Upscaling the diffusion equations in particulate media made of highly conductive particles. I. Theoretical aspects

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Many analytical and numerical works have been devoted to the prediction of macroscopic effective transport properties in particulate media. Usually, structure and properties of macroscopic balance and constitutive equations are stated *a priori*. In this paper, the upscaling of the transient diffusion equations in concentrated particulate media with possible particle-particle interfacial barriers, highly conductive particles, poorly conductive matrix, and temperature-dependent physical properties is revisited using the homogenization method based on multiple scale asymptotic expansions. This method uses no *a priori* assumptions on the physics at the macroscale. For the considered physics and microstructures and depending on the order of magnitude of dimensionless Biot and Fourier numbers, it is shown that some situations cannot be homogenized. For other situations, three different macroscopic models are identified, depending on the quality of particle-particle contacts. They are one-phase media, following the standard heat equation and Fourier's law. Calculations of the effective conductivity tensor and heat capacity are proved to be uncoupled. Linear and steady state continuous localization problems must be solved on representative elementary volumes to compute the effective conductivity tensors for the two first models. For the third model, i.e., for highly resistive contacts, the localization problem becomes simpler and discrete whatever the shape of particles. In paper II [Vassal *et al.*, Phys. Rev. E **77**, 011303 (2008)], diffusion through networks of slender, wavy, entangled, and oriented fibers is considered. Discrete localization problems can then be obtained for all models, as well as semianalytical or fully analytical expressions of the corresponding effective conductivity tensors.

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I. INTRODUCTION

The analysis of diffusion phenomena (such as thermal or electrical conduction) in heterogeneous materials made of assemblies of connected granular or fibrous particles plunged into a continuous matrix has been a subject of great interest for several decades. Many theoretical and numerical works have been conducted in order to obtain exact analytical solutions or rigorous bounds of the macroscopic effective properties for such heterogeneous media [1–4]. These studies are of great importance in many applications. For instance, improving thermal or electrical conductivity of polymer composites using carbon, aluminum, or copper particles becomes an interesting solution for industrial applications such as heat sinks, electronic components, breaking systems, etc. These types of heterogeneous media display a very high contrast between the conductivities of the matrix and of the particles, so that predictions given by well-known bounds are usually not satisfactory [5–7]. A possible way to circumvent the difficulty to predict their effective transport properties is to assume that conduction in and between contacting or almost contacting particles is much higher than that inside the surrounding matrix: it is then possible to neglect the contribution of the bulk matrix to the overall macroscopic conduction [8,9]. Hence, by using this assumption, many discrete conduction models have been established analytically or numerically [4,8–25].

It must be underlined that all the mentioned models *a priori* assume that the equivalent macroscopic continua are one-phase media, i.e., with a one-temperature (or electric potential) field obeying to a standard macroscopic diffusion equation with a standard Fourier's (or Ohm's) law between macroscopic temperature (or electric potential) gradient and macroscopic heat flow (or electric current). Nevertheless, by studying the transient diffusion in heterogeneous media made of connected phases with the homogenization method with multiple scale expansions [26–28], i.e., without *a priori* assumption at macroscale, some works have shown that the above macroscopic postulates could sometimes break down. For example, if the characteristic wavelength of the macroscopic excitation with respect to the length of the local heterogeneities are of the same order of magnitude, the problem may not be homogenized, i.e., there is no macroscopic equivalent continuum [28]. Moreover, depending on the contrast between local conductivities and volumetric heat capacities, the structure of the macroscopic transient diffusion equation may deviate from its standard form, exhibiting memory effects [29]. Lastly, increasing thermal resistances of interfacial barriers between phases may result in multiphase models at macroscale, i.e., with multiple macroscopic temperature (or electric potential) fields, balances, and con-

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stitutive equations [30]. It would be interesting to see whether similar behaviors arise in case of particulate media or not.

Within that context, this two parts contribution revisits via the homogenization method with multiple scale expansions, the macroscopic behavior of a concentrated particulate medium submitted to transient diffusion phenomena when conduction in and between contacting or almost contacting particles is predominant. Different qualities of particle-particle contacts are considered, as well as possible dependence of local physical properties with temperature (or electrical potential). From the unique knowledge of local physics, the aim is (i) to determine theoretically the structures and properties of possible macroscopic description(s) corresponding to such media, (ii) to formulate well-posed localization problems in order to evaluate the effective macroscopic properties, and (iii) to analyze quantitatively from this theoretical study the effective properties of networks of slender, wavy, and entangled fibers in order to size the role of the fiber content and orientation up. The transient diffusive thermal problem is treated, but strong analogies with other types of physics can be established.

In paper I, the theoretical upscaling is performed starting from the dimensionless description of the physics at the particle scale (Sec. II), the homogenization method with multiple scale expansions is used (Sec. III) and discussed (Sec. IV). Depending on the order of magnitude of dimensionless Fourier and Biot numbers, three interesting situations are studied, leading to three different macroscopic models. A discrete formulation of both localization problems and macroscopic heat flow is obtained for the third model, whatever the considered particulate medium. Paper II [35] will be dedicated to the application of theoretical results to entangled fibrous media.

II. PROBLEM STATEMENT

A. Description of the considered heterogeneous medium

We consider an heterogeneous medium made of fixed and rigid solid particles surrounded by a stagnant matrix. In order to establish homogenization based principles for prediction of effective properties over the macroscopic medium, it is supposed to be made of a periodic assembly of N_{REV} repetitions (see Fig. 1) of a representative elementary volume (REV) of the microstructure. The volume of the REV is noted Ω_{REV} and its finite characteristic length l_{REV}. It is made of a set $\mathcal{P}_{\text{REV}}$ of P_{REV} particles p_α. Each particle is supposed to have a constant density and to be contained in a volume $\Omega_\alpha < \Omega_{\text{REV}}$ which characteristic length l_α is such that $l_\alpha < l_{\text{REV}}$. In the following, $i\alpha\beta$ ($=i\beta\alpha$) will represent the ith connection or contact in the REV between particles p_α and p_β. The set of the C_{REV} connections $i\alpha\beta$ in the REV will be noted $\mathcal{C}_{\text{REV}}$ and that of the C_α connections of particle p_α will be denoted by $\mathcal{C}_\alpha$. The external surface of a particle p_α can be split in: Γ_α, the surface of the particle in contact with the matrix, and $\Gamma_{i\alpha\beta}$ of characteristic area Γ_c, the surface of the ith contact in the REV, between particles p_α and p_β. We assume that the volume fraction, geometry, and spatial distribution of particles are such that there is no isolated particle

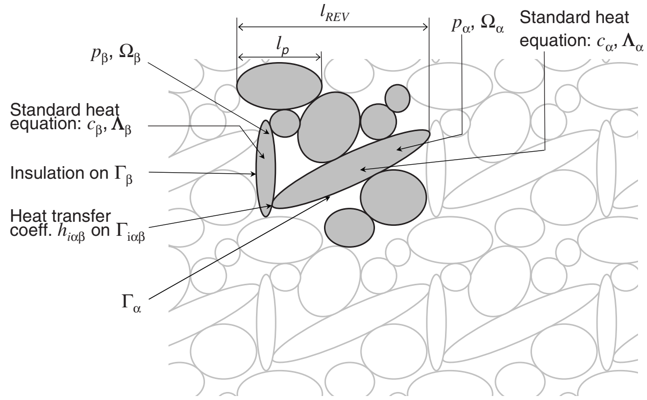

FIG. 1. Scheme of the studied microstructure and local physical description. The gray particles belong to the representative elementary volume (REV). The volume of the REV is denoted Ω_{REV} and its finite characteristic length l_{REV}. It is made of P_{REV} particles p_α of volume Ω_α. c_α represents the volumetric heat capacity and $\mathbf{\Lambda}_\alpha$ the conductivity tensor of the particle p_α. Its surface splits into Γ_α the surface in contact with the matrix on which heat transfers are neglected and $\Gamma_{i\alpha\beta}$ the surface in contact with a particle p_β on which heat transfer is governed by the heat transfer coefficient $h_{i\alpha\beta}$.

or group of particles in the REV. It is also supposed that there is a good separation of scales between the smallest "macroscopic" characteristic length L_c of the studied medium (e.g., characteristic size of the considered macroscopic volume and/or length upon which macroscopic temperature gradients occur) and the "microscopic" characteristic length of the physics at local scale l_c (e.g., characteristic length upon which microscopic temperature gradients occur). This results in the following condition:

$$\varepsilon = \frac{l_c}{L_c} \ll 1, \tag{1}$$

which introduces the separation of scales parameter ε. For the sake of simplicity, it will be assumed that l_c, l_{REV}, and l_α are of the same order of magnitude, i.e., $l_c = O(l_\alpha) = O(l_{\text{REV}})$.

B. Physics at the particle scale

This rigid particulate medium is subjected to a transient thermal loading. Only heat transfers by conduction are considered. Following assumptions stated in Ref. [8], it is supposed that conduction phenomena in and between contacting (or almost contacting) particles are much higher than those occurring elsewhere in the stagnant matrix. Thereby, the thermal balance of the medium is governed by a standard transient heat equation which in any point of a given particle p_α reads

$$c_\alpha \dot{T}_\alpha = -\nabla \cdot \mathbf{q}_\alpha + r_\alpha, \tag{2}$$

in Ω_α, where ∇ is the differential operator with respect to the space variable $\mathbf{X}$, $T_\alpha(\mathbf{X},t)$ is the temperature at the considered point, $\dot{T}_\alpha = \partial T_\alpha / \partial t$, c_α represents the volumetric heat capacity of particle p_α, and r_α is a volumetric heat source (characteristic value r_c). The heat capacities are assumed to

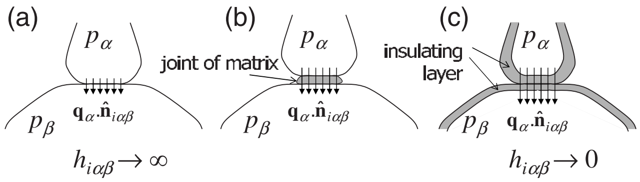

FIG. 2. Scheme of possible basic heat transfer mechanisms that may occur in contact zones and of their influence on the heat transfer coefficient $h_{i\alpha\beta}$.

be of the same order of magnitude (characteristic value c_c), i.e., $\forall\ \alpha\ \varepsilon < c_\alpha / c_c < \varepsilon^{-1}$. The c_α and r_α are given and they can be $\mathbf{X}$ dependent. The c_α's can also be temperature dependent. The heat flow vector $\mathbf{q}_\alpha$ is supposed to follow the standard linear Fourier's law

$$\mathbf{q}_\alpha = -\mathbf{\Lambda}_\alpha \cdot \boldsymbol{\nabla} T_\alpha, \tag{3}$$

in Ω_α, where $\mathbf{\Lambda}_\alpha$ is the symmetric and positive thermal conductivity tensor of the particles. The principal values $(\mathbf{\Lambda}_\alpha)_k$ $(k \in \{\mathrm{I}, \mathrm{II}, \mathrm{III}\})$ of these tensors may be $\mathbf{X}$ dependent, T dependent, and are of the same order of magnitude (characteristic value Λ_c). Likewise, heat transfers on the surfaces Γ_α are neglected compared to heat transfers on the surfaces $\Gamma_{i\alpha\beta}$ of contact zones which are supposed to be correctly modeled by a mixed Cauchy-type boundary condition involving local heat transfer coefficients $h_{i\alpha\beta}$. These coefficients can be $\mathbf{X}$ and T dependent and are assumed to be positive quantities of the same order of magnitude (characteristic value h_c). For examples, the $h_{i\alpha\beta}$ can reflect three basic mechanisms (see Fig. 2): (a) thermal conduction through the contact area between two touching particles, (b) thermal conduction through a thin entrapped matrix layer between two almost contacting particles, and (c) thermal conduction through an insulating layer (for example, an oxide layer) between two contacting particles. These three elementary mechanisms may occur together in contact zones so that the exact determination of $h_{i\alpha\beta}$ may be very complex [8,15,31] and will not be studied in this article. Hence the physics at the particle scale results in the following set of boundary conditions:

$$\mathbf{q}_\alpha \cdot \hat{\mathbf{n}}_\alpha = 0 \ \text{ on } \ \Gamma_\alpha, \qquad \left.\begin{aligned} \mathbf{q}_\alpha \cdot \hat{\mathbf{n}}_{i\alpha\beta} &= \mathbf{q}_\beta \cdot \hat{\mathbf{n}}_{i\alpha\beta} \\ \mathbf{q}_\alpha \cdot \hat{\mathbf{n}}_{i\alpha\beta} &= -h_{i\alpha\beta}\Delta_{\alpha\beta}T \end{aligned}\right\} \text{ on } \ \Gamma_{i\alpha\beta}, \tag{4}$$

where $\Delta_{\alpha\beta}T = T_\beta - T_\alpha$ and where $\hat{\mathbf{n}}$ are external unit normal vectors to the considered surfaces. It is also assumed that at the initial time t_0, the temperature at any point M is equal to T_0:

$$\forall M \in \Omega_\alpha, \quad T_\alpha(t_0) = T_0. \tag{5}$$

Lastly, the temperature variations in the particles are supposed to be of the same order of magnitude:

$$\forall M, \forall\ \alpha, \forall\ \beta, \quad T_\alpha - T_0 = O(T_\beta - T_0). \tag{6}$$

The set of Eqs. (2)–(5) forms the local physical description of the problem. It is worth noticing that the form of Eqs. (3)–(5) displays strong analogies with other transient (or not) and diffusive physical phenomena (see the examples given in Table I). The theoretical developments carried out in this work can be easily transposed to such local physics without major difficulties [4,34].

C. Dimensionless form of the local physics

In this subsection as well as in the following one, for the sake of simplicity, only the case of constant physical properties with no volumetric heat source will be developed. Temperature-dependent properties and local heat sources will be considered in Secs. III F and III G, respectively. Hence, by adopting the method proposed in Ref. [28], the set of dimensionless variables

$$\mathbf{X}^* = \mathbf{X}/l_c, \quad t^* = (t - t_0)/\Delta t_c, \quad T^* = (T - T_0)/\Delta T_c,$$

$$\mathbf{\Lambda}_\alpha^* = \mathbf{\Lambda}_\alpha/\Lambda_c, \quad h_{i\alpha\beta}^* = h_{i\alpha\beta}/h_c, \quad c_\alpha^* = c_\alpha/c_c, \tag{7}$$

is introduced in Eqs. (2)–(5) (subscripts "c" denote characteristic values). In the above expressions, $\Delta t_c = O(t - t_0)$ represents a typical time interval during which macroscopic thermal loading is applied, $\Delta T_c = O(T - T_0)$ the typical tem-

TABLE I. Examples of analogies (at the particle scale) with the studied thermal problem. The fields T_α, τ_α, P_α, and V_α represent the temperature, solute concentration, pressure, and electric potential, respectively. ϕ_α is the porosity of particle α, ρ the density of the flowing fluid, μ its viscosity, $C_\alpha^P(P_\alpha)$ the particle fluid retention capacity, $k_{r\alpha}$ the relative permeability, ω the pulsation. $\mathbf{J}_\alpha$ is the solute diffusion tensor, $\mathbf{K}_\alpha$ the permeability tensor, $\boldsymbol{\varepsilon}_\alpha$ the permittivity tensor, and $\boldsymbol{\sigma}_\alpha$ the electrical conductivity tensor.

Physics at the particle scale	Field	Capacity	Diffusion	Interfacial coefficient
Heat diffusion [Eqs. (3)–(5)]	T_α	c_α	$\mathbf{\Lambda}_\alpha$	$h_{\alpha\beta}$
Solute diffusion	τ_α	1	$\mathbf{J}_\alpha$	$h_{\alpha\beta}^{\tau}$
Slow flow of compressible Newtonian fluids through saturated (s) porous particles	P_α	$\phi_\alpha \frac{\partial\rho(P_\alpha)}{\partial P_\alpha}$	$\frac{\rho(P_\alpha)}{\mu}\mathbf{K}_\alpha$	$h_{\alpha\beta}^{P_s}$
Slow flow of incompressible Newtonian fluids through unsaturated (u) porous particles	P_α	$C_\alpha^P(P_\alpha)$	$\frac{k_{r\alpha}(P_\alpha)}{\mu}\mathbf{K}_\alpha$	$h_{\alpha\beta}^{P_u}$
Electrostatics—nonconductive particles (ε)	V_α		$\boldsymbol{\varepsilon}_\alpha$	$h_{\alpha\beta}^{V_\varepsilon}$
Electrostatics—conductive particles (σ)	V_α		$\boldsymbol{\sigma}_\alpha$	$h_{\alpha\beta}^{V_\sigma}$
Quasistatics—time harmonic current	V_α		$\boldsymbol{\sigma}_\alpha + i\omega\boldsymbol{\varepsilon}_\alpha$	$h_{\alpha\beta}^{V_\sigma} + i\omega h_{\alpha\beta}^{V_\varepsilon}$

perature variation in the sample. Therewith, the following dimensionless local form of the physics at the particle scale is obtained:

$$c_\alpha^* \dot{T}_\alpha^* = -\mathbb{F}_c \boldsymbol{\nabla}^* \cdot \mathbf{q}_\alpha^* \quad \text{in } \Omega_\alpha^*, \tag{8a}$$

$$\mathbf{q}_\alpha^* = -\boldsymbol{\Lambda}_\alpha^* \cdot \boldsymbol{\nabla}^* T_\alpha^* \quad \text{in } \Omega_\alpha^*, \tag{8b}$$

$$T_\alpha^*(t_0) = 0 \quad \text{in } \Omega_\alpha^*, \tag{8c}$$

$$\mathbf{q}_\alpha^* \cdot \hat{\mathbf{n}}_\alpha = 0 \quad \text{on } \Gamma_\alpha^*, \tag{8d}$$

$$\mathbf{q}_\alpha^* \cdot \hat{\mathbf{n}}_{i\alpha\beta} = \mathbf{q}_\beta^* \cdot \hat{\mathbf{n}}_{i\alpha\beta} \quad \text{on } \Gamma_{i\alpha\beta}^*, \tag{8e}$$

$$\mathbf{q}_\alpha^* \cdot \hat{\mathbf{n}}_{i\alpha\beta} = -\mathbb{B}_c h_{i\alpha\beta}^* \Delta_{\alpha\beta} T^* \quad \text{on } \Gamma_{i\alpha\beta}^*, \tag{8f}$$

where the differential operator $\boldsymbol{\nabla}^*$ is defined in the dimensionless space and calculated with $\mathbf{X}^*$. This system of equations reveals two dimensionless numbers. The first is the Biot number $\mathbb{B}_c$

$$\mathbb{B}_c = \frac{h_c l_c}{\Lambda_c} = \mathbb{A}_c \mathbb{B}, \tag{9}$$

by noting

$$\mathbb{A}_c = \frac{S_c}{\Gamma_c} \quad \text{and} \quad \mathbb{B} = \frac{l_c}{S_c \Lambda_c} / \frac{1}{\Gamma_c h_c} = \frac{R_{\text{particle}}}{R_{\text{contact}}}. \tag{10}$$

In the above relations, l_c can be interpreted as the typical length upon which gradients occur inside the particle, whereas S_c may be seen as the associated characteristic cross section involved in the conduction process. For example, in case of fibrous media, S_c is close to the fiber cross section and l_c is the average distance between two adjacent fiber-fiber contacts on a fiber (see paper II). Moreover, $R_{\text{particle}} = l_c / S_c \Lambda_c$ and $R_{\text{contact}} = 1/\Gamma_c h_c$ can be seen as resistors characterizing the conduction inside the particles and through the particle-particle connections, respectively. The order of magnitude of the dimensionless Biot number $\mathbb{B}$ involved in Eqs. (9) and (10) indicates the predominating physical phenomena at the local scale: (i) a high Biot number $\mathbb{B}$ corresponds to a physics ruled by conduction inside the particles ($R_{\text{particle}} \gg R_{\text{contact}}$), (ii) when $\mathbb{B} = O(1)$, particle-particle contacts start curbing heat transfers ($R_{\text{particle}} \approx R_{\text{contact}}$), and (iii) a small Biot number $\mathbb{B}$ corresponds to a local physics governed by heat transfer at particle-particle contacts ($R_{\text{particle}} \ll R_{\text{contact}}$).

Only three situations of interest will be explored in the following, i.e.,

$$\mathbb{B}_c = O(\varepsilon^m), \quad m \in \{-1, 0, 1\}. \tag{11}$$

Indeed, it can be shown that (i) values of m lower than -1 correspond to the same macroscopic description as $m = -1$ and (ii) values of m greater than 1 lead to nonconductive macroscopic media. The second dimensionless number is the Fourier number $\mathbb{F}_c$,

$$\mathbb{F}_c = \left(\frac{D_c}{l_c}\right)^2 \quad \text{with} \quad D_c = \sqrt{\frac{\Lambda_c \Delta t_c}{c_c}}, \tag{12}$$

which is the ratio between a characteristic macroscopic diffusion length D_c and the characteristic physical microscopic length l_c. In order to upscale the above local transient physics, the smallest macroscopic diffusion length D has to be introduced. Depending on the nature of particle-particle contacts, this length has two expressions. When $m \leq 0$, the diffusion is governed by conduction in particles so that the smallest diffusion length reads $D = D_c = \sqrt{\Lambda_c \Delta t_c / c_c}$. When $m > 0$, the diffusion is governed by heat transfers at particle-particle contacts so that the smallest diffusion length becomes $D = \sqrt{h_c \Delta t_c l_c / c_c}$.

It is important to notice that a macroscopic description can be obtained only if there is a good separation of scale which implies that the smallest characteristic macroscopic diffusion length D is large with respect to l_c, i.e., when

$$\mathbb{F} = \left(\frac{D}{l_c}\right)^2 = O(\varepsilon^k), \quad k \leq -2. \tag{13}$$

If this condition breaks down, the above local physics cannot be upscaled, i.e., no homogenized solution exists. Considering the nature of the particle-particle contacts, the previous fundamental condition reads as follows. When $m \leq 0$

$$\mathbb{F}_c = O(\varepsilon^k), \quad k \leq -2. \tag{14}$$

When $m > 0$, considering Eqs. (12) and (9),

$$\mathbb{F}_c = O(\varepsilon^k)/\mathbb{B}_c, \quad k \leq -2. \tag{15}$$

In this work, the only explored cases correspond to $k = -2$. Other situations ($k < -2$) correspond to steady state conduction problems at the macroscopic scale and can be easily deduced from the latter. Hence, from the above dimensionless analysis, three interesting situations must be further explored (see next section).

III. UPSCALING

A. Asymptotic expansions

As a result of the separation of scales (1), a "microscopic" space variable $\mathbf{y}^* = \mathbf{X}/l_c$ and a "macroscopic" space variable $\mathbf{x}^* = \varepsilon \mathbf{y}^* = \mathbf{X}/L_c$ are introduced, $\mathbf{X}$ being the physical space variable. If Eq. (1) is satisfied, then $\mathbf{y}^*$ and $\mathbf{x}^*$ appear as two independent space variables and the physical variables of the problem, i.e., the temperature fields, can then be seen as *a priori* functions of $\mathbf{y}^*$ and $\mathbf{x}^*$, i.e., $T_\alpha^*(\mathbf{X}^*, t^*) = T_\alpha^*(\mathbf{x}^*, \mathbf{y}^*, t^*)$. Hence, the spatial differential operator $\boldsymbol{\nabla}^*$ can be written as

$$\boldsymbol{\nabla}^* = \boldsymbol{\nabla}_{y^*} + \frac{l_c}{L_c} \boldsymbol{\nabla}_{x^*} = \boldsymbol{\nabla}_{y^*} + \varepsilon \boldsymbol{\nabla}_{x^*}, \tag{16}$$

where $\boldsymbol{\nabla}_{y^*}$ and $\boldsymbol{\nabla}_{x^*}$ are calculated with $\mathbf{y}^*$ and $\mathbf{x}^*$, respectively. Thereby, we now assume that the temperature fields can be looked for in the form of asymptotic expansions in powers of ε [26,27]:

$$T_\alpha^*(\mathbf{X},t^*) = T_\alpha^{[0]*}(\mathbf{x}^*,\mathbf{y}^*,t^*) + \varepsilon T_\alpha^{[1]*}(\mathbf{x}^*,\mathbf{y}^*,t^*) + \varepsilon^2 T_\alpha^{[2]*}(\mathbf{x}^*,\mathbf{y}^*,t^*) + \cdots, \quad (17)$$

where the functions $T_\alpha^{[i]*}$ are supposed to be Ω_{REV} periodic with respect to the dimensionless microscopic space variable $\mathbf{y}^*$. The method of multiple scale expansions then consists in (i) introducing Eq. (17) into the dimensionless local Eqs. (8), (ii) identifying terms with the same power of ε, and (iii) solving boundary value problems that arise at successive orders of ε.

B. Model I: $\mathbb{B}_c = O(\varepsilon^{-1})$ while $\mathbb{F}_c = O(\varepsilon^{-2})$

In this situation, thermal contacts between particles are excellent so that they do not affect heat transfers. For example, such a situation would be well suited for heat transfers in foams, cellular materials, or in ceramic or metallic powders near the end of the sintering process, i.e., when grains are welded and grain-grain contact surfaces are not too small. This case extends the results obtained in Ref. [30] for composite materials with connected phases to the case of particulate media.

(i) The temperatures $T_\alpha^{[0]*}$ do not depend on the considered particle and are not functions of the microscopic variable $\mathbf{y}^*$:

$$T_\alpha^{[0]*}(\mathbf{x}^*,\mathbf{y}^*,t^*) = T^{[0]*}(\mathbf{x}^*,t^*). \quad (18)$$

(ii) The first order temperatures $T_\alpha^{[1]*}$ are the solutions of the following boundary values problems written on each particle p_α contained in the REV:

$$\nabla_{y^*} \cdot \mathbf{q}_\alpha^{[1]*} = 0 \quad \text{in } \Omega_\alpha^*, \quad (19a)$$

$$\mathbf{q}_\alpha^{[1]*} = -\boldsymbol{\Lambda}_\alpha^* \cdot (\boldsymbol{\nabla}_{y^*} T_\alpha^{[1]*} + \boldsymbol{\nabla}_{x^*} T^{[0]*}) \quad \text{in } \Omega_\alpha^*, \quad (19b)$$

$$\mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_\alpha = 0 \quad \text{on } \Gamma_\alpha^*, \quad (19c)$$

$$T_\alpha^{[1]*} = T_\beta^{[1]*} \quad \text{on } \Gamma_{i\alpha\beta}^*, \quad (19d)$$

$$\mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = \mathbf{q}_\beta^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} \quad \text{on } \Gamma_{i\alpha\beta}^*, \quad (19e)$$

where $\boldsymbol{\nabla}_{x^*} T^{[0]*}$ here appears as a given macroscopic thermal loading which is constant in the whole REV. Multiplying Eq. (19a) by an appropriate test function T', see Ref. [29], integrating over Ω_α^*, using the divergence theorem and the periodicity, it is possible to obtain a weak variational formulation of this problem for each particle p_α:

$$\forall T', \quad \int_{\Omega_\alpha^*} \mathbf{q}_\alpha^{[1]*} \cdot \boldsymbol{\nabla}_{y^*} T' dV^* = \sum_{\mathcal{C}_\alpha} \int_{\Gamma_{i\alpha\beta}^*} \mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} T' dS^*, \quad (20)$$

where the set $\mathcal{C}_\alpha$ contains all the connections involving the particle p_α. Such a weak formulation allows us to prove the uniqueness of $T_\alpha^{[1]^*}$ and shows that $T_\alpha^{[1]*}$ are linear functions of $\boldsymbol{\nabla}_{x^*} T_\alpha^{[0]*}$, to an arbitrary REV-independent value $\bar{T}^{[1]*}$ [29]:

$$T_\alpha^{[1]*} = T^{[1]*} = \boldsymbol{\theta}^{[1]*} \cdot \boldsymbol{\nabla}_{x^*} T^{[0]*} + \bar{T}^{[1]*}, \quad (21)$$

where the values of the components $(\boldsymbol{\theta}^{[1]*})_k$ of the vector $\boldsymbol{\theta}^{[1]*}$ correspond to the temperature fields $T_\alpha^{[1]*}$ obtained for macroscopic temperature gradients $\boldsymbol{\nabla}_{x^*} T^{[0]*} = \hat{\mathbf{e}}_k$ with $k \in \{1,2,3\}$, respectively.

(iii) At the first order of approximation, the equivalent macroscopic medium is a one phase medium, whose thermal equilibrium is ruled by a standard heat equation, here written in its nondimensional form

$$c^{e*} \dot{T}^{e*} = -\boldsymbol{\nabla}_{x^*} \cdot \mathbf{q}^{e*}, \quad (22)$$

where $T^{e*} = T^{[0]*}$,

$$c^{e*} = \langle c_\alpha^* \rangle = \frac{1}{\Omega_{\text{REV}}^*} \sum_{\mathcal{P}_{\text{REV}}} \int_{\Omega_\alpha^*} c_\alpha^* dV^*, \quad (23)$$

and

$$\mathbf{q}^{e*} = \langle \mathbf{q}_\alpha^{[1]*} \rangle = \frac{1}{\Omega_{\text{REV}}^*} \sum_{\mathcal{P}_{\text{REV}}} \int_{\Omega_\alpha^*} \mathbf{q}_\alpha^{[1]*} dV^*. \quad (24)$$

Introducing

$$\langle \boldsymbol{\Lambda}_\alpha^* \rangle = \frac{1}{\Omega_{\text{REV}}^*} \sum_{\mathcal{P}_{\text{REV}}} \int_{\Omega_\alpha^*} \boldsymbol{\Lambda}_\alpha^* dV^* \quad (25)$$

and using Eqs. (19b) and (21) yield

$$\mathbf{q}^{e*} = -\left[\langle \boldsymbol{\Lambda}_\alpha^* \rangle + \frac{1}{\Omega_{\text{REV}}^*} \sum_{\mathcal{P}_{\text{REV}}} \int_{\Omega_\alpha^*} \boldsymbol{\Lambda}_\alpha^* \cdot \boldsymbol{\nabla}_{y^*}^T \boldsymbol{\theta}^{[1]*} dV^* \right] \cdot \boldsymbol{\nabla}_{x^*} T^{e*}. \quad (26)$$

Consequently, the macroscopic heat flow obeys a standard Fourier's law, whose effective thermal conductivity tensor

$$\boldsymbol{\Lambda}^{e*} = \langle \boldsymbol{\Lambda}_\alpha^* \rangle + \frac{1}{\Omega_{\text{REV}}^*} \sum_{\mathcal{P}_{\text{REV}}} \int_{\Omega_\alpha^*} \boldsymbol{\Lambda}_\alpha^* \cdot \boldsymbol{\nabla}_{y^*}^T \boldsymbol{\theta}^{[1]*} dV^* \quad (27)$$

is definite, positive, and symmetric [29]. The first contribution $\langle \boldsymbol{\Lambda}_\alpha^* \rangle$ is simply a volume average of the conductivities in the REV. The second contribution takes into account the exact morphology of the particulate medium (i.e., distribution of positions, size, shape, and orientation of both particles and contacts between them). One should also stress that $\boldsymbol{\Lambda}^{e*}$ is independent of heat transfer coefficients $h_{i\alpha\beta}^*$ in this model.

C. Model II: $\mathbb{B}_c = O(1)$ while $\mathbb{F}_c = O(\varepsilon^{-2})$

Now the quality of contacts between particles decreases, due to the decrease of contact surfaces (Γ_c) or to the decrease of the interfacial heat transfer coefficients (h_c). Briefly, most of the above results remain valid, the only difference concerns Eq. (19d) which now reads

$$\mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = -h_{i\alpha\beta}^* \Delta_{\alpha\beta} T^{[1]*} \quad \text{on } \Gamma_{i\alpha\beta}^*, \quad (28)$$

where the $T_\alpha^{[1]*}$'s are still linear functions of $\boldsymbol{\nabla}_{x^*} T^{[0]*}$ to an arbitrary constant $\bar{T}_\alpha^{[1]*}$:

$$T_\alpha^{[1]*} = \boldsymbol{\theta}_\alpha^{[1]*} \cdot \boldsymbol{\nabla}_{x^*} T^{[0]*} + \bar{T}_\alpha^{[1]*}. \tag{29}$$

Integrating Eq. (19a) over Ω_α^*, applying the divergence theorem, and taking into account Eqs. (19c) and (19e) yield the following compatibility condition:

$$\sum_{\mathcal{C}_\alpha} \int_{\Gamma_{i\alpha\beta}^*} \mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} dS^* = 0. \tag{30}$$

By introducing $\tilde{h}_{i\alpha\beta}^*$ as the local averages of the heat transfer coefficients $h_{i\alpha\beta}^*$, i.e.,

$$\tilde{h}_{i\alpha\beta}^* = \frac{1}{\Gamma_{i\alpha\beta}^*} \int_{\Gamma_{i\alpha\beta}^*} h_{i\alpha\beta}^* dS^*, \tag{31}$$

and by accounting for Eqs. (28) and (29), (30) yields

$$\sum_{\mathcal{C}_\alpha} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* \Delta_{\alpha\beta} \bar{T}^{[1]*} + \boldsymbol{\nabla}_{x^*} T^{[0]*} \cdot \sum_{\mathcal{C}_\alpha} \int_{\Gamma_{i\alpha\beta}^*} h_{i\alpha\beta}^* \Delta_{\alpha\beta} \boldsymbol{\theta}^{[1]*} dS^* = 0. \tag{32}$$

This represents a system of linear equations from which the $\bar{T}_\alpha^{[1]*}$'s can be calculated, up to an arbitrary constant. Moreover, Eq. (32) shows that $\Delta_{\alpha\beta}\bar{T}^{[1]*}$ can be put in the form

$$\Delta_{\alpha\beta} \bar{T}^{[1]*} = \Delta_{\alpha\beta} \bar{\boldsymbol{\theta}}^{[1]*} \cdot \boldsymbol{\nabla}_{x^*} T^{[0]*}, \tag{33}$$

where the value of the kth component $(\Delta_{\alpha\beta}\bar{\theta}^{[1]*})_k$ of the vector $\Delta_{\alpha\beta}\bar{\boldsymbol{\theta}}^{[1]*}$ equals the solution $\Delta_{\alpha\beta}\bar{T}^{[1]*}$ when $\boldsymbol{\nabla}_{x^*}T_0^* = \hat{\mathbf{e}}_k$ $(k \in \{1,2,3\})$. As a consequence, the forms of the macroscopic thermal equilibrium (22) and thermal conductivity tensor (27) remain unchanged. However, because of Eq. (28), the macroscopic conductivity tensor $\boldsymbol{\Lambda}^{e*}$ depends on heat transfer coefficients $h_{i\alpha\beta}^*$. As for model I, the calculation of the components of $\boldsymbol{\Lambda}^{e*}$, requires the determination of the $\boldsymbol{\theta}_\alpha^{[1]*}$. This can be achieved by solving the localization problem (19), by replacing Eq. (19d) with Eq. (28), for three given independent macroscopic temperature gradients $\boldsymbol{\nabla}_{x^*}T^{[0]*} = \hat{\mathbf{e}}_k$.

D. Model III: $\mathbb{B}_c = O(\varepsilon^1)$ while $\mathbb{F}_c = O(\varepsilon^{-2})/\mathbb{B}_c$

This case corresponds to heat transfers governed by interfacial barriers in contact zones and has not been treated elsewhere. The identification procedure at the successive orders of ε leads to the following boundary value problems.

The boundary value problem for $T_\alpha^{[0]*}$ is

$$\boldsymbol{\nabla}_{y^*} \cdot \mathbf{q}_\alpha^{[0]*} = 0 \quad \text{in } \Omega_\alpha^*, \tag{34a}$$

$$\mathbf{q}_\alpha^{[0]*} = -\boldsymbol{\Lambda}_\alpha^* \cdot \boldsymbol{\nabla}_{y^*} T_\alpha^{[0]*} \quad \text{in } \Omega_\alpha^*, \tag{34b}$$

$$\mathbf{q}_\alpha^{[0]*} \cdot \hat{\mathbf{n}}_\alpha = 0 \quad \text{on } \Gamma_\alpha^*, \tag{34c}$$

$$\mathbf{q}_\alpha^{[0]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = \mathbf{q}_\beta^{[0]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} \quad \text{on } \Gamma_{i\alpha\beta}^*, \tag{34d}$$

$$\mathbf{q}_\alpha^{[0]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = 0 \quad \text{on } \Gamma_{i\alpha\beta}^*. \tag{34e}$$

Multiplying Eq. (34a) by $T_\alpha^{[0]*}$, integrating over Ω_α^*, applying the divergence theorem, and accounting for Eqs. (34b)–(34e) yields

$$\int_{\Omega_\alpha^*} \boldsymbol{\nabla}_{y^*} T_\alpha^{[0]*} \cdot \boldsymbol{\Lambda}_\alpha^* \cdot \boldsymbol{\nabla}_{y^*} T_\alpha^{[0]*} dV^* = 0. \tag{35}$$

As the tensors $\boldsymbol{\Lambda}_\alpha^*$ are definite and positive, it is concluded from Eq. (35) that $\boldsymbol{\nabla}_{y^*}T_\alpha^{[0]*} = \mathbf{0}$, i.e., the macroscopic temperature field of each particle is $\mathbf{y}^*$ independent:

$$T_\alpha^{[0]*}(\mathbf{x}^*, \mathbf{y}^*, t^*) = T_\alpha^{[0]*}(\mathbf{x}^*, t^*). \tag{36}$$

The boundary value problem for $T_\alpha^{[1]*}$ and compatibility condition for $T_\alpha^{[0]*}$ are

$$\boldsymbol{\nabla}_{y^*} \cdot \mathbf{q}_\alpha^{[1]*} = 0 \quad \text{in } \Omega_\alpha^*, \tag{37a}$$

$$\mathbf{q}_\alpha^{[1]*} = -\boldsymbol{\Lambda}_\alpha^* \cdot (\boldsymbol{\nabla}_{x^*} T_\alpha^{[0]*} + \boldsymbol{\nabla}_{y^*} T_\alpha^{[1]*}) \quad \text{in } \Omega_\alpha^*, \tag{37b}$$

$$\mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_\alpha = 0 \quad \text{on } \Gamma_\alpha^*, \tag{37c}$$

$$\mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = \mathbf{q}_\beta^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} \quad \text{on } \Gamma_{i\alpha\beta}^*, \tag{37d}$$

$$\mathbf{q}_\alpha^{[1]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = -h_{i\alpha\beta}^* \Delta_{\alpha\beta} T^{[0]*} \quad \text{on } \Gamma_{i\alpha\beta}^*. \tag{37e}$$

Integrating Eq. (37a) over Ω_α^*, taking into account Eq. (36) as well as conditions (37c)–(37e), the following compatibility condition is obtained:

$$\sum_{\mathcal{C}_\alpha} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* \Delta_{\alpha\beta} T^{[0]*} = 0. \tag{38}$$

Multiplying the last equation by $T_\alpha^{[0]*}$, summing over all particles in the REV, the following expression is obtained:

$$\sum_{\mathcal{C}_{\mathrm{REV}}} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* (\Delta_{\alpha\beta} T^{[0]*})^2 = 0. \tag{39}$$

As $\Gamma_{i\alpha\beta}^* > 0$ and $\tilde{h}_{i\alpha\beta}^* > 0$, the last relation implies

$$T_\alpha^{[0]*}(\mathbf{x}^*, t^*) = T_\beta^{[0]*}(\mathbf{x}^*, t^*) = T^{[0]*}(\mathbf{x}^*, t^*). \tag{40}$$

Consequently, at the first order, the equivalent macroscopic medium is still a one-phase medium, as in models I and II. Likewise, one can notice that system (37) is a boundary value problem in which the temperatures $T_\alpha^{[1]*}$ are unknowns and where the macroscopic temperature gradient $\boldsymbol{\nabla}_{x^*}T^{[0]*}$ is given. Multiplying Eq. (37a) by an appropriate test function T', integrating over Ω_α^* and considering Eqs. (37b)–(37e) as well as Eq. (40) the following weak variational formulation is obtained:

$$\forall T' \quad \int_{\Omega_\alpha^*} \boldsymbol{\Lambda}_\alpha^* \cdot (\boldsymbol{\nabla}_{x^*} T^{[0]*} + \boldsymbol{\nabla}_{y^*} T_\alpha^{[1]*}) \cdot \boldsymbol{\nabla}_{y^*} T' dV^* = 0. \tag{41}$$

From this formulation it is possible to prove the uniqueness of the following solution $T_\alpha^{[1]*}$, up to an arbitrary $\mathbf{y}^*$-independent constant $\bar{T}_\alpha^{[1]*}$. This solution is such that

$$\mathbf{q}_\alpha^{[1]*} = -\mathbf{\Lambda}_\alpha^* \cdot (\nabla_{x^*} T_\alpha^{[0]*} + \nabla_{y^*} T_\alpha^{[1]*}) = \mathbf{0} \tag{42}$$

and can be written as

$$T_\alpha^{[1]*} = -\mathbf{y}_\alpha^* \cdot \nabla_{x^*} T^{[0]*} + \bar{T}_\alpha^{[1]*}(\mathbf{x}^*, t^*), \tag{43}$$

where $\mathbf{y}_\alpha^* = \mathbf{G}_\alpha^* \mathbf{M}^*$ and $\mathbf{G}_\alpha^*$ is the center of mass of particle p_α.

The boundary value problem for $T_\alpha^{[2]*}$ and compatibility condition for $T_\alpha^{[1]*}$ are

$$\nabla_{y^*} \cdot \mathbf{q}_\alpha^{[2]*} = 0 \quad \text{in } \Omega_\alpha^*, \tag{44a}$$

$$\mathbf{q}_\alpha^{[2]*} = -\mathbf{\Lambda}_\alpha^* \cdot (\nabla_{x^*} T_\alpha^{[1]*} + \nabla_{y^*} T_\alpha^{[2]*}) \quad \text{in } \Omega_\alpha^*, \tag{44b}$$

$$\mathbf{q}_\alpha^{[2]*} \cdot \hat{\mathbf{n}}_\alpha = 0 \quad \text{on } \Gamma_\alpha^*, \tag{44c}$$

$$\mathbf{q}_\alpha^{[2]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = \mathbf{q}_\beta^{[2]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} \quad \text{on } \Gamma_{i\alpha\beta}^*, \tag{44d}$$

$$\mathbf{q}_\alpha^{[2]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = -h_{i\alpha\beta}^* \Delta_{\alpha\beta} T^{[1]*} \quad \text{on } \Gamma_{i\alpha\beta}^*. \tag{44e}$$

Integrating Eq. (44a) over Ω_α^*, applying the divergence theorem as well as using Eqs. (44c) and (44d) yield the following compatibility conditions:

$$\sum_{\mathcal{C}_\alpha} \int_{\Gamma_{i\alpha\beta}^*} \mathbf{q}_\alpha^{[2]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} \mathrm{d}S^* = 0. \tag{45}$$

By noting $\mathbf{y}_{\alpha\beta}^* = \mathbf{G}_\alpha^* \mathbf{G}_\beta^*$, and by accounting for Eqs. (43) and (44e), the last relation is equivalent to

$$\sum_{\mathcal{C}_\alpha} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* (\Delta_{\alpha\beta} \bar{T}^{[1]*} + \mathbf{y}_{\alpha\beta}^* \cdot \nabla_{x^*} T^{[0]*}) = 0. \tag{46}$$

This represents a linear system of $P_{\mathrm{REV}}-1$ independent equations with P_{REV} unknowns $\bar{T}_\alpha^{[1]*}$. By fixing arbitrarily the value of one temperature fluctuation, this system has a unique solution. Likewise, Eq. (46) shows that the $\Delta_{\alpha\beta}\bar{T}^{[1]*}$ may be put in the following form:

$$\Delta_{\alpha\beta} \bar{T}^{[1]*} = \Delta_{\alpha\beta} \bar{\boldsymbol{\theta}}^{[1]*} \cdot \nabla_{x^*} T^{[0]*}, \tag{47}$$

where the value of the kth component $(\Delta_{\alpha\beta}\bar{\theta}^{[1]*})_k$ of the vector $\Delta_{\alpha\beta}\bar{\boldsymbol{\theta}}^{[1]*}$ equals the solution $\Delta_{\alpha\beta}\bar{T}^{[1]*}$ when $\nabla_{x^*} T^{[0]*} = \hat{\mathbf{e}}_k$ ($k \in \{1,2,3\}$). Vectors $\Delta_{\alpha\beta}\bar{\boldsymbol{\theta}}^{[1]*}$ therefore verify

$$\sum_{\mathcal{C}_\alpha} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* (\mathbf{y}_{\alpha\beta}^* + \Delta_{\alpha\beta} \bar{\boldsymbol{\theta}}^{[1]*}) = \mathbf{0}. \tag{48}$$

By multiplying each of these last expressions by a test vector $\boldsymbol{\tau}'_\alpha$, by summing them for all particles in the REV and by noting $\Delta_{\alpha\beta}\boldsymbol{\tau}' = \boldsymbol{\tau}'_\beta - \boldsymbol{\tau}'_\alpha$, the following expression is obtained:

$$\forall \boldsymbol{\tau}'_\alpha, \forall \boldsymbol{\tau}'_\beta, \quad \sum_{\mathcal{C}_{\mathrm{REV}}} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* (\mathbf{y}_{\alpha\beta}^* + \Delta_{\alpha\beta} \bar{\boldsymbol{\theta}}^{[1]*}) \cdot \Delta_{\alpha\beta} \boldsymbol{\tau}' = 0. \tag{49}$$

If we now choose successively $\Delta_{\alpha\beta}\boldsymbol{\tau}' = (y_{\alpha\beta}^*)_k \hat{\mathbf{e}}_l$ and then $\Delta_{\alpha\beta}\boldsymbol{\tau}' = (y_{\alpha\beta}^*)_l \hat{\mathbf{e}}_k$ ($k \in \{1,2,3\}$ and $l \in \{1,2,3\}$), three interesting relations can be established when $k \neq l$ and will be used in the next point:

$$\sum_{\mathcal{C}_{\mathrm{REV}}} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* [(\Delta_{\alpha\beta} \bar{\theta}^{[1]*})_l (y_{\alpha\beta})_k - (\Delta_{\alpha\beta} \bar{\theta}^{[1]*})_k (y_{\alpha\beta})_l] = 0. \tag{50}$$

The boundary value problem for $T_\alpha^{[3]*}$ and compatibility condition for $T_\alpha^{[2]*}$ are

$$c_\alpha^* \dot{T}^{[0]*} = \nabla_{y^*} \cdot \mathbf{q}_\alpha^{[3]*} + \nabla_{x^*} \cdot \mathbf{q}_\alpha^{[2]*} \quad \text{in } \Omega_\alpha^*, \tag{51a}$$

$$\mathbf{q}_\alpha^{[3]*} = -\mathbf{\Lambda}_\alpha^* \cdot (\nabla_{x^*} T^{[2]*} + \nabla_{y^*} T_\alpha^{[3]*}) \quad \text{in } \Omega_\alpha^*, \tag{51b}$$

$$\mathbf{q}_\alpha^{[3]*} \cdot \hat{\mathbf{n}}_\alpha = 0 \quad \text{on } \Gamma_\alpha^*, \tag{51c}$$

$$\mathbf{q}_\alpha^{[3]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = \mathbf{q}_\beta^{[3]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} \quad \text{on } \Gamma_{i\alpha\beta}^*, \tag{51d}$$

$$\mathbf{q}_\alpha^{[3]*} \cdot \hat{\mathbf{n}}_{i\alpha\beta} = -h_{i\alpha\beta}^* \Delta_{\alpha\beta} T^{[2]*} \quad \text{on } \Gamma_{i\alpha\beta}^*. \tag{51e}$$

Integrating Eq. (51a) over the whole REV, applying the divergence theorem and using Eqs. (51c)–(51e) yield the following compatibility condition, which represents the heat balance equation of the macroscopic equivalent continuous medium at the first order of approximation

$$c^{e*} \dot{T}^{e*} = -\nabla_{x^*} \cdot \mathbf{q}^{e*}, \tag{52}$$

where $T^{e*} = T^{[0]*}$ and $\mathbf{q}^{e*} = \langle \mathbf{q}^{[2]*} \rangle$. By taking into account Eq. (44a), one can use the following relation:

$$\mathbf{q}_\alpha^{[2]*} = (\mathbf{y}_\alpha^* \otimes \mathbf{q}_\alpha^{[2]*}) \cdot \nabla_{y^*} \tag{53}$$

and the divergence theorem to write

$$\mathbf{q}^{e*} = \frac{1}{\Omega_{\mathrm{REV}}^*} \sum_{\mathcal{P}_{\mathrm{REV}}} \sum_{\mathcal{C}_\alpha} \int_{\Gamma_{i\alpha\beta}^*} (\mathbf{y}_\alpha^* \otimes \mathbf{q}_\alpha^{[2]*}) \cdot \hat{\mathbf{n}}_{i\alpha\beta} dS^*. \tag{54}$$

By taking into account Eq. (44e), and by noting that the double summation in $\mathcal{P}_{\mathrm{REV}}$ and $\mathcal{C}_\alpha$ can be replaced by the summation on the set $\mathcal{C}_{\mathrm{REV}}$ of the particle-particle connections in the REV one obtains

$$\mathbf{q}^{e*} = -\frac{1}{\Omega_{\mathrm{REV}}^*} \sum_{\mathcal{C}_{\mathrm{REV}}} \int_{\Gamma_{i\alpha\beta}^*} h_{i\alpha\beta}^* \Delta_{\alpha\beta} T^{[1]*} dS^* \mathbf{y}_{\alpha\beta}^*. \tag{55}$$

Finally, by accounting for Eqs. (43) and (47), it can be shown that the macroscopic heat flow $\mathbf{q}^{e*}$ follows a standard Fourier's law at the first order of approximation

$$\mathbf{q}^{e*} = -\mathbf{\Lambda}^{e*} \cdot \nabla_{x^*} T^{e*}, \tag{56}$$

where the macroscopic conductivity tensor is defined as

$$\mathbf{\Lambda}^{e*} = \frac{1}{\Omega_{\mathrm{REV}}^*} \sum_{\mathcal{C}_{\mathrm{REV}}} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* \mathbf{y}_{\alpha\beta}^* \otimes (\mathbf{y}_{\alpha\beta}^* + \Delta_{\alpha\beta} \bar{\boldsymbol{\theta}}^{[1]*}) \tag{57}$$

or, by introducing $C_1 = C_{\mathrm{REV}}/\Omega_{\mathrm{REV}}^*$ as the number of connections per unit of volume,

$$\mathbf{\Lambda}^{e*} = C_1 \left[\frac{1}{C_{\mathrm{REV}}} \sum_{\mathcal{C}_{\mathrm{REV}}} \Gamma_{i\alpha\beta}^* \tilde{h}_{i\alpha\beta}^* \mathbf{y}_{\alpha\beta}^* \otimes (\mathbf{y}_{\alpha\beta}^* + \Delta_{\alpha\beta} \bar{\boldsymbol{\theta}}^{[1]*}) \right]. \tag{58}$$

The macroscopic conductivity tensor $\mathbf{\Lambda}^{e*}$ does not depend on $\mathbf{\Lambda}_\alpha^*$. Its symmetry results from Eq. (50). Its components can be determined from the calculation of the $\Delta_{\alpha\beta}\overline{\boldsymbol{\theta}}^{[1]*}$. This is achieved by solving the linear system of Eqs. (46) and (47) for three given independent macroscopic temperature gradients $\hat{\mathbf{e}}_k$ ($k\in\{1,2,3\}$).

E. Simplified expressions of the conductivity tensor for model III

Simpler expressions of the macroscopic conductivity tensor can be obtained for model III in case of elementary microstructures. For example, let us consider that REV's are made of spherical particles of identical radius a^* with identical averaged heat transfer coefficient $\tilde{h}^*$ and contact surface Γ^* which can be approximated as a disk of radius ka^* (k being a constant) with a normal unit vector $\hat{\mathbf{e}}_{\alpha\beta}$ such as $\mathbf{y}^*_{\alpha\beta}=2a^*\hat{\mathbf{e}}_{\alpha\beta}$. Then, $\boldsymbol{\Lambda}^{e*}$ can be approximated as

$$\boldsymbol{\Lambda}^{e*} = 4\pi C_1 \tilde{h}^* k^2 a^{*4}\left(\mathbf{A} + \frac{1}{C_{\text{REV}}}\sum_{\mathcal{C}_{\text{REV}}} \hat{\mathbf{e}}_{\alpha\beta}\otimes\frac{\Delta_{\alpha\beta}\overline{\boldsymbol{\theta}}^{[1]*}}{2a^*}\right), \tag{59}$$

where

$$\mathbf{A} = \frac{1}{C_{\text{REV}}}\sum_{\mathcal{C}_{\text{REV}}} \hat{\mathbf{e}}_{\alpha\beta}\otimes\hat{\mathbf{e}}_{\alpha\beta}, \tag{60}$$

stands for the second order fabric tensor [33] characterizing the orientation of contacts between touching particles and $C_1 = C_{\text{REV}}/\Omega^*_{\text{REV}}$ is the number of contacts per unit of volume. Notice that for a similar type of local physics and microstructures (monodispersed spherical particles, steady state conditions, and small contact surfaces), Batchelor, O'Brien, and O'Brien [8] assumed that temperature variation $\Delta_{\alpha\beta}T^*$ between particles p_α and p_β could be estimated as affine functions of the mean imposed temperature gradient. At the first order, this is equivalent to

$$\Delta_{\alpha\beta}T^* \approx \Delta_{\alpha\beta}T^{[1]*} \approx \mathbf{y}^*_{\alpha\beta}\cdot\boldsymbol{\nabla}_{x^*}T^{[0]}. \tag{61}$$

As shown from Eq. (46), such an assumption can be confirmed from some regular types of particle arrangements (square packing, for example). In general, however, its validity must be discussed from numerical results [13]. If it applies, the macroscopic conductivity tensor should then simply reads

$$\boldsymbol{\Lambda}^{e*} = 4\pi C_1 k^2 \tilde{h}^* a^{*4}\mathbf{A} \tag{62}$$

and should hence be directly deduced from the unique knowledge of the microstructure. A similar analysis will be conducted in paper II in the case of slender, wavy, and entangled fibers.

F. Temperature dependent thermal properties

The above theoretical developments have been achieved for temperature independent heat capacities c^*_α, conductivities $\boldsymbol{\Lambda}^*_\alpha$, and heat transfer coefficients $h^*_{i\alpha\beta}$. In many applications, however, thermal properties are considered as temperature-dependent variables, i.e., $c^*_\alpha(T^*_\alpha)$ and/or $\boldsymbol{\Lambda}^*_\alpha(T^*_\alpha)$ and/or $h^*_{i\alpha\beta}(T^*_\alpha)$. If these functions satisfy

$$\forall k\geq 1,\quad O\left(\frac{1}{k!}\left\|\left[\frac{\partial^k\chi^*_\alpha}{\partial T^{*k}_\alpha}\right]_{T^{[0]*}}\right\|\right)\leq O(\varepsilon^{1-k}), \tag{63}$$

χ^*_α being equal to c^*_α, $\boldsymbol{\Lambda}^*_\alpha$, and $h^*_{i\alpha\beta}$, respectively, they can be taken into account in the last upscaling process. Indeed, by using the following Taylor expansions of the functions χ^*_α around $T^{[0]*}$:

$$\chi^*_\alpha(T^*_\alpha) = \chi^*_\alpha(T^{[0]*}) + \left[\frac{\partial\chi^*_\alpha}{\partial T^*_\alpha}\right]_{T^{[0]*}}\varepsilon(T^{[1]*}_\alpha + \varepsilon T^{[2]*^2}_\alpha + \cdots) + \cdots + \frac{1}{k!}\left[\frac{\partial^k\chi_\alpha}{\partial T^{*k}_\alpha}\right]_{T^{[0]*}}\varepsilon^k(T^{[1]*}_\alpha + \varepsilon T^{[2]*^2}_\alpha + \cdots)^k + \cdots, \tag{64}$$

they can be expressed as asymptotic expansions [32]

$$\chi^*_\alpha(T^*_\alpha) = \chi^{[0]*}_\alpha + \varepsilon\chi^{[1]*}_\alpha + \cdots, \tag{65}$$

where, in particular, $\chi^{[0]*}_\alpha = \chi^*_\alpha(T^{[0]*}_\alpha)$. Condition (63) implies that for $n\geq 1$, the $\chi^{[n]*}_\alpha$'s will never arise in the boundary value problem in $T^{[0]*}$. From a physical point of view, this means that close to $T^{[0]*}$, the variation of χ^*_α with T^*_α remains weak. Therefore, it can be shown that previously established theoretical results, i.e., localization problems, structures, and properties of macroscopic heat balance and constitutive equations, still remain valid, simply replacing c^*_α, $\boldsymbol{\Lambda}^*_\alpha$, $h^*_{i\alpha\beta}$, c^{e*}, and $\boldsymbol{\Lambda}^{e*}$ by $c^*_\alpha(T^{[0]*})$, $\boldsymbol{\Lambda}^*_\alpha(T^{[0]*})$, $h^*_{i\alpha\beta}(T^{[0]*})$, $c^{e*}(T^{e*})$, and $\boldsymbol{\Lambda}^{e*}(T^{e*})$, respectively.

G. Local thermal heat sources

For the sake of simplicity, possible volumetric heat sources r_α (characteristic value r_c) in the right-hand side of local heat balance Eq. (2) have been neglected until now. It is possible to take them into account in the upscaling process. For that purpose a dimensionless term $\mathbb{R}_c r^*_\alpha$ is added in the right-hand side of Eq. (8a), where the dimensionless heat source r^*_α is defined as $r^*_\alpha = r_\alpha/r_c$ and where the dimensionless number $\mathbb{R}_c = r_c\Delta t_c/c_c\Delta T_c$. By using physical arguments identical to those conducted for $\mathbb{F}_c$, it can be shown that homogenizable situations correspond to $\mathbb{R}_c = O(\mathbb{F}_c)$. Also, heat sources r^*_α are supposed to be expressed in the form of asymptotic expansions in powers of ε, in a way similar to that conducted for the temperatures in Eq. (17):

$$r^*_\alpha(\mathbf{X}^*,t^*) = r^{[0]*}_\alpha(\mathbf{x}^*,\mathbf{y}^*,t^*) + \varepsilon r^{[1]*}_\alpha(\mathbf{x}^*,\mathbf{y}^*,t^*) + \varepsilon^2 r^{[2]*}_\alpha(\mathbf{x}^*,\mathbf{y}^*,t^*) + \cdots. \tag{66}$$

It can then be shown that the unique modification in the results obtained in the above upscaling process is the introduction of the volume average $r^{e*} = \langle r^{[0]*}_\alpha\rangle$ in the right-hand side of the macroscopic balance Eqs. (22) and (52), in a way similar to what was done for the heat capacities

$$c^{e*}\dot{T}^{e*} = -\boldsymbol{\nabla}_{x^*}\cdot\mathbf{q}^{e*} + r^{e*}. \tag{67}$$

Hence, for the considered transient thermal problem and the considered particulate media, calculations of the effective properties c^{e*}, r^{e*}, and $\boldsymbol{\Lambda}^{e*}$ are uncoupled.

IV. CONCLUDING REMARKS

When neglecting heat transfers in the bulk matrix, the transient and diffusive heat transfers through a network of connected and highly conductive particles having interfacial thermal barriers on their contacting zones have been studied theoretically with the homogenization method of multiple scale expansions. Theoretical results obtained in the previous section bring up the following comments.

(i) Depending on both the separation of scales parameter and the quality of the contacts between touching particles, the existence of three different macroscopic equivalent media has been established for the considered local physics and particulate microstructures. Such media are one-phase continua that obey standard transient heat balance equations and Fourier's law. These models have been established without any *a priori* assumption concerning the structures and properties of the macroscopic balances and constitutive equations.

(ii) The developments carried out to obtain models I and II (corresponding, respectively, to highly or rather conductive contacts) are identical to those achieved previously in the case of composite materials made of connected phases [30]. Due to the particulate nature of the considered microstructures and to the considered highly resistive contacts, model III is different than the model obtained in Ref. [30], and the media behave as insulators for lower Biot numbers. It is important to notice that the last results may break down for some other particulate media. For example, let us consider the case of continuous fibers, i.e., fibers that can cross the REV. In this situation, the upscaling process would become similar to that conducted in Ref. [30]. This would result in multiphase macroscopic descriptions for lower Biot numbers, i.e., with P_{REV} macroscopic temperature fields $T_\alpha^{[0]*}(\mathbf{x}^*,t^*)$ and P_{REV} coupled macroscopic heat balance equations. Identical theoretical results might also be gained by considering that the REV contains clusters or chains that are made of short particles linked with excellent particle-particle contacts, that cross the REV and that are touching other chains with poorer chain-chain contacts.

(iii) Even if a transient and weakly nonlinear physics is studied at the microscale and results in a transient and weakly nonlinear physics at the macroscale, calculations of the effective macroscopic volumetric heat capacity c^{e*}, heat sources r^{e*}, and conductivity tensor $\mathbf{\Lambda}^{e*}$ are uncoupled and can be achieved quite easily. Indeed, c^{e*} and r^{e*} are trivial volume averages of the local heat capacities and heat sources, whereas $\mathbf{\Lambda}^{e*}$ is determined by solving steady state and linear localization problems, independently from local heat capacities and heat sources.

(iv) In case of models I and II, the calculation of the macroscopic conductivity tensor $\mathbf{\Lambda}^{e*}$ requires (i) solving the partial differential equation system (19d) [replacing Eq. (19) by Eq. (28) for model II] for three unit vectors $\boldsymbol{\nabla}_{x^*}T^{[0]*}=\hat{\mathbf{e}}_k$ ($k\in\{1,2,3\}$) and (ii) computing the averaged heat flux $\mathbf{q}^{e*}=\langle\mathbf{q}_\alpha^{[1]*}\rangle$ from the knowledge of the temperatures $T_\alpha^{[1]*}=(\boldsymbol{\theta}_\alpha^{[1]*})_k$. Typically, this could be achieved with 3D usual numerical schemes such as finite elements, differences, or volumes methods. Depending on the number of particles contained in REV's as well as their geometry, localization problems to be solved can rapidly become cumbersome, and time and memory consuming. The simplification of these problems in the case of spherical particles have already been proposed in previous studies for linear and steady state conditions (for example, Refs. [15,18]), leading to a discrete formulation of the conduction problem. In paper II [35], such a simplification will be proposed in the case of fibrous materials.

(v) By contrast, localization problem in case of model III is considerably simplified: whatever the considered particulate medium, solving the linear discrete system of algebraic Eq. (46) is required to compute the temperatures $\Delta_{\alpha\beta}\overline{T}^{[1]*}=(\Delta_{\alpha\beta}\overline{\theta}^{[1]*})_k$, and then the macroscopic conductivity tensor is obtained from Eq. (58).

From this theoretical work, paper II of this contribution will explore analytically and numerically the effective diffusive properties of networks of high aspect ratio, wavy, and entangled fibers.

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