Strain effects at solid surfaces near the melting point

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Abstract

We investigate the effects of strain on a crystal surface close to the bulk melting temperature $T_m$, where surface melting usually sets in. Strain lowers the bulk melting point, so that at a fixed temperature below but close to $T_m$ the thickness of the quasi-liquid film is expected to grow with strain, irrespective of sign. In addition, a strain-induced solid surface free energy increase/decrease takes place, favoring/disfavoring surface melting depending on the sign of strain relative to surface stress. In the latter case one can produce a strain-induced prewetting transition, where for increasing temperature the liquid film suddenly jumps from zero to a finite thickness. This phenomenology is illustrated by a realistic molecular dynamics simulation of strained Al(110).

KEYWORDS: Surface thermodynamics, Surface melting, Surface stress, Prewetting, Aluminum, Molecular dynamics
1 Melting of a Strained Surface: Phenomenological Theory

We consider the fate of the surface of a strained solid just below the bulk melting temperature, and focus in particular on surface melting, that is on the possibility that a microscopically thin surface film could melt before the bulk. The phenomenological surface free energy variation (per unit area) produced by melting the solid surface, subject to a small bulk strain $\varepsilon$ (assumed parallel to the surface), to a thickness $l$ of liquid can be written as

$$\Delta G = l\rho \lambda \left(1 - \frac{T}{T_m}\right) + (\gamma_{SL} + \gamma_{LV} - \gamma_{SV}) + V(l) - \frac{1}{2} Y' l \varepsilon^2 - \sigma^{(s)} \varepsilon .$$

Here $\lambda$ is the enthalpy of fusion per unit mass and $\rho$ is the liquid density; thus the first, positive term represents an increase of free energy ($T < T_m$) required for melting a surface unstrained solid film to become a liquid film of thickness $l$. The second, $\Delta \gamma_\infty \equiv (\gamma_{SL} + \gamma_{LV} - \gamma_{SV})$, is the free energy variation caused by replacing, at zero strain, the solid-vapor interface with the solid-liquid and the liquid-vapor pair of interfaces. When $\Delta \gamma_\infty < 0$ ordinary, strain-free surface melting takes place, with $l > 0$ close to $T_m$. The third term $V(l)$ represent effective interaction, usually repulsive, between the solid-liquid and the liquid-vapor interfaces. Its typical behaviour for small $l$ is $V(l) = |\Delta| e^{(-2l/\xi)}$ ($\Delta$ is a parameter comparable with $\Delta \gamma_\infty$, $\xi$ is the correlation length in the liquid [2]), while a crossover to the asymptotic form $V(l) = H/l^2$ appears at larger $l$’s. The fourth term represents the decrease of the elastic energy stored in the strained solid, $(1/2) Y' l \varepsilon^2$, since the molten film is free to expand or contract along the surface normal ($Y'$ is proportional and close to the Young modulus $Y$). Finally $\sigma^{(s)} \varepsilon$ is a surface free energy change – in principle affecting both solid-vapor and solid-liquid interfaces – caused by a generally nonzero surface stress $\sigma^{(s)}$.

Eq. (1) can be rewritten as

$$\Delta G(l) = \rho \lambda \left(\frac{T_{m}^*(\varepsilon) - T}{T_m}\right) l - (|\Delta \gamma_\infty| + \sigma^{(s)} \varepsilon) + V(l) ,$$

1 The exact value of $Y'$ depends on how the strain is applied. If the surface is strained in the $y$ direction ($\varepsilon_{yy} = \varepsilon$) and the $x$ direction is free ($\sigma_{xx} = 0$) in the absence of shear ($\varepsilon_{xy} = 0$), then $\sigma_{yy} = Y \varepsilon_{yy}$ and $Y' = (\rho/\rho_{solid})Y$. The density ratio enters because $l$, the thickness of the molten film, is larger than the thickness of the original solid film.
where $T_m^*$, is defined as

$$T_m^*(\varepsilon) = \left(1 - \frac{\gamma'}{2\rho \lambda} \varepsilon^2\right) T_m.$$  \hspace{1cm} (3)

As the temperature reaches $T_m^*$, the thickness of the molten layer diverges: $T_m^*(\varepsilon)$ is the melting temperature of the solid under strain $\varepsilon$. Actually the strain enhances the free energy of the solid phase without altering that of the liquid phase. Thus the latter is favoured and $T_m^* < T_m$. We note that $\Delta G(0) = 0$ but $\lim_{l \to 0^+} \Delta G(l) \equiv G(0^+) = -(|\Delta \gamma_{\infty}| + \sigma^{(s)} \varepsilon) + V(0^+)$ which does not generally vanish. In fact equations (1) and (2) cease to hold for $l$ comparable with a monolayer or less.

The predicted strain-temperature phase diagram for realistic parameters mimicking aluminium, and obtained minimizing the $\Delta G(l)$ with respect to $l$ is shown in Fig. 1. At $T = T_m^*(\varepsilon)$ (solid line) there is melting of the strained bulk. The quadratic decrease of $T_m^*$ with increasing strain is visible. Surface melting appears below $T_m^*$ when, for increasing $T$, $\Delta G(l)$ first develops a minimum for a finite value of $l$. The nominal onset temperature for surface melting – the temperature where the solid surface is first wetted by an infinitesimal liquid film – is attained at $T = T_w$ where $d(\Delta G)/dl = 0$ at $l = 0$. This wetting temperature (dot-dashed line) is, similarly to bulk melting, quadratically depressed by strain.

Between these two temperatures, $T_w$ and $T = T_m^*$, the quasi-liquid film thickness grows from zero to infinity. The divergence at $T_m^*$ is power law $l \sim (T_m^* - T)^{-1/3}$ for $H > 0$, but only logarithmic $l \sim \log(T_m^* - T)$ for $H = 0$. A crossover between the two regimes appears when the derivative of $H/l^2$ with respect to $l$ becomes comparable with that of $|\Delta \gamma_{\infty}|e^{-2l/\xi}$: in Al $H \sim 0.56 \times 10^{-21}$ Joule$^3$ and this crossover should take place at about 0.5 K below the melting point, with $l \sim 14 \text{Å}$.

A continuous growth of the liquid film thickness is typical of regular, complete wetting of the solid substrate by its own melt. For other surfaces or materials wetting may not occur at all before bulk melting ($T_w = T_m^*$), and we have the so-called surface non-melting$^4,^5,^6$. A discontinuous growth, with a jump in the liquid thickness, could theoretically take place in case of a so-called prewetting $^7$ transition. The strain-free surfaces that have been studied so far, experimentally as well as theoretically, were found to exhibit mostly complete surface melting, or surface nonmelting. An intermediate type of behavior known as incomplete surface melting, where the liquid film...
Figure 1: The phase diagram of the Al(110) interface. The circles show the melting temperatures of the strained solid obtained by the molecular dynamics simulations. The prewetting line has been obtained by assuming $V(l) = |\Delta \gamma_\infty| e^{-2l/\xi}$ in equation (1). Note the large strains we are considering.
thickness levels off to a finite value below $T = T_m$, discontinuously jumping to infinity at $T = T_m$, has also been described \[8\] and can be seen as a rather special case of prewetting. However no case of regular prewetting, with a finite jump of the liquid film thickness, has so far been described in surface melting.

As it turns out, our simple model also predicts that surfaces that exhibit complete surface melting could be caused to develop a prewetting transition by means of external strain. That is due to the inevitable presence of nonzero surface stress at the solid surface, or more correctly at all interfaces involving the solid.\[9\] The $\sigma \varepsilon$ term provokes a shift, linear to first order in the strain, of the interface free energy balance $\Delta \gamma_\infty$. Depending on that shifted value the minimum of $\Delta G(l)$ can be either negative with respect to the crystalline surface – thus supporting a stable liquid film – or positive, in which case the liquid film is metastable, supporting a stable dry solid surface. In that case there is a whole range of strain values where $\Delta G(l)$ changes its sign from positive to negative for increasing temperature, generating a prewetting transition phase line, where $l$ jumps from zero to a finite value. For even larger negative strain magnitudes the surface behavior is eventually predicted to become nonmelting.

2 Simulations of Strained Surface Melting

To verify the above simple theory, we simulated the thermal behavior of Al(110) close to the melting point, in presence of unidirectional in-plane strain. Molecular dynamics simulations of Al(110) were done in the slab geometry, both flat and bent, \[10\] and the Ercolessi-Adams many body potential for Al, whose bulk melting temperature is 943 K (to be compared with an experimental $T_m$ of 933 K) was used. Strain was introduced by expanding the flat simulation box along the [0 0 1] direction, or alternatively by bending the simulated slab, while keeping it fixed in the orthogonal direction.

The simulations, conducted with standard canonical methods confirmed first of all the decrease of $T = T_m^*(\varepsilon)$ with strain. Fig. \[2\] shows the large increase of the melted film occurring at fixed temperature for symmetrically positive and negative strains.

Subsequently, to investigate the possible presence of a prewetting transition, we carried out \[11\] a series of microcanonical simulations, where at each given strain the internal energy was increased stepwise. (Fixing the en-
\[ T_{m-T} = 4 \text{ K} \]

**unstrained**

\[ \varepsilon = -0.012 \]

**compressed**

\[ \varepsilon = +0.012 \]

**stretched**

Figure 2: Single snapshots of the simulations of Al(110): side view of three samples at the same temperature. Both negative and positive strain increase the molten film thickness, reflecting lowering of the melting temperature by strain. Samples size: \( 14 \times 20 \times 16 \) cells. The atom stacking in the 20-atom rows orthogonal to the picture clearly distinguishes the liquid by the solid phases.
The effective melting temperature $T_m - T_m^*(\pm 1K)$ is extracted, by determining the vertical asymptote in the plot of temperature versus molten film thickness. Data reported in Table 1 show a good agreement with our formula (3), the discrepancy at the larger positive strains being due to anharmonic effects. In this kind of simulation the possible occurrence of prewetting will show up, as with any other first order transition, by hysteresis, as well as by the occurrence of an inhomogeneous two-phase coexistence of dry and wet portions of the surface. Because the surface stress of Al(110) is positive (here about 0.052 eV/Å$^2$ at a temperature of 900 K, but ab initio calculations of Needs [12] at $T = 0$ provide a value of 0.115 eV/Å$^2$), it is expected that prewetting could appear in an important way at negative strain, i.e., under compression.

Fig. 3 shows the effective liquid thickness against temperature as obtained in each simulation, for strains of -3%, 0, and +3%. The expected overheating of the solid surface is indeed observed for strains -3%, 0, but not for +3%, in agreement with the snapshots. We conclude, as detailed in Ref. [11], that the Ercolessi-Adams model potential predicts a prewetting transition in the surface melting of compressed and of strain free Al(110). The prewetting jump in the liquid layer thickness disappears form the huge positive strain of +3%. The agreement with Fig. 4 is qualitatively correct, although the prewetting

| strain | $T_m - T_m^*(\pm 1K)$ | $Y'/(2\rho\lambda) T_m\varepsilon^2$ |
|--------|-----------------|-----------------|
| -0.03  | 23.0            | 22.5            |
| -0.02  | 11.1            | 10.0            |
| -0.015 | 5.5             | 5.6             |
| -0.01  | 2.3             | 2.5             |
| +0.01  | 2.5             | 2.5             |
| +0.015 | 5.6             | 5.6             |
| +0.02  | 12.4            | 10.0            |
| +0.03  | 27.2            | 22.5            |

Table 1: The decrease of the effective melting temperature with strain. The third column is obtained by formula (4), with $Y'/(2\rho\lambda) = 26.6$ for the Ercolessi-Adams potential.
Figure 3: Thickness of the molten layer vs Temperature. Continuous and dashed lines are the predictions, without considering the prewetting, for unstrained and strain $\epsilon = \pm 0.03$ slabs respectively.
region turns out to be larger than expected, unexpectedly including zero strain.

3 Discussion and Conclusions

Bulk strain depresses the melting point of a solid, whose surfaces will tend, at a given fixed temperature, to melt more readily than in the absence of strain. Since a tiny strain of order 0.0006 suffices in Al to lower $T_m$ by one hundredth of a degree – the typical accuracy of a surface melting experiment [13] – this suggests that random strains could represent an important source of uncertainty in these experiments. A combination of strained regions, resulting e.g. from surface treatments, could lead to patchy behaviour close to melting, where portions of the surface would melt and others would not.

Another consequence of strain-induced surface melting is the related possibility to give rise to potentially interesting side effects. If strain were introduced through a bulk longitudinal wave for example of sufficiently low frequency $\omega$ and wavevector $k$, one could expect a corresponding surface liquid thickness modulation of frequency $2\omega$ and wavevector $2k$. There would also be associated frictional damping effects worth investigating.

A newer effect of strain is the possibility to cause a prewetting transition in surface melting. That is of interest, in view of the fact that prewetting has never so far emerged in surface melting. Although it might prove difficult for the crystal to sustain large strains particularly so very close to the melting point, nevertheless the entirely theoretical possibility of strain-induced prewetting seems worth addressing experimentally, as the stress needed might in fact be quite small. In the case of Al(110) used here as a test case, our simulations indicated prewetting already at zero strain. While that may be an artifact of the potential used – existing experiments have shown no evidence of prewetting on Al(110) [6] – it seems possible that prewetting could appear with a relatively modest compression, as suggested by Fig. 1. Prewetting is further discussed in Ref. 11.

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