International Journal of Engineering Science 74 (2014) 143–150

Contents lists available at ScienceDirect

International Journal of Engineering Science

journal homepage: www.elsevier.com/locate/ijengsci

On cross-correlation between thermal gradients and electric fields

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ARTICLE INFO

Article history:

Communicated by M. Kachanov

Keywords:
Effective properties
Cross-correlations
Heterogeneous materials

ABSTRACT

An important phenomenon in the field of thermoelectric conversion in certain materials is the *Seebeck* effect, which is characterized by an electrical field, $\boldsymbol{E}$ being produced by a temperature gradient, $\boldsymbol{E} = S\nabla\theta$, where S is known as the (isotropic) Seebeck number. The objective of this note is to develop bounds on the effective thermoelectric Seebeck property for heterogeneous mixtures of materials. Specifically, we develop bounds on $\langle \boldsymbol{E} \rangle_\Omega = S^* \langle \nabla\theta \rangle_\Omega$, where S^* is the effective Seebeck number for the mixture, where the averaging operator is defined as $\langle\cdot\rangle_\Omega \stackrel{\text{def}}{=} \frac{1}{|\Omega|}\int_\Omega (\cdot)\, d\Omega$ over a statistically representative volume element with domain Ω, using only the pointwise cross-correlation properties of the material and the average thermal fields. .

1. Introduction and objective

A cross-correlation phenomenon that has recently become of high interest is thermoelectricity, which deals with the conversion of thermal energy into electrical energy, and vice versa.[1] Unlike Joule-heating, the effects can be reversible. Essentially, one can generate current from a temperature difference. One important phenomena in this area is the *Seebeck Effect*, which is characterized by an electrical field, $\boldsymbol{E}$ being produced by a temperature gradient

$$\boldsymbol{E} = S\nabla\theta, \tag{1.1}$$

where S is known as the (isotropic) Seebeck number and where the thermal heat flux is related to the temperature gradient, for example, by $\boldsymbol{q} = \mathbb{K}\nabla\theta$, where $\mathbb{K}$ is the thermal conductivity. The objective in this note is to derive bounds for the effective Seebeck number for a heterogeneous materials, such as particulate-doped mixtures of materials (Fig. 1).

$$\langle \boldsymbol{E} \rangle_\Omega = S^* \langle \nabla\theta \rangle_\Omega, \tag{1.2}$$

where S^* is the effective Seebeck number for the mixture, where the averaging operator is defined as $\langle\cdot\rangle_\Omega \text{def} = \frac{1}{|\Omega|}\int_\Omega (\cdot)\, d\Omega$ over a statistically representative volume element with domain Ω, with only knowledge of the pointwise relations and the $\mathbb{K}^*$ is the effective thermal conductivity, relating the volume averaged thermal heat flux $\langle \boldsymbol{q} \rangle_\Omega$ to the temperature gradient $\langle \nabla\theta \rangle_\Omega$, $\langle \boldsymbol{q} \rangle_\Omega = -\mathbb{K}^* \langle \nabla\theta \rangle_\Omega$. As a model problem, we will consider a two-phase heterogeneous material. The analysis will proceed by developing phase field concentration functions for the thermal gradient in each component in the heterogeneous material and then using the concentration functions to develop estimates for the overall Seebeck number.

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[1] In particular, this interest is driven by thermal scavaging applications.

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http://dx.doi.org/10.1016/j.ijengsci.2013.09.003

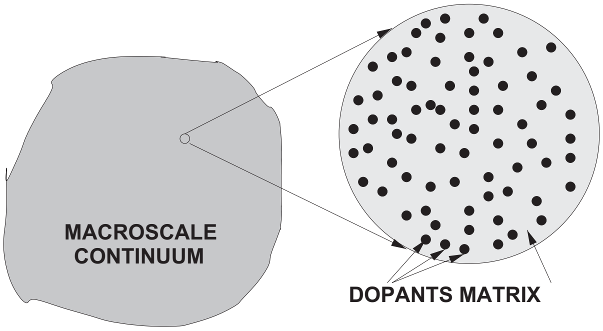

Fig. 1. A material doped with second phase particles.

Remark 1. Cross-correlations can be rather involved, for example in elastic applications, and we refer the reader to the extensive works of Kachanov, Sevostianov, and Shafiro (2001) and Sevostianov and Kachanov (2001, 2002, 2003, 2008a, 2008b, 2009a, 2009b) for cross-correlation property analysis connecting elastic and conductive properties. We note that in those works, the cross-correlated properties are not based on point-wise cross-correlations.

2. Phase-wise field decompositions

In this paper, as a model problem, we will consider a statistically representative volume element (RVE of volume $|\Omega|$) of a two-phase medium, as depicted in Fig. 1. The microscale properties are characterized by a spatially variable thermal conductivity $\mathbb{K}(\boldsymbol{x})$, electrical conductivity $\boldsymbol{\sigma}(\boldsymbol{x})$ and Seebeck $S(\boldsymbol{x})$ number. For example, for such a sample, one can decompose the thermal field carried by each phase in the material as follows

$$\langle \nabla\theta \rangle_\Omega = \frac{1}{|\Omega|}\left(\int_{\Omega_1} \nabla\theta\, d\Omega + \int_{\Omega_2} \nabla\theta\, d\Omega\right) = v_1 \langle \nabla\theta \rangle_{\Omega_1} + v_2 \langle \nabla\theta \rangle_{\Omega_2} \tag{2.1}$$

and for the electrical field

$$\langle \boldsymbol{E} \rangle_\Omega = \frac{1}{|\Omega|}\left(\int_{\Omega_1} \boldsymbol{E}\, d\Omega + \int_{\Omega_2} \boldsymbol{E}\, d\Omega\right) = v_1 \langle \boldsymbol{E} \rangle_{\Omega_1} + v_2 \langle \boldsymbol{E} \rangle_{\Omega_2}, \tag{2.2}$$

where Ω_1 is the domain of phase one and Ω_2 is the domain of phase two. v_1 and v_2 are the volume fractions of phases one and two respectively ($v_1 + v_2 = 1$). We denote $v_1\langle \nabla\theta \rangle_{\Omega_1}$ and $v_2\langle \nabla\theta \rangle_{\Omega_2}$ as the "thermal load shares", since[2]

$$v_1 \langle \nabla\theta \rangle_{\Omega_1} + v_2 \langle \nabla\theta \rangle_{\Omega_2} = \langle \nabla\theta \rangle_\Omega. \tag{2.3}$$

A key to obtaining the effective Seebeck number is to determine the load-shares as functions of known (a priori) quantities

$$\langle \nabla\theta \rangle_{\Omega_1} = \mathcal{F}_1(v_1, \mathbb{K}_1, \mathbb{K}_2, \langle \nabla\theta \rangle_\Omega) \tag{2.4}$$

and

$$\langle \nabla\theta \rangle_{\Omega_2} = \mathcal{F}_2(v_1, \mathbb{K}_1, \mathbb{K}_2, \langle \nabla\theta \rangle_\Omega), \tag{2.5}$$

where $\mathbb{K}_1$ and $\mathbb{K}_2$ are the conductivities of phase one and phase two respectively.

3. Concentration functions and load shares

A useful quantity that arises in the analysis of heterogeneous materials is the effective conductivity, $\mathbb{K}^*$, defined via[3]

$$\langle \mathbf{q} \rangle_\Omega = -\mathbb{K}^* \cdot \langle \nabla\theta \rangle_\Omega, \tag{3.1}$$

which is the macroscopic "property". Decomposing the righthand side yields

[2] For solids with cracks and non-spherical pores, such as thin platelets, the volume fraction is an inadequate microstructural parameter. For an indepth analysis of the proper microstructural parameters, we refer the reader to Kachanov (1999).

[3] Implicitly, we assume that (a) the contact between the phases is perfect and (b) the ergodicity hypothesis is satisfied (see Kröner (1972) or Torquato (2002)).

$$-\mathbb{K}^* \cdot \langle \nabla\theta \rangle_\Omega = \langle \boldsymbol{q} \rangle_\Omega = v_1 \langle \boldsymbol{q} \rangle_{\Omega_1} + v_2 \langle \boldsymbol{q} \rangle_{\Omega_2} = -\left(v_1 \mathbb{K}_1 \cdot \langle \nabla\theta \rangle_{\Omega_1} + v_2 \mathbb{K}_2 \cdot \langle \nabla\theta \rangle_{\Omega_2} \right)$$

$$= -\left(\mathbb{K}_1 \cdot (\langle \nabla\theta \rangle_\Omega - v_2 \langle \nabla\theta \rangle_{\Omega_2}) + v_2 \mathbb{K}_2 \cdot \langle \nabla\theta \rangle_{\Omega_2} \right) = -\left(\underbrace{(\mathbb{K}_1 + v_2(\mathbb{K}_2 - \mathbb{K}_1) \cdot \mathbf{C}_{\theta,2})}_{\mathbb{K}^*} \cdot \langle \nabla\theta \rangle_\Omega \right), \tag{3.2}$$

where

$$\underbrace{\left(\frac{1}{v_2} (\mathbb{K}_2 - \mathbb{K}_1)^{-1} \cdot (\mathbb{K}^* - \mathbb{K}_1) \right)}_{\stackrel{\text{def}}{=} \mathbf{C}_{\theta,2}} \cdot \langle \nabla\theta \rangle_\Omega = \langle \nabla\theta \rangle_{\Omega_2}. \tag{3.3}$$

$\mathbf{C}_{\theta,2}$ is known as the gradient concentration tensor. Thus, the product of $\mathbf{C}_{\theta,2}$ with $\langle \nabla\theta \rangle_\Omega$ yields $\langle \nabla\theta \rangle_{\Omega_2}$. *Once either $\mathbf{C}_{\theta,2}$ or $\mathbb{K}^*$ are known, the other can be computed.*

In order to determine the concentration tensor for phase one, from Eq. (2.1), we have

$$\langle \nabla\theta \rangle_{\Omega_1} = \frac{\langle \nabla\theta \rangle_\Omega - v_2 \langle \nabla\theta \rangle_{\Omega_2}}{v_1} = \frac{(\mathbf{1} - v_2 \mathbf{C}_{\theta,2}) \cdot \langle \nabla\theta \rangle_\Omega}{v_1} \stackrel{\text{def}}{=} \mathbf{C}_{\theta,1} \cdot \langle \nabla\theta \rangle_\Omega, \tag{3.4}$$

where

$$\mathbf{C}_{\theta,1} = \frac{1}{v_1} (\mathbf{1} - v_2 \mathbf{C}_{\theta,2}) = \frac{\mathbf{1} - v_2 \mathbf{C}_{\theta,2}}{1 - v_2}. \tag{3.5}$$

Note that Eq. (3.5) implies

$$\underbrace{v_1 \mathbf{C}_{\theta,1}}_{\text{phase-1 contribution}} + \underbrace{v_2 \mathbf{C}_{\theta,2}}_{\text{phase-2 contribution}} = \mathbf{1}. \tag{3.6}$$

Summarizing, we have the following results:

- $\mathbf{C}_{\theta,1} \cdot \langle \nabla\theta \rangle_\Omega = \langle \nabla\theta \rangle_{\Omega_1}$ where $\mathbf{C}_{\theta,1} = \frac{1}{v_1} (\mathbf{1} - v_2 \mathbf{C}_{\theta,2}) = \frac{\mathbf{1} - v_2 \mathbf{C}_{\theta,2}}{1 - v_2}$,
- $\mathbf{C}_{\theta,2} \cdot \langle \nabla\theta \rangle_\Omega = \langle \nabla\theta \rangle_{\Omega_2}$ where $\mathbf{C}_{\theta,2} = \frac{1}{v_2} (\mathbb{K}_2 - \mathbb{K}_1)^{-1} \cdot (\mathbb{K}^* - \mathbb{K}_1)$.

Remark 2. The overall volume averages, $\langle \nabla\theta \rangle_\Omega$ and $\langle \boldsymbol{q} \rangle_\Omega$, are considered known, since they can be determined by standard averaging theorems, discussed in Appendix A.

Remark 3. In many cases, the thermal flux in each phase is of interest, particularly in particulate-doped materials where matrix ligament overheating and damage is a concern. The thermal flux in each phase can be derived from the thermal gradient concentration function (Appendix B).

4. Bounds on the concentration functions

4.1. The effective thermal response

Because the concentration functions depend on $\mathbb{K}^*$, which in turn depends on $\mathbb{K}_1, \mathbb{K}_2, v_2$, and the microstructure, we need to employ estimates for $\mathbb{K}^*$. One class of estimates are the Hashin–Shtrikman bounds Hashin and Shtrikman (1962) for two isotropic materials with an overall isotropic response

$$\underbrace{\mathbb{K}_1 + \frac{v_2}{\frac{1}{\mathbb{K}_2 - \mathbb{K}_1} + \frac{1 - v_2}{3\mathbb{K}_1}}}_{\mathbb{K}^{*,+}} \leqslant \mathbb{K}^* \leqslant \underbrace{\mathbb{K}_2 + \frac{1 - v_2}{\frac{1}{\mathbb{K}_1 - \mathbb{K}_2} + \frac{v_2}{3\mathbb{K}_2}}}_{\mathbb{K}^{*,+}}, \tag{4.1}$$

where the thermal conductivity of phase two (with volume fraction v_2) is larger than phase one ($\mathbb{K}_2 \geqslant \mathbb{K}_1$). Provided that the volume fractions and constituent conductivities are the only known information about the microstructure, the expressions in Eq. (4.1) are the tightest bounds for the overall isotropic effective responses for two phase media, where the constituents are both isotropic. A critical observation is that the lower bound is more accurate when the material is composed of high conductivity particles that are surrounded by a low conductivity matrix (denoted case 1) and the upper bound is more accurate for a high conductivity matrix surrounding low conductivity particles (denoted case 2). The last comments on the accuracy of the lower or upper bounds can be qualitatively explained by considering the two cases with 50% low conductivity material and 50% high conductivity material. A material with a continuous low conductivity binder (50%) will isolate the high conductivity particles (50%), and the overall system will not conduct heat well (this is case 1 and the lower bound is more accurate), while a material formed by a continuous high conductivity binder (50%) surrounding low conductivity particles (50%, case 2) will, in an overall sense, conduct heat better than case 1. Thus, case 2 is more closely approximated by the upper bound and case 1 is closer to the lower bound.

Remark 4. The literature on methods to estimate the overall macroscopic properties of heterogeneous materials dates back at least to Maxwell (1867, 1873) and Rayleigh (1892), For an authoritative review of (a) the general theory of random heterogeneous media see, for example, Torquato (2002), (b) for more mathematical homogenization aspects, see Jikov, Kozlov, and Olenik (1994), (c) for solid-mechanics inclined accounts of the subject see, for example, Hashin (1983), Mura (1993) or Markov (2000) and (d) for computational aspects see Ghosh (2011),hosh and Dimiduk (2011) and Zohdi and Wriggers (2008).

4.2. The concentration functions

We consider isotropic materials. Consequently, for the concentration functions, we have.

- $C_{\theta,1}\langle\nabla\theta\rangle_{\Omega} = \langle\nabla\theta\rangle_{\Omega_1}$ where $C_{\theta,1} = \frac{1-v_2 C_{\theta,2}}{1-v_2}$,
- $C_{\theta,2}\langle\nabla\theta\rangle_{\Omega} = \langle\nabla\theta\rangle_{\Omega_2}$ where $C_{\theta,2} = \frac{1}{v_2}\frac{\mathbb{K}^*-\mathbb{K}_1}{\mathbb{K}_2-\mathbb{K}_1}$.

The bounds on the effective thermal reponse immediately provide bounds on the second phase concentration function

$$C^{-}_{\theta,2}(\mathbb{K}^{*,-}) \leqslant C_{\theta,2}(\mathbb{K}^{*}) \leqslant C^{+}_{\theta,2}(\mathbb{K}^{*,+}), \tag{4.2}$$

where we define

- $C_{\theta,2}(\mathbb{K}^*) = \frac{1}{v_2}\frac{\mathbb{K}^*-\mathbb{K}_1}{\mathbb{K}_2-\mathbb{K}_1}$ with argument $\mathbb{K}^*$,
- $C^{+}_{\theta,2}(\mathbb{K}^{*,+}) = \frac{1}{v_2}\frac{\mathbb{K}^{*,+}-\mathbb{K}_1}{\mathbb{K}_2-\mathbb{K}_1}$ with argument $\mathbb{K}^{*,+}$ and
- $C^{-}_{\theta,2}(\mathbb{K}^{*,-}) = \frac{1}{v_2}\frac{\mathbb{K}^{*,-}-\mathbb{K}_1}{\mathbb{K}_2-\mathbb{K}_1}$ with argument $\mathbb{K}^{*,-}$.

These expressions provide upper and lower bounds for the first phase concentration function:

$$C^{-}_{\theta,1}(\mathbb{K}^{*,+}) \leqslant C_{\theta,1}(\mathbb{K}^{*}) \leqslant C^{+}_{\theta,1}(\mathbb{K}^{*,-}), \tag{4.3}$$

where

$$C_{\theta,1}(\mathbb{K}^*) = \frac{1 - v_2 C_{\theta,2}(\mathbb{K}^*)}{1-v_2} \leqslant \frac{1 - v_2 C^{-}_{\theta,2}(\mathbb{K}^{*,-})}{1-v_2} \stackrel{\text{def}}{=} C^{+}_{\theta,1}(\mathbb{K}^{*,-}) \tag{4.4}$$

and

$$C_{\theta,1}(\mathbb{K}^*) = \frac{1 - v_2 C_{\theta,2}(\mathbb{K}^*)}{1-v_2} \geqslant \frac{1 - v_2 C^{+}_{\theta,2}(\mathbb{K}^{*,+})}{1-v_2} \stackrel{\text{def}}{=} C^{-}_{\theta,1}(\mathbb{K}^{*,+}). \tag{4.5}$$

5. Bounds on the effective Seebeck number

5.1. The effective Seebeck number

In order to determine the effective overall Seebeck number, defined via $S^*\langle\nabla\theta\rangle_{\Omega}$, we decompose the overall electric field into the portions in phase one and phase two:

$$\begin{aligned} S^*\langle\nabla\theta\rangle_{\Omega} = \langle\boldsymbol{E}\rangle_{\Omega} &= \frac{1}{|\Omega|}\left(\int_{\Omega_1}\boldsymbol{E}\,d\Omega + \int_{\Omega_2}\boldsymbol{E}\,d\Omega\right) = v_1\langle\boldsymbol{E}\rangle_{\Omega_1} + v_2\langle\boldsymbol{E}\rangle_{\Omega_2} = v_1\langle S\nabla\theta\rangle_{\Omega_1} + v_2\langle S\nabla\theta\rangle_{\Omega_2} \\ &= v_1 S_1\langle\nabla\theta\rangle_{\Omega_1} + v_2 S_2\langle\nabla\theta\rangle_{\Omega_2} = v_1 S_1 C_{\theta,1}\langle\nabla\theta\rangle_{\Omega} + v_2 S_2 C_{\theta,2}\langle\nabla\theta\rangle_{\Omega} = \underbrace{(v_1 S_1 C_{\theta,1} + v_2 S_2 C_{\theta,2})}_{S^*}\langle\nabla\theta\rangle_{\Omega}. \end{aligned} \tag{5.1}$$

Thus, by definition, the multiplier of $\langle\nabla\theta\rangle_{\Omega}$, is the effective overall Seebeck number

$$S^* = (v_1 S_1 C_{\theta,1} + v_2 S_2 C_{\theta,2}). \tag{5.2}$$

Now we use the definitions of the bounds on the concentration functions in the previous section to obtain bounds on the effective Seebeck number, $S^{*,-} \leqslant S^* \leqslant S^{*,+}$, explicitly as

$$\underbrace{v_1 S_1 C^{-}_{\theta,1} + v_2 S_2 C^{-}_{\theta,2}}_{S^{*,-}} \leqslant \underbrace{v_1 S_1 C_{\theta,1} + v_2 S_2 C_{\theta,2})}_{S^*} \leqslant \underbrace{v_1 S_1 C^{+}_{\theta,1} + v_2 S_2 C^{+}_{\theta,2}}_{S^{*,+}}. \tag{5.3}$$

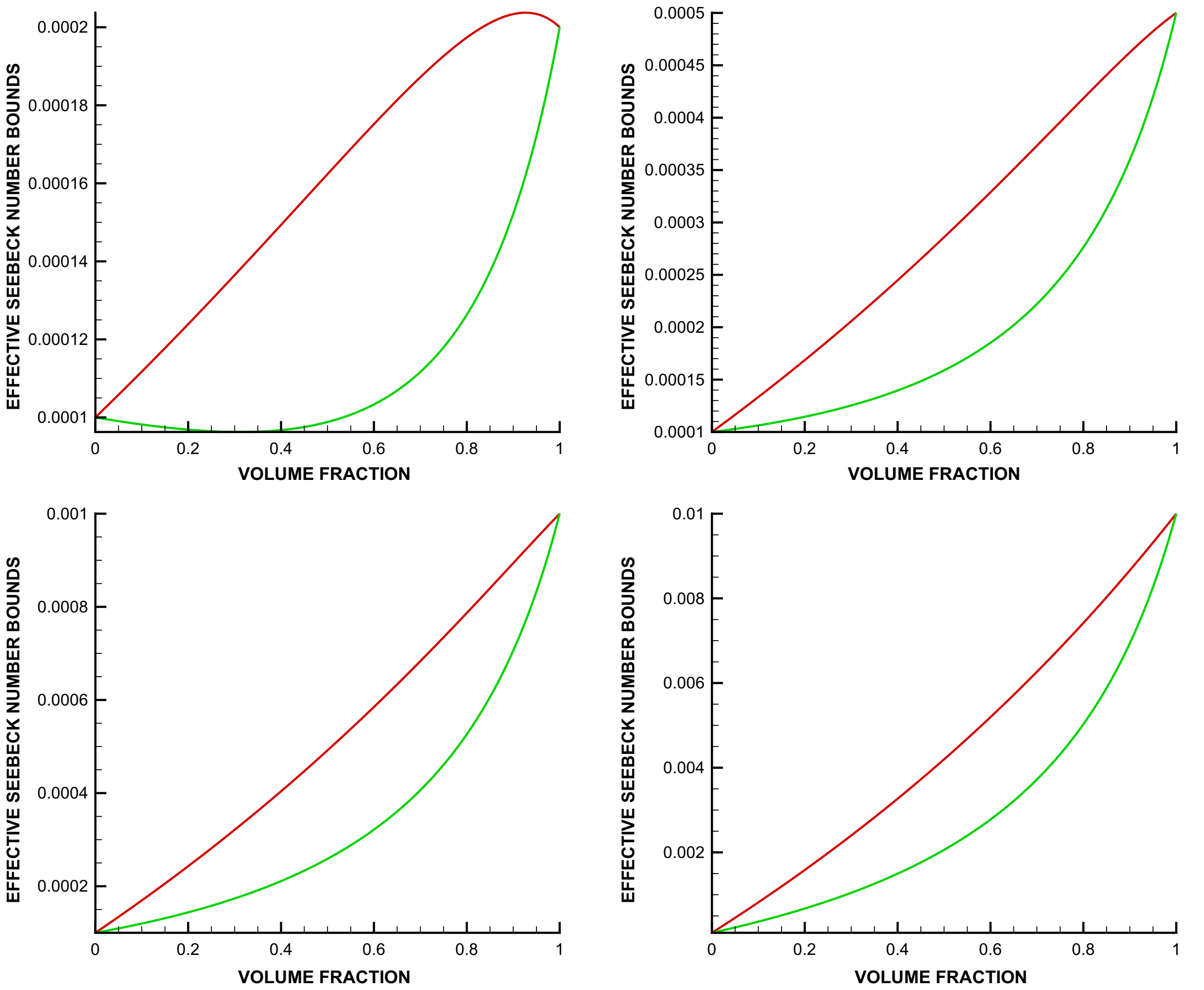

Fig. 2. Varying the pointwise Seebeck number: The bounds on the effective Seebeck number S^* for (top to bottom and left to right) $S_2/S_1 = 2$, $S_2/S_1 = 5$, $S_2/S_1 = 10$ and $S_2/S_1 = 100$, with $\mathbb{K}_2/\mathbb{K}_1 = 10$.

5.2. Numerical examples

To illustrate the behavior of the previously derived expressions, the following (mid-range) parameter selections for phase one were chosen, namely (a) $S_1 = 100 \times 10^{-6}$ V/K and (b) $\mathbb{K}_1 = 1$ W/mK. We considered parameter studies:

Case 1: Fixing the thermal conductivity mismatch, $\mathbb{K}_2/\mathbb{K}_1 = 10$ and varying $2 \leqslant S_2/S_1 \leqslant 100$, as well as the volume fraction $0 \leqslant v_2 \leqslant 1$. Fig. 2 illustrates the behavior of the bounds on the effective Seebeck number S^* for $S_2/S_1 = 2$, $S_2/S_1 = 5$, $S_2/S_1 = 10$ and $S_2/S_1 = 100$, with $\mathbb{K}_2/\mathbb{K}_1 = 10$.
Case 2: Fixing the Seebeck number mismatch, $S_2/S_1 = 10$ and varying $2 \leqslant \mathbb{K}_2/\mathbb{K}_1 \leqslant 100$, as well as the volume fraction $0 \leqslant v_2 \leqslant 1$. Fig. 3 illustrates the behavior of the bounds on the effective Seebeck number S^* for (top to bottom and left to right) $\mathbb{K}_2/\mathbb{K}_1 = 2$, $\mathbb{K}_2/\mathbb{K}_1 = 5$, $\mathbb{K}_2/\mathbb{K}_1 = 10$ and $\mathbb{K}_2/\mathbb{K}_1 = 100$, with $S_2/S_1 = 10$.

Notice that for certain parameter selections, such as $S_2/S_1 = 2$ and $\mathbb{K}_2/\mathbb{K}_1 = 10$ and, to a much milder extent, $S_2/S_1 = 10$ and $\mathbb{K}_2/\mathbb{K}_1 = 100$, there is a nonmononic dependency of the effective Seebeck number on the volume fraction v_2. Generally speaking, the bounds for the effective Seebeck number in Figs. 2 and 3, for various mismatch ratios, provide a guide to thermo-electric material combination selection. Further enhancement of these estimates is discussed next.

6. Summary and extensions

This work derived estimates and bounds for the effective Seebeck number for heterogeneous materials, S^* using only the pointwise cross-correlation properties of the material and the average thermal fields. The derived relations provide a useful

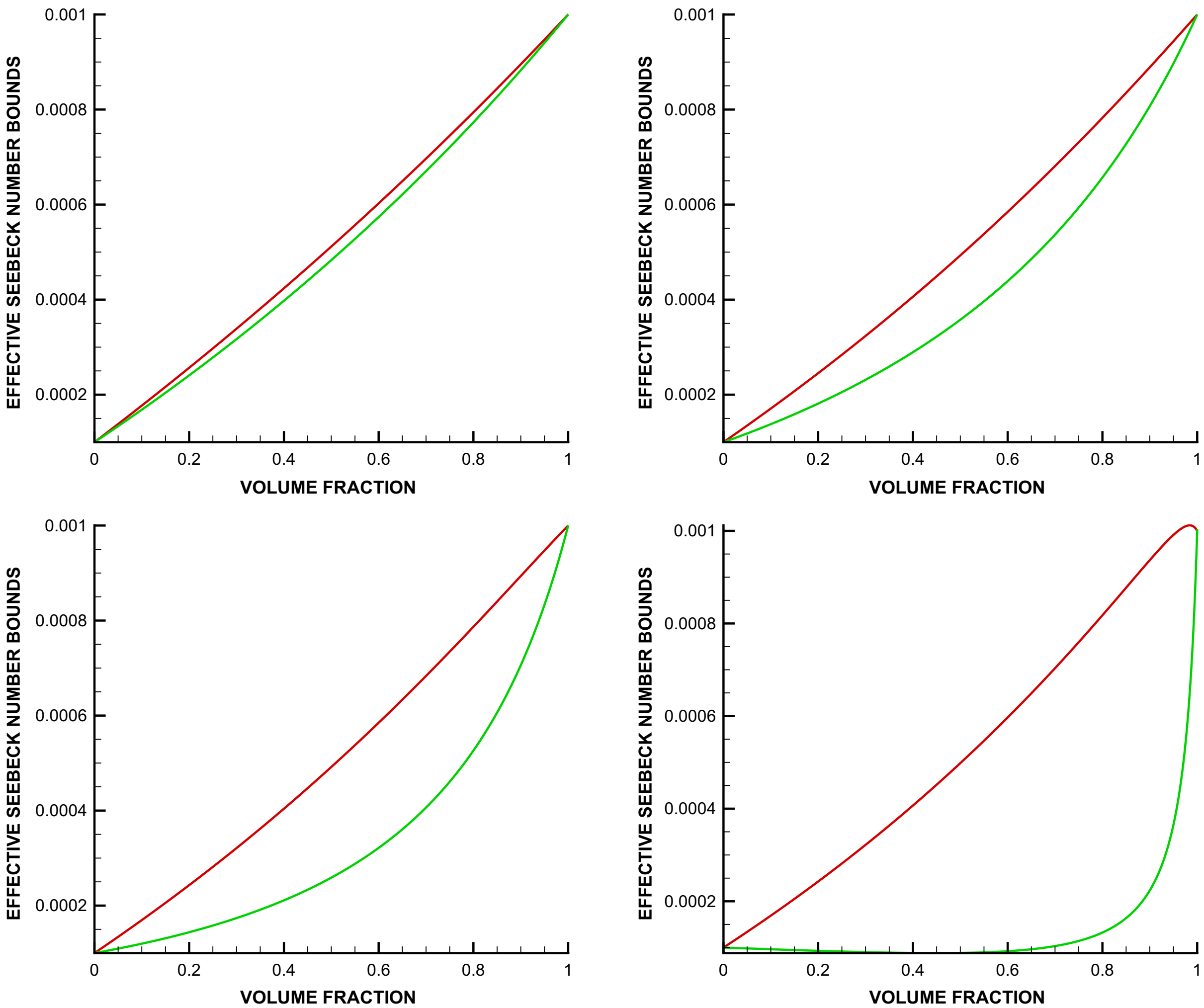

Fig. 3. Varying the pointwise thermal conductivity: The bounds on the effective Seebeck number S^* for (top to bottom and left to right) $\mathbb{K}_2/\mathbb{K}_1 = 2$, $\mathbb{K}_2/\mathbb{K}_1 = 5$, $\mathbb{K}_2/\mathbb{K}_1 = 10$ and $\mathbb{K}_2/\mathbb{K}_1 = 100$, with $S_2/S_1 = 10$.

qualitative guide to the developement of new thermoelectric materials. We remark that for a material to be acceptable from both a power generation and cooling point of view, a material needs a high Seebeck number, and also a high electrical conductivity (σ), as well as a low thermal conductivity ($\mathbb{K}$), thus motivating the definition of a thermoelectric figure of merit, $\mathcal{Z} \stackrel{\text{def}}{=} \frac{S^2\sigma}{\mathbb{K}}$. Oftentimes, in material design, one combines heterogeneous materials to produce a hybrid material. The objective of this paper is to derive bounds and estimates on the effective thermoelectric figure of merit for such materials, $\mathcal{Z}^* \stackrel{\text{def}}{=} \frac{(S^*)^2\sigma^*}{\mathbb{K}^*}$, where S^* is the effective Seebeck number for the mixture, $\mathbb{K}^*$ is the effective thermal conductivity and σ^* is the effective electrical conductivity. However, as with all thermoelectric phenomena, there is concern with localized heating effects, in particular due to the heterogenity of the material. For example, in particulate-doped materials, the determination of high heat concentration in the matrix ligaments between particles ("hot spots") must be explored via numerical simulation. To determine the generation of transient electromagnetic fields, temperature fields, stress fields (due to both Joule-heating and thermal stresses) and possible chemical reaction fields, this requires the coupled solution to the time-transient forms of Maxwell's equations, the first law of thermodynamics, the balance of linear momentum and reaction–diffusion laws. For general heterogeneous material systems, in order to accurately capture the coupled (transient) electromagnetic, thermal, mechanical and chemical behavior of a complex material, Zohdi (2010) has recently developed direct FDTD (Finite Difference Time Domain) numerical methods to extract effective coupled responses of a heterogeneous material. The application of such an approach to investigate local events in the microstructure is under current investigation by the author.[4]

[4] There are other computational electromagnetic methods that may be suitable for the class of problems of interest, such as *the Finite Element Method*, which is based on discretization of variational formulations and which are ideal for irregular geometries. In particular, see Demkowicz (2006, 2007) for the state of the art in adaptive Finite Element Methods for Maxwell's equations.

Appendix A. The controllable quantities-$\langle\nabla\theta\rangle$ and $\langle \boldsymbol{q}\rangle$

Two physically important boundary ($\partial\Omega$) loading states are notable on a sample of heterogeneous material (Fig. 1): (1) applied thermal fields of the form: $\theta|_{\partial\Omega} = \mathcal{T}\cdot\boldsymbol{x}$ and (2) applied thermal flux field of the form: $\boldsymbol{q}\cdot\boldsymbol{n}|_{\partial\Omega} = \mathcal{F}\cdot\boldsymbol{n}$, where $\mathcal{T}$ and $\mathcal{F}$ are constant thermal gradient and heat flux field vectors, respectively. Clearly, for these loading states to be satisfied within a macroscopic body under nonuniform external loading, the sample must be large enough to possess small boundary field fluctuations relative to its size. Therefore, applying (1)- or (2)-type boundary conditions to a large sample is a way of reproducing approximately what may be occurring in a statistically representative microscopic sample of material within a macroscopic body.

The following two results render $\langle\boldsymbol{q}\rangle_\Omega$ and $\langle\nabla\theta\rangle_\Omega$ as controllable quantities, via the boundary loading:

- *The Average Field Theorem*: Consider a sample with boundary loading $\theta|_{\partial\Omega} = \mathcal{T}\cdot\boldsymbol{x}$ where $\mathcal{T}$ is a constant vector, then

$$\begin{aligned}\langle\nabla\theta\rangle_\Omega &= \frac{1}{|\Omega|}\int_\Omega \nabla\theta\, d\Omega \\ &= \frac{1}{|\Omega|}\left(\int_{\Omega_1}\nabla\theta\, d\Omega + \int_{\Omega_2}\nabla\theta\, d\Omega\right) \\ &= \frac{1}{|\Omega|}\left(\int_{\partial\Omega_1}\theta\boldsymbol{n}\, dA + \int_{\partial\Omega_2}\theta\boldsymbol{n}\, dA\right) \\ &= \frac{1}{|\Omega|}\left(\int_{\partial\Omega}(\mathcal{T}\cdot\boldsymbol{x})\boldsymbol{n}\, dA + \int_{\partial\Omega_1\cap\partial\Omega_2}]|\theta[|\boldsymbol{n}\, dA\right) = \mathcal{T},\end{aligned} \tag{A.1}$$

where $]|\theta[|$ describes thermal jumps at the interfaces between Ω_1 and Ω_2, which are zero, since the temperature is continuous for the problems under consideration.

- *The Average Flux Theorem:* Again we consider a body with $\boldsymbol{q}\cdot\boldsymbol{n}|_{\partial\Omega} = \mathcal{F}\cdot\boldsymbol{n}$, where $\mathcal{F}$ is a constant vector. Since there are no source terms, $\nabla\cdot(\mathbb{K}\cdot\nabla\theta) = \nabla\cdot\boldsymbol{q} = 0$, and we can make use of the identity

$$\nabla\cdot(\boldsymbol{q}\otimes\boldsymbol{x}) = (\nabla\cdot\boldsymbol{q})\otimes\boldsymbol{x} + \boldsymbol{q}\cdot\nabla\boldsymbol{x} = \boldsymbol{q}\cdot\boldsymbol{1} = \boldsymbol{q} \tag{A.2}$$

and substitute this into the definition of the average flux

$$\begin{aligned}\langle\boldsymbol{q}\rangle_\Omega &= \frac{1}{|\Omega|}\left(\int_\Omega \nabla\cdot(\boldsymbol{q}\otimes\boldsymbol{x})\, d\Omega - \int_\Omega \underbrace{(\nabla\cdot\boldsymbol{q})}_{=0}\otimes\boldsymbol{x}\, d\Omega\right) \\ &= \frac{1}{|\Omega|}\int_\Omega \nabla\cdot(\boldsymbol{q}\otimes\boldsymbol{x})\, d\Omega \\ &= \frac{1}{|\Omega|}\int_{\partial\Omega}(\boldsymbol{q}\otimes\boldsymbol{x})\cdot\boldsymbol{n}\, dA \\ &= \frac{1}{|\Omega|}\int_{\partial\Omega}(\mathcal{F}\otimes\boldsymbol{x})\cdot\boldsymbol{n}\, dA = \mathcal{F},\end{aligned} \tag{A.3}$$

where, since there are no source terms, $\nabla\cdot(\mathbb{K}\cdot\nabla\theta) = \nabla\cdot\boldsymbol{q} = 0$. Thus, $\langle\boldsymbol{q}\rangle_\Omega = \mathcal{F}$.

Remark 5. The importance of the *Average Field Theorem* and the *Average Flux Theorem* is that we can consider $\langle\nabla\theta\rangle_\Omega$ and $\langle\boldsymbol{q}\rangle_\Omega$ to be controllable quantities, via $\mathcal{T}$ or $\mathcal{F}$ on the boundary. Applying these boundary conditions should be made with the understanding that these idealizations reproduce what a representative volume element (which is much smaller than the structural component of intended use) would experience within the system of intended use. Uniform loading is an idealization and would be present within a vanishingly small microstructure relative to a finite-sized engineering (macro) structure. These types of loadings are somewhat standard in computational analyses of samples of heterogeneous materials (see Ghosh (2011), Ghosh & Dimiduk (2011), Zohdi (2010) and Zohdi & Wriggers (2008)).

Appendix B. concentration function for the thermal flux

In order to determine the thermal flux in in each phase, concentration functions can be derived from the thermal gradient concentration functions by writing

$$\langle\boldsymbol{q}\rangle_\Omega = -\mathbb{K}^*\cdot\langle\nabla\theta\rangle_\Omega \Rightarrow \mathbb{K}^{*-1}\cdot\langle\boldsymbol{q}\rangle_\Omega = -\boldsymbol{C}_{\theta,2}^{-1}\cdot\langle\nabla\theta\rangle_{\Omega_2} = \boldsymbol{C}_{\theta,2}^{-1}\cdot\mathbb{K}_2^{-1}\cdot\langle\boldsymbol{q}\rangle_{\Omega_2}. \tag{B.1}$$

Thus,

$$\underbrace{\mathbb{K}_2\cdot\boldsymbol{C}_{\theta,2}\cdot\mathbb{K}^{*-1}}_{\boldsymbol{C}_{F,2}}\cdot\langle\boldsymbol{q}\rangle_\Omega = \langle\boldsymbol{q}\rangle_{\Omega_2} \tag{B.2}$$

and

$$\boldsymbol{C}_{F,1} \cdot \langle \boldsymbol{q} \rangle_{\Omega} = \langle \boldsymbol{q} \rangle_{\Omega_1}, \tag{B.3}$$

where

$$\boldsymbol{C}_{F,1} = \frac{\mathbf{1} - v_2 \boldsymbol{C}_{F,2}}{1 - v_2} = I\!K_1 \cdot \boldsymbol{C}_{\theta,1} \cdot I\!K^{*-1}. \tag{B.4}$$

We remark that Eq. (B.4) implies

$$\underbrace{v_1 \boldsymbol{C}_{F,1}}_{\text{phase-1 contribution}} + \underbrace{v_2 \boldsymbol{C}_{F,2}}_{\text{phase-2 contribution}} = \mathbf{1} \tag{B.5}$$

and in summary:

- $\boldsymbol{C}_{F,1} \cdot \langle \boldsymbol{q} \rangle_{\Omega} = \langle \boldsymbol{q} \rangle_{\Omega_1}$ where $\boldsymbol{C}_{F,1} = \frac{\mathbf{1} - v_2 \boldsymbol{C}_{F,2}}{1 - v_2} = I\!K_1 \cdot \boldsymbol{C}_{\theta,1} \cdot I\!K^{*-1}$,
- $\boldsymbol{C}_{F,2} \cdot \langle \boldsymbol{q} \rangle_{\Omega} = \langle \boldsymbol{q} \rangle_{\Omega_2}$ where $\boldsymbol{C}_{F,2} = I\!K_2 \cdot \boldsymbol{C}_{\theta,2} \cdot I\!K^{*-1}$.

The thermal flux in each phase is an important quantity to characterize for thermoelectric phenomena for heterogeneous media since localized heating is a concern.

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