Premelting of thin wires

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We have investigated the melting behavior of thin lead wires using molecular dynamics. We find that—in analogy with cluster melting—the melting temperature $T_m(R)$ of a wire with radius R is lower than that of a bulk solid T_m^b by $T_m(R) = T_m^b - c/R$. Surface melting effects, with formation of a thin skin of highly diffusive atoms at the wire surface, are observed. The diffusivity is lower over (111)-oriented faces, and higher at (110) and (100) rounded areas. The possible relevance to recent results on nonrupturing thin necks between a scanning tunnel microscope tip and a warm surface is addressed.

It is well known—experimentally and theoretically—that small atomic clusters have a melting temperature T_m which is lower than that, T_m^b, of the infinite bulk solid of the same element.[1] The main physical reason for this is that the liquid-vapor interface free energy γ_{lv} is generally lower than the average solid-vapor interface free energy γ_{sv}. Therefore, when the particle size is decreased, its surface to volume ratio increases, and T_m decreases as a consequence of the improved free energy at the cluster surface.

Thin wires with a microscopic diameter should exhibit a similar melting behavior—although with significant differences due to their cylindrical symmetry and infinite extension along the axis—but they have not been extensively investigated so far, probably due to lack of practical motivations. However, considerable interest in the thermal behavior of thin wires has been recently raised by some scanning-tunneling-microscopy[2] (STM) experiments. Abrupt changes of the tunnel resistance have been observed when the tip-surface separation distance becomes sufficiently small, indicating jump into contact.[3] Molecular dynamics (MD) computer simulation studies[4-6] have indicated that contact is often realized by means of a narrow "neck" connecting the tip with the sample surface. In an MD study of a Au tip interacting with a Pb(110) surface at high temperature,[6] this neck is seen to be liquid in nature in its thinner portion, even when the temperature is considerably lower than T_m. Moreover, the jump to contact between tip and surface via such a partly liquid neck was predicted, because of this, to occur more readily as temperature was raised. Recent STM experiments by Kuipers and co-workers[7,8] also performed on Pb(110) using a W tip over a temperature range from about $0.5\,T_M$ to surface melting, indicate that the neck elongates up to considerable lengths (several thousand Å), depending on the retraction speed and on temperature before breaking. To shed some light on the behavior of such a thin and long neck, we have started an investigation of cylindrical metallic wires.

(i) Simple theory: For spherical particles of radius R, a melting temperature $T_m(R)$ is obtained phenomenologically[9] by equating the Gibbs free energies of solid and liquid spherical clusters, assuming constant pressure conditions:

$$\frac{T_m^b - T_m(R)}{T_m^b} = \frac{2}{\rho_s L^b R}\left[\gamma_{sv} - \left(\frac{\rho_s}{\rho_l}\right)^{2/3}\gamma_{lv}\right], \qquad (1)$$

where ρ_s and ρ_l are the solid and liquid densities, L^b is the bulk latent heat of melting, and γ_{sv} and γ_{lv} are the solid-vapor and liquid-vapor interface energies, respectively. The surface energy anisotropy of the solid is not taken into account, and the possibility of inhomogeneous phases (such as a liquid skin wetting the solid cluster) is also neglected. In spite of these approximations, the $1/R$ behavior is approximately correct for clusters of sufficiently large size, although in some systems T_m drops faster than predicted.[1,10,13] In the case of Pb, which is the subject of our MD study, deviations from $\sim 1/R$ appear to be small even at small sizes.[11,12] For a wire, following a similar procedure, we equate the Gibbs free energies per unit length of the solid and liquid wires at constant pressure and temperature, $G_s = N\mu_s + 2\pi R\gamma_{sv}$ and $G_l = N\mu_l + 2\pi R\gamma_{lv}$, where N is the number of atoms per unit length, μ_s and μ_l are the chemical potentials of the solid and liquid phases, respectively, and R is the wire radius. Since near T_m^b, $N(\mu_s - \mu_l) = V\rho_s L^b(T - T_m^b)/T_m^b$, we obtain for the melting temperature $T_m(R)$ of a thin wire

$$\frac{T_m^b - T_m(R)}{T_m^b} = \frac{1}{\rho_s L^b R}\left[\gamma_{sv} - \left(\frac{\rho_s}{\rho_l}\right)^{1/2}\gamma_{lv}\right]. \qquad (2)$$

Hence, the melting temperature of a wire should be depressed by approximately half the corresponding amount for a spherical cluster. In this simple model the latent heat of melting per atom (averaged on all atoms) decreases with exactly the same law when the size is decreased:

$$\frac{L^b - L(R)}{L^b} = \frac{1}{\rho_s L^b R}\left[\gamma_{sv} - \left(\frac{\rho_s}{\rho_l}\right)^{1/2}\gamma_{lv}\right]. \qquad (3)$$

These relations imply the existence of a critical radius $R_c = [\gamma_{sv} - (\rho_s/\rho_l)^{1/2}\gamma_{lv}]/(\rho_s L^b)$ corresponding to $T_m(R_c) = 0$, $L(R_c) = 0$, below which the solid wire is not stable.

(ii) MD simulation: For our simulation we have chosen lead, and a (110) orientation for the wires. Pb was a natural choice as the melting properties of its surfaces and clusters have been extensively investigated both experimentally and theoretically. Interestingly, Pb(111), Pb(100), and Pb(110) exhibit different melting properties, that is, respectively, nonmelting, incomplete melting, and surface melting.[14-16] On small Pb particles, the formation of a liquid skin as a
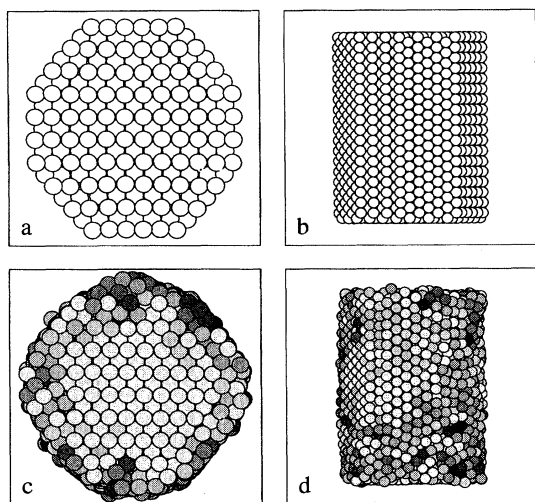
FIG. 1. Snapshot views of the MD sample with $N = 3294$ and $R \simeq 22.5$ Å. (a) and (b) are the initial sample at 0 K. (a) is the top view of the wire cross section. Wire axis (z direction) is perpendicular to this cross section. (b) is the side view from an angle such that all different laterals are seen. (c) and (d) are corresponding views at a temperature just below the melting temperature. The grayness of each atom is proportional to its square displacement during a MD run. White indicates a nondiffusing, crystalline behavior.
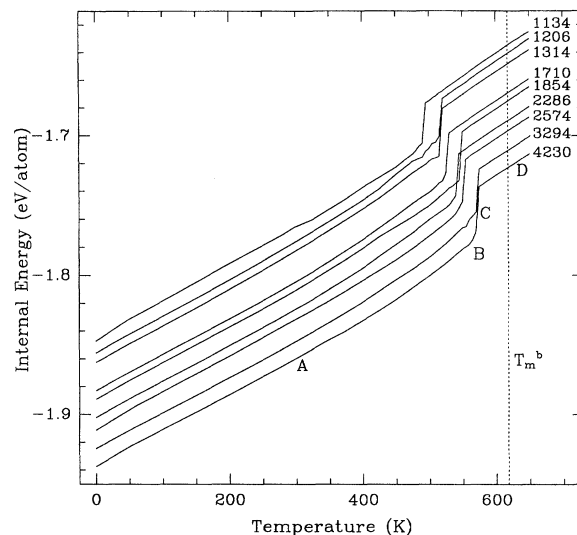

FIG. 2. Internal energy as a function of temperature is shown for different wire samples. Numbers labeling the curves are the number of atoms in MD cell. Dashed vertical line indicates the bulk melting temperature for lead determined from MD. Discontinuity in the curves shows the melting transition.

premelting effect has been observed by microscopy experiments.[11] We have used a many-body potential that has already tested in previous surface[6,17,18] and cluster[12] studies. In particular, the different melting behavior of the main surfaces of Pb was reproduced, in excellent agreement with experimental results. Because the model potential is untested (and therefore unreliable) at really low coordination numbers, we restrict our study to $R \geqslant 10$ Å. By choosing a (110) wire axis, (111), (100), and (110) orientations are simultaneously present on the cylindrical surface of the wire. The different melting behavior of these facets can make the details of premelting phenomena particularly interesting. Moreover, Pb(110) is the system on which the STM experiments discussed above[7,8] have been done, and one could conjecture that the neck might retain the same (110) orientation of the sample surface.

We have performed several MD runs at different temperatures and for different wire radii. All samples are made up by 36 (110) layers, repeated along the wire axis z by periodic boundary conditions. The initial configurations are prepared by including all atoms in an fcc lattice whose distance from the axis is smaller than an assigned radius. At $T = 0$ K, well-defined (100), (110), and (111) facets are present (Fig. 1). This roughly cylindrical geometry is expected to be relatively close to the equilibrium situation, since the surface energy anisotropy of Pb is known to be rather small.[12] For the system sizes investigated, this procedure typically results in octagonal cross sections. We have studied nine samples, with a total number of atoms $N = 1134$, 1206, 1314, 1710, 1854, 2286, 2574, 3294, and 4230, with radii between $R = 13$ Å and $R = 25$ Å.

All MD runs were performed at constant temperature and constant wire length, where the box length along z is ad-

justed according to the bulk thermal expansion curve. While it would also seem possible to operate at constant axial stress and varying length, it is not feasible to achieve stability under such conditions when the wire becomes liquid. The time step is $\Delta t = 7.32 \times 10^{-15}$ s. The initial samples with atoms in ideal fcc positions were first relaxed by simple quenching. Then, an annealing cycle at room temperature, followed by a quench to 0 K, is done to check the stability of the original structure. In most cases, due to creation of defects during the annealing, the final energy was slightly higher than that of the previous relaxed structure. The absence of any major structural changes indicates that the original structure was optimal or nearly optimal. Each system was then heated by MD runs of 20 000 time steps (147 ps) with a temperature step of 50 K up to 300 K and of 25 K above 300 K. In proximity of T_m we further reduced the temperature step to 5 K and used longer equilibration runs of 40 000 time steps (293 ps) at each temperature. We monitored several quantities, such as the internal energy E and the diffusivity as a function of T.

The caloric curves $E(T)$ for all the wires investigated are shown in Fig. 2. The dashed vertical line indicates the bulk melting temperature of our model determined using the phase coexistence method[17] from bulk MD runs at zero pressure, $T_m^b = 618 \pm 4$ K (to be compared with 600.7 K of real Pb). In each curve one can identify four regions, labeled as A, B, C, D in Fig. 2. In region A the wire is solid, and the slope corresponds to the Dulong-Petit specific heat. Visual examination of the samples confirms that diffusion is nonexistent, or very low in this region. In region B, $E(T)$ exhibits an upward curvature, where the specific heat gradually increases by a small fraction of the total heat of melting. This increase is associated with loss of solid rigidity, and onset of diffusion at the wire surface. For example, the wire cross section in Fig. 1(c), taken at $T = 570$ K for a wire with $R = 22.5$ Å, clearly shows that melting starts first at the wire

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surface, while the inner region is still ordered. The surface diffusivity is anisotropic and appears to be lower in correspondence with (111) facets. This is reasonable in view of the known nonmelting behavior of Pb(111).[16,17] The lateral view [Fig. 1(d)] also shows the presence of (111) crystalline patches on the wire surface. Presumably, the wire size is too small to exhibit complete crystallinity of (111) facets, which should be expected in the limit of macroscopic sizes. (100) patches are also sometimes observed. (110) faces appear to be the first to melt with increasing T, followed by (100) and then (111). Another interesting feature shown by Fig. 1(c) is that (110) facets—and, to a lesser extent, (100) faces—have shrunken in size with respect to the low-temperature shape, and are considerably rounded. A rounded profile is characteristic of a roughened surface, where steps can proliferate freely. This observation is therefore qualitatively consistent with the experimental observation of a roughening transition of Pb(110) around 415 K,[19] and is further corroborated by surface simulations results.[18] Region C consists of an abrupt nearly vertical jump corresponding to the melting transition of the whole wire, and its temperature and magnitude are discussed below. In region D the wire is completely liquid, and $E(T)$ grows again linearly.

It is interesting to note that the internal energy jump (region C), corresponding to the latent heat, remains sharp and discontinuous: the wire suddenly melts when its melting temperature is reached, regardless of the quantity of solid at the surface which is already melted. The presence of surface melted regions implies absence of large overheating for the wire. Only a minor amount of overheating can be detected, e.g., on curve of 1854 particles wire of Fig. 2. The sharp energy jump yields a rather precise value of T_m for all the sizes investigated. There is a clear decrease of T_m with decreasing wire radius (Fig. 2). To verify the predicted approximately factor of two between Eqs. (1) and (2) we compare the behavior of wires with that of Pb clusters investigated by Lim et al.[12] using the same force model. Figure 3 reports T_m as a function of $1/R$ for wires (solid circles) and clusters (open squares). The dashed lines correspond to the simple thermodynamical models of Eqs. (1) and (2), using $\gamma_{sv} = 544$ mJ/m^2, $\gamma_{lv} = 476$ mJ/m^2, $\rho_s = 0.0321$ atom/Å^3, $\rho_l = 0.031$ atom/Å^3, and $L^b = 0.0494$ eV/atom. For both geometries, the $1/R$ behavior is followed with fairly good accuracy, as well as the approximate ratio 2 between the slopes.

The energy jump on melting corresponds to the latent heat $L(R)$. As a result of the premelting effects discussed above, this jump is slightly smaller than the latent heat that would be obtained if the system were entirely crystalline just below T_m.[20] In order to verify the prediction of Eq. (3), where premelting effects are not considered, we have constructed a modified latent heat $L^*(R)$, defined as the difference between the energy of the liquid and the energy of a hypothetical complete solid at T_m, obtained by ignoring surface melting and extrapolating linearly $E(T)$ from its low-temperature behavior. $L^*(R)$ normalized by the bulk latent heat, $L^b = 0.056$ eV/atom determined from our model, is plotted in Fig. 4 as a function of $1/R$ (solid circles), together with the data relative to spherical clusters from Ref. 12 (open squares) and with Eq. (3) (dashed line). For both geometries the $1/R$ behavior is again approximately true, although not quite as accurate as for T_m. However, deviations from Eq.
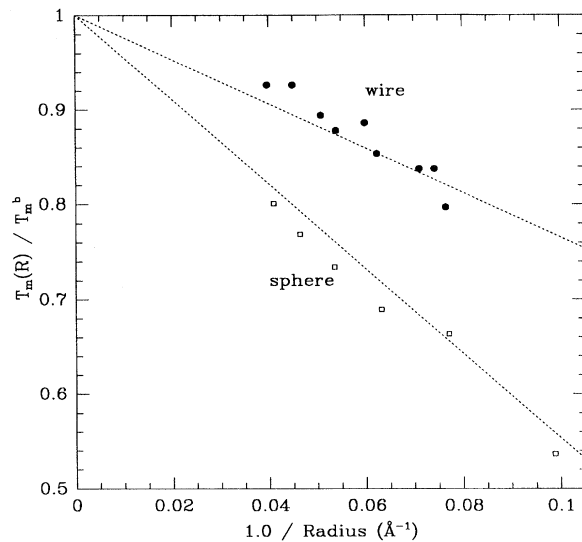

FIG. 3. Melting temperature of different clusters as a function of inverse radius. Solid circles refer to wires, open squares to spherical clusters, the dashed lines are the predictions of the simple phenomenological theory (see text).

(3) are more noticeable for clusters than for wires, and for all the smaller sizes. A faster decrease of L compared with T_m with decreasing size has been also observed in previous Au clusters simulations.[13] These deviations can be tentatively attributed to the reduced entropy of atoms at the liquid metal surface compared with those in the bulk liquid.

Our results on wire melting may be of relevance to the neck between an STM tip and a metal surface. While a thick crystalline neck can still be slowly pulled out of a surface via tip-induced diffusion, as explained in Refs. 7 and 8, it is possible, as indicated by MD simulations[6] that at least a part
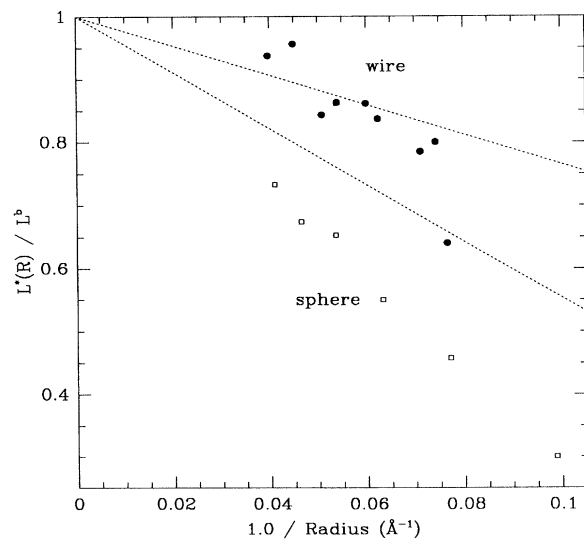

FIG. 4. Latent heat of melting for different clusters as a function of inverse radius. Solid circles refer to wires, open squares to spherical clusters, the dashed lines are the predictions of the simple phenomenological theory (see text).

of the neck could be extremely thin, $R \sim 5$ Å. Our extrapolated melting temperature for such a very thin Pb wire is lower than room temperature. Hence, that neck portion would be completely liquid above 300 K, allowing matter to flow freely along its axis even under fast traction. The possible existence of these ultrathin necks might be checked by looking for, e.g., transversally quantized electronic levels and related jumps in the I-V characteristics, and their liquid nature could be of importance for friction problems.

In conclusion, thin wires, like small clusters, melt at a temperature $T_m(R)$ which is lower than the bulk melting temperature, and is found to be approximately a decreasing linear function of inverse radius. The latent heat follows a similar law, but drops slightly faster with decreasing size. Wire melting is preceded by surface melting effects of its outer skin, similar to those exhibited by flat surfaces and by spherical clusters. Possible relevance to the nature of thin tip-surface necks has been pointed out.

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