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Effective thermal conductivity of composite spheres in a continuous medium with contact resistance

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Abstract

The self-consistent field concept is extended to the determination of the effective thermal conductivity of mixtures containing composite spheres randomly distributed in a continuous medium. Contact resistance is allowed for at the interface between the spheres and the continuous phase. A simple, yet exact, analytical solution is derived by first determining the temperature distribution for particle/continuous phase spheres as they are surrounded by an extensive effective medium. Special cases of the general solution are developed which correspond to various types of ideal particle/continuum behaviors. One category-perfect contact with negligible core gas heat conduction-is a useful model for many *syntactic foams*. Under these conditions, it is shown that the ratio of the effective conductivity of the medium to the conductivity of the continuous phase depends on a single parameter. The 'critical value' of this parameter is determined for which this ratio is unity. The result is consistent with prior studies of critical conditions in composite media.

1. Introduction

Various approaches for characterizing the effective thermal, electrical, and elastic properties of composite media have been introduced since Maxwell's seminal work on spherical particle suspensions more than a century ago [1]. Apart from the large number of results which are based on either highly approximated micro-models or *ad hoc* mixing rules, several approaches based on reasonable physical models have also been established and refined to include the effects of various particle shapes plus imperfect thermal contact between the particle surface and the continuous medium. Such studies include: exact mathematical analysis of dilute systems in which bounds are established on the effective properties, and asymptotic behavior is determined (see, for example, Beasley and Torquato [2], and Thovert and Acrivos [3]); exact mathematical analysis of various regular arrays of particles (see, for example, McKenzie et al. [4], Gu and Tao [5], Gu and Liu [6], Torquato and Rintoul [7], and Cheng and Torquato[8]); numerical simulation of Brownian diffusion of pulsed sources through particle arrays (see, for example, Torquato and Kim [9], and Kim and Torquato [10]); the self-consistent field concept for analyzing non-dilute, non-regularly spaced particles (see, for example, Hashin [11], Benveniste and Miloh [12], and Benveniste [13]); and the technique of 'successive embedding of effective media' to treat multi-coated cylinders or spheres (see, for example, Schulgasser [14], and Milgrom and Shtrikman [15]).

The purpose of the present study is to establish within the self-consistent field model, an analytical solution for the effective conductivity of a medium in which *composite* spheres are randomly distributed throughout a continuous phase. The *composite* spheres are taken to have a homogeneous core surrounded by a homogeneous spherical shell of a thermally different material. Also, contact resistance is allowed to exist between the outer surface of the shell and the continuous medium in which it is embedded. The motivation for this study was the analysis of *syntactic foam insulation* produced by mixing hollow glass microspheres into various plastic resins. Hence, computations using parameters which are characteristic of such systems will also be presented.

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Nomenclature

h	contact conductance
$\boldsymbol{H}$	negative of temperature gradient
k	thermal conductivity
k_{mn}	thermal conductivity ratio ($= k_m/k_n$)
P_m	Legendre polynomial, mth order
$\boldsymbol{q}$	heat flux
r	radial coordinate
T	temperature
v_f	particulate volume fraction ($= (r_2/r_1)^3$)
v	volume fraction
v_{mn}	volume fraction ratio ($= v_m/v_n$)
V	cell volume ($= 4\pi r_1^3/3$)

Greek symbols

α	magnitude of $\boldsymbol{H}$ in the effective medium
β	dimensionless contact conductance ($= hr/k$)
δ	particle wall thickness
θ	polar angle

Subscripts

0	effective medium's numerical index
1	continuous medium
2	particle shell
3	particle core
c	critical condition ($k_{\text{eff}} = k_1$)
eff	effective medium
z	z-component of vector

Superscript

overbar	volume average

2. The self-consistent approximation

The self-consistent approximation is based on the following concept. Consider a slab of material composed of composite spheres distributed throughout a continuous phase. A temperature difference is imposed across the slab and causes a flow of heat through the medium. The effective thermal conductivity of the medium is defined as the ratio of the induced heat flux to the imposed temperature difference, and the effective temperature gradient is the imposed temperature difference divided by the slab thickness. Using these effective quantities, the mixture of continuous phase and spheres is then represented as an effective homogeneous medium.

To determine the effective thermal conductivity of this medium in terms of the thermal conductivities of the constituent phases and their spatial distribution, the following concept is used. Consider one sphere to be surrounded by a volume of continuous medium in the same proportion as in the mixture as a whole (i.e., the same volume fraction). Treat this sphere-continuum composite unit as being embedded in the macroscale effective homogeneous medium. Then, impose a uniform temperature gradient in the surrounding macroscale effective medium and compute the heat transfer occurring through the sphere-continuum composite unit that is embedded in it. The ratio of the average flux in the unit to the average temperature gradient in the unit then defines the effective thermal conductivity. It will depend on the thermal conductivities and volumetric distributions of the constituent phases.

An essential question regards the shape to use for the continuous phase that surrounds the sphere. For media in which the spheres are distributed in a regular lattice arrangement, this shape would be dictated by the shape of a unit cell. For randomly oriented spheres, however, some average shape is needed. Conventionally, the shape taken for the continuous phase in the basic unit is spherical. Therefore, the geometry to be analyzed in the present application of the self-consistent field theory is as shown in Fig. 1.

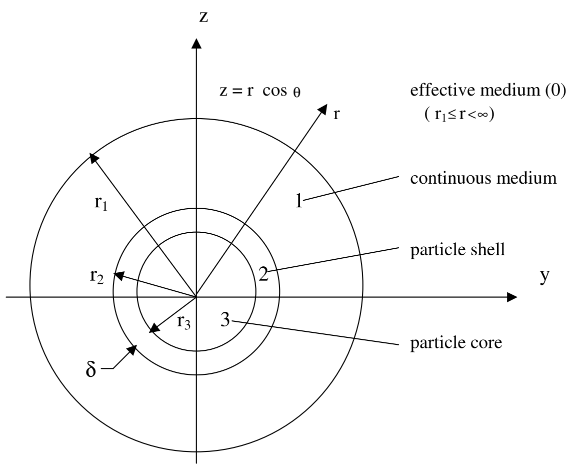

Fig. 1. Geometry of cell for self-consistent field analysis of composite spheres randomly mixed into a continuum. The cell ($0 \leqslant r \leqslant r_1$) is embedded in the effective medium ($r_1 \leqslant r < \infty$). The temperature distribution is azimuthally independent.

3. Analysis

A uniform temperature gradient is imposed in the effective medium at large distances from the spherical unit embedded in it. The spherical unit is comprised of a composite particle surrounded by a layer of the continuous medium (see Fig. 1). Thermal contact resistance exists at the interface of the sphere and the surrounding continuous phase, but not at the core/shell interface within the particle.

The temperature distribution is defined by azimuthally independent steady-state heat conduction:

$$\nabla^2 T_n = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T_n}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T_n}{\partial\theta}\right) = 0 \tag{1}$$

where $n = 0, 1, 2, 3$, with 0 designating the effective medium surrounding the spherical cell (i.e., $k_0 = k_{\text{eff}}$). The solution of Eq. (1) in each medium may be written as

$$T_n = \sum_{m=0}^{\infty}\left(a_{n,m}r^m + b_{n,m}r^{-(m+1)}\right)P_m(\cos\theta) \tag{2}$$

where $P_m(\cos\theta)$ is the mth degree Legendre polynomial. Note that in the effective medium far from the sphere, the temperature gradient and heat flux are constants. Taking these to be aligned with the z-direction:

$$\boldsymbol{H}_{\text{eff}} \equiv -(\nabla T)_{\text{eff}} = \hat{k}\alpha, \quad \text{const.} \tag{3}$$

$$\boldsymbol{q}_{\text{eff}} = k_{\text{eff}}\boldsymbol{H}_{\text{eff}} = \hat{k}q_0, \quad \text{const.} \tag{4}$$

Therefore, the asymptotic boundary condition on the temperature may be written as

$$\lim_{(r\to\infty,\theta)} T_0(r,\theta) = -\alpha z = -\alpha r\cos\theta \tag{5}$$

Noting that $P_1(\cos\theta) = \cos\theta$, it is seen that in the effective medium (0), the infinite series of orthogonal polynomials reduces to just the $n = 1$ term. The boundary conditions connecting each medium then impose this same reduction to each $T_n(r,\theta)$, resulting in

$$T_n(r,\theta) = (A_n r + B_n r^{-2})\cos\theta \tag{6}$$

Applying the asymptotic boundary condition ($r \to \infty$) results in: $A_0 = -\alpha$. Also, since the solution must be finite at $r = 0$, $B_3 = 0$. The six boundary conditions required for determining the remaining six coefficients are

$$\begin{aligned} &-k_{n+1}(\partial T_{n+1}/\partial r)_{r_{n+1},\theta} \\ &\quad = -k_n(\partial T_n/\partial r)_{r_{n+1},\theta} \quad (n = 0,1,2) && (7)\\ &\quad = h_{21}[T_2(r_2,\theta) - T_1(r_2,\theta)] \quad (n = 1) && (8)\end{aligned}$$

$$T_{n+1}(r_{n+1},\theta) = T_n(r_{n+1},\theta) \quad (n = 0,2) \tag{9}$$

where h_{21} is the contact conductance at the interface between the sphere and the continuous medium.

The six equations above were solved algebraically. Introducing the following definitions: $A'_n \equiv A_n/\alpha$, $(n = 1,2,3)$; $B'_n \equiv (r_n^{-3}/\alpha)B_n$, $(n = 1,2)$; $B'_0 \equiv (r_1^{-3}/\alpha)B_0$, the coefficients in the temperature distribution are found to be

$$B'_0 = [-(k_{01} - 1) + 3B'_1]/(2k_{01} + 1) \tag{10}$$

$$A'_1 = -[3k_{01} + 2(k_{01} - 1)B'_1]/(2k_{01} + 1) \tag{11}$$

$$\begin{aligned} B'_1 = 3\{[-(\beta_2^{-1} + 1) + k_{21}]v_{f3}(k_{32} + 2) - [(2\beta_2^{-1} - 1) \\ - 2k_{21}](k_{32} - 1)\}/D \end{aligned} \tag{12}$$

$$A'_2 = -9v_f^{-1}v_{f3}(k_{32} + 2)/D \tag{13}$$

$$B'_2 = 9v_f^{-1}(k_{32} - 1)/D \tag{14}$$

$$A'_3 = -27v_f^{-1}v_{f3}/D \tag{15}$$

where

$$\begin{aligned} D = &-[(2k_{01} + 1) - 2v_f(k_{01} - 1)](k_{32} - 1) \\ &\times [2 - \beta_2(2k_{21} + 1)]/(v_f\beta_2 k_{01}) + 3(k_{32} - 1) \\ &\times [2(2k_{01} + 1) - \beta_2(2k_{01} + 1)]/(v_f\beta_2 k_{01}) \\ &+ v_{f3}(k_{32} + 2)\{[2 + \beta_2(k_{21} + 2)](2k_{01} + 1) \\ &+ 2v_f[1 - \beta_2(k_{21} - 1)](k_{01} - 1)\}/(v_f\beta_2 k_{01}) \end{aligned} \tag{16}$$

in which

$$k_{mn} = k_m/k_n \tag{17}$$

$$\beta_2 = h_{21}r_2/k_2 \tag{18}$$

$$v_f = (r_2/r_1)^3 = \text{volume fraction of particles} \tag{19}$$

$$v_{f3} = v_f/v_3 = (r_2/r_3)^3 \tag{20}$$

It is to be noted that

$$r_3 = r_2 - \delta \tag{21}$$

$$v_{3f} = v_{f3}^{-1} = (1 - \delta/r_2)^3 \tag{22}$$

where δ is the wall thickness and $0 \leqslant v_{3f} \leqslant 1$.

Using the above coefficients, the temperature distribution in each material may then be written from Eq. (6). The distributions of temperature gradient and heat flux then follow by differentiation.

For the effective medium, noting that ($k_{\text{eff}} \equiv k_0$),

$$\boldsymbol{H} \equiv -\nabla T = \hat{\boldsymbol{\varepsilon}}_i H_i \tag{23}$$

$$\boldsymbol{q} \equiv k_{\text{eff}}\boldsymbol{H} = \hat{\boldsymbol{\varepsilon}}_i q_i \tag{24}$$

where $\hat{\boldsymbol{\varepsilon}}_i$ is the unit vector in the ith coordinate direction. From the results for the temperature distribution within the basic cell, the effective thermal conductivity is evaluated as

$$k_{\text{eff}} = \overline{q_i}/\overline{H_i} \tag{25}$$

where the overbar indicates a volume average over the cell volume, $V = (4\pi r_1^3/3)$:

$$\bar{f} = (1/V)\int_V f\,\mathrm{d}V \tag{26}$$

Due to symmetry, only the averaged z-components are non-zero. They are given by

$$\bar{q}_z = \bar{q}_{z,1}v_1 + \bar{q}_{z,2}v_2 + \bar{q}_{z,3}v_3 \tag{27}$$

where

$$\bar{q}_{z,n} = k_n\overline{H}_{z,n} \tag{28}$$

in which

$$\overline{H}_z = H_z^0 = \overline{H}_{z,1}v_1 + \overline{H}_{z,2}v_2 + \overline{H}_{z,3}v_3 + J_z^{(12)}v_{\mathrm{f}} \tag{29}$$

where the last term in Eq. (29) arises from the temperature discontinuity at the interface between materials 1 and 2 (at $r = r_2$); it is given by

$$J_z^{(12)} = (A_2 - A_1) + (B_2 - B_1)r_2^{-3} \tag{30}$$

In the above equations,

$$\bar{f}_n = (1/V_n)\int_{V_n} f_n\,\mathrm{d}V_n \tag{31}$$

which is the volume average of function f_n over the volume of the nth material, and

$$v_n = (V_n/V) \tag{32}$$

which is the volume fraction of the nth material in the cell. The value of v_n is traditionally taken to be the same as the volume fraction of the nth material in the composite medium as a whole. Therefore, the cell composition is identical to that of the bulk medium. This, in turn, defines the value of cell volume V and hence r_1.

Consequently,

$$\bar{q}_z = k_{\mathrm{eff}}H_z^0 = k_1\overline{H}_{z,1}v_1 + k_2\overline{H}_{z,2}v_2 + k_3\overline{H}_{z,3}v_3 \tag{33}$$

and, therefore, the effective conductivity of the medium becomes:

$$k_{\mathrm{eff}} = \frac{k_1\overline{H}_{z,1}v_1 + k_2\overline{H}_{z,2}v_2 + k_3\overline{H}_{z,3}v_3}{\overline{H}_{z,1}v_1 + \overline{H}_{z,2}v_2 + \overline{H}_{z,3}v_3 + J_z^{(12)}v_{\mathrm{f}}} \tag{34}$$

Using Eq. (33), this also can be written as

$$k_{\mathrm{eff}} = k_1 + (k_2 - k_1)\frac{\overline{H}_{z,2}}{H_z^0}v_2 + (k_3 - k_1)\frac{\overline{H}_{z,3}}{H_z^0}v_3 - k_1\frac{J_z^{(12)}}{H_z^0}v_{\mathrm{f}} \tag{35}$$

Note from Eq. (3) that $H_z^0 = \alpha$.

With the temperature distributions in each material being of the form:

$$T_n(r,\theta) = (A_n r + B_n r^{-2})\cos\theta \tag{36}$$

the corresponding z-components of the temperature gradients may be written as

$$-H_{z,n} = \frac{\partial T_n}{\partial z} = A_n + (\sin^2\theta - 2\cos^2\theta)r^{-3}B_n \tag{37}$$

The average of the above over the volume of the nth material follows directly:

$$\overline{H}_{z,n} = -A_n \tag{38}$$

Then, by combining Eqs. (10)–(16), (30), (35) and (38), and performing considerable algebraic manipulation, the following simple expression may be derived for the effective thermal conductivity:

$$k_{\mathrm{eff}} = \left[\frac{2(1 - v_{\mathrm{f}})F - 3\beta_2\Phi}{(2 + v_{\mathrm{f}})F - 3\beta_2\Phi}\right]k_1 \tag{39}$$

where F and Φ are functions that naturally occur while performing the algebra:

$$F \equiv (k_{32} - 1)[2 - \beta_2(2k_{21} + 1)] + (k_{32} + 2) \times [1 - \beta_2(k_{21} - 1)]v_{\mathrm{f3}} \tag{40}$$

$$\Phi = 2(1 - v_{\mathrm{f3}})k_{21} - (2 + v_{\mathrm{f3}})k_{31} \tag{41}$$

This 'primary' form of the result is most useful to those who perform analyses using the effective medium theory since the manner in which it is written provides an indication of the algebraic steps used derive it.

On the other hand, when applying the result it is of interest to group together terms proportional to the contact conductance ($\beta_2 = h_{21}r_2/k_2$). Doing this results in the following form for the effective thermal conductivity:

$$k_{\mathrm{eff}} = \left[\frac{2(1 - v_{\mathrm{f}})\Psi + \beta_2\Theta_{\mathrm{N}}}{(2 + v_{\mathrm{f}})\Psi + \beta_2\Theta_{\mathrm{D}}}\right]k_1 \tag{42}$$

where

$$\Psi = (2 + v_{\mathrm{f3}})k_{32} - 2(1 - v_{\mathrm{f3}}) \tag{43}$$

and

$$\Theta_{\mathrm{N}} = (1 - v_{\mathrm{f}})[2(1 + 2v_{\mathrm{f3}}) - 2(1 - v_{\mathrm{f3}})k_{32}] + (1 + 2v_{\mathrm{f}})[(2 + v_{\mathrm{f3}})k_{31} - 2(1 - v_{\mathrm{f3}})k_{21}] \tag{44}$$

$$\Theta_{\mathrm{D}} = (2 + v_{\mathrm{f}})[(1 + 2v_{\mathrm{f3}}) - (1 - v_{\mathrm{f3}})k_{32}] + (1 - v_{\mathrm{f}})[(2 + v_{\mathrm{f3}})k_{31} - 2(1 - v_{\mathrm{f3}})k_{21}] \tag{45}$$

Simplification of the above general result to forms that correspond to various ideal physical models will now be considered.

4. Special cases

4.1. Ideal thermal contact ($\beta_2 \to \infty$)

When the contact resistance between the particles and the continuum is negligible, the contact conductance, h_{21}, tends toward infinity, resulting in $\beta_2 \to \infty$. In this limit, k_{eff} is given by

$$k_{\mathrm{eff}} = (\Theta_{\mathrm{N}}/\Theta_{\mathrm{D}})k_1 \tag{46}$$

4.2. Ideal conducting particles ($k_{21} \to \infty$ and $k_{23} \to \infty$; $\beta_2 \neq 0$)

This limit, which corresponds to the case of hollow metal particles dispersed in a dielectric continuum, is given by

$$k_{\mathrm{eff}} = \left(\frac{1+2v_{\mathrm{f}}}{1-v_{\mathrm{f}}}\right)k_1 \tag{47}$$

4.3. Ideal insulating particles ($k_{21} \to 0$ and $k_{23} \to 0$; or $\beta_2 \to 0$)

Particles may inhibit the flow of heat throughout their entire cross section by having either a thermal conductivity of the outer shell which is vanishingly small, $k_{21} = (k_2/k_1) \to 0$ and $k_{23} = (k_2/k_3) \to 0$, or by experiencing an infinite contact resistance with the continuum ($h_{21} \to 0$). Either of these conditions is physically equivalent to having voids of radius r_2 distributed throughout the continuum. The limiting form for the effective conductivity in these cases (i.e. $k_{21} \to 0$ and $k_{23} \to 0$; or $\beta_2 \to 0$) is given by

$$k_{\mathrm{eff}} = \left[\frac{2(1-v_{\mathrm{f}})}{(2+v_{\mathrm{f}})}\right]k_1 \tag{48}$$

This agrees with Hashin's [11] result.

4.4. Uniform particle ($k_{32} = 1$)

The composite sphere will behave as a uniform sphere when the shell and core have the same thermal conductivity ($k_3 = k_2$). In this limit, $k_{32} = 1$ and $k_{31} = k_{21}$. The effective conductivity is then given by

$$k_{\mathrm{eff}} = \frac{2(1-v_{\mathrm{f}}) + \beta_2[2(1-v_{\mathrm{f}}) + (1+2v_{\mathrm{f}})k_{21}]}{(2+v_{\mathrm{f}}) + \beta_2[(2+v_{\mathrm{f}}) + (1-v_{\mathrm{f}})k_{21}]}k_1 \tag{49}$$

This agrees with the result of Benveniste [13].

4.5. Ideal hollow particle ($k_3 = 0$)

Hollow spheres generally contain residual gas in their cores due to the nature of the various processes used to produce such particles. The thermal conductivity of this gas, k_3, is usually much smaller than the conductivity of the solid shell that surrounds it, k_2. Hence, a useful limit is one for which $k_{32} = 0 = k_{31}$. In this limit, the effective thermal conductivity becomes:

$$k_{\mathrm{eff}} = 2\left[\frac{2+\beta_2(\omega_{\mathrm{f3}} + \omega_{\mathrm{f}}k_{21})}{2\omega_{\mathrm{f}}^* + \beta_2(\omega_{\mathrm{f}}^*\omega_{\mathrm{f3}} + 2k_{21})}\right]k_1 \tag{50}$$

where

$$\omega_{\mathrm{f}} = (1+2v_{\mathrm{f}})/(1-v_{\mathrm{f}}) \tag{51}$$

$$\omega_{\mathrm{f}}^* = (2+v_{\mathrm{f}})/(1-v_{\mathrm{f}}) \tag{52}$$

$$\omega_{\mathrm{f3}} = (2v_{\mathrm{f3}}+1)/(v_{\mathrm{f3}}-1) \tag{53}$$

4.6. Typical hollow microspheres: ideal ($k_{31} = 0 = k_{32}$); no contact resistance ($\beta_2 \to \infty$)

Actual particle dispersions may often be characterized by assuming that the continuous phase is in intimate contact with the particles ($\beta_2 \to \infty$) and that the residual gas in the hollow core contributes little to the conduction of heat across the sphere ($k_{31} = 0 = k_{32}$). The effective conductivity under these conditions follows directly from the previous result:

$$k_{\mathrm{eff}} = \left[\frac{2(\omega_{\mathrm{f3}} + \omega_{\mathrm{f}}k_{21})}{(\omega_{\mathrm{f}}^*\omega_{\mathrm{f3}} + 2k_{21})}\right]k_1 \tag{54}$$

Upon further rearrangement, using Eqs. (51)–(53), a surprisingly simple form is obtained for this case:

$$k_{\mathrm{eff}} = \left(\frac{1+2\Omega v_{\mathrm{f}}}{1-\Omega v_{\mathrm{f}}}\right)k_1 \tag{55}$$

where

$$\Omega = (\eta - 1)/(\eta + 2) \tag{56}$$

in which

$$\eta = 2k_{21}/\omega_{\mathrm{f3}} \tag{57}$$

Eq. (55) demonstrates that the dimensionless effective conductivity ($k_{01} = k_{\mathrm{eff}}/k_1$) for this category of composites depends on only a single variable: (Ωv_{f}). This relation is plotted in Fig. 2.

Although the single line result in Fig. 2 is the complete solution, when the performance of several composites are to be compared, it is useful to plot instead the $k_{\mathrm{eff}}(v_{\mathrm{f}})$ curve for each material. Fig. 3 illustrates the nature of plotting the data this way. The present theory

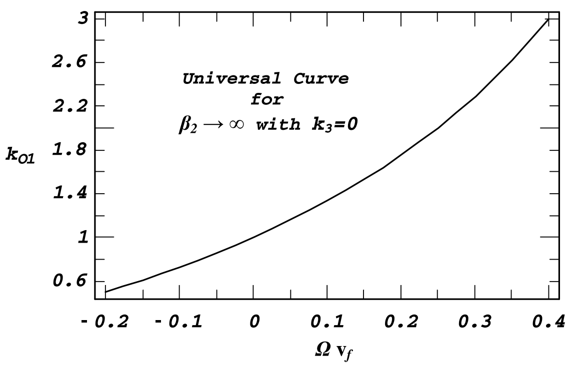

Fig. 2. Excellent thermal contact with the continuum ($\beta \to \infty$) and negligible core gas conduction ($k_{32} = 0 = k_{31}$). The effective thermal conductivity ($k_{01} = k_{\mathrm{eff}}/k_1$) depends only on ($\Omega v_{\mathrm{f}}$).

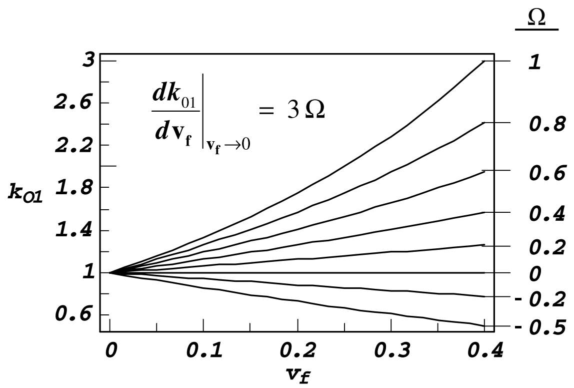

Fig. 3. Excellent thermal contact with the continuum ($\beta \to \infty$) and negligible core gas conduction ($k_{32} = 0 = k_{31}$). Plot of k_{01} as $k_{01}(v_f)$ with Ω as a parameter enables the graphical determination of Ω from experimental data. Different types of particles have different Ω.

shows that for such plots, each composite is represented by a constant-Ω line. Further, Eq. (55) indicates that the Ω-value for a given composite may be obtained from the experimentally measured slope of $k_{01}(v_f)$ in the limit of vanishing particle concentration $v_f \to 0$,

$$(\mathrm{d}k_{01}/\mathrm{d}v_f)|_{v_f\to 0} = 3\Omega \tag{58}$$

The range of physically allowable values for Ω may be determined as follows. First, it is useful to transform from the variable v_{f3}, which has a semi-infinite range (1 to ∞), to its inverse, $v_{3f} = 1/v_{f3}$, whose range is bounded ($0 \leqslant v_{3f} < 1$). The variable v_{3f} is given by

$$v_{3f} = (r_3/r_2)^3 = (1-\delta/r_2)^3 \tag{59}$$

The variables ω_{f3} and Ω may then be written in terms of v_{3f} and k_{21}:

$$\omega_{f3} = (2+v_{3f})/(1-v_{3f}) \tag{60}$$

$$\Omega = \frac{2(1-v_{3f})k_{21} - (2+v_{3f})}{2(1-v_{3f})k_{21} + 2(2+v_{3f})} \tag{61}$$

Since $0 \leqslant v_{3f} < 1$, it follows that the ranges across which Ω varies are given by

$$-\frac{1}{2} < \Omega \leqslant \left(\frac{k_{21}-1}{k_{21}+2}\right)\begin{cases} \leqslant 0, & 0 \leqslant k_{21} \leqslant 1 \\ \leqslant 1, & 1 \leqslant k_{21} \end{cases} \tag{62}$$

Note that $|\Omega| \leqslant 1$, and therefore $|\Omega v_f| < 1$. Hence, many composites will be characterized by $|\Omega v_f| \ll 1$ across the entire range of v_f in which they will be used. When this is the case, Eq. (55) reduces to

$$k_{01}(v_f)_{\mathrm{eff}}|_{(\Omega v_{f3})\ll 1} \simeq 1 + 3\Omega v_f(1+\Omega v_f) \approx 1 + 3\Omega v_f \tag{63}$$

indicating that a linear dependence of k_{01} on (Ωv_f) should often be observed.

4.7. *Critical condition ($k_{eff} = k_1$) for typical hollow microspheres ($k_3 = 0$ with $\beta_2 \to \infty$)*

The condition under which the effective conductivity of the composite medium equals the conductivity of the pure continuous phase is known as the *critical condition* [1,7]. In the present context, the *critical condition* indicates whether it will be possible to augment or diminish the thermal conductivity of a medium by mixing into it various types of particles.

The critical condition (c) is found by evaluating Eq. (55) for $k_{\mathrm{eff}} = k_1 (k_{01} = 1)$:

$$\left.\begin{array}{l}\Omega_c = 0 \text{ or} \\ \eta_c = (2k_{21}/\omega_{f3})_c = 1\end{array}\right\} \quad c \Rightarrow (k_{\mathrm{eff}} = k_1) \tag{64}$$

In terms of the usual design variables this may be written as

$$2\left(\frac{k_2}{k_1}\right)_c \left[\frac{1-(1-\delta/r_2)_c^3}{2+(1-\delta/r_2)_c^3}\right] = 1 \tag{65}$$

Note that $k_{\mathrm{eff}} \gtreqless k_1$ according to $\Omega \gtreqless 0$ or $(2k_{21}/\omega_{f3}) \gtreqless 1$.

4.7.1. *Microballoons/microbubbles*

Further simplification follows for thin-walled hollow microspheres, $(\delta/r_2) \ll 1$. Such hollow microspheres are commonly referred to as either *microballoons* or *microbubbles*. For these particles, $(1-\delta/r_2)^3 \sim [1-3(\delta/r_2)]$ and, hence, the *critical condition* reduces to

$$2(k_2/k_1)_c(\delta/r_2)_c = 1 \quad (\delta/r_2) \ll 1 \tag{66}$$

It is to be noted that the above relation corresponds to the 'critical conductance' found in [7] under the condition of vanishing 'sphere conductivity, σ_2'.

From Eq. (66) it is seen to be possible to *reduce* (*increase*) the conductivity of a given continuum (k_1) by adding *microballoons* of wall thickness (δ/r_2) when they are made of a material whose thermal conductivity is *smaller* (*larger*) *than* the critical value: $k_2 < 0.5k_1/(\delta/r_2)$. Similarly, for a given continuum (k_1) and particle material (k_2), the effective thermal conductivity of the medium (k_{eff}) can be *reduced* (*increased*) from k_1 when the *microballoons* have wall thicknesses *smaller* (*larger*) *than* the critical value: $(\delta/r_2) < 0.5(k_1/k_2)$.

5. Calculations

The dimensionless effective thermal conductivity ($k_{01} = k_{\mathrm{eff}}/k_1$) for composite spheres that are randomly distributed in a continuum and have contact resistance at the sphere-continuum interface is seen to depend on the following dimensionless quantities:

$$k_{01} = f(v_f, v_{f3}, k_{21}, k_{31}, \beta_2) \tag{67}$$

Parametric variations involving three variables at a time will now be considered. Since many applications involve the use of *hollow* spheres, the following limited set of calculations are presented for the condition $k_{31} = 0 = k_{32}$. Also, the volume fraction of particles is held fixed at $v_f = 0.35$ throughout. The ranges considered for the continuum and sphere thermal conductivities are taken to correspond to a dielectric continuua ($k_1 \sim 0.2$ W/m K) and glass/ceramic particles at partial to full density ($k_2 \sim 0.4$–2 W/m K); the corresponding range of the relative conductivity is $2 \leqslant k_{21} \leqslant 10$. The wall thickness is nominally taken to range from fully solid particles ($\delta = r_2$) to *microballoons*, for which 100 μm diameter particles ($r_2 \sim 50$ μm) typically have sub-micron thick walls ($\delta \sim 0.5$ μm) [16]; hence, $0.01 \leqslant (\delta/r_2) \leqslant 1$ and, correspondingly, $0.97 \geqslant v_{3f} \geqslant 0$.

Fig. 4 illustrates the dependence of the effective conductivity (k_{01}) on the contact conductance (β_2) for various wall thicknesses (v_{3f}). Note that at small β_2, the curves for all wall thicknesses converge to $k_{01} = 0.55$, consistent with Eq. (48). At large β_2, each v_f curve converges to the appropriate $\beta_2 \to \infty$ value given by Eq. (54) or (55). Fig. 5 illustrates the markedly different graphical appearance which the same results acquire when plotted in terms of level contours of the effective conductivity. As will be discussed below, this type of plot can be useful when assessing the effectiveness of different types of particles in achieving a thermal design requirement.

The influence of particle wall thickness and thermal conductivity on the effective thermal conductivity are demonstrated in Figs. 6 and 7. Here it is assumed that there is excellent thermal contact between the particles and the medium ($\beta_2 \to \infty$). Fig. 6 highlights thin-walled spheres including *microballoons* ($v_{3f} \geqslant 0.9$, i.e. $(\delta/r_2) \leqslant 0.35$). It should be noted that when written in these variables, the general solution given by Eq. (54), becomes:

$$k_{01} = 2\left[\frac{(1-v_f)(2+v_{3f}) + (1+2v_f)(1-v_{3f})k_{21}}{(2+v_f)(2+v_{3f}) + 2(1-v_f)(1-v_{3f})k_{21}}\right] \quad (68)$$

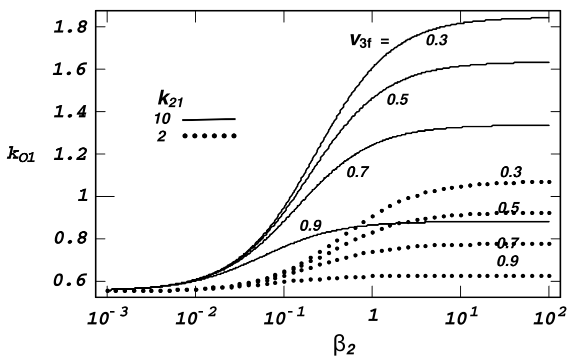

Fig. 4. The influence of thermal contact conductance, $\beta_2 = (h_{21}r_2/k_2)$, and particle wall thickness, $v_{3f} = (1-\delta/r_2)^3$, on the effective thermal conductivity ($k_{01} = k_{eff}/k_1$). Negligible core gas conduction ($k_{32} = 0 = k_{31}$) and $v_f = 0.35$. Note: for $\beta_2 \ll 1$, curves converge according to Eq. (60); for $\beta_2 \gg 1$, behavior follows Eq. (66) or (67).

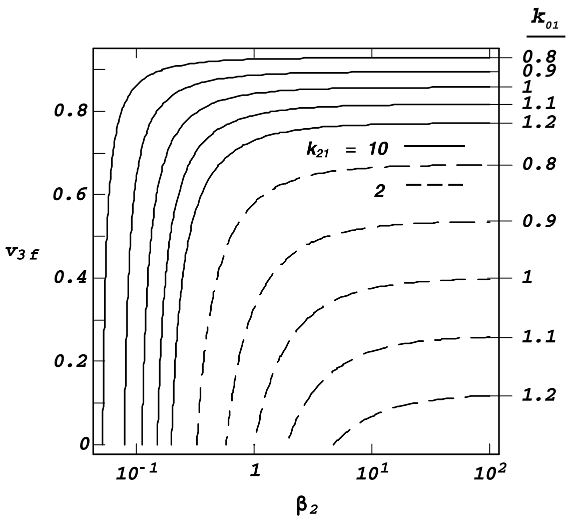

Fig. 5. Alternative method for plotting the interrelationship between the three variables (k_{01}, β_2, v_{3f}). Same data as for Fig. 4.

A practical point should also be noted with respect to the format used for this figure. That is, this type of plot can be helpful in assessing which, if any, particles are capable of meeting a design requirement for the effective thermal conductivity. A given type of particle is characterized by its relative thermal conductivity ($k_{21} = k_2/k_1$) and dimensionless wall thickness ($v_{3f} = (1-\delta/r_2)^3$). Since these are the axes of this plot, each type of particle will be represented by a different point on the plane and may be judged acceptable or unacceptable according to which side of the required iso-k_{01} curve it falls.

Finally, Fig. 7 shows the same basic interrelation $k_{01}(k_{21}, v_{3f})$ but by using ω_{f3} as the wall thickness variable in place of v_{3f}. This was done since, as indicated by the derivation of Eqs. (50) and (54), ω_{f3} is the 'natural' mathematical variable for describing this phenomena in contrast to v_{f3}, which is the more physically meaningful variable. The mathematical form of the variation depicted in Fig. 7 may be deduced from Eq. (54) by using the definitions in Eqs. (51)–(53). Arranging the variables into the form $k_{21}(\omega_{f3})$ with k_{01} as a parameter, the relation becomes:

$$k_{21} = \frac{1}{2}\left(\frac{2 - k_{01}\omega_f^*}{k_{01} - \omega_f}\right)\omega_{f3} \quad (69)$$

Note that unlike the relation between k_{21} and v_{3f}, the relation between k_{21} and ω_{f3} is linear.

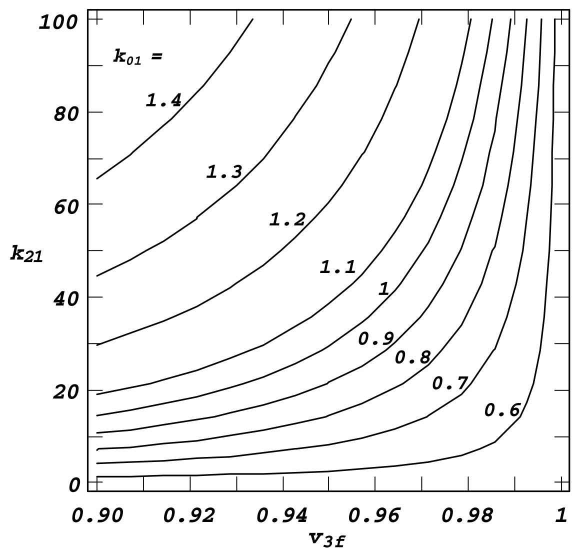

Fig. 6. The interrelationship between the effective conductivity, $k_{01} = k_{\text{eff}}/k_1$, the particle conductivity, $k_{21} = k_2/k_1$, and the particle wall thickness, $v_{3f} = (1 - \delta/r_2)^3$ for thin-walled spherical shells including *microballoons* ($(\delta/r_2) \sim 0.01$, or $v_{3f} \sim 0.97$). $\beta_2 \to \infty$; $k_{32} = 0 = k_{31}$; $v_f = 0.35$.

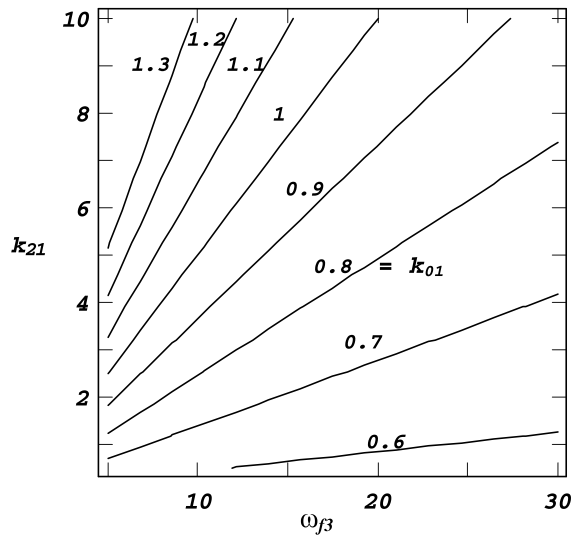

Fig. 7. An alternative plot for the (k_{01}, k_{21}, v_{3f}) data of Fig. 6. Note that the relationship between k_{21} and ω_{f3} is linear—Eq. (69).

6. Conclusions

The self-consistent field theory was employed to derive the effective thermal conductivity of mixtures produced by randomly distributing composite spheres throughout a continuum, and having imperfect thermal contact between the surfaces of the spheres and the continuous phase. The present result extends previous studies which considered such spheres to be homogeneous. An exact, yet simple, analytical result was obtained. Also derived were relations which apply to various idealizations. For the case representative of many *syntactic foams*, it was found that the dimensionless effective conductivity depends on a single variable (Ωv_f), and that the conductivity of the continuum may be increased or decreased by adding hollow spheres to it depending on whether the Ω-value for the spheres is greater or less than zero, respectively.

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