

Surface melting on small particles

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Surface melting on small particles was detected using x-ray diffraction from Pb crystallites of 50 nm diam in ultrahigh vacuum. Since the melting temperature depends on particle size, it can be difficult to distinguish between the melting and surface melting. A sharp crystallite size distribution is obtained by melting the smaller particles while a liquid skin forms on the remaining crystallites. When the sample is cooled slightly, the liquid particles remain liquid while the liquid skin on the crystallites solidifies. *In situ* x-ray diffraction reveals that the liquid skin thickness changes reversibly. © 1997 American Institute of Physics. [S0003-6951(97)04742-6]

The melting mechanism remains “a mystery” although much progress has been made.^{1,2} Faraday’s hypothesis that a liquid skin forms on solid surfaces below the melting temperature³ has been experimentally confirmed for some flat surface orientations of Pb and disproved for others.^{4–6} Surface melting may differ on small crystallites,^{7–17} whose energetics and structure can be altered by the high surface curvature.^{11,18–22} Physically, the differences may arise because of the distribution of surface orientations, the high surface-to-volume ratio, capillarity effects, enhanced surface step-step interaction, and finite-size effects. Small particles are known to exhibit size-dependent melting temperatures,^{7–15,20,23–28} latent heats,^{20–22} and quasimelting,^{18,29} i.e., rapid structural fluctuations. Different theories^{7–15,23,24} and experiments^{9,11,20,23,25–28} show that the melting temperature [$T_m(D)$] depends on the crystallite diameter (D), as follows:

$$T_m(D) = T_m(\infty) - \alpha/D, \quad (1)$$

where $T_m(\infty)$ is the bulk melting temperature, and α is some constant. An experimental study of size-dependent melting for Pb particles gave $\alpha = 360$ nm K under ultrahigh vacuum conditions.³⁰

There are different theories predicting how small-particle surface melting may differ from flat-surface melting, i.e., liquid skin growth below the melting temperature, $T_m(D)$.^{7–9,12–17,23,31} Molecular dynamics simulations of Au nanoparticles show this phenomenon as enhanced surface diffusivity and atomic displacements below $T_m(D)$.^{21,22} Structural proof of surface melting in small particles is still lacking despite several experimental studies^{9,11,20,28,32–35} (and references therein). For an assembly of crystallites, any size distribution leads to a distribution in melting temperature and liquid skin thickness, thus complicating interpretation.

To separate small-particle surface melting from size-dependent melting, we rely on the phenomenon of undercooling of liquid particles without solidification.³⁶ Consider a stable distribution of particles with maximum particle diameter, D_{\max} . A sharp crystallite size distribution is created close to D_{\max} by heating the sample to slightly below

$T_m(D_{\max})$ (see shaded area in Fig. 1). Most particles are molten while the remaining crystallites might have a liquid skin. The sample is then cooled slightly (ΔT in Fig. 1) to solidify the liquid skin without nucleating solid in the wholly melted particles. *In situ* x-ray diffraction can then provide the changes in the average crystallite size and hence, the liquid skin thickness.

All experiments were performed inside an ultrahigh vacuum chamber (base pressure $\sim 3 \times 10^{-9}$ Torr) which has an x-ray transparent beryllium window.³⁷ Pb was chosen for this study because of its low vapor pressure at the bulk melting point (4×10^{-9} Torr at 600 K), large x-ray scattering factor, and its well-characterized surface melting on flat surfaces.^{4–6} A single-crystal (532)-oriented Si substrate with its native oxide supported the Pb particles yet contributed little to the x-ray scattering background.

The sample was prepared by evaporating 99.9999% pure Pb (Johnson Matthey) onto the substrate in the ultrahigh vacuum chamber. At the system base pressure, Pb remained atomically clean for tens of hours,^{38,39} as verified by Auger electron spectroscopy. After deposition, we raised the substrate temperature above 600 K to melt all particles, followed by cooling to resolidify them. *Ex situ* field-emission scanning electron microscopy showed that the Pb particles are nearly spherical, as expected from the nearly isotropic surface energy of Pb.^{6,40} All measurements were performed using Cu $K_{\alpha 1}$ radiation from an 18 kW rotating anode x-ray source. A linear position-sensitive detector was used to collect diffraction signals from the 111 and 200 peaks simultaneously over a 2θ range of 10° in 60 s snapshots. Diffraction from an *in vacuo* Pb standard provided calibration of the instrumental resolution [full-width at half-maximum (FWHM) = 0.155°]. The substrate temperature was determined by a thermocouple pressed onto the sample surface.

After sample preparation, a thermal cycle was performed in which the sample was heated to 99.5% $T_m(D_{\max})$, cooled to 96.0%, heated again to $T_m(D_{\max})$, and finally cooled to 93.5% $T_m(D_{\max})$ (see insert in Fig. 2). Profile *c* was taken after reaching $T_m(D_{\max})$. Here, the diffraction intensity has vanished due to the melting of the entire sample. Profiles *c* and *d* are statistically equivalent, demonstrating that the melted particles do not crystallize for the undercooling employed in these experiments. Indeed, liquid undercooling down to 77% $T_m(D_{\max})$ without solidification was observed.

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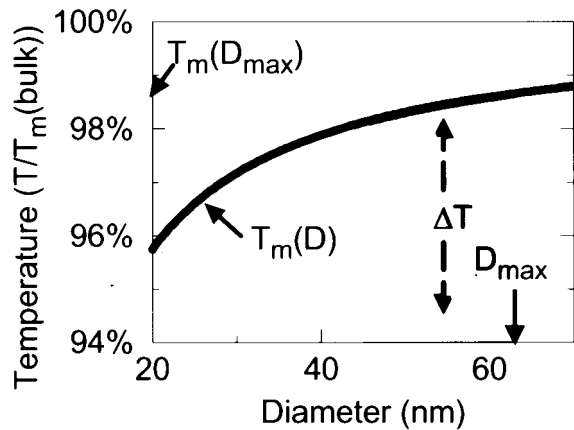


FIG. 1. Melting temperature vs particle diameter for Pb [bold line labelled $T_m(D)$]. The ratio, $T/T_m(D)$, determines the state of a particle—liquid, crystalline, or crystalline with a liquid skin of some thickness. The largest particles have diameter, D_{\max} , and melt at $T_m(D_{\max})$. Upon heating to $T = 99.5\% T_m(D_{\max})$, the crystallite size distribution and the melting temperature distribution become narrow (shaded area). Upon cooling by $\Delta T = 3.5\%$, the liquid skin solidifies while wholly melted particles would remain liquid.

The temperature was reduced by 3.5% from a to b , and Fourier analysis of the x-ray diffraction peaks⁴¹ indicated that the area-averaged crystallite diameter was 52 ± 2 nm at both temperatures. If the liquid skin thickness (τ) were to change during this temperature excursion, this should result in a change of the apparent crystallite diameter as follows:

$$-\frac{\Delta(\langle D \rangle)}{\langle D \rangle} = \frac{2\Delta\tau}{\langle D \rangle}. \quad (2)$$

Equation (2) establishes that the upper limit change in liquid skin thickness, $\Delta\tau$, would be less than one nanometer over this temperature excursion [from 96% to 99.5% $T_m(D_{\max})$].

Figure 3 gives the integrated intensity values (with background subtracted) and the corresponding temperature variation as a function of time. This was repeated four times. The peak intensity is normalized to 100%, and the uncertainty is 1.0% due to counting statistics and the background.⁴² Coin-

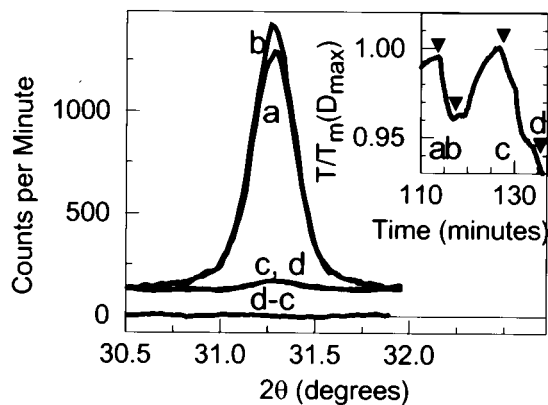


FIG. 2. *Insert:* Temperature-time program. Temperature is given relative to $T_m(D_{\max})$. $T_m(D_{\max}) \approx 98.8\% T_m(\infty)$ based on Eq. (1) in the text. *Main:* Four x-ray scattering “snapshots,” intensity vs 2θ , at the Pb 111 diffraction peak position. In c , the entire sample has melted. The liquid droplets do not solidify on cooling by 6% to d . Therefore, the difference between a and b is mainly due to solidification of a 0.5 nm liquid skin enveloping the 52 nm crystallites.

cident with the 3.5% temperature decrease from 99.5% $T_m(D_{\max})$, the integrated intensity increases by $7.0 \pm 1.5\%$. This intensity change is reversible with the temperature excursion. Some of this intensity change (ΔI) is due to thermal vibrations (Debye–Waller factor), according to⁴³

$$\frac{\Delta I}{I} = -0.265 \frac{\Delta T}{T_m(\infty)} \quad (3)$$

for small ΔT and the Pb 111 x-ray diffraction peak from 52 nm crystallites, including the extra contribution from surface atoms. Accordingly, at most, 1% of the intensity change may be attributed to thermal vibrations over the 3.5% temperature excursion. Also, as the sample was thermally equilibrated above 90% $T_m(D_{\max})$ for several hours, it is unlikely that this reversible intensity change is due to crystallite reorientation or grain growth.

We attribute the remaining 6.0% intensity change to the variation in the liquid skin thickness, $\Delta\tau$. Since the integrated diffraction intensity is proportional to the diffracting crystalline volume, we have

$$\frac{\Delta I}{I} = \left(\frac{\langle D \rangle - 2\Delta\tau}{\langle D \rangle} \right)^3 - 1 \approx -\frac{6\Delta\tau}{\langle D \rangle}. \quad (4)$$

Using Eq. (4), the liquid skin thickness increases by 0.5 nm between 96.0% and 99.5% $T_m(D_{\max})$. This is the first demonstration of a liquid skin growth on free surfaces of nano-scale particles.

This result can be compared with a previous transmission electron microscopy study which showed that the liquid skin thickness on a 100 nm Pb particle grows from 19 nm at 94.7% $T_m(\infty)$ to 25 nm at 95.2% $T_m(\infty)$ before the particle melts entirely at 1% higher temperature.³² The liquid skin thickness change is much larger than what we detected in our measurements. One explanation^{33,34} is that these Pb particles were embedded in a silica matrix. It can be shown^{33,34} that the hydrostatic stresses exerted on the Pb particles due to thermal expansion mismatch may have caused the melting

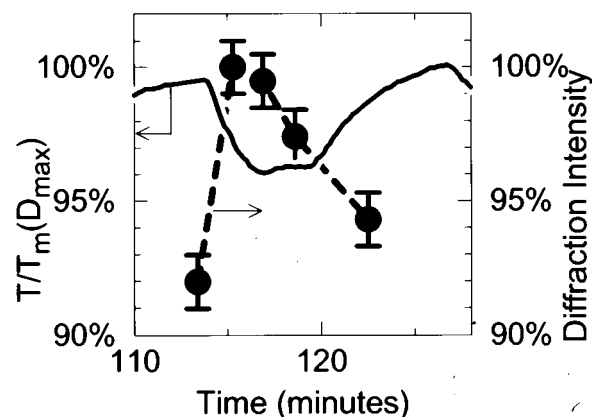


FIG. 3. Temperature program and Pb 111 x-ray diffraction integrated intensity vs time. Liquid skin growth of 0.5 nm causes most of the intensity change.

temperature to shift according to the classical Clausius–Clapeyron equation, and hence the larger liquid skin thickness at a given temperature.

Surface melting has been demonstrated on small Pb particles in ultrahigh vacuum. The liquid skin thickness increases near the size-dependent melting temperature. The surface melting is isolated by undercooling the sample slightly from near the melting temperature so that the liquid skin solidifies. X-ray diffraction from 52 nm Pb crystallites reveals reversible liquid skin growth as a change in the crystallite volume.

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