Heat Conduction in Saturated Granular Materials

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Heat conduction in granular materials varies with the conductivities and volumetric proportions of the constituents. Thermal conductivities predicted by leading equations that utilize these factors are compared with reported values for quartz sand, glass beads, and lead shot, each saturated with various liquids. Only the equation of de Vries and a series/parallel flow equation proposed by Woodside and Messmer approximate the data over a range of conductivity ratio and porosity. Neither equation, however, is based on a fully rational model. An equation proposed by Kunii and Smith utilizes a better physical model but is weakened by its dependence on the regular packing of spheres.

The series/parallel approach is altered to incorporate three additional propositions: (a) the quantity of fluid that conducts heat in the series branch approaches zero at the extremes of porosity; (b) interfacial material invariably resides between this fluid and a grain, or between two grains; and (c) the possibility of contact resistance (limited surface conductance) exists at each such interface. The resulting equation is tested against the literature data and is shown to give a better understanding of heat conduction in granular materials. The equation also serves to indicate areas in which further research is needed.

•THERE IS a need for a rational theory to predict the effective thermal conductivity of granular materials found in conjunction with various fluids. Such a theory would be applicable to a wide range of engineering and geological problems, including the freezing and thawing of soils beneath highways, the dissipation of heat from building foundations or from buried utility systems, the conduction of heat through water- or oil-bearing sands, the design of insulating or refractory materials, and many others.

Many of the techniques in use at present are openly empirical, while others of a more rational development incorporate matching factors that have only a quasi-physical basis. Moreover, apparently no approach has taken into account the effect of thermal resistance between grains and fluid. A recent study (1) indicated that the thermal conductivity of a mixture of ice and sand was limited by poor thermal transfer across ice/sand boundaries. It is very likely that thermal resistance is present to some degree at all boundaries between differing materials, and particularly where foreign substances are adsorbed. A rational theory of heat conduction should make provision for the influence of this factor on overall conductivity.

Previous solutions for the thermal conductivity of granular materials have tended to fall into three major categories:

1. Empirical averaging techniques, in particular modifications built on the weighted geometric mean of the conductivities of the phases;

2. Modified parallel-flow equations based on Maxwell's electrical conductivity equation for spheres in a continuous liquid; and

3. Series/parallel flow equations.

In this paper, leading equations in each of these categories are compared with conductivity data of Woodside and Messmer (2). The data cover a large range of porosities and conductivity ratios and were obtained by means of the probe method of transient heating. This method is judged to be the most reliable technique for measuring the conductivity of multi-phase materials. All of the equations take into consideration the conductivities and volumetric proportions of the constituents, factors which together constitute the first requirement of a rational theory.

Other equations have been proposed that are not included here because they do not satisfy certain initial requirements; many of these have been reviewed elsewhere (2,3). Some have not considered the proportions of the constituents. Others have been empirically involved or based on questionable assumptions (4). Still others have utilized geometrical models that incorporate dubious estimates of the contact area between grains (5, 6).

The degree to which each equation predicts or fails to predict the experimental data is shown and the reasons analyzed. A conductance equation is then developed that attempts to correct for the inadequacies of previous solutions. This equation is based on a series/parallel flow model; however, the development differs from previous approaches in that the existence of true solid-to-solid contact between grains is discounted, while the possibility of interfacial resistance is recognized.

GEOMETRIC MEAN EQUATIONS

The basic geometric mean equation, attributed to Lichtenecker (7), is given by

$$K = K_f^n \cdot K_S^\lambda \tag{1}$$

or

$$\log K = n \log K_f + \lambda \log K_S$$

where K_f and K_S are the bulk conductivities of a continuous fluid phase and a dispersed granular phase, respectively; n is the porosity or volume fraction of saturating fluids; and $\lambda = (1-n)$ is the volume fraction of solids. Asaad (8) proposed a variation to the geometric mean equation,

$$K = K_f^{pn} \cdot K_S^{1-pn} \tag{2}$$

where p varies in the neighborhood of unity and has the effect of altering the porosity corresponding to a particular value of K. Legg and Given (9) and Brown (10) proposed other variations.
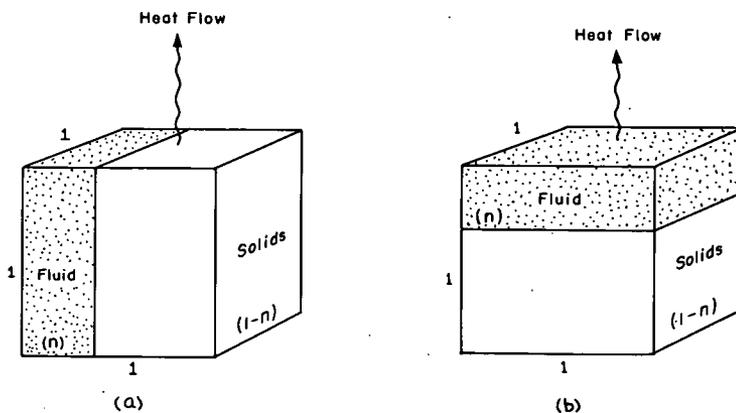
Figure 1. Schematic models of parallel flow (a) and series flow (b).
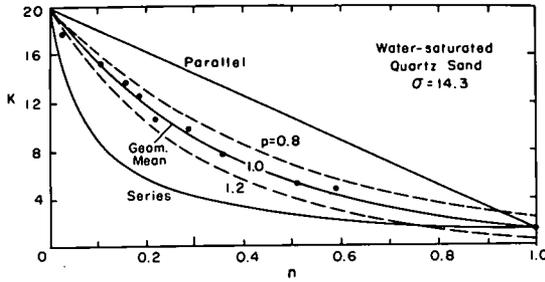
Figure 2. Conductivity (K), mcal/deg C-cm-sec, vs porosity (n); parallel, geometric mean, and series equations.

Each of these equations is an empirical compromise between two physically limiting cases, namely, parallel (maximum) flow:

$$K = nK_f + \lambda K_s \qquad (3)$$

and series (minimum) flow:

$$K^{-1} = nK_f^{-1} + \lambda K_s^{-1} \qquad (4)$$

Schematic diagrams of parallel and series flow are shown in Figure 1; no simple diagram representing geometric mean flow can be drawn.

A comparison of Eqs. 1 through 4 is shown in Figure 2. The curves were calculated for the case of water-saturated quartz sand (K_s = 20, K_f = 1.4 mcal/deg C-cm-sec at 20 C; $\sigma = K_s K_f^{-1}$ = 14.3). The data are taken from Woodside and Messmer (2), Parts I and II, for quartz sands and quartzitic sandstones; both types of sands were found to give equal conductivities for equal porosities when water-saturated and are therefore plotted together. Equation 2 was calculated with several values of p. This equation reduces to Eq. 1 when p is unity.

Figure 2 shows the rather striking agreement of calculated geometric mean values with experimental data when the conductivity ratio ($K_s K_f^{-1}$) is less than 20. Nevertheless, the appeal of the approach is primarily based on convenience, inasmuch as little insight is provided into the physical processes involved. In a later comparison, the geometric mean equation is shown to overestimate conductivity by successively larger margins as the conductivity ratio is increased.

MODIFIED MAXWELL EQUATIONS

A second approach, and one that has received a great deal of attention, involves modifying Maxwell's electrical conductivity equation to fit presumably analogous heat conductivity situations. Maxwell's equation, rewritten in terms of conductances rather than the original specific resistances, is given by

$$K = K_f \cdot \frac{K_s + 2K_f + 2\lambda (K_s - K_f)}{K_s + 2K_f - \lambda (K_s - K_f)} \qquad (5)$$

Equation 5 was derived by Maxwell to express the compound electrical conductivity of a mixture of uniform spheres dispersed in a continuous conducting fluid. An important stipulation of the derivation was that the spheres were of radii small compared with their distances, so that "their effects in disturbing the course of the current may be taken as independent of each other" (11, p. 440). Maxwell's equation is directly applicable only when the percentage of solids is well below 50 percent.

Rayleight (12) derived a similar formula for spheres arranged cubically. The derivation was extended by Burger (13) to ellipsoidal particles and by Eucken (14) to several phases dispersed in a single continuous phase. Eucken was apparently one of the first to suggest an analogy with heat flow. Most recently, de Vries (15, 16) has applied the extended equation to the thermal conductivity of soils. De Vries' equation for a fluid medium with dispersed ellipsoidal solids is

$$K = \frac{nK_f + F\lambda K_s}{n + F\lambda} \qquad (6)$$
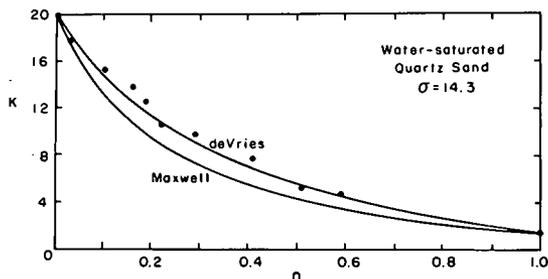
Figure 3. Conductivity (K) vs porosity (n); de Vries and Maxwell equations.

where

$$F = \frac{1}{3} \sum_{x=1}^{3} \left[1 + g_x \left(\frac{K_s}{K_f} - 1 \right) \right]^{-1}$$

(6a)

and

$$\sum_{x=1}^{3} g_x = 1$$

(6b)

Equation 6 has the form of Eq. 3 for parallel flow, with the exception that the factor F is different from unity. It has been suggested that F is related to the ratio of the effective temperature gradients in the continuous and dispersed phases. However, for packed granular materials, which are those to which Eq. 6 has been applied by de Vries, F is only slightly more than a weighting factor by which the equation can be fitted to a given set of data.

The empirical nature of F becomes clear when the factor g_x is considered: $g_x = g_1$, g_2, g_3 expresses the axial lengths of the ellipsoidal particle. For spherical particles, $g_x = \frac{1}{3}, \frac{1}{3}, \frac{1}{3}$, and Eq. 6 reduces to Maxwell's equation. Whereas Maxwell's equation typically underestimates experimental data for granular soils (Fig. 3), de Vries found that the assumption of $g_x = \frac{1}{8}, \frac{1}{8}, \frac{6}{8}$ results in good agreement with measured values. Nevertheless, the presumed particle, with a major axis six times the length of each minor axis, does not in reality approximate the particles of the soils to which the equation is usually applied.

It is instructive to cast Maxwell's equation into the form of Eq. 6 and to compare Maxwell's F-value with that of de Vries. When this is done, Maxwell's factor is given by

$$F(1:1:1) = \left[1 + \frac{1}{3}(\sigma - 1) \right]^{-1} = \frac{3}{\sigma + 2}$$

(7a)

while de Vries' factor is

$$F(1:1:6) = \frac{4}{3} \left(\frac{11 + 13}{3\sigma^2 + 22\sigma + 7} \right)$$

(7b)

As before, $\sigma = K_s K_f^{-1}$. The two F-factors are plotted against σ in Figure 4. With the exception of the point where $K_s = K_f$, de Vries' factor is everywhere larger than Maxwell's. Mineral soils fall into the lower right quadrant, where F is less than unity. For water-wet sand ($\sigma = 14.3$), $F(1:1:1)$ is 0.184 and $F(1:1:6)$ is 0.281. In effect, de Vries finds the solid fraction in real soils more effective in conducting heat than Maxwell's equation would predict. This result is what we would expect for particles in close association; however, the manner in which the result is obtained is to some degree arbitrary.
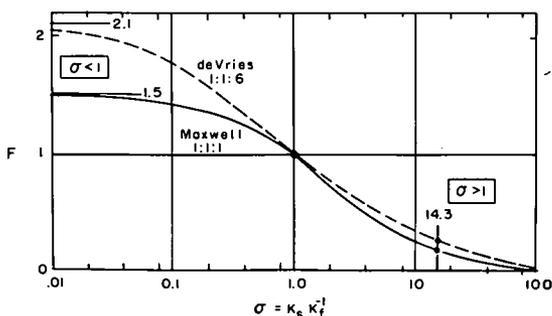
Figure 4. F-factor (F) vs conductivity ratio (σ); de Vries and Maxwell equations.
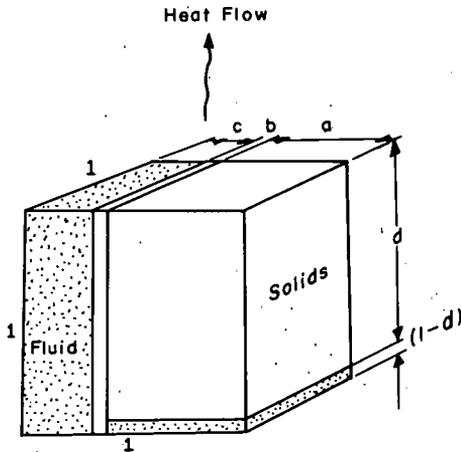
Figure 5. Schematic model of the resistor equation.

SERIES/PARALLEL EQUATIONS

A third approach accounts more directly for the mechanisms governing heat transfer from particle to particle. This approach is based on the recognition of at least two distinct paths of conduction through a granular material: a continuous path through the major portion of the fluid, and a series path through the solid particles that are thought to be bridged by a small portion of the fluid. Many investigators have postulated a third path by way of solid-to-solid connections between particles; however, as discussed later, it is unlikely that such a path actually exists except in rare instances.

The series/parallel approach differs from that of Maxwell and related equations in that a true series path is discerned. Properly applied, Maxwell's approach treats those cases where the continuous path is predominant; the series/parallel approach can potentially treat all cases from full parallel to full series flow with equal rigor.

Figure 5 shows a schematic model of series/parallel flow as proposed by Wyllie and Southwick (17). This model has been called the equivalent resistor model because it was originally proposed for electrical conductivity; the model has since been applied to the calculation of thermal conductivity. In Figure 5 fluid areas are stippled and areas representing solids are white. It will be noted that the model incorporates a continuous path through the solids in addition to the series path. As illustrated, the volumes of the various elements are expressed in terms of four ratios, a, b, c, d.

The equation for the resistor model as given by Wyllie and Southwick is

$$K = \frac{aK_s K_f}{(1-d)K_s + (d)K_f} + bK_s + cK_f \tag{8}$$

where

$$a + b + c = 1 \tag{8a}$$

Converting to the symbols used earlier for the volumetric ratios of solids and saturating fluids, we find respectively

$$\lambda = b + ad$$
$$n = 1 - b - ad = c + a(1 - d) \tag{8b}$$

In practice, it is necessary to supplement relations 8a and 8b with certain experimental measurements before the dimensions of the equivalent resistor model can be determined. To evaluate b, Wyllie and Southwick proposed evacuating the pores to make the fluid nonconducting (K_f equal to zero). Thus b was thought to be $K_v K_s^{-1}$, where K_v was the observed conductivity in a vacuum. However, the relation is not exact because, with no fluid in the pores, radiation between grains is no longer negligible; an experimentally determined value of K_v will always be higher than conduction

would account for. Thus, a small but finite K_V does not necessarily indicate the presence of a conducting path.

Since the solids could not be made nonconducting, an empirical estimate of c was necessary. Kimura (18) assumed $c = n^{1.3}$ and $b = 0$, but disregarded Eqs. 8b. Woodside and Messmer (2) also assumed $b = 0$, but calculated the value of c required to match the resistor model to experimental data. For porosities from 20 to 60 percent they found c to be virtually independent of the conductivity ratio and to take the value $(n - 0.03)$ to a close approximation. Woodside and Messmer concluded that when the following empirical relations were incorporated,

$$b = 0$$
$$c = n - 0.03$$
$$a = 1 - c = (1 - n) + 0.03 \tag{8c}$$
$$d = (1 - n)/a$$

an equation resulted that predicted the thermal conductivity of granular materials with good agreement over the range studied. With the addition of Eqs. 8c, the resistor equation becomes

$$K = (n - 0.03)K_f + (\lambda + 0.03)\left[\frac{\lambda}{\lambda + 0.03}\left(\frac{1}{K_s}\right) + \frac{0.03}{\lambda + 0.03}\left(\frac{1}{K_f}\right)\right]^{-1} \tag{9}$$

Equation 9 was termed the modified resistor equation by these investigations.

It is evident from Figure 5 that the resistor approach does not take into account the geometry of the particles or the specific arrangement of the pore fluids that enter into the series flow. Kunii and Smith (19) proposed a series/parallel equation in which they made a semi-empirical estimate of the extent of the series fluid. This equation was an updated version of an earlier one proposed by Yagi and Kunii (20) that included a term for the contact area between grains but neglected the continuous fluid path. In the later equation, Kunii and Smith sought to provide for conductive heat transfer through actual contact surfaces by introducing an empirical coefficient; nevertheless, the coefficient indirectly depended on contact area. Two other coefficients represented radiative transfer between particles and between voids. The authors took all these coefficients to be zero in a comparison with experimental data.

Kunii and Smith's equation, neglecting radiation and possible contact area, is

$$K = nK_f + \lambda\left[\frac{\varphi}{\beta}\left(\frac{1}{K_f}\right) + \frac{\gamma}{\beta}\left(\frac{1}{K_s}\right)\right]^{-1} \tag{10}$$

in which the parameters β, γ, and φ are ratios with the average diameter of a particle, D. Thus β D is the effective distance between centers of adjacent particles, γ D is the effective length of a particle, and φ D is the effective length of the series fluid. The value of each parameter was estimated through a comparison with open and close packings of uniform spheres: β was assumed to be between 0.9 and 1.0, but was taken as unity in the authors' calculations; γ was assigned the value of $\frac{2}{3}$, corresponding to the length of a cylinder having the same diameter and volume as a spherical particle; φ, as a function of porosity and conductivity ratio, was linearly interpolated between φ_1 and φ_2 calculated for the two packings. Outside the porosity range 48 to 26 percent, φ was assumed to retain the values φ_1 and φ_2.

The calculation of φ_1 and φ_2 represented an attempt to determine the amount of series fluid that would be effective in each of the reference packings. Although not wholly
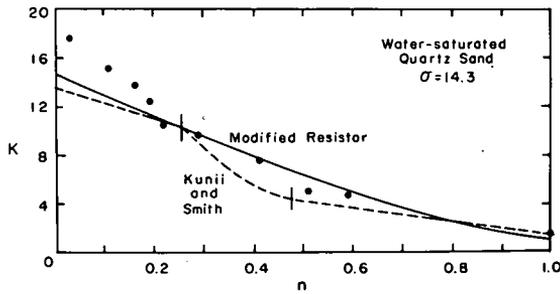
Figure 6. Conductivity (K) vs porosity (n); modified resistor and Kunii and Smith equations.
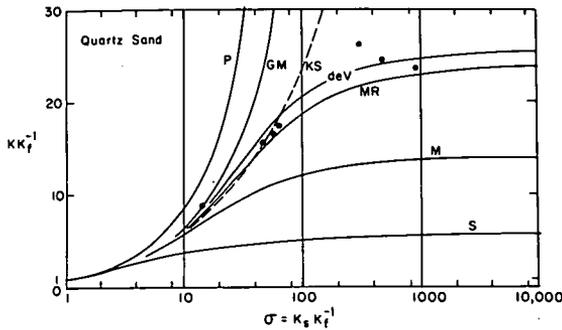
Figure 7. Comparison of conductivity equations; n = 19 percent.
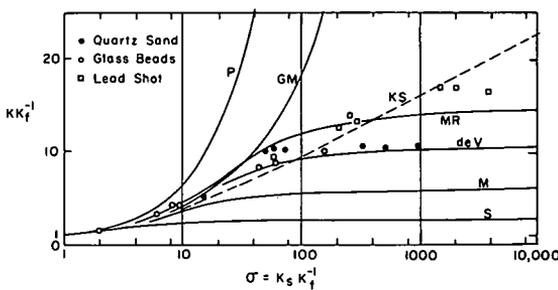
Figure 8. Comparison of conductivity equations; n = 38 percent.

rigorous, it is interesting for being the only known effort directed toward deriving such a value from basic principles. The calculation involved several steps. The first was the introduction of a conductance equation derived elsewhere [presumably by Yagi and Kunii (21), in Japanese] that represented the integral heat flow within a circular column bounded by the external surfaces of two spherical particles in contact ($\beta = 1$). In this equation the conductivity ratio was taken as a variable but apparently was used only to determine the ratio of the temperature gradients in the fluid and solid phases. The limitation placed on the extent of the conducting column by the refraction of flow lines at the spherical surfaces was not considered, inasmuch as parallel flow was assumed throughout.

The cross section of an equivalent series fluid column in each packing was estimated by weighting the total heat flow through a single hemisphere according to the number of contact points on that hemisphere, the direction of the normal to the surface at each contact point, and the total cross-sectional area of the packing perpendicular to each normal. The area of the average conducting column in the direction of general heat flow was calculated to be 70 percent of the projected area of a particle for open packing (n = 48 percent) and 15 percent for close packing (n = 26 percent). That these areas were independent of the conductivity ratio was an error arising from the assumption of parallel flow on each side of the spherical surface. The integral equation was then used to calculate the equivalent length of a cylindrical prism of series fluid having the cross-sectional area so determined, which gave the value of φD required for each packing. Thus φ_1 and φ_2 were functions of conductivity ratio—the larger the conductivity ratio the shorter the equivalent column. According to this development, conductivity ratio altered the length of the column of series fluid but had no effect on its width.

Kunii and Smith compared their equation with experimental data reported by nine previous investigators. These data covered a broad range of materials, but porosities varied only between 38 and 50 percent. One of their figures indicated that the calculated values fell within a band extending some 15 percent on each side of the observed values.

Kunii and Smith's equation with $\beta = 1$ and $\gamma = \frac{2}{3}$ is compared in Figure 6 with Woodside and Messmer's data for water-saturated sand. The modified resistor equation is

also plotted. It is apparent that at a conductivity ratio of 14.3 neither equation closely predicts the data over a wide range of porosities. For the most part Kunii and Smith's equation underestimates the data, except at a porosity of 26 percent where there is also an abrupt change of slope. The modified resistor equation lies both above and below the data but may be said to be a fair approximation, considering the whole scale of porosities. Neither equation reproduces the value K_s at n = 0, nor does the modified resistor equation predict the value K_f at n = 1.

COMPARISON OF EQUATIONS AGAINST CONDUCTIVITY RATIO

In Figures 7, 8, and 9, the conductivity equations are compared with experimental data for quartz sand, glass beads, and lead shot, as reported by Woodside and Messmer (2). The figures show the influence of the conductivity ratio, σ, for three selected porosities: 19, 38, and 59 percent. The following equations are compared:

Geometric mean	(GM)	Eq.	1
Parallel flow	(P)	Eq.	3
Series flow	(S)	Eq.	4
Maxwell	(M)	Eq.	5
De Vries	(deV)	Eq.	6
Modified resistor	(MR)	Eq.	9
Kunii and Smith	(KS)	Eq.	10

The parallel and series results are included because they represent upper and lower limiting cases, although they do not actually approximate the data.

Several relations are immediately evident. When σ is less than 10 there is little to choose quantitatively among the equations (disregarding the limiting cases) inasmuch as they all converge to the value $K = K_s = K_f$. On the other hand, with increasing σ the geometric mean and Kunii and Smith equations are concave upward, in a manner similar to the parallel flow equation. The geometric mean equation agrees with the data up to a value of σ approximately equal to the porosity in percentage, beyond which the calculated values diverge rapidly from the observed values. Kunii and Smith's equation lies below the data at low σ, passes through at σ between 50 and 500, and continues upward. The remainder of the equations show quite a different behavior; on a semi-logarithmic plot they all have inflections beyond which they approach horizontal asymptotes. These latter equations are characterized by series-type flow at high conductivity ratios.

The series flow equation and Maxwell's equation consistently underestimate the data at all values of σ. Only the de Vries and the modified resistor equations may be said to approximate the data over a large portion of the conductivity range. Both equations fit quite well at a porosity of 19 percent. At the intermediate porosity of 38 percent, the combined data for 1.2 mm lead shot, 40/50 mesh glass beads, and 20/30 mesh quartz sand give the appearance of at least two relationships, portions of which seem to fit both equations. At a porosity of 59 percent, the de Vries equation lies well below the data when σ exceeds 20, while the modified resistor equation continues to fit fairly closely.

The reason for the failure of the de Vries equation when porosity and the conductivity ratio exceed certain limits lies with the F-factor and its dependence on g_x. Figure 3 indicated that the F-factor with g_x = 1:1:6 is essentially correct for all porosities when σ is as low as 14.3. However, at a porosity of 59 percent (Fig. 9), comparison with the position of Maxwell's equation indicates that an ellipsoidal particle even more strongly elongated would be required in order to approximate the data.
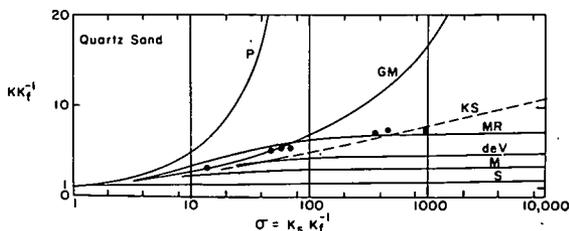
Figure 9. Comparison of conductivity equations; n = 59 percent.

Calculation gives g_x = 1:1:10, which is obviously at variance with the actual particles of sand. The conclusion is inescapable that the de Vries equivalent particle is too slender precisely because Maxwell's stipulation does not hold: the particles do indeed disturb the course of the current, even at porosities as high as 60 percent. The ellipsoidal shape is an empirical device for accounting for the large amounts of heat conducted by the fluid between adjacent grains.

De Vries, of course, has characterized his method as approximate (22). The remarkable fact is that it approximates such a large body of data with relatively small changes in the shape of the presumed particle. This circumstance leads one to speculate that the flow lines derived from a truer physical model will in some way correspond to those derived for the 1:1:6 particle.

The resistor model and the model of Kunii and Smith each take account of the series bridging fluid and its thermal effect, the first model in a qualitative way and the second in an ingenious but not wholly satisfactory quantitative way. The Kunii and Smith method results in a volume of series fluid that is variable with porosity and conductivity ratio, but which because of certain assumptions is of incorrect magnitude. The modified resistor method assumes the volume of continuous fluid to be (n - 0.03), which has the effect of assigning a constant volume (3 percent of the gross volume) to the series fluid. Except for the ambiguity in the data at n = 38 percent (Fig. 8), this equation is a good approximation for all conductivity ratios when porosity is between 19 and 59 percent. On the other hand, Figure 6 indicated that outside this porosity interval the assumption of constant series fluid volume was no longer valid, inasmuch as the end points were not reproduced. It is evident from a physical standpoint that the volume of series fluid should be zero at the porosity limits, independently of conductivity ratio. It follows, then, that if 3 percent is the approximate mean value over the entire range of porosities, there are some porosities for which the volume of series fluid will exceed this value.

THE SERIES CONDUCTING PATH

The foregoing illustrates that there is as yet no fully rational solution for the thermal conductivity of granular materials. Nevertheless, several of the equations currently in use produce strikingly close approximations to certain measured conductivities. There is therefore little purpose in proposing yet another equation that would perform the same function but in a slightly different manner. On the contrary, a new approach is needed that more closely describes the physical situation and thereby permits confident predictions over a broader range of variables; in this connection, empiricisms utilized as a temporary expedient should be of such nature that they can also be made the subject of theoretical inquiry. It is in this context that a heat conduction equation for granular materials is developed here.

It may be anticipated that such an approach will be generically similar to the series/parallel approaches of Wyllie and Southwick or Kunii and Smith, in which the series path carries a major portion of the heat flow. However, a true series path will incorporate a feature that does not appear in any of the equations previously discussed, namely, the possibility of thermal resistance across the particle interfaces bordering the series fluid.

Ingersoll, Zobel, and Ingersoll (23, p. 27) state, "In any practical consideration of heat transfer it is disastrous to overlook the contact resistance that is offered to heat flow by any discontinuity of material; here we have a phenomenon which is really a temperature discontinuity at the gas-solid boundary and which greatly increases resistance." Similarly, Van Rooyen and Winterkorn (3, p. 200) state, "In granular systems the discontinuity of energy and temperature that exists on a solid-gas interface has been recognized and experimentally proven. It is reasonable to assume that a similar phenomenon exists between a solid and a liquid phase." Birch and Clark (24) took account of contact resistance at a gas-solid interface in measuring the thermal conductivity of rock. Sakiadis and Coates (25) took account of resistance at a liquid-solid interface, stating that surface irregularities as small as 0.0005 in. (12μ) introduce considerable error in thin-liquid-layer apparatus.
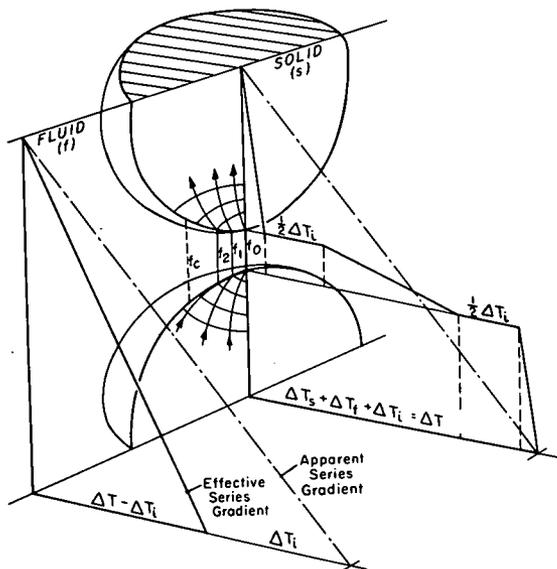
Figure 10. Series heat flow between grains.

Interfacial resistance (or equiv-alently, low surface-layer conduc-tance) is caused by the molecular discontinuity that occurs at the in-terface where two differing materi-als meet. Foreign molecules ad-sorbed by the interfaces are also likely to reduce surface conductance. Thus, interfacial resistance and its effects must be considered a definite pos-sibility in connection with surface-active granular solids. The outward effect is a reduction in the overall conductivity of the mixture. The previously mentioned ambiguity in the data of Figure 8 most likely arises from this cause.

A secondary result of the presence of boundaries and adsorbed layers in granular materials is that at every point of apparent contact there will remain two interfaces. Only in rare instances, such as in out-gassed sin-tered materials where recrystalliza-tion has progressed across crystal boundaries, will there be an obliteration of original grain surfaces leading to a true molecular matching. In the great majority of granular materials the physical reality is that there is no point at which heat can pass from grain to grain without crossing two boundaries, no matter how compact the packing may be. In other words, there is in general no solid-to-solid contact; in the resistor model equation, for example, the factor b is identically zero.

Figure 10 illustrates schematically a point of close approach between two grains in a saturated granular material. For clarity the grains are shown separated, with a finite fluid length, f_0, at the midpoint. Other fluid lengths, f_1 and f_2, occur at succes-sively greater distances from the midpoint. Each of these lengths decreases as the particles are moved closer together, the distance f_0 eventually becoming zero. Never-theless, because of the presence of the grain boundaries the flow path at the midpoint continues to be of the same character as each of the others. All flow paths between grains are therefore similar, the only variables being the distance across the inter-vening fluid and the angle at which a flow line intercepts the grain surface. No solid-to-solid connections are postulated.

A calculation made by Maxwell (11, Art. 312) indicates that currents passing through the grains will for the most part be contained by the granular boundaries, breaking through only at discrete points of high potential. Maxwell's example was that of a thin spherical shell of conductivity different from that of the media enclosed by it and sur-rounding it. His calculations led him to conclude that if the shell is a better conductor than the rest of the medium it tends to equalize the potential around the inner sphere; if it is a poorer conductor, it tends to prevent currents from reaching the inner sphere at all. In either case, the shell acts as a barrier to currents that would otherwise cross the space occupied by it. In the present context, the surface of the particle and the adsorbed layers constitute the shell of differing conductivity; the granular particle is analogous to the region within the shell.

Woodside and Kuzmak (26) demonstrated that the points of highest potential are pre-cisely those where another grain comes into near contact. Using a large model com-posed of marble hemispheres surrounded by silica gel (simulating quartz grains in moisture-saturated air) they found that temperature gradients within a radius of $\frac{1}{4}$ grain diameter from the midpoint were more than 20 times greater than the average gradient as measured in the remote fluid. It is therefore apparent that only a small

portion of the total fluid in the system will be spatially situated to contribute to the heat flow between the grains.

The lateral extent of the series conducting fluid was considered by Kunii and Smith (19) as previously mentioned; however, these investigators failed to take into account the refracting influence of the conductivity ratio of the solids and fluid. According to the law of refraction of flow lines (11, Art. 310),

$$\frac{\tan \theta_s}{\tan \theta_f} = \frac{K_s}{K_f} = \sigma \tag{11}$$

where θ_s and θ_f are the angles that the flow lines in the solid and fluid, respectively, make with the normal to the surface of separation. With $\sigma > 1$, Eq. 11 indicates that a flow line in passing from solid to fluid to solid will be refracted as shown in Figure 10. For a given value of σ there is a flow line, f_c, for which the angle of refraction in leaving the fluid equals the inclination of the solid surface; the flow surface of which this flow line is a part does not penetrate the interior of the solid and therefore marks the lateral limit of the series fluid for that region. The higher the ratio of conductivities the closer will f_c be to the midpoint, and hence the smaller will be the total volume of fluid (for a given porosity) that can be utilized as a series connection for heat passing through the grains. With $\sigma < 1$, the reverse will be true, but this situation does not generally occur with mineral solids.

THE BASIC CONDUCTANCE EQUATION

The general condition of heat flow through a granular material saturated with fluid is taken to be as shown in Figure 11. The paths of the series flow in an internal sheet one-half grain diameter in thickness are shown by solid flow lines; the paths pass through successive points of near contact, shown schematically at the near surface of the element. The mean temperature on the upper surface of the sheet is T_2, and on the lower surface T_1; the mean temperature gradient in the direction of the general heat flow is $-(T_1 - T_2)/\Delta L$, which for ΔL sufficiently large is equal to the average temperature gradient between the remote external surfaces.

In addition to the series paths there are continuous paths through the fluid, indicated by dashed flow lines passing into and out of the sheet. Maxwell's analogy of the thin shell indicates that these latter paths do not intercept the particles but in all likelihood lie entirely within the fluid. There are thus two main paths for the conduction of heat through a granular material.

A general equation describing the heat flow in Figure 11 will be of the form

$$K = f(n) K_f + f(\lambda) K_{gs} \tag{12}$$

where $f(n)$ and $f(\lambda)$ are volume functions of the fluid and solids respectively, K_f is the conductivity of the bulk fluid, and K_{gs} is the apparent conductivity over the granular series path; K_{gs} will be a function of the bulk conductivities of solids and fluid, the porosity, the amount of fluid involved in

Figure 11. General heat flow through an aggregate of grains.

the series flow, and the interfacial resistance. An expression for K_{gs} may be derived with the aid of Figures 10 and 11.

In Figure 11, between the upper and lower surfaces and along a single flow line traversing several grains, there will be a total temperature differential ΔT_n across the solids, $\Delta T_n'$ across the intervening fluid, and $\Delta T_n''$ across the interfacial regions, such that

$$\Delta T_n + \Delta T_n' + \Delta T_n'' = T_1 - T_2 = \Delta T \tag{13}$$

Assuming steady flow with no internal sinks or sources, the heat flow in a single flow tube will be given by

$$q_n = K_s \cdot \frac{\Delta T_n}{s_n} \cdot \bar{a}_n = K_f \cdot \frac{\Delta T_n'}{f_n} \cdot \bar{a}_n' = K_i \cdot \frac{\Delta T_n''}{i_n} \cdot \bar{a}_n''$$

$$= K_{gs} \cdot \frac{\Delta T}{s_n + f_n} \cdot \frac{s_n \bar{a}_n + f_n \bar{a}_n'}{s_n + f_n} \tag{14}$$

where s_n and f_n are the actual lengths of the flow tube in the domains of the solids and fluid, respectively. The thickness of the interfacial regions, i_n, is taken to be negligible compared with the values of s_n and f_n. The mean areas of the flow tube are $\bar{a}_n$, $\bar{a}_n'$ and $\bar{a}_n''$ in the solid, fluid, and interfacial domains. With $\sigma > 1$, a_n will be generally larger than a_n', whereas $a_n' \approx a_n''$ for a single flow tube. K_i is the interfacial conductance.

The volume of the flow tube in each of the domains is given by

$$v_n = \bar{a}_n s_n \; ; \; v_n' = \bar{a}_n' f_n' \; ; \; v_n'' = \bar{a}_n'' i_n \tag{15}$$

where the series interfacial volume, v_n'', is very much smaller than v_n and v_n'. Substitution into Eq. 14 gives, for the heat flow in a single tube,

$$q_n = K_s \cdot \frac{\Delta T_n}{s_n} \cdot \frac{v_n}{s_n} = K_f \cdot \frac{\Delta T_n'}{f_n} \cdot \frac{v_n'}{f_n} = K_i \cdot \frac{\Delta T_n''}{i_n} \cdot \frac{v_n''}{i_n}$$

$$= K_{gs} \cdot \frac{\Delta T}{s_n + f_n} \cdot \frac{v_n + v_n'}{s_n + f_n} \tag{16}$$

The heat flow in the entire volume of N flow tubes is then

$$Q = \sum_{n=1}^{N} q_n = K_s \cdot \frac{\Delta T_s}{s} \cdot \frac{v_s}{s} = K_f \cdot \frac{\Delta T_f}{f} \cdot \frac{v_f}{f} = K_i \cdot \frac{\Delta T_i}{i} \cdot \frac{v_i}{i}$$

$$= K_{gs} \cdot \frac{\Delta T}{s + f} \cdot \frac{v_s + v_f}{s + f} \tag{17}$$

where ΔT_s, ΔT_f, and ΔT_i are the overall mean temperature differentials across the various phases; s, f, and i are the overall mean lengths of the flow tubes in these phases; v_s, v_f, and v_i are the actual volumes of solids, series fluid, and series interfacial material. Again, i and v_i are very small.

If ΔT_i represents the summation of the interfacial temperature differentials in the volume considered, then

$$\Delta T_s + \Delta T_f = \Delta T - \Delta T_i \tag{18}$$

which may be combined in the following way with Eq. 17 to yield an expression for K_{gs}. From Eq. 17,

$$\Delta T_f = \Delta T_s \cdot \sigma \cdot \frac{v_s}{v_f} \left(\frac{f}{s}\right)^2 \tag{19}$$

Substitution into Eq. 18 gives

$$\Delta T_s = (\Delta T - \Delta T_i) \left[1 + \sigma \cdot \frac{v_s}{v_f} \left(\frac{f}{s}\right)^2 \right]^{-1} \tag{20}$$

and a combination of Eqs. 20 and 17 results in

$$K_{gs} = \left(1 - \frac{\Delta T_i}{\Delta T} \right) K_s \left(1 + \frac{f}{s} \right)^2 \left(1 + \frac{v_f}{v_s} \right)^{-1} \left[1 + \sigma \cdot \frac{v_s}{v_f} \left(\frac{f}{s}\right)^2 \right]^{-1} \tag{21}$$

A comparison of the first term of Eq. 21 with Figure 10 shows that the effect of ΔT_i is to reduce the mean effective temperature gradient along the series path. When interfacial resistance is negligible owing to a high surface conductance, ΔT_i approaches zero and K_{gs} approaches its highest value as determined by the other variables. Conversely, as interfacial resistance increases, ΔT_i approaches ΔT and K_{gs} approaches zero. The quantity $(1 - \Delta T_i/\Delta T)$ thus modifies the series heat flow irrespective of K_s, K_f, or the geometry. It is convenient to specify an interfacial efficiency applicable to the series path through a granular material as follows:

$$\epsilon = 1 - \frac{\Delta T_i}{\Delta T} \; ; (0 \leq \epsilon \leq 1) \tag{22}$$

With the incorporation of this relation, Eq. 21 becomes

$$K_{gs} = \epsilon K_s \left(1 + \frac{f}{s} \right)^2 \left(1 + \frac{v_f}{v_s} \right)^{-1} \left[1 + \sigma \cdot \frac{v_s}{v_f} \left(\frac{f}{s}\right)^2 \right]^{-1} \tag{23}$$

Equation 23 is the basic equation for the compound conductivity of the series path. The values of s and f are in general unknown, inasmuch as they depend on the geometry of a given system. However, the following approximation may be nearly correct in many instances:

$$\frac{f}{s} \approx \frac{v_f}{v_s} \equiv \frac{n_c}{\lambda} \tag{24}$$
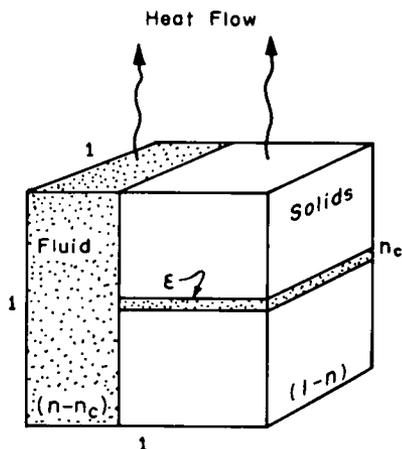
Figure 12. Schematic model of the saturated conductance equation.

where n_c is the volume fraction of fluid utilized as a series member. Substitution of Eq. 24 into Eq. 23 results in a macroscopic approximation of K_{gs} in terms of the conductivities and volumetric proportions of the constituents:

$$K_{gs} = \epsilon \, K_s \cdot \frac{\lambda + n_c}{\lambda + \sigma n_c} \qquad (25)$$

This expression is equivalent to a linear relation in terms of resistances,

$$\frac{1}{K_{gs}} = \frac{1}{\epsilon} \left[\frac{\lambda}{\lambda + n_c} \cdot \frac{1}{K_s} \right.$$

$$\left. + \frac{n_c}{\lambda + n_c} \cdot \frac{1}{K_f} \right] \qquad (25a)$$

Thus, the total series resistance is increased when ϵ is less than unity.

Referring again to Eq. 12, it remains to add the contribution to overall conductivity of the continuous paths through the fluid. Equation 25a indicates that the fractional volume of material utilized in the series path is $(\lambda + n_c)$; the remainder of the fluid volume is therefore $(n - n_c)$. Hence, with the approximation of Eq. 24, Eq. 12 becomes

$$K = (n - n_c) K_f + (\lambda + n_c) K_{gs} \qquad (26)$$

Equations 25 and 26 together describe the macroscopic heat flow in the mixture. They may be combined to give the following expression for the thermal conductivity of a saturated granular material:

$$K = (n - n_c) K_f + (\lambda + n_c) \frac{\epsilon \, K_s (\lambda + n_c)}{\lambda + \sigma n_c} \qquad (27)$$

where $\sigma = K_s K_f^{-1}$.

Equation 27 is similar in form to the modified resistor equation with $b = 0$. However, there are two important differences: (a) the effects of interfacial conductance are accounted for, and (b) the volume of series fluid is as yet unspecified, being free to vary with grain size and shape, porosity, and the conductivity ratio. A prismatic model of Eq. 27 is shown in Figure 12, which may be compared with Figure 5.

Derivations of n_c and ϵ should be possible. However, the first step will be to gain some idea of their values for particular materials. The manner in which this may be accomplished is discussed in the following.

DISCUSSION

Experimental data reported by Woodside and Messmer (2) for quartz sand, glass beads, and lead shot were previously compared with selected equations for thermal conductivity. In Figures 13, 14, and 15 these data are compared with Eq. 27. The data presented are for seven different saturants at three porosity levels. In the order of increasing conductivity ratio, the saturants are water (H_2O), hydrogen (H), helium
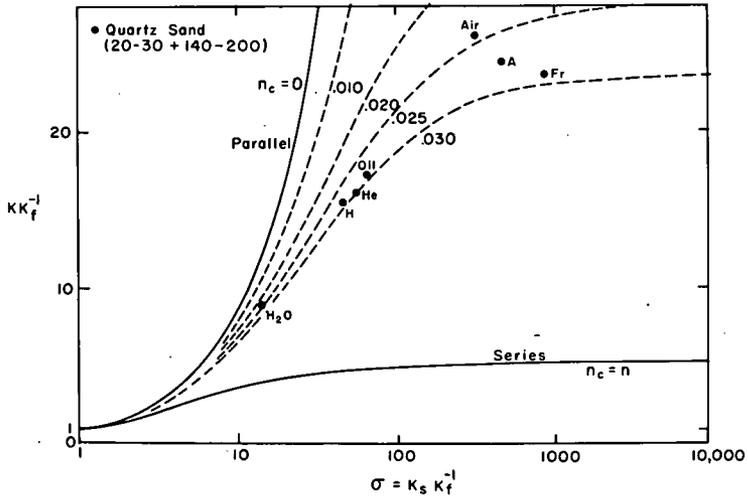
Figure 13. Comparison of the conductance equation with reported data; n = 19 percent , ϵ = 1.

(He), n-heptane (Oil), dry air (Air), argon (A), and Freon-12 (Fr), all at atmospheric pressure.

The figures show familes of curves corresponding to the calculation of conductivity with two variables, n_c and σ; ϵ was taken to be unity. If in the physical system interfacial resistance is negligible, the value of n_c read from the curves is the correct value. If in reality ϵ is less than unity, the actual value of n_c is lower than the apparent value. Curves corresponding to the parallel and series combinations of the constituents are also included. These curves are the upper and lower limits of conductivity, respectively, for ϵ = 1. They are also solutions to the conductance equation when n_c = 0 and n_c = n, respectively. The parallel and series relationships are therefore special cases of Eq. 27.

The curves labeled n_c = 0.030 are solutions to the modified resistor equation, Eq. 9. Clearly a constant value of n_c does not fit all the data. An envelope has been drawn
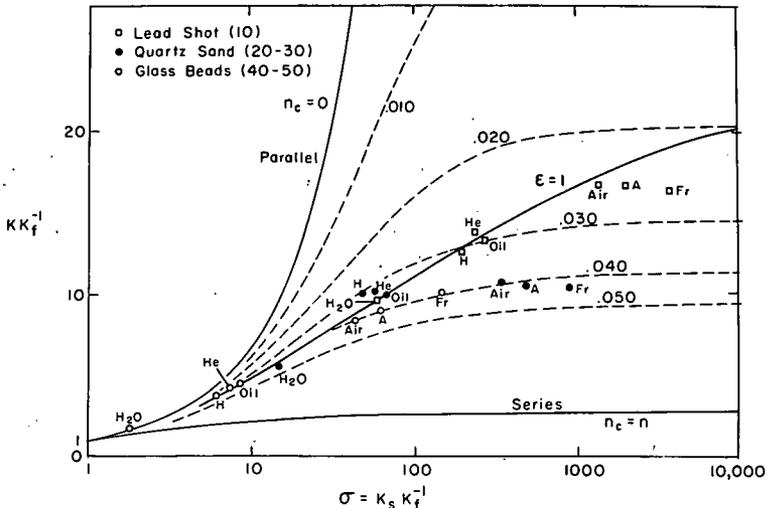
Figure 14. Comparison of the conductance equation with reported data; n = 38 percent, ϵ = 1.
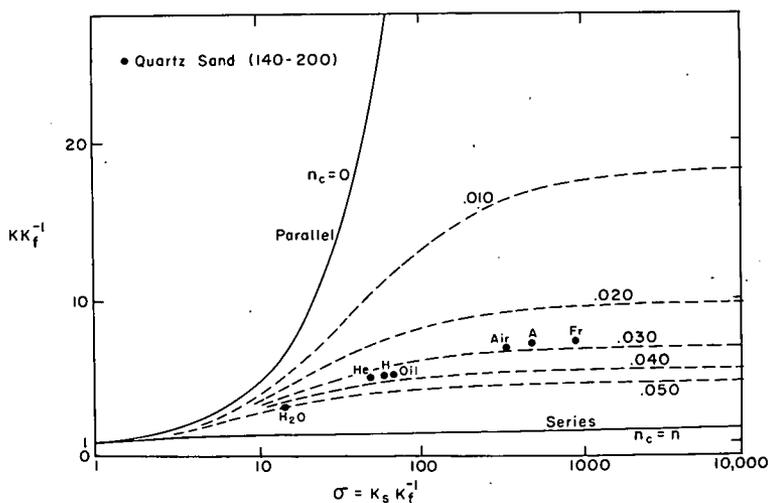
Figure 15. Comparison of the conductance equation with reported data; n = 59 percent, $\epsilon = 1$.

through the composite data of Figure 14 for 38 percent porosity. The position of this envelope is remarkably similar to the position of Kunii and Smith's estimation in Figure 8. Considering the variety of mixtures involved, it may be presumed that the envelope corresponds approximately to an efficiency of unity, and therefore to the true values of n_c. It is apparent that, at a single porosity, n_c decreases with conductivity ratio, a result that is consistent with the deduced influence of refraction. In addition, there is evidence that ϵ for dry air, argon, and Freon is less than unity; the experimental data for all three types of particles with these saturants falls below the envelope.

Envelope curves have not been drawn in Figures 13 and 15; Figure 14 illustrates that data from than one type of particle will normally be needed to define the position of the n_c-envelope for a given porosity.

Figure 16 shows the variation of n_c with n for water-saturated quartz sand ($\sigma = 14.3$). The upper curve represents the solution of Eq. 27, with $\epsilon = 1$, that fits the data shown in Figure 2. As anticipated, n_c is zero at both extremes and reaches a maximum of approximately 0.05; the mean value over the entire porosity range is very close to 0.03 for this combination of materials, as was expected. Also shown is a partial relationship for quartz sand and oil ($\sigma = 67$),

Figure 16. Volume of series fluid (n_c) vs porosity (n).
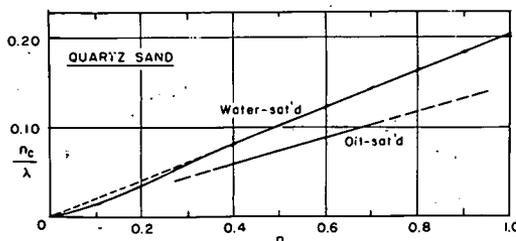
Figure 17. Volume ratio (n_c/λ) vs porosity (n).

assuming $\epsilon = 1$. For sand saturated with oil, the mean value of n_c is approximately 0.02.

Figure 17 shows the variation of the volumetric ratio, n_c/λ, with porosity. For porosities greater than 40 percent this ratio is proportional to n, being 0.20n for sand with water and 0.14n for sand with oil. The relationship is different for porosities less than 40 percent. As particles become more tightly packed, proportionately less connecting fluid is utilized.

A final remark may be made concerning the conductivity of unsaturated materials. Although Eq. 27 was derived with the assumption of full saturation, the adaptation to unsaturated conditions should require only a few additional considerations. One of the most important is the proper assessment of the volume of fluid taken up by adsorbed films at low degrees of saturation. Most of the adsorbed fluid will be part of the continuous fluid network, with only a small fraction contributing to the series connections. It may therefore be anticipated that the total volumetric water content necessary for full development of the series paths will be somewhat in excess of the actual series fluid.

SUMMARY AND CONCLUSIONS

Selected equations for calculating the thermal conductivity of granular materials have been analyzed and compared with experimental data. None of the equations was found to have a truly rational basis, although the de Vries equation and the modified resistor equation predicted the data to a fair degree. An equation by Kunii and Smith seemed to be the closest to a physical solution in form but was encumbered by empirical estimates that made it a poor approximation.

A conductance equation was then derived for saturated granular materials, based on the hypothesis that there are only two paths for heat flow through these materials: a series path through the granular network, aided by a portion of the pore fluid that acts to transfer heat from grain to grain, and a continuous path through the remainder of the fluid. A third path through continuous solid material connected at grain contact points was considered to be generally nonexistent. Every series path was assumed to cross two interfacial regions in passing from one grain to another; temperature differentials across the interfaces had the effect of reducing conductivity. The series and parallel flow equations were found to be special cases of the derived equation.

The volume of fluid brought into action as a thermal connection was found to vary with porosity and the conductivity ratio of the constituents. For systems in which the bulk conductivity of the solids exceeds that of the fluid, the maximum amount of series connecting fluid effective in any condition appeared to be approximately 5 percent by total volume.

At constant porosity, the effective volume of connecting fluid decreased with the conductivity ratio (solids to fluid). At a single conductivity ratio (14.3) the volume of connecting fluid varied from zero at porosities of 0 and 100 percent to a maximum at a porosity of 50 percent.

A transfer efficiency coefficient was defined to express the influence of thermal resistance at fluid-grain interfaces. Transfer efficiency appeared to vary with the saturating fluid. Water, hydrogen, helium, and oil had an efficiency of unity with quartz sand, glass beads, and lead shot. Dry air, argon, and Freon were less efficient with each of the three solid materials.

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