

Thermal conductivity of crystalline particulate materials

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In order to explore the relationship between effective thermal conductivity of an evacuated powder and the bulk thermal conductivity of the same material, the effective thermal diffusivities of particulate NaCl and Dianin's inclusion compound with ethanol guests (abbrev. ED) with effective porosities ≈ 0.5 were measured and used to determine their effective thermal conductivities below 300 K. Calculations showed that contact heat conduction is the predominant mechanism, i.e., heat transfer by radiation and by conduction through the gas phase are negligible in the measurement conditions. The effective thermal conductivity of particulate as-synthesised ED powder was found to be proportional to the bulk thermal conductivity for three different samples. On the other hand, the effective thermal conductivity of NaCl powder was found to have a softer temperature dependence than the bulk thermal conductivities reported for measurements of NaCl single crystals. This was related to increased concentration of structural defects formed during mechanical grinding of the NaCl sample. © 2000 Kluwer Academic Publishers

1. Introduction

Particulate (or granular) materials are ubiquitous in nature and also are used extensively in many technologies. Modelling of granular materials in various applications, from materials processing to geophysical and astrophysical environments, often requires knowledge of the effective thermal diffusivity, D_{eff} , and effective thermal conductivity, κ_{eff} . Dramatic differences in properties of bulk and finely divided matter have even led some scientists to refer to the latter as a separate state of matter [1]. Although the problem of heat conduction through particulate matter has been discussed for more than 100 years [2], several problems remain unresolved. Furthermore, given the difficulty in obtaining single crystals for the measurement of intrinsic thermal conductivities, it is useful to explore the relationship between the (more accessible) powder thermal conductivity and that of the bulk for well-characterized systems.

The important contributors to thermal conductivity in particulate matter can be conduction through the gas, conduction within the solid and across solid-solid contacts, and radiation. The nature of the solid material, the gas pressure, temperature, particle size, particle morphology and effect of radiation all could play roles in determining the effective thermal conductivity of particulate materials. Removal of the gas can simplify the situation somewhat and, at ambient conditions, the effective thermal conductivity of evacuated non-metallic powders can be as low as one percent of the intrinsic (bulk) thermal conductivity, κ_s [3]. According to a widely accepted [4] conjecture [5], the effective thermal

conductivity through evacuated particulate materials is virtually independent of chemical composition and can be described as the sum of a temperature-independent contact thermal conductivity term and a dominating radiative thermal conductivity term that is proportional to T^3 . This concept seems to be supported by measurements of disordered materials with low degrees of crystallinity in which the intrinsic thermal conductivity is effectively temperature independent in the temperature range between 100 and 500 K [6–8]. On the other hand, some models of heat transfer through particulate materials have assumed that the effective thermal conductivity of evacuated particles is proportional to the bulk thermal conductivity [3].

In order to delineate the relationship, if any, between effective thermal conductivity of evacuated crystalline particulate materials and intrinsic thermal conductivity, we have determined the effective thermal conductivity of two evacuated highly crystalline non-metallic powders, NaCl and a molecular crystal (Dianin's inclusion compound with ethanol guests), in the temperature range from ca. 40 K to 300 K. Most studies of thermal conductivity of particulate materials have focussed on refractory materials, and, to a lesser extent, on metals; the present investigation increases the scope to molecular materials as a step towards understanding thermal conductivity of softer particulate matter.

2. Experimental methods

Values of thermal conductivity, κ , were obtained from measured thermal diffusivity, D , and reported values of

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heat capacity, C_p , and density, ρ , according to

$$\kappa = D \cdot C_p \cdot \rho. \quad (1)$$

Thermal diffusivity was measured using a highly sensitive apparatus for modulated thermal measurements of low thermal diffusivity particulate materials at sub-ambient temperatures. This apparatus, which had been shown with solid benzene to give measurements for low thermal diffusivity materials (in the range 1×10^{-8} to $5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$), reliable within $\pm 30\%$, is described in detail elsewhere [9, 10].

Powdered NaCl of grain size less than 0.074 mm was obtained by grinding ACS grade (99% pure) polycrystalline NaCl material in a ball mill. The powder was heated for 24 hours at 420 K and then evacuated for 24 hours after placement in the cell to remove adsorbed gases. The resulting particulate material was characterized by $50 \pm 2\%$ porosity [porosity p is defined as $p = (\rho_{\text{bulk}} - \rho_{\text{eff}}) / \rho_{\text{bulk}}$].

The particulate sample of the molecular solid was Dianin's inclusion compound [4-(3,4-dihydro-2,2,4-trimethyl-2H-1-benzopyran-4-yl)phenol] with ethanol as guest (abbrev. ED) [11], obtained by recrystallization of ED from ethanol solution (quench of a near-boiling saturated solution in an ice bath, followed by cooling to 260 K). The maximum size of needle-shaped crystals in the unsieved sample, called ED-I, was around 0.6 mm by 0.05 mm. Another two samples, ED-IIa and ED-IIb, were prepared by the same method but with smaller quantities, and this produced more homogeneous particles sizes, an order of magnitude smaller than in ED-I. Each sample was placed in the cell and tapped lightly for 5 min; then the cell was evacuated briefly with a roughing pump to remove air and to establish saturated vapour conditions. The effective porosity for each was $50 \pm 2\%$, i.e. essentially the same as for NaCl.

3. Results and discussion

3.1. Effective thermal conductivities

The measured thermal diffusivities were used to determine the effective thermal conductivities using Equation 1. For NaCl, using the literature data for heat capacity [12] and thermal expansion [13, 14] gave the values of κ_{eff} shown in Fig. 1. Similarly, known values of heat capacity [15] and thermal expansion [16],

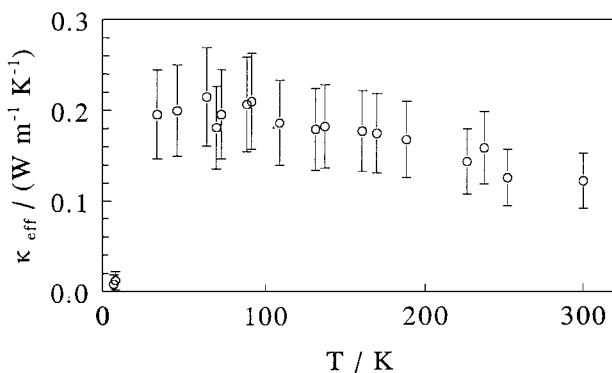


Figure 1 Effective thermal conductivity of milled NaCl powder in vacuum as a function of temperature. Error bars represent both systematic and random uncertainties.

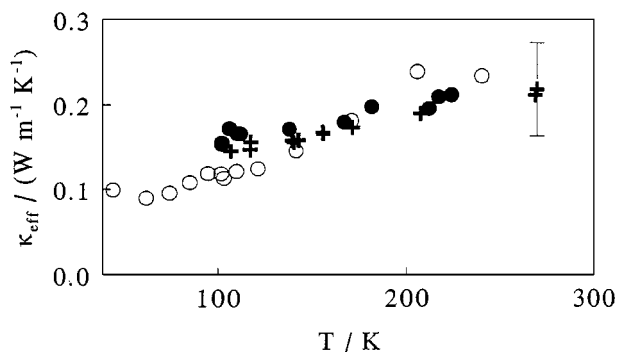


Figure 2 Effective thermal conductivities of evacuated, powdered samples of the Dianin inclusion compound with ethanol guests, as functions of temperature. The error bar represents total uncertainty (random and systematic). + ED-I; \circ ED-IIa; \bullet , ED-IIb.

allowed the conversion of thermal diffusivity to κ_{eff} for ED, as shown in Fig. 2. Before comparing effective and bulk thermal conductivities, it is necessary to estimate contributions of heat transfer by conduction through the gas phase and by radiation to the total thermal conduction.

3.2. Heat conduction through the gas phase

The thermal conductivity of a gas phase at such low pressures that the gas exhibits properties of a discontinuous medium [this critical Knudsen pressure can be found as $P_{\text{Kn}} = 2^{3/2} k_B T / (\pi \sigma_{\text{cs}}^2 d)$, where σ_{cs} is the effective collision cross-section of a gas molecule and d is the effective dimension of pore space, $d \approx \eta / 100$, where η is the mean particle diameter] [17] can be estimated from [18]

$$\kappa_f = Y'' \cdot P \cdot d \cdot T^{-1/2}, \quad (2)$$

with the coefficient Y'' given by

$$Y'' = \frac{Z(\gamma_g + 1)C_v V_{\text{mol}}}{2(2 - Z)\sqrt{2\pi R}} \quad (3)$$

where Z is the accommodation coefficient, R is the gas constant, V_{mol} is the molar volume and γ_g is the ratio of heat capacities ($\gamma_g = C_p / C_v$).

It is illustrative to calculate the thermal conductivity through helium gas at 300 K, the largest contribution to heat transfer through the gas phase for the present experiments. The critical Knudsen pressure can be estimated to be $8 \times 10^4 \text{ Pa}$ for $\eta = 0.05 \text{ mm}$ (thus, $d = 5 \times 10^{-7} \text{ m}$) and $\sigma_{\text{cs}} = 2.18 \text{ \AA}$ [19]. Assuming ideal gas conditions, $\gamma_g = 5/3$ and $C_v = 3R/2$, the parameter Y'' is $36.4 \text{ m}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$ for ideal conductive heat transfer from incident gas molecules to the surface of the solid particles, i.e. $Z = 1$. At 100 Pa, the upper limit of the pressure in the present experiments, the effective thermal conductivity of the gas phase, κ_f , is $2.1 \times 10^{-5} \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Thus, for sodium chloride powder with an effective thermal conductivity at 300 K of ca. $0.13 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, conduction through the gas phase constitutes less than 0.02% of the heat transfer at pressures less than 100 Pa. For ED, this contribution is even less, ca. 0.01%.

3.3. Heat conduction through radiation

To estimate the radiative contribution to the total heat transfer, the Rosseland formula [20] for radiative thermal conductivity can be used:

$$\kappa_R = 16n_R^2\sigma_R T^3/[3(\alpha_R + \beta_R)], \quad (4)$$

where n_R is the refractive index of a solid, α_R and β_R are, respectively, the effective absorption and scattering coefficients of the heterogeneous material, and σ_R is the Stefan-Boltzmann constant. It has been shown [8] for spherical particles at 300 K that the effective scattering coefficient, β_R , can be estimated as $12(1-p)/[\eta(2-p)]$. Radiation absorption at these temperatures is negligible for sodium chloride powder [21], and therefore, the radiative thermal conductivity coefficient can be written as

$$\kappa_R = 4n_R^2\sigma_R T^3\eta(2-p)/[9(1-p)]. \quad (5)$$

At 300 K, the maximum radiation intensity is at a wavelength of 9.64×10^{-6} m according to Wien's displacement law [22], and the refractive index of sodium chloride for this wavelength is 1.49 [21]. Thus, the estimated pre-temperature term in the expression for radiative thermal conductivity in a powder of porosity 0.5 is $1.66 \times 10^{-11} \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-4}$, and, at 300 K, $\kappa_R = 4.5 \times 10^{-4} \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Therefore, radiation constitutes only 0.6% of the heat transfer in this sodium chloride powder at ambient conditions (and less at lower temperatures), and this mode can be neglected. A similar situation would be expected for ED.

3.4. Contact thermal conductivity

We have shown above that heat transfer through radiation and gas thermal conduction is negligible in these conditions, so the conduction through the solid sample is the dominant mechanism. The coefficients of contact thermal conductivity, A_{cont} , defined as

$$A_{\text{cont}} = \kappa_{\text{eff}}/\kappa_s \quad (6)$$

where κ_{eff} and κ_s are the effective and bulk thermal conductivities, can be investigated as functions of temperature. A_{cont} is shown in Figs 3 and 4 for NaCl and ED, respectively.

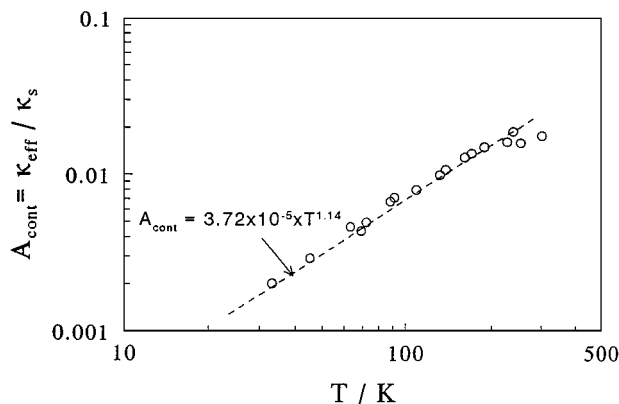


Figure 3 Contact thermal conductivity of evacuated, milled NaCl powder as a function of temperature.

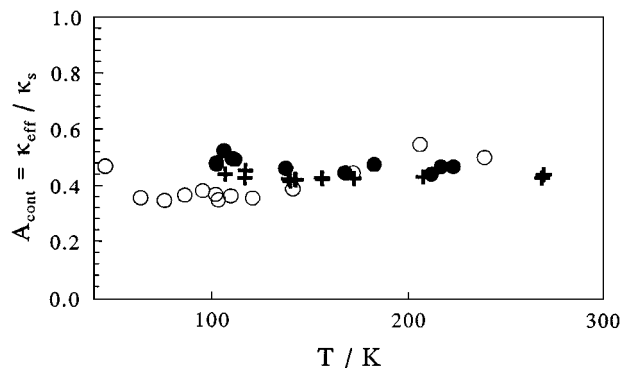


Figure 4 Contact thermal conductivity of evacuated, powdered samples of the Dianin inclusion compound with ethanol guests, as functions of temperature. + ED-I; o ED-IIa; • ED-IIb.

3.4.1. NaCl

Bulk thermal conductivities for NaCl were from measurements [23] of a 1 cm single crystal. In order for A_{cont} to be meaningful, the value of κ_s used in its derivation should be representative of the particulate sample, which probably is not the case here. The basis of this remark is that the maximum in the effective thermal conductivity of the present sodium chloride powder was found at ca. 75 K, while in single crystals the maximum is observed at ca. 15 K [23], which shows that the NaCl powder has been degraded. The change in κ likely is related to an increase in the concentration of structural defects in NaCl, produced during milling in the mechanical ball mill. Calculations suggest that local pulsed pressures created in such mills can be as high as 7 GPa [10], and mechanical grinding has been shown to induce phase transformations with critical pressure of up to 20 GPa [24]. Apparently, even grinding in a mortar can initiate transformations that have transition pressures of up to 1.5 GPa at room temperature [25]. (Grinding of Dianin's compound has been shown to induce irreproducible structural changes [11], and for this reason the ED samples in this work were not mechanically treated. Molecular solids likely are even more susceptible to damage by grinding than ionic salts: solid state amorphization of organic molecular crystals has been shown to occur in a vibrating mill [26].) Although sodium chloride exists as only one polymorph with rock-salt structure at ambient conditions, and milling is unlikely to lead to the pressure-induced CsCl structure (requiring a pressure of 26.8 GPa) [27, 28], an elevated concentration of structural defects can be expected after milling the NaCl sample. Most of the temperature-dependence of A_{cont} in powdered NaCl ($A_{\text{cont}} \propto T^{1.14}$, see Fig. 3) can be attributed to κ_s : fit to the experimental values of bulk thermal conductivity of sodium chloride [23] in the temperature range between 50 K and 400 K gives $T^{-1.23}$ dependence, and $\kappa_{\text{eff}} \propto T^{-0.1}$ at $T > 100$ K. A very weak temperature dependence of κ_{eff} for microcrystalline conglomerates has been reported and related to various kinds of structural disorder [29, 30]. A slightly positive or zero temperature gradient of thermal conductivity has been observed in the "ultimately" disordered amorphous solids [31]. Another example of softening of the temperature dependence of thermal conductivity has been observed for

local disorder induced by irradiation in quartz crystals [32]. Calculations, based on the experimentally determined parameters describing phonon relaxation processes in NaCl [23], indicate an effective NaCl crystallite dimension of 10^{-4} mm, less than 1% of the true dimension, again supporting the concept of a high concentration of mechanical defects. Therefore, it seems likely that the strong temperature dependence of A_{cont} observed for powdered NaCl is attributable to the temperature dependence of κ_s .

3.4.2. Ethanol-Dianin

The values of κ_s used to determine A_{cont} for ED were from measurements [33] along the c -axis of a single crystal of effective dimension ca. 1 cm and, as indicated above, the preparation of ED powder should not have introduced defects. Therefore, A_{cont} for ED should allow a test of the relationship between κ_{eff} and κ_s for an evacuated molecular crystal. From Fig. 4, A_{cont} can be seen to be essentially temperature independent, and also independent of the samples (ED-I, ED-IIa, ED-IIb). The difference in the values of contact thermal conductivity for NaCl (ca. 0.02 at 300 K) and ED (ca. 0.4 at all temperatures) can be related to a number of factors, especially the larger contact area in ED powder due to the needle-like shape of ED crystals and the larger compressibility compared to NaCl (1.3×10^{-10} Pa $^{-1}$ vs. 3.9×10^{-11} Pa $^{-1}$) [34, 35]. Additional phonon scattering from structural defects in NaCl powder (*vide supra*) also can contribute to the reduction of the contact thermal conductivity.

A_{cont} for all three samples of ED remains essentially independent of temperature (Fig. 4), similar to the behaviour observed for microcrystalline conglomerates [36]. It is possible to apply the semi-empirical cellular model [37], one of the few models of heat transfer in particulate materials applicable to evacuated powders, to deduce information about the effective contact area between particles. This model relates contact thermal conductivity of evacuated particulate materials to porosity as

$$A_{\text{cont}} = \zeta(1 - p)^{1/2}, \quad (7)$$

where ζ is a flattening coefficient ($\zeta = 23\eta_c / [\eta(1 + 22(\eta_c/\eta)^{4/3})]$) for effectively spherical particles with η_c as the mean diameter of the contact between two particles). The value of A_{cont} in ED suggests that the equivalent flattening coefficient is 0.6, which is significantly larger than found for powders of highly crystalline framework silicates (0.2 for the dehydrated zeolite, NaA) [10].

4. Conclusions

The present experiments delineate contact thermal conductivity of powdered samples, i.e. radiation and heat conduction through the gas phase are shown to be negligible. In these conditions, the ED results show that the effective thermal conductivities of highly crystalline as-synthesised powders of a molecular solid are propor-

tional to the bulk thermal conductivity, and therefore measurements of powder samples yield direct information concerning the temperature-dependence of the bulk sample. On the other hand, the temperature dependence of the effective thermal conductivity of NaCl powder obtained by mechanical grinding is softened compared to the bulk thermal conductivities of single crystals, and this is related to the formation of high concentrations of structural defects in grains of particulate materials giving rise to enhanced phonon scattering and consequently to a less negative temperature gradient of the effective thermal conductivity of the grains. Therefore, for effective thermal conductivities of evacuated powders to be representative of the bulk thermal conductivity, the effects of radiation must be negligible, and the sample must be representative of the bulk material, especially with respect to structural defects.

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