EFFECTIVE THERMAL CONDUCTIVITY OF GRANULAR MATERIALS

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Calculations are made of the effective thermal conductivity for macroscopic heat transfer in a composite material consisting of a continuous medium (binder) with spherical particles (filler) randomly distributed through it.

In investigating transfer processes in composite materials having a complex internal structure it is often admissible to regard the material as a continuous medium characterized by certain effective values of the corresponding transfer coefficients. As a result there arises the problem of determining these values as functions of the geometric parameters of the material and the physical transfer coefficients for the individual components of this material. This problem was formulated by Maxwell and Rayleigh for granular materials in connection with the determination of the dielectric constant of dilute dispersions. In spite of the considerable number of papers on this subject (cf. summary in [1, 2]) a rigorous solution of this problem exists only for materials with a small volume concentration of filler. Attempts to generalize this solution to materials of high or medium concentrations are clearly phenomenological in character.

We present an approximate theory of the thermal conductivity of high-concentration granular materials based on the representation of a filler particle as a thermal dipole perturbing the temperature distribution in the binder. In view of the analogy of the mathematical formulations of the corresponding problems, the results obtained are applicable to calculations of the electrical conductivity, the dielectric constant, and the magnetic permeability of a granular material, and also the effective diffusion coefficient of some admixture in it.

1. We consider a granular material consisting of a continuous binder with a thermal conductivity λ_1 and spherical filler particles. The number and volume densities of particles are n and ρ respectively, and the distribution function for particles of radius a and thermal conductivity λ_2, normalized to unity, is denoted by $\psi(a, \lambda_2)$. For any configuration of material the temperature distribution in the binder and filler can in principle be obtained by solving the appropriate heat-conduction equations and satisfying certain initial and external boundary conditions and conditions for the continuity of the temperature and heat flux at the surfaces of all particles. Such a problem cannot be solved at the present time. Further difficulties arise from the fact that the detailed disposition of the particles in actual materials (i.e., their configuration) is generally unknown and can only be described statistically.

However, if the characteristic linear scale L of the variation of n and ρ is much larger than the scale characterizing the microstructure of the material, and the same order of magnitude as the average distance between particles $l \sim a_0\rho^{-1/3} > a_0$, where a_0 is a typical value of the radius of a particle, it is generally not necessary to go into a detailed determination of the microscopic temperature distribution. Actually in this case there exists a physically small volume which contains a representative number of particles sufficient for averaging, and the material within this volume can be assumed macroscopically homogeneous.

For simplicity we assume that the material is also macroscopically isotropic. If the temperature of the material obtained by averaging over such a volume changes significantly over distances of the order of L or, in any case, much larger than l, the idea of an effective thermal conductivity of a granular material λ can be introduced as a proportionality factor between the average values of the heat flux and the tempera-

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ture gradient, i.e.,

$$[\mathbf{Q}] = -\lambda [\nabla T] = -\lambda \nabla [T] \tag{1.1}$$

From now on, square brackets denote averaging over a physically small volume. Clearly we can write

$$\begin{aligned} [\mathbf{Q}] &= (1-\rho)[\mathbf{Q}_1] + n \iint v(a)\, \psi(a, \lambda_2)\, [\mathbf{Q}_2](a, \lambda_2)\, da d\lambda_2 \\ \nabla [T] &= (1-\rho) \nabla [T_1] + n \iint v(a)\, \psi(a, \lambda_2) \nabla [T_2](a, \lambda_2)\, da\, d\lambda_2 \end{aligned} \tag{1.2}$$

where v(a) is the volume of a particle, and the subscripts 1 and 2 refer to the binder and filler respectively. It is clear that

$$[\mathbf{Q}_1] = -\lambda_1 \nabla [T_1], \quad [\mathbf{Q}_2](a, \lambda_2) = -\lambda_2 \nabla [T_2](a, \lambda_2) \tag{1.3}$$

If Eq. (1.1) is satisfied, the equation describing macroscopic heat transfer in the material is

$$\partial [T] / \partial t = \nabla (\lambda \nabla [T_2]) \tag{1.4}$$

where for simplicity we have taken the specific heat as unity.

From (1.4) we have $\omega \sim \lambda L^{-2} \sim \lambda_1 L^{-2}$, where ω is the characteristic frequency of the process. From this and the inequality $L \gg l \gg a$, there follows a restriction on the frequency ω of the heat-transfer process, which by using (1.1)-(1.4) can be considered as occurring in a homogeneous medium with thermal conductivity λ. We obtain

$$\omega \ll \lambda a^{-2} \sim \lambda_1 a^{-2} \tag{1.5}$$

This inequality holds also when the effective thermal conductivity depends on ω, i.e., when (1.1) and (1.4) are satisfied, for example, for the Fourier components of [Q] and ∇[T] but not for these quantities themselves.

It follows from (1.2) and (1.3) that the value of λ characterizing the isotropic granular material under consideration can be determined by finding the relation between the average temperature gradient in particles of radius a and thermal conductivity λ_2 and the average temperature gradient in the binder. Therefore it is reasonable to replace the original problem of determining the true microscopic temperature distribution in the material by a simpler problem formulated for the average macroscopic temperatures of the binder and filler.

To this end, we consider an ensemble of N particles of the material in a volume $V \gg l^3$ such that within this volume the possibility of n and ρ depending on $\mathbf{r}$ can be neglected, i.e., the material can be considered statistically homogeneous. We introduce the N-particle distribution function of the ensemble $\varphi(B_N)$, normalized to unity, where B_N denotes the set of radius vectors to the centers of the N particles of the ensemble and their radii and thermal conductivities. In addition we introduce the ensemble distribution functions $\varphi(B_{N-1}|\mathbf{r}, a)$ and $\varphi(N_{N-2}|\mathbf{r}, a; \mathbf{r}', a')$.

The first function is the conditional probability density of the configuration B_{N-1} of all N − 1 particles of the ensemble except a certain selected one, if it is known that the center of the selected particle is at the point $\mathbf{r}$ and its radius is a. The second distribution function is the probability density of the configuration B_{N-2} when there are two selected particles of radii a and a' at the points $\mathbf{r}$ and $\mathbf{r}'$. These distribution functions permit the determination of the ensemble average of any quantity F which depends on the coordinates, radii, and thermal conductivities of many particles. We have

$$\begin{gathered} \langle F \rangle = \langle F \rangle_N = \int F \varphi(B_N)\, dB_N, \quad \langle F \rangle'_{N-1} = \int F \varphi(B_{N-1} | \mathbf{r}, a)\, dB_{N-1} \\ \langle F \rangle''_{N-2} = \int F \varphi(B_{N-2} | \mathbf{r}, a; \mathbf{r}', a')\, dB_{N-2} \end{gathered} \tag{1.6}$$

The properties of the ensemble distribution functions and the corresponding averages in (1.6) were considered, for example, in [3-5] in the analysis of the slow flow of a fluid in a cloud of spherical particles. The following properties are important in what follows.

There are the identities

$$\begin{gathered} \varphi(B_N) = \varphi(\mathbf{r}, a, \lambda_2)\, \varphi(B_{N-1} | \mathbf{r}, a) \\ \varphi(B_{N-1} | \mathbf{r}, a) = \varphi(\mathbf{r}', a', \lambda_2 | \mathbf{r}, a)\, \varphi(B_{N-2} | \mathbf{r}, a; \mathbf{r}', a') \end{gathered} \tag{1.7}$$

where $\varphi(\mathbf{r}, a, \lambda_2)$ and $\varphi(\mathbf{r}, a, \lambda_2|\mathbf{r}'; a')$ are the unconditional and conditional single-particle (unary) distribution functions normalized to unity. Since it has been assumed that the material in the vicinity of any particle can be considered statistically homogeneous, we have the approximate relation between $\varphi(\mathbf{r}, a, \lambda_2)$ and the function $\psi(a, \lambda_2)$ introduced earlier:

$$\varphi(\mathbf{r}, a, \lambda_2) \approx V^{-1}\psi(a, \lambda_2) \tag{1.8}$$

From the assumptions of the statistical homogeneity of the material and the random packing of particles in it there follows

$$\varphi(\mathbf{r}, a, \lambda_2|\mathbf{r}', a') = \begin{cases} \varphi(\mathbf{r}, a, \lambda_2), & |\mathbf{r}-\mathbf{r}'| > a + a' \\ 0, & |\mathbf{r}-\mathbf{r}'| < a + a' \end{cases} \tag{1.9}$$

Finally in accordance with the analysis in [3-5] we consider a quantity F such that each individual particle affects F very slightly, and only the effect of many particles is significant. For such a quantity we can write asymptotic equations valid for $N \gg 1$

$$\langle F\rangle''_{N-2} = \langle F\rangle'_{N-1} + O_1(N^{-1}) = \langle F\rangle + O_2(N^{-2}) \tag{1.10}$$

which express the properties of statistical stability of the ensemble. If Eq. (1.10) is not satisfied, for example, for the temperature in a granular material the very concept of a statistical description of the heat-transfer process in the material becomes meaningless.

2. Let us consider next the transfer of heat in the vicinity of a certain test particle selected from the ensemble of N particles. Let the center of this particle be at the point $\mathbf{r} = 0$ and its radius be a. In view of the linearity of the heat-conduction equation, the temperatures in the binder can be written as

$$T_1(t, \mathbf{r}) = T_0(t, \mathbf{r}) + \sum_{j=1}^{N-1} T^{(j)}(t, \mathbf{r}; \mathbf{r}^{(j)}, a^{(j)}, \lambda_2^{(j)}) \tag{2.1}$$

Here T_0 is the temperature of the binder, unperturbed by the particles, and $T^{(j)}$ is the perturbation introduced by the j-th particle. The quantities introduced in Eq. (2.1) satisfy the equations

$$\partial T_0/\partial t = \lambda_1 \Delta T_0, \qquad \partial T^{(j)}/\partial t = \lambda_1 \Delta T^{(j)} + G^{(j)} \tag{2.2}$$

where $G^{(j)}$ is the heat source simulating the effect of the j-th particle on the temperature distribution in the binder. This quantity can be written in the form

$$G^{(j)} = \oint_{s_j} q(t, \mathbf{r})\,\delta(\mathbf{r} - \mathbf{R}^{(j)})\,d\mathbf{R}^{(j)} = \lambda_0 \oint_{s_j} \mathbf{n}\nabla T^{(j)}(t, \mathbf{r})\,\delta(\mathbf{r} - \mathbf{R}^{(j)})\,d\mathbf{R}^{(j)}$$
$$(\mathbf{R}^{(j)} = \mathbf{r}^{(j)} + \mathbf{a}^{(j)}) \tag{2.3}$$

Here $\boldsymbol{a}^{(j)}$ is the vector connecting the center $\mathbf{r}^{(j)}$ of the particle and an arbitrary point on its surface s_j, $\mathbf{n}$ is the outward normal, and $\mathbf{q}$ is the heat flux density at s_j corresponding to the temperature perturbation due to the j-th particle.

Expanding the delta function in (2.3) in a power series in the components of the vector $\boldsymbol{a}^{(j)}$, we obtain

$$G^{(j)} = \oint_{s_j} q(t, \mathbf{R}^{(j)}) \sum_m \frac{(-1)^m}{m!} (\mathbf{a}^{(j)}\nabla)^m\, \delta(\mathbf{r} - \mathbf{r}^{(j)})\, d\mathbf{a}^{(j)} = \sum_m {}^m G_{ik\ldots p}(t, \mathbf{r}^{(j)}) \frac{\partial}{\partial r_i} \cdots \frac{\partial}{\partial r_p} \delta(\mathbf{r} - \mathbf{r}^{(j)})$$
$${}^m G_{ik\ldots p}(t, \mathbf{r}^{(j)}) = \frac{(-1)^m}{m!} \oint_{s_j} q(t, \mathbf{R}^{(j)})\, a_i^{(j)} a_k^{(j)} \ldots a_p^{(j)}\, d\mathbf{a}^{(j)} \tag{2.4}$$

The m-th order tensors ${}^m G$ are the multipole moments of the source $G^{(j)}$ distributed over the surface of the j-th particle, and Eq. (2.4) is the expansion of this source in point multipoles. The particles neither produce nor absorb heat and therefore for steady-state heat flow the first term (monopole) in expression (2.4) is identically zero. In a nonstationary process this term describes the exchange of heat between the binder and the filler particles and is generally different from zero. However, it can be shown that it is of the order $(a/L)^2$ and should be omitted. The following terms in (2.4) corresponding to the dipole, quadrupole, and higher moments of the source $G^{(j)}$ are generally not zero. Henceforth we shall take account only of the dipole term, neglecting all the others. This corresponds to replacing the real perturbation due to the j-th particle by the perturbation produced by a point thermal dipole at the point $\mathbf{r}^{(j)}$.

Thus we have from (2.2)-(2.4)

$$\begin{gathered}\partial T_0 / \partial t = \lambda_1 \Delta T_0, \quad \partial T^{(j)} / \partial t = \lambda_1 \Delta T^{(j)} - \mathbf{D}^{(j)} \nabla \delta(\mathbf{r} - \mathbf{r}^{(j)}) \\ \mathbf{D}^{(j)} = \lambda_1 \oint_{s_j} \mathbf{n} \nabla T^{(j)} \big|_{\mathbf{r}=\mathbf{R}^{(j)}} \mathbf{a}^{(j)} d\mathbf{a}^{(j)}\end{gathered} \tag{2.5}$$

Summing Eqs. (2.5) and using (2.1) we obtain

$$\frac{\partial T_1}{\partial t} = \lambda_1 \Delta T_1 - \sum_{j=1}^{N-1} \mathbf{D}^{(j)} \nabla \delta(\mathbf{r} - \mathbf{r}^{(j)}) \tag{2.6}$$

This equation determines the temperature in the spaces between the particles in the dipole approximation.

We average Eq.(2.6) with the conditional distribution function $\varphi(B_{N-1} | 0, a)$. Using Eqs. (1.6)-(1.10) and the fact that the vector $\mathbf{D}^{(j)}$ depends strongly on the parameters of the j-th particle so that Eqs. (1.10) are not necessarily true for this vector, we have

$$\begin{gathered}\langle \partial T_1 / \partial t \rangle'_{N-1} = \partial \langle T_1 \rangle / \partial t, \ \langle \Delta T_1 \rangle'_{N-1} = \Delta \langle T_1 \rangle \\ \langle \mathbf{D}^{(j)} \nabla \delta(\mathbf{r} - \mathbf{r}^{(j)}) \rangle'_{N-1} = \frac{1}{V} \iiint \langle \mathbf{D}^{(j)} \rangle''_{N-2} H(|\mathbf{r} - \mathbf{r}^{(j)}| - a^{(j)} - a) \times \\ \times \nabla \delta(\mathbf{r} - \mathbf{r}^{(j)}) \psi(a^{(j)}, \lambda_2^{(j)}) \, da^{(j)} d\lambda_2^{(j)} d\mathbf{r}^{(j)} = \\ = \nabla \left\{ \frac{1}{V} \iint \langle \mathbf{D}^{(j)} \rangle''_{N-2} H(|\mathbf{r} - \mathbf{r}^{(j)}| - a^{(j)} - a) \psi(a^{(j)}, \lambda_2^{(j)}) \, da^{(j)} d\lambda_2^{(j)} \right\}\end{gathered} \tag{2.7}$$

where H(x) is the Heaviside function.

All of the equations involved are essentially linear so that one can expect a linear dependence of $\langle \mathbf{D}^{(j)} \rangle_{N-2}''$ on $\langle T_1 \rangle_{N-2}''$. On the other hand the only distinguishable direction close to the j-th particle is determined by the vector $\nabla \langle T_1 \rangle_{N-2}''$. Therefore it is natural to assume

$$\langle \mathbf{D}^{(j)} \rangle''_{N-2} = A(a^{(j)}, \lambda_2^{(j)}) \nabla \langle T_1 \rangle''_{N-2} = A(a^{(j)}, \lambda_2^{(j)}) \nabla \langle T_1 \rangle \tag{2.8}$$

The last equality in (2.8) follows from (1.10). Thus from (2.6)-(2.8) we obtain an equation for the average heat transfer in the vicinity of the test particle

$$\begin{gathered}\partial \langle T_1 \rangle / \partial t = \nabla \{ \lambda'(\mathbf{r}, a) \nabla \langle T_1 \rangle \} \\ \lambda'(\mathbf{r}, a) = \lambda_1 - n \iint A(a', \lambda_2) H(r - a - a') \psi(a', \lambda_2) \, da' \, d\lambda_2\end{gathered} \tag{2.9}$$

Here $\lambda'(\mathbf{r}, a)$ plays the role of the apparent thermal conductivity of the medium surrounding the test particle and consisting of the binder and the point thermal dipoles dispersed in it and simulating the other filler particles. Thus, the problem of thermal conductivity in a real binder in the spaces between the particles is replaced, in the statistical sense and within the framework of the dipole approximation, by another problem for a certain fictitious homogeneous medium occupying all of space and having a thermal conductivity different from the thermal conductivity of the binder.

The derivation presented for Eq. (2.9) can be regarded as a rigorous theoretical justification of the phenomenological concept of a fictitious medium surrounding each particle of a granular material, an idea which has been used in one form or another in all the papers on the thermal conductivity of concentrated granular materials known to the author (cf. summary in [1, 2]). However, the apparent thermal conductivity of this medium, $\lambda'(\mathbf{r}, a)$, is not equal to the effective thermal conductivity of the material itself, as was assumed without justification in all the papers mentioned above, but depends in general on the distance from the test particle. We note that the concept of a layer of variable thermal conductivity around a test particle follows also from the Kerner [6] phenomenological model proposed to determine the electrical conductivity of granular materials.

Equation (2.9) must be solved together with the equation

$$\partial \langle T_2 \rangle / \partial t = \lambda_2 \Delta \langle T_2 \rangle \tag{2.10}$$

which holds inside the test particle, and the boundary conditions

$$\langle T_1\rangle = \langle T_2\rangle, \ \lambda'(\mathbf{a},\ a)\,\mathbf{n}\,\nabla\langle T_1\rangle = \lambda_2\mathbf{n}\,\nabla\langle T_2\rangle (r=a)$$
$$\nabla\langle T_1\rangle \to \mathbf{E}\ \ (r\to\infty), \qquad \langle T_2\rangle < \infty (r=0) \tag{2.11}$$

where E is the specified temperature gradient at an infinite distance from the test particle, $a\lambda'(a, a) \equiv \lambda_1$.

The solution of problem (2.9)-(2.11) determines $\langle T_2\rangle$ as a function of E and enables one to express the effective thermal conductivity of the material λ in accordance with (1.1)-(1.3). Actually the ensemble averages of T_1 and T_2 describing the temperatures of the binder and filler can be identified with the corresponding volume averages appearing in (1.2) and (1.3). At the same time the quantity $-\lambda'\nabla\langle T_1\rangle$ ($\lambda' = \lim \lambda'(\mathbf{r}, a)$ as $r \to \infty$) describes the average heat flux in the binder, taking account of the effect of the dispersed filler particles; i.e., it must be identified with the volume averaged heat flux in the granular material. Thus we have

$$\langle T_1\rangle = [T_1], \ \langle T_2\rangle = [T_2], \ -\lambda'\nabla\langle T_1\rangle = [\mathbf{Q}] \tag{2.12}$$

The last equation in (2.12) shows why the apparent thermal conductivity λ' differs from both the true thermal conductivity of the binder λ_1 establishing the relation between $[\mathbf{Q}_1]$ and $\nabla[T_1]$ of (1.3), and from the effective thermal conductivity λ of the material, relating [Q] and $\nabla[T]$ in accord with (1.1).

The unknown coefficient $A(a, \lambda_2)$ appears in the basic equation (2.9). Therefore all quantities obtained by solving problem (2.9)-(2.11) will depend on this coefficient as on a parameter. In order to obtain the equation for this parameter and thus to complete the theory we apply the condition of self-consistency. That is, we use the solution of problem (2.9)-(2.11) to calculate the dipole moment **D** of the test particle in accord with (2.7), which we write in a form analogous to (2.8) with a coefficient depending on $A(a, \lambda_2)$. Equating this coefficient to $A(a, \lambda_2)$ we obtain the required equation.

3. For simplicity we consider first a granular material containing particles of the same size and the same thermal conductivity. In this case we have for $\lambda'(\mathbf{r}, a)$ from (2.9)

$$\lambda'(\mathrm{r}, a) = \begin{cases} \lambda' = \lambda_1 - \alpha, & r > 2a \\ \lambda_1 & , \ r \leqslant 2a, \end{cases} \quad \alpha = nA \tag{3.1}$$

Thus the test particle is located in a medium with a thermal conductivity λ', but separated from it by a concentric layer of thickness a and thermal conductivity λ_1. The existence of such a layer was first suggested in [6] from phenomenological considerations and widely used subsequently, but the thickness of the intervening layer remained unknown.

The linear scale of the temperature perturbation introduced by the test particle is of the order of a. Therefore it follows from Eq. (2.9) that

$$\left|\frac{\partial\langle T_1\rangle/\partial t}{\nabla(\lambda\nabla\langle T_1\rangle)}\right| \sim \frac{\omega a^2}{\lambda} \sim \frac{\omega a^2}{\lambda_1} \ll 1$$

Here ω is estimated from (1.5). Thus the time derivative in (2.9) should be omitted.

Two cases are possible: $\lambda_2 \gtrsim \lambda_1$ and $\lambda_2 \ll \lambda_1$. In the first case the time derivative should be omitted in Eq. (2.10) also, so that we actually have a stationary heat-conduction problem around the test particle. It is clear that in this case the effective thermal conductivity of the material does not depend on ω, and Eqs. (1.1) and (1.4) are valid. In the second case the two terms in (2.10) can be of the same order of magnitude and relations of the type (1.1) hold only for the individual Fourier components of the average temperature gradient and the average heat flux, and the coefficients in these relations are different for different components.

We consider the first case. Taking account of (3.1), problem (2.9)-(2.11) takes the form

$$\begin{aligned}
&\Delta\langle T_1\rangle = 0\,(r > 2a); \quad \Delta\langle T_1\rangle_* = 0 \quad (a < r < 2a)\\
&\Delta\langle T_2\rangle = 0 \quad (r < a)\\
&\langle T_1\rangle = \langle T_1\rangle_*, \quad \lambda'\mathbf{n}\nabla\langle T_1\rangle = \lambda_1\mathbf{n}\nabla\langle T_1\rangle_* \quad (r = 2a)\\
&\langle T_1\rangle_* = \langle T_2\rangle, \quad \lambda_1\mathbf{n}\nabla\langle T_1\rangle_* = \lambda_2\mathbf{n}\nabla\langle T_2\rangle \quad (r = a)\\
&\langle T_1\rangle \to \mathbf{Er} \quad (r\to\infty), \quad \langle T_2\rangle < \infty \quad (r = 0)
\end{aligned} \tag{3.2}$$

where E is the given gradient of the temperature $\langle T_1\rangle$ at an infinite distance from the test particle. The solution of problem (1.2) has the form

$$\begin{gathered}\langle T_1\rangle = \{1 - 4\,\Delta^{-1}\,[\beta\,(7\,\varkappa + 17) - 2\,(5\,\varkappa + 7)]\,(a\,/\,h)^3\}\,\mathrm{Er}\\ \langle T_1\rangle_* = 12\,\beta\Delta^{-1}\,[\varkappa + 2 - (\varkappa - 1)\,(a\,/\,r)^3]\,\mathrm{Er}\\ \langle T_2\rangle = 36\,\beta\Delta^{-1}\mathrm{Er},\ \varkappa = \lambda_2\,/\,\lambda_1,\ \beta = \lambda'\,/\,\lambda_1,\\ \Delta = \beta\,(7\,\varkappa + 17) + 5\,\varkappa + 7\end{gathered} \tag{3.3}$$

From (2.3) the heat flux density q at the surface of the test particle is

$$q = -\lambda_1\mathbf{n}\,(\nabla\,\langle T_1\rangle - \mathrm{E})_{r=a} = -\lambda_1\Delta^{-1}\,[\beta\,(29\,\varkappa - 17) - 5\,\varkappa - 7] \tag{3.4}$$

Calculating the dipole moment of the test particle from (2.7), comparing the result with (2.8), and using (3.1), we obtain

$$\alpha = -\rho q,\ \lambda' = \lambda_1 + \rho q \tag{3.5}$$

The second of Eqs. (3.5) with q from (3.4) is the equation for the unknown apparent thermal conductivity λ', or the coefficient $\beta = \lambda'/\lambda_1$, whose solution is

$$\begin{gathered}\beta = [2\,(7\,\varkappa + 17)]^{-1}\,\{(2 + 29\,\rho)\,\varkappa + 10 - 17\,\rho\\ + [((2 + 29\,\rho)\,\varkappa + 10 - 17\,\rho)^2 + 4\,(1 - \rho)\,(5\,\varkappa + 7)\,(7\,\varkappa + 17)]^{1/2}\}\end{gathered} \tag{3.6}$$

From (1.2), (2.12) and (3.3) we have

$$\begin{gathered}[\mathbf{Q}] = -\lambda_1\,(1 - \rho + 36\,\rho\varkappa\beta\Delta^{-1})\,\mathbf{E}\\ \nabla\,[T] = (1 - \rho + 36\,\rho\beta\Delta^{-1})\,\mathbf{E}\end{gathered} \tag{3.7}$$

where Δ and β, and $\varkappa$ are found from (3.3) and (3.6) respectively. The expression for the effective thermal conductivity λ follows from (1.1) and (3.7):

$$\frac{\lambda}{\lambda_1} = \frac{\beta\Delta}{(1-\rho)\,\Delta + 36\rho\beta} = \frac{(7\varkappa + 17)\,\beta + 5\varkappa + 7}{(1-\rho)\,[(7\varkappa + 17)\,\beta + 5\varkappa + 7] + 36\rho\beta}\,\beta \tag{3.8}$$

where β is given by (3.6).

It is also easy to prove that the flux $[\mathbf{Q}]$ from (3.7) is identically equal to $-\lambda'\mathbf{E} = -\lambda_1\beta\mathbf{E}$, as noted at the end of the last section. As an illustration Fig. 1 shows λ/λ_1 as a function of $\varkappa = \lambda_2/\lambda_1$ for various values of ρ (solid curves). From (3.8) it is easy to obtain approximate expressions for λ/λ_1 which are valid for small ρ and small and large $\varkappa$.

We note that the intervening layer separating the test particle from the fictitious medium with thermal conductivity λ' results from the fact that the filler particles cannot overlap. Taking account of this fact is naturally not very important when the concentration of filler is rather small. In this case, instead of (3.2), the problem becomes the simpler one of a test particle immersed in a homogeneous medium with thermal conductivity λ'. The corresponding expressions for λ/λ_1 and $\beta = \lambda'/\lambda_1$ are

$$\begin{gathered}\lambda\,/\,\lambda_1 = \beta\,(\varkappa + 2\,\beta)\,[(1 - \rho)\,(\varkappa + 2\,\beta) + 3\,\rho\beta]^{-1}\\ \beta = {}^1\!/_4\,\{2\,(1 - \rho) - \varkappa\,(1 - 3\,\rho) + [(2\,(1 - \rho) - \varkappa\,(1 - 3\,\rho))^2 + 8\,\varkappa\,(1 - \rho)]^{1/2}\}\end{gathered} \tag{3.9}$$

For $\rho > 1/3$ both these quantities become infinite as $\varkappa \to \infty$. This strange result is of course due to the fact that the overlapping of particles is permitted within the framework of the model leading to (3.9). The open curves in Fig. 1 are for λ/λ_1 from Eq. (3.9). It is clear that if ρ is not very large and $|\varkappa|$ is not too different from unity the results from the simplified model under discussion are close to those from the exact formula (3.8).

If the particles in the granular material have the same size a but different thermal conductivities, i.e., $\psi(a', \lambda_2) = \psi(\lambda_2)\,\delta(a' - a)$, it is easy to generalize (3.6) and (3.8) by using the above method. We obtain the following equation for β and the expression for λ/λ_1:

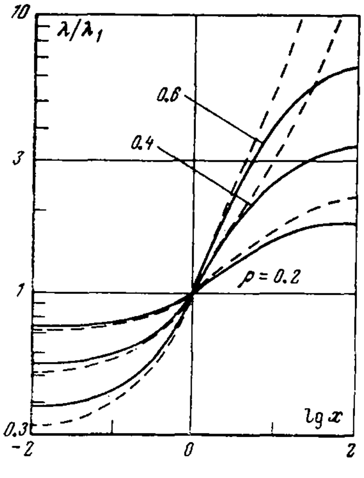

Fig. 1

$$\beta = 1 + \int \rho(\lambda_2) \frac{(7\varkappa - 17)\beta - 5\varkappa - 7}{(7\varkappa + 17)\beta + 5\varkappa + 7} d\lambda_2$$

$$\frac{\lambda}{\lambda_1} = \beta \left[1 - \rho + 36\beta \int \frac{\rho(\lambda_2)\, d\lambda_2}{(7\varkappa + 17)\beta + 5\varkappa + 7}\right]^{-1} \qquad (3.10)$$

$$(\rho(\lambda_2) = v(a)\, n\psi(\lambda_2))$$

The quantity λ/λ_1 from (3.8) and (3.10) has the important property of being independent of the radius of the filler particles as a consequence of the fact that (3.3) is a self-similar solution of problem (3.2). Therefore if the granular material contains particles of various sizes Eqs. (3.8) and (3.10) hold as before in the first approximation. To find the exact relation for λ/λ_1 in this case it is of course necessary to solve problem (2.9)-(2.11) with the apparent thermal conductivity $\lambda'(\mathbf{r}, a)$ as a function of $\mathbf{r}$. We note that the approximate formula (3.9) for λ/λ_1 corresponding to the model of nonoverlapping spheres in principle does not depend either on the average size of the filler particles or on their size distribution.

We now consider the second case when $\lambda_2 \ll \lambda_1$. In this case Eq. (1.1) does not hold in general. A relation of this type is satisfied only by the Fourier transforms of the average thermal flux and the average temperature gradient. For simplicity we limit our discussion to a material with grains of the same size and the same thermal conductivity. Using (3.1) we obtain from (2.9)-(2.11) the following problem for the Fourier transforms τ_1 and τ_2 of $\langle T_1 \rangle$ and $\langle T_2 \rangle$:

$$\begin{aligned} &\Delta\tau_1 = 0 \quad (r > 2a), \quad \Delta\tau_{1*} = 0 \quad (a < r < 2a), \quad i\omega\tau_2 = \lambda_2 \Delta\tau_2 \quad (r < a) \\ &\tau_1 = \tau_{1*}, \quad \lambda' \mathbf{n}\nabla\tau_1 = \lambda_1 \mathbf{n}\nabla\tau_{1*} \quad (r = 2a) \\ &\tau_{1*} = \tau_2, \quad \lambda_1 \mathbf{n}\nabla\tau_{1*} = \lambda_2 \mathbf{n}\nabla\tau_2 \quad (r = a) \\ &\nabla\tau_1 \to \varepsilon \quad (r \to \infty), \quad \tau_2 < \infty \quad (r = 0) \end{aligned} \qquad (3.11)$$

where ε is the Fourier transform of E.

The solution of (3.11) is

$$\begin{aligned} &\tau_1 = [1 + B_1 (a/r)^3]\, \varepsilon\mathbf{r}, \quad \tau_{1*} = [C_* + B_* (a/r)^3]\, \varepsilon\mathbf{r} \\ &\tau_2 = C_2' r^{-1/2} J_{3/2} (\sqrt{-i}\, c\xi)\, \varepsilon\mathbf{r} = C_2 R(c\xi)\, \varepsilon\mathbf{r} \\ &R(x) = \frac{3}{-ix^2}\left(\frac{\sin\sqrt{-i}\, x}{\sqrt{-i}\, x} - \cos\sqrt{-i}\, x\right), \quad c = \left(\frac{\omega a^2}{\lambda_2}\right)^{1/2}, \ \xi = \frac{r}{a} \end{aligned} \qquad (3.12)$$

Here we have introduced the notation

$$\begin{aligned} &B_1 = 4\Delta^{-1} [-\beta (7\varkappa R_2 + 17 R_1) + 2(5\varkappa R_2 + 7 R_1)] \\ &B_* = -12\beta\Delta^{-1} (\varkappa R_2 - R_1) \\ &C_* = 12\beta\Delta^{-1} (\varkappa R_2 + 2R_1), \qquad C_2 = 36\beta\Delta^{-1} \\ &R_1 = R(c), \quad R_2 = (\xi d/d\xi + 1) R(c\xi)|_{\xi=1} \end{aligned} \qquad (3.13)$$

where the parameters κ, β, and Δ are found from (3.3). The solution of the steady-state problem (3.3) is obtained from (3.12) and (3.13) by letting $c \to 0$.

The equation for β obtained by the above method agrees with the similar equation of the steady-state problem so that β as before is expressed by using (3.6). In the case under discussion $\lambda_2 \ll \lambda_1$ so that $\varkappa \approx 0$. Then it follows from (3.6) that

$$\beta \approx 1 - \rho \qquad (3.14)$$

By using the above method to determine the Fourier transforms of the average heat flux and the average temperature gradient in the material corresponding to the solution (4.12) we obtain for the effective thermal conductivity of the material $\lambda(\omega)$

$$\frac{\lambda(\omega)}{\lambda_1} = \frac{24 - 17\rho}{24 + (36\sigma - 17)\rho}, \quad z = \sqrt{-i}\, c = \left(-\frac{i\omega a^2}{\lambda_2}\right)^{1/2} \qquad (3.15)$$

$$\sigma = \frac{1}{v(a) R_1} \int\limits_{r<a} R(c\xi)\, d\mathbf{r} = 3\frac{\operatorname{Si} z - \sin z}{\sin z - \cos z}, \quad \operatorname{Si} z = \int\limits_0^z \frac{\sin\zeta}{\zeta} d\zeta$$

Here the contour of integration C encloses the points 0 and z in the complex z plane. Equation (3.14) was used in deriving (3.15).

The relation between [Q] and $\nabla[T]$ which replaces Eq. (1.1) in the present case is

$$[\mathbf{Q}] = -\int e^{i\omega t}\lambda(\omega)\nabla\tau\, d\omega, \quad \nabla\tau = \int e^{-i\omega t}\nabla[T]\, dt \tag{3.16}$$

The equation of macroscopic transfer in a granular material becomes (see (1.4)]

$$\frac{\partial[T]}{\partial t} = \nabla\int\int e^{i\omega(t-t')}\lambda(\omega)\nabla[T]_{t=t'}\, d\omega\, dt' \tag{3.17}$$

where $\lambda(\omega)$ is given by (3.15).

Thus when the thermal conductivity of the filler is much smaller than that of the binder there is an appreciable frequency dispersion of the effective thermal conductivity of the granular material. This has a pronounced effect on nonstationary heat transfer in such granular materials and must be taken into account, for example, in analyzing the results of dynamic experiments with composite materials, granular, dense, and pseudo fluidized beds, etc. (see, for example, [7, 8]).

In conclusion we note some possible ways of generalizing the proposed theory. First it seems appropriate to investigate in more detail the degree of applicability of the dipole approximation used above. As follows from the discussion in [1] the next (quadrupole) term in expansion (2.4) can become important for $\varkappa \gg 1$ or $\varkappa \ll 1$. We note that the contribution of point thermal quadrupoles in the expression for λ/λ_1 depends strongly on the radius of the particles. However, since the experimental values of the effective thermal conductivity of granular materials vary slowly with grain size it can be concluded that the quadrupole moments have a relatively insignificant effect on heat transfer in a granular material.

The general method described above can be applied to the investigation of granular materials of a more complex structure containing nonspherical filler particles with various distribution functions for the parameters characterizing the orientation of the particles. In particular if this function is anisotropic the effective thermal conductivity of the granular material becomes a tensor instead of a scalar.

Finally in a number of practical problems it is important to take account of the contact thermal resistance between contiguous filler grains, the radiation component of the heat transfer, and a possible temperature jump at grain surfaces in beds filled with low-pressure gas. None of these phenomena were taken into account above.

We note also that the formulas obtained for λ/λ_1 can be used directly to calculate the effective diffusion coefficient of a substance in a granular material and also to calculate effective steady-state values of the electrical conductivity and the dielectric constant or magnetic permeability of granular conductors and dielectrics because these quantities are completely analogous to λ in (1.1)-(1.3), and the corresponding mathematical problems for the concentration of matter and the electric or magnetic potentials have exactly the same form as in problem (2.9)-(2.11) for the temperature.

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