Comment on "Melting of Isolated Tin Nanoparticles"

In a recent Letter, Bachels, Güntherodt, and Schäfer (BGS) [1] present new experimental results on the melting of unsupported tin nanoparticles. For a $N = 430$ atoms particle (radius $R \simeq 14$ Å) they found, compared to bulk values, a 25% lowering of the melting temperature T_m together with a 45% lowering of the latent heat Δu^{ls}. BGS interpret their results with the help of our phenomenological model [2] and of previous experiments of Lai *et al.* [3]. They conclude that melting occurs abruptly without surface melting, which should explain why their particles, although smaller than the ones of Lai, have a higher Δu^{ls}. After some general considerations, we will discuss the validity of the comparison between both experimental studies, and give finally a different interpretation of the BGS results.

In the last decade, surface melting has been shown to play a key role in the melting of nanoparticles, and several phenomenological models have been derived [2,4,5]. As expected for finite size systems, the first-order character of the bulk solid-liquid (SL) transition is altered by the presence of surface melting. More surprisingly, these models predict that premelting effects should disappear below a critical radius R_c, and hence that a reentrance of the first-order SL transition should occur for the smallest systems. Nevertheless, one can doubt the validity of these phenomenological modelizations for sizes at which this transition is expected, and no clear experimental observation supports this prediction. As the size is decreased, experiments and simulations rather show a dynamical coexistence between different phases [6,7].

The conclusions of BGS are essentially based on a comparison with the experimental study of Lai *et al.* If it is true that the unsupported tin particles of BGS have a spherical shape, this is certainly not the case for the supported particles of Lai *et al.* Indeed, it has been shown [8] that, on similar substrates, island growth of Sn rather gives truncated spheres (close to half spheres). As a first consequence, the real number of atoms in a particle is unknown and overestimated by Lai *et al.* As a second consequence, because Lai's particles partially wet the substrate, surface energy difference between the substrate-solid and the substrate-liquid, at melting, should be taken into account in the release of latent heat. Obviously, this is not the case for BGS's unsupported particles. Finally, it has also been shown [9] that the melting temperature of a supported particle strongly depends on its wetting angle. These important differences between both experimental systems do not permit any reasonable comparison.

Now, we propose an alternative interpretation of the decrease of Δu^{ls}. It is clear from Fig. 1 of BGS that they get Δu^{ls} through the measure of the total heat which is necessary to go from the asymptotic full solid state to the full liquid one at $T = T_m$. The consideration of the different surface terms in the free energies of the spherical particle permits one to extract the size dependence of the latent heat of fusion. Neglecting the density and caloric capacity differences between the solid and the liquid, one can find that $\Delta u^{\mathrm{ls}}(R)$ satisfies

$$\Delta u^{\mathrm{ls}}(R) = \Delta u^{\mathrm{ls}}(\infty) - \frac{3\Delta\sigma}{\rho R}, \tag{1}$$

where $\Delta\sigma = \sigma_{\mathrm{sv}} - \sigma_{\mathrm{lv}}$ and ρ is the density. With two values of $\Delta\sigma$ found in the literature ($\Delta\sigma = 0.084\ \mathrm{J\,m^{-2}}$ [10] and $\Delta\sigma = 0.11\ \mathrm{J\,m^{-2}}$ [1]), we respectively found $\Delta u^{\mathrm{ls}} = 42$ meV/atm and $\Delta u^{\mathrm{ls}} = 32$ meV/atm. This is in good agreement with the experimental measurement of BGS: $\Delta u^{\mathrm{ls}} = (40 \pm 10)$ meV/atm. We thus demonstrate here that the decrease of Δu^{ls} with the size is simply justified by surface energy considerations. Note that we did not make any assumption on the scenario of the transition. Whether it is abrupt or not, the measured latent heat is the same.

For what concerns the melting temperature, the nature of the transition should here have an influence on the $T_m(R)$ curve. Indeed, phenomenological models predict a crossover between two qualitatively different behaviors. Unfortunately, the single size measurement of BGS does not permit such an observation. At this point one cannot conclude on the existence or not of a reentrant first-order SL transition for small nanoparticles. We hope this Comment will motivate further necessary measurements of the latent heat of fusion on free nanoparticles.

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