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Thermal conductivity of a partially wet granular material

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We report an experimental study of the thermal conductivity of a granular material when water is added to the system. Because of the formation of liquid bridges at the contacts between grains, the thermal conductivity increases. Below a critical amount of water, the number of bridges increases. Any additional water simply flows by gravity to the bottom of the container. Simple theoretical models account for both the critical amount of water and the measured thermal conductivity.

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Granular media exhibit amazing behavior, when at rest, these systems are known to be metastable, and, for instance, their mechanical properties depend on their history [1]. If a large enough shear stress is applied, they can flow almost like liquids, but they exhibit solid-like frictional properties [2]. As well as the understanding of their mechanical properties, the study of the transport coefficients in granular matter addresses interesting and puzzling questions. In particular, the physics of the contact between grains, as well as the nature of the granular packing, play an important role in the thermal and electrical conductivities in these systems [3]. These properties are of great practical importance both in nature and in industry because they determine, for instance, the electrical conduction of a carbon powder used as contact, or the efficiency of sand buffers used in nuclear-waste deposits. Studying the effect of humidity at the contact scale could also help in understanding the effect of humidity on the thermal properties of glasswool commonly used as thermal insulators. Experimental and theoretical studies of the thermal conduction in a dry granular material have already been reported [3–5]. Humidity can modify significantly the ability of these systems to conduct heat. In the following, we extend these experimental studies to the case of partially wet granular matter and suggest theoretical explanations of our findings.

The principle of the experiment is similar to the one used in Refs. [4,5]. We measure the energy loss through a column of granular material in the steady state. We impose the temperature of the outer surface T_0 while we inject a given heating power P per unit length along the axis. In the steady state, the asymptotic temperature T_i of the material along the axis depends on the thermal conductivity k of the material. The larger k is, the smaller T_i is.

The experimental setup (Fig. 1) consists of a copper tube (length: 15 cm, outer radius: 3 cm, inner radius: $R_0 = 0.6$ cm) maintained at constant temperature $T_0 = 50.00 \pm 0.05\,^\circ\mathrm{C}$ by a temperature regulator. A second copper tube (outer radius : $R_i = 0.2$ cm), placed along the axis of the first one, contains a heating wire (constantan) used as both heating element and temperature sensor. The heating wire goes back and forth from one end to the other of the inner tube insuring that energy is homogeneously injected along the whole length of the system. The granular material fills the gap between the two tubes and two PTFE caps seal the system.

The samples are prepared by pouring a mass $m = 20$ g of granular material in the cylinder. The apparatus is then tapped in order to reach a reference state. The initial compaction of the granular material is then large enough to prevent a significant increase of its density later during the experiment. Repeatedly adding a small amount of distilled water to the system makes it possible to measure the thermal conductivity of the same granular packing with different water content (volume of water $V = 0$ to 3 ml). Each time we add water, we seal the system and set the temperature T_0 to 120 °C for 6 h in order to help the water to invade homogeneously the space between the grains. We then set the temperature T_0 to 50 °C and wait for 2 more hours (during which the water condenses homogeneously in the system) before starting the measurements.

The experiment consists in measuring the asymptotic temperature T_i of the inner cylinder for different values of the heating power P injected along the axis of the column. A power supply injects a constant current I in the heating wire. The additional measurement of the voltage U between two points A and B (distance from A to B: $d = 1$ cm) located near the half of the cylinder length gives the heating power per unit length $P = UI/d$ and the local temperature of the heating wire T_i, that we deduce from the wire resistivity per unit length $\rho = U/dI$ ($d \log \rho / dT = 3.99 \times 10^{-3}$ K^{-1}). Three

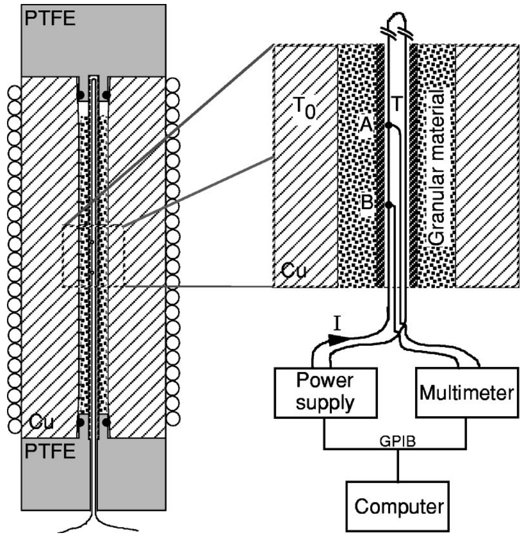

FIG. 1. Experimental setup.

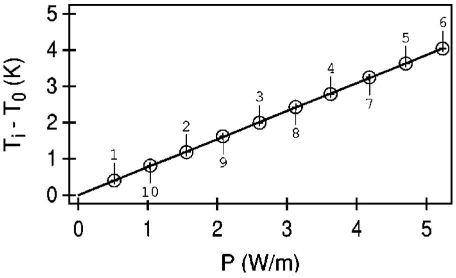

FIG. 2. Temperature difference vs heating power. We check that the thermal conductivity is not significantly modified during the measurements by increasing and, then, decreasing the heating power P (the experimental points are numbered in the order they are measured).

multimeters, connected to a computer *via* a GPIB interface, make it possible to measure simultaneously T_0, I, U for different values of I and, thus, to obtain the temperature difference $T_i - T_0$ (within 5×10^{-3} K) as a function of P. We measure the temperature difference $T_i - T_0$ in the steady regime for ten values of the heating power P (Fig. 2).

The thermal conductivity k of the granular material filling the gap between the cylinders is deduced from the experimental data as follows: the measurements are performed, far from the sealing caps, in a region where we expect the temperature field to be radial. If the temperatures of the cylinders are homogeneous, the temperature difference $T_i(P) - T_0$ is given by

$$T_i(P) - T_0 = \frac{\ln\left(\frac{R_i}{R_0}\right)}{2\pi k} P \equiv \frac{\beta}{k} P. \tag{1}$$

The thermal conductivity k is given, within a multiplicative geometrical constant β, by the slope of the linear law $T_i(P) - T_0$. Using the experimental value $R_i/R_0 = 1/3$, Eq. (1) leads to $\beta = 17.5$. We calibrated, in addition, the system by measuring the known thermal conductivity of a viscous silicon oil (Rhodorsil 47V10000 which, because of its high viscosity, avoids convection) and obtained $\beta = 18.5$. Convection would lead to underestimate β whereas the 5% discrepancy can easily originate in the uncertainty on the geometry (radii, length d between the solders in A and B, homogeneity of cylinders temperatures, . . .). In the following, we use $\beta = 18.5$.

The granular materials consist of three samples of spherical glass beads (typical diameters 45, 125, and 360 μm), and of crushed glass grains (mean size 125 μm). We use clean glass grains without any specific surface treatment. We give in Table I the size, the typical volume fraction of glass Φ, and the thermal conductivity k_0 of each of the *dry* sample.

The thermal conductivity k_0 measured in the *dry* samples of glass beads is compatible with theoretical predictions, and with former experimental results. The thermal conduction in granular packing is mainly governed by the conduction at the contact points between the grains when the thermal conductivity of the grains [$k_g = 1.4$ W/(m K) for glass] is large compared to the thermal conductivity of the material filling the space between them [$k_a = 0.025$ W/(mK) for air]. The temperature is then roughly constant within a grain except in a thin region of thickness h and radius R^* around the contact point. Assuming that the granular material is homogeneous and that its thermal properties are isotropic, Batchelor and O'Brien [3] showed that

$$\frac{k_0}{k_a} = 1 + \frac{1}{2}\Phi p\left[\ln\left(\frac{k_g}{k_a}\right)^2 + K - 3.9\right], \tag{2}$$

where p is the number of neighbors at contact with one bead, and $K = 2\ln(R^*/R)$ a constant of the order of unity. This result holds true for $k_g \gg k_a$. In a random granular packing $p \simeq 6.5$ and $\phi \simeq 0.63$ so that Eq. (2) leads to $k_0 = 0.13$ W/(mK) with $K = -2.1$ as suggested in Ref. [3]. The discrepancy between the theoretical prediction and our experimental result is about 25%. Using the usual values of p and Φ, the mean experimental value $k_0 \simeq 0.18$ W/(mK) and Eq. 2 lead to $K \simeq -1$ so that $R^*/R \simeq 0.6$ and $h/R \simeq 0.2$. The size of the region associated with a contact point is not very small compared to the bead size, but this result is not surprising as the value of the ratio $k_g/k_a = 56$ is not very large : the temperature field extends in depth in the glass bead. (We point out that the experimental value $K = -2.1$ reported for the experimental examples in Ref. [3] leads to $R^*/R = 0.35$, and then to a penetration depth $h/R = 0.06$, only three times smaller than our experimental value.) Moreover, we assumed that the surface area of the contact between two glass beads is zero (neglecting then the direct heat transfer from glass-to-glass through the Hertz' contact). Nevertheless, we can conclude that our experimental results and the theoretical description of the thermal conductivity in granular packing agree quantitatively. The discrepancy originates in the fact that the theoretical description does not account for the detailed temperature field around a contact. On the other hand, the thermal conductivity is expected not to depend significantly on the shape of the grains as long as the local shape and number of the contacts are not drastically changed. The experimental results obtained in the sample of crushed glass grains are qualitatively in agreement with this prediction.

TABLE I. Mean diameter of the grains $2R$, volume fraction of glass in the granular packing Φ, and thermal conductivity k_0 for each of the *dry* samples.

Type of grains	$2R$ (μm)	Φ	k_0 [W/(m K)]
Glass beads	045 ± 20	0.62	0.17
	125 ± 50	0.64	0.17
	360 ± 30	0.68	0.22
Crushed glass	125 ± 50	0.58	0.17

The thermal conductivity k of the granular materials depends on the water content of the system. The experimental results are given as functions of the volume fraction $f \equiv V/V_0$ of water in the free space between the grains (V is the volume of water added to the system and V_0 the free

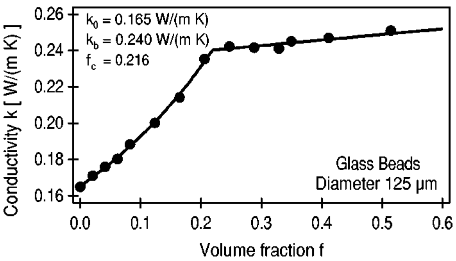

FIG. 3. Thermal conductivity k as a function of the volume fraction f in the case of spherical glass beads. Dots; experimental data. Line; interpolation [Eq. (4)].

volume available between the grains). As expected, due to the larger thermal conductivity of water $k_w=0.64$ W/(mK) (compared to air), the thermal conductivity k increases as water replaces air in the free space between the grains (Fig. 3). We point out that the results, obtained in the different samples of beads, do not depend significantly on the characteristic radius R of the grains (Table II). The most interesting feature is that the experimental data exhibit two different regimes: at small additional volume ($f<f_c\simeq 0.25$), the thermal conductivity k increases significantly (typically by 50% at f_c, we write k_b the value of k at f_c) whereas a smaller increase is observed at larger volumes ($f>f_c$). The formation of liquid bridges between grains accounts for the existence of a critical volume fraction f_c, and for the quantitative variation of k.

Indeed, in a humid granular material, the water tends to form liquid bridges where their nucleation is the easiest (i.e., at the points of contact between grains). In the experiments reported herein, the additional amount of water is always large enough to insure that the air between the grains is always vapor saturated. Thus, the geometrical characteristics of a single liquid bridge are entirely determined by the thermodynamical condition of zero pressure difference between the inside and the outside of the bridge, by the wetting condition on glass, and by the geometry of the grains. The individual volume of the liquid bridges v_b is given, provided that the size and shape of the grains are the same within the sample, and that the bridges form only where the grains are in contact (because of a high energetic barrier, the spontaneous nucleation of one bridge is difficult when the grains are apart). The number of bridges in the system is given by $N_b=V/v_b$, where V is the volume of water added to the sample. The total number of contacts in the system can be written as $N=\frac{1}{2}pm/(\frac{4}{3}\pi R^3\rho_g)$, where p is the number of contacts per grain, m the mass of grains, R the radius of one grain, and $\rho_g=2.19\ \mathrm{g/cm^3}$ the specific mass of glass. As long as $N_b<N$, the addition of water increases the number of bridges. When $N_b=N$, every available nucleation site (i.e., point of contact) is used and there is not any remaining possibility to form a new bridge. For $N_b>N$, the water added to the system simply fills the remaining free space between the grains, and flows to the bottom of the container. This feature accounts for the existence of a critical volume fraction f_c. The condition $N_b=N$ leads to

$$v_b=\frac{8}{3}\pi R^3\frac{f_c}{p}\left(\frac{1}{\Phi}-1\right). \tag{3}$$

TABLE II. Critical volume fraction f_c, thermal conductivities k_0 and k_b [Eq. (4)], volume pv_b/R^3 of water per grain, and typical number of contacts per grain p.

Type	Diameter (μm)	f_c	k_0 [W/(m K)]	k_b [W/(m K)]	pv_b/R^3	p
Glass	045	0.22	0.17	0.27	1.13	6.8
beads	125	0.23	0.17	0.24	1.08	6.5
	360	0.28	0.22	0.31	1.09	6.6
Crushed	125	0.26	0.17	0.23		

We report in Table II, the values of the typical volume of water in the bridges around a grain pv_b/R^3 deduced from Eq. 3 and from the experimental values of R and Φ. In the case of spherical glass beads, we computed $v_b/R^3=0.166$ for the experimental value of the wetting angle $\alpha\simeq 35°$ (measured, in addition, in the case of water droplets deposited on a glass plate). We then obtain the experimental value of $p=6.6\pm 0.2$ (Table II) that is in good agreement with the typical number of contacts around a bead in the case of random packing.

The formation of liquid bridges also accounts for the values of the thermal conductivity measured experimentally. Within the granular sample, there exists an isotropic random network of grains bounded by a total number N of contacts, and the thermal conductivity of the partially wet granular packing k satisfies, provided that $N_b<N$,

$$\frac{N}{k}=\frac{N-N_b}{k_0}+\frac{N_b}{k_b}, \tag{4}$$

where k_b is the thermal conductivity of the system when every point of contact is surrounded by a liquid bridge ($N=N_b$). The experimental values of k_b deduced from Eq. (4), and from the experimental data (Fig. 3) are reported in Table II [6].

We can estimate k_b by studying the thermal conductivity of a hexagonal packing of glass spheres partially bounded by water bridges. The previous theoretical description leading to Eq. (2) does not apply here because the bridges are large and the contact not independent of each other. We will assume that the system is globally isotropic so that we can calculate the thermal conductivity along any direction. We choose, for convenience, an axis perpendicular to a dense plane Π (temperature T_0), and we will estimate the mean heat flux per unit surface area assuming that the temperature of the next dense plane Π' is T_1 (Fig. 4). The temperature gradient is given by

$$\nabla T=\frac{(T_1-T_0)}{2\sqrt{\frac{2}{3}}R}. \tag{5}$$

Each grain of the plane Π accounts for a surface area $S=2\sqrt{3}R^2$, so that the heat flux through a grain H

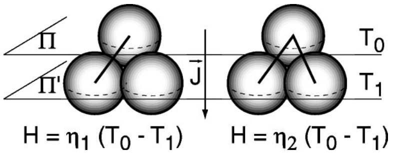

FIG. 4. Sketch of thermal conduction for hexagonal packing. On the left hand side, the grain belonging to the dense plane (Π) is connected to a single grain belonging to the next dense plane (Π′). On the right hand side, the grain is connected to two grains.

$=2\sqrt{3}R^2J$, where $J\equiv-k_b\nabla T$ denotes the heat current perpendicular to Π. The mean number of bridges around a single grain equals 6.5, so that a grain belonging to Π is statistically connected to 1.625 grains belonging to Π′. We will assume that this situation corresponds to a grain that is connected to 1 or 2 grains of Π′ with weights 0.375 and 0.625. If we define the coefficient η_1 (η_2) by $\eta_1\equiv H/(T_0-T_1)$ $[\eta_2\equiv H/(T_0-T_1)]$ when the grain is connected to a single grain (two grains) of Π′, the heat flux is given by

$$H=(0.375\eta_1+0.625\eta_2)(T_0-T_1). \tag{6}$$

As a consequence, the thermal conductivity k_b of the wet granular packing is given by

$$k_b=\sqrt{\frac{2}{3R}}(0.375\eta_1+0.625\eta_2). \tag{7}$$

We obtain, in addition, an estimate of η_1 by studying the heat flux through two glass spheres in contact connected by a cylinder of water (length $2u_0$ along the z axis, radius r_0; Fig. 5). We then do not take into account the detailed shape of the liquid bridge. Even in this simplified geometry, the determination of the exact temperature profile is not straightforward and, in order to get an estimate of the heat flux, we assume that the stream lines are parallel to the z axis.The mean thermal conductivity along the stream line located at a distance r from the axis can be written as

$$k=\frac{k_gk_wu}{k_wu+(k_g-k_w)z}, \tag{8}$$

where u is the position of the water-glass interface ($r^2=2uR-u^2$). The total heat flux H is given by

$$\frac{H}{\pi(T_0-T_1)}=\frac{k_gk_w}{k_g-k_w}\left((R+A)\log\frac{A+u_0}{A}-u_0\right), \tag{9}$$

with $A=[k_w/(k_g-k_w)]R$. In our experimental conditions, for a cylindrical bridge having the same volume as the catenoidal bridge, $u_0=0.17R$, so that $\eta_1=1.25R$ (one would find the same result within 1% with r_0 equal to the radius of the catenoidal bridge at the saddle point). The coefficient η_2 corresponds to the situation of a grain connected to two of its neighbors in the next dense plane Π′. One can estimate, by application of the superposition theorem, that $\eta_2=\frac{4}{3}\eta_1$.

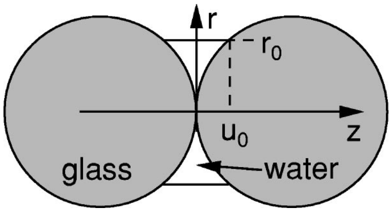

FIG. 5. Two beads bounded by a cylindrical bridge.

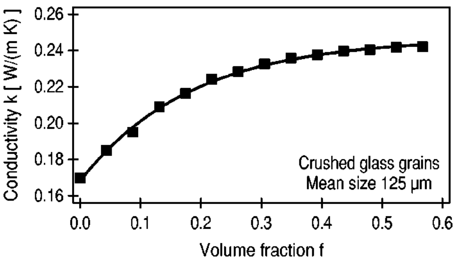

FIG. 6. Thermal conductivity k as a function of the volume fraction f in the case of crushed glass grains. Dots; experimental data. Line; exponential interpolation (see text).

The theoretical estimate of $k_b\simeq0.35$ W/m K given by Eq. (7) agrees to within 30% of the mean experimental value $k_b\simeq0.27$ W/mK. The accuracy of our estimation of k_b does not make it possible to validate our description of the thermal conduction through the contact. Nevertheless, the model accounts for the observation that adding a small amount of water (about 6% of the total volume) can produce a large variation in the thermal conductivity. It also shows that the thermal conductivity of the system remains much smaller than that of either glass or water alone. The model illustrates again the importance of the physics of contacts for the physical properties of granular packings, but the theoretical description of the thermal conductivity in such systems needs further development in order to get a more reliable estimate of k_b.

The results qualitatively change when the shape of the grains is changed. When water is added to the sample of crushed glass grains (Fig. 6), the thermal conductivity of the sample increases continuously and there does not appear a well defined critical volume of water. This result is in agreement with the variability of the size and shape of the contacts between the grains. The decreasing slope dk/df suggests that the small bridges form first. Indeed, the computation of v_b and k_b [obtained from Eq. (7)] shows that dk_b/dv_b is a decreasing function of v_b, and thus, that the small bridges are the most efficient (i.e., they induce the same change in k using less water than large bridges). The slope dk/df is always smaller for crushed glass grains than for glass beads having the same typical size, suggesting that the bridges are typically larger in this case. The thermal conductivity tends roughly exponentially to its asymptotic value with a characteristic volume fraction $f_c=0.26$ (Table II). The total variation of the thermal conductivity compares to the variation observed in samples of glass beads; assuming that k tends exponentially to its asymptotic value, and taking into account the linear increase of the measured value of k above f_c, we estimate $k_b=0.23$ W/(mK). This value of k_b is smaller than the value measured in glass beads, again in agreement with the facts that the bridges are larger in this case and that only a part of the contacts are surrounded by liquid bridges for

$f = f_c$ (the number of contacts between grains is not known in this case). We nevertheless point out that, even if the behavior of k as a function of f is qualitatively different, the total variation of the thermal conductivity k compares with the variation measured in samples of glass beads.

In summary, we have measured the effect of additional water on the thermal conductivity of packing of grains having different size and shape. The main features are as follows:

(1) The experimental value of the thermal conductivity of the *dry* samples of glass beads is in agreement with Batchelor's theoretical description of the thermal conduction of random packing of beads. The shape of the grains does not change significantly the thermal conductivity of the material.

(2) When water is added to the system, the increase of the thermal conductivity originates from the formation of liquid bridges at the points where the grains are in contact. As long as there exists in the system contacts between grains that are not surrounded by a liquid bridge, the addition of water leads to the formation of new bridges. For a larger additional volume, the excess of water, driven by gravity, simply flows to the bottom of the container where it fills the space between the grains.

(3) A simple geometrical model accounts for the experimental value of the critical volume for which every contact between grains is surrounded by a liquid bridge.

(4) A simple thermal model accounts for the measured thermal conductivities.

We plan to extend this study to the effects of both a change in the wetting properties and of an applied mechanical stress on the thermal properties of granular materials. We checked that the qualitative behavior described above (existence of a critical volume) remains true when the wetting ability of water on glass surface is changed (perfect wetting for grains cleaned in sulfochromic acid and weak partial wetting for grains whose surface is treated with silane). However, the quantitative results are not reliable because water tends to accumulate on the walls or at the bottom of the container when the wetting ability of water on the glass surface is decreased. In addition, our experimental configuration does not make it possible to apply a well-controlled mechanical stress. We expect, in this case, the grains to deform, leading to an increase in the surface area and in the number of the contacts between grains. Quantitative studies will be the subject of a further publication as they require the design of a different experimental setup.

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[6] For $f > f_c$, we still measure an increase of the thermal conductivity because the excess of water then fills the remaining space between the grains. In this case, the water flows to the bottom of the container and the sample is not homogeneous. We showed experimentally, by partially filling the system, that the measured thermal conductivity increases almost linearly with the quantity of material. In order to interpolate the experimental data, we assume that k varies linearly with f for $f > f_c$. Measurements of the thermal conductivity are then not reliable, and we will exclude this case from our study.