Comment on “Large Melting-Point Hysteresis of Ge Nanocrystals Embedded in SiO$_2$”

In their Letter [1], Xu et al. study the melting behavior of Ge nanocrystals (NC) in a SiO$_2$ matrix. The observed melting-point hysteresis around the bulk melting point $T_m$ is used with classical nucleation theory (CNT) to estimate the liquid-solid (LS) surface tension of Ge, $\gamma_{LS}$. We reconsider some of the numbers and arguments of [1].

(i) A key quantity is the latent heat of fusion $L$, but the value used in [1] is not given. On one hand, one can infer $L$ from the discussion of Turnbull’s value for $\gamma_{LS}$. From the supercooling limit of Ge and a calculated $L = 25.5$ kJ mol$^{-1}$, he deduced from CNT $\gamma_{LS} = 0.181$ J m$^{-2}$ $\propto L^{2/3}$ [2]. Xu et al. explain that a rescaling gives $\gamma_{LS} = 0.23$ J m$^{-2}$, which indicates the use of $L_1 = 36.94$ kJ mol$^{-1}$, the currently accepted value [3]. On the other hand, to reproduce their values for the nucleation barriers with $\gamma_{LS} = 0.26$ J m$^{-2}$ [1], one needs to use $L_2 = 31.8$ kJ mol$^{-1}$, but this is the average of two inconsistent early determinations [4]. $L_1$ should be preferred and leads to $\gamma_{LS} = 0.285$ J m$^{-2}$. Coming back to Turnbull, we note that he studied Ge on a SiO$_2$ flake [5]: nucleation was heterogeneous as in [1]. Assuming a contact angle of $\pi/2$ on SiO$_2$ [1], we modify his analysis [2] by dividing the energy barrier by 2 and replacing the number of atoms $n$ by $n^{2/3}$, the number of atoms at the surface: $\gamma_{LS}$ becomes 0.26 J m$^{-2}$, close to 0.285 J m$^{-2}$.

(ii) As Ge shrinks upon melting, Xu et al. consider the possibility that a gap opens between the molten droplet and the matrix. For a spherical vapor shell, they find that the surface energy cost is higher than the elastic strain energy, and conclude that a gap will not open. However, the vapor does not wet the matrix completely: the contact angle $\theta_c = \cos^{-1}[\gamma_{LM} - \gamma_{MV}]/\gamma_{LV}$ is between 34° and 61° (based on tensions from [1]). The increase in surface energy can thus be lowered by creating a lenticular bubble rather than a spherical shell. A complete analysis should take the elasticity of the matrix into account, but it is complicated by the loss of spherical symmetry. To give an idea, we consider a rigid matrix and expand the liquid chemical potential linearly in density to calculate the change in density to calculate the change in

$\gamma_{LM}$.

(iii) Finally, we consider the effect of annealing. The stress in the sample is relieved by annealing for 14 h at 1073 K [8]. When all the NCs are melted at 1450 K, the matrix is put under stress; using the thermally activated model from [8], we estimate that the stress relaxes in 34 s at this temperature, less than the 5 min duration of a temperature step in [1]. In this case, when cooling down, solidification results in a compressive stress. The above argument about $\Delta T$ can be invoked, but with a different value of the strain and the bulk modulus of the solid [3]. For $f = 0.6$ J m$^{-2}$ (respectively $1$ J m$^{-2}$), $\Delta T$ is shifted by $+24$ K (respectively $+28$ K) for $r_0$ and by $+43$ K (respectively $+47$ K) for $r = 0.5$ nm. If such a mechanism is relevant, the whole picture would have to be modified, leading to different values for $\gamma_{LM} - \gamma_{SM}$ and $\gamma_{LS}$.

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