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Thermal Conductivity of Porous Media and Soils

A Review of Soviet Investigations

Yurii A. Kovalenko and Stephen N. Flanders

May 1991

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PREFACE

This report was prepared by Dr. Yurii A. Kovalenko, Institute of Thermophysics, Siberian Branch of the U.S.S.R. Academy of Sciences, and Stephen N. Flanders, Research Civil Engineer, Civil and Geotechnical Engineering Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory.

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CONTENTS

ILLUSTRATIONS

NOMENCLATURE

a	Thermal diffusivity (m^2/s)
c	Specific heat capacity [J/(kg K)]
C	Relative bar size
C_1	Contiguity (or contact degree)
E	Modulus of elasticity
K_{12}	Ratio of averaged temperature gradients in binary heterogeneous system, $K_{12} = \lvert \Delta\langle T\rangle_1 \rvert / \lvert \Delta\langle T\rangle_2 \rvert$
L	Scale of the problem (m)
Le	Lewis number
L_{pr}	Process length (m)
L_{sp}	Specimen length (m)
l	Molecular scale (m)
m_i	Mass fraction of the ith component
n	Number of dimensions
N_c	Number of particle contacts
N_p	Number of particles
p	Pressure of compaction (Pa)
P_{ef}	Modulus of elasticity or pressure of compaction (Pa)
P_c	Contact value of modulus of elasticity per unit of contact area (Pa)
$\vec{q}$	Local thermal flux density (W/m^2)
$\vec{r}$	Coordinates (m)
S_c	Contact surface area of a particle (m^2)
S_{cont}	Contact surface area (m^2)
S_{compl}	Sum of particle surface areas (m^2)
S_{nom}	Nominal section area of the specimen (m^2)
S_p	Surface area of a particle (m^2)
S_{pr}	Surface contact area projected on the section plane (m^2)
t	Time (s)
T	Temperature (K)
$T\rvert_B$	Boundary value of temperature (K)
$\dot{T}$	Heating rate (K/s)
v_i	Partial specific volume of the ith component (m^3/kg)
z	Distance normal to surface (m)
α	Relative contact section of molded (or sintered) materials. The ratio of contact area projected onto a cross section to the area of the cross section of the specimen
β	Empirical parameter, relating to hardness. $\beta \approx 1.2$ for soft materials, like aluminum, and $\beta \approx 4$ for hard metals
Δ	Scale of a subregion of the problem (m)
δ	Inhomogeneity scale (m)
ε	Ratio of the scale of the inhomogeneity to the scale of the problem
θj	Angle between the jth contact plane and the normal to the section plane
ν	Ratio of thermal conductivities for a binary heterogeneous system
Π	Porosity
Π_o	Bulk porosity
ρ	Density (kg/m^3)
ϕ_i	Area or volume fraction of the ith component
χ	For random $\ln\lambda$ and their mean value, $\langle\ln\lambda\rangle$, χ is $\ln\lambda - \langle\ln\lambda\rangle$, where probability ($\chi$) is a normal distribution
λ_c	Contact thermal conductivity (W/m K)
λ_{ef}	Effective thermal conductivity (W/m K)
λ_m	Maxwell's solution for effective thermal conductivity (eq 24)
$\langle\ \rangle$	Average

Thermal Conductivity of Porous Media and Soils
A Review of Soviet Investigations

YURII A. KOVALENKO AND STEPHEN N. FLANDERS

INTRODUCTION

The thermal conductivity of soils and other dispersed porous materials of natural and artificial origin depends, first of all, on the composition and geometric microstructure of a system. Besides structure and composition, thermal conductivity is influenced by interphase (intercomponent) interactions. Heat transfer occurs primarily by conduction in systems with pores of conventional size (< 10^{-4} m), with temperatures ranging from –50 to 100°C and subject to ordinary temperature gradients. Convective and radiative heat exchange in pores can be estimated (Chudnovskii 1962, Dulnev and Zarichnyak 1974) and is generally negligible, except in materials with large pores, such as thermal insulation, and some structural construction materials, notably the large-celled concrete found in the Soviet Union.

Porous media and soils belong to a large class of Heterogeneous Media (HM), for which the theory of heat transfer allows the investigator to take an approach typical of continuous media: first, introduction of averaged characteristics of the medium and the process (volume content of components, temperature, heat flow, heat capacitance and thermal conductivity), and second, formulation of principal physical laws in terms of these characteristics. Such a continuous approach, applied independently of the order or disorder of the real heterogeneous system, rests on the assumption that the scale of typical inhomogeneities (δ) is miniscule compared with the scale of the system (L):

$$\delta << L . \tag{1}$$

This continuous approach uses the concepts of an infinitesimal volume (Lifshitz and Pitaevskii 1979) and of incorporated continua. Any such averaged description, as an alternative to a detailed description of processes in HM, considerably simplifies the problem solution, provided that the regular microstructure is known. It allows the solution of practical problems when the inner structure is non-regular and unknown (by the statistical method in Landau and Lifshitz [1976]). The difficulty of describing processes in this case is in obtaining averaged equation coefficients for energy, momentum and mass (analogous to obtaining closure for hydrodynamic equations [Lifshitz and Pitaevskii 1979]). Being random variables for $\delta \leq L$, these coefficients become single-valued characteristics of the medium when the conditions of eq 1 are satisfied (the so-called self-averaging of specific extensive quantities and kinetic coefficients as $\delta/L \rightarrow 0$ from Lifshitz et al. [1982]).

Several further concepts of HM classification are useful. Many classifications by different indicators exist (for example, Chudnovskii 1962, Dulnev and Zarichnyak 1974, Dulnev 1979, Heifitz and Neimark 1982). The principal indicators are:

1. The occurrence of binary or multi-component mixtures.
2. The occurrence of inert mechanical mixtures, alloys, solutions, HM with chemical interactions, etc.
3. The topology of the microstructure—including the degree of surface contact and the distribution of component sizes within the medium, ranging from uniform to varied.
4. The degree of order or randomness in the HM.
5. The uniformity or variety of the components within the HM, ranging from weakly to strongly heterogeneous. This includes the physical qualities of the components and their arrangement within the medium.

These classifications are conventional and in practice the given types of systems are mixed, with a high degree of disorder of components being typical. In this respect porous media and soils are similar to other types of HM.

The first investigations in which the continuous approach was extended from homogeneous gases, solutions and liquids to heterogeneous media with inner structure are in works by Maxwell (1873) and Rayleigh (1892), which focused on calculation of the effective electric field in a medium with spherical inclusions that are located at the nodes of a cubic lattice. Burger* studied the case of ellipsoidal inclusions. In 1887 Arrhenius* studied the analogous problem for the viscosity of binary liquid solutions and suggested the formula for the "logarithmic law of viscosity mixing." Later the same approach appeared again in Lichtenecker's work (1909, 1924, 1926, 1929) on conductivity. Eycken* (1912) apparently was the first to study the equivalent problem for heat transfer. Analogous problems connected with various physical fields were also studied by Wiener* (1912), Fricke* (1924), Voight* (1928), Reuss* (1929), Bruggeman (1935) and others (Odelevskii 1951, Chudnovskii 1962, Vasiliev and Tanaeva 1971, Dulnev and Zarichnyak 1974, Dulnev et al. 1976, Bakhvalov and Panasenko 1984, Shvidler 1985). A modern introduction to the formal study of physical characteristics that are analogous to conductivity (the dielectric constant and magnetic permeability, viscosity, electrical and thermal conductivity, diffusion and filtration coefficients, and moduli of elasticity), is found in Odelevskii (1951).

Investigations conducted in the U.S.S.R. may be divided into two large groups: 1) ad-hoc experiments investigating the thermal conductivity of specific materials and media, and 2) theoretical calculations to determine general solutions for effective thermal conductivity and overall conductance in wide classes of HM.

CONTINUOUS DESCRIPTION OF THERMAL PROCESSES IN HETEROGENEOUS MEDIA AND THE CONCEPT OF EFFECTIVE CHARACTERISTICS

The fundamental distinction between averaged descriptions of HM, and macroscopic descriptions of molecular systems rests with the heterogeneity of the HM being much larger than molecular scale (l):

$$\delta >> l. \tag{2}$$

The averaging technique used allows one to approximate a continuous medium with the same form of conservation of energy equations as for the HM and its internal heterogeneities, each having its own local physical coefficients.

Even if the contact area on the interface between components in a micro-heterogeneous system is large, one may often neglect the interaction of components within it over a large temperature span. In such temperature intervals, HM are mechanical mixtures and heat transfer is described by the pure conduction equations:

$$\operatorname{div} \vec{q} + c\rho \frac{\partial T}{\partial t} = 0 \tag{3}$$

$$\vec{q} = -\lambda \operatorname{grad} T \tag{4}$$

$$T(\vec{r},0) = T_0(\vec{r}),\ T|_B = T(\vec{r}_B,t). \tag{5}$$

Here specific heat $c(\vec{r})$, density $\rho(\vec{r})$ and thermal conductivity $\lambda(\vec{r})$ have rapidly changing coordinate functions (with periodical or random variables). As $c\rho(\vec{r})$ and $\lambda(\vec{r})$ are discontinuous in HM, the solution of the eq 3 through 5 is considered to be a general solution satisfying corresponding integral relations (Bakhvalov and Panasenko 1984). It is necessary to assume a temperature and heat flux continuum along interfaces between components

$$[T] = 0,\ \left[\lambda \frac{\partial T}{\partial z}\right] = 0$$

where [ ] is the function jump on the surface of a contact and $\partial T/\partial z$ is the partial derivative of temperature normal to the surface.

In principle, a detailed knowledge of the HM microstructure that determines the functions $c(\vec{r})$, $\rho(\vec{r})$ and $\lambda(\vec{r})$ would allow one to solve the problem accurately. With the assumption of eq 1 and if the structure is rather complicated, then such a detailed solution would be difficult to model on a computer. However, such a computation would rely on a detailed knowledge of the microstructure of the HM, which is unknown in detail. Instead, collective general properties of the microstructure are typically known. Thanks to this knowledge, a detailed solution is not usually required and an averaged description of the medium and the processes taking place within is typically the only appropriate method. It is also advisable to average the processes in simple, periodic media, as was done in Bakhvalov and Panasenko (1984) and Dulnev et al. (1976).

Now we'll cover isotropic and macroscopically homogeneous systems, that is, the systems in which the scale of heterogeneity δ and the averaged parameters (the volume of the components and so on) do not depend on global coordinates. In terms of the multiple scales method that is applied to averaged processes in periodical media (Bakhvalov and Panasenko 1984), these so-called "slow variables" are on the scale of L, unlike "quick variables," which are inside heterogeneities and are on the scale of δ.

Averaging can be carried out by several methods. The method strongly depends on the microstructure of the HM. It may be 1) statistical averaging over an ensemble of similar systems, where $c\rho(\vec{r})$ and $\lambda(\vec{r})$ are random functions, 2) averaging over a physically small volume Δ^3, $\delta << \Delta << L$, or 3) averaging over an elementary cell that is in a periodic structure. No matter how the averaging is done, it essentially uses the disintegration of the solution from Bakhvalov and Panasen-

* Citation not available.

ko (1984) or the parabolic operator of equations from Kozlov (1978), Shvidler (1986) and Zhikov et al. (1981), sequentially, into a power series of the parameter $\varepsilon = \delta/L$. Averaged equations of the zeroth order corresponding to eq 3 and 4 are expressed as follows

$$\operatorname{div} \langle q \rangle + \langle c\rho \rangle \frac{\partial \langle T \rangle}{\partial t} = 0 \tag{6}$$

$$\langle q \rangle = -\lambda_{ef} \operatorname{grad} \langle T \rangle \tag{7}$$

where the operations div and grad are taken only by global variables. In eq 6–8 the symbols < > mean averaging 1) over an ensemble of similar systems with random fields, $c\rho(\vec{r})$ and $\lambda(\vec{r})$, 2) of a physically small volume Δ^3, or 3) using the periodicities of regularities within the structure. In order to solve for $\langle T \rangle$ approximately in eq 6 and 7 to solve for T in eq 3–5

$$\max |T - \langle T \rangle| \le C_0 \varepsilon$$

must be satisfied, where C_0 is a quantity of the first order of magnitude. One must establish boundary conditions so that they coincide with their averaged analogue

$$\langle T \rangle|_B = T(\vec{r}_B, t). \tag{8}$$

We now look at the concept of effective thermal conductivity λ_{ef}, which is discussed as a special-case ancillary problem in Bakhvalov and Panasenko (1984), Shvidler (1985) and Shvidler (1986). Characterizing λ_{ef} is not trivial and represents the main challenge in this whole topic. Many works are devoted to the theoretical determination of λ_{ef}. However, experimentation is the most reliable way for determining λ_{ef}.

The other thermal coefficient derived from averaged equations, average thermal capacitance $\langle c\rho \rangle$ in eq 6, is determined simply by additivity. In fact, by dividing regions of integration into separate subregions occupied by individual components, it is easy to show that

$$\langle c\rho \rangle = \frac{1}{\Delta^3} \iiint\limits_{(\Delta^3)} c\rho dr^3 = \sum_i c_i \rho_{ci} \phi_i \tag{9}$$

where c_i and ρ_{ci} = specific heat capacity and density
i = component
ϕ_i = volume fraction i-component (averaged over the characteristic volume Δ^3).

By introducing partial density (the concentration of the i^{th}-component), $\rho_i = \phi_i \rho_{ci}$, equation 9 may be expressed as

$$\langle c\rho \rangle = \sum_i c_i \rho_i .$$

Another derivation of averaged volume heat capacity is possible by using the effective specific heat and an averaged density of the HM. Let's first determine the mass content of the components in their mixture

$$m_i = \rho_i / \sum_i \rho_i \tag{11}$$

and then the partial specific volume

$$v_i = m_i / \rho_{ci} .$$

By using v_i, we determine the volume content of the i^{th}-component in a manner analogous to eq 11

$$\phi_i = v_i / \sum_i v_i .$$

Then, introducing the effective specific thermal capacity of the HM as

$$c_{ef} = \sum_i c_i m_i \tag{12}$$

and the average density

$$\langle \rho \rangle = \sum_i \phi_i \rho_{ci} = \sum_i \rho_i = \left(\sum_i v_i \right)^{-1} \tag{13}$$

from eq 10–13 it is easy to show that

$$\langle c\rho \rangle = c_{ef} \langle \rho \rangle . \tag{14}$$

Note that the effective specific heat c_{ef} does not coincide with the averaged specific heat, as determined by the mean of individual specific heats, namely $c_{ef} \neq \langle c \rangle$. The same is true for $\lambda_{ef} \neq \langle \lambda \rangle$. In the particular case of layered HM, as we'll see below, $\lambda_{ef} = \langle \lambda \rangle$. These quantities agree only for volume-specific properties.

Note the following limitation on the applicability of eq 6 and 7 to non-steady-state processes. Their validity may be accepted only when the local temperature within the medium differs only a little from the temperature of the local thermal equilibrium. They are unconditionally valid only when the medium is close to steady state, that is, at $\partial T/\partial t \approx 0$ in Rubinshtein (1948). Hence, it follows that they can describe only rather slow non-steady-state thermal processes with typical response times much longer than the time constants of the heterogeneities within the medium, that is

$$t_{char} >> \frac{\delta^2}{a_{min}} \tag{15}$$

where $a_{min} = \min(a_i)$ and can be described by averaged eq 6 and 7. The condition (eq 15) can also be obtained from the estimate of the terms of eq 6 and 7 using the inequality of eq 1 (Buevich 1973). The effective thermal conductivity in eq 7 for non-steady-state processes, tested against the condition in eq 15, coincides with the steady-state effective thermal conductivity.

If one cannot adhere to the assumptions of local thermal equilibrium, then one has to resort to a more detailed description—for example, a multi-temperature model (Rubinshtein 1948, Schvidler 1986). In such a model, heat transfer terms that are linear functions of temperature are added to eq 6 for each temperature within the individual components.

Summing up, let us reformulate the conditions of the applicability of homogenization of both steady-state and non-steady-state thermal problems in HM, including mechanical mixtures and also dispersed systems with possible phase and chemical reactions (Kovalenko 1987).

With the inequality of eq 1 as the principal condition, the smallest of the following two dimensions must be chosen as the typical problem scale: 1) minimal size of specimen L_{sp}, or 2) the typical process length L_{pr}, that is: $L = \min(L_{sp}, L_{pr})$. The condition $L >> \delta$ must be observed for any steady-state (this usually allows $L = L_{sp}$) or non-steady-state process. In this latter case the condition of eq 1 can be rewritten by the substitution

$$L = \sqrt{t_{char} \cdot a}$$

as the condition of eq 15, in which the $L = L_{sp}$, the characteristic time is simply equal to L_{sp}^2/α. When $L = L_{pr}$, the characteristic time can be expressed by other parameters. So, for HM undergoing phase endothermal change from thawing, $t_{char} = \Delta T/\dot{T}$ can be introduced, where ΔT is the liquid characteristic temperature difference in the phase diagram (melting phase), and where $\dot{T}$ is the heating rate. The value t_{char} not only represents eq 15 but exceeds the diffusion time in the heterogeneity scale. The latter condition is thanks to the fact that a Lewis number, $Le \leq 10^{-3} << 1$, in condensed media appears sufficient for homogenized modeling of the medium (in this case the condition of eq 15 is deliberately observed). With such a homogenization, we understand the description of the medium with the help of lumped, effective characteristics.

THEORETICAL METHODS FOR THE DETERMINATION OF EFFECTIVE THERMAL CONDUCTIVITY

By definition the effective thermal conductivity is a coefficient that relates the averaged values for heat flux and the gradient of the average temperature (eq 7)

$$\langle q \rangle = -\lambda_{ef} \operatorname{grad} \langle T \rangle.$$

Most calculation methods are based on this definition. The problem then is the determination of the fields of $\langle q \rangle_i$ and $\langle T \rangle_i$ averaged by the components within the HM.

Exact solutions and approximate methods

Exact solutions to the problem of the definition of the effective thermal conductivity are known only for a few cases. In the first place, these are one-dimensional layered structures for which the longitudinal conductivity is as follows

$$\lambda_{||} = \langle \lambda \rangle \tag{16}$$

and transverse

$$\lambda_{\perp} = \langle \lambda^{-1} \rangle^{-1}. \tag{17}$$

For more complex structures, especially for non-regular ones, it is complicated enough to calculate the effective thermal conductivity on the basis of the information about field structures of $\langle q \rangle_i$ and $\langle T \rangle_i$, so exact solutions are very rare. However, one may occasionally avoid awkward and sometimes unsuccessful calculations for systems that are not strongly heterogeneous. This possibility relies on using variational principles for estimating the bounds of effective characteristics (Dykhne 1967, Shvidler 1985). The simplest expression of such bounds is

$$\langle \lambda^{-1} \rangle^{-1} \leq \lambda_{ef} \leq \langle \lambda \rangle \tag{18}$$

which was probably determined for the first time by Wiener and later was ascertained by Hill* (1964) for the modulus of elasticity and pliability and by Dykhne (1967) for conductivity.

Dykhne (1970) obtained an interesting result in his work, in which he proved that for a flat isotropic system, covered on the average by geometrically equivalent regions with different conductivities λ_1 and λ_2, the effective conductivity satisfies the functional equation

$$\lambda_{ef}(\phi_1) \cdot \lambda_{ef}(\phi_2) = \lambda_1 \lambda_2$$

where ϕ_i is the area fraction (in a two-dimensional model) for regions with conductivity λ_i and $\phi_1 + \phi_2 = 1$. Hence at $\phi_1 = \phi_2 = 1/2$ it follows

$$\lambda_{ef}(1/2) = \sqrt{\lambda_1 \lambda_2}. \tag{19}$$

In the above mentioned work by Dykhne and also a paper by Kozlov (1979), the case when, for the random

* Citation not available.

variable λ, the distribution of the value $\chi = \ln\lambda - \langle\ln\lambda\rangle$ is an even function of χ, is studied for different possibilities. The precise value of the effective thermal conductivity is obtained as

$$\lambda_{ef} = \exp \langle\ln\lambda\rangle. \tag{20}$$

This result with its particular case of eq 19 represents the empirical logarithm-mixing formula by Arrhenius (also suggested later by Lichtenecker) which, thus, is accurate for two-dimensional bicomponent systems with specialized conductivity distribution functions. Equation 20 can be represented by (Shvidler 1985)

$$\lambda_{ef} = (\langle\lambda\rangle \langle\lambda^{-1}\rangle^{-1})^{1/2}. \tag{21}$$

This is a geometric mean that is between the arithmetic and harmonic means for thermal conductivity.

In the work in Ivanov (1967), eq 21 is generalized to other dimensions n with the help of the additional results of the perturbation method

$$\lambda_{ef} = \langle\lambda\rangle^{\left(1-\frac{1}{n}\right)} \langle \lambda^{-1} \rangle^{\left(-\frac{1}{n}\right)}. \tag{22}$$

At $n = 1$ this formula is accurate for any distribution, at $n = 2$ it is accurate if the distribution of χ is even and at $n = 3$, according to Shvidler (1985), "one can expect the formula to be accurate enough for normal distributions of $\ln\lambda$."

The approach made in the early works of Maxwell (1873) and Rayleigh (1892), which present an approximation of a small concentration of inclusions dispersed either regularly or randomly within the matrix, gave rise to a great number of publications in which different asymptotic formulae for λ_{ef} were obtained. Maxwell (1873) derived the first term of a decomposition of effective thermal conductivity as a function of the volumetric fractions of the inclusions

$$\lambda_{ef} = \lambda_2 \cdot \frac{\nu(1+2\phi_1) + 2(1-\phi_1)}{\nu(1-\phi_1) + 2 + \phi_1} \tag{23}$$

where the subscript 1 refers to the inclusions, 2 refers to the matrix, and $\nu = \lambda_1/\lambda_2$. Rayleigh (1892) studied the problem of spherical inclusions at the nodes of a regular cubic lattice. He obtained the first two terms of an expansion of λ_{ef} by degrees of ϕ_1; the first and principal term of this expansion disregarded the mutual influence of inclusions, and coincided with Maxwell's (1873) solution (eq 23). Rayleigh's solution was rendered more precise by adding two more terms of the expansion in Berdichevskii (1979).

Hashin and Strikman (1962) narrowed the limits of effective parameters beyond those in eq 18 using the variational principle. For the isotropic two-phase system with $\lambda_1 \leq \lambda_2$, the limits coincide with asymptotic formulae by Maxwell (1873)

$$\lambda_1 \cdot \frac{\frac{\lambda_2}{\lambda_1}(1+2\phi_1) + 2\phi_1}{\frac{\lambda_2}{\lambda_1}\phi_1 + 2 + \phi_2} = \lambda_m^- \leq \lambda_{ef} \leq \lambda_m^+$$

$$= \lambda_2 \cdot \frac{\frac{\lambda_1}{\lambda_2}(1+2\phi_1) + 2\phi_2}{\frac{\lambda_1}{\lambda_2}\phi_2 + 2 + \phi_1}. \tag{24}$$

This is not a casual coincidence. In fact, as shown in Berdichevskii (1979), if the thermal conductivity of inclusions λ_1 is less than that of the medium λ_2, then the accurate value of effective conductivity of a periodically structured medium with spherical inclusions is less than or equal to the first term, λ_m of the Rayleigh–Berdichevskii formula in Berdichevskii (1979) that coincides with Maxwell's solution (eq 23). If $\lambda_1 \geq \lambda_2$, then $\lambda_{ef} \geq \lambda_m$.

Unlike the universal bounds for λ_{ef} in eq 18, Hashin–Strikman's expression (eq 24) for the three-dimensional heterogeneous system gives approximate bounds, which, however, are considerably narrower than the former (eq 18). Using such bounds it is possible, when necessary, to construct approximate solutions, as in eq 24. Shvidler (1985) further recommends that if component connectivity is identical (mutually penetrative components), then we can take as an approximate value of

$$\lambda_{ef} = \left(\lambda_m^- + \lambda_m^+\right)/2.$$

For isotropic matrix HM, he recommends the assumption $\lambda_{ef} = \lambda_m^+$, if the matrix thermal conductivity is more than the inclusion conductivity, and $\lambda_{ef} = \lambda_m^-$ in the opposite case. If no single component is simply connected, but the components' connectivities are different, then the estimate for λ_{ef} is $\lambda_{ef} = \sqrt{\lambda_m^- \lambda_m^+}$.

The perturbation method for determining thermal conductivity in Landau and Lifshitz (1982) is similar to the Maxwell (1873) method for approximating small concentrations of inclusions. The perturbation method gives good results for any concentration of components but only for weakly heterogeneous systems.

In addition to the perturbation method, the self-consistent effective field method is another important technique. In a number of cases it gives better results. The first self-consistent parameters were probably calculated by Bruggeman (1935). Later, Odelevskii (1951) in the U.S.S.R., Landauer (1952) and others developed this method for other systems. The efficiency of the self-consistent field method is shown by direct numerical computations (Shvidler 1983) and by comparison with experiments (Odelevskii 1951). Shvidler (1985) gives tables for the values of λ_{ef}/λ_1 calculated by this method for different values of λ_2/λ_1 and ϕ_i and for different dimensional ratios of spheroidal inclusions.

Note that in the strongly heterogeneous HM, percolation causes threshold effects (Efros 1982, Shvidler 1985). One can describe conductance behavior near the threshold in such systems, using power laws for scaling according to percolation theory. Critical indexes and values of the threshold concentration ϕ_c for simple problems can be obtained analytically, but more often they are computed by the Monte Carlo method. Self-consistent parameters at $\nu = 0$ or at $\nu = \infty$ in some concentration areas get non-physical, negative values. While this is certainly the result of approximation, it is also an indicator for the percolation effect (Shvidler 1985). Thus, the formula for binary HM with equal components derived in Odelevskii (1951) by the effective media method

$$\lambda_{ef} = \frac{\lambda_1}{4} \{(3\phi_1-1) + \nu(3\phi_2-1) + \sqrt{[(3\phi_2-1) + \nu(3\phi_2-1)]^2 + 8\nu}\} \tag{25}$$

where $\nu = \lambda_2/\lambda_1$ gives the estimate of percolation threshold $\phi_c = 1/3$ as $\nu \to 0$

$$\text{when } \phi_1 \le \phi_c \qquad \lambda_{ef} = 0$$

$$\text{when } \phi_1 > \phi_c \qquad \lambda_{ef} = \lambda_1(3\phi_1-1)/2. \tag{26}$$

In engineering practice the methods of structural modeling (Chudnovskii 1962, Vasiliev and Tanaeva 1971, Dulnev and Zarichnyak 1974, Dulnev et al. 1976, Dulnev 1979) are often used. The real HM structure is modeled by the most suitable ordered structure in which an elementary cell is separated, and its thermal conductivity is calculated precisely using a computer as in Bakhvalov and Panasenko (1984) or approximately as in Dulnev and Zarichnyak (1974). Approximate calculations of λ_{ef} for the elementary cell are usually made by dividing a cell into separate fragments, containing only one of the components with surfaces that are orthogonal to the direction of heat flow. Then the thermal resistance of a complete elementary cell is made of parallel and serial connections of fragment resistances and calculated by the rules of Kirchhoff's chain. A number of formulae sufficiently useful for engineering calculations are obtained by this method in Dulnev and Zarichny (1974). Thus, a model was suggested for structures with interpenetrating components, in which one of the components presents a cubic lattice or frame with bars of a constant square section. To determine the conductivity of such a system by the method described, the estimates of λ_{ef} were obtained with the help of two different fragment thermal resistance connections within the elementary cell

$$\lambda_{ad} = \lambda_1\left[C^2+\nu(1-C)^2 + 2\nu C(1-C)(\nu C+1-C)^{-1}\right]$$

$$\lambda_{isot} = \lambda_1\left[\frac{1-C}{C^2+\nu(1-C^2)} + \frac{C}{C(2-C)+\nu(1-C^2)}\right]^{-1}$$

where the subscripts *ad* and *isot* refer to adiabatic and isothermal, respectively, and C is the relative bar size, which is a root of the equation

$$2C^3 - 3C^2 + 1 - \phi_2 = 0.$$

With the arithmetic mean of these values from Dulnev and Zarichnyak (1974), one can determine the effective value of λ for any relationship of the component thermal conductivities, the result being rather near to the results of numerical computations. Maximum calculation error is attained when $\nu = 0$ or $\nu = \infty$, yet it doesn't exceed ~15% (Dulnev and Zarichnyak 1974).

These methods include the averaged element technique (Dulnev and Zarichnyak 1974). This technique introduces a set of assumptions about the HM structure and then averages the parameters of the structure. The complexity and subjectivity of the procedure to define such an averaged element substantially explains why this method was not widely adopted.

In some applied problems, it is necessary to take into account the statistical distribution of heterogeneities in HM leading to deviations in thermal conductivity values from the average value λ_{ef}. Zhirov's work (1976) focuses on this problem.

The success of the application of all these formulas to real HM depends on how well one has characterized the system structure, e.g., the distribution of λ for random mixtures or for geometrical structures. Variational estimates based on universally used principles are relatively simple and require minimal information about the HM studied. Therefore, they apply to wide classes of HM. This is their advantage and at the same time a limitation on their efficiency when they lead to wide bounds in estimating effective conductivity. One can obtain positive results provided that $0.2 < \nu < 5$ for the Hashin–Strikman estimate and $0.5 < \nu < 2$ for the universal relationship are both true. Attempts to include in the analysis more detailed information about specific features of the systems studied, in order to narrow the limits of estimates, instead make the variational estimates method considerably more cumbersome.

Semi-empirical methods

All the estimates of effective thermal conductivity given above have the form $\lambda_{ef}(\phi_i, \lambda_i)$ and do not contain the parameters that directly reflect the real structure of the material. Therefore, they adequately represent such factors that affect heat transfer as the forms of inclusions, the dispersion of their sizes, the effects of thermal contact, etc.

Some missing information about actual HM structures can come from direct observations and measurements. Thus, we come to the semi-empirical methods for estimating effective thermal conductivity, which allow one to take into account known specific features of the HM structure by introducing additional semi-empirical parameters.

Some semi-empirical methods (Dulnev 1979, Malter et al. 1980) are based on the representation of the definition λ_{ef} from eq 7 in the form

$$\lambda_{ef} = \frac{|<q>|}{|\nabla<T>|} = \lambda_i \cdot \frac{K_{12}\phi_1 + \nu\phi_2}{K_{12}\phi_1 + \phi_2} \tag{27}$$

where $\nu = \lambda_2/\lambda_1$, and $K_{12} = |\nabla<T>_1| / |\nabla<T>_2|$ is the ratio of the averaged temperature gradients in the two components of a binary heterogeneous system (after Shvidler 1986). A number of properties of K_{12} can be set. Thus, using eq 18 it is easy to show that this value is limited by the bounds for K_{12} of 1, ν and, hence, when $\nu = 1$, then $K_{12} = 1$. With the help of such boundary relationships for dielectric polarization from Odelevskii (1951) and Landau and Lifshitz (1982), we obtain the value of the derivative when $\nu = 1$

$$\frac{\partial K_{12}}{\partial \nu} = \frac{1}{3}.$$

There exist generalized experimental data from Malter et al. (1980) that indicate that, for a wide class of systems, when $\nu = 0$ or $\nu = \infty$ the boundary values of K_{12} (ν) do not depend on the volume fraction over a wide range and satisfy the condition

$$0.4 \le K_{12}(0) + K_{12}(\infty) \le 0.67$$

$\left(K_{12} = K_{21}^{-1}\right)$.

Assuming similar properties of the ratio K_{12}, Malter et al. (1980) suggested a four-parameter approximate equation for K_{12} (ν), considering it independent of the concentration. Assuming that K_{12} is independent of ϕ_i, it is possible to determine this constant for the given ν and from eq 27 if the value of λ_{ef} has been measured for certain values of ϕ_i; then for the other values of ϕ_i the thermal conductivity can be calculated by using the derived value of K_{12}.

Also of interest are the works of Serykh and Kolesnikov (1982) and Kolesnikov (1985), which suggest use of stereological analysis for obtaining the additional information about HM structures. Thus, for determination of effective thermal conductivity in porous granular systems when $\nu = 0$, Serykh and Kolesnikov (1982) derive the following formula

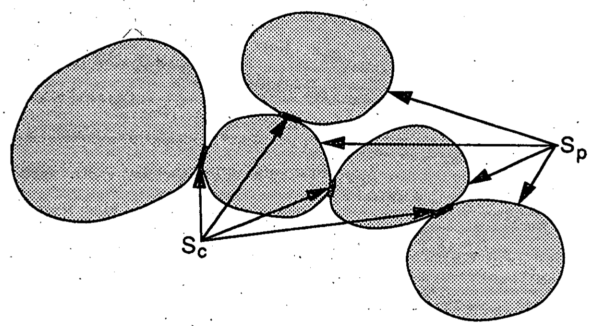

Figure 1. Determination of C_1, the ratio of contact surface area to the total area of the particle surfaces.

$$\lambda_{ef} = \lambda_i \phi_i \sqrt{C_1}\ . \tag{28}$$

Here C_1 is called contiguity or degree of contact. It is the ratio of the contact surface area to the total area of the particle surface (Fig. 1)

$$C_1 = 2\, S_{cont}/S_{total} \tag{28a}$$

$$\text{where } S_{cont} = \sum_{j=1}^{N_c} (S_c)j \tag{28b}$$

S_c = contact surface area
N_c = number of contacts

and

$$S_{total} = \sum_{j=1}^{N_p} (S_p)j \tag{28c}$$

S_p = particle surface area
N_p = number of particles.

C_1 is determined from the stereological analysis of a microsection specimen. This method can sometimes simplify thermal experiments for porous granular systems, but usually direct measurement of thermal conductivity is simpler.

In Balshin's work (1948, 1972) the following formula for the conductivity properties of porous materials is suggested

$$\lambda_{ef} = \lambda_1 \sqrt{\phi_1 \alpha}\ . \tag{29}$$

in which

$$\alpha = S_{pr} / S_{nom} \tag{29a}$$

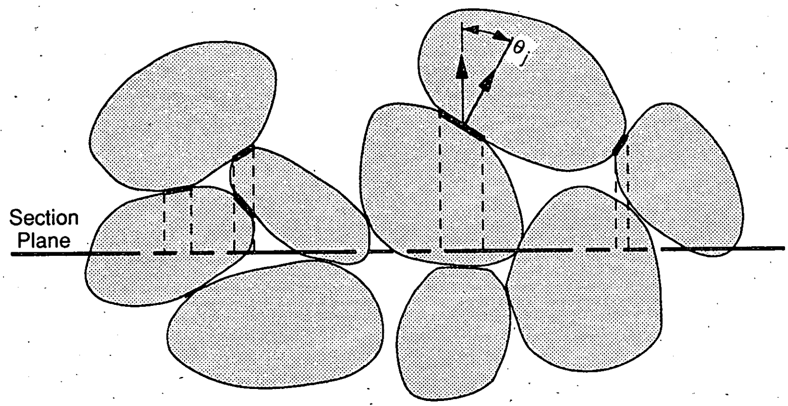

Figure 2. Determination of α, the ratio of projected areas of contact to the section area of the specimen.

and

$$S_{pr} = \sum_{j=1}^{N_c} (S_c)_j \cos\theta_j \tag{29b}$$

where N_c is the number of contacts, θ_j is the angle between the normal to the j^{th} contact plane and the normal to the section plane, and S_{nom} is the nominal section area of the specimen (Fig. 2). Balshin used the concept of contact sections to describe the physical and mechanical properties of compressed materials in uniform positions. Their characteristics are expressed by α with a simple formula

$$P_{ef} = P_c\alpha. \tag{30}$$

Here P_{ef} may be the modulus of elasticity E, the strength, or the pressure of compaction p. Each of these represent a resistance property for forming the material. P_c is the corresponding contact value for this property. For E, P_c is the corresponding modulus of elasticity of the frame* material. For p, P_c is a corresponding value between the material frame strength and the yield point of this material (Balshin 1948, 1972). The weight of the experimental evidence in Balshin (1972) suggests an approximation of the contact section value through measured parameters either for porosity Π and the initial bulk porosity Π_o or corresponding values of the volume fraction of the solid phase ϕ_1

$$\alpha = (1-\Pi)^2 (1-\Pi/\Pi_o)^\beta \tag{31}$$

where β depends empirically on the hardnesses of the material species.

The stereological definition of the contact section is described by eq 29a. Using this definition, Serykh and Kolesnikov (1982) and Kolesnikov (1985) connected the values C_1 and α with the help of the stereological approach

$$C_1 = \alpha/\phi_1 . \tag{32}$$

Hence, one can derive the formula for the effective thermal conductivity identical to eq 29 from eq 28. Thus, one might match both approaches and determine α by stereological means.

The formulas for λ_{eff} in eq 28 and 29 are based on some lax assumptions that do not account for the physical state of the contacts. This probably overestimates the thermal conductivity in some cases, for example, for compressed metal powders with high porosity. These systems were studied by Aleksandrov et al. (1985), Gruzdev and Kovalenko (1987, 1988a) and Gruzdev et al. (1989), using compressed powders of nickel, zirconium and their mixtures with aluminum powder as examples. In Aleksandrov et al. (1985) and Gruzdev et al. (1989), experiments determined that a good analogy exists between heat transfer and mechanical stress transfer in these systems, as determined by the degree of contact present. A lattice model of a powder body demonstrates the analogy theoretically in Gruzdev and Kovalenko (1987, 1988a). The thermal versus mechanical analogy between the molding pressure and thermal conductivity is based on the similarity of dependence on specimen porosity. Employing the relationship of porosity to mechanical properties in eq 30, and the thermal versus mechanical analogy for thermal conduction, we can write

$$\lambda = \lambda_c\, \alpha(\Pi,\Pi_o). \tag{33}$$

Parameter β, which enters into the function α (Π,Π_o) (from eq 31), depends on the hardnesses of the material

* The frame refers to the solid skeleton of a porous material, exclusive of the voids within it.

species (Gruzdev et al. 1989). It ranges from $\beta = 1$ to $\beta = 1.5$ for soft metals, such as aluminum, to $\beta \approx 4$ for hard metals. Experimentation confirms a clear similarity of relationship between $P(\Pi,\Pi_o,\beta)$ and $\lambda_{ef}(\Pi,\Pi_o,\beta)$. As follows from the above described thermal–mechanical analogy, the porosity Π, the bulk porosity Π_o, which characterizes the precompaction structure, and the parameter β are criteria for similarity (Kutateladze 1986) between the mechanical and thermal properties of porous, compressed powdered metals. The contact thermal conductivity λ_c is determined empirically. This analogy and the formula in eq 33 are limited by the condition that the area of inter-particle contacts be small in comparison with the sizes of species. Hence, porosity should be in the range of $\Pi \geq 0.25 \pm 0.05$.

EXPERIMENTAL INVESTIGATIONS

Non-steady-state methods are generally used for measuring effective thermal conductivity and thermal diffusivity of dispersed and porous media, as in Artykpaev (1968) and Lyalikov (1965), for example. These methods can be conventionally divided into several groups: 1) methods using monotonic (Platunov 1973) and periodical (Filippov 1984) heating, 2) methods using equilibration at an exponential rate, e.g., the "regular regime of Kondratiev" (Chudnovskii 1962) and 3) probe methods (see, e.g., Sigalova 1965, Bakenov et al. 1972, Zaitzev et al. 1989). Steady-state methods are more laborious and inaccurate and are therefore used less often. For temperature intervals in which HM or their separate components (for example, thawing soils) undergo phase transformations, traditional methods do not work because the thermal conductivity equation is nonlinear. For such cases the methods based on computer solutions of the corresponding inverse problems are suggested in Pavlov et al. (1980), Kovalenko (1986) and Gruzdev and Kovalenko (1988b).

Experimental investigations have, as a rule, been individual, ad-hoc efforts. Their purpose in each case has been to study thermal conductivity of a narrow class of materials. There are practically no experimental investigations for modeled media.

The thermal conductivity of soils (clays, sandstones) and various rock deposits is investigated in the works by Bogomolov (1941), Sigalova (1965), Bakenov et al. (1972), Sidorov (1979), Nikiolaev et al. (1987) and Zaitzev et al. (1989). An attempt to summarize thermal conductivity of three- or four-component soils (hard frame with air, water and oil) is made in the works of Volkov et al. (1982). The works of Franchuk (1941), Kaufman (1955), Vasiliev and Fraiman (1967), Zabrodskii et al. (1968), Garnashevich (1974), Frantsevich (1976), Litovskii and Puchkelevich (1982) and Strelov (1982) are dedicated to experimental study of the thermal conductivities of thermal insulation and other building materials. Zarichnyak (1970) summarizes experimental data for the thermal conductivity of such systems. Metal–ceramic and compressed metal-powder materials are considered in the works of Lyalikov (1965), Skorokhod (1967), Demidchenko (1972), Andreev (1975), Aleksandrov et al. (1985) and Gruzdev et al. (1989).

Experimental investigations can be unsatisfactory when the materials studied are insufficiently characterized. Also, the amount of experimental data is insufficient to favor one or another calculational model for specific classes of porous, dispersed materials.

CONCLUSION

A review of Soviet studies of thermal conductivity of porous materials and soils shows that theoretical investigations are more common than experimental. Many models are not adequately validated with the meager experimental data that exist for different classes of systems. In fact, there are no systematic experimental investigations of the whole classes of HM, as they are modeled. Investigators give preference to calculations. The lack of 1) thermal measurement apparatuses, 2) accurate methods to characterize structure, and 3) a common data bank for individual experimental results reinforces this syndrome.

Methods available for determining the effective thermal conductivity of HM by theoretical calculation probably exceed in scope the whole range of various HM classes. Choosing between models for specific cases is therefore a major problem in predicting of HM thermal properties.

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A Review of Soviet Investigations

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This review concentrates on works published over the past 10–15 years, but includes important earlier publications. The authors do not claim bibliographic completeness but only aim to embrace different trends of investigations carried out in the U.S.S.R. in the field of thermal conductivity and generalized conductivity of dispersed materials and porous media, the latter two being considered mechanical mixtures without phase changes or chemical reactions among the components.

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