

Size-dependent superheating in confined Pb(111) films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 53

(<http://iopscience.iop.org/0953-8984/17/1/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 19:30

Please note that [terms and conditions apply](#).

Size-dependent superheating in confined Pb(111) films

J I Akhter

Physics Research Division, Pakistan Institute of Nuclear Science and Technology, PO Nilore, Islamabad, Pakistan

E-mail: jiakhter@yahoo.com and akhterji@pinstech.org.pk

Received 20 September 2004, in final form 19 November 2004

Published 10 December 2004

Online at stacks.iop.org/JPhysCM/17/53

Abstract

Molecular dynamics simulations have been carried out to explore superheating in Pb(111) films confined in an Al(111) matrix. The size dependence of the superheating has been investigated by varying the film size and keeping the host matrix unchanged. Melting is found to initiate in the interior of the film, which suggests intrinsic homogeneous nucleation. The superheating is found to be dependent on the size of the film. Superheating up to 115 K above the bulk melting temperature is achieved. A good agreement between the theoretical calculations, experimental value and the simulated results is obtained.

1. Introduction

Over the years there has been considerable interest in the atomic level understanding of superheating in crystalline solids. The melting behaviour of small metallic clusters and thin films has been addressed, both experimentally and theoretically [1–6], to obtain a comprehensive understanding of the stability, structure and size effects. The melting temperature of clusters has been found to be dependent on the degree of packing of surface planes. The absence of free surface, as in the case of encapsulating of crystallites within a higher melting point host matrix, is found to enhance the melting point [7–11]. The more open surfaces assist the nucleation of liquid phase at the surface. This is due to the fact that different metal surfaces have shown quite different melting behaviours, either melting point depression (such as premelting) or melting point elevation (i.e. superheating). The surface melting of Pb, Al and Pd has been shown to be orientation dependent, with more open surface like (110) premelts at temperatures much lower than the bulk melting temperature [12–15]. It is well known that the melting temperature of a small cluster with free surface, i.e., an isolated cluster in vacuum, is lower than that of the infinite bulk solid due to the increase in surface to volume ratio [16]. However, for the embedded clusters the situation is different, and considerable superheating has been achieved by suppressing the free surface effects [2]. Evidence of shape-dependent superheating of entrained nanosized Pb particles in a Zn matrix has been reported, and the importance of crystallography and morphology at the microlevel at the interface has

Table 1. Melting temperatures of various film sizes.

Number of (111) planes in the film	Number of atoms in the film	Number of atoms in the computational cell	Film thickness (μm)	Melting temperature (K)	Superheating (K)
6	864	6144	18	745	115
9	1296	6576	27	725	85
12	1728	7008	36	705	65

been emphasized [13]. It has been reported [1] that the melting temperature revealed only by the diffraction intensity results becomes unreliable due to crystal reorientation near melting. Computer simulation methods, and, in particular, molecular dynamics (MD), have been proven to be excellent tools for investigating the melting phenomenon in detail, as one can follow the evolution of the system as a function of time. The physical properties can be examined not only at a global level but also locally. For example, the melting behaviour of Pb(110) film embedded in an Al matrix was explored, and it was shown that the orientation of the matrix plays an important role in the melting behaviour of the film [14]. The Pb(110) film adopted the low energy orientation, i.e. (111), when embedded in an Al(111) matrix, and the reoriented film was superheated up to 300 K above the bulk melting temperature. This high superheating of the reoriented Pb(111) film was in contrast to the experimental evidence of Herman and Elsayed-Ali [17], who reported a superheating of 120 K in laser-heated Pb(111). The superheating was attributed to the fast heating due to the laser beam. The present study was conducted by MD simulation to investigate superheating in Pb(111) embedded coherently in an Al(111) matrix. The structural changes taking place at different temperatures are reported in detail. The effect of film size on the superheating is explored without changing the size of the matrix.

2. Simulation technique

The Sutton–Chen glue potentials for Al and Pb [18] were employed to conduct the present simulation studies. The potential for the Al–Pb alloy was the same as that defined in previous studies [2, 4, 19]. The melting behaviour of the Al(111)/Pb(111) immiscible system was examined under the conditions of constant pressure (NPT). The atomic positions, i.e. the initial configuration, were generated by using the lattice parameters for Al and Pb, calculated from separate NPT simulations for these metals. The MD cells were constructed from 24 (111) layers of Al, with 220 atoms in each layer, and three film sizes containing 6, 9 and 12 (111) layers of Pb with 144 atoms per layer. The number of atoms in each film and in the respective computational cell is given in table 1 along with the film thickness. The Pb film was located symmetrically in the middle of the Al matrix. The number of layers of Pb(111) film was chosen so that the stacking sequence of the host Al remained unchanged with the introduction of the Pb film. In this way the film forms two coherent interfaces with the host. The Al–Pb interlayer distance was set close to the average of the interlayer distances for Al and Pb. Periodic boundary conditions were applied in all three directions. A Verlet velocity algorithm with a time step of 5×10^{-15} s was employed for solving the equations of motion. The system was equilibrated at 100 K for 8000 time steps, by NVT simulation, before heating up to 800 K at a rate of 5×10^{12} K s $^{-1}$ in 28 000 simulation steps. The potential energy per atom at zero pressure was recorded during each temperature interval of 1 K.

3. Results and discussion

The melting temperatures of the low-index free surfaces of Pb, i.e. (110), (100) and (111), reported by Jin *et al* [2] are 600, 610 and 640 K, respectively. The average energy per atom

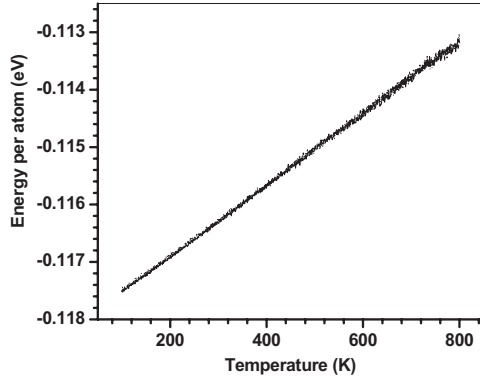


Figure 1. Variation of potential energy per atom for the host Al(111).

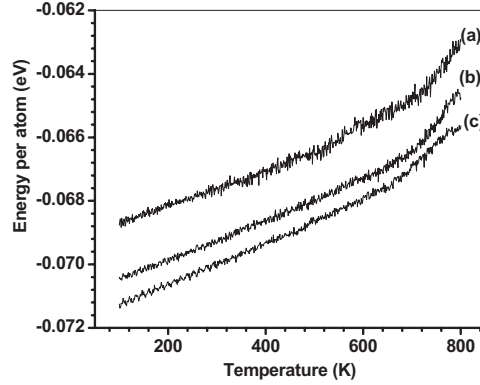


Figure 2. Variation of potential energy per atom for the film with (a) 6 layers, (b) 9 layers and (c) 12 layers.

was calculated as a function of temperature and plotted in figures 1 and 2 for the host Al(111) and for three thicknesses of Pb(111) film, respectively. The energy varies in a linear manner for the host during the whole range of temperature. Furthermore, the position of the energy–temperature curve for the host remains the same for the three configurations. For the film, the energy per atom increases with the decrease in film size. However, the trend is the same for the three films, and the change in energy remains linear with increase in temperature up to a certain temperature in all cases, and then there is an upward rise in the slope. The melting temperature of the film is estimated from the appearance of an abrupt change in the slope. From figure 2 the melting temperatures of the films are found to lie close to the temperatures listed in table 1. In all three films the melting of the film takes place above the melting temperature of the Pb film with free surfaces, i.e. 640 K as calculated previously by MD simulation using the Sutton–Chen potential [2]. Furthermore, the melting temperature for the smallest thickness film, i.e. the film with six Pb(111) planes, is even found to be 20 K above the bulk melting temperature for Pb, i.e. 725 K, calculated by MD [2].

In order to reveal the structural changes taking place in the film, the number density of the atoms along the perpendicular direction, i.e. the z -direction in the present case, has been calculated at various temperatures. These are plotted in figures 3(a)–(c) for three film thicknesses. The film remains ordered at temperatures below melting for all three films, as manifested by the well defined sharp peaks, and then disordering takes place above melting, which is indicated by the spread in the peaks. For the 12-layer film, melting takes place inside the film between 690 and 705 K, as depicted by the spread in the interior peaks at 720 K in figure 3(a). For the nine-layer film, melting again initiates inside the film after 720 K, and most of the film is melted at 750 K, as indicated in figure 3(b). The film with six Pb(111) layers is the most stable one. The number density results for this film in figure 3(c) suggest that the melting initiates again inside the film but at a higher temperature. In this case the film shows some ordering even at 740 K. One common observation in all these films is that the outer layers remain intact, and no disordering occurs at the film/host interface. In order to obtain fully relaxed film structures before and after melting, a conjugate gradient energy minimization procedure was adopted. The relaxed atomic configurations of the film and the host were recorded at selected temperatures to demonstrate that the melting is initiated homogeneously within the interior of the film rather than from the film–host interface. The y – z projections of the atomic positions are plotted in figures 4 and 5 for 12-layer and 6-layer films, respectively. It is again clear that

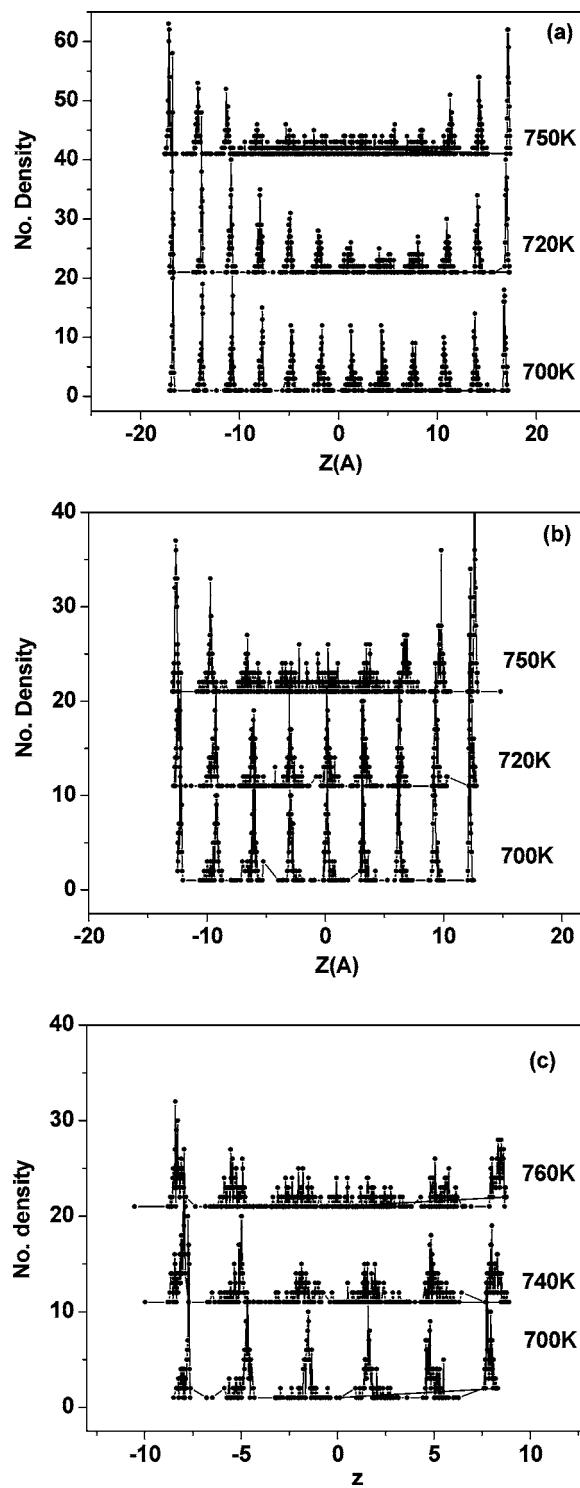


Figure 3. Atomic number density profiles along the z direction at selected temperatures for films with (a) 12 layers, (b) 9 layers and (c) 6 layers.

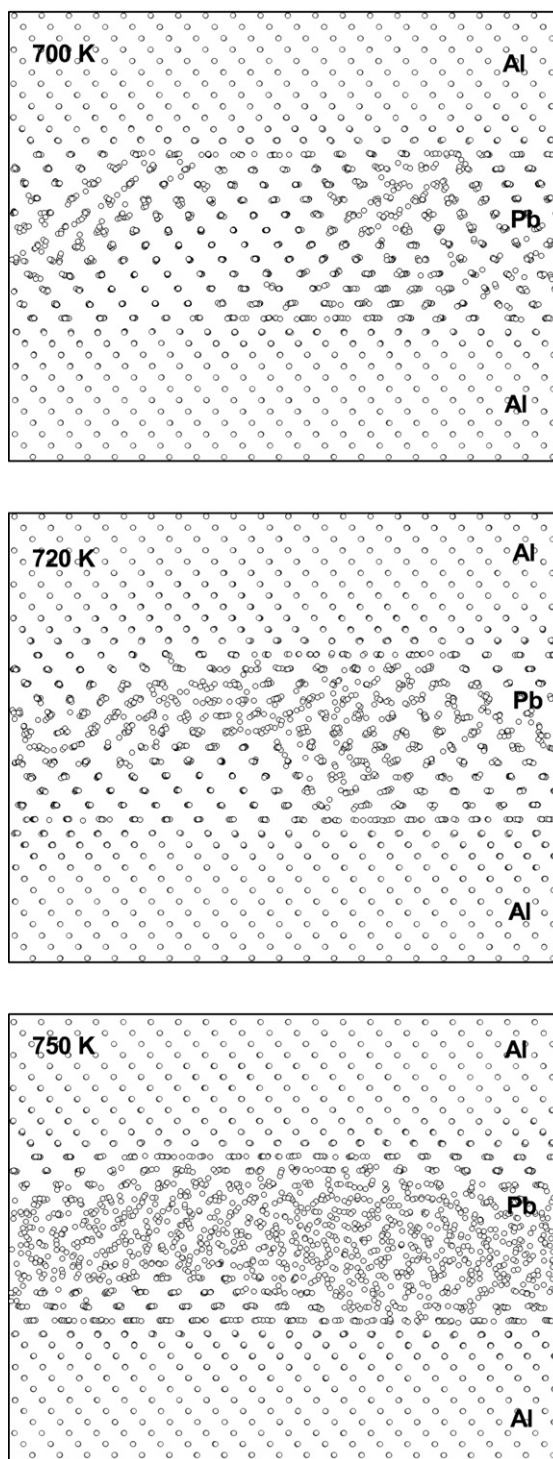


Figure 4. Snapshots of atomic positions projected onto the x - z plane for confined film with 12 layers.

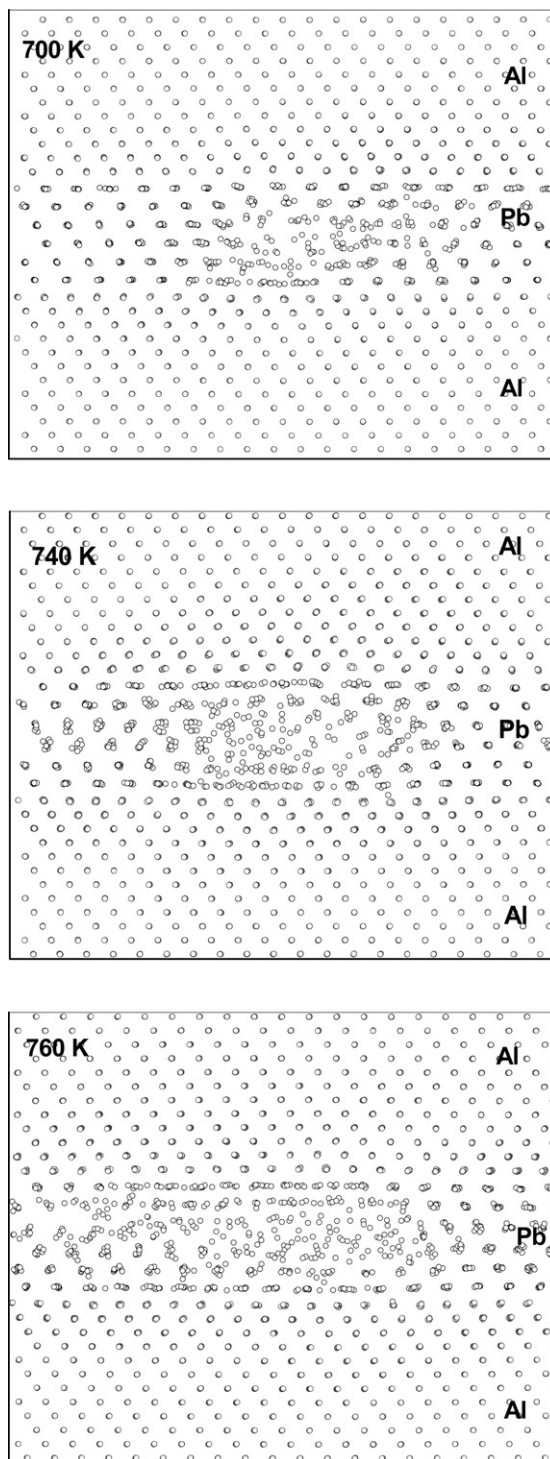


Figure 5. Snapshots of atomic positions projected onto the $x-z$ plane for confined film with 6 layers.

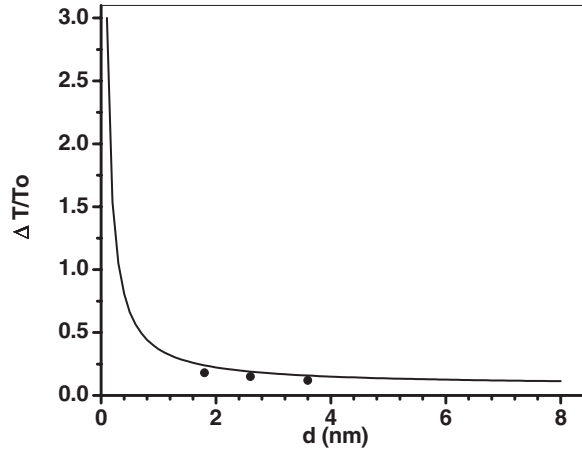


Figure 6. The degree of superheating $\Delta T/T$ versus film thickness for Pb(111). The solid curve shows the theoretical values calculated by homogeneous nucleation theory and the solid circles represent the simulated results.

the outer layers tend to survive on both interfaces up to much higher temperatures, showing no signal for a thermal evolution. The existence of one or two non-melting monolayers stiffened to the matrix lattice can modify interfacial energies and stresses. It can provide effective barriers in preventing interdiffusion between the confined and hosting atoms. The smaller size film again shows melting in the interior at a higher temperature compared to the greater thickness film.

The results imply that superheating in the film can be achieved under perfect confinement conditions, and the melting of the system is controlled by intrinsic homogeneous mechanisms such as vacancy–interstitial pairs and large vibrational amplitudes. The size-dependent nature of the superheating is also evident from the difference in the melting temperature of the films with different thicknesses. In all cases the melting nucleated in the interior of the film. Assuming that the melting of the superheated film is homogeneous in nature, the applicability of homogeneous nucleation theory [20] has been examined by comparing the simulated MD results. According to homogeneous nucleation theory, for a pure substance the Gibbs free-energy difference between a crystalline and a liquid embryo of spherical shape of radius r can be written as

$$\Delta G = \frac{4}{3}\pi r^3(-L_0\Delta T/T_0 + \Delta E) + 4\pi r^2(\gamma_{lm} - \gamma_{sm}) \quad (1)$$

where T_0 is the thermal equilibrium melting temperature, L_0 is the latent heat at T_0 , γ_{lm} and γ_{sm} are the liquid and solid interfacial energies, ΔT is the degree of superheating and ΔE represents the strain effects caused by the volume change on melting [11]. From $\partial(\Delta G)/\partial r = 0$, a relationship between the critical radius r_c and ΔT is obtained:

$$\Delta T/T_0 = [2(\gamma_{lm} - \gamma_{sm})/r_c + \Delta E]/L_0. \quad (2)$$

For a thin film of thickness d sandwiched between semi-infinite solid matrices, a similar relation can be written:

$$\Delta T/T_0 = [2(\gamma_{lm} - \gamma_{sm})/d + \Delta E']/L_0 \quad (3)$$

where $\gamma_{lm} - \gamma_{sm} = 0.038 \text{ J m}^{-2}$ [2] is the difference between the liquid–matrix and solid–matrix interfacial energy, and it is smaller than $\gamma_s = 0.046 \text{ J m}^{-2}$ [1] for Pb because of the semi-coherent nature of the Pb–Al interface, and $\Delta E'$ denotes the strain effects caused by

volume expansion as well as by the thermal expansion mismatch on melting. Using the data for Pb from the literature, $L_0 = 4.81 \text{ kJ mol}^{-1}$ [21] and $\Delta E = 0.1L_0$, ΔT is calculated, and the theoretical curve is given in figure 6. The simulated results for the three films are given in table 1 and plotted in figure 6, which indicates good agreement with the theoretical results. The superheating achieved for the smallest film is 115 K above the free surface melting point, and it also compares very well with 120 K, obtained experimentally by Herman and Elsayed-Ali for Pb(111) [17]. It is, however, interesting to note that this superheating is smaller than that for the reoriented Pb(110) film reported previously [4]. This may be due to the fact that the Pb(111) film created in this study is less dense as compared to the film generated after the reorientation of Pb(110). Furthermore, the asymmetry in the film–host interface is less in the present case as compared to the previous case of Pb(110). A detailed analysis of the atomic configurations suggests that the reoriented structure in the case of Pb(110) has very small disorder even at 650 K, and therefore it requires much energy to generate mean square displacements in the lattice before melting. Thus melting occurs at a much higher temperature. However, the atoms in the Pb(111) film have large mean square displacements at 650 K, and the film melts after gaining a small amount of energy at low temperature.

4. Conclusions

In conclusion, superheating has been obtained in a Pb(111) confined film. The degree of superheating is dependent on the film thickness and it decreases with increase in the film size. The maximum superheating obtained is 115 K, which is very close to the experimental value and that predicted by homogeneous nucleation theory.

References

- [1] Peters K F, Cohen J B and Chung Y W 1998 *Phys. Rev. B* **57** 13430
- [2] Jin Z H, Sheng H W and Lu K 1999 *Phys. Rev. B* **60** 141
- [3] Goswami R and Chattopadhyay K 1993 *Phil. Mag. Lett.* **68** 223
- [4] Akhter J I, Jin Z H and Lu K 2001 *J. Phys.: Condens. Matter* **13** 7969
- [5] Daeges J, Gleiter H and Perepezko J H 1986 *Phys. Lett. A* **119** 79
- [6] Jin Z H, Gumbsch P, Lu K and Ma E 2001 *Phys. Rev. Lett.* **87** 055703
- [7] Zhang D L and Cantor B 1990 *Phil. Mag. A* **62** 557
- [8] Sheng H W, Ren G, Peng L M, Hu Z Q and Lu K 1996 *Phil. Mag. Lett.* **71** 197
- [9] Zhang D L and Cantor B 1991 *Acta Metall. Mater* **39** 1591
- [10] Allen G L, Gile W W and Jesser W A 1986 *Thin Solid Films* **144** 297
- [11] Allen G L, Gile W W and Jesser W A 1985 *Acta Metall.* **28** 1695
- [12] Pluis B, Denier van der Gon A W, Frenken J W M and van der Veen J F 1990 *Surf. Sci.* **239** 265
- [13] Pluis B, Denier van der Gon A W, Frenken J W M and van der Veen J F 1987 *Phys. Rev. Lett.* **59** 2678
- [14] Jin Z H and Lu K 1998 *Phil. Mag. Lett.* **78** 29
- [15] Akhter J I, Yaldram K and Ahmad W 1996 *Solid State Commun.* **98** 1043
- [16] Borel J P 1981 *Surf. Sci.* **106** 1
- [17] Herman J W and Elsayed-Ali H E 1992 *Phys. Rev. Lett.* **69** 1228
- [18] Sutton A P and Chen J 1990 *Phil. Mag. Lett.* **61** 139
- [19] Rafi-Tabar H and Sutton A P 1991 *Phil. Mag. Lett.* **63** 217
- [20] Uhlmann D R 1980 *J. Non-Cryst. Solids* **41** 347
- [21] Porter D A and Easterling K E 1980 *Phase Transformations in Metals and Alloys* (London: Van Nostrand-Reinhold) p 171