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LETTER TO THE EDITOR

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Abstract
The melting temperature of nano-ice confined in micropores of MCM-41 is predicted by use of our simple model based on the Lindemann criterion. The model takes into consideration the density of the OH bonds of MCM-41 pores; its prediction is consistent with the experimental results for the melting temperature of nano-ice. The applicability of the Gibbs–Thompson equation to nanocrystals in the mesoscopic size range is compared with that of our model and a modification of that same equation is compared with our model.

Recently, a new kind of microporous material, MCM-41, with uniform channels has been synthesized; pores with radii ranging from 0.8 and 5 nm cover the full mesoscopic size range, but a proportion of them have microscopic size [1, 2]. The pores are of cylinder-like nature, and are arranged parallel to each other in a honeycomb-type lattice. The absence of pore channel intersection guarantees that pore-networking effects are negligible [1–8]. Thus, MCM-41 is used as a model material for measuring melting temperatures of nanocrystals in the mesoscopic and microscopic size ranges. Using this model material, the melting temperature of nano-ice has been measured recently to test the validity of the Gibbs–Thompson equation in this size range [2–8]. The results show that the melting temperature of nano-ice decreases as the scale decreases. However, this decrease cannot fully agree with the Gibbs–Thompson equation for a free surface particle, which has the following form [9]:

$$T_m(r)/T_m(\infty) = 1 - C/r \tag{1}$$

where $T_m(r)$ and $T_m(\infty)$ are the melting temperatures of crystals with pore radius r and the corresponding bulk crystals, while r is equal to the inner radius of the pores [2–8]. C denotes a constant. Note that the existence of OH-bond interactions between the surface of ice and the pore wall leads to a fraction of the surface molecules of the ice being no longer fully free. This effect is equivalent to an increase of size of the nanocrystals affecting the surface/volume ratio and increasing the values of $T_m(r)$ for the ice. Thus, some modifications must be made to extend equation (1) to make it applicable in the mesoscopic size range. One of the modifications is as follows [6, 8]:

$$T_m(r)/T_m(\infty) = 1 - C'/(r - t) \tag{2}$$

where C' is a constant and t is assumed to be the thickness of the so-called 'inter-phase' existing between the inner surfaces of pore walls and the solid-ice-like phase in the middle of the pores, which is estimated to be about two molecules thick [6, 8]. The existence of the inter-phase may be due to the polarity of the ice molecules [2–8]. The experimental results seem to support this suggestion, since freezing of water in MCM-41 occurs at two different temperatures and equation (2) corresponds well to experimental results [4, 6–7]. However, the density of the OH bonds on the surface of the pore walls of MCM-41 is only a tenth of that on the surface of the nano-ice. Thus, most of the molecules on the surface of ice are free of chemical interaction with the pore walls [6]. Moreover, this chemical interaction, which is weaker than that among ice molecules themselves, should not lead to the appearance of a new phase. To understand the nature of the melting of nano-ice in MCM pores and the physical background of equation (2), a thermodynamic model for the size dependence of the melting of ice should be established, which should help us to understand the size range for which the Gibbs–Thompson equation is applicable. This is the goal of this contribution. Based on the size-dependent amplitude of the atomic thermal vibrations of nanocrystals according to the Lindemann criterion, our model for the $T_m(r)$ function for nanoparticles is developed using the following form [9, 10]:

$$\frac{T_m(r)}{T_m(\infty)} = \frac{\sigma^2(\infty)}{\sigma^2(r)} = \exp\left[\frac{-(\alpha - 1)}{r/r_0 - 1}\right] \qquad (3)$$

where r_0 is a critical radius at which almost all atoms of a particle are located on its surface, $\sigma^2(r)$ and $\sigma^2(\infty)$ are the averaged mean square displacement (msd) of atoms for a crystal with the pore radius r and that for the corresponding bulk crystal, respectively. r_0 in equation (3) is dependent on the dimension of the crystal, d: $d = 0$ for nanocrystals, $d = 1$ for nanowires and $d = 2$ for thin films. For a nanoparticle, r has the usual meaning of the radius. For a nanowire, r is taken as its radius. For a thin film, r denotes its half-thickness. Let h be the atomic or molecular diameter; r_0 is given by [9, 10]

$$r_0 = (3 - d)h. \qquad (4)$$

Since a crystal is characterized by its long-range order, the smallest nanocrystal should have at least half of its atoms or molecules located within the nanocrystal. Hence, the smallest r is defined as $2r_0$ [9, 10]. One could argue that even a monolayer film may exist in a crystalline state due to its two-dimensional long-range order. However, all atoms of the film are located on the surface and the thermal vibration of the film should differ from that of the corresponding bulk crystals. In fact, when r for Bi film decreases to $2r_0 = 2h = 0.40$ nm, the crystallinity disappears [11]. For Pb nanowire in carbon nanotubes, $2r_0 = 4h = 1.56$ nm with $h = 0.39$ nm [12], which again is fully consistent with the observation that the crystallinity of Pb vanishes at $r = 1.5$ nm [13]. For ice in MCM-41 pores, when $r < 1.0$–1.2 nm, crystallization of water does not occur [3, 4, 6–8]. Since the molecular separation in ice with a hexagonal lattice is 0.276 nm [14], and $d = 1$ due to the cylindrical nature of MCM-41 pores, $2r_0 = 4h = 1.104$ nm, which is consistent with the above experimental results.

In equation (1), α is a ratio between the msd of atoms on the surfaces of nanocrystals ($\sigma_s^2(r)$) and that for atoms within the nanocrystals ($\sigma_v^2(r)$) [9, 10], i.e., $\alpha = \sigma_s^2(r)/\sigma_v^2(r)$. According to equation (3), when $\alpha < 1$, $T_m(r) > T_m(\infty)$. When nanocrystals are embedded in a matrix where the melting temperature of the matrix $T_M(\infty)$ is higher than $T_m(\infty)$ and the interfaces between the nanocrystals and the matrix are coherent, α takes its smallest value of α_{min} [15]:

$$\alpha_{min} = \{[h_M^2/h^2]T_m(\infty)/T_M(\infty) + 1\}/2 \qquad (5)$$

where h_M is the atomic diameter of the matrix. On the other hand, when the surface of the nanocrystals is free, $\alpha > 1$ and $T_m(r) < T_m(\infty)$ where α takes its largest value of α_{max} [9, 10]:

$$\alpha_{max} = 2S_m(\infty)/(3R) + 1 \tag{6}$$

where $S_m(\infty)$ is the melting entropy of the corresponding bulk crystal and R is the ideal-gas constant.

Since there exist silanol protons on the pore walls of MCM-41 [6], and the OH bonds of the silanol protons are interchangeable with those of the surface ice molecules [3, 4, 6], the msd of this fraction of the surface molecules should be similar to that of the interior ice molecules. If the corresponding molecule number is n, and the total number of surface ice molecules is N, let

$$\beta = n/N \qquad \alpha = [(1 - \beta)\sigma_s^2(r) + \beta\sigma_v^2(r)]/\sigma_v^2(r).$$

Note that $\sigma_s^2(r)$ is the msd of molecules on a free surface and $\alpha_{max} = \sigma_s^2(r)/\sigma_v^2(r)$; we have

$$\alpha = \alpha_{max}(1 - \beta) + \beta. \tag{7}$$

Because $\beta \leqslant 1$ and $\alpha = 1 + (1 - \beta)\{2S_m(\infty)/[3R]\} > 1$ according to equation (6), supercooling of the water in MCM-41 pores always occurs. In the limit case of $\alpha = \beta = 1$, the msd of the surface molecules is equal to that of the interior molecules and $T_m(r) = T_m(\infty)$. In this case, a quasi-bulk system consisting of the nano-ice and the pores is formed.

For nano-ice in MCM-41 pores, $\beta \approx 1/10$ [6]. As a first-order approximation, the second term on the right-hand side of equation (7) may be neglected and the equation now reads, using equation (6),

$$\alpha = \alpha_{max}(1 - \beta) = [2S_m(\infty)/(3R) + 1](1 - \beta). \tag{8}$$

Using equation (8) and the mathematical relation $\exp(-x) \approx 1 - x$ when x is small, equation (3) can be compared with equations (1) and (2). Under the conditions $\beta \approx 0$ and $r \gg r_0$,

$$T_m(r)/T_m(\infty) \approx 1 - 4hS_m(\infty)/(3rR) = 1 - C/r \tag{9}$$

where $r_0 = 2h$ due to the cylindrical shape of MCM-41 pores. Note that the thermodynamic freezing temperature $T_f(r)$ for micropores has been deduced to be [16]

$$T_f(r)/T_m(\infty) = 1 - 2\gamma V/[H_m(\infty)r] \tag{10}$$

where γ is approximately the solid–liquid interface energy, V is the gram-atomic volume and $H_m(\infty)$ is the melting enthalpy of bulk crystal. Substituting [17]

$$\gamma = 2hS_m(\infty)H_m(\infty)/(3VR) \tag{11}$$

into equation (10), $T_f(r) = T_m(r)$ in the micropores according to equation (9). Since the derivation of equation (10) was carried out under conditions of thermodynamic equilibrium, $T_f(r)$ has the same meaning as $T_m(r)$. Thus, equation (9) or equation (1) is an approximate result of equation (3) when $\beta \approx 0$ and $r \gg r_0$. If $\beta \neq 0$ and r is comparable with r_0 ($2r_0 \approx 1.1$ nm; see the above discussion),

$$T_m(r)/T_m(\infty) \approx 1 - r_0(\alpha - 1)/(r - r_0) = 1 - C'/(r - t) \tag{12}$$

where $C' = r_0(\alpha - 1)$ and $t = r_0$ by comparison with equation (2). Thus, equation (12) or equation (2), which is utilized to interpret experimental results on $T_m(r)$ for nano-ice in MCM-41 pores [3–8], has indeed extended the Gibbs–Thompson equation to the mesoscopic size range according to our model of equation (3).

The model prediction of equation (3) and the experimental data on $T_m(r)$ [8] and $T_f(r)$ [3, 6] for nano-ice are shown in figure 1. Note that the measured values of $T_f(r)$ [3, 6] are systematically higher than the measured values of $T_m(r)$ [8], where distinct measuring methods
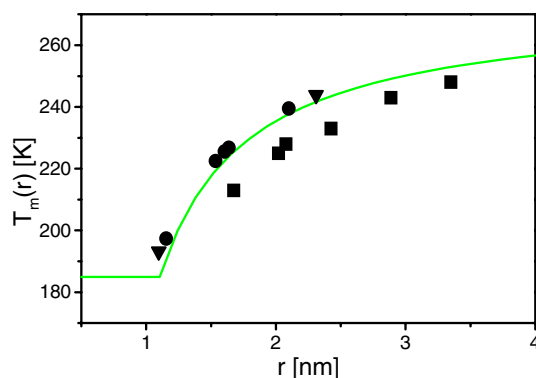
Figure 1. The size-dependent melting temperature of nano-ice. The line is the theoretical prediction according to equations (3), (6) and (8) where $d = 1$ since the morphology of MCM-41 is cylindrical [1]. Thus, $r_0 = 2h = 0.552$ nm ($h = 0.276$ nm [14]) according to equation (4). β is calculated as follows: for ice, the number of OH bonds is 3.34×10^{22} g^{-1} when one takes the molar volume of ice as 18.02 g mol^{-1} and the density as 1 g cm^{-3}. When $r = 1.42$ nm, the ratio of number of surface molecules to total number of molecules for ice is 0.477. Thus, the number of surface molecules is 1.59×10^{22} g^{-1} and 12.7% of the surface ice molecules are in contact with the OH bonds of the pore wall, where the concentration of OH bonds on the surface of the pore wall is 2.02×10^{21} g^{-1} [6], i.e., $\beta = 0.127$. According to equation (6), $\alpha_{max} = 1.59$ where $S_m(\infty) = 7.37$ J (g atom)$^{-1}$ K^{-1} and $R = 8.314$ J (g atom)$^{-1}$ K^{-1} [16]. According to equation (8), $\alpha = 1.39$. $T_m(\infty) = 273.15$ K [16]. The symbols ● [6], ■ [8] and ▼ [3] denote the experimental results for nano-ice.

were used in the different references cited. However, the results from the two methods (that of [3, 6] and that of [8]) correspond well (within the measurement error range) to the model prediction: $T_m(r)$ diminishes with decrease in scale although the lowest measured $T_m(r)$ of 193 K is a little higher than the prediction of 185 K. Theoretically, $T_f(\infty) < T_m(\infty)$, due to the non-equilibrium process of nucleation during the freezing. However, when $r = 1$ to 5 nm, the nucleation barrier or Gibbs free energy of melting approaches zero [9] and thus $T_f(r) \approx T_m(r)$ in experiments [18].

Inserting numerical values of r_0 and α into equation (12) (as regards the details of the calculations, see the figure caption), $C' = 0.215$ nm and $t = 0.552$ nm, while the experimental fitting parameters are $C' = 0.19$ nm and $t = 0.59$ nm, respectively [6]; these are in quite surprisingly agreement with our model predictions, considering the assumptions and limitations of the model. Note that t in our model is not related to the thickness of the inter-phase, but is a certain material parameter related to r_0. Thus, the inter-phase is a part of the nano-ice. In fact, this is an advantage of our model, as no consideration of the possible thickness of the inter-phase is involved. Since the application of our model is limited to cases where surface melting of the nano-ice does not occur, the physical nature of the inter-phase remains an open question and needs to be studied further.

In conclusion, nano-ice confined in MCM-41 micropores exhibits a reduced melting temperature. Reasonable agreement between the experimental data for nano-ice and the prediction of our model has been found. This correspondence implies that the Gibbs–Thompson equation cannot be simply extended to the mesoscopic size range. Moreover, the model shows a way to consider the effect of the OH concentration of pore walls on the melting temperature of ice.

References

[1] Beck J S, Vartuli J C, Roth W J, Leonowicz M E, Kresge C T, Schmitt K D, Chu C T-W, Olson D H, Sheppard E W, McCullen S B, Higgins J B and Schlenker J L 1992 *J. Am. Chem. Soc.* **114** 10 834

[2] Schmidt R, Hansen E W, Stöcker M, Akporiaye D and Ellestad O H 1995 *J. Am. Chem. Soc.* **117** 4049

[3] Akporiaye D, Hansen E W, Schmidt R and Stöcker M 1994 *J. Phys. Chem.* **98** 1926

[4] Hansen E W, Schmidt R, Stöcker M and Akporiaye D 1995 *J. Phys. Chem.* **99** 4148

[5] Stapf S and Kimmich R 1995 *J. Chem. Phys.* **103** 2247

[6] Hansen E W, Stöcker M and Schmidt R 1996 *J. Phys. Chem.* **100** 2195

[7] Hansen E W, Tangstad E, Myrvold E and Myrstad T 1997 *J. Phys. Chem.* B **101** 10 709

[8] Morishige K and Kawano K 1999 *J. Chem. Phys.* **110** 4867

[9] Jiang Q, Shi H X and Zhao M 1999 *J. Chem. Phys.* **111** 2176

[10] Wen Z, Zhao M and Jiang Q 2000 *J. Phys.: Condens. Matter* **12** 8819

[11] Mitch M G, Chase S J, Fortner J, Yu R Q and Lannin J S 1991 *Phys. Rev. Lett.* **67** 875

[12] King H W 1970 *Physical Metallurgy* ed R W Cahn (Amsterdam: North-Holland) p 60

[13] Ajayan P M and Iijima S 1993 *Nature* **361** 233

[14] Dosch H, Lied A and Bilgram J H 1996 *Surf. Sci.* **366** 43

[15] Jiang Q, Zhang Z and Li J C 2000 *Chem. Phys. Lett.* **322** 549

[16] Awschalom D D and Warnock J 1987 *Phys. Rev.* B **35** 6779

[17] Jiang Q, Shi H X and Zhao M 1999 *Acta Mater.* **47** 2109

[18] Zhang Z, Li J C and Jiang Q 2000 *J. Mater. Sci. Lett.* **19** 1893