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# Heat and mass transfer in disperse media—II. Constitutive equations

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**Abstract**—The problem of expressing all the quantities, which are involved in the averaged field equations governing heat and mass transport in a disperse medium, in terms of the unknown variables of these equations and of physical parameters is investigated. Its constructive solution is obtained by means of formulating an accessory problem determining perturbations induced by a single particle in the mean temperature and concentration fields of an admixture. This is done on the basis of essentially the same reasoning as that applied when deriving the averaged equations themselves. By way of example, solutions of the latter problem under steady transfer conditions are considered thus permitting the effective thermal conductivity and the admixture diffusivity to be calculated as functions of physical parameters.

## 1. INTRODUCTION

It is well known that there have been an enormous number of attempts to find thermal and electric conductivities, diffusivity, electric and magnetic permeabilities and other effective transport properties of a disperse mixture consisting of discrete particles immersed in an ambient continuous medium. Such attempts date back to the classical Maxwell model and are being undertaken up until now; a review of the early work on the subject can be found, for example, in refs. [1, 2]. However refined and ingenious some of the physical models underlying those endeavours may be or appear to be, they usually employ a wide variety of partial concepts which should be proved independently. These will not be discussed below.

An alternative approach may consist in looking upon the determination of the effective transfer properties of a disperse system under stationary conditions as a part of a much more general problem of closing the averaged conservation equations describing unsteady heat or mass transfer in phases of the system, the exchange between the phases being taken into account along with the transient flux of heat or mass of an admixture. It is just the latter problem which makes up the main topic of what follows. While solving it, use is made of the same methods of averaging over configurational ensembles of the dispersed particles as those employed in the first part of the paper [3]. To make the matter simpler, the discussion is restricted to motionless macroscopically uniform and isotropic disperse mixtures containing equal spherical particles with no internal heat release or consumption. Then the averaging over the unconditional ensemble results in the following field equations associated with transfer in the phases of a mixture (the nomenclature of ref. [3] is retained):

$$c_0\epsilon\partial\tau_0/\partial t = -\nabla\mathbf{q}+\sigma, \quad c_1\rho\partial\tau_1/\partial t = -\sigma \tag{1}$$

where

$$q(t,\mathbf{r}) = -\lambda_0\nabla\tau-(\lambda_1-\lambda_0)\int_{|\mathbf{r}-\mathbf{r}'|\leqslant a} n(\mathbf{r}')\nabla_{\mathbf{r}}\tau_{\mathbf{r}'}\,d\mathbf{r}',$$

$$\sigma(t,\mathbf{r}) = \int_{|\mathbf{r}-\mathbf{r}'|\leqslant a} n(\mathbf{r}')\nabla_{\mathbf{r}}\mathbf{q}_{\mathbf{r}'}\,d\mathbf{r}', \quad \tau = \epsilon\tau_0+\rho\tau_1,$$

$$\sigma_{\mathbf{r}'} = \sigma(t,\mathbf{r}|\mathbf{r}'), \quad \mathbf{q}_{\mathbf{r}'} = \mathbf{q}(t,\mathbf{r}|\mathbf{r}'). \tag{2}$$

Here $\mathbf{q}$ and $\sigma$ denote the mean transient heat flux and the mean heat exchange between the phases per unit volume of the mixture, respectively, and $\tau$ is the mean temperature of the mixture as a whole. The variables carrying the subscript $\mathbf{r}'$ are obtained by averaging over the configurational ensemble conditioned by the presence at the point $\mathbf{r}'$ of the centre of a sphere. Thus, the closing of the averaged heat transfer equation (1) is reduced, in accordance with equation (2), to the determination of the mean temperature and heat flux inside a chosen test particle. There exist several reliable approaches to the calculation of these quantities. Either by means of considering interparticle thermal interactions with subsequent averaging over possible positions of all the spheres except the test one, or on the basis of more or less plausible assumptions about the influence of all the other particles upon the temperature field within each of them. Before going into details of the general method of closure adopted here, it is reasonable to review briefly the key ideas exploited previously when attacking the problem.

## 2. HIERARCHY OF HEAT TRANSFER EQUATIONS AND CLUSTER EXPANSIONS

Let us consider the temperature field inside the test sphere with its centre at the point $\mathbf{r}'$ surrounded by other spheres placed arbitrarily in the ambient matrix.

## NOMENCLATURE

| | |
|---|---|
| $a$ | radius of spheres |
| $B$ | interphase heat exchange divided by $\rho$ |
| $b$ | shell radius |
| $c$ | heat capacity per unit volume |
| $\mathbf{D}$, $\mathbf{d}$ | dipole moments |
| $\mathbf{F}$ | correction to mean heat flux |
| $l$ | mean distance between centres of neighbouring particles |
| $N$ | total number of particles |
| $n$ | number concentration of particles |
| $\mathbf{q}$ | heat flux |
| $T$ | fine-grained temperature field |
| $U^{(j)}$ | heat source associated with the $j$th particle |
| $\mathbf{x}$ | distance from test sphere centre |
| $z$ | $x/a$. |

Greek symbols

| | |
|---|---|
| $\beta$ | effective heat conductivity related to that of matrix, $\lambda/\lambda_0$ |
| $\kappa$ | $\lambda_1/\lambda_0$ |
| $\lambda$ | heat conductivity |
| $\mu$, $\nu$ | self-consistency coefficients |
| $\rho$ | concentration of particles by volume |
| $\sigma$ | interphase heat exchange |
| $\tau$ | temperature |
| $\phi$ | probability distribution function |
| $\psi$ | relative volume concentration of dispersed phase near test sphere |
| $\omega$ | frequency. |

Subscripts

| | |
|---|---|
| 0 | ambient matrix |
| 1 | dispersed phase |
| $\mathbf{r}'$ | quantities conditioned by presence of test sphere centre at $\mathbf{r}'$. |

Superscripts

| | |
|---|---|
| * | perturbation to mean field |
| ^ | temperature field inside test sphere |
| ¯ | Fourier transformations. |

If the exact configuration of the system of these other spheres is known, then one has to study a boundary problem for conventional one-phase equations of heat conduction with appropriate boundary conditions at the surfaces of the spheres. The surfaces being presumed to be thermally inactive, these conditions require continuity of the temperature and of the normal component of heat flux.

The temperature distribution inside the test sphere, corresponding to a given arrangement of other spheres, stems from the solution of the boundary problem complying with this arrangement. To obtain the mean temperature field in a single sphere of a randomly packed disperse mixture one has to average such a distribution over the conditional ensemble of surrounding spheres. This is to be done with the help of the probability density function $\phi(C_{N-1}|\mathbf{r}')$ introduced in ref. [3]. Unfortunately, the precise solution of the boundary problem involving many particles is at present impossible so one can only hope to get an approximate solution when the mixture is sufficiently dilute (the ratio $a/l$ is small compared with unity, $a$ and $l$ being the sphere radius and the mean distance between the centres of neighbouring spheres). Thus, results obtained by direct solution of the multiparticle boundary problem mentioned can be only accurate, at most, for mixtures of small volume concentration of the dispersed phase.

In the alternative approach, the solution of the boundary problem does not precede averaging the temperature field inside the test sphere, but contrariwise, the averaging of local conduction equations is first. This gives rise to a new problem of deriving effective averaged equations which would govern heat transfer in the vicinity of the test sphere. The derivation can be done in a similar way to the field equations (1) if one uses the conditional distribution function $\phi(C_{N-1}|\mathbf{r}')$ rather than the unconditional one, $\phi(C_N)$. The result is

$$\epsilon_{\mathbf{r}'}c_0(\partial/\partial t)\tau_{0,\mathbf{r}'} = -\nabla_{\mathbf{r}}\mathbf{q}_{\mathbf{r}'}+\sigma_{\mathbf{r}'},$$
$$\rho_{\mathbf{r}'}c_1(\partial/\partial t)\tau_{1,\mathbf{r}'} = -\sigma_{\mathbf{r}'} \qquad (3)$$

where

$$\mathbf{q}_{\mathbf{r}'} = -\lambda_0\nabla_{\mathbf{r}}\tau_{\mathbf{r}'}$$
$$-(\lambda_1-\lambda_0)\int_{|\mathbf{r}-\mathbf{r}'|\leqslant a,\,|\mathbf{r}'-\mathbf{r}''|>2a} n(\mathbf{r}''|\mathbf{r}')\nabla_{\mathbf{r}}\tau_{\mathbf{r}',\mathbf{r}''}\,\mathrm{d}\mathbf{r}''$$
$$\sigma_{\mathbf{r}'} = \int_{|\mathbf{r}-\mathbf{r}'|\leqslant a,\,|\mathbf{r}'-\mathbf{r}''|>2a} n(\mathbf{r}''|\mathbf{r}')\nabla_{\mathbf{r}}\mathbf{q}_{\mathbf{r}',\mathbf{r}''}\,\mathrm{d}\mathbf{r}''. \qquad (4)$$

The integrands contain ensemble averages conditioned by the presence of two sphere centres at prescribed positions compatible with the requirement of non-overlapping of the spheres. The integration itself allows averaging of these quantities over the pair distribution function $\phi(\mathbf{r}'', \mathbf{r}) = N^{-1}n(\mathbf{r}''|\mathbf{r}')$. Similarly, integration in equation (2) means, in fact, averaging over the distribution function $\phi(\mathbf{r}') = N^{-1}n(\mathbf{r}')$ for one sphere. Definition of all the distribution functions is considered in detail in ref. [3].

By repeating this procedure it is possible to arrive at the whole hierarchy of equations for conditional averages corresponding to the fixation of the positions of various numbers of the spheres. In a general case equations the unknown variables of which are conditional averages with $M$ fixed spheres include integral terms the integrands of which include averages of the next level when $M+1$ spheres occupy given positions. The equations in sets (1) and (2), and in (3) and (4) symbolize the first and the second levels, respectively.

Usually, when an infinite series of equations appears, one needs to enforce either closing or truncation of the series at a certain level and, after that, to solve the equations in succession starting with those of the highest level. Classical examples of such a situation can be found in the statistical physics of liquids and dense gases as well as in the field of the statistical theory of turbulence.

On the first level the problem is calculating the temperature inside and outside a single sphere, the presence of all the other spheres being totally left out. This fits very dilute mixtures the particles of which do not interact so that the test sphere can be regarded as immersed in a pure matrix. The desired temperature fields can then be found from a standard boundary problem with proper conditions of continuity at the test sphere surface; at infinity the temperature must coincide asymptotically with its unconditional representation near the point occupied by the centre of the test sphere. The solution enables one to determine the integrands on the right-hand sides of the relations in set (2) and, thus, to close the averaged equations of heat conservation (1). As a supplementary result, one gets an expression for the effective bulk thermal conductivity of the mixture. The well-known Maxwellian formula embodies just this reasoning.

On the second level the truncation is carried out with respect to equations for the mean phase temperatures under the condition that two spheres are fixed. This amounts to allowance for binary interactions of pairs of spheres, ternary, quadruple and other interactions being neglected. The problem is now to find the temperature in a system composed of the matrix with two immersed spheres. The boundary condition at infinity remains unchanged and the continuity conditions are imposed now at two spherical surfaces. The resulting expressions for $\tau_{\mathbf{r}',\mathbf{r}''}$ and $\mathbf{q}_{\mathbf{r}',\mathbf{r}''}$ are to be used in equations (4) and this correctly defines the boundary problem for the test particle, heat conduction in its vicinity being governed by the first equation in set (3). This equation can be formally thought of as being associated with a certain fictitious medium, the properties of which reflect those of both matrix and particles simultaneously and, moreover, depend upon the distance from the test sphere centre. Solving the boundary problem for the test sphere surrounded by the fictitious ambient medium leads, as before, to certain expressions for $\tau_{\mathbf{r}'}$ and $\mathbf{q}_{\mathbf{r}'}$ to be used in equation (2) and then in equation (1). Again this ensures the closure of the averaged heat transfer equations.

As far as the present author is aware, so far nobody has considered the problem on the third or higher levels. Nevertheless, a rather systematic formal approach to the closure problem on any level of the hierarchy is by no means impossible, as it has been convincingly demonstrated by Jeffrey [4]. His procedure consists of independent introduction of main contributions to a given physical quantity (e.g. the bulk heat flux) stemming from thermal interaction within groups containing one, two and more particles. It resembles in essential features the group expansion method of the statistical mechanics. Some other methods involving the ordering of multiparticle interactions have been proposed, mostly while dealing with hydrodynamic problems related to the rheology of suspensions of free particles and to filtration flows in beds of motionless particles. The present author feels that the original paper by Howells [5] should be mentioned in this connection. It seems that all the methods of accounting for joint interactions within limited groups of particles which have been put forward until recently are to be looked upon as versions of the cluster expansions encountered in statistical physics. This has been emphasized and discussed earlier [6].

An actual realization of any cluster procedure for disperse media has never been explained beyond the second hierarchical level. Even so rather serious difficulties arise when evaluating the integrals in equation (4). They are due mostly to long-range effects of either thermal or hydrodynamic interaction of pairs of particles resulting in the integrals being not absolutely convergent. Schemes devised to overcome these difficulties sometimes lead to contradictory final results. This means that some correct renormalization procedure has to be brought into practice in order to bypass the problem of non-absolute convergency. An elegant procedure of the kind has been suggested in connection with the problem of the sedimentation of suspensions [7] and extended further to a number of other problems, including that of determining the effective thermal conductivity [8]. An important exception is presented only by the problem of the hydraulic resistance and permeability of granular beds where the long-range effects vanish [9].

It should be stressed here that different attempts to employ the cluster expansion method would result at best in determining polynomial expressions for effective mixture properties in degrees of the particle concentration by volume. Really, interactions on the $M$th level pertaining to be the cooperative influence of $M$ particles give rise to terms of the order of $\rho^M$ in such expressions. It is clear, therefore, that conceivable results of such attempts, however rigorous and reliable, are bound to be confined to dilute mixtures. That is, a pragmatic importance of such an approach is limited and one should look in another direction to receive conclusions valid in a more broad range of the particle volume concentration.

## 3. SELF-CONSISTENT APPROXIMATION AND MULTIPOLE EXPANSIONS

Another general method devised to treat mixtures of moderate or high concentration and, in particular, to calculate $\tau_{\mathbf{r}'}$ and $\mathbf{q}_{\mathbf{r}'}$ appearing in the integrands in equation (2) is founded on ideas common to the theory of self-consistent fields [10]. The basic underlying assumption is that a typical particle can be regarded as being embedded in a fictitious homogeneous medium whose properties are representatives of those of the whole mixture. Such a scheme is essentially empirical. In addition to the simplest possible model when the fictitious medium is thought of as being identical to the mixture in the sense that it is fully characterized by the bulk properties of the latter, there exist versions of the self-consistent scheme when the test particle is separated from the medium by a concentric layer filled with the pure matrix material, the layer thickness being unknown [10].

According to this method, the conditional averages appearing in the integrands in equation (2) are to be found straightforwardly by solving a boundary problem for the test particle immersed into the fictitious medium with a given temperature distribution at infinity. The problem for the spherical particle at a point $\mathbf{r}'$ is formulated under steady conditions in the following manner:

$$\begin{gathered}
\Delta\tau^{(1)} = 0, \quad x > b; \quad \Delta\tau^{(2)} = 0, \quad a < x < b; \\
\Delta\tau^* = 0, \quad x < a; \quad \lim \tau^{(1)} = \tau(\mathbf{r}') + \mathbf{E}(\mathbf{r}')\mathbf{x}, \\
x \to \infty, \quad \mathbf{E}(\mathbf{r}') = \nabla\tau|_{x=0}; \quad \tau^{(2)} = \tau^*, \\
\lambda_0 \mathbf{n}\nabla\tau^{(2)} = \lambda_1 \mathbf{n}\nabla\tau^*, \quad x = a; \quad \tau^{(1)} = \tau^{(2)}, \\
\lambda \mathbf{n}\nabla\tau^{(1)} = \lambda_0 \mathbf{n}\nabla\tau^{(2)}, \quad x = b; \quad \tau^* \neq \infty, \\
x = 0; \quad \mathbf{x} = \mathbf{r} - \mathbf{r}'. \qquad (5)
\end{gathered}$$

Here the mean temperature field of the mixture, $\tau(\mathbf{r})$, near the point $\mathbf{r}'$ is regarded as an outer asymptotic expansion of $\tau^{(1)}(\mathbf{r})$. The external radius $b$ of the concentric spherical layer seems to be principally indeterminable within the frames of the self-consistent theory; usually it is taken equal to $a\rho^{-1/3}$. Note some affinity of these schemes with the known cell model which utilizes the concept of an individual shell surrounding each particle as well.

A certain substantiation of the self-consistent approach may be advocated with the aid of a multipole expansion procedure [11]. By virtue of linearity of the heat conduction equation the fine-grained temperature field, $T_0(t, \mathbf{r}|C_N)$, in the matrix region can be presented as a sum of a matrix temperature $T^0(t, \mathbf{r})$ as it would be if the particles were absent and of quantities $T^{(j)}(t, \mathbf{r}, \mathbf{r}^{(j)})$, $j = 1, \ldots, N$ where each $T^{(j)}$ is a temperature perturbation induced by the $j$th particle. Then, if one considers the situation near the test sphere,

$$T_0(t, \mathbf{r}|C_{N-1}) = T^0(t, \mathbf{r}) + \sum_{j=1}^{N-1} T^{(j)}(t, \mathbf{r}, \mathbf{r}^{(j)}). \qquad (6)$$

The fields $T^0(t, \mathbf{r})$ and $T^{(j)}(t, \mathbf{r}, \mathbf{r}^{(j)})$ satisfy within the matrix the equations

$$\begin{gathered}
c_0 \partial T^0/\partial t = -\lambda_0 \Delta T^0, \\
c_0 \partial T^{(j)}/\partial t = -\lambda_0 \Delta T^{(j)} + U^{(j)}, \qquad (7)
\end{gathered}$$

where by definition

$$U^{(j)}(t, \mathbf{r}^{(j)}) = \lambda_0 \int \mathbf{n}\nabla T^{(j)}(t, \mathbf{r}, \mathbf{r}^{(j)})\delta(\mathbf{r} - \mathbf{r}^{(j)} - \mathbf{a})\,\mathrm{d}\mathbf{a}, \qquad (8)$$

$\mathbf{a}$ being a vector connecting the sphere centre with a point on its surface and $\mathbf{n}$ denoting the unit normal vector. It is evident that $U^{(j)}$ describes a heat source imitating the thermal influence of the $j$th sphere. By expanding the vector delta-function in the integrand one arrives at a multipole expansion

$$\begin{aligned}
U^{(j)}(t, \mathbf{r}^{(j)}) &= \lambda_0 \int \mathbf{n}\nabla T^{(j)}(t, \mathbf{r}^{(j)} + \mathbf{a}, \mathbf{r}^{(j)}) \\
&\qquad \times \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \delta(\mathbf{r} - \mathbf{r}^{(j)})\,\mathrm{d}\mathbf{a} \\
&= \sum_{m=0}^{\infty} U^{(j)}_{m,ik\ldots p} \frac{\partial}{\partial r_i} \frac{\partial}{\partial r_k} \cdots \frac{\partial}{\partial r_p} \delta(\mathbf{r} - \mathbf{r}^{(j)}), \\
U^{(j)}_{m,ik\ldots p}(t, \mathbf{r}^{(j)}) & \\
&= \frac{(-1)^m}{m!} \lambda_0 \int \mathbf{n}\nabla T^{(j)}(t, \mathbf{r}^{(j)} + \mathbf{a}, \mathbf{r}^{(j)}) a_i a_k \ldots a_p\,\mathrm{d}\mathbf{a}. \qquad (9)
\end{aligned}$$

The tensor quantity represents multipole moments of the thermal source $U^{(j)}(t, \mathbf{r}^{(j)})$ distributed over the $j$th spherical surface. If the particles do not produce or absorb heat by themselves, then the zeroth monopole term vanishes. But it is not so under unsteady conditions of the interphase heat exchange. The following terms in equation (9) correspond to dipole, quadrupole, etc., moments of the $j$th thermal source, all the multipoles being located at the points occupied by the centres of the spheres.

The simplest possible way to treat the problem under stationary conditions is to substitute all $U^{(j)}$ by the corresponding dipole terms neglecting all the other multipoles in sum (9). Then, by collecting together equations (6)–(9), one gets

$$\begin{gathered}
\lambda_0 \Delta T_0 - \sum_{j=1}^{N} \mathbf{D}^{(j)} \nabla\delta(\mathbf{r} - \mathbf{r}^{(j)}) = 0, \\
\mathbf{D}^{(j)}(\mathbf{r}^{(j)}) = \lambda_0 \int \mathbf{n}\nabla T^{(j)}(\mathbf{r}^{(j)}) + \mathbf{a}, \mathbf{r}^{(j)}\mathbf{a}\,\mathrm{d}\mathbf{a}. \qquad (10)
\end{gathered}$$

By means of averaging equations (10) over possible configurations of all the spheres except the test one positioned at the point $\mathbf{r}'$ one obtains further

$$\begin{gathered}
\lambda_0 \Delta\tau_{0,\mathbf{r}'} - \nabla\mathbf{d}_{\mathbf{r}'} = 0, \\
\mathbf{d}_{\mathbf{r}'} = \mathbf{d}(\mathbf{r}/\mathbf{r}') = N \int \langle\mathbf{D}\rangle_{\mathbf{r}'} \phi(\mathbf{r}, \mathbf{r}')\delta(\mathbf{r} - \mathbf{r}'')\,\mathrm{d}\mathbf{r}'' \\
= \langle\mathbf{D}\rangle_{\mathbf{r}'} n_{\mathbf{r}'}, \quad n_{\mathbf{r}'} = n(\mathbf{r}|\mathbf{r}'), \\
\langle\mathbf{D}\rangle_{\mathbf{r}'} = \lambda_0 \int \mathbf{n}\nabla\tau_{\mathbf{r}'}(\mathbf{r}^{(j)} + \mathbf{a}, \mathbf{r}^{(j)})\mathbf{a}\,\mathrm{d}\mathbf{a}. \qquad (11)
\end{gathered}$$

Here the fact that the point dipoles are substituted for the real particles of finite volume is explicitly taken into account.

Bearing in mind the concept of tensor dimensionality as well as the linearity of the heat conduction equations, it is easy to conclude that $\langle \mathbf{D} \rangle_{\mathbf{r}'}$ in a macroscopically isotropic system must be proportional to a unique vector quantity—the gradient of the mean field $\tau_{0,\mathbf{r}'}$, that is, $\langle \mathbf{D} \rangle_{\mathbf{r}'} = A\nabla\tau_{0,\mathbf{r}'}$ so that it is possible to transform the equation in equations (11) to a more familiar form. Adding the heat conduction equation inside the test particle one arrives at a boundary problem

$$\begin{gathered}
\nabla(\lambda_0 - An_{\mathbf{r}'})\nabla\tau_{0,\mathbf{r}'} = 0, \quad x > a; \\
\Delta\tau^* = 0, \quad x < a; \\
\lim \tau_{0,\mathbf{r}'} = \tau_0(\mathbf{r}') + \mathbf{E}_0(\mathbf{r}')x, \quad x \to \infty, \\
\mathbf{E}_0(\mathbf{r}') = \nabla\tau_0|_{x=0}; \\
\tau_{0,\mathbf{r}'} = \tau^*, \quad (\lambda_0 - An_{\mathbf{r}'})\mathbf{n}\nabla\tau_{0,\mathbf{r}'} = \lambda_1\mathbf{n}\nabla\tau^*, \\
x = a; \quad \tau^* \neq \infty, \quad x = 0; \quad \mathbf{x} = \mathbf{r} - \mathbf{r}'. \qquad (12)
\end{gathered}$$

This problem resembles that represented by equations (5) except that $\tau_{0,\mathbf{r}'}$ plays here a role of $\tau^{(1)} = \tau_{\mathbf{r}'}$. For macroscopically homogeneous mixtures $n_{\mathbf{r}'} = n(x)$. If $n(x) = 0$ when $a < x < 2a$ and $n(x) = n = \text{const.}$ when $x > 2a$, which is quite natural to assume when neglecting fine details of multiparticle interactions, then one infers that $\lambda_0 - An_{\mathbf{r}'} = \lambda_0 - An = \lambda^0$ outside the sphere $x = 2a$ and $\lambda_0 - An_{\mathbf{r}'} = \lambda_0$ in the concentric layer $a < x < 2a$. Thus, the value of $b$ appearing in equations (5) becomes definite. The interconnection between $\mathbf{E}_0$ and $\mathbf{E}$ as well as between $\lambda^0$ and $\lambda$ remains unknown, however. Therefore, some supplementary hypothesis about averages associated with the mixture as a whole and only with its matrix is still needed. Two examples of such a hypothesis linking those averages, both hardly being successful, can be pointed out [11, 12]. For instance, the authors of ref. [12] have drawn a conclusion that the well-known Maxwellian formula for the effective conductivity is valid not only for very dilute systems but also for disperse mixtures of any concentration. Although they have succeeded in mending this mistake later on, they have made other errors of principal nature stemming from an inadequate understanding of the origin and the essence of the phenomenon of non-absolutely convergent integrals mentioned above [13].

A reasonable way of dealing with this obstacle is to put $\mathbf{E}_0 = \mathbf{E}$ (and hence $\lambda^0 = \lambda$) and so turn from equations (12) to problem (5), the thickness of the concentric layer being now specified. Then, as before, the solution of the problem yields the field $\tau^*(\mathbf{x}) = \tau_{\mathbf{r}'}$ and the heat flux $\mathbf{q}_{\mathbf{r}'}$ inside the test particle which are to be used in the definition of $\langle \mathbf{D} \rangle_{\mathbf{r}'}$ in equations (11). From this and from the relation $\langle \mathbf{D} \rangle_{\mathbf{r}'} = A\nabla\tau_{0,\mathbf{r}'}$ a transcendent algebraic equation for $A$ follows again, and this gives an opportunity to derive $\lambda = \lambda^0$ as a function of physical parameters. Thus, one arrives in a quite natural manner at the condition of self-consistency.

A general inference resulting from the analysis above is that both the self-consistent scheme and the multipole expansion method require a rigorous substantiation by means of some independent consideration or need to be confirmed by direct comparison with either experiments or results obtained with the help of other methods. It is expedient to point out in this connection that the multipole expansion method in its latter formulation is able to provide for results of high reliability. For example, components of the tensor of effective thermal conductivity in a mixture of aligned spheroidal particles calculated with this method in ref. [14] happen to differ negligibly from their values derived in a more rigorous fashion [15].

## 4. THE TEST PARTICLE PROBLEM

Let the centre of the test sphere of a macroscopically uniform and isotropic system to be placed, as before, at the point $\mathbf{r}'$. It is evident that $\epsilon = 1 - \rho$ and $\rho$ are constant whereas the conditional concentrations of the continuous and the dispersed phases may be expressed as functions of $x = |\mathbf{r} - \mathbf{r}'|$, that is $\epsilon_{\mathbf{r}'} = 1 - \rho_{\mathbf{r}'} = \epsilon(x)$ and $\rho_{\mathbf{r}'} = \rho(x)$. The problem is to represent the integrals over the test sphere volume involved in equations (4) through $\rho(x)$ in the same manner as those in equations (2) are being expressed in terms of $\rho$.

The local situation near any physical point of the system is fully determined under accepted assumptions by a set of the scalar unknown variables $\tau_0$ and $\tau_1$ and of their time derivatives of various orders. Since the original heat conduction equations in the materials of the phases are linear, dependences of the integrals in equations (2) on those derivatives must be linear as well. Taking into account that both integrals have to include terms of appropriate tensor dimensionality, one obtains

$$\begin{aligned}
&\int_{|\mathbf{r}-\mathbf{r}'|<a} n(\mathbf{r}')\nabla_{\mathbf{r}}\mathbf{q}_{\mathbf{r}'}\,\mathrm{d}\mathbf{r}' \\
&= \rho B\left(\tau_0, \quad \tau_1, \quad \frac{\partial\tau_0}{\partial t}, \quad \frac{\partial\tau_1}{\partial t}, \ldots\right)\int_{|\mathbf{r}-\mathbf{r}'|<a} n(\mathbf{r}')\nabla_{\mathbf{r}}\tau_{\mathbf{r}'}\,\mathrm{d}\mathbf{r}' \\
&= \rho\mathbf{F}\left(\nabla\tau_0, \quad \nabla\tau_1, \quad \frac{\partial\nabla\tau_0}{\partial t}, \quad \frac{\partial\nabla\tau_1}{\partial t}, \ldots\right) \qquad (13)
\end{aligned}$$

$B$ and $\mathbf{F}$ being certain unknown linear functions of their arguments and $n_{\mathbf{r}'} = n = \text{const.}$

Let us make allowance now for the fact that $\tau_1$ can be unequivocally expressed through $\tau_0$ with the help of the second equation in set (1) so that its derivatives may be excluded from equations (13). This gives

$$B = -\sum_{j=0}^{\infty} \mu_j \frac{\partial^j \tau_0}{\partial t^j}, \quad \mathbf{F} = \sum_{j=0}^{\infty} \nu_j \frac{\partial^j \nabla \tau_0}{\partial t^j}, \tag{14}$$

$\mu_j$ and $\nu_j$ being unknown constant coefficients. Under stationary conditions all the time derivatives equal zero so that only $\mu_0$ and $\nu_0$ remain. In a general case it is reasonable to use the Fourier transform (or another linear integral transform) which reduces equations (14) to

$$\bar{B} = -\mu \bar{\tau}_0, \quad \bar{\mathbf{F}} = \nu \nabla \bar{\tau}_0,$$

$$\mu = \sum_{j=0}^{\infty} (i\omega)^j \mu_j, \quad \nu = \sum_{j=0}^{\infty} (i\omega)^j \nu_j, \tag{15}$$

where the overbar marks Fourier transformations of corresponding functions and $i\omega$ stands for the operator $\partial/\partial t$. Thus, the problem is to find only two coefficients $\mu$ and $\nu$ in any case. Note that equations (13)–(15) define also $\mathbf{q}$ and $\sigma$ in accordance with equations (2).

In order to express $\mathbf{q}_{\mathbf{r}'}$ and $\sigma_{\mathbf{r}'}$ in a similar form, it is necessary to single out those parts of conditional fields of the type of $\tau_{0,\mathbf{r}'} = \tau_0(t, \mathbf{r}|\mathbf{r}')$ and $\tau_{1,\mathbf{r}'} = \tau_1(t, \mathbf{r}|\mathbf{r}')$ which are due to the presence of the surface of the test particle in its capacity of an external boundary. This is possible to do by incorporating into the analysis perturbation fields of the type of $\tau^*_{0,\mathbf{r}'} = \tau^*_0(t, \mathbf{r}|\mathbf{r}')$ and $\tau^*_{1,\mathbf{r}'} = \tau^*_1(t, \mathbf{r}|\mathbf{r}')$ characterizing mean deviations of $\tau_0(t, \mathbf{r}|\mathbf{r}')$ and $\tau_1(t, \mathbf{r}|\mathbf{r}')$ from $\tau_0(t, \mathbf{r})$ and $\tau_1(t, \mathbf{r})$ caused by such a boundary; by following ref. [3] one obtains

$$\langle \theta T \rangle_{\mathbf{r}'} = \epsilon \tau_0(t, \mathbf{r}) + \epsilon(x) \tau^*_0(t, \mathbf{r}|\mathbf{r}'),$$
$$\langle (1-\theta) T \rangle_{\mathbf{r}'} = \rho \tau_1(t, \mathbf{r}) + \rho(x) \tau^*_1(t, \mathbf{r}|\mathbf{r}'), \tag{16}$$

where $\theta$ is the characteristic function equating zero inside the particles and unity otherwise and $T$ is the fine-grained field of temperature. In just the same manner one gets

$$\int_{|\mathbf{r}-\mathbf{r}'| \leqslant a,\, |\mathbf{r}'-\mathbf{r}''| > 2a} n(\mathbf{r}''|\mathbf{r}') \nabla_{\mathbf{r}} \mathbf{q}_{\mathbf{r}',\mathbf{r}''} \, \mathrm{d}\mathbf{r}'' = \rho B + \rho(x) B^*_{\mathbf{r}'},$$

$$\int_{|\mathbf{r}-\mathbf{r}'| \leqslant a,\, |\mathbf{r}'-\mathbf{r}''| > 2a} n(\mathbf{r}''|\mathbf{r}') \nabla_{\mathbf{r}} \tau_{\mathbf{r}',\mathbf{r}''} \, \mathrm{d}\mathbf{r}'' = \rho \mathbf{F} + \rho(x) \mathbf{F}^*_{\mathbf{r}'}, \tag{17}$$

where $B^*_{\mathbf{r}'}$ and $\mathbf{F}^*_{\mathbf{r}'}$ are linear function dependent on $\tau^*_{0,\mathbf{r}'}$ and on its time derivatives in exactly the same way as $B$ and $\mathbf{F}$ depend on $\tau_0$ in accordance with equations (14). That the mean volumetric concentration $\rho(x)$ of the dispersed phase in the close vicinity of the test sphere deviates from its asymptotic value $\rho$ is, thus, explicitly accounted for. The formulae (18) help in expression $\mathbf{q}_{\mathbf{r}'}$ and $\sigma_{\mathbf{r}'}$ involved in equations (3) as

$$\mathbf{q}_{\mathbf{r}'} = \mathbf{q} + \mathbf{q}^*_{\mathbf{r}'}, \quad \sigma_{\mathbf{r}'} = \rho B + \rho(x) B^*_{\mathbf{r}'},$$
$$\mathbf{q} = -\lambda_0 \nabla \tau - (\lambda_1 - \lambda_0) \rho \mathbf{F},$$
$$\mathbf{q}^*_{\mathbf{r}'} = -(\lambda_1 - \lambda_0) \rho(x) \mathbf{F}^*_{\mathbf{r}'}. \tag{18}$$

These formulae enable one to present the averaged field equations (1) in the form

$$c_0 \epsilon \partial \tau_0 / \partial t = \lambda_0 \Delta \tau + (\lambda_1 - \lambda_0) \rho \nabla \mathbf{F} + \rho B,$$
$$c_1 \partial \tau_1 / \partial t = -B \tag{19}$$

and to do the same with the equations in set (3) as well. Further, by subtracting equations (19) from equations (3) one derives

$$c_0 \epsilon(x) \partial \tau^*_{0,\mathbf{r}'} / \partial t = \lambda_0 \Delta \tau^*_{\mathbf{r}'}$$
$$+ (\lambda_1 - \lambda_0) \nabla (\rho(x) \mathbf{F}^*_{\mathbf{r}'}) + \rho(x) B^*_{\mathbf{r}'},$$
$$c_1 \partial \tau^*_{1,\mathbf{r}'} / \partial t = -B^*_{\mathbf{r}'},$$
$$\tau^*_{\mathbf{r}'} = \epsilon(x) \tau^*_{0,\mathbf{r}'} + \rho(x) \tau^*_{1,\mathbf{r}'}; \tag{20}$$

these equations govern the perturbation fields $\tau^*_{0,\mathbf{r}'}$ and $\tau^*_{1,\mathbf{r}'}$.

The quantities $B$ and $\mathbf{F}$ in equations (19) as well as $B^*_{\mathbf{r}'}$ and $\mathbf{F}^*_{\mathbf{r}'}$ in equations (20) are expressible through $\tau_0$ and $\tau^*_{0,\mathbf{r}'}$ in compliance with equations (14) and (15). This is why set (19) can be reduced to a single field equation for $\tau_0$ and set (20) is equivalent, in essence, to a closed equation for the perturbation $\tau^*_{0,\mathbf{r}'}$. The latter equation together with that of conventional heat conduction inside the test sphere gives an opportunity to formulate the test particle problem in a consistent way. Boundary conditions imposed on the surface of the test sphere have to allow for continuity of both temperature and heat flux whereas that at infinity must require the perturbation to tend to zero. The solution of the problem determines the integrands in equations (2) as functions of the unknown coefficients $\mu$ and $\nu$. The subsequent integration enables one to obtain alternative representations for $B$ and $\mathbf{F}$ depending on $\mu$ and $\nu$ as on parameters. At last, the identification of these representations with equations (14) or (15) leads to transcendent algebraic equations whose solution gives explicit expressions for both unknown coefficients and, thereby, defines $\mathbf{q}$ and $\sigma$ involved in the field equations (1). This brings the analysis to an end. Such a method seems to have been discussed for the first time in ref. [16].

Before proceeding to the determination of $\rho(x)$ possible semi-empirical hypotheses about this function will be pointed out. First of all, if one neglects the non-overlapping property of the spheres, there is no reason to distinguish between $\rho(x)$ and $\rho$. This corresponds to the model of homogeneous fictitious medium and may happen to be agreeable for mixtures of moderate concentrations. That it is actually the case is evidenced by comparison with experimental data. Another phenomenological assumption may consist in postulating that $\rho(x) = \rho$ when $x > b$ and $\rho(x) = 0$ otherwise, which returns the reader directly to problem (5). This model has been considered at $b = 2a$ in ref. [17].

It is evident in a general case that the conditional number concentration $n(t, \mathbf{r}|\mathbf{r}') = N\phi(t, \mathbf{r}, \mathbf{r}')$, $\phi(t, \mathbf{r}, \mathbf{r}')$ being the binary correlation function for a

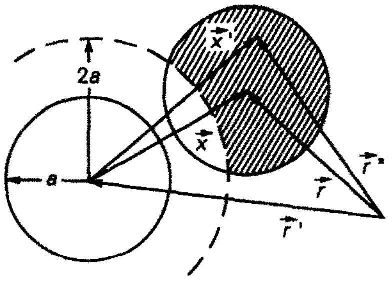

FIG. 1. Region of integration in equations (4) and (21).

pair of the spheres [3]. For macroscopically isotropic and time-independent $n(t, \mathbf{r}|\mathbf{r}') = n(x)$, $\mathbf{x} = \mathbf{r}-\mathbf{r}'$ and

$$\rho(x) = \int_{|\mathbf{x}-\mathbf{x}'|\leqslant a,\, x'>2a} n(x')\,\mathrm{d}\mathbf{x}',$$

$$\mathbf{x} = \mathbf{r}-\mathbf{r}', \quad \mathbf{x}' = \mathbf{r}''-\mathbf{r}'. \tag{21}$$

The simplest model of $n(x)$, amounting to neglect of joint interactions of more than two spheres, yields [17]

$$n(x) = n, \quad x > 2a; \quad n(x) = 0, \quad a < x \leqslant 2a. \tag{22}$$

Then the integration in equation (21) can be easily performed to get

$$\rho(x) = \rho\psi(z), \quad z = x/a,$$

$$\psi(z) = (16z)^{-1}(27-56z+30z^2-z^4),$$

$$1 < z \leqslant 3a, \tag{23}$$

and $\psi(z) = 1$ at $z > 3$. Other and more elaborate models must take into account the consequences of interactions within groups of several spheres. Such models (e.g. those by Kirkwood *et al.* the hypernetted one) are well known in the statistical mechanics of dense gases and liquids and result in oscillating functions $\psi(z)$ and $\rho(x)$ [18]. The region of integration according to equations (21) is shown in Fig. 1 and characteristic functions $\psi(z)$ are given in Fig. 2.

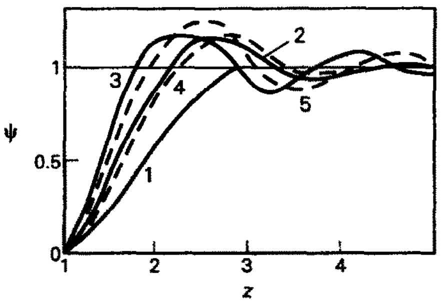

FIG. 2. Relative volume concentration of dispersed phase near the test sphere surface; 1, equations (23); 2,3, model by Percus and Yevick at $\rho = 0.2618, 0.4712$; 4,5, model by Kirkwood at $\rho = 0.2314, 0.4840$.

## 5. AN EXAMPLE: EFFECTIVE CONDUCTIVITY UNDER STEADY CONDITIONS

Let us apply the above consideration to a familiar problem of calculating the effective thermal conductivity of a macroscopically uniform and isotropic disperse medium with equal spherical particles. In view if the identity of corresponding mathematical formulations, the result to be obtained must be valid also for the effective diffusivity, the effective electrical conductivity as well as for effective electric and magnetic permeabilities of the medium.

Under stationary conditions the quantity $\sigma$ turns to zero and the mean heat flux is to be presented, in compliance with equations (2), (13) and (14), in the following form:

$$\mathbf{q} = -\lambda\nabla\tau, \quad \lambda = \beta\lambda_0, \quad \beta = 1+(\kappa-1)\nu\rho,$$

$$\kappa = \lambda_1/\lambda_0, \tag{24}$$

where $\lambda$ is the effective conductivity under question. Relations (18) lead to a complementary expression

$$\mathbf{q}_{\mathbf{r}'}^* = -\lambda^*(x)\nabla\tau_{\mathbf{r}'}^*, \quad \lambda^*(x) = \beta(x)\lambda_0,$$

$$\beta(x) = 1+(\kappa-1)\nu\rho\psi(z) \tag{25}$$

which defines the first equation in set (20), $\psi(z)$ being expressed in accordance with equations (23) or in agreement with a more elaborate scheme (Fig. 2). Now it is possible to state the boundary problem for perturbations produced by the test sphere. Without going into details the final result will be presented:

$$\nabla[\beta(x)\nabla\tau^*] = 0, \quad x > a; \quad \Delta\hat{\tau} = 0, \quad a \geqslant x \geqslant 0;$$

$$\tau^*+\tau = \hat{\tau}, \quad \lambda^*(a)\mathbf{n}\nabla\tau^*+\lambda\mathbf{n}\nabla\tau = \lambda_1\mathbf{n}\nabla\hat{\tau}, \quad x = a;$$

$$\tau^* \to 0, \quad x \to \infty; \quad \hat{\tau} \neq \infty, \quad x = 0, \tag{26}$$

$\hat{\tau}$ being the mean temperature inside the sphere. The subscript $\mathbf{r}'$ is dropped for simplicity. If $\tau = \mathbf{Ex}$, then $\tau^*$ and $\hat{\tau}$ can be shown to be proportional to $\mathbf{Ex}$ as well and, further,

$$\tau^* = f(x)\mathbf{Ex}, \quad \hat{\tau} = \nu\mathbf{Ex}, \tag{27}$$

where the function $f(x)$ is understood as a solution to the problem

$$x\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}+4\frac{\mathrm{d}f}{\mathrm{d}x}+\frac{\mathrm{d}\ln\beta(x)}{\mathrm{d}x}\left(x\frac{\mathrm{d}f}{\mathrm{d}x}+f\right) = 0,$$

$$f = \nu-1, \quad a(\mathrm{d}f/\mathrm{d}x) = \varepsilon(\kappa-1), \quad x = a;$$

$$f \to 0, \quad x \to \infty. \tag{28}$$

Thus, there are three conditions for an ordinary differential equation of the second order. Problem (28) determines, therefore, not only $f(x)$ but also the parameter $\nu$ playing the role of eigenvalue.

In a general case of a complicated function $\beta(x)$ (or $\psi(z)$) the desired solution of equation (28) is to be obtained numerically. However, if simplified versions of $\psi(z)$ are utilized, the solution can be derived in an analytical form. For moderately concentrated systems ($\psi(z) = 1$) one readily gets

$$v = \frac{3\beta}{\kappa+2\beta}, \quad \beta = 1 + \frac{3(\kappa-1)\beta}{\kappa+2\beta}\rho, \tag{29}$$

the latter equation yielding

$$\beta = (1/4)\{2-3\rho-\kappa(1-3\rho)+[(2-3\rho - \kappa(1-3\rho))^2+8\kappa]^{1/2}\}. \tag{30}$$

If $\psi(z)$ is substituted by a step function ($\psi(z)-1$, $z > 2$ and $\psi(z) = 0$, $1 < z \leqslant 2$), one obtains [17] instead of equation (30)

$$\beta = [7\kappa(1-\rho)+17+7\rho]^{-1}\{\kappa(1+11\rho) + 5 - 11\rho + ([\kappa(1+11\rho)+5-11\rho]^2 + [7\kappa(1-\rho)+17+7\rho][\kappa(5+7\rho) + 7(1-\rho)])^{1/2}\}. \tag{31}$$

These expressions define completely $\beta$ and $\lambda$ within the scope of the approximation indicated. It should be stressed that equation (31) leads to a good agreement with experiments for composite materials and other disperse mixtures in the case $\kappa \leqslant 1$. An example is presented in Fig. 3 where the theoretical curve for $\beta$ as a function of $\rho$ at $\kappa = 0$ is drawn together with the experimental data on diffusion in granular beds collected in ref. [17]. It is worth noting that formula (31) gives an opportunity to find an analytical expression for the tortuosity factor usually introduced when describing diffusional processes in heterogeneous media.

The situation is different if $\kappa \gg 1$. In this case the model resulting in equation (31) seems to be insufficient because it underestimates the effective conductivity, and a more thorough analysis based on either equations (23) or models specific to the statistical mechanics is necessary. The correlation between values of $\beta$ obtained from equation (31) and those computed with the help of equations (23) is illustrated by Fig. 4. Model (23) gives quite acceptable results which are, however, slightly different from ones corresponding to more exact forms of the binary correlation function. To demonstrate this, dependences of $\beta$ on $\rho$ conforming with different models of randomly packed mixtures are given in Fig. 5. Note that the curves derived from the model by Kirkwood and by Percus and Yevick are practically indistinguishable [19].

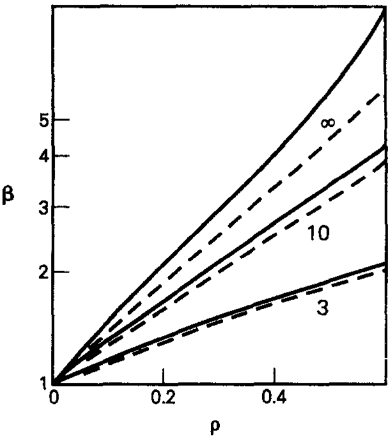

FIG. 4. Relative heat conductivity in accordance with equations (31) and (23) (dashed and solid curves, respectively) at different $\kappa$ (figures on the curves).

The compliance of the theory of this paper with the experiments on the effective electric conductivity of emulsions carried out in refs. [20–23] is confirmed in

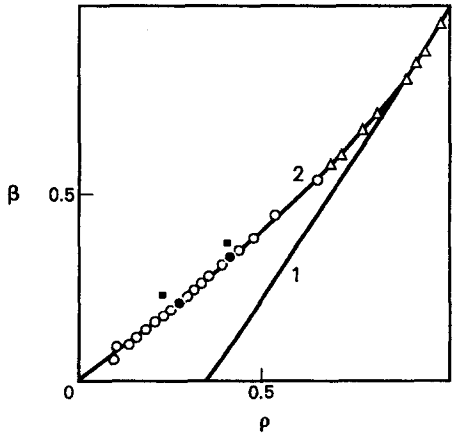

FIG. 3. Effective relative heat conductivity as a function of concentration of particles by volume at $\kappa = 0$; 1, equations (30); 2, equation (31); points, experiments on diffusion presented in ref. [15].

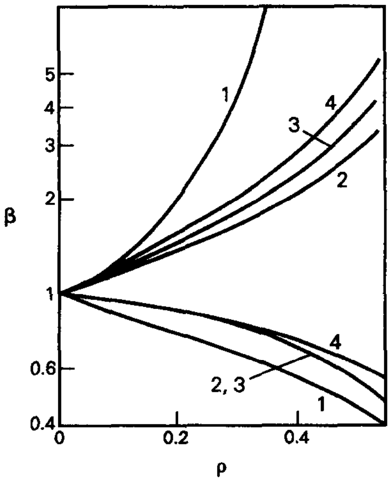

FIG. 5 Relative heat conductivity for different structural models of binary correlations at $\kappa = 0.1$, 100; 1, equations (30); 2, equation (31); 4, Percus–Yevick and Kirkwood models; 3, model (23).

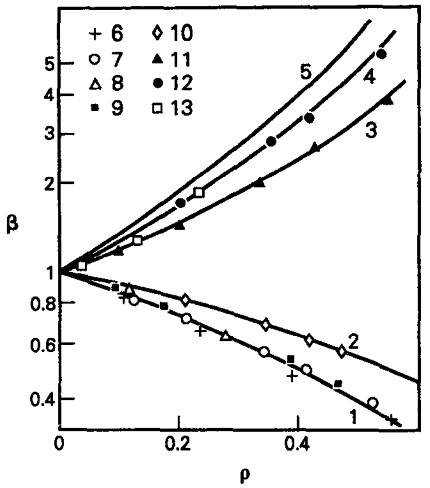

FIG. 6. Comparison of the theory experiments on electric conductivity of emulsions; 1–5 correspond to the Percus–Yevick model at $\kappa = 0, 0.172, 15.7, 100$ and $\infty$, respectively; 6–9, different experimental results at $\kappa = 0$ [20–23]; 10–13, results for $\kappa = 0.172, 15.7, 101$ and $\infty$, respectively [23].

Fig. 6. The theoretical curves have been obtained by using the Percus–Yevick model [19]. A general conclusion from the above is that the theory suggested gives reliable results concerning the stationary effective conductivity.

## 6. CONCLUDING REMARKS

A significant and rather attractive feature of the theory developed to close the averaged equations of heat and mass transfer consists in that its field of applicability is restricted by neither steady transport processes nor monodisperse systems of motionless spheres. In the remainder of the paper we would like to point out briefly some recent results revealing feasible directions of future work on the subject.

First of all, the theory can be used with equal success when studying effective transfer properties in mixtures containing particles of other forms, as that is evidenced by the analysis of dispersions of spheroids in ref. [15]. Such a dispersion ceases to be macroscopically isotropic in a general case and its effective conductivity coefficients form a tensor of the second order depending on the degree of ordered alignment of the spheroids.

When applied to the calculation of effective transfer properties under non-stationary conditions, new representations for both the transient heat flux $q$ and the mean heat exchange $\sigma$ between the phases per unit volume of a disperse mixture are attained. These quantities happen to involve terms containing time derivatives of the mean temperature and enable one to describe certain important relaxation processes occurring in the mixture in full accordance with experimental evidence. An example of treatment of this kind is provided for in ref. [24] where the self-consistency conditions have been formulated by means of using the Fourier transform in accordance with the formulae in set (15).

The statement of the test particle problem can be generalized to situations when specific interfacial properties of dispersed particles are of importance (e.g. the surface conductivity especially peculiar to some emulsions and colloidal systems) and direct transfer through contacts of the particles plays a significant role (as may be the case for closely packed systems). Both these factors have been taken into account in ref. [25] and a satisfactory agreement with available experimental data has been gained.

Of more interest, the same reasoning is quite applicable to combined processes of heat and mass transfer accompanied by internal heat and mass release and by chemical reactions and phase transitions both in the bulk of either a matrix or particles and on the interface. All these factors are able to influence effective mixture properties to a considerable extent. An example of a successful application of the theory to the description of diffusion and of diffusionally induced phase transitions in a solid disperse mixture in connection with problems of the thermochemical processing of heterogeneous metals is to be found in ref. [26].

A possible sphere of application of the theory is by no means exhausted by the examples indicated and much remains to be done along all the lines mentioned. It is expedient to stress in this respect that the theory under discussion gives a principal opportunity to treat these and other problems with a sound hope to succeed whereas that could hardly be said about particular models of various nature devised previously with limited aims in view.

The test particle problem needs to be reformulated somewhat in a case of infiltrated fixed granular beds when convective transfer to or from surfaces of the granules must be accounted for. The above results are approximately valid if the particle Peclet number is small compared with unity and, in the general case, one has to incorporate convective terms in equations (20) and to change the boundary condition of heat flux continuity at the test particle surface.

Much more complicated problems arise if dispersed particles are not at rest so that their binary correlation function cannot be thought of as a given quantity. Moreover, it depends essentially on the type of flow around the test particle affected to a great extent by hydrodynamic and other interactions with neighbouring particles. This is why the binary correlation function has to be understood as one of the unknown variables to be determined while solving the rheological problem for a disperse mixture under study alongside with all the other unknown variables. An informative discussion of the latter problem is presented in ref. [27].

In conclusion it should be indicated that the developed general method of closing the averaged field equations is applicable also while dealing with transfer of a vector quantity, such as momentum. Therefore, the same approach serves a useful purpose in the determination of rheological properties of flowing mixtures, moduli of elasticity of composite materials and so forth. By way of example, refer to paper [28] where effective characteristics of thermo-elasticity of composite materials have been successfully investigated.

## REFERENCES

1. G. N. Dulnev and Yu. P. Zarichnyak, *Thermal Conductivity of Mixtures and Composite Materials*. Energiya Press, Leningrad (1974) (in Russian).
2. S. S. Dukhin and V. N. Shilov, *Dielectric Phenomena and Double Layer in Disperse Systems and Polyelectrolytes*. Naukova Dumka Press, Kiev (1975) (in Russian).
3. Yu. A. Buyevich, Heat and mass transfer in disperse media—I. Averaged field equations, *Int. J. Heat Mass Transfer* **35,** 2445–2451 (1992).
4. D. J. Jeffrey, Group expansions for the bulk properties of statistically homogeneous suspensions, *Proc. R. Soc.* **A338,** 503–516 (1974).
5. I. D. Howells, Drag due to the motion of a Newtonian fluid through a sparse random array of small fixed rigid objects, *J. Fluid Mech.* **64,** 449–475 (1974).
6. R. Herczynski and I. Pienkowska, Toward a statistical theory of suspensions, *Ann. Rev. Fluid Mech.* **12,** 237–269 (1980).
7. G. K. Batchelor, Sedimentation in a dilute suspension of spheres, *J. Fluid Mech.* **52,** 245–265 (1972).
8. D. J. Jeffrey, The physical significance of non-convergent integrals in expressions for effective transport properties. In *Continuum Models of Discrete Systems*, pp. 653–674. Univ. Waterloo Press (1977).
9. H. C. Brinkman, A calculation of the viscous force exerted by a flowing fluid on a dense swarm of particles, *Appl. Sci. Res.* **A1,** 27–39 (1947).
10. Z. Hashin, Assessment of the self consistent scheme approximation. Conductivity of particulate composites, *J. Composite Materials* **2,** 284–300 (1968).
11. Yu. A. Buyevich, On the thermal conductivity of granular materials, *Chem. Engng Sci.* 29–48 (1974).
12. A. M. Golovin and V. E. Chizhov, On the effective thermal conductivity of a suspension, *Vestnik MGU, Ser. Matem., Mekhanika* No. 1, 89–94 (1978) (in Russian).
13. A. M. Golovin and V. E. Chizhov, To the calculation of sedimentation velocity of a homogeneous suspension, *Prikl. Matem. Mekhanika* **42,** 105–113 (1978) (in Russian).
14. I. N. Shchelchkova, Effective thermal conductivity of a heterogeneous mixture with ellipsoidal particles, *Zh. Prikl. Mekh. Tekhn. Fiz.* **1,** 107–111 (1974) (in Russian).
15. Yu. A. Buyevich, A. Yu. Zubarev and S. A. Naidanova, Effective transfer coefficients in a disperse system with ellipsoidal inclusions, *Inzh.-Fiz. Zh.* **51,** 75–83 (1986) (in Russian).
16. Yu. A. Buyevich, Yu. A. Korneev and I. N. Shchelchkova, On heat or mass transfer in a dispersed flow, *Inzh.-Fiz. Zh.* **30,** 979–985 (1976) (in Russian).
17. Yu. A. Buyevich and Yu. A. Korneev, Effective thermal conductivity of a disperse system at small Peclet number, *Inzh.-Fiz. Zh.* **31,** 607–612 (1976) (in Russian).
18. C. A. Croxton, *Liquid State Physics—a Statistical Mechanical Introduction*. Cambridge Univ. Press, Cambridge (1974).
19. B. S. Endler, On effective viscosity and thermal conductivity of a disperse medium, *Inzh.-Fiz. Zh.* **37,** 110–117 (1979) (in Russian).
20. V. P. Mashovets, Influence of non-conducting inclusions upon electric conductivity of an electrolyte, *Zh. Prikl. Khimii* **24,** 353–360 (1951) (in Russian).
21. C. A. R. Peagre, The electrical conductivity and permittivity of mixtures with spherical particles with reference to emulsions of water in fuel oil, *Br. J. Appl. Phys.* **6,** 113–120 (1955).
22. R. E. Meredith and C. W. Tobias, Resistance to potential flow through a cubical array of spheres, *J. Appl. Phys.* **31,** 1270–1273 (1960).
23. R. E. Meredith and C. W. Tobias, Conductivities in emulsions, *J. Electrochem. Soc.* **108,** 286–290 (1961).
24. Yu. A. Buyevich, To the theory of transfer in heterogeneous media, *Inzh.-Fiz. Zh.* **54,** 770–779 (1988) (in Russian).
25. A. A. Belyaev, A. Yu. Zubarev, E. S. Kats and V. M. Kiseev, On the effective thermal conductivity of dispersions of contacting particles, *Inzh.-Fiz. Zh.* **55,** 122–130 (1988) (in Russian).
26. Yu. A. Buyevich and S. L. Komarinsky, On the macrokinetics of diffusional transformations in metals with a dispersed phase, *Inzh.-Fiz. Zh.* **56,** 596–604 (in Russian).
27. G. K. Batchelor and J. T. Green, The determination of the bulk stress in a suspension of spherical particles to order $c^2$, *J. Fluid Mech.* **56,** 401–427 (1972).
28. Yu. A. Buyevich and A. Yu. Zubarev, On thermo-elastic effects in a disperse medium, *Inzh.-Fiz. Zh.* **51,** 248–255 (1986) (in Russian).

## TRANSFERT DE CHALEUR ET DE MASSE DANS LES MILIEUX DISPERSES—II. EQUATIONS CONSTITUTIVES

**Résumé**—On étudie le problème de formulation de toutes les grandeurs impliquées dans les équations de champ moyen qui gouvernent le transfert de chaleur et de masse dans un milieu dispersé, en fonction des variables inconnues de ces équations et des paramètres physiques. La solution est obtenue en formulant un problème annexe qui détermine les perturbations induites par une seule particule dans les champs moyens de température et de concentration. Au moyen d'exemples, les solutions, dans les conditions de transfert permanent, sont considérées et elles permettent de calculer la conductivité thermique effective et la diffusivité en fonction des paramètres physiques.

# WÄRME- UND STOFFTRANSPORT IN DISPERSEN MEDIEN—II. DIE BESCHREIBENDEN GLEICHUNGEN

**Zusammenfassung**—In den gemittelten Feldgleichungen für den Wärme- und Stofftransport in einem dispersen Medium kommen Größen vor, die in Abhängigkeit von den unbekannten Variablen dieser Gleichungen und von physikalischen Parametern beschrieben werden müssen. Dieses Problem wird in der vorliegenden Arbeit untersucht. Die Lösung beruht auf der Formulierung eines Hilfsproblems zur Bestimmung von Störungen, die durch ein einzelnes Partikel in den Feldern für die gemittelte Temperatur und Konzentration ausgelöst werden. Dies geschieht im wesentlichen auf derselben Grundlage wie bei der Ableitung der gemittelten Gleichungen selbst. Mit Hilfe eines Beispiels werden die Lösungen des Problems unter stationären Bedingungen betrachtet, was die Ermittlung der effektiven Wärmeleitfähigkeit und der Diffusivität in Abhängigkeit von den physikalischen Parametern erlaubt.

# ТЕПЛО- И МАССОПЕРЕНОС В ДИСПЕРСНЫХ СРЕДАХ—II. ОСНОВНЫЕ УРАВНЕНИЯ

**Аннотация**—Исследована проблема представления всех величин, появляющихся в усредненных полевых уравнениях тепло- и массопереноса в дисперсной среде, в виде функций неизвестных переменных этих уравнений и физических параметров. Конструктивное решение проблемы получено при помощи формулировки вспомогательной задачи о возмущениях, вносимых какой-либо одной частицей в средние поля температуры и концентрации примеси. Последнее делается на основе существенно тех же соображений, что и используемые при выводе самих усредненных уравнений. В качестве примера рассмотрены решения указанной задачи при стационарных условиях, что позволяет вычислить эффективные теплопроводность и коэффициент диффузии примеси как функции физических параметров.