volume-averaged value K_0, so that

$$K(\mathbf{r})=K_0+\sum_{\mathbf{k}}K(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{3}$$

The temperature field will be obtained from the equation of heat conduction in terms of the components $K(\mathbf{k})$, and the rate of entropy production and effective thermal conductivity will likewise be expressed in terms of these components. The effective thermal conductivity will have a simple form; see Eq. (13) below. It will be seen that K_e cannot exeed the volume average K_0. Some simple cases are discussed.

2. TEMPERATURE FIELD

As a result of the inhomogeneous nature of $K(r)$, the temperature gradient is also inhomogeneous. Let the temperature field be of the form

$$T=\mathbf{r}\cdot\nabla T_0+\sum_{\mathbf{q}}T(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}} \tag{4}$$

so that

$$\text{grad } T=\nabla T_0+i\sum_{\mathbf{q}}\mathbf{q}T(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}} \tag{5}$$

The components $T(\mathbf{q})$ and $K(\mathbf{k})$ are related by the equation of heat condition,

$$\operatorname{div} K(\mathbf{r}) \operatorname{grad} T = 0 \tag{6}$$

From Eqs. (3) and (5)

$$\begin{aligned} K \operatorname{grad} T = & -K_0 \nabla T_0 + iK_0 \sum_{\mathbf{q}} \mathbf{q} T(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \\ & + \nabla T_0 \sum_{\mathbf{k}} K(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} + i \sum_{\mathbf{q},\mathbf{k}} \mathbf{q} K(\mathbf{k})\, T(\mathbf{q}) e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} \end{aligned} \tag{7}$$

Therefore

$$\begin{aligned} \operatorname{div} K(\mathbf{r}) \operatorname{grad} T = & -K_0 \sum_{\mathbf{q}} q^2 T(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \\ & + i \sum_{\mathbf{k}} (\nabla T_0 \cdot \mathbf{k})\, K(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - \sum_{\mathbf{k},\mathbf{q}} \mathbf{q}\cdot(\mathbf{k}+\mathbf{q})\, K(\mathbf{k})\, T(\mathbf{q}) e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} \end{aligned} \tag{8}$$

In the first iteration one can disregard the nonlinear term in $K(\mathbf{k})\, T(\mathbf{q})$. Equating each Fourier component separately to zero and writing $\mathbf{q} \cdot \nabla T_0 = q |\nabla T_0| \cos\theta$, one obtains

$$T(\mathbf{q}) = i |\nabla T_0| \cos\theta (K_0 q)^{-1}\, K(\mathbf{q}) \tag{9}$$

This relates the fluctuations in the temperature field to the spatial variations in the thermal conductivity. The neglect of the nonlinear terms can now be justified. If this iteration is substituted into Eq. (8) and one then integrates over space, the only contributions to the double sum come from terms such that $\mathbf{k}+\mathbf{q}=0$, so that $\mathbf{q}\cdot(\mathbf{k}+\mathbf{q})=0$. Hence not only are nonlinear terms of second order in $|\nabla T_0|$, but also they vanish in a spatial average.

3. EFFECTIVE THERMAL CONDUCTIVITY

To obtain the effective thermal conductivity from Eq. (2), one must integrate $\operatorname{grad} T \cdot K(\mathbf{r}) \operatorname{grad} T$ over unit volume. Using Eq. (5) for $\operatorname{grad} T$ and Eq. (3) for $K(\mathbf{r})$, and then integrating,

$$\begin{aligned} & \langle \operatorname{grad} T \cdot K(\mathbf{r}) \operatorname{grad} T \rangle \\ & = K_0 (\nabla T_0)^2 + \sum_{\mathbf{q}} \Big\{ K_0 q^2 T(\mathbf{q})\, T(-\mathbf{q}) + 2i\mathbf{q}\cdot\nabla T_0 T(\mathbf{q})\, K(-\mathbf{q}) \\ & \quad + 2i\mathbf{q}\cdot\nabla T_0 K_0 \int e^{i\mathbf{q}\cdot\mathbf{r}} T(\mathbf{q})\, d\mathbf{r} + (\nabla T_0)^2 \int e^{i\mathbf{q}\cdot\mathbf{r}} K(\mathbf{q})\, d\mathbf{r} \Big\} \\ & \quad \sum_{\mathbf{q},\mathbf{q}',\mathbf{k}} (\mathbf{q}\cdot\mathbf{q}')\, T(\mathbf{q})\, T(-\mathbf{q}')\, K(\mathbf{k}) \int e^{i(\mathbf{q}+\mathbf{k}-\mathbf{q}')\cdot\mathbf{r}}\, dr \end{aligned} \tag{10}$$

The last term is of third order in $|\nabla T_0|$ and is neglected. The fourth and fifth terms vanish on integration over **r**. Using Eq. (9)

$$2i\mathbf{q}\cdot\nabla T_0 T(\mathbf{q})\,K(-\mathbf{q}) = -2(\nabla T_0)^2\frac{\cos^2\theta}{K_0}K(\mathbf{q})\,K(-\mathbf{q}) \tag{11a}$$

$$K_0 q^2 T(\mathbf{q})\,T(-\mathbf{q}) = (\nabla T_0)^2\frac{\cos^2\theta}{K_0}K(\mathbf{q})\,K(-\mathbf{q}) \tag{11b}$$

so that

$$\langle \text{grad}\, T\cdot K(\mathbf{r})\,\text{grad}\, T\rangle = K_0(\nabla T_0)^2 - \frac{(\nabla T_0)^2}{K_0}\sum_{\mathbf{q}}\cos^2\theta K(\mathbf{q})\,K(-\mathbf{q}) \tag{12}$$

By comparison with Eq. (2) one finally obtains the effective thermal conductivity,

$$K_e = K_0 - \frac{1}{K_0}\sum_{\mathbf{q}} K(\mathbf{q})\,K(-\mathbf{q})\cos^2\theta \tag{13}$$

where $\cos\theta$ is the direction cosine of **q** with respect to the overall temperature gradient.

It is of interest to note that the effective thermal conductivity K_e is always less than the volume-averaged conductivity K_0. The only exception occurs when $\cos\theta = 0$ for all significant Fourier components of $K(\mathbf{r})$, i.e., when the inhomogeneities have cylindrical symmetry and are in the plane normal to the temperature gradient. In that special case one can add all heat currents so that $K_e = K_0$.

4. STRIATIONS

In this case all significant Fourier components of $K(\mathbf{r})$ point in the same direction, so that all values of $\cos\theta$ are the same, and $K(\mathbf{r})$ is constant over all planes normal to one direction in space. In the case when $\cos\theta = 0$, $K_e = K_0$, as before. In the opposite case, when $\cos\theta = 1$, one must average the thermal resistivity over volume. One can readily show that K_e is less than K_0, so that

$$K_e = K_0 - \Delta K \tag{14}$$

where

$$\Delta K = \frac{1}{K_0}\sum_{\mathbf{k}} K(\mathbf{k})\,K(-\mathbf{k}) \tag{15}$$

since all values of **k** lie in one direction.

If the direction of the temperature gradient makes an angle θ with the direction normal to the striation planes,

$$K_e = K_0 - \Delta K \cos^2 \theta \tag{16}$$

5. INHOMOGENEOUS SOLUTE DISTRIBUTION

Solutes depress the thermal conductivity of solids. The variation of thermal conductivity with solute content c for a small change δc is thus of the form

$$\delta K = -\beta K(c)\, \delta c \tag{17}$$

In the case of metals and dilute alloys

$$\beta \sim 100(300/T) \tag{18a}$$

where T is the absolute temperature. In the case of mixed dielectric crystals,

$$\beta \sim 30(300/T)^{1/2} \tag{18b}$$

In the case of concentrated alloys, where the thermal conductivity is partly electronic and partly due to lattice waves, β is intermediate between $\beta \sim 1/c$ and the value of Eq. (18b). In these equations c is the fraction of solutes per atom [2].

If one can express the spatial variation of solute content about an average value c_0 in terms of a Fourier expansion,

$$c(\mathbf{r}) - c_0 = \sum_{\mathbf{k}} c(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{19}$$

then $K(\mathbf{k})$ of Eq. (3) becomes

$$K(\mathbf{k}) = -\beta K_0 c(\mathbf{k}) \tag{20}$$

A case of interest is when $c(\mathbf{r})$ is a function of radial distance r only; this corresponds to solute clusters of spherical symmetry such that there is no correlation in the position of neighboring clusters. In this case $c(k)$ is independent of the direction of k. For a domain of unit volume, now taken as a sphere of radius $R = (4\pi/3)^{-1/3}$,

$$c(k) = \int_0^R c(r)(2\pi/k) r \sin(kr)\, dr \tag{21}$$

and

$$\sum_{\mathbf{k}} c(\mathbf{k})\, c(-\mathbf{k}) = \int_0^{2\pi/R} (2\pi)^{-3} 4\pi k^2 [c(k)]^2\, dk \tag{22}$$

This formalism is particularly suited to treat homogenization of the solute content by diffusion. Let the diffusion coefficient for the solutes at the temperature of homogenization be D, and let that temperature be applied for a time t. Diffusion reduces each Fourier component according to

$$\frac{\partial}{\partial t} c(k) = -k^2 D c(k) \tag{23}$$

so that, treating $c(k)$ as function of t with an initial value $c(k, 0)$,

$$c(k, t) = c(k, 0) e^{-k^2 Dt} \tag{24}$$

Diffusion will remove all Fourier components with $k > (Dt)^{-1/2}$. The effective thermal conductivity, using Eqs. (13) and (20), can be written as

$$K_e = K_0 \left[1 - \beta^2 \sum_{\mathbf{k}} c(\mathbf{k})\, c(-\mathbf{k}) \right] \tag{25}$$

so that inhomogeneities reduce the thermal conductivity. Diffusion, by reducing the contribution of higher Fourier components, will thus increase the thermal conductivity, provided of course that no additional solutes or impurities are introduced into the solid while it is being heated. Thus, for solute clusters of spherical symmetry, diffusion effectively reduces the upper limit of integration in Eq. (22) to $k = (Dt)^{-1/2}$.

Consider, for example, an alloy containing N cluster per unit volume, each having a solute concentration

$$c(r) = r_0/r \tag{26}$$

so that, for one cluster in unit volume, according to Eq. (21),

$$c(k) = 2\pi r_0/k^2 \tag{27}$$

Thus for a single cluster according to Eq. (22),

$$\sum_{\mathbf{k}} c(\mathbf{k})\, c(-\mathbf{k}) = 2r_0^2 \left[\frac{1}{k_{\min}} - \frac{1}{k_{\max}} \right] \tag{28}$$

For N clusters per unit volume, if their relative position is not correlated,

$$\sum_{\mathbf{k}} c(\mathbf{k})\, c(-\mathbf{k}) = 2r_0^2 N[2\pi N^{-1/3} - 1/k_{\max}] \tag{29}$$

If the material was not homogeneized, $1/k_{\max}=0$. After homogenization for a time t with a diffusion coefficient D, $1/k_{\max}=(Dt)^{1/2}$ and

$$\sum_{\mathbf{k}} c(\mathbf{k})\, c(-\mathbf{k}) = 2r_0^2 N[2\pi N^{-1/3} - (Dt)^{1/2}] \tag{30}$$

Now let $\beta^2 = 1\times 10^4$, $r_0 = 1\times 10^{-7}$ cm, and $N = 10^{12}$ cm^{-3}, then from Eqs. (30) and (25),

$$\Delta K = K_0 - K_e = 0.04 K_0 \tag{31}$$

provided no diffusion had occurred. It would require homogenization for a time such that $(Dt)^{1/2}$ was about 6×10^{-4} cm to reduce ΔK to zero.

Longer annealing would make $(Dt)^{1/2}$ larger than $1/k_{\min}$, and expression (29) would be zero.

The crition for effective homogenization, that

$$(Dt)^{1/2} > {\sim} N^{-1/3} \tag{32}$$

does of course also follow from the need that the distance of diffusion should exceed the average separation between clusters.

6. SUMMARY

By expressing the variations of the thermal conductivity in Fourier components, a simple expression was obtained for the effective thermal conductivity. This effective value is usually less than the volume average of the thermal conductivity and cannot exceed it. The formalism is well suited to cases when inhomogeneous solute distributions cause inhomogeneities in the thermal conductivity, especially since changes due to diffusion can be represented simply in terms of Fourier components.

While this paper addressed itself explicitly to thermal conductivity, the same method can also be used for the effects of inhomogeneity on electrical conductivity.

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REFERENCES

1 J. E. Parrott and A. D. Stuckes, *Thermal Conductivity of Solids* (Pion, London, 1976).
2. P. G. Klemens and R. K. Williams, *Int. Metals Rev.* **31**:197 (1986).