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Damped Thermoelectric Waves

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Abstract

Dynamic measurement techniques such as ac resistivity and the Cahill 3-ω [1] thermal conductivity method induce periodic currents in materials. In thermoelectric materials the coupling between electrical and thermal effects means the normal mode excitations are generally attenuated waves of mixed electrical/thermal character. Since ZT is one measure of the coupling between the electrical and thermal effects it is perhaps not surprising that ZT is also a measure of the mixing. This paper examines solutions to the coupled thermoelectric diffusion problem and discusses some implications for measurements.

Introduction

Diffusion of heat and charge in solids is ordinarily well described by the approximate diffusion equations

$$\begin{aligned} \dot{h} &= d_e \nabla^2 h \\ \dot{T} &= d_q \nabla^2 T \end{aligned} \qquad (1)$$

where *h* is the electrical potential (or more precisely, the electrochemical potential), *T* is the temperature, and d_e and d_q are the electrical and thermal diffusivities. These diffusion equations derive from conservation of energy and charge considerations, with only a few simplifying assumptions.

In thermoelectric materials heat and electricity are coupled, an effect neglected above. This paper seeks to identify when the above expressions are adequate and when a more complete treatment is required.

First, the coupled diffusion equations are derived and the characteristic eigenvalue problem is solved to identify the normal modes. The resulting eigenvalues represent diffusivity values for coupled temperature-potential diffusion and the eigenvectors indicate the degree to which temperature and potential diffusion are mixed in the normal modes. Next the behavior of the normal mode diffusion constants is examined as a function of coupling. And as an example, the coupled boundary-value problem corresponding to the 'flash' method of determining the thermal diffusivity is considered.

Thermoelectric Diffusion Equations

The first task is to write the problem in terms of measurable properties. Start with conservation of charge and energy

$$\begin{aligned} \dot{r} + \nabla \cdot \bar{i} &= 0 \\ \dot{U} + \nabla \cdot \bar{U} &= 0 \end{aligned} \qquad (2)$$

and definitions of the entropy flux ($\bar{S}$) and time rate of change of the entropy density ($\dot{S}$)

$$\begin{aligned} T\bar{S} &= \bar{U} - h\bar{i} \\ T\dot{S} &= \dot{U} - h\dot{r} \end{aligned} \qquad (3).$$

Combining (2) and (3) and defining an entropy source term, *s*,

$$\begin{aligned} s &\equiv \frac{1}{T}\left(\bar{S} \cdot (-\nabla T) + \bar{i} \cdot \bar{E}\right) \\ \dot{S} &+ \nabla \cdot \bar{S} = s \end{aligned} \qquad (4)$$

allows connection to the ordinary transport coefficients, assuming the currents are linearly proportional to the gradients of the potentials, by

$$\begin{aligned} \bar{i} &= s\left(\bar{E} - a\bar{\nabla} T\right) \\ \bar{S} &= a\bar{i} - \left(\frac{l}{T}\right)\bar{\nabla} T \end{aligned} \qquad (5).$$

Using a more compact matrix notation.

$$\begin{pmatrix} \bar{i} \\ \bar{S} \end{pmatrix} = L \begin{pmatrix} \bar{E} \\ -\bar{\nabla} T \end{pmatrix} \qquad (6)$$

with the transport matrix *L* given by

$$L = \begin{pmatrix} s & sa \\ sa & l g_L / T \end{pmatrix} \qquad (7).$$

Here ***i*** is the electric current density, ***E*** is the electric field, ∇*T* is the temperature gradient, *s* is the electrical conductivity, α is the Seebeck coefficient and *l* is the thermal conductivity (measured under the condition $\bar{i}=0$). g_L is a convenient measure of the relative strength of the thermoelectric effects

$$\begin{aligned} g_L &\equiv 1 + \frac{L_{12}{}^2}{L_{11}L_{22} - L_{12}{}^2} \\ &= 1 + \frac{sa^2 T}{l} \\ &\equiv 1 + ZT \end{aligned} \qquad (8)$$

where ZT is the dimensionless thermoelectric figure of merit.

Within the same linear response regime, the time variations as can be written

$$\begin{aligned} \dot{r} &= C_{11}\dot{h} + C_{12}\dot{T} \\ \dot{S} &= C_{21}\dot{h} + C_{22}\dot{T} \end{aligned} \qquad (9)$$

which is conveniently summarized in matrix form as

$$\begin{pmatrix} \dot{r} \\ \dot{S} \end{pmatrix} = C \begin{pmatrix} \dot{h} \\ \dot{T} \end{pmatrix} \qquad (10).$$

with the capacity matrix, *C*, given by various thermodynamic derivatives.

The symmetry of *C* is a consequence of the second law of thermodynamics and the off-diagonal elements (C_{12} and C_{21}) are exactly equal. C_{22}-$C_{12}{}^2/C_{11}$ is essentially the heat capacity. C_{11} is related to the carrier concentration although in general it is a slightly more complex quantity. C_{21} represents the change in entropy (or heat) when the charge is changed isothermally and C_{12} represents the change in charge with temperature, keeping the electrochemical potential constant. In principle each coefficient can be both calculated and measured, although the cross coefficients rarely are.

A 'γ' can be defined for the C matrix as well

$$g_C = 1 + \frac{C_{12}{}^2}{C_{11}C_{22} - C_{12}{}^2},$$

which again is a convenient measure of the relative magnitude of the cross effects.

Combining conservation of energy and charge with linear response considerations yields the coupled diffusion equations

$$\left[C\frac{\partial}{\partial t} - \nabla L \nabla\right]\begin{bmatrix} h \\ T \end{bmatrix} = \begin{bmatrix} 0 \\ s \end{bmatrix} \qquad (11).$$

For the remainder of this paper the entropy source term will be neglected and the C and L matrices will be treated as constants, independent of chemical potential and temperature. The non-linearities so neglected, however, can in principle lead to a variety of interesting behavior.

The coupled diffusion problem may be solved using the usual methods. Solutions which oscillate in space and decay with time like

$$\begin{bmatrix} h \\ T \end{bmatrix} = \begin{bmatrix} h_o \\ T_o \end{bmatrix} e^{-ak^2t + jkx} \qquad (12)$$

or which oscillate in time and decay exponentially in space like

$$\begin{bmatrix} h \\ T \end{bmatrix} = \begin{bmatrix} h_o \\ T_o \end{bmatrix} e^{jwt + (j-1)\sqrt{\frac{w}{2a}}x} \qquad (13)$$

are possible. The first case is often useful for initial value problems, where for example the potential and temperature distribution are known at some initial time and one wishes to know the future time evolution of these functions. This case will be examined below. The second case occurs in methods where the potential (or temperature) is forced to oscillate at a fixed frequency, such as in an ac resistivity measurement (or an Ångstrom [2] or Cahill 3-ω [1] thermal conductivity measurement).

Solution of the characteristic equation yields the eigenvalues

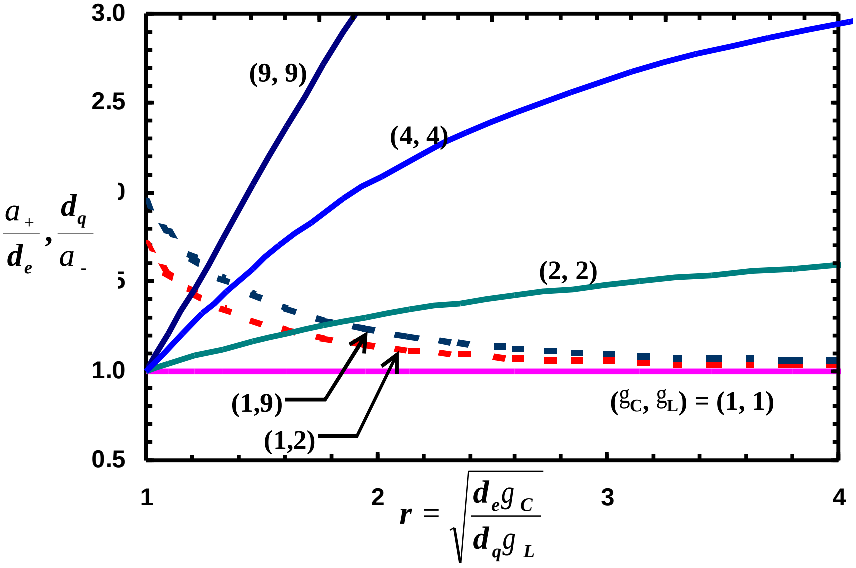

Figure 1: Actual diffusivity values a_+ and a_- as functions of the diffusion constants d_e and d_q neglecting coupling and the magnitude of thermoelectric coupling (g_C, g_L).

$$a_{\pm} = \frac{1}{2}\sqrt{d_e d_q g_C g_L}\left(b \pm \sqrt{b^2 - 4/g_C g_L}\right)$$

$$b = r + 1/r - 2\sqrt{\left(1 - \frac{1}{g_C}\right)\left(1 - \frac{1}{g_L}\right)} \qquad (14)$$

$$r = \sqrt{\frac{d_e g_C}{d_q g_L}}$$

where

$$d_e = \frac{L_{11}}{C_{11}}$$

$$d_q = \frac{L_{22} - L_{12}{}^2/L_{11}}{C_{22} - C_{12}{}^2/C_{11}} \qquad (15)$$

are the usual electrical and thermal diffusivity values for the respective uncoupled diffusion problems.

Thus the eigenvalues depend on the two uncoupled diffusivity values and on the coupling between electrical and thermal effects represented by the two γ values.

The two eigenvectors are given by

$$\frac{h_{o\pm}}{T_{o\pm}} = -\frac{(a_{\pm}C_{12} - L_{12})}{(a_{\pm}C_{11} - L_{11})} \qquad (16),$$

which again illustrates that in the absence of thermoelectric coupling (C_{12}=L_{12}=0), the solutions uncouple to one purely electrical diffusion solution and another purely temperature diffusion solution.

Behavior of the eigenvalues

The two eigenvalues a_+ and a_- represent two diffusion constants which appear in two independent solutions of the form given by Eqs. 12 or 13. In a great many materials the electrical diffusivity (d_e) is greater than the thermal diffusivity (d_q), sometimes very much greater, so it is natural to identify the larger eigenvalue a_+ as an 'electric-like' diffusion coefficient and the smaller eigenvalue, a_-, as a 'heat-like' diffusion coefficient. It is important to note, however, that so long as thermoelectric coupling is not zero each solution involves time and spatial variations of both the electrochemical potential and the temperature. Further, when $d_e < d_q$ (which is true for some poor mobility materials) the identification of 'electric-like' or 'heat-like' can become ambiguous and the roles of a_+ and a_- can reverse.

The constants d_e and d_q represent the diffusivity values expected in the absence of thermoelectric effects, but a_+ and a_- are the diffusivity values which one observes in dynamic laboratory measurements. Fig. 1 illustrates how the observed diffusivity values (a_+ and a_-) depend on d_e and d_q and on the degree of coupling.

Fig. 1 shows the thermoelectric coupling can significantly modify the actual diffusivity values compared to the values expected in the absence of coupling. The situation is particularly severe when both types of coupling are large (i.e. when g_C and g_L>>1). For most materials, however, thermoelectric coupling is small (g_C and g_L only slightly greater than 1) and the actual diffusivity values are little modified from the uncoupled values d_e and d_q.

For d_e>>d_q the first order corrections to the diffusivity is given by

$$a_+ \cong d_e g_C + d_q\left(g_L - \frac{1}{g_C}\right) - 2\sqrt{d_e d_q (g_C - 1)(g_L - 1)} \qquad (17).$$
$$a_- = d_e d_q / a_+$$

Eq. 17 illustrates that the corrections depend on the departure from no coupling (i.e. g_C-1 and g_L-1), a delicate balance between the two types of thermoelectric coupling (g_C vs. g_L), and on the relative magnitudes of the two uncoupled diffusivity values (d_e and d_q).

Thermal Flash Diffusivity

The flash technique (Fig. 2) developed by Parker et al [3] for determining thermal diffusivity is relatively simple, fast and insensitive to heat loss.

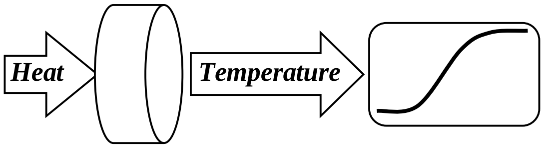

Figure 2: 'Flash' methods determine thermal diffusivity on thin, disk-shaped samples from the temperature vs. time response of the front face.

The boundary conditions for the flash method are that no heat or charge enters or leaves the sample, except during a brief period (short compared with any characteristic internal diffusion time) when heat is deposited on the rear face of the sample. The mathematical problem including the effects of thermoelectric coupling is solved using techniques essentially identical to a heat flow problem discussed by Carslaw and Jaeger [4], except that here two independent solutions are required to conserve charge. The time dependence of the electrochemical potential and temperature of back face of the sample are given by

$$\begin{aligned} h &= T_\infty\left\{A_+ B_+ f\left(a_+ t/L^2\right) + A_- B_- f\left(a_- t/L^2\right)\right\} \\ T &= T_\infty\left\{A_+ f\left(a_+ t/L^2\right) + A_- f\left(a_- t/L^2\right)\right\} \end{aligned} \qquad (18)$$

with

$$A_\pm = \mathbf{m}\frac{\left(\dfrac{C_{12}}{C_{11}} + B_{\mathbf{m}}\right)}{\left(B_+ - B_-\right)}$$
$$B_\pm = -\frac{\left(a_\pm C_{12} - L_{12}\right)}{\left(a_\pm C_{11} - L_{11}\right)} \qquad (19)$$
$$f(x) = 1 + 2\sum_{n=1}^{\infty}(-1)^n e^{\left(-n^2 p^2 x\right)}$$

and

$$T_\infty = \frac{Q_o/T_o}{C_{22} - C_{12}{}^2/C_{11}} \qquad (20)$$

Q_o is the total heat deposited in the sample at temperature T_o. These solutions ensure that no electrical charge enters or leaves the surfaces at any time, even during the heat flash itself.

The time dependence of the temperature of the back face is given by the sum of two terms: 1) an 'electric-like' term with amplitude A_+ propagating with a characteristic diffusion time governed by $\alpha_+$and 2) a 'heat-like' term with amplitude A_- propagating with a characteristic diffusion time governed by α_-. Fig. 3 illustrates how the amplitude of more slowly propagating 'heat-like' portion of the temperature response varies with relative magnitude of the two uncoupled diffusivity values (d_e and d_q) and the degree thermoelectric coupling (represented by g_C and g_L).

Again, thermoelectric coupling significantly modifies the results compared to the values expected in the absence of coupling. When both types of coupling are large (i.e. when g_C and g_L>>1) the 'heat-like' contribution can actually become a small faction of total temperature response. For most materials, however, thermoelectric coupling is small (g_C and g_L only slightly greater than 1) and the 'heat-like' component dominates the temperature response, as expected

When corrections are large

From the above discussion it appears that no special precautions are required when interpreting diffusivity measurements when both types of thermoelectric coupling are small (i.e., when g_C and g_L are only slightly greater than 1) When only one type of coupling is strong (i.e. g_C>>1 or g_L >>1, but not both) the actual diffusivity values will be given by the uncoupled values (d_e or d_q) except when these are similar in magnitude. In other cases, the full roots given by Eq. 14 are required.

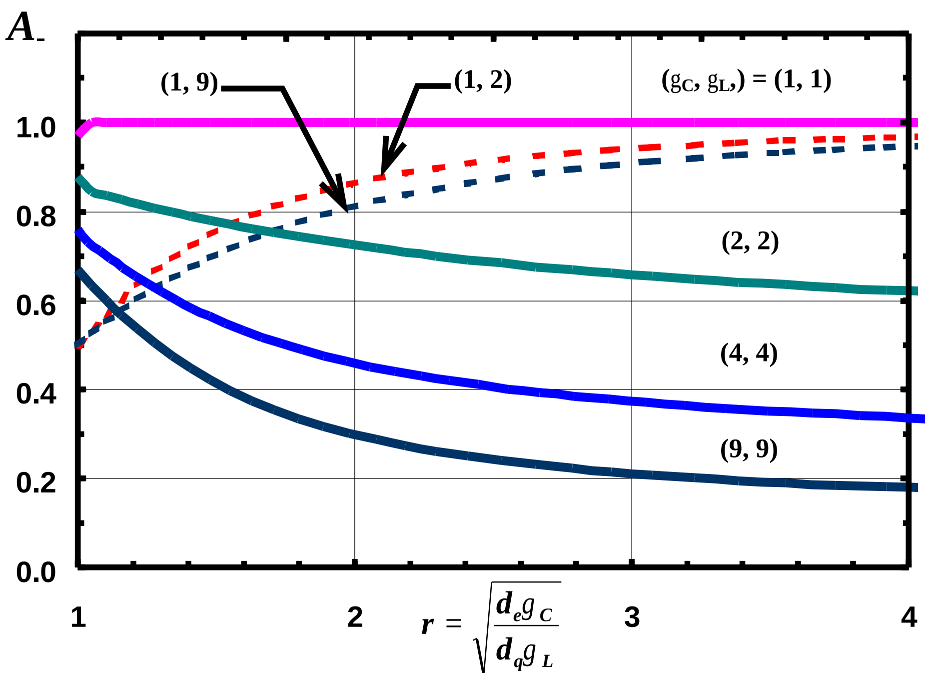

Figure 3: Amplitude of the 'heat-like' response as a function of the diffusion constants neglecting coupling (d_e and d_q) and the magnitude of the coupling (g_C and g_L).

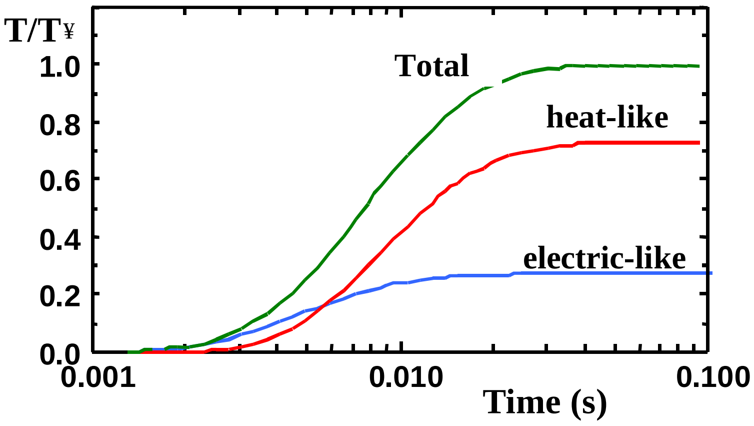

Figure 4: Temperature vs. time response for a flash diffusivity measurement on a hypothetical metal 1 mm thick with $\gamma_C \sim 2$ and $\gamma_L \sim 2$.

Fig. 4 illustrates one kind of error which can occur in extreme cases. Here, diagonal coefficients corresponding approximately to Pd have been combined with hypothetical off-diagonal coefficients to give $\gamma_C \sim 2$ and $\gamma_L \sim 2$ and the results of a flash diffusivity experiment on this hypothetical metal was calculated. While the total time dependence of the back face looks qualitatively similar to the uncoupled case (which has the shape of either of the individual contributions labeled 'heat-like' and 'electric-like'), it is acually much more complex depending on three new materials parameter (d_e,, γ_C, and γ_L) in addition to the uncoupled thermal diffusivity (d_q).

This example is not intended to represent realistic properties, but it illustrates some difficulties which may be encountered. Ordinarily, a key advantage of diffusivity measurements is that only a single number (such as $t_{0.5}$, the time required for the backface temperature to reach 1/2 of its' final value) is required. Times can be determined with great precision and accuracy, so a simple measurement of times can yield important experimental information.

In the case of thermoelectric coupling, four materials parameters (two diffusivities and two coupling parameters) determine the time dependence of the temperature of the backface temperature and more careful analysis is required to extract the material properties. Indeed, when other corrections such as heat loss and finite duration of the flash are considered (as has been done for the uncoupled problem [3]), extraction of reliable values for materials properites becomes problematic.

Conclusion

Characterization of electrical and thermal properties of materials using dynamic methods (i.e. using time dependent external perturbations) is more complex in materials with strong thermelectric effects because the response generally exhibits both 'electric-like' and 'heat-like' components, each with characteristic diffusion constants modified compared to the uncoupled diffusion constants. In most materials thermoelectric coupling will be negligible but it would be of interest to confirm the effects described in this paper by analysis of high-precision diffusivity experiments on, for example, metallic thermocouple .materials where the coupling effects may be within experimental resolution.

References

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