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Effect of the interphase zone on the conductivity or diffusivity of a particulate composite using Maxwell's homogenization method

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ABSTRACT

An analytical model is developed for the conductivity (diffusivity, permeability, *etc.*) of a material that contains a dispersion of spherical inclusions, each surrounded by an inhomogeneous interphase zone in which the conductivity varies radially according to a power law. The method of Frobenius series is used to obtain an exact solution for the problem of a single such inclusion in an infinite matrix. Two versions of the solution are developed, one of which is more computationally convenient for interphase zones that are less conductive than the pure matrix, and *vice versa*. Maxwell's homogenization method is then used to estimate the effective macroscopic conductivity of the medium. The developed model is used to analyze some data from the literature on the ionic diffusivity of concrete. Use of the model in an inverse mode permits the estimation of the local diffusivity variation within the interphase, and in particular at the interface with the inclusion.

1. Introduction

Most modeling of the behavior of composite materials is carried out under the assumption that the "matrix" and "inclusions" are both homogenous, and that there is a clearly defined interface between them. The usual interface conditions are that all relevant fields (traction, displacement, temperature, heat flux, *etc.*) are continuous across the matrix/inclusion interface. But there are many situations in which either the interface is not sharp, or else one of the two components (matrix, inclusion) has a gradient in its physical properties. For example, a binding agent is sometimes applied to the fibers in a polymer composite, so as to promote adhesion between the fiber and the matrix (Drzal, Rich, Koenig, & Lloyd, 1983). This binding agent diffuses into the matrix during the curing process, leading to a gradient in resin concentration, which in turn may lead to gradients in physical properties within the so-called "interphase zone". Another well known and technologically important example of materials containing such interphase zones is concrete, in which the local porosity in the cement paste increases in the vicinity of the aggregate or sand inclusions, leading to a local variation of all properties that depend on porosity, such as the elastic moduli and the transport properties (Crumbie, 1994; Lutz, Monteiro, & Zimmerman, 1997).

In a seminal paper on the effective properties of materials that possess spatially-varying local properties, Kanaun and Kudryavtseva (1986) used Green's functions to analyze the stresses and displacements in a spherically-layered inclusion,

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located in a homogeneous matrix, and subjected to uniform far-field stress. This model of an inclusion composed of thin concentric layers, each having its own set of physical properties, has been widely used since then, for both the calculation of effective elastic (*i.e.,* Hervé, 2002) and conductive (*i.e.,* Caré & Hervé, 2004) properties.

Another model that is often used to account for the effect of an interphase zone can be traced back to another early paper by Kanaun (1984), on so-called "singular inclusions". Developed originally in the context of elasticity, when translated into the context of conductivity problems, Kanaun's method considers, for example, a very thin interphase shell that has a very high conductivity. In the limit in which the thickness of the zone goes to zero, and the conductivity becomes infinite, so that their *product* approaches some constant value, the annular shell can be replaced by a "flux discontinuity" boundary condition at the interface between a homogeneous inclusion and a homogeneous matrix. The case in which the conductivity and the thickness of the interphase each go to zero, while their *ratio* approaches a finite value, leads to an interface condition in which the temperature undergoes a jump discontinuity. This type of model has been used in conductivity problems by, for example, Cheng and Torquato (1997), Benveniste and Miloh (1999), Hashin (2001), and Benveniste (2012), among others.

Numerous other methods have been proposed to analyze the problem of an inclusion surrounded by a thin interphase zone. Sevostianov and Kachanov (2007), for example, considered the addition of a thin layer around a spherical inclusion, and aimed to replace this "inner sphere plus thin shell" by an equivalent homogeneous inclusion. In the limit of an infinitesimally thin shell, this led to an ordinary differential equation for the evolution of the conductivity of the equivalent homogeneous inclusion. A similar method had been applied in the elasticity context by Shen and Li (2005).

The present paper will approach this problem along the lines developed by Lutz and Zimmerman (1996, 2005). Instead of modeling the interphase zone as a region of finite thickness, having uniform or piecewise-uniform properties, the conductivity outside of the inclusion will be assumed to vary smoothly according to a power-law variation, approaching that of the "pure matrix" phase at far distances from the inclusion. The problem of a single such spherical inclusion subjected to an otherwise uniform external gradient can be solved exactly using the power series method of Frobenius. The effective conductivity of a material containing a dispersion of such spherical inclusions will be estimated by using Maxwell's effective medium method to approximately account for the finite concentration of inclusions.

The mathematical problem of calculating the "effective conductivity" has application to numerous transport-type processes that are governed by mathematically analogous sets of constitutive and balance equations. For example, according to the classical theory of heat conduction, the heat flux is proportional to the temperature gradient, through a constant of proportionality known as the thermal conductivity. Under steady-state conditions, the divergence of the heat flux must vanish. For a homogeneous material with a piecewise-uniform thermal conductivity, this leads to a Laplace equation for the temperature. For a material with a smoothly varying thermal conductivity, the conductivity appears inside the flux term, and cannot be factored out to yield a Laplace equation (see Section 2). Other physical processes that are governed by exactly analogous sets of equations include electrical conduction, ionic diffusion, and fluid flow of a slightly compressible fluid through a porous medium (Table 1).

For specificity, and since heat conduction lends itself to a simple physical interpretation and simple verbal discussion, the problem described above will be presented and solved within the context of thermal conductivity, although the results will be immediately applicable to other transport properties. The developed model will then be used to analyze some data from the literature, on the ionic diffusivity of concrete.

2. Single inclusion surrounded by a radially inhomogeneous interphase zone

The effective thermal conductivity problem can be analyzed by solving the basic problem of an inclusion that perturbs a uniform temperature gradient of magnitude G in an otherwise homogeneous body. A spherical coordinate system (r, θ, ϕ) is used, with its origin at the center of the inclusion, and the z-axis aligned with the far-field temperature gradient. The thermal conductivity is assumed to be a function of the radial co-ordinate, r. In the steady state, this problem is governed by (see Table 1)

$$\nabla \cdot [k(r)\nabla T(r,\theta,\phi)] = 0. \tag{1}$$

Using the expression for the gradient operator in spherical co-ordinates (Arfken & Weber, 2012), Eq. (1) takes the form

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 k(r)\frac{\partial T}{\partial r}\right] + \frac{k(r)}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial T}{\partial\theta}\right] + \frac{k(r)}{r^2\sin^2\theta}\frac{\partial^2 T}{\partial\phi^2} = 0. \tag{2}$$

Table 1
Transport processes governed by analogous constitutive and conservation laws.

Process	Potential	Flux	Constitutive law	Constitutive parameter	Conservation law
Heat conduction	Temperature, T	Heat flux, q	Fourier's law, $q = -k\nabla T$	Thermal conductivity, k	$\nabla \cdot q = 0$
Electrical conduction	Electric field, E	Electrical current, i	Ohm's law, $i = -\sigma\nabla E$	Electrical conductivity, σ	$\nabla \cdot i = 0$
Solute diffusion	Concentration, c	Solute mass flux, q	Fick's law, $q = -D\nabla c$	Diffusivity, D	$\nabla \cdot q = 0$
Fluid flow in porous media	Pressure, p	Volumetric flowrate, q	Darcy's law, $q = -(k/\mu^*)\nabla p$	Permeability, k	$\nabla \cdot q = 0$

$^*\mu$ = fluid viscosity.

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