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Melting of clusters approaching 0D

R. Kofman[1,a], P. Cheyssac[1], Y. Lereah[2], and A. Stella[3]

[1] Laboratoire de Physique de la Matière Condensée – CNRS UMR 6622, Université de Nice-Sophia Antipolis, Parc Valrose, F-06108 Nice Cedex 2, France
[2] Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Israel
[3] Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica "A. Volta", Universita di Pavia, Via Bassi 6, I-27100 Pavia, Italy

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Abstract. Recently, new experiments have allowed us to understand the melting scenario of very small crystals. Down to sizes of 5–8 nm, surface melting amplified by curvature effects is observed; the melting process is initially continuous and reversible (first-order transition with critical phenomena due to confinement). When the inner solid core reaches a critical radius r_m, final melting occurs discontinuously and irreversibly. For clusters of sizes smaller than 5–8 nm, surface melting disappears and the melting process is discontinuous.

Experiments yielding new information will be discussed for the different size ranges of the clusters and compared with models of melting taking surface melting into account. Issues requiring clarification will be stressed, particularly the problem of the limit (if any) of the lowering of the melting temperature.

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1 Introduction

The lowering of the melting temperature of a cluster is a phenomenon known as the "thermodynamic size effect" which becomes observable for cluster sizes of 100 nm and is very large when their size reaches the nm range. This phenomenon is relevant since, for example, a Pb cluster of size 6 nm (about 1800 atoms) has a melting temperature lowered by 200 K compared to the bulk one ($T_\mathrm{B} = 600\,\mathrm{K}$). From a qualitative point of view, it is easy to understand that the ratio between the number of surface atoms and the total number of atoms of a cluster increases when the size of the cluster decreases. In the case of a free cluster, these surface atoms are more weakly bound to their neighbours than bulk atoms and the simple application of the Lindemann [1] criterion explains why the melting temperature T_m of a free cluster must lower when its size decreases.

The first scientists to be interested in this problem were W. Thomson (Lord Kelvin) in 1870 and J.J. Thomson [2] in 1888 but the phenomenon was only experimentally demonstrated by Takagi [3] in 1954 using electron diffraction. Up to 1980, many groups measured the lowering of T_m for metals such as Pb, Sn, Bi, In, Au. The classic work in this period was done by Buffat and Borel [4] on Au using electron diffraction. The essential feature of these studies was that clusters, though deposited on a substrate (generally amorphous carbon), were approximated as spheres and only their melting temperature was under consideration. These experimental results lead to the law $T_\mathrm{B} - T_\mathrm{m}(R) \sim 1/R$ where R is the radius of the cluster and T_B is the melting temperature of the bulk.

From a theoretical point of view, Pawlow (1901) [5] was the first to analyse the system constituted by two clusters of radius R, one being solid, the other liquid, in equilibrium with their vapor. Following this idea, Hanszen [6] derived a formula which verifies the $1/R$ law for the decrease of T_m. This formula which was later improved by Buffat and Borel [4] uses as main data the surface energies γ_sv (solid/vapor) and γ_lv (liquid/vapor). Other hypotheses have been used such as a solid cluster in equilibrium with the liquid phase (Semenchenko's model [7]) which uses the solid/liquid interfacial energy γ_sl, or a solid cluster in equilibrium with a liquid surface layer of constant thickness (Wronski's model [8]).

Due to their different hypotheses, these models, though all verifying the $1/R$ law, agree well or less well with the experimental results, as we will see later.

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[a] Corresponding author. e-mail: `kofman@unice.fr`

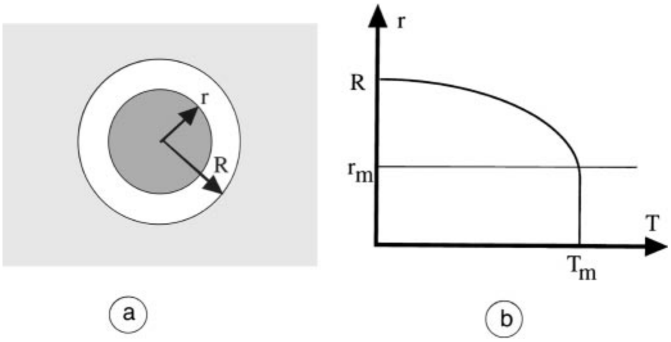

Fig. 1. Scheme summarizing the scenario of melting of a cluster. (a) A spherical cluster of radius R with a liquid layer at the surface. (b) Evolution of the radius r of the solid/liquid interface versus T.

2 Experiment

The samples were prepared by evaporation-condensation of high purity materials in ultra high vacuum. Substrates are sapphire slides for optical measurements and copper grids covered by a carbon film for electron microscopy. The temperature of the substrate is controlled for the nucleation of the particles taking place in the liquid state. After freezing, a distribution of crystals shaped as truncated spheres is obtained. The precise shape of the crystals can be obtained by measuring the contact angle on the substrate [9]. New experiments based on high sensitivity optical reflectivity or dark-field electron microscopy (Kofman *et al.* [10,11]) have allowed us to understand the scenario of melting for relatively large particles (∅ > 5–8 nm). This has been observed with amorphous substrates for supported or embedded clusters. Melting starts at the surface of the as-spherical cluster by a decrease of the radius r of the solid core down to a value r_m where complete melting occurs suddenly (Fig. 1). For $R > r > r_\mathrm{m}$, the process is reversible; for $r < r_\mathrm{m}$, it is irreversible; freezing occurs only upon a decrease of the temperature of the order of 100 K. Moreover, experiments on non-spherical clusters show that the liquid surface layer has a thickness which depends on the local curvature of the cluster. This is clearly visible on supported clusters which wet the substrate differently: for example Sn clusters on a $\mathrm{SiO_2}$ substrate have a geometry close to a sphere because Sn does not wet $\mathrm{SiO_2}$ (Fig. 2). In contrast to this, Ga clusters wet SiO_x ($x \approx 1$) and the cluster has the shape of a truncated spheroid whose height is only a small fraction of the radius (Fig. 3). Figures 2 and 3 show the surface melting in both cases and it gives evidence that high curvature regions, which exist in Ga clusters, enhance surface melting.

These observations have allowed the introduction for clusters of the concept of surface melting (SM) which was already known for bulk. In contrast to the bulk [12] where SM is limited to some atomic layers, here it affects an important part of the cluster depending obviously on curvature.

This has allowed the melting process of clusters to be understood as a nucleation–growth phenomenon of the liquid on the solid. This phenomenon is favoured if the liquid wets the solid, i.e. if there is a gain in energy when a solid surface layer is replaced by a liquid one.

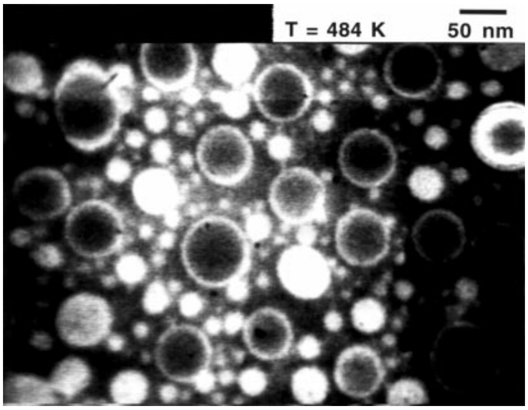

Fig. 2. Dark-field electron microscopy for Sn clusters on $\mathrm{SiO_2}$. Clusters with a bright ring around a dark core have a liquid layer at the surface. White (and smaller) clusters are melted.

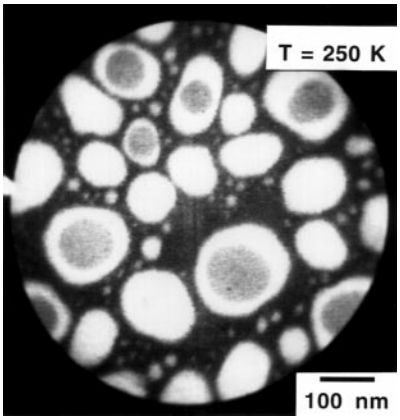

Fig. 3. Dark-field electron microscopy for Ga clusters on SiO_x. The liquid layer is larger than in the system $\mathrm{Sn/SiO_2}$. Note that Ga clusters are in a metastable phase (β, δ,...) whose bulk melts at about 260 K while bulk Ga (α phase) melts at 303 K.

For clusters of smaller sizes (∅ < 5–8 nm), these experiments reveal an interesting behaviour: Both SM and irreversibility in freezing disappear (Fig. 4). These small clusters have also been observed by high resolution electron microscopy. In addition to the fact that no liquid surface layer can be detected, we observe that the structure of the crystal fluctuates (Fig. 5). This is revealed by the appearance and disappearance of moving defects whose activity depends on size and temperature. We have shown that the positions of the (111) planes of Pb clusters [13] were not random but were characteristic defects of the CFC structure. Since these positions of the (111) planes do not change with time, we conclude that the cluster retains the "memory" of its structure when it jumps to another one. This excludes total (but not partial) melting between two different structures of the cluster. For very small clusters (∅ < 3–4 nm for Pb), electron microscopy shows that they are liquid at room temperature. The evaluation of the influence of the observation technique appears to be an

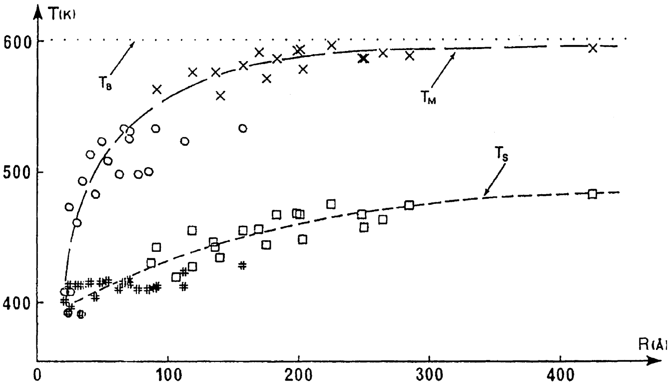

Fig. 4. Experimental melting (T_m) and freezing (T_s) temperature versus radius R through high-sensitivity reflectance measurements (results for lead [9]). T_B is the bulk melting temperature. The data points are deduced from: ○, the beginning of melting; ×, the end of melting; □, the beginning of solidification; #, the end of solidification.

essential step of the measurement procedure. This is a difficult task with electron microscopy and it appears useful to develop new and less perturbing observation techniques for very small clusters. Haberland [14] has developed a photofragmentation technique that he applied to a beam of Na clusters. He found the melting temperature of Na_{139}^+ ($\varnothing = 2.2$ nm) to be $T_m = 267$ K while $T_B = 371$ K. We have no results on supported Na clusters to compare with this result, but it can be noted that the decrease in melting temperature with respect to the bulk is 28% while higher decreases (about 33%) on larger supported clusters of other materials (Pb, Ga,...) have been found. To go further, it would be very interesting to have results by this technique not only for one size but for a range of sizes (see the paper of Haberland *et al.* in this issue).

3 Theory

The model we have developed has been described elsewhere [10] and we shall give only the main ideas necessary for discussion. It starts with a spherical geometry and three phases: solid, liquid, vapor or matrix. The important fact is that we introduce a short range interaction between both solid/liquid and liquid/vapor (or matrix) interfaces. This interaction is described by a characteristic length ξ. In this way, it is possible to obtain a minimum in the free energy of the three-phase system which means that, for a given solid/liquid interface radius r and temperature $T(r)$, a stable equilibrium for the liquid surface layer exists. The relation between r and $T(r)$ has been calculated (L is the latent heat and ϱ the volume mass):

$$1-\frac{T(r)}{T_B}=\frac{2\gamma_{sl}}{\varrho L r}(1-e^{-\delta/\xi})+\frac{S'R^2}{\varrho L\xi r^2}e^{-\delta/\xi}$$

$$\text{with } \delta = R-r \text{ and } S'=\gamma_{sv}-\left[\gamma_{lv}+\gamma_{sl}\left(\frac{r}{R}\right)^2\right] .$$

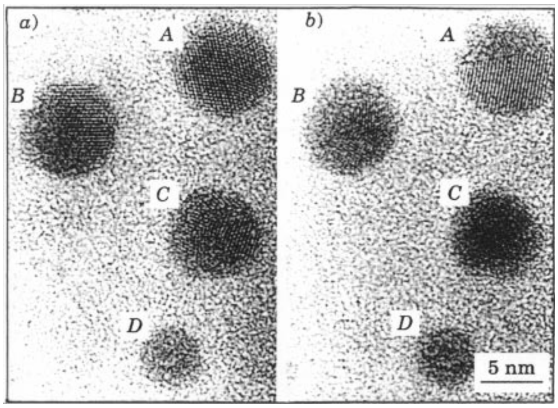

Fig. 5. (a) High resolution electron microscopy picture of four Pb clusters at room temperature; (b) the same field after 10 s. (Pictures by LAMEL, Bologna).

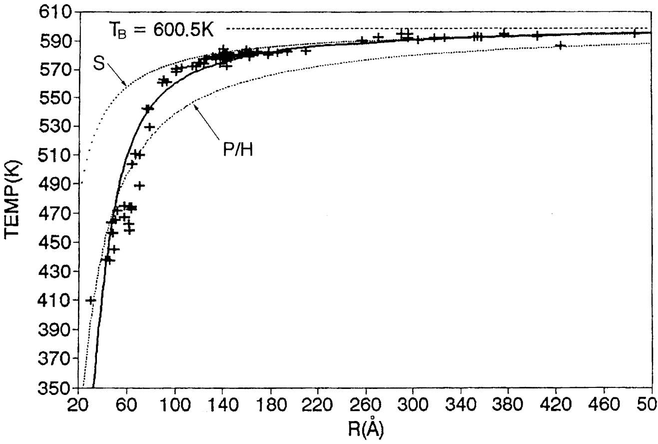

Fig. 6. +: Experimental melting points obtained for lead through dark-field electron microscopy [10]. P/H: Pawlow/Hanszen's model [5, 6]. S: Semenchenko's model [7]. Full line: Kofman *et al.*'s model [9, 10] with the following data used for Pb: $L = 22\,990$ J/kg, $\varrho = 10\,950$ kg/m^3, $\gamma_{sv} = 0.61$ J/m^2, $\gamma_{lv} = 0.48$ J/m^2, $\gamma_{sl} = 0.05$ J/m^2, $\xi = 0.63$ nm.

It allows one to corroborate the experimental observations: r decreases slowly from $r = R$ to $r = r_m$ and for this value (where $T = T_m$) r jumps suddenly to zero. The curve $T_m(R)$ is the best fit to experimental points. In this model it is possible to take into account a nonspherical geometry by describing the shape by a functional [15]. On Fig. 6, which has been applied to Pb, it can be shown that while Pawlow/Hanszen's model [6] does not fit the experimental points, Semenchenko's model [7] agrees with experiments for large clusters; this is not surprising because the approximations adopted in the present model (R large, $r_m \sim R$ and $\xi \ll r_m$) lead to the model of Semenchenko.

An interesting point has been raised by Vanfleet and Mochel [16] on a similar model: On the one hand, it is possible to find the beginning of SM by drawing the curve where one monolayer of liquid exists on the surface of the cluster. On the other hand, it is possible to find the freezing curve. These results are in excellent agreement with the experimental data. The limit of SM is the point where the freezing curve joins the melting curve $R_{\mathrm{exp}} = 2.5\,\mathrm{nm}$, $T_{\mathrm{exp}} = 392\,\mathrm{K}$ and $R_{\mathrm{th}} = 2.5\,\mathrm{nm}$, $T_{\mathrm{th}} = 429\,\mathrm{K}$ for Pb. Note that the values of the interface energies for Pb, which have been taken from the literature, are not known with a sufficient accuracy, which explains the differences in T.

Another model by Sakai [17] agrees with these results.

4 Discussion

There is now broad agreement on the melting scenario of clusters. Melting of clusters for $\varnothing > 5\,\mathrm{nm}$ (for Pb) is a first-order transition with a critical phenomenon induced by the surface. The order parameter in the system (density, crystallinity,...) evolves continuously with radial coordinate but discontinuously with temperature. The surface liquid layer starts with a continuous growth and suddenly invades the cluster at $T = T_{\mathrm{m}}$ and $r = r_{\mathrm{m}}$. There is a critical value R_{c} of the radius of the cluster where both SM and irreversibility in freezing disappear. For clusters with $R < R_{\mathrm{c}}$ ($\varnothing < 5\,\mathrm{nm}$ for Pb) the solid–liquid transition is sharp (no SM when increasing T, no hysteresis when decreasing T). In this range of sizes, the cluster can easily switch to liquid and vice-versa. The fluctuations of structure that we observe may be due to a decrease of the latent heat of the material at these sizes which could explain why thermal fluctuations are sufficient to induce clusters to approach melting but there is no decisive proof of this. More experimental results are needed to understand the behaviour of clusters of sizes lower than 5 nm.

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