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A mixture theory for heat conduction in ⁷**heterogeneous media**

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Abstract-A mixture theory based on the ensemble-averaging technique is proposed for studying the thermal behaviour of heterogeneous media. Balance equations with partial heat fluxes and interaction terms are introduced for a two-component medium. Relations between these quantities and the ensembleaveraged (mean) temperatures of separate components are derived. The limits of application of widely used postulates of proportionality of the interaction term to difference in mean temperature of components is discussed. The effective conductivities of components in the mixture and the interaction coefficient are introduced and related to the so-called microstructure functions, which are functions of the microgeometry of the medium and the thermal properties of its components. Examples of the application of the theory to the calculation of the mean properties of a heterogeneous medium are presented.

1. INTRODUCTION

The behaviour and properties of heterogeneous media have attracted the attention of many investigators due to.the complexity of the problem and the wide occurrence of the media in engineering applications. The macroscopic approach to the description of the processes is usually followed and two different continuum models have been proposed. The first model, often called the *pseudohomogeneous* model, treats the heterogeneous material as a single phase with certain effective properties. Examples of this model can easily be found, for example, in many problems of heat conduction in heterogeneous media [l-4]. It was found that the medium, when looked at from the macroscopic point of view, behaves in a nonlocal and memory way [3]. The boundary effects can also be observed [5].

In the second model, called the *mixture* model, components of the heterogeneous medium are envisioned as forming continua coexisting at every point in the medium $[6-10]$. These continua are described by different effective properties and are mutually interacting. This way of modelling processes in heterogeneous media is popular, for example, in conduction-convection problems of heat transfer, flow problems of suspensions, filtration in porous media, and many others. Naturally, it is suspected that this way of continuum modelling a heterogeneous medium will also lead to a similar kind of effect as met with the pseudohomogeneous model. However, it is interesting what kind of deeper relations exist between the mixture and pseudohomogeneous models, and to calculate macroscopic properties of a heterogeneous medium knowing the microstructure of the medium and the properties of its components.

If we focus on a heat transfer process and the mixture approach then description of the process must include :

- (i) Formulation of energy balance equations in which mean (partial) heat fluxes and temperatures of the separate phases appear as well as terms of the energy exchange between them.
- (ii) Constitutive relations between the mean (partial) heat fluxes and phase energy interchange term and mean temperatures of the components.

The answer to the above problems is by no means simple and often based on more or less reliable postulates. If it is treated rigoriously it can be analyzed only when a cohduction mode of heat transfer is present. Even then the microgeometry of the heterogeneous medium places serious limitations on the solution of the problems. Thus, originally only two- [l **1,121** and three-component [131 laminates have been studied. The mixture formulation was then applied to unidirectional fiber-reinforced composites of different fiber cross-section and different fiber distribution in a matrix [14, 151. The nonlinear form of the mixture theory for this kind of heterogeneous media, following on from the temperature dependence of the fiber properties, has been proposed in ref. [16]. The results of these investigations proved to be very useful in forecasting temperature fields in these kinds of composite. In all of the above-mentioned approaches the periodicity assumption for the structure of the media and the volume-averaging technique have been utilized. Moreover, only conduction along laminae and fibers has been studied.

It is also worth mentioning another approach to solving previously discussed problems associated with

NOMENCLATURE

mixture formulation of heat transfer in heterogeneous **2. THE ENERGY BALANCE EQUATIONS FOR** media as proposed by Buyevich and coworkers [17 **THE MIXTURE FORMULATION** 211. With this approach the mean heat transfer in different components of the medium is not treated on the same footing. For example, in the two-component, granular medium studied the continuum phase associated with grains is assumed to be non-conductive, the conductive mode being only retained for heat transfer in the matrix. However, it is then not clear what kind of limitations, besides strictly geometrical ones, are associated with such an assumption.

In this paper heat conduction in a two-component medium is studied using the mixture formulation. No a *priori* limitations referring to the medium microgeometry are assumed. In Section 2 the ensembleaveraging technique is used to formulate the energy balance equations describing heat transfer processes in two components. In Section 3 the problem of existing relations between mean (partial) heat fluxes in the components, the energy interchange term and the mean temperatures of the components is addressed and thoroughly discussed. In Section 3 it is shown how quantities appearing in the previously proposed, pseudohomogeneous formulation of heat conduction in heterogeneous materials [3] can be utilized in the study of problems of heat transfer in heterogeneous media when the mixture formulation is applied. Section 4 presents examples of application of the theory in calculation of the interaction coefficient for different kind of composite materials. Finally, Section 5 provides a brief summary of the main results.

 $(nabla)$

Consider an inhomogeneous medium Ω . This medium is thermally affected by the environment on its boundary. The inner structure of the medium may be regular (periodic) or irregular (chaotic). One strictly determined distribution of components in volume Ω with respect to its boundary is understood as a different configuration $\mathscr A$ and treated as an element of the sample space [3]. The configuration may be described, for example, by the so-called characteristic function $\theta_i(\mathbf{x} \mid \mathcal{A})$ which assumes a value equal to unity inside the *j*th component, and zero otherwise.

The ensemble-averaged (mean) value of any function $f(t, \mathbf{x} | \mathcal{A})$ over the sample space may be defined as

$$
\{f(t, \mathbf{x})\} = \int f(t, \mathbf{x} \mid \mathcal{A}) p(\mathcal{A}) d\mathcal{A} \tag{1}
$$

where $p(\mathcal{A})$ is the probability density function for configuration $\mathscr A$.

For each configuration $\mathscr A$ of a two-component medium the heat conduction equation can be formally written as

$$
-\nabla \cdot \mathbf{q}(t, \mathbf{x} \mid \mathscr{A}) = c(\mathbf{x} \mid \mathscr{A}) \partial_t T(t, \mathbf{x} \mid \mathscr{A}) \qquad (2)
$$

$$
-q(t, \mathbf{x} \mid \mathcal{A}) = \lambda(t, \mathbf{x} \mid \mathcal{A}) \nabla T(t, \mathbf{x} \mid \mathcal{A}) \tag{3}
$$

where

$$
\lambda(t, \mathbf{x} \mid \mathcal{A}) = \lambda_1 \theta_1(\mathbf{x} \mid \mathcal{A}) + \lambda_2 \theta_2(\mathbf{x} \mid \mathcal{A}) \tag{4}
$$

$$
c(t, \mathbf{x} \mid \mathscr{A}) = c_1 \theta_1(\mathbf{x} \mid \mathscr{A}) + c_2 \theta_2(\mathbf{x} \mid \mathscr{A}). \tag{5}
$$

The initial and boundary conditions are assumed to 3. **CONSTITUTIVE RELATIONS FOR MIXTURE** be as follows : **THEORY**

$$
T(0, \mathbf{x} \mid \mathcal{A}) = T_0 \quad \text{in} \, \Omega \, \text{for} \, t = 0 \tag{6}
$$

$$
\mathbf{q}(t, \mathbf{x} \mid \mathscr{A}) \cdot \mathbf{n} + \alpha(\mathbf{x}) T(t, \mathbf{x} \mid \mathscr{A}) = \beta(t, \mathbf{x}) \quad \text{on } \partial \Omega.
$$

(7)

Dirichlet-, Neumann- and Cauchy-type boundary conditions may be obtained by the proper choice of functions α and β . Both of these functions are treated as independent of the configuration of the components.

Equations (2) , (3) , (6) and (7) were multiplied in turn by $\theta_1(\mathbf{x} \mid \mathcal{A})$ and $\theta_2(\mathbf{x} \mid \mathcal{A})$, and subsequently ensemble-averaged over all possible configurations of the heterogeneous medium. In this way two energy balance equations, each corresponding to a separate component, were obtained. After some manipulation the equations may be written as follows :

$$
\nabla \cdot \lambda_1 (\nabla \{ \theta_1 T \} + \tau_1) - c_1 \partial_t \{ \theta_1 T \} = \mathcal{F}
$$
 (8)

$$
\nabla \cdot \lambda_2^3 (\nabla \{\theta_2 T\} + \tau_2) - c_2 \partial_t \{\theta_2 T\} = -\mathscr{T}
$$
 (9)

where

$$
\tau_i = -\{\nabla \theta_i T\} \quad i = 1, 2 \tag{10}
$$

and

$$
\mathcal{T} = -\{\nabla \theta_1 \cdot \mathbf{q}\} = \{\nabla \theta_2 \cdot \mathbf{q}\}.
$$
 (11)

The quantities $\{\theta_1 T\}$ and $\{\theta_2 T\}$ appearing in the above equations are proportional to the mean (partial) temperatures of the components. Noting that

$$
\{\theta_1 T\} + \{\theta_2 T\} = \{T\} \tag{12}
$$

the mean temperatures of the components may be defined as

$$
\{T\}_1 = \{\theta_1 T\}/v_1 \quad \{T\}_2 = \{\theta_2 T\}/v_2 \quad (13)
$$

where v_1 and v_2 are the volume fractions of each component.

The gradients of the characteristic functions θ_i in definitions (10) and (11) have non-zero values only in the component interphases. The vectors τ_1 and τ_2 are related to the change in the mean temperature gradient in each of component of the medium due to a tortuous way of heat flow in each phase, and are subsequently called "*tortuosity vectors*". The quantity \mathcal{T} is known as the *"interaction term"* and gives the value of the local interchange of energy between the components during conduction of heat in the medium.

The set of equations (8) and (9) cannot be solved by any method (either analytical or numerical) unless relations (constitutive relations) between $\tau_1, \tau_2, \mathscr{T}$ and the mean temperatures of the components are known. These relations constitute the "closure problem" for the mixture formulation of heat transfer in a heterogeneous medium. However, even for the process of heat conduction with an arbitrary medium microstructure, they are unfortunately not known exactly. This problem will be studied in detail in Section 3.

The relations between the tortuosity vectors and the interaction term on the one hand and the mean temperatures of the components on the other should in general be nonlocal [3]. This means that $\tau_1(\mathbf{x}, t)$, $\tau_2(\mathbf{x}, t)$ and $\mathcal{T}(\mathbf{x}, t)$ should depend not only on the gradients or time derivatives of $\{\theta_1 T\}$ and $\{\theta_2 T\}$ at point x and time t , but also on the whole temperature distribution $\{\theta_1 T\}$ and $\{\theta_2 T\}$ and its variation with time, i.e. its history. It can also be observed easily that the pertinent constitutive relations could be derived directly from definitions (10) and (11) if the relation between the local temperature $T(t, x | \mathcal{A})$ and the component mean temperature $\{T\}_i$ (or $\{\theta_i T\}$) is known. In this paper a special case of slowly varying (in time and space) temperature fields $\{T\}_i$ will be considered. It is the case that was studied in the majority of papers on the subject [11, 12, 16].

In a previous paper [3] the pseudohomogeneous formulation of heat conduction in heterogeneous media was discussed in detail. Some of the intermediate results of the theory presented in ref. [3] will now be utilized in order to simplify the derivations. This procedure will also give an opportunity to analyze mutual connections between the formulations, i.e. the pseudohomogeneous and the mixture one. In the above-mentioned paper it was shown that the following, integral-type relation between the local temperature $T(t, \mathbf{x} | \mathcal{A})$ and the mean temperature $\{T\}$ holds :

$$
T(t, \mathbf{x} | \mathcal{A}) = \{T(t, \mathbf{x})\}
$$

+
$$
\int_{\Omega} \varphi(\mathbf{x}, \mathbf{x} | \mathcal{A}) \cdot \nabla \{T(t, \mathbf{x}') d\mathbf{x}
$$

+
$$
\int_{0}^{t} \int_{\Omega} \psi(t, \mathbf{x}; t', \mathbf{x}' | \mathcal{A})
$$

$$
\times \partial_{t}' \{T(t', \mathbf{x}') d\mathbf{x}' dt'
$$
 (14)

where φ and ψ , called "the microstructure functions", are solely dependent on the microgeometry and thermal properties of the components of the heterogeneous medium. Both functions can be obtained from solution of the integro-differential equations given in ref. [3].

If one of the components of the heterogeneous medium (for example denoted by 1) appear in the form of separate particles (or fibers), the characteristic function $\theta_1(\mathbf{x} \mid \mathcal{A})$ can then be expressed as

$$
\theta_1(\mathbf{x} \mid \mathcal{A}) = \sum \theta_{1j}(\mathbf{x} \mid \mathcal{A}) \tag{15}
$$

where summation extends over all particles of the component for the assumed configuration \mathcal{A} , and the function θ_{1j} is equal to unity in the *j*th particle and to zero otherwise. Now consider a point in the medium determined by a location vector x. For a definite configuration $\mathscr A$ one of the particles is nearest to the point system ξ , bound with this particle, is introduced [3]: it can be cast in the form

$$
\xi(\mathbf{x} \mid \mathcal{A}) = [\mathbf{x} - \mathbf{x}_s(\mathcal{A})] / l. \tag{16}
$$

It is obvious that ξ depends on $\mathscr A$ and may thus be treated as a random variable. A microdimension 1 nondimensionalizing ξ may be understood as a mean interparticle distance, a cell dimension in periodic structures or a correlation length associated with the description of a random structure. If the nonlocality is weak then relation (14), using ξ , can be cast in the following form [3] :

$$
T(t, \mathbf{x} | \mathcal{A}) = \{T(t, \mathbf{x})\}+ l\varphi_1(\mathbf{x}, \xi | \mathcal{A}) \cdot \nabla_g \{T(t, \mathbf{x})+ l^2[\overline{\varphi}_2(\mathbf{x}, \xi | \mathcal{A}) : \nabla_g^{(2)} \{T(t, \mathbf{x})+ \psi_{20}(\mathbf{x}, \xi | \mathcal{A}) \partial_t \{T(\mathbf{x}, \xi) + O(l^2) \} (17)
$$

where $\nabla_{g}^{(n)}$ denotes an *n*th-order gradient calculated in the global (x) coordinate system.

The reduced "microstructure functions" φ_1 , $\overline{\varphi_2}$ and ψ_{20} then satisfy the equations :

$$
\varphi_1(\mathbf{x}, \xi \mid \mathscr{A}) = -\int_{\Omega} \nabla_1 G(\xi, \eta)
$$

$$
\cdot [\lambda'(\eta \mid \mathscr{A})(\overline{1} + \nabla_1 \varphi_1(\mathbf{x}, \eta \mid \mathscr{A}))
$$

$$
- \{\lambda'(\eta \mid \mathscr{A})(\overline{1} + \nabla_1 \varphi_1(\mathbf{x}, \eta \mid \mathscr{A}))\}]\,d\eta \quad (18)
$$

$$
\overline{\varphi}_2(\mathbf{x}, \xi | \mathcal{A}) = - \int_{\Omega} \nabla_1 G(\xi, \eta)
$$

$$
\cdot [\lambda'(\eta | \mathcal{A})(\overline{1}\varphi_1(\mathbf{x}, \eta | \mathcal{A}) + \nabla_1 \overline{\varphi}_2(\mathbf{x}, \eta | \mathcal{A}))
$$

$$
- \{\lambda'(\eta | \mathcal{A})(\overline{1}\varphi_1(\mathbf{x}, \eta | \mathcal{A}) + \nabla_1 \overline{\varphi}_2(\mathbf{x}, \eta | \mathcal{A}))\}]\,d\eta
$$
(19)

$$
\psi_{20}(\mathbf{x}, \xi | \mathscr{A}) = -\int_{\Omega} \nabla_1 G(\xi, \eta)
$$

$$
\left\{ \lambda'(\eta | \mathscr{A}) \nabla_1 \psi_{20}(\mathbf{x}, \eta | \mathscr{A}) \right\}
$$

$$
-\left\{ \lambda'(\eta | \mathscr{A}) \nabla_1 \psi_{20}(\mathbf{x}, \eta | \mathscr{A}) \right\} \right\} d\eta
$$

$$
+\int_{\Omega} G(\xi, \eta) \cdot \left[c(\eta | \mathscr{A}) - \left\{ c(\eta | \mathscr{A}) \right\} \right] d\eta \qquad (20)
$$

$$
\{\phi_1\} = 0 \quad \{\overline{\phi}_2\} = 0 \quad \{\psi_{20}\} = 0 \tag{21}
$$

where $\bar{1}$ is the unit second-order tensor, $\lambda' = \lambda - \lambda_r$, and $G(\xi, \eta)$ and ∇_i are the Green function and gradient calculated in local coordinates ξ , respectively. The Green function is a solution of the following problem :

$$
\nabla_1 \lambda_r \nabla_1 G(\xi, \eta) + \delta(\xi, \eta) = 0 \quad \text{in } \Omega
$$

-\lambda_r \nabla_1 G(\xi, \eta) \cdot \mathbf{n} + \alpha G(\xi, \eta) = 0 \quad \text{on } \partial \Omega. \quad (22)

In the above equations $\delta(\xi, \eta)$ denotes a Dirac pseudofunction, **n** is a normal, external vector to $\partial\Omega$, and λ , is a certain reference conductivity.

x and influences most the local temperature and heat In order to derive the relation between the local flux around it. A certain characteristic point \mathbf{x}_s has $T(t, \mathbf{x} | \mathcal{A})$ and the mean temperature $\{T(t, \mathbf{x})\}_1$ of the been chosen inside the particle (for example the centre first component, equation (17) has been multiplied by of the spherical particle), and the local coordinate $\theta_1(\mathbf{x} \mid \mathcal{A})$, and ensemble-averaged. After rearranging

$$
\{T\} = \{T\}_1 - I\{\theta_1\}^{-1} \{\theta_1 \varphi_1\} \cdot \nabla_g \{T\}
$$

$$
-I^2 [\{\theta_1\}^{-1} \{\theta_1 \overline{\varphi}_2\} \cdot \nabla_g^{(2)} \{T\}
$$

$$
+ \{\theta_1\}^{-1} \{\theta_1 \psi_{20}\} \partial_t \{T\}] - O(I^3). \quad (23)
$$

The successive gradients and time derivatives (of growing order) for the left-hand side of equation (23) were then calculated and used to eliminate the pertinent quantities on the right-hand side of equation (23). In this way the following relation between $\{T\}$ and $\{\theta_1 T\}$ has been obtained:

$$
\{T\} = \{T\}_1 - l\zeta_1 \cdot \{\theta_1\}^{-1} \nabla_g \{\theta_1 T\}
$$

$$
-l^2 [\overline{\zeta}_2 : \{\theta_1\}^{-1} \nabla_g \{\theta_1 T\}
$$

$$
+ \chi_{20} {\{\theta\}_1^{-1} \partial_t {\{\theta_1 T\}} - O(l^3) \quad (24)
$$

where

$$
\zeta_1 = \{\theta_1\}^{-1} \{\theta_1 \varphi_1\} \tag{25}
$$

$$
\overline{\zeta}_2 = {\theta_1}^{-1} {\theta_1 \overline{\phi}_2} - {\zeta_1} {\theta_1}^{-1} {\theta_1 \varphi_1}
$$
 (26)

$$
\chi_{20} = \{\theta_1\}^{-1} \{\theta_1 \psi_{20}\}.
$$
 (27)

Finally, substituting $\{T\}$ from equation (24) into equation (17) the following relation was obtained :

$$
T(t, \mathbf{x} | \mathcal{A}) = \{T(t, \mathbf{x})\}_1 + l\phi_1(\mathbf{x} | \mathcal{A})
$$

$$
\cdot \{\theta_1\}^{-1} \nabla_{\mathbf{g}} \{\theta_1(\mathbf{x}) T(t, \mathbf{x})\} + l^2 [\overline{\phi}_2(\mathbf{x} | \mathcal{A})
$$

$$
\cdot \{\theta_1\}^{-1} \nabla_{\mathbf{g}} \{\theta_1(\mathbf{x}) T(t, \mathbf{x})\} + X_{20}(\mathbf{x} | \mathcal{A})
$$

$$
\cdot \{\theta_1\}^{-1} \partial_t \{\theta_1(\mathbf{x}) T(t, \mathbf{x})\} + O(l^3)
$$
(28)

where

$$
\begin{aligned}\n\boldsymbol{\phi}_1 &= \boldsymbol{\varphi}_1 - \boldsymbol{\zeta}_1 \\
\overline{\phi}_2 &= \overline{\phi}_2 - \boldsymbol{\varphi}_1 \boldsymbol{\zeta}_1 - \overline{\boldsymbol{\zeta}}_2 \\
X_{20} &= \psi_{20} - \chi_{20}.\n\end{aligned}
$$
\n(29)

In an identical way the relation between $T(t, x | \mathcal{A})$ and $\{T(t, x)\}\$ can be derived. It is worth noting that the above relation, equation (28), can also be obtained directly from equation (14) by multiplying this equation by θ_1 , ensemble averaging and a proper expansion in a power series of l to obtain equation (24).

When the relations between the local temperature *T* and the mean temperatures of the components are known derivation of the constitutive relations is straightforward. In order to do that definitions (10) and (11) for τ_1 and $\mathcal T$ were rewritten using the local coordinate system ξ (Appendix 1) as

$$
\tau_1 = l^{-1} v_1 \langle \langle \nabla_1 T \rangle^* \rangle_1 \tag{30}
$$

$$
\mathcal{T} = l^{-1} v_1 \langle {\{\nabla_1 \cdot \bar{q}\}}^* \rangle_1 \tag{31}
$$

where $\langle \rangle$ means averaging over a volume of the

reference particle that is nearest to point x in the medium and $\{ \}^*$ means ensemble averaging over all possible shapes of the reference particle as well as over all possible configurations of the neighbouring particles when location of the reference particle and its shape is fixed. Subsequently, after substitution of equation (2) for q and equation (28) for *T* into the above equations and making use of the following relation $[3]$:

$$
\nabla T(t, \mathbf{x} \mid \mathcal{A}) = \nabla_{\mathbf{g}} T + l^{-1} \nabla_{\mathbf{l}} T \tag{32}
$$

expressions (30) and (31) are cast in the form

$$
\tau_1(t, \mathbf{x}) = v_1 \langle \{ \nabla_1 \phi_1 \}^* \rangle_1 \cdot \{ \theta \}^{-1} \nabla_{\mathbf{g}} \{ \theta_1 T \} + \mathcal{O}(t)
$$

= $v_1 \langle \{ \nabla_1 \phi_1 \}^* \rangle_1 \cdot \{ \theta_1 \}^{-1} \nabla_{\mathbf{g}} \{ \theta_1 T \} + \mathcal{O}(t)$ (33)

$$
\mathcal{J}(t, \mathbf{x}) = -\lambda_1 v_1 [\langle \{V_1 + \nabla_1 \overline{\phi}_2\}^* \rangle_1 \cdot {\theta_1}^2]^{-1} \nabla_g^{(2)} {\theta_1 T}
$$

+ $\langle {\nabla_1 \cdot \nabla_1 X_{20}}^* {\theta_1}^2]^{-1} \partial_t {\theta_1 T}^2 + O(t)$
= $-\lambda_1 v_1 [\langle {\nabla_1 \cdot (\overline{\Pi} \varphi_1 + \nabla_1 \overline{\varphi}_2} - (\overline{\Pi} + \nabla_1 \varphi_1) {\theta_1}^2]^{-1} {\theta_1 \varphi_1}])^* \rangle_1$
 $\cdot {\theta_1}^2 {}^{-1} \nabla_g^{(2)} {\theta_1 T}$
+ $\langle {\nabla_1 \cdot \nabla_1 \psi_{20}}^* {\theta_1}^2]^{-1} \partial_t {\theta_1 T}^2 + \langle {\nabla_1 \cdot \nabla_1 \psi_{20}}^* {\theta_1}^2]^{-1} \partial_t {\theta_1 T}^2 + O(t)$. (34)

Formulas similar to equation (33) can be obtained for the tortuosity vector τ_2 corresponding to the second component. If a relation between *T* and $\{\theta_2 T\}$ identical to equation (28), with θ_1 in equations (25)-(29) changed to θ_2 , is used then τ_2 can be expressed as

$$
\tau_2(t, \mathbf{x}) = -v_1 \langle {\nabla}_1 \varphi_1 \rangle^* \rangle_2 \cdot {\nabla}_2 {\nabla}_2 \{\theta_2\}^{-1} \nabla_g {\nabla}_2 f \rangle + O(l). \tag{35}
$$

Equation (34) can be simplified when the differential form of equations (18) and (19) is utilized, i.e.

$$
\nabla_{\mathbf{i}} \cdot \lambda (\mathbf{T} + \nabla_{\mathbf{i}} \boldsymbol{\varphi}_{\mathbf{i}}) = 0
$$

$$
\nabla_{\mathbf{i}} \cdot \lambda (\mathbf{T} \boldsymbol{\varphi}_{\mathbf{1}} + \nabla_{\mathbf{i}} \overline{\boldsymbol{\varphi}}_{\mathbf{2}}) = \lambda_{\mathbf{r}} \nabla_{\mathbf{i}} \boldsymbol{\varphi}_{\mathbf{1}}.
$$

Then the interaction term can be expressed as

$$
\mathcal{F}(t, \mathbf{x}) = -\lambda_{\tau} v_1 \langle {\nabla_{1} \boldsymbol{\varphi}_{1}} \rangle^* \rangle_{1} : {\nabla_{1} \boldsymbol{\varphi}_{1}}^{-1} \nabla_{\boldsymbol{\varphi}}^{(2)} {\nabla_{1} T}
$$
\n
$$
-\lambda_{1} v_1 \langle {\nabla_{1} \boldsymbol{\cdot} \nabla_{1}} \boldsymbol{\psi}_{20} \rangle^* \rangle_{1} {\nabla_{1} \boldsymbol{\varphi}_{1}}^{-1} \partial_{\tau} {\nabla_{1} T} + O(l). \quad (36)
$$

The above formula is the most general expression for the interaction term. Further simplifications can be obtained when additional assumptions are made. If it is assumed that the heterogeneous medium can be treated as statistically (i.e. on the macroscopic scale) homogeneous and isotropic then the following relation holds (Appendix 2) :

$$
\overline{1}: \nabla_{g}^{(2)} \{ \theta_{1} T \} = a_{\text{ef}}^{-1} \partial_{t} \{ \theta_{1} T \}
$$
 (37)

where a_{eff} is the effective thermal diffusivity defined by

$$
a_{\rm ef} \overline{1} = \overline{\lambda}_{\rm ef} / c_{\rm ef} = {\lambda(\overline{1} + \nabla_{\rm i}\varphi_1)}/{\langle c \rangle}. \qquad (38)
$$

It should be noted that a relation similar to equation

(37) is also satisfied for macroscopically anisotropic media (for example layered or reinforced with unidirectionally aligned fibres) when the bulk heat flow occurs along one of the principal axes of the effective conductivity tensor $\bar{\lambda}_{\text{ef}}$. Equation (37) allows for the elimination of $\nabla_{\mathbf{g}}^{(2)} \{ \theta_1 T \}$ from expression (36), which leads to

$$
\mathcal{F} = -\lambda_{\tau} v_1 [\langle \{ |\nabla_{\mathbf{I}} \varphi_1 | \}^* \rangle / a_{\rm cf} + \lambda_1 / \lambda_{\rm r} \langle \{ \nabla_{\mathbf{I}} \cdot \nabla_{\mathbf{I}} \psi_{20} \}^* \rangle_1] \{ \theta \}^{-1} \partial_{\rm t} \{ \theta_1 T \} + \mathbf{O}(l) \quad (39)
$$

where the notation $\nabla_1 \varphi_1 = |\nabla_1 \varphi_1|$ $\bar{\bar{\mathbf{I}}}$ is used for isotropic media.

In many papers dealing with the application of the mixture theory to the description of heat transfer in heterogeneous media, the interaction term is postulated to be proportional to the difference in the mean temperatures of the phases [4, 10, 22]. In order to verify this postulate the time derivative of $\{\theta_1, \theta_2\}$ should be eliminated from equation (39). Multiply the expression for the local temperature, equation (28), by the characteristic function $\theta_2(\mathbf{x} \mid \mathcal{A})$ and ensemble average the product. Then the following relation holds :

$$
\begin{aligned} \{\theta_2 T(t, \mathbf{x})\} &= \{\theta_2\} \{T\}_1 + l \{\theta_2 \phi_1\} \\ \cdot \{\theta_1\}^{-1} \nabla_{\mathbf{g}} \{\theta_1 T\} + l^2 [\{\theta_2 \overline{\phi}_2\} : \{\theta_1\}^{-1} \nabla_{\mathbf{g}}^{(2)} \{\theta_1 T\} \\ &+ \{\theta_2 X_{20}\} \{\theta_1\}^{-1} \partial_t \{\theta_1 T\} + \mathcal{O}(l^3). \end{aligned} \tag{40}
$$

If definitions (29), equation (37) and the relations

$$
\begin{aligned} \{\theta_1 \varphi_1\} &= 0\\ \{\theta_1 \overline{\varphi}_2\} &= \{\theta_1 | \varphi_2\} \overline{1} \end{aligned}
$$

valid for macroscopically homogeneous and isotropic media are taken into account, then equation (40), after multiplication by $-\{\theta_1\}$ and reordering, can be written as

$$
\{\theta_2\} \{\theta_1 T\} - \{\theta_1\} \{\theta_2 T\} = l^2 [\{\theta_1 | \varphi_2\}] / a_{\text{cf}}
$$

+
$$
\{\theta_1 \psi_{20}\}] \partial_{\tau} \{\theta_1 T\} + O(l^3).
$$
 (41)

If, additionally, the analysis is limited to terms of order l^2 then elimination of $\partial_t \{\theta_i T\}$ between equations (39) and (41) leads to the following expression for the interaction term :

$$
\mathcal{F}(t, \mathbf{x}) = -\lambda_{\rm r} v_1 l^{-2} [\langle \{ | \nabla_1 \varphi_1 | \}^* \rangle_1 / a_{\rm ef} \n+ \lambda_1 / \lambda_{\rm r} \langle \{ \nabla_1 \cdot \nabla_1 \psi_{20} \}^* \rangle_1] \cdot [\{\theta_1 | \overline{\varphi}_2 | \} / a_{\rm ef} \n+ \{\theta_1 \psi_{20}\}]^{-1} [\{\theta_2\} \{\theta_1 T\} - \{\theta_1\} \{\theta_2 T\}].
$$
\n(42)

Now introduce a definition of the "effective (partial) conductivity of the *i*th component":

$$
\overline{\lambda}_{\text{ref}} = \lambda_i (\overline{\mathbf{I}} + {\theta_i \nabla_1 \varphi_1}/{\theta_i})
$$
 (43)

and note that, according to Appendix 1,

$$
\{\theta_1 f(t, \mathbf{x})\} = v_1 \langle \{f(t, \mathbf{x})\} \rangle_1^*.
$$
 (44)

Then, using definitions of the mean temperatures of the components [equations (13)] a set of equations for the mixture theory of heat conduction in heterogeneous media can be, finally, cast in the form

$$
\nabla_{\mathbf{g}} \cdot \overline{\lambda}_{\text{ref}} \cdot \nabla_{\mathbf{g}} \{T\}_1 - \mathbf{c}_1 \,\partial_t \{T\}_1 = \mathcal{R}(\{T\}_1 - \{T\}_2)/v_1
$$
\n(45)

$$
\nabla_{\mathbf{g}} \cdot \overline{\lambda}_{2\epsilon\mathbf{f}} \cdot \nabla_{\mathbf{g}} \{T\}_2 - c_2 \, \partial_{\mathbf{t}} \{T\}_2 = -\mathcal{R}(\{T\}_1 - \{T\}_2)/v_2
$$
\n(46)

with boundary conditions

$$
(\overline{\lambda}_{i\in f} \cdot \nabla_{g} \{T\}_{i}) \cdot \bar{n} + \alpha \{T\}_{i} = f(t, \mathbf{x}) \quad i = 1, 2
$$

where the interaction coefficient \mathcal{R} is defined by

$$
\mathcal{R} = -\lambda_r v_1 v_2 l^{-2} [\langle \{ |\nabla_1 \varphi_1| \}^* \rangle / a_{\text{ef}} \n+ \lambda_1 / \lambda_r \langle \{ \nabla_1 \cdot \nabla_1 \psi_{20} \}^* \rangle_1] [\langle \{ |\overline{\varphi}_2| \}^* \rangle_1 / a_{\text{ef}} \n+ \langle \{ \psi_{20} \}^* \rangle_1]^{-1}.
$$
 (47)

The set of equations (45) and (46), approximately describing a heat conduction process in a heterogeneous medium within the mixture formulation, can be solved numerically or analytically, for example using a method proposed in ref. [23]. The effective partial thermal conductivities λ_{1cf} and λ_{2cf} and the interaction coefficient $\mathcal R$ needed for it can be calculated after solving equations (19) – (21) for the microstructure functions φ_1 , $\overline{\varphi}_2$ and ψ_{20} . These microstructure functions are the same as those appearing in the pseudohomogeneous formulation of the macroscopic theory of heat conduction in heterogeneous media presented in ref. [3]. If distribution of the mean temperature of the first component is found from equation (28) the approximate distribution of the local temperature $T(t, x | \mathcal{A})$ in the medium can be calculated for any configuration \mathcal{A} .

4. EXAMPLES OF THE APPLICATION OF THE THEORY

The utility of the theory presented in the Sections 2 and 3 can be illustrated, for example, by forecasting the effective properties of a heterogeneous medium, i.e. $\lambda_{1ef}, \lambda_{2ef}$ and \mathscr{R} . However, out of these three properties, the last is the most interesting. This happens because the effective conductivities of components can be obtained directly from a knowledge of the effective thermal conductivity $\lambda_{\rm ef}$ appearing in the pseudohomogeneous formulation. Two relations are then helpful :

$$
\overline{\lambda}_{\text{ef}} = \lambda_2 \overline{T} + (\lambda_1 - \lambda_2) v_1 \overline{\lambda}_{\text{1ef}} / \lambda_1 \tag{48}
$$

$$
(\overline{\lambda}_{1\text{cf}} - \lambda_1 \overline{1}) v_1 / \lambda_1 + (\overline{\lambda}_{2\text{cf}} - \lambda_2 \overline{1}) v_2 / \lambda_2 = 0. \quad (49) \quad \overset{\text{DOS}}{\longrightarrow}
$$

These relations follow directly from the definitions of $\overline{\lambda}_{\text{ref}}$ [equation (43)] and $\overline{\lambda}_{\text{ef}}$ [equation (38)], and the properties of the characteristic functions θ_i . Expressions (48) and (49) can also be used for calculating $\overline{\lambda}_{\text{ref}}$ when $\overline{\lambda}_{\text{cf}}$ is known from measurements, which is usually the case. In the following part of Section 4 attention is thus focused on the interaction coefficient \mathcal{R} . In all of the examples presented the

reference conductivity λ_r appearing in equation (47) is assumed to be equal to the thermal conductivity of the second component, λ_2 .

4.1. Interaction coefficient for periodic, laminated com*posite*

Consider an infinite, laminated composite with each component appearing in the form of identical laminae with a thickness corresponding to the volume fraction of the component. The origin of the local coordinate system ξ is placed in the centre of the laminae of component 1. An assumption is made that the bulk (macroscopic) heat flow is one-dimensional, occurring either along or perpendicular to the laminae. The Green function G_{∞} for the infinite space, needed for the solution of equations (19) – (21) , can be written in the following form consistent with the shape of the laminae [24] :

$$
G_{\infty}(\xi_1, \eta_1) = 0.5[(a - \xi_1 + \eta_1) H(\xi_1 - \eta_1) + (a + \xi_1 - \eta_1) H(\eta_1 - \xi_1)]/\lambda_r
$$
 (50)

where ξ_1 and η_1 are coordinates of a point in the composite along an axis perpendicular to the laminae, a is an arbitrary constant, and *His* the Heaviside step function. The origin of the local coordinate system is placed in the centre of the reference lamina of component 1. This Green function is a solution of the following problem :

$$
\lambda_{r} \partial_{\xi\xi} G_{\infty} + \delta(\xi, \eta) = 0
$$

$$
G_{\infty}(\xi - \eta = \pm a) = 0
$$

where *a* is an arbitrary constant.

Due to the assumption that $\lambda_r = \lambda_2$ integration of the right-hand side of equations (19) and (20) is carried out only over the volume of component 1. The functions φ_1 , $\bar{\varphi}_2$ and ψ_{20} inside this component have been chosen as follows :

$$
\varphi_1 = C_{11}\xi_1 \mathbf{1}_1
$$

\n
$$
\overline{\varphi}_2 = (D_{20} + D_{21}\xi_1^2)\mathbf{1}_1 \mathbf{1}_1
$$

\n
$$
\psi_{20} = E_{20} + E_{21}\xi_1^2
$$
\n(51)

where C_{11} , D_{20} , D_{21} , E_{20} and E_{21} are constants to be determined from equations (19)-(21), and $\mathbf{1}_1$ is a unit vector along the coordinate axis ξ_1 . It should be noted that, in postulating the form of the microstructure functions, symmetrical and antisymmetrical properties of these functions, as discussed in ref. [3], have been used together with the periodicity of the composite structure. From the periodicity of the composite it also follows that, for a fixed location x, at the centre of the reference lamina, only one configuration is possible, so that, for an arbitrary function f ,

$$
\langle \{f\}^* \rangle_1 = \langle f \rangle_1.
$$

After calculating the constants C_{11} , D_{20} , D_{21} , E_{20} and E_{21} , and substituting expressions (51) for φ_1 , $\bar{\varphi}_2$ and ψ_{20} in formula (47), the following relations for the interaction coeffient have been obtained :

$$
\mathscr{R}^{\parallel} = 12[v_1/\lambda_1 + v_2/\lambda_2]^{-1}/l^2 \tag{52}
$$

for heat flow along laminae, and

$$
\mathcal{R}^{\perp} = 12\lambda_1 l^{-2} [(\sigma_c - 1)\sigma_{\lambda} - (\sigma_{\lambda} - 1)(1 + (\sigma_c - 1)v_1)]
$$

.
$$
\cdot [(\sigma_{\lambda} - 1)^2 v_1 (1 + (\sigma_c - 1)v_1) + (\sigma_c - 1)\sigma_{\lambda} (v_1 + \sigma_{\lambda} v_2)]^{-1} \quad (53)
$$

where $\dot{\sigma}_{\lambda} = \lambda_1/\lambda_2$, and $\dot{\sigma}_c = c_1/c_2$, for heat flow perpendicular to laminae.

Formula (52) is identical with the expression for \mathcal{R} obtained by Nayfeh [12] but by a different method.

4.2. *Interaction coefjcient for a composite reinforced with unidirectionally aligned fibres*

Let a composite consist of a set of identical, unidirectionally aligned fibres of circular cross-section. The fibres have a thermal conductivity and volumetric specific heat equal to λ_1 and c_1 , respectively. The are embedded in a matrix characterized by the thermal properties λ_2 and c_2 . If the volume fraction of fibres is not too high then the so-called "well-separated" model of fibre distribution can be assumed. In this model each fibre is surrounded by a cylindrical layer of the matrix. The diameter of this external layer is roughly equal to the distance of fibre separation 21. In the local coordinate system ξ , with the origin located on the axis of the reference fibre, the surface of the fibre is described by a coordinate ξ_1 (perpendicular to the fibre axis) equal to $v_1^{1/2}$. The composite is also assumed to fill the infinite space. The appropriate Green function G_{∞} satisfying equation (22) and consistent with the fibre geometry can then be assumed, according to ref. [25], to be in the form of a series of trigonometric functions in the cylindrical system of coordinates $(\xi_1, \vartheta), (\eta_1, \vartheta)$:

$$
G_{\infty}(\xi_{1}, \vartheta; \eta_{1}, \vartheta)
$$

=
$$
[\ln (\eta_{1})^{-1} + \sum_{n=1}^{\infty} (\xi_{1}/\eta_{1})^{n} \cos n(\vartheta - \vartheta)]
$$

$$
\times H(\eta_{1} - \xi_{1})/(2\pi n \lambda_{1})
$$

+
$$
[\ln (\xi_{1})^{-1} + \sum_{n=1}^{\infty} (\eta_{1}/\xi_{1})^{n} \cos n(\vartheta - \vartheta)]
$$

$$
\times H(\xi_{1} - \eta_{1})/(2\pi n \lambda_{1})
$$
 (54)

where 9 is the azimuthal angle.

In order to solve equations (19) – (21) for the microstructure functions a form for these functions inside the reference fibre is needed. Due to the assumed model of fibre distribution, the microstructure functions should be axisymmetrical, i.e. they can be written as

$$
\varphi_1 = C_{11}\xi_1 \mathbf{1}_1
$$

\n
$$
\overline{\varphi}_2 = (D_{20} + D_{21}\xi_1^2)\mathbf{1}_1 \mathbf{1}_1 + D_{22}\xi\xi
$$

\n
$$
\psi_{20} = E_{20} + E_{21}\xi_1^2
$$
\n(55)

where, from the constants C_{ij} , D_{ij} and E_{ij} , the constants

 D_{21} and D_{22} are components of an isotropic fourthrank tensor. The constants discussed are determined from equations (19) – (21) after introducing into these equations expressions (54) and (55) and making use of the assumption that all the cells consist of a fibre surrounded by a matrix are identical. The explicit expressions for constants in equation (55) are not given because of their complicated, lengthy form. The microstructure functions φ_1 , $\overline{\varphi}_2$ and ψ_{20} when substituted into equation (47) lead to

$$
\mathcal{R}^{\parallel} = 8[1/\lambda_1 - (1 + 2/v_2 + \ln v_1^2/v_2^2)/\lambda_2]/l^2 \quad (56)
$$

for heat flow along fibres, and

$$
\mathcal{R}^{\perp} = 8\lambda_1 l^{-2} (\sigma_c - 2\sigma_{\lambda} + \sigma_c \sigma_{\lambda})
$$

$$
\times [(\sigma_{\lambda} - 1)^2 (v_2 + \sigma_c v_1) + (\sigma_c - 1)
$$

$$
\cdot (\sigma_{\lambda}^{-1} - (1 + 2/v_2 + \ln v_1^2/v_2^2)) \sigma_{\lambda} (\sigma_{\lambda} + v_2 + \sigma_{\lambda} v \perp)]^{-1}
$$
 (57)

for heat flow perpendicular to fibres.

The expression for the interaction coefficient given in equation (56) is identical with the result of Maewal *et al.* [14] for the same composite geometry.

4.3. Interaction coefficient for a composite with dis*persion of spherical inclusions*

In the third example the composite is assumed to consist of identical, spherical inclusions of thermal conductivity λ_1 and volumetric specific heat c_1 embedded in a matrix of thermal properties denoted by λ_2 and c_2 . The distribution of the inclusions is similar to the previous example, i.e. "the well-separated" model of inclusion distribution is assumed. The separation of the two nearest inclusions is taken to be equal to 2*l*. When the local coordinate system ξ has the origin located in the centre of the reference particle (with coordinate ξ_1 perpendicular to the surface of this inclusion) the value of ξ_1 corresponding to the external surface of the inclusion is equal to $v_1^{1/3}$. When the infinite space of the composite is considered the proper Green function consistent with the shape of the inclusion and satisfying conditions (22) can be found in ref. [25]. It can be expressed in the spherical coordinate system $(\xi_1, \vartheta, \beta)$, $(\eta_1, \vartheta, \beta')$ in the form of an expansion of the spherical harmonics $Y_{lm}(9, \beta)$ as

$$
G_{\infty}(\xi_1, \vartheta, \beta; \eta_1, \vartheta, \beta)
$$

=
$$
\sum_{l=0}^{\infty} \sum_{m=-l}^{m=1} [\xi_1^l \eta_1^{-(l+1)} H(\eta_1 - \xi_1) + \xi_1^{-(l+1)} \eta_1^l
$$

$$
\cdot H(\xi_1 - \eta_1) \cdot Y_{lm}(\vartheta, \beta) \hat{Y}_{lm}(\vartheta, \beta) / \lambda_2 \quad (58)
$$

where \hat{Y}_{lm} is a complex function conjugated to Y_{lm} , and θ and β are angles defining the location of a point in the local, spherical coordinate system.

Due to the spherical symmetry of the reference inclusion and a layer of the matrix surrounding it, the microstructure functions appearing in equation (47) have been assumed to be in a form identical to that

Fig. 1. Nondimensionalized interaction coefficient $\mathcal{R}/\mathcal{R}_{\text{lam}}^{\parallel}$ as a function of the volume fraction v_1 of component 1: (1) bulk heat flow \perp to lamina for laminated composite, (2) bulk heat flow \perp to fibres for unidirectionally fibre-reinforced composite, (3) bulk heat flow \parallel to fibres for unidirectionally fibre reinforced composite, (4) composite with spherical inclusions.

presented in equation (55). Together with the abovegiven Green function they were introduced into equations (19)-(21) and, after manipulations similar to those described in the previous example, the following expression for the interaction coefficient was obtained :

$$
\mathscr{R} = 15\lambda_1 l^{-2} v_1^{1/3} [(\sigma_c - 1)(2 + \sigma_{\lambda}) + 2(\sigma_{\lambda} - 1)v_1
$$

-(\sigma_{\lambda} - 1)((\sigma_c - 1)v_1 + 1)] \cdot [(\sigma_{\lambda} - 1)^2 (1 + (\sigma_c - 1)v_1)
+(\sigma_c - 1)(\sigma_{\lambda}^{-1} - (v_1^2 - 5v_1 + 9v_1^{1/3} - 5)/v_2^2)
\cdot \sigma_{\lambda} (2 + \sigma_{\lambda}) + 2(\sigma_{\lambda} - 1)v_1]. \tag{59}

As can be judged from the examples presented the interaction coefficient depends on the thermal conductivity σ_{λ} and the volumetric specific heat $\sigma_{\rm c}$ ratios of the components, the volume fraction v_1 and thermal conductivity λ_1 of the component existing in the form of particles, the characteristic microdimension l equal to the half-distance between the particles, and the type of microgeometry of the heterogeneous medium. It increases when the particle conductivity increases and when the characteristic microdimension *l* decreases. The influence of other parameters is shown in Figs. 1-3. Due to the simplest form of expression for the interaction coefficient $\mathscr{R}^{\parallel}_{\text{lam}}$ for the laminated composite with bulk heat flow occurring along laminae and its anticipated greatest value because of high thermal coupling between the lamina of two components, the value of $\mathscr{R}^{\parallel}_{\text{lam}}$ was assumed to be the reference one in Figs. l-3. Thus, all the interaction coefficients were nondimensionalized with \mathcal{R}_{lam} , assuming that *l* is the same for each type of composite microgeometry. The interaction coefficient, except for heat flow along laminae or fibres, is very sensitive to the volumetric specific heat ratio $\sigma_c = c_1/c_2$. Depending on σ_c it can take both positive or negative values, and even approach infinity.

Equations (19) - (21) for the microstructure functions φ_1 , $\overline{\varphi}_2$ and ψ_{20} can be solved for many types of

Fig. 2. Nondimensionalized interaction coefficient $\mathcal{R}/\mathcal{R}_{\text{lam}}^{\parallel}$ as a function of the thermal conductivity ratio $\sigma_{\lambda} = \lambda_1/\lambda_2$ (other symbols identical to Fig. 1).

distribution of fibres or spherical inclusions in the matrix, and can allow the study of the influence of the details of the microstructure on the interaction coefficient. Examples of the influence of the crosssection of fibres and fibre distribution on \mathcal{R}^{\parallel} for composites reinforced with unidirectionally aligned fibres and the bulk heat flow occurring along them are given in refs. [15] and [26].

5. **CONCLUSIONS**

The method used in ref. [3] for obtaining an approximate, macroscopic description of heat conduction in heterogeneous materials within the pseudohomogeneous formulation can also be utilized in the study of the process when another, mixture, formulation is used. The latter formulation was presented

Fig. 3. Nondimensionalized interaction coefficient $\mathcal{R}/\mathcal{R}_{\text{lam}}$ as a function of the volumetric specific heat ratio $\sigma_c = c_1/c_2$ (other symbols identical to Fig. 1).

in this paper for the two-component medium when the nonlocality associated with the heat conduction process in the heterogeneous medium is weak, i.e. when the variation of the mean temperatures of the components is slow enough. The method allowed the formulation of energy balance equations for the mixture formulation and the finding of the constitutive relations between partial heat fluxes or the interaction term and mean temperatures of the components. The partial heat flux gives a mean value of the heat flux of each component of the medium in any place and time, while the interaction term describes the amount of heat exchanged locally between the components during the heat conduction process.

The proposed method also enabled the analysis of the well-known postulate that the interaction term depends on a difference in the mean temperatures of components. It was concluded that the assumption is really valid only if the heterogeneous medium is statistically homogeneous and isotropic. It is also valid for a statistically homogeneous but anisotropic medium if the bulk heat flow occurs along one of the principal directions of the effective thermal conductivity tensor, for example along or perpendicular to unidirectionally aligned fibres or laminae. In the light of this study it may also be concluded that the common assumption that the mean temperatures of components are equal in the steady-state heat transfer is only valid for the same conditions as mentioned above.

Comparison of the presented mixture theory with the pseudohomogeneous formulation described in ref. [3] for the case of weak nonlocality of the bulk heat conduction process leads to the conclusion that the first theory is a higher-order one than the zeroth-order pseudohomogeneous theory known as the quasihomogeneous (effective) theory. This can be justified by the appearance of the characteristic microdimension l in the final equations of the mixture theory.

In the presented mixture theory the bulk properties of the heterogeneous medium are described by the effective (partial) thermal conductivities of the component, λ_{ref} . It was shown how these properties can be obtained from usually determined effective thermal conductivity of the medium. Finally, some examples of the calculation of another bulk thermal property of an heterogeneous medium, the interaction coefficient \mathcal{R} , were given. This coefficient is a proportionality factor between the interaction term and the difference in the mean temperatures of the components. Some of the results obtained happened to be identical with those previously presented in the literature, which allows one to place confidence in the theory and use it in other situations when strictly analytical solutions are not possible.

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APPENDIX 1: SOME RELATIONS FOR THE ENSEMBLE AVERAGES CONTAINING THE CHARACTERISTIC FUNCTION θ_1

The ensemble average of a product of the characteristic function $\theta_1(\mathbf{x}|\mathcal{A})$ and an arbitrary function $f(t, \mathbf{x}|\mathcal{A})$ can be defined as follows :

$$
\{\theta_1(\mathbf{x})f(t,\mathbf{x})\} = \int \theta_1(\mathbf{x}|\mathscr{A})f(t,\mathbf{x}|\mathscr{A})p(\mathscr{A}) d\mathscr{A} \quad (1.1)
$$

where integration extends over the set of all possible configurations of the heterogeneous medium. If component 1 exists in the form of particles (grains) then the characteristic function can be written as

$$
\theta_1(\mathbf{x}|\mathcal{A}) = \sum_j \theta_{1j}(\mathbf{x} - \mathbf{x}_j|\mathcal{A})
$$
 (1.2)

where θ_{1i} is equal to unity inside and zero outside *j*th particle, x_i is the distinguished point in the *j*th particle (for instance the centre of the spherical particle), and the summation extends over all particles for a certain configuration $\mathcal A$. From all possible distributions of particles in the medium (configuration \mathcal{A}) a subset was chosen in which configurations differ only by translation of the set of x_i , along an arbitrary vector. The random event of finding the distinguished point of the kth particle in location x_k is independent of the event that the distinguished point of other particles can have the same location : thus, equation (1.1) can be cast in the form

$$
\{\theta_1(\mathbf{x})f(t,\mathbf{x})\} = \sum_{k} \int_{\Omega} \int \theta_1(\mathbf{x}|\mathscr{A})
$$

$$
\times f(t,\mathbf{x}|\mathscr{A}) p(\mathscr{A}|\mathbf{x}_k) p(\mathbf{x}_k) d(\mathscr{A}|\mathbf{x}_k) d\mathbf{x}_k \quad (1.3)
$$

where
$$
p(\mathcal{A}|\mathbf{x}_k)
$$
 is the probability density function for con-

figuration $\mathscr A$ if the position of the distinguished point of the kth particle is fixed, and $p(\mathbf{x}_k)$ is the probability density function for the location of the distinguished point of the k th particle (the single particle distribution function). If the distinguished point of the kth particle can have any location within the medium then $p(\mathbf{x}_k) = \Omega^{-1}$.

Equation (1.2) is then introduced into equation (1.3) . This, after rearranging, leads to

$$
\{\theta_1(\mathbf{x})f(t,\mathbf{x})\} = \Omega^{-1} \sum_{k} \int_{\Omega} \int \theta_{ik}(\mathbf{x} - \mathbf{x}_{ks}|\mathscr{A})
$$

$$
\times f(t,\mathbf{x}|\mathscr{A}) \, p(\mathscr{A}|\mathbf{x}_{ks}) \, d(\mathscr{A}|\mathbf{x}_{ks}) \, d\mathbf{x}_{ks} \quad (1.4)
$$

where x_{ks} denotes the location of the characteristic point of the particle that is the nearest to point x. Noting the properties of the function θ_{1k} and a definition of the conditional ensemble average

$$
\{f(t, \mathbf{x})\}^* = \int f(t, \mathbf{x}|\mathscr{A}) p(\mathscr{A}|\mathbf{x}) d(\mathscr{A}|\mathbf{x})
$$

expression (1.4) can be written as

$$
\{\theta_1(\mathbf{x})f(t,\mathbf{x})\} = \Omega^{-1} \sum_{k} \left\{ \int_{\Omega_{k}} f(t,\mathbf{x}) d\mathbf{x} \right\}^* \tag{1.5}
$$

in which integration is carried out over the volume Ω_{k} of the particle that is nearest (for the considered configuration \mathcal{A}) to point x. Then the right-hand side of equation (1.5) was divided by Ω_{ks} and multiplied by Ω_1 , the volume of all the particles. This leads to the following final result :

$$
\{\theta_1(\mathbf{x})f(t,\mathbf{x})\} = v_1\{\langle f(t,\mathbf{x})\rangle_1\}^*.
$$
 (1.6)

Statistical averaging over all possible shapes and dimensions of the particles was included in the conditional ensemble average appearing on the right-hand side of equation (1.6).

If, instead of θ_1 , its gradient $\nabla \theta_1$ is considered in the ensemble average of type (1.1) then steps (1.2) and (1.3) are the same as in the previous derivation. They lead to a formula

$$
\begin{aligned} \{\nabla \theta_1(\mathbf{x}) f(t, \mathbf{x})\} &= \Omega^{-1} \sum_{k} \int \int \nabla \theta_1(\mathbf{x} - \mathbf{x}_{ks} | \mathcal{A}) \\ &\times f(t, \mathbf{x} | \mathcal{A}) \, p(\mathcal{A} | \mathbf{x}_{ks}) \, d(\mathcal{A} | \mathbf{x}_{ks}) \, d\mathbf{x}_{ks}. \end{aligned} \tag{1.7}
$$

The gradient of the function θ_k calculated with respect to the particle that is nearest to point x can expressed in the form

$$
\nabla \theta_k(\mathbf{x} - \mathbf{x}_{ks}) = -\mathbf{n}(\mathbf{x}) \,\delta(\mathbf{x}, \mathbf{x}_{ks}) \tag{1.8}
$$

where $n(x)$ is the external unit vector to the surface of the k th particle and δ denotes the Dirac pseudofunction taking infinite values on the surface of the kth particle. Equation (1.8) was subsequently introduced into equation (1.7), which leads to the formula

$$
\left\{\nabla\theta_1(\mathbf{x})f(t,\mathbf{x})\right\} = -\Omega \sum_{k} \left\{\int \mathbf{n}(\mathbf{x}_{ks})f(t,\mathbf{x}) \, \mathrm{d}\mathbf{x}_{ks}\right\}^* \quad (1.9)
$$

in which integration is carried out over the surface of the kth particle nearest (for the configuration considered) to point x. The use of the Green theorem and the definition of the local coordinate system ξ allows one to put equation (1.9) in the final form

$$
\{\nabla \theta_1(\mathbf{x}) f(t, \mathbf{x})\} = -l v_1 \{\langle \nabla_1 f(t, \mathbf{x}) \rangle_1\}^* \qquad (1.10)
$$

where, similarly to formula (1.6), $\{_\ \}^*$ denotes statistical averaging over all possible shapes, dimensions of the reference particle and averaging over all possible distributions of the neighbouring particles when the location of the reference particle is fixed. A similar result is valid when f is a vector function and the product is a vector one.

APPENDIX 2. JUSTIFICATION FOR RELATION (37)

In order to justify relation (37) ensemble averaging was applied directly to equations $(2)-(5)$:

$$
\nabla \cdot \{\lambda \nabla T\} = \{c \,\partial_t T\}.
$$
 (2.1)

Subsequently the relation between local *T* and $\{\theta_1 T\}$, i.e. equation (28), was introduced to both sides of the above equation. When, additionally, the relation between gradients expressed in global and local coordinates, equation (32), was included then equation (2.1) can be written as

$$
\nabla_{g} \cdot \{\lambda(\overline{T} + \nabla_{1} \phi_{1})\} \cdot \nabla_{g} \{\theta_{1} T\} = \{c\} \partial_{t} \{\theta_{1} T\} \tag{2.2}
$$

when only the first term in the expansion of the growing powers of *l* was retained. Then the formula for ϕ_1 , equation (29), the definition of the effective thermal conductivity

$$
\overline{\lambda}_{\rm cf} = \{ \lambda (\overline{1} + \nabla_1 \varphi_1) \}
$$
 (2.3)

and the effective volumetric specific heat

$$
c_{\rm ef} = \{c\} = c_1 v_1 + c_2 v_2 \tag{2.4}
$$

were introduced into equation (2.2). This leads to the following expression :

$$
\nabla_{\mathbf{g}} \cdot \overline{\lambda}_{\mathrm{ef}} \cdot \nabla_{\mathbf{g}} \{ \theta_1 T \} = c_{\mathrm{ef}} \, \partial_1 \{ \theta_1 T \}. \tag{2.5}
$$

For statistically homogeneous and isotropic media the following relation holds

$$
\nabla_{\mathbf{g}} \cdot \lambda_{\mathrm{cf}} \overline{\mathbf{I}} \cdot \nabla_{\mathbf{g}} \{ \theta_1 T \} = \lambda_{\mathrm{ef}} \overline{\mathbf{I}} \cdot \nabla_{\mathbf{g}}^{(2)} \{ \theta_1 T \}
$$
(2.6)

From the last two equations relation (37) follows.