Melting thermodynamics of organic nanocrystals

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The size-dependent melting temperature and the size-dependent melting entropy of organic nanocrystals are predicted by use of our simple model being free of any adjustable parameter. The model predictions for the size-dependent melting temperature and the size-dependent melting entropy are supported by the experimental results on benzene, chlorobenzene, heptane, and naphthalene nanocrystals. © *1999 American Institute of Physics.* [S0021-9606(99)51328-7]

INTRODUCTION

In 1954, Takagi demonstrated for the first time that ultrafine metallic particles melt below their corresponding bulk melting temperature.[1] It is now known that the melting temperature of all low-dimensional crystals, including metallic,[2–6] semiconductor,[7–8] and organic crystals,[9,10] depends on their sizes. Although there are relatively extensive investigations on the size-dependent melting of nanocrystals, it has not been accompanied by the necessary investigation of the size-dependent thermodynamics of nanocrystals.[2–4,9,11,12] Such an investigation should deepen our understanding of the size effect of melting. In particular, a complete understanding of the melting transition in nanocrystals cannot be obtained without a clear understanding of the entropy of melting, which reflects the change in the degree of order upon melting.

Recently, a model for the size-dependent melting temperature was developed based on the size-dependent amplitude of the atomic thermal vibrations of nanocrystals in terms of Lindemann criterion.[4–6] Furthermore, in terms of the above model for size-dependent melting and Mott's expression for the vibrational entropy of melting for metallic crystals at melting temperature,[13,14] a model for the size-dependent melting entropy of metallic nanocrystals is derived.[3] The model suggests that the size dependence of the melting entropy for nonsemiconductor nanocrystals is determined by the size dependence of the vibrational part of the melting entropy of nanocrystals, which decreases as the size of the crystal decreases.

In this contribution, the above model is extended to organic nanocrystals due to similar melting nature for both metallic and organic nanocrystals. To extend this model to the melting temperature and melting entropy of organic crystals, the diameter of atoms in metallic crystals is modified as the mean diameter of molecules in organic crystals. With this modification, the model is also applicable for organic nanocrystals. The theoretical prediction of the model for the size-dependent melting temperature and the size-dependent melting entropy has been found to be consistent with experimental evidence on benzene, chlorobenzene, heptane, and naphthalene nanocrystals.[9]

MODEL

The size-dependent melting temperature of metallic nanocrystals $T_m(r)$ can be described by the following model,[4–6]

$$T_m(r)/T_m(\infty) = \sigma^2(\infty)/\sigma^2(r)$$
$$= \exp[-(\alpha-1)/(r/r_0-1)], \qquad (1)$$

where r is the radius of the crystal, $T_m(\infty)$ is the melting temperature for the corresponding bulk crystal, r_0 denotes a critical radius at which all atoms of the particle are located on its surface, $\sigma^2(r)$ is the average mean-square displacement (msd) of atoms for a particle with a radius of r, $\sigma^2(\infty)$ is the msd of atoms for the corresponding bulk crystals, α shows a ratio between the msd of surface atoms of the crystal and that of interior atoms of the crystal.

For low-dimensional crystals, it is clear that r_0 in Eq. (1) should be dependent on the dimension of the crystal d: $d = 0$, for nanocrystals, $d=1$ for nanowires, and $d=2$ for thin films. In general, the dimension can be fractal.[4] For a nanoparticle, r has a usual meaning of radius. For a nanowire, r is taken as its radius. For a thin film, r denotes its half thickness. Let h be the atomic diameter, r_0 is given by (i) $r_0 = 3h$ for $d=0$ since $4\pi r_0^2 h = 4\pi r_0^3/3$; (ii) $r_0 = 2h$ for $d=1$ since $2\pi r_0 h = \pi r_0^2$; and (iii) $r_0 = h$ for $d=2$ since $2h = 2r_0$. In short, the relationship between d and r_0 is given by,[4,5]

$$r_0 = (3-d)h. \qquad (2)$$

Since a crystal is characterized by its long-range order, the smallest metallic nanocrystal should have at least a half of the atoms located within the nanocrystal. Hence, the smallest r is $2r_0$.[4,5] This estimation is consistent with experimental results for Bi film[15] and Pb nanowire in a carbon nanotube.[16,17]

Equation (1) differs from all previous models in that it is able to explain not only the experimental observation of both the melting temperature suppression and superheating in nanocrystals,[6] but also the melting behavior for nanocrystals smaller than 10 nm.[3–6] The above model has predicted the

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size-dependent melting for metallic nanoparticles,[6] for metallic thin films,[4] for metallic nanowires in carbon nanotubes,[5] and for the related size-dependent initial sintering temperature of metallic nanocrystals.[18] The predicted results are confirmed by the available experimental evidences.

Based on Mott's expression for the vibrational entropy of melting $S_{vib}(\infty)$ of bulk crystals at melting temperature[13,14] and the above model, the size-dependent melting entropy of metallic crystals and α in Eq. (1) could also be developed.[3,4] According to Mott,[13] the vibrational entropy of melting of a bulk crystal $S_{vib}(\infty)$ was shown as,[13,14]

$$S_{vib}(\infty) = (3k/2)\ln\{T_m(\infty)$$
$$\times [C_s(\infty)/C_l(\infty)]^2 [\pi^4/(6N_0)]^3/M\}, \quad (3)$$

where $C_l(\infty)$ and $C_s(\infty)$ are the ultrasound propagation velocities of the bulk liquid and the bulk crystal, respectively, N_0 is Avogadro's number, M is the molecular number, k denotes the Boltzmann constant. The size-dependent vibrational entropy of melting $S_{vib}(r)$ of a nanocrystal with a radius of r can be obtained as a generalization of Eq. (3), i.e., $S_{vib}(r) - S_{vib}(\infty) = (3k/2)\ln\{[T_m(r)/T_m(\infty)] [C_s(r)/C_l(r)]^2/ [C_s(\infty)/C_l(\infty)]^2\}$, where $C_l(r)$ and $C_s(r)$ are the size-dependent ultrasound propagation velocities of the liquid and the crystal. Instead of treating $C_l(r)$ and $C_s(r)$ to be size-dependent, respectively, the ratio of $C_l(r)/C_s(r) \approx C_l(\infty)/C_s(\infty)$ is approximately taken as a size-independent value. Hence,

$$S_{vib}(r) - S_{vib}(\infty) = (3k/2)\ln[T_m(r)/T_m(\infty)]. \quad (4)$$

Substituting Eq. (1) into Eq. (4) reads,

$$S_{vib}(r) = S_{vib}(\infty) - (3k/2)(\alpha-1)/(r/r_0-1). \quad (5)$$

For semiconductor crystals, if the melting is accompanied by the semiconductor-to-metal transition, the entropy of electronic origin should strongly contribute the overall entropy of melting.[14] However, it is known that the entropy of melting for metallic crystals is mainly vibrational in nature.[14] Hence, although $S_{vib}(r)$ represents only one of several contributions to the overall entropy of melting, one may suggest that the overall entropy of melting for metallic nanocrystals, $S_m(r)$, follows the same size dependence as $S_{vib}(r)$,

$$S_m(r) = S_m(\infty) - (3k/2)(\alpha-1)/(r/r_0-1). \quad (6)$$

The parameter α in Eq. (6) now can be expressed in terms of $S_m(\infty)$. This is because in the limit of $r \rightarrow 2r_0$, $S_m(r) \rightarrow 0$,[3,4] the degree of the order for the liquid and the solid state is the same. Hence,

$$\alpha = [2S_m(\infty)/(3k)] + 1. \quad (7)$$

Eliminating the parameter α from Eq. (6) by means of Eq. (7), one has,

$$S_m(r)/S_m(\infty) = 1 - 1/(r/r_0-1). \quad (8)$$

Equation (8) is remarkably simple and more importantly, free of any adjustable parameter. Equation (8) has been supported by the experimental results on Sn (Ref. 11) and Al (Ref. 12) nanocrystals and the first-principle calculations on Al nanocrystals.[2] In Eq. (8), $S_m(r)$ decreases as r decreases.

This trend is expected for two reasons. First, the surface fraction of molecules in a nanocrystal increases with decreasing size, and consequently its entropy, $S_c(r)$, increases as the size decreases. At the limit of $2r_0$, the nanocrystal has the same structure of the liquid particle due to the fact that the short-range order of the particle appears, $S_c(r)$ equals the entropy of a liquid particle of the same size, $S_l(r)$, i.e., $S_m(2r_0) = 0$. Second, it is conceivable that the size dependence of $S_l(r)$ is much weaker than that of $S_c(r)$. Consequently, $S_m(r)$ decreases with a decrease in size.

Equations (1) and (8) should also be utilized for organic nanocrystals due to their similar melting nature, i.e., the melting entropy of organic crystals is essentially contributed by a vibrational part. However, since organic crystals are molecular ones, h or r_0 stated above must be newly defined. A simple generalization is that h is defined as the mean diameter of the organic molecule, which implies that a molecule in organic crystals takes a similar effect of an atom in metallic crystal. Hence, when a molecule is located on the surface of the organic crystal, the amplitude of the thermal vibration of the full molecule is larger than that of molecules within the crystal.

Since the shape of an organic molecule is usually not spherical, h as a mean diameter of a molecule is simply shown as,

$$h = \frac{1}{3}\sum_{i=1}^{3} h_i, \quad (9)$$

where the subscript i is taken from 1 to 3 denoting the x-, y-, and z-axis of a molecule, h_i is the length of the molecule along the corresponding direction. For the organic molecules not having any regular shapes, the direction of the longest size is defined as the x-axis and the shortest size is defined as another axial direction. Different choices of the axes only lead to little difference of h, which changes $T_m(r)$ and $S_m(r)$ functions little, especially when r/h is large enough (for instance, usually $r > 2$ nm in experiments and $h < 0.5$ nm for most organic crystals).

RESULTS AND DISCUSSION

Organic nanocrystals can be obtained by filling the corresponding organic liquids to porous materials,[9,10] whose thermal properties are measurable by a usual calorimeter. Among different porous materials, the controlled porous glass has a narrow size distribution with morphology of a network of cylindrical pores.[9,10] The calorimetric experimental results for organic molecules filled in the controlled porous glass are highly reproducible and permit the size-dependent melting temperature and the size-dependent melting enthalpy to be accurately determined. Hence, this kind of experimental result will be used to test our model.

Since the morphology of the controlled porous glass is in a cylindrical type,[9] $d = 1$ and $r_0 = 2h$ in terms of Eq. (2). The measured results of four molecular nanocrystals of benzene, chlorobenzene, heptane, and naphthalene are utilized to examine our model,[9,10] whose geometric shapes are simpler and thus whose h_i and axis direction can be easily determined without any arguments.

TABLE I. Averaged bond lengths in nanometer and bond angles used for calculating h (Ref. 20).

Bond type	Bond length	Bond type	Bond length	Bond type	Bond angle
Heptane		Naphthalene[a]	0.1373	Heptane	
C^1–C^2	0.1533		0.1416	H–C–C	110.7°
C^2–C^3	0.1539		0.1422	C–C–C	112.8°
C–H	0.1091		0.1421	H–C–H	107.0°
Benzene		Chlorobenzene		Benzene	120°
C–C	0.1395	C–Cl	0.178[b]		
C–H	0.1100	C–C	0.1395	Chlorobenzene	120°
		C–H	0.1100		

[a]For naphthalene, there are four different bond lengths.
[b]C–Cl bond length is cited from Ref. 21.

The geometric shape of benzene is disk-like,[19] thus, $h_x = h_y$. According to the bond lengths of molecules listed in Table I, for benzene, $h_x(h_y)$ is equal to the sum of the two C–C bond lengths and two C–H bond lengths, and $h_x = h_y = 0.4990$ nm. h_z is the bond length of C–C, which is 0.1395 nm. In terms of Eq. (9), $h = 0.3792$ nm.

A similar consideration above can be applied on chlorobenzene. The only structural difference between chlorobenzene and benzene is that one C–H bond is substituted by a C–Cl bond, i.e., its h_x is equal to the sum of the two C–C bond lengths, one C–H bond length, and one C–Cl bond length. In terms of Table I, $h_x = 0.5670$ nm. The h_y and h_z values of chlorobenzene are the same as that of benzene. Thus, $h_y = 0.4990$ nm and $h_z = 0.1395$ nm. Hence, $h = 0.4018$ nm for chlorobenzene is obtained by use of Eq. (9).

The geometric shape of heptane is rod-like.[19] Hence, the length of the rod is taken as h_x, the diameter of the rod is considered as h_y and h_z. In terms of Table I, h_x is a sum of seven C–C bond lengths and two C–H bond lengths with related bond angles. With a simple calculation, h_x
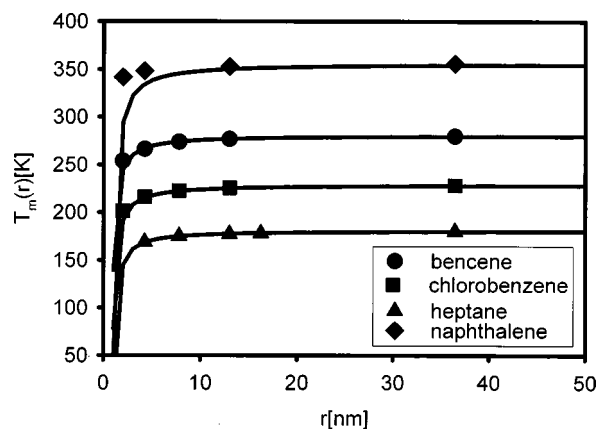

FIG. 1. Size-dependent melting temperatures of benzene, chlorobenzene, heptane, and naphthalene. The lines are theoretical predictions in terms of Eqs. (1) and (7). ●, ■, ▲, and ◆ denote the experimental results of benzene, chlorobenzene, heptane, and naphthalene, respectively (Ref. 9). $T_m(\infty)$ values of benzene, chlorobenzene, heptane, and naphthalene in K are 280.8, 229.1, 181.0, 356.1, respectively (Ref. 9). The corresponding $S_m(\infty)$ values in Jg-atom^{-1} K^{-1} are 2.842, 3.375, 3.042, and 2.920, respectively (Ref. 9). r_0 is taken as $2h$ (for the calculations of h values, see the text). The corresponding r_0 values in nm are 0.7584, 0.8036, 0.9650, and 0.9024.
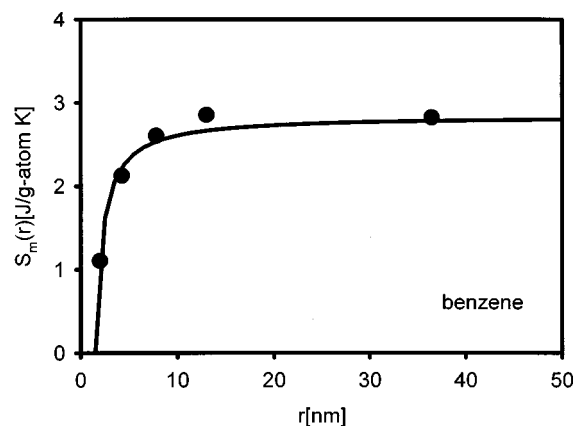

FIG. 2. Size-dependent melting entropy of benzene. The line is a model prediction based on Eqs. (8) and (7). ● denotes the experimental results of benzene (Ref. 9). For the corresponding r_0 and $S_m(\infty)$ values, see the caption of Fig. 1.

$= 0.9474$ nm. h_y or h_z is a sum of two C–H bond lengths and a fraction of C–C bond length due to the existence of the bond angle, $h_y = h_z = 0.2501$ nm. Finally, $h = 0.4825$ nm in terms of Eq. (9).

The geometric shape of naphthalene is similar to benzene being disk-like, which could be considered as a joining of two benzene rings. h_x thus is taken as the length of the molecule across two benzene rings and h_y is the length along one benzene ring. Taking the data in Table I, $h_x = 0.7128$ nm and $h_y = 0.5014$ nm. h_z has the same value of benzene, i.e., the C–C bond length of 0.1395 nm. $h = 0.4512$ nm for naphthalene based on Eq. (9).

After the determination of h, the size-dependent melting temperature $T_m(r)$ of the four organic nanocrystals may be calculated in terms of Eqs. (1) and (7). Figure 1 shows this model prediction and the experimental observation.[9] It is evident that the model prediction is consistent with the experimental observation: The melting temperature decreases with a decrease in size. The only exception is that when $r < 4.5$ nm, the model prediction of $T_m(r)$ for naphthalene is a little lower than the experimental results. In addition, $T_m(r)$ for different organic nanocrystals is also dependent on their critical size of r_0 and their bulk melting entropy of $S_m(\infty)$. The larger r_0 and $S_m(\infty)$ are, the deeper the undercooling of the nanocrystal. However, the lowest value of $T_m(r)$, i.e., $T_m(2r_0)$, is only determined by its bulk melting entropy in terms of Eqs. (1) and (7). A larger value of $S_m(\infty)$ of the crystal leads to a lower value of $T_m(2r_0)$. Since $S_m(\infty)$ values for four organic crystals are only a third of that for metallic crystals, the values of $T_m(2r_0)$ for organic crystals, which is typically $0.6T_m(\infty)$, is larger than that of metallic crystals $[0.5T_m(\infty)]$. Note that r_0 in our model is dimension-dependent. A lower dimension of the crystal brings about a larger value of ΔT, i.e., a particle has a larger undercooling than a thin film has at the same r. This difference comes from different ratios between the surface molecules and the interior molecules in different dimensions.

Most phenomenological models for $T_m(r)$, regardless of their initial assumptions, predict a change of $T_m(r)$ following the relation of $T_m(r)/T_m(\infty) \sim 1 - 1/r$.[4,6,9] All these theo-
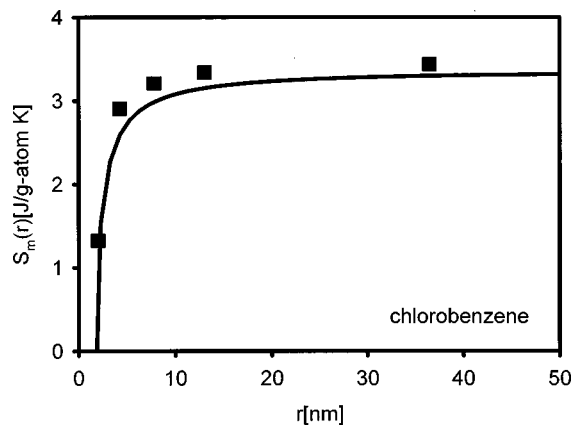
FIG. 3. Size-dependent melting entropy of chlorobenzene. The line is a model prediction based on Eqs. (8) and (7). ■ shows the experimental results of chlorobenzene (Ref. 9). For the corresponding r_0 and $S_m(\infty)$ values, see the caption of Fig. 1.

FIG. 5. Size-dependent melting entropy of naphthalene. The line is a model prediction based on Eqs. (8) and (7). ◆ presents the experimental results of naphthalene (Ref. 9). For the corresponding r_0 and $S_m(\infty)$ values, see the caption of Fig. 1.

ries are in good agreement with the experimental data when $r \geqslant 10$ nm. Under this condition ($r \geqslant 10 r_0$ where $r_0 \approx 1$ nm for $d=1$), Eq. (1) is the same phenomenological model as $T_m(r)/T_m(\infty) \sim 1-1/r$ in terms of a mathematical relation of $\exp(-x) \approx 1-x$. However, these phenomenological models fail for smaller nanocrystals without the lowest limit of $T_m(r)$ at the critical size of r_0, and cannot explain a dimensional dependent $T_m(r)$. Against that, our model can illustrate all of the above phenomena.

Figures 2–5 present a comparison between the prediction of Eq. (8) and the experimental results of $S_m(r)$ for four organic nanocrystals.[9] The theoretical model is in good agreement with experimental evidences although the theoretical prediction of $S_m(r)$ for chlorobenzene is a little lower than the experimental results.[9]

In Figs. 2–5, the melting entropy decreases as size of the crystals decreases. This fact confirms that the assumption that the vibrational entropy is dominating the size dependence of $S_m(r)$ not only for metallic nanocrystals, but also for organic nanocrystals, is reasonable. The decrease of melting entropy is decided only by its r and r_0 without any in-

fluence of $S_m(\infty)$ itself. Hence, the ratio between the percentage of surface molecules and that of the interior molecules, which is a function of the size of the nanocrystal, is the only factor to determine the decrease of the melting entropy.

SUMMARY

In conclusion, organic nanocrystals exhibit reduced melting temperature and melting entropy since the vibrational spectrum of the surface region differs from the bulk. The maximum phonon wavelength truncated by the crystallite size and the surface region has enhanced configurational entropy. With decreasing crystal size the relative significance of all of these effects increases. Although Eq. (8) as a function of crystal size is derived by formally extending Mott's estimate of the melting entropy of an infinite metallic crystal to metallic crystals of finite size, they can be utilized not only for metallic nanocrystals, but also for organic nanocrystals. Reasonable agreement between the experimental data for organic nanocrystals confined in porous glass and the estimated melting temperature and melting entropy of our model has been found.
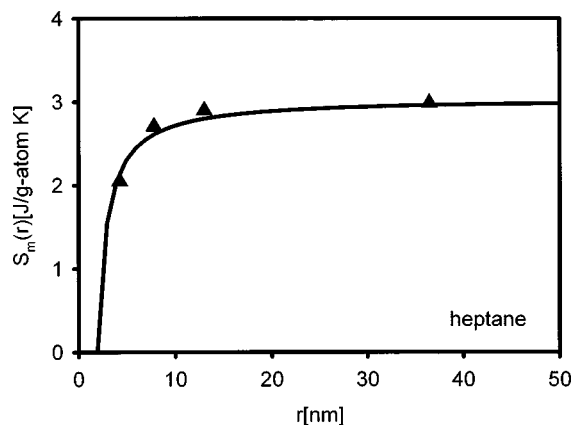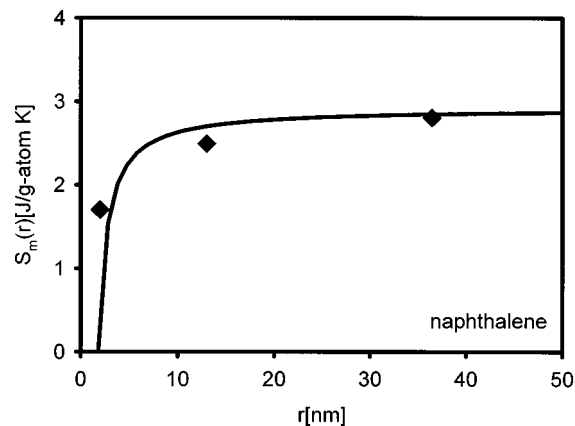
ACKNOWLEDGMENTS

FIG. 4. Size-dependent melting entropy of heptane. The line is a model prediction based on Eqs. (8) and (7). ▲ gives the experimental results of heptane (Ref. 9). For the corresponding r_0 and $S_m(\infty)$ values, see the caption of Fig. 1.

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