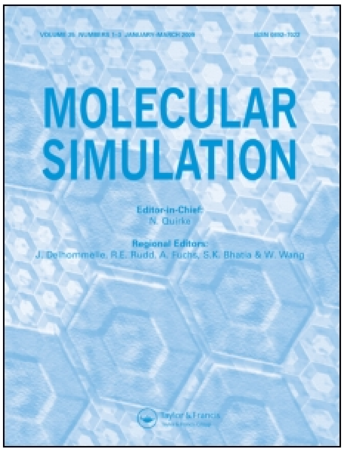

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Heat Transfer of Premelted Ice in Micro- and Nanometer-sized Powders

Nanxia Rao[a]; Da-Ming Zhu[b]
[a] Department of Physics, University of Missouri-Kansas City, Kansas City, MO, USA [b] Department of Modern Physics, University of Science and Technology of China, Hefei, China

To cite this Article Rao, Nanxia and Zhu, Da-Ming(2004) 'Heat Transfer of Premelted Ice in Micro- and Nanometer-sized Powders', Molecular Simulation, 30: 2, 183 — 188

To link to this Article: DOI: 10.1080/0892702031000152082

URL: http://dx.doi.org/10.1080/0892702031000152082

Molecular Simulation, Vol. 30 (2–3), 15 February–15 March 2004, pp. 183–188

Heat Transfer of Premelted Ice in Micro- and Nanometer-sized Powders

NANXIA RAO[a] and DA-MING ZHU*[,b]

[a]*Department of Physics, University of Missouri-Kansas City, 5110 Rockhill Road, Kansas City, MO 64110, USA;* [b]*Department of Modern Physics, University of Science and Technology of China, Hefei, China*

(Received October 2002; In final form January 2003)

Heat transfer properties of premelted ice in silica powders were studied in a temperature range slightly below 0°C. The thermal conductivity of the ice was found to be much smaller than that of bulk ice. A drop in the thermal conductivity is observed at the melting, similar to bulk behavior, but the magnitude of the drop is much smaller than that found in the bulk phase. The heat transfer rate versus temperature gradient of ice in silica powders was found to deviate slightly from a perfectly linear behavior. The deviation could be due to a disruption of homogeneity of the powder media, due to a thermomolecular pressure. Such an effect needs to be further confirmed by future experiments.

Keywords: Thermal conductivity; Interfacial melting; Powders; Heat transfer

INTRODUCTION

The melting of ice in porous media, which plays important roles in many thermal, biological, chemical, and geological processes of natural environment [1,2], has been investigated extensively in recent years using various techniques [3–11]. The results all show that a thin water layer exists at temperatures below 0°C at the ice-particle interfaces or in small voids, and the thickness of the water layer or the volume fraction of the water increase as temperature approaches to the bulk melting point [2,3]. This behavior is called premelting, and is attributed to the combination of a finite size effect and an interfacial melting mechanism in which the competition of interfacial free energies causes a thin layer of ice at the interface being converted to water below the bulk melting temperature [2]. The phenomenon is not unique to ice; finite size effect is a general property of matters confined in small pores, and the evidences of interface and surface melting have been found in several other types of solids including metals and rare gas solids [12–14].

Recent studies of premelting phenomena have been extended to the flow and other non-equilibrium properties of interface (surface)-melted layers [15–17]. Premelted water layers are found to flow spontaneously from warmer to colder regions. The flow is explained as being due to a thermomolecular pressure induced by the temperature gradient. Such a flow is believed to be the cause of *frost heave* [1,2], a common and somehow mysterious phenomenon which refers to the deformation of wet soil during freezing weather. Again, frost heave is not unique to ice; the phenomenon has been recently observed in He confined in porous glass and Ar in silica powders [18–20].

In this paper, we present the results of a preliminary study of heat transport, another non-equilibrium property, of premelted ice in micro- and nanometer-sized silica powders. Several experimental studies demonstrated that premelted water exists at the interface between ice and silica powder below the ice point, and water fraction in a silica powder compacts can be as high as 10% at temperatures several degrees below 0°C [3,8,10]. Frost heave of ice in silica powders was also demonstrated in well-controlled laboratory experiments [21]. As will be discussed below, heat transfer carried by the flow of a premelted liquid is directly associated with the mass flow in frost heave. This study focused on a relatively narrow temperature range below 0°C. The purpose of the study is to investigate how the thermal transport properties of ice are affected by

---

*Corresponding author. E-mail: zhud@umkc.edu

ISSN 0892-7022 print/ISSN 1029-0435 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/0892702031000152082

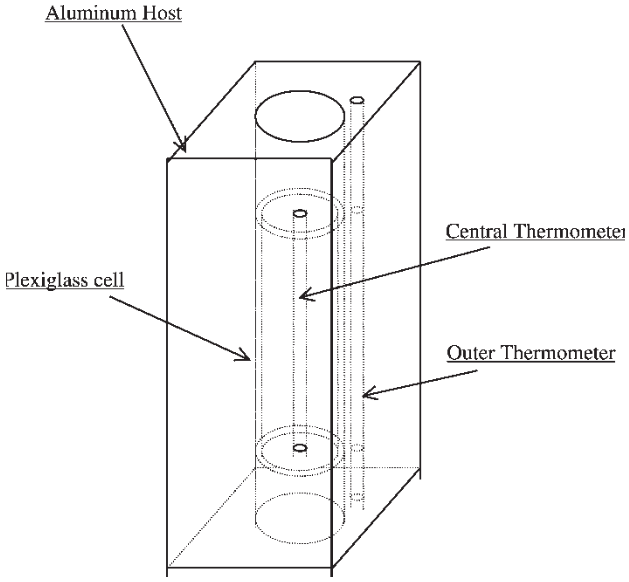

FIGURE 1 Experimental cell configuration. The aluminum host was attached to a temperature controlled cold stage.

premelting in powder media and if the heat transfer carried by the frost heave flow of premelted ice can be detected by a conventional technique used in measuring thermal conductance.

EXPERIMENTAL

The experimental configuration used in measuring thermal conductance of ice in silica powders was similar to that used in a typical "hot wire" method [22]. Silica powders were packed in a thin wall cylindrical plexiglass cell of 2.5 cm long and 0.7 cm in diameter with a wall thickness of 0.12 cm. The cell was placed in an aluminum host, as illustrated in Fig. 1. A thin layer of vacuum grease was applied to the outside surface of the plexiglass cell to ensure a good thermal contact between the cell and the aluminum host. The aluminum host is open at both ends so the cell contacts with the host only through the sidewall. A platinum thermometer tightly fitted in a thin wall copper tubing jacket was placed along the central axial position of the cell, as shown in the figure. A second platinum thermometer was embedded in a position close to the inner edge of the aluminum host. Both thermometers were calibrated against a standard thermometer. A removable cap was placed on the top of the tube after the tube was packed with the powders. The amount of the powders was carefully weighed and the packing ratio was calculated using the measured dimensions of the cell and the thermometer.

Two types of silica powders were used in the study. One is mono-sized spherical powder with a diameter of 5.3 μm,[†] the other has an averaged diameter of 12 nanometer (nm) with a 40% size dispersion.[‡] Both types of powders were used as received. The packing processes were handled carefully to assure the uniformity and the absence of void in the packed powders. The cell was not packed full with the powders, a space was left above the top of the powder and below the cap, so the pressure generated within the powder compact would push silica particulates to move upwards. The packing ratios were calculated using the measured mass of the cell before and after being packed with powders and their volume. The volume-packing ratio is 0.34 for the 5.3 μm powders and 0.16 for the 12 nm powders.

A steady-state method was used in measuring the thermal conductance of the powders [22]. The temperature of the aluminum host was controlled to a precision of 0.01 K using a temperature controller. The central platinum thermometer serves a dual purpose of a thermometer and a resistance heater. During each measurement, the temperature of the aluminum host was kept at a constant while a heating current was supplied to the central platinum thermometer. The current causes the thermometer to self-heat and the resistance of the thermometer determines its temperature. By varying the current supplied to the central thermometer, its temperature can be varied. As mentioned above, the thermal linkage from the two ends of the cell to the surroundings is very weak, so heat generated in the central thermometer flow mainly in radial directions inside the plexiglass cell. Solving the heat conduction equation describing the heat flow radially through different layers of materials in the cell yields an expression of heat transfer [23]:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{2\pi L(T_1 - T_2)}{\frac{1}{\kappa}\ln\left(\frac{r_1}{r_2}\right) + \frac{1}{\kappa_\mathrm{p}}\ln\left(\frac{r_2}{r_3}\right) + \frac{1}{\kappa_\mathrm{c}}\ln\left(\frac{r_t}{r_1}\right)} \tag{1}$$

where L is the height of the cell, r_t and r_1 the inner and outer radiuses of the copper tubing, r_2 and r_3 the inner and outer radiuses of the plexiglass cell, κ the thermal conductivity of silica powder compacts, κ_p and κ_c the thermal conductivities of plexiglass and copper, respectively, T_1 and T_2 the temperature measured by the two thermometers. The contribution from the term involving κ_c can be neglected since copper's thermal conductivity is much higher than that of plexiglass and silica powders. It should be mentioned that in the derivation of Eq. (1) the thermal resistance at boundaries between different layers are neglected.

[†] The 5.6 μm monosized silica powders were obtained from Professor Dash's group at the University of Washington.

[‡] Degussa Corp., Silica Division, 65 Challenger Rd, Ridgefield Park, NJ 07660, USA.

Using the known thermal conductivities of plexiglass and copper and the measured dimensions of the components of the cell, the thermal conductivity κ of the powders, or ice mixed with the powders, can be derived using Eq. (1).

In this study, the thermal conductivities of the dry powders were measured first. Then purified water was added to the plexiglass cell. The amount of the water added was determined by weighing the cell before and after the water was added. The mass ratios of water versus powders were cross checked with the volume-packing ratios and were found to be consistent. The thermal conductivities of ice in powders were then measured using the exactly same measuring procedure.

RESULTS AND DISCUSSIONS

Thermal Conductance of Ice in Silica Powders

Figure 2 displays the thermal conductivities of dry silica powders. The missing volumes in the powders were corrected using the measured filling factors. Also plotted is the thermal conductivity of bulk silica for comparison [24]. The thermal conductivities of the two types of silica powders are about a factor of four smaller than that of bulk silica. We think this is due to large interface area involved in the media. The total interface areas are about 34 m^2 and 6400 m^2 for the 5.3 μm and 12 nm powder compacts, respectively. The large interface area divides the medium into a large number of layers, resulting a significant boundary thermal resistance in the medium. It is surprising that the thermal conductivities of the two types of silica powders, although their sizes differ significantly, are quite close to each other. However, phonon mean free path in silica at these temperature is less than 1 nm [25], so the size difference here would not strongly affect the bulk contribution to the thermal conductance. The fact that the effects from interfaces between particles are similar suggests that the thermal conductance in the powders are dominated by the contact areas in neighboring particles and the total contact areas between neighboring particles of the powder compacts as a whole are not strongly dependent on particle sizes.

Adding water to a powder media introduces additional thermal paths, thus the thermal conductivity of ice in powders is derived by considering that ice is connected in parallel to the powders in conducting heat. Figure 3 plots the thermal conductivity of ice as a function of temperature, after being scaled by the filling factors which take into account the volume occupied by the powders. Also plotted is the thermal conductivity of bulk crystal ice and water [26]. The data show a reduction in the thermal conductivity of ice confined in the powders. Since the thermal conductivity of water is smaller than that of ice, the reduction can be due to both boundary resistance and/or premelting of ice. It is interesting to note that the temperature dependence of ice in 5.3 μm powders is similar to that of a bulk crystal, while the temperature dependence of ice in 12 nm powders resembles that of amorphous ice [26], suggesting that ice in nanometer powders used contains a significant amount of disorder. In both cases, the thermal conductivity shows a small drop at the melting temperature.

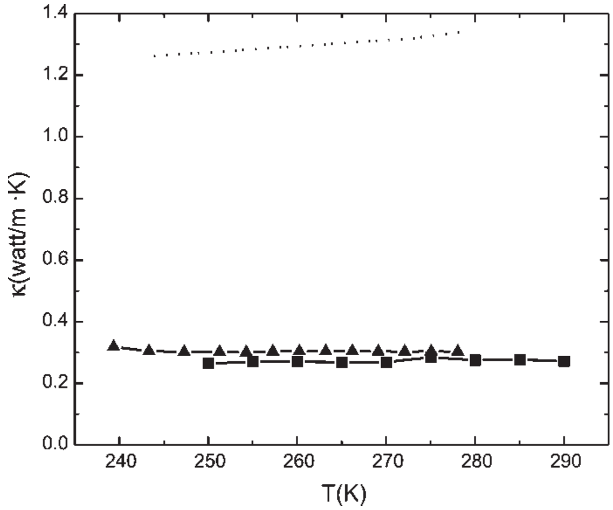

FIGURE 2 Thermal conductivity of silica powders (▲) 5.3 μm; (■) 12 nm. The dotted line represents the thermal conductivity of bulk silica [24]. The solid lines are the guides to the eyes.

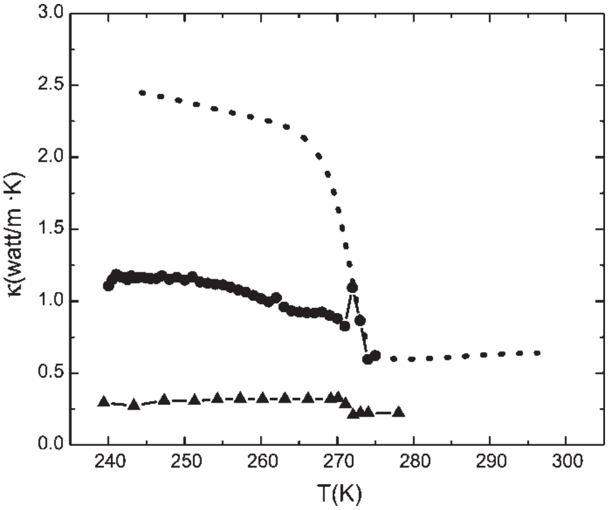

FIGURE 3 Thermal conductivity of ice and water in silica powders (●) 5.3 μm (▲) 12 nm. The dotted line represents the thermal conductivity of bulk ice crystal and water [26]. The solid lines are the guides to the eyes.

Non-linear Heat Transfer Associated with Frost Heave

As mentioned above, the main purpose of the study is to search for evidence of non-linear heat transfer associated with frost heave of ice in powder media. The fundamental mechanism of frost heave has been recently explained in terms of an interfacial melting theory [1,2,17–19]. The theory assumes that a premelted liquid layer, due to interfacial melting and/or curvature effect, exists at an ice-particle wall interface. A temperature gradient applied in parallel to the interface induces a thermomolecular pressure which drives the liquid to flow towards lower temperatures. The liquid layer thickness is determined by local temperature. Under a stable condition, the liquid flown to lower temperatures has to be converted to solid to maintain a constant liquid thickness profile. Thus solid "lens" starts to grow in the colder region. The liquid continues to flow until a sufficient pressure build-up in the region to counteract the flow. Usually the ground soil (or the porous media in general) would be broken open before this maximum frost heave pressure is reached, which allows more liquid to flow into the region and being frozen, resulting a growing bulk solid [2,15,16].

The flow of premelted liquid from warmer to colder regions generates additional heat transfer channels, thus enhances the thermal conductance of the system. The enhancement comes from two contributions. The first is due to the flow of premelted liquid itself. The liquid flows through a distance Δx with a temperature difference ΔT, cools as it flows, transporting heat $c\Delta T$ across the distance, where c is the heat capacity per unit volume of the liquid. The heat transfer rate across the distance Δx due to this component is

$$\frac{\mathrm{d}Q_1}{\mathrm{d}t} = cV_f A\Delta T,$$

where A is the cross sectional area of the liquid and V_f the speed of the liquid along the direction of the temperature gradient. The second contribution is from the deposition of latent heat of fusion as the flowing liquid converting to solid. The heat transfer rate due to this component is

$$\frac{\mathrm{d}Q_2}{\mathrm{d}t} = qV_f\left(\frac{\mathrm{d}A}{\mathrm{d}T}\right)\Delta T,$$

where q is the latent heat of fusion of the liquid. Combining the two contributions, the total enhancement to the heat transfer rate can be expressed as

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \left(cA + q\frac{\mathrm{d}A}{\mathrm{d}T}\right)V_f\Delta T.$$

Assuming the flow of a premelted liquid obeys Darcy's law [27], the flow speed can be written as

$$V_f = \left(\frac{k}{\mu}\right)\left(\frac{\Delta P}{\Delta x}\right)$$

where k is the permeability of the medium, and μ the viscosity of the liquid. In this equation, ΔP is the thermomolecular pressure created due to ΔT [2]:

$$\Delta P = \rho q\frac{\Delta T}{T_0},$$

where ρ is solid-state density and T_0 the bulk melting temperature. Combining these equations yields the heat transfer rate due to the heat transfer associated with the flow of premelted liquid:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \left(cA + q\frac{\mathrm{d}A}{\mathrm{d}T}\right)\left(\frac{k}{\mu}\right)\rho q\frac{(\Delta T)^2}{T_0\Delta x}. \tag{2}$$

A unique feature of this excess heat transfer is its non-linear dependence on the temperature difference across Δx, which distinguishes itself from the conventional thermal conductance of solids. The non-linear heat transfer rate would give rise to a temperature-gradient dependent component in the thermal conductance of the system.

Obviously, the magnitude of the excess heat transfer depends on the properties of a premelted liquid and the medium that hosts the liquid. Although premelting has been observed in a number of systems, the properties of the premelted liquids are largely unknown. The results from computer simulations show that all the properties of a premelted liquid are intermediate between those of the bulk solid and liquid phases [28,29]. In particular, the properties of a premelted liquid are affected by the presence of neighboring solid walls that impose a layer-like order in the liquid [28,29]. The ordering affects the dynamic and the thermodynamic properties of premelted liquids, causing an anisotropic decrease in mobility of the liquid and a reduced entropy change, and thus a much smaller latent heat, as the solid being converted to a premelted liquid [2,14]. The viscosity of a thin water film on a solid surface can also be much larger that of the bulk water [30]. Unfortunately, these properties have not yet been determined quantitatively, which makes the estimate of the magnitude of the excess heat transfer difficult.

In order to observe the non-linearity of heat transfer rate versus temperature gradient, an experiment needs to be designed so that there is a continuous fluid supply and flow path. The current experimental setup does not provide that. But, a temperature gradient along the radial direction would disrupt the homogeneity of the powder media, causing the powder in the high thermomolecular pressure region to be pushed upwards,

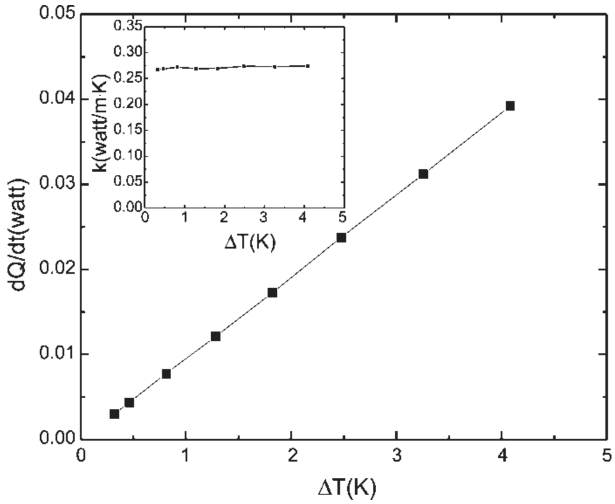

FIGURE 4 Heat transfer rate in dry silica powders versus temperature gradient across the radius of the cylindrical cell at $T = 270\,\mathrm{K}$. The inlet is the thermal conductivity of the dry powders versus temperature gradient. The solid lines are the guides to the eyes.

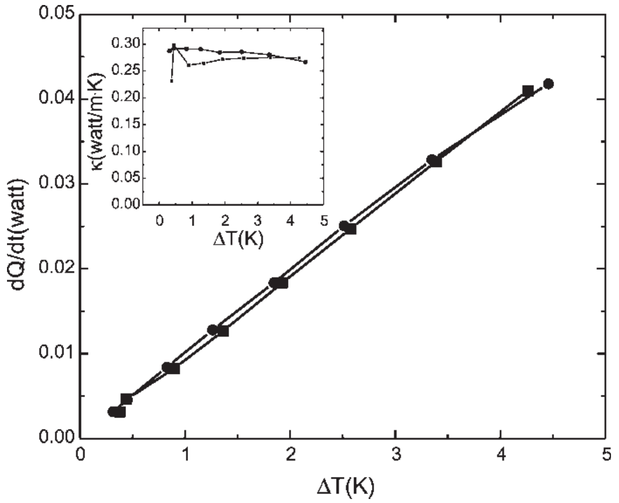

FIGURE 5 Heat transfer rates of silica powders filled with ice versus temperature gradient across the radius of the cell: (●) 5.3 μm, $T = 270\,\mathrm{K}$; (■) 12 nm, $T = 272\,\mathrm{K}$. The inlet shows the thermal conductivity of ice in powders versus temperature. The solid lines are the guides to the eyes.

resulting a slightly decrease in the thermal conductance.

In this study, we have measured a series of heat transfer rates versus temperature difference across the sample cell at different temperatures. In the measurements, we applied variable heating powers to the central heater while keeping the temperature of the sample host constant. The variable heating power created a variable temperature difference ΔT across the sample cell, so the heat transfer rate $\mathrm{d}Q/\mathrm{d}t$ versus ΔT can be measured. Figure 4 plots the heat transfer rate and the thermal conductance of dry powder sample. In this case, we do not expect any non-linear behavior. As shown in the figure, the heat transfer rate clearly has a perfect linear dependence on the temperature difference across the sample within the experimental uncertainty.

The heat transfer rates versus ΔT for ice in silica powders were also measured carefully at different temperatures. The data does not reveal any convincing non-linear behavior. Figure 5 displays two representative curves of the heat transfer versus temperature difference for ices in 5.3 μm powders and in 12 nm powders at temperatures a few degrees below 0°C. The curves deviate slightly from a perfectly linear behavior, but the deviation does not show a clear trend of increasing with ΔT, as shown in Fig. 5 (see the inlet). The deviation could be caused by a disruption of the homogeneity of the powder compacts due to a thermomolecular pressure. Certain degree of the disruption to the powder media in the cell was seen after the measurements. However, the deviation does not seem to increase with the temperature gradient. Therefore, other possibilities cannot be ruled out. Further study will be needed to confirm the phenomenon observed here.

In summary, thermal conductance of ice in silica powders have been measured. The thermal conductivities of ice and silica powders, after appropriate scaling, are much smaller than the corresponding bulk values, indicating a significant boundary thermal resistance between powder particles and between particles and ice. The thermal conductivity of ice in silica powders shows a drop at 0°C, similar to bulk behavior. The heat transfer rates versus temperature gradient demonstrate a nearly perfect linear behavior for dry powders, but the same rates for ice in powders were found to deviate slightly from a linear dependence.

Acknowledgements

This work is supported by a grant from University of Missouri Research Board (BK-000095). Acknowledgement is made to the donors of the Petroleum Research Fund, administered by American Chemical Society for supporting this research.

References

[1] Dash, J.G. (1999) "Ice Physics and the Natural Environment", In: Wettlaufer, J.S., Dash, J.G. and Untersteiner, N., eds, *NATO ASI* Ser. I (Springer-Verlag, Heidelberg) Vol. **56**.

[2] Dash, J.G., Fu, H.-Y. and Wettlaufer, J.S. (1995) "The premelting of ice and its environmental consequences", *Rep. Prog. Phys.* **58**, 115.

[3] Fu, H.-Y., *Investigation of the Role of Surface Melting of Ice in Frozen Media*, Ph.D. Thesis.

[4] Li, J.-C., Ross, D.K. and Heenan, R.K. (1993) "Small-angle neutron-scattering studies of the transition between water and ice in a restricted geometry", *Phys. Rev. B* **48**, 6716.

[5] Hills, B.P. and Le Floc'h, G. (1994) "NMR studies of non-freezing water in randomly packed beds of porous particles", *Mol. Phys.* **82**, 751.

[6] Handa, Y.P., Zakrzewski, M. and Fairbridge, C. (1992) "Effect of restricted geometries on the structure and thermodynamic properties of ice", *J. Phys. Chem.* **96**, 8594.

[7] Morishige, K. and Nobuoka, K. (1997) "X-ray diffraction studies of freezing and melting of water confined in a mesoporous adsorbent (MCM-41)", *J. Chem. Phys.* **107**, 6965.

[8] Ishizaki, T., Maruyama, M., Furukawa, Y. and Dash, J.G. (1996) "Premelting of ice in porous silica glass", *J. Cryst. Growth* **163**, 455.

[9] Cahn, J.W., Dash, J.G. and Fu, H.-Y. (1992) *J. Cryst. Growth* **123**, 101.

[10] Gay, J.-M., Suzanne, J., Dash, J.G. and Fu, H. (1992) "Premelting of ice in exfoliated graphite: a neutron diffraction study", *J. Cryst. Growth* **125**, 33.

[11] Maruyama, M., Bienfait, J.G., Dash, G. and Goddens, G. (1992) "Interfacial melting of ice in graphite and talc powders", *J. Cryst. Growth* **118**, 33.

[12] Pluis, B., van der Gon, A.W., Frenken, J.W.M. and van der Veen, J.F. (1987) "Crystal-face dependence of surface melting", *Phys. Rev. Lett.* **59**, 2678.

[13] Da-Ming Zhu and Dash, J.G. (1986) "Surface melting and roughening of adsorbed argon film", *Phys. Rev. Lett.* **57**, 2959.

[14] Da-Ming Zhu and Dash, J.G. (1988) "Surface melting of neon and argon films: profile of the crystal-melt interface", *Phys. Rev. Lett.* **60**, 432.

[15] Wilen, L.A. and Dash, J.G. (1995) "Frost heave dynamics at a single crystal interface", *Phys. Rev. Lett.* **74**, 5076.

[16] Wettlaufer, J.S., Worster, M.G., Wilen, L.A. and Dash, J.D. (1996) "A theory of premelting dynamics for all power law forces", *Phys. Rev. Lett.* **76**, 3602.

[17] Rempel, A.W., Wettlaufer, J.S. and Worster, M.G. (2001) "Interfacial premelting and the thermomolecular force: thermodynamic buoyancy", *Phys. Rev. Lett.* **87**, 88501.

[18] Hiros, M., Mizusaki, T., Tsuneto, T., Hirai, A. and Eguchi, K. (1989) "Frost-heave phenomena of 4He on porous glasses", *Phys. Rev. B* **40**, 6581.

[19] Mizusaki, T. and Hiroi, M. (1995) "Frost Heave in He", *Physica B* **210**, 403.

[20] Zhu, D.-M., Vilches, O.E., Dash, J.G., Sing, B. and Wettlaufer, J.S. (2000) "Frost heave in argon", *Phys. Rev. Lett.* **85**, 4908.

[21] Dash, J.G., Hodgkin, V.A. and Wettalufer, J.S. Unpublished.

[22] Takahashi, H., Hiki, Y. and Kogure, Y. (1994) "An improved transient hot-wire method for studying thermal transport in condensed matter", *Rev. Sci. Instrum.* **65**, 2901.

[23] Kakac, S. and Yener, Y. (1993) *Heat Conduction*, 3rd Ed. (Taylor & Francis, Washington, DC).

[24] Touloukian, Y.S., Powell, R.W., Ho, C.Y. and Klemens, P.G. (1970) *Thermal Conductivity Nonmatallic Solids* (IFI/Plenum Press, New York, WA), p 183.

[25] Anderson, A.C. (1981) "Thermal conductivity", In: Phillips, W.A., ed, *Amorphous Solids* (Springer-Verlag, Berlin).

[26] Andersson, O. and Suga, H. (2002) "Thermal conductivity of amorphous ices", *Phys. Rev. B* **65**, 140201.

[27] Phillips, O.M. (1991) *Flow and Reaction in Permeable Rocks* (Cambridge University Press, Cambridge, England).

[28] Broghton, J.Q., Boinssent, A. and Abraham, F.F. (1981) "The FCC (111) and (100) crystal-melt interfaces: A comparison by molecular dynamics simulation", *J. Chem. Phys.* **74**, 4029.

[29] Lowen, H. (1994) "Melting, freezing and colloidal suspensions", *Phys. Rep.* **237**, 249–324.

[30] Yingxi Zhu and Granick, Steve (2001) "Viscosity of interfacial water", *Phys. Rev. Lett.* **87**, 96104.