

Molecular dynamics study of surface premelting in adsorbed argon films on graphite

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

1989 J. Phys.: Condens. Matter 1 2709

(<http://iopscience.iop.org/0953-8984/1/16/007>)

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

Download details:

IP Address: 94.79.44.176

The article was downloaded on 10/05/2010 at 18:09

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

LETTER TO THE EDITOR

Molecular dynamics study of surface premelting in adsorbed argon films on graphite

Y J Nikas† and C Ebner

Department of Physics, Ohio State University, Columbus, OH 43210, USA

Received 16 January 1989

Abstract. We have studied surface premelting in thin solid argon films adsorbed on a graphite substrate using molecular dynamics simulations. The interaction between the atoms assumes the truncated Lennard-Jones form. We have found that the top layers of the film begin to melt at $0.27 T_t$ below the triple-point temperature T_t , and that the thickness of the quasi-liquid layer grows as the temperature approaches T_t .

The term surface melting refers to the wetting of a solid–vapour interface by a layer of liquid at temperatures approaching the bulk triple-point temperature from below. This phenomenon has long been known [1], but recently, new interest has been evoked by the first direct observation of melted layers on a Pb(100) crystal surface [2]. Also, experiments on adsorbed films O₂/Gr [3], CH₄/MgO [4] and Ar/Gr, Ne/Gr [5] have provided convincing evidence of this effect. Computer simulations have also shown the existence of a liquid-like layer at a solid–vapour interface [6]. Furthermore, various theories based on a Landau free-energy expansion [7] and a mean-field approximation [8] have predicted that as the temperature approaches the triple-point temperature T_t , the thickness of the liquid layer grow as $(T_t - T)^{-1/3}$ for van der Waals solids and as $|\log(T_t - T)|$ for materials whose molecules interact via short-range forces. However, detailed simulation of adsorbed films that can be compared directly with the experimental results is still lacking. It is the purpose of this Letter to report our molecular dynamics (MD) simulation results for the melting of solid argon films adsorbed on graphite.

The MD simulation techniques are well documented in the book by Allen and Tildesley [9]. In our study, we have followed the algorithm for an isobaric–isothermal (constant-NPT) ensemble described by Brown and Clarke [10].

The system consists of five layers, with 64 atoms in each layer, originally lying on an FCC (ABC stacking) lattice, and the periodic boundary condition was imposed in both x and y directions. The atoms interact via a Lennard-Jones potential $v(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, with the cut-off radius 3σ , where $\sigma = 3.405 \text{ \AA}$ and $\varepsilon/k = 119.8 \text{ K}$, which are the widely used values for argon. Throughout the Letter, the temperature and the energy will be in units of ε . The time step Δt is taken to be 10^{-14} s . The graphite substrate is located at the $z = 0$ plane. The interaction between argon atoms and graphite assumes the form proposed by Cole and Klein [11] where the potential depends only on the

† Née Y Jiang.

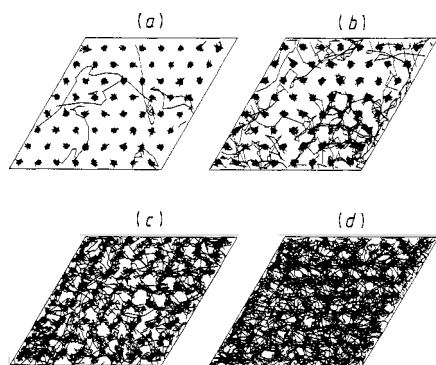


Figure 1. The xy trajectories of atoms in the first layer at (a) $T = 0.500$, (b) $T = 0.530$, (c) $T = 0.551$ and (d) $T = 0.613$.

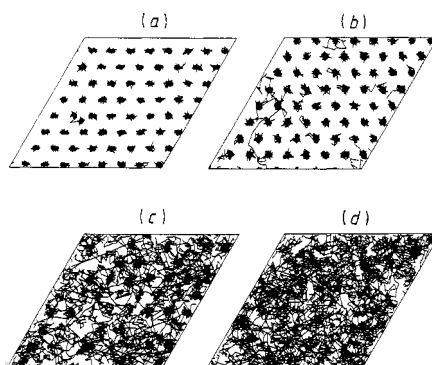


Figure 2. The xy trajectories of atoms in the second layer at (a) $T = 0.551$, (b) $T = 0.613$, (c) $T = 0.652$ and (d) $T = 0.674$.

distance from the graphite surface to the adatoms. A hard wall is placed at $z = 10\sigma$ to fix the size in the z direction, and the area is allowed to relax in such a way that the lateral pressure of the system is held constant. Since the lateral components of the pressure tensor are larger than the z component and the former are set at the solid–vapour coexistence values [12], the simulations are performed in the region slightly below the real solid–vapour coexistence line. We chose to monitor the lateral components rather than the normal component of the pressure tensor because the pressure at solid–vapour coexistence is close to zero, and the fluctuation of the latter is of the same order of magnitude as the pressure itself. However, for the melting process, including all quantities reported here, the effect of varying the pressure by a few atmospheres is negligible (a few runs at different pressure values have confirmed this).

A typical run consists of 12 000 time steps (120 ps) for the system to equilibrate and another 120 ps for calculating the statistical averages. In order to characterise liquid and solid states, we have plotted the trajectories of atoms in different layers separately and calculated the 2D radial distribution functions $g(r)$, the static structure factor $S(Q)$ and the 2D diffusion coefficients within each layer.

To begin with, we present the trajectory plots since direct information about the mobility of the atoms and about the disordering of the lattice can be extracted from them. Figures 1 and 2 show the xy projections of trajectories of atoms in layers 1 and 2 for different temperatures (layer 1 is the farthest from the substrate). The time interval between two successive positions is $120 \Delta t$. The plots show that the mobility of the atoms in the topmost layer starts increasing gradually from $T = 0.50$, but the lattice structure is partially retained until $T = 0.613$, when the second layer begins to melt. It seems that the melting of one layer is a continuous phase change, and that the film melts layer by layer. In the duration of a single run, the effect of interlayer exchange of atoms between the first and second layers does not become obvious until the second layer begins to melt.

During the melting process, the retention of the inlayer lattice structure before disordering begins in the underlying layer can also be seen from the plots of the 2D radial distribution functions (figures 3 and 4). The surface disordering causes a coalescence of the split peaks and a decrease in the peak height; the layer by layer disordering sequence can be seen clearly. In addition, these figures along with the trajectory plots suggest that

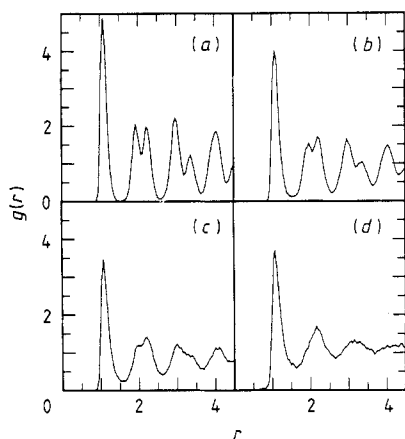


Figure 3. The 2D radial distribution functions of the first layer at (a) $T = 0.500$, (b) $T = 0.530$, (c) $T = 0.551$ and (d) $T = 0.613$.

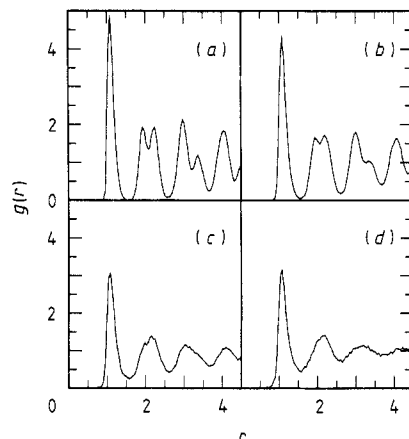


Figure 4. The 2D radial distribution functions of the second layer at (a) $T = 0.551$, (b) $T = 0.613$, (c) $T = 0.652$ and (d) $T = 0.674$.

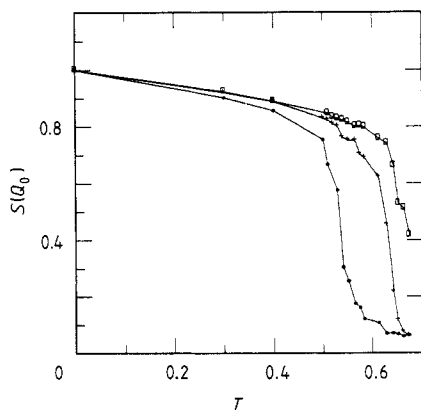


Figure 5. The height of Bragg peak $\langle 10 \rangle$ as a function of temperature for the layers one (\cdot), two ($+$), and three (\square).

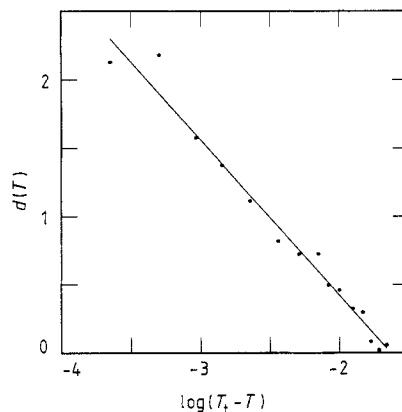


Figure 6. The film thickness as a function of temperature. The full line is the least-squares fit to the data.

the so-called liquid layer at the solid–vapour interface is not in a true liquid state; rather, it can be viewed as ‘quasi-liquid’ because the underlying lattice plays an important role in determining the structure of this layer and the mobility of the atoms in it.

The structure factor $S(Q)$ is another characterisation of the degree of disordering of the lattice, and it can be measured directly by the neutron scattering technique. Unfortunately, one cannot observe the melting process by monitoring the variation in scattering intensity of the $\langle 10 \rangle$ Bragg peak’s height $S_i(Q_0)$, because when the momentum transfer Q is parallel to the (111) face of an FCC lattice, this peak gives identical heights for a five-layer and a four-layer solid film. For this reason, we show in figure 5 the variation of $S_i(Q_0)$ with temperature for the first three layers individually. From the figure, the temperature ranges in which each layer ‘melts’ can be easily identified, but

we are not able to estimate the number of atoms that are in the quasi-liquid state because the magnitude of the lattice vibrations is beyond the range in which the harmonic approximation is still applicable.

One possible way to obtain a quantitative estimate of the liquid film thickness is by evaluating the atomic mobility through the diffusion coefficients. The 2D diffusion coefficients are defined as

$$2tD_i = \frac{1}{2} \lim_{t \rightarrow \infty} \langle (x_i(t) - x_i(0))^2 + (y_i(t) - y_i(0))^2 \rangle \quad (1)$$

where $(x_i(t), y_i(t), z_i(t))$ is the position of an atom in the i th layer at the time t . We find that $D_i(T)$ increase steadily with the temperature starting from $T = 0.51, 0.565, 0.629$ for layers 1, 2, and 3 respectively. These temperatures can be identified as the temperatures at which each layer begins to melt. Since the mean-square displacements in the long-time limit are constants for atoms vibrating near the lattice sites, the finite diffusion coefficients can be attributed to the atoms which are in the liquid state. Thus we have $D_i(T) = f_i^l(T)D_i^l$, where $f_i^l(T)$ is the number fraction of atoms in the liquid-like state in the i th layer, and D_i^l is the diffusion coefficient for these atoms; its value is equal to $D_i(T)$ at the temperature where the entire layer is melted. The thickness d (number of layers) of the quasi-liquid film can be written as

$$d(T) = \sum_{i=1}^L f_i^l. \quad (2)$$

The plot of $d(T)$, figure 6, with respect to $\ln[1/(T_i - T)]$ shows a reasonably good fit to the logarithmic function. From the fit, we obtain

$$d(T) = d_0 \ln[0.28T_i/(T_i - T)] \quad (3)$$

where $d_0 = 1.14$. This relation agrees with Broughton and Gilmer's estimation from surface free energy considerations [6]. In making the fit, we have used the experimental value $T_i = 0.698$. The triple-point temperature for truncated Lennard-Jones systems is still a subject of controversy. Recent molecular dynamics simulations in systems with periodic boundary conditions imposed in all dimensions overestimate T_i by at least 10% [13, 14], as compared with earlier MD [15] and MC [16] simulations which give values slightly lower than or very close to that of the real system. Consequently, it seemed appropriate to us to use the experimental value; in any event, figure 6 is not significantly affected by a small (a few per cent) change in T_i ; certainly the basic conclusion is not altered.

This logarithmic growth of the liquid layer with temperature is not surprising because of the truncated interactions between the atoms and the limited thickness of the film. For an adsorbed film of reasonable thickness and in which the particles interact via true long-range Lennard-Jones interactions, power-law growth is expected to be seen [8]. Calorimetric measurements on Ar and Ne films [5] have confirmed the power-law growth; however, logarithmic growth in liquid film thickness has been observed in neutron diffraction experiments on O₂ films adsorbed on graphite [3]. It is believed that in the latter case it is the short-range interaction that dominates because the films studied in the experiments are very thin, and there will be a crossover from logarithmic to power-law growth as the total film thickness increases. However, in order to study the premelting at the surface of real van der Waals solids by computer simulations, systems with considerably larger sizes will be required.

In summary, we have studied the surface premelting effect in a thin Ar film adsorbed on a graphite substrate. We have provided some evidence that the liquid layer at the solid-vapour interface still retains some characteristics of the solid; in this case, there is not a simple distinction between the solid and liquid regimes. We have also shown that the film melts layer by layer, and from our results the thickness of the melted layer seems to grow logarithmically as the temperature approaches T_1 in systems with finite interaction range.

One of the authors (YJN) wishes to thank J Suzanne for helpful discussions. The Ohio Supercomputer Center is gratefully acknowledged for providing CPU time on Cray X-MP where the simulation was performed. This work is partially supported by National Science Foundation under the grant No NSF DMR 8705606.

References

- [1] Ubbelohde A R 1978 *The Molten State of Matter* (New York: Wiley)
- [2] Frenken J W M and van der Veen J F 1985 *Phys. Rev. Lett.* **54** 134
Frenken J W M, Marée P M J and van der Veen J F 1986 *Phys. Rev. B* **34** 7506
- [3] Krim J, Coulomb J P and Bouzidi J 1987 *Phys. Rev. Lett.* **58** 583
Chiarello R, Coulomb J P, Krim J and Wang C L unpublished
- [4] Bienfait M 1987 *Europhys. Lett.* **4** 79
- [5] Zhu Da-Ming and Dash J G 1986 *Phys. Rev. Lett.* **57** 2959; 1988 *Phys. Rev. Lett.* **60** 432
- [6] Broughton Q and Gilmer G H 1983 *Acta Metall.* **31** 845; 1983 *J. Chem. Phys.* **79** 5119
- [7] Lipowsky R 1982 *Phys. Rev. Lett.* **49** 1575
Lipowsky R and Speth W 1983 *Phys. Rev. B* **28** 3983
- [8] Trayanov A and Tosatti E 1987 *Phys. Rev. Lett.* **59** 2207
- [9] Allen M P and Tildesley D J 1987 *Computer Simulation of Liquids* (Oxford: Clarendon)
- [10] Brown D and Clarke J H R 1984 *Mol. Phys.* **51** 1243
- [11] Cole M W and Klein J R 1983 *Surf. Sci.* **124** 547
- [12] Flubacher P, Leadbetter A J and Morrison J A 1961 *Proc. Phys. Soc. London* **78** 1449
- [13] Nosé S and Yonezawa F 1986 *J. Chem. Phys.* **84** 1803
- [14] Chokappa D and Clancy P 1987 *Mol. Phys.* **61** 617
- [15] Ladd A J C and Woodcock L V 1978 *Mol. Phys.* **36** 611
- [16] Hansen J-P and Verlet L 1969 *Phys. Rev.* **184** 151