DOF Phase Separation of the Lennard-Jones fcc(111) Surface

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Abstract

Recent lattice model calculations have suggested that a full-layered crystal surface may undergo, under canonical (particle-conserving) conditions, a preroughening-driven two-dimensional phase separation into two disordered flat (DOF) regions, of opposite order parameter. We have carried out extensive classical molecular dynamics (MD) simulations of the Lennard-Jones fcc(111) surface, to check whether these predictions are relevant or not for a realistic continuous system. Very long simulation times, a grid of temperatures from $(2/3)T_m$ to $T_m$, and unusually large system sizes are employed to ensure full equilibrium and good statistics. By examining layer-by-layer occupancies, height fluctuations, sublattice order parameter and X-ray structure factors, we find a clear anomaly at $\sim 0.83T_m$. The anomaly is distinct from roughening (whose incipiency is also detected at $\sim 0.94T_m$), and is seen to be consistent with the preroughening plus phase separation scenario.

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The surfaces of a rare-gas solid such as Ar are reasonably well modeled by those of a (truncated) Lennard-Jones (LJ) fcc solid. The behavior of the LJ surfaces as a function of temperature, particularly in the vicinity of the melting point $T_m$, has been the subject of a large number of studies, mostly by classical Molecular Dynamics (MD) [1]. Based on these studies, the general consensus until recently was that the LJ surfaces begin to disorder, with increasing temperature $T$, in a very gradual manner. As $T \gtrsim (2/3) T_m$, surface anharmonicities [3] and defects [1] first build up. In particular, there is a progressive growth in the number of surface adatoms/vacancies in the region $T \sim 0.7 \div 0.8 T_m$ and above. Their presence undermines the surface crystalline state [3]. Eventually, a microscopic quasi-liquid surface film is formed, which leads to surface melting as $T_m$ is approached [4]. En route to surface melting, a surface roughening transition at $T_R < T_m$ should also appear [3], owing to a step free energy softening in presence of the quasi-liquid film. On Ar(111), for example, it is known that $T_R \approx 0.94 T_m$ [6].

Subsequently, however, experimental evidence has appeared [7–10], followed by theoretical work [11–16] which upsets this gradual picture, and suggests that surface disordering occurs instead through a singularity. In connection with statistical mechanics models introduced by Den Nijs in the 80’s [17], this singularity is probably best understood as “preroughening” (PR). At PR, the originally ordered flat surface turns into a disordered flat (DOF) state, where surface steps proliferate, albeit with strict up-down alternation. In this way surface flatness is preserved while still gaining entropy from disorder, in particular from step meandering [11]. Due to the resulting checkerboard texture of steps, a DOF surface phase exhibits, at least in the lattice models, a striking half-integer occupancy in the topmost layer.

More recently, grand canonical Monte Carlo simulations [18,19] have confirmed the occurrence of a PR phase transition, and of an associated coverage jump at the LJ(111) surface, in the neighborhood of $0.83 T_m$.

The questions we address in this note are the following. Can we first of all detect preroughening and roughening in a standard canonical (that is, particle-conserving) realistic surface MD simulation? And, if the PR scenario is indeed correct for the LJ surfaces, how do PR and the appearance of a DOF phase exactly manifest themselves? Finally, why did such an important singularity go unnoticed in so many previous, good-quality MD simulations?

We surmised recently [20] that the answer might be that in MD, the singularity is masked by particle conservation, turning a sharp critical onset into a subtler, Ising-like phase separation. A Monte Carlo study of a lattice RSOS (restricted solid-on-solid) model did indeed show that under canonical, particle-conserving conditions, an initially full surface monolayer spontaneously phase separates above $T_{PR}$ into two DOF regions, each of which has essentially population $1/2$ in the top layer [20]. However, lattice models may be oversimplified, and a more realistic study of this question is strongly needed.

Here, we describe new extensive canonical MD simulations of the LJ fcc(111) surface, specifically aimed at understanding whether the DOF phase separation is real or not. Anticipating our conclusions, we shall find that the answer is affirmative. However we also find that the evidence can only be obtained by employing large sizes, long simulation times, and size scaling, usually not considered in previous work. A corollary is that these kinds of precautions, aimed at detecting possible DOF surface phase separation, appear mandatory for future studies of warm surfaces using canonical MD simulation.

We conducted all our simulations in a slab geometry, with $N_L$ fully mobile layers of
$M$ particles/layer and $(x, y)$ periodic boundary conditions. Three rigid fcc(111) layers are added at the bottom of the slab. To account for thermal expansion, the $(x, y)$ simulation cell size was expanded with temperature according to an expansion coefficient extracted from an independent set of bulk simulations. Since we are aiming at describing a solid-vapor interface at full thermodynamic equilibrium, our simulation allowed an approximately equal volume of LJ gas above the solid surface. The gas particles were contained and backscattered by a perfectly reflecting wall placed at a distance $N_V$ “layers” in the vacuum above the last crystal layer.

We studied in detail three samples: (i) SF (small full) where $M = 120$ particles/layer, $N_L = 13$, $N_V \simeq 10$; (ii) LF (large full) where $M = 504$, $N_L = 25$, $N_V \simeq 15$; (iii) LH (large half) where $M = 504$, $N_L = 24.5$, $N_V \simeq 15$. The interparticle interaction was 12-6 LJ, truncated at $2.5\sigma$. The bulk melting temperature for this system was determined to be $k_B T_m \simeq 0.7\epsilon$, by observing that at this temperature a relatively large number ($\approx 4$) of melted layers were stable while the rate of growth of the liquid film was maximal (full melting of the slab being prevented by the three bottom rigid layers).

A standard fifth-order predictor-corrector algorithm was used for the time integration of Newton’s equation, with a time step of 0.01 LJ units, amounting to $2.15 \times 10^{-14}$ s in the case of Ar ($\epsilon/k_B = 120$ K, $\sigma = 3.40$ Å). Temperature control based on velocity rescaling was used to heat or cool the system. However, all the equilibration and data collection runs were done in constant energy, microcanonical conditions.

In each case, the standard procedure adopted was to equilibrate the system for $10^5$ steps, at each temperature $T$ chosen in the interval $\sim 0.7T_m \div T_m$. During this time (amounting to about 2 ns for Ar) some surface atoms evaporated and others recondensed. However, their number (less than 10 in all cases) was negligible in comparison with one monolayer, so that the solid underneath was basically running under particle conserving conditions. Since surface evolution in these conditions is strictly determined by diffusion, long equilibration times are dictated by the requirement that the lateral diffusion length of a surface particle should be roughly comparable to half the $(x, y)$ cell size. With a diffusion coefficient of the order of $0.2 \times 10^{-4}$ cm$^2$/s for Ar at $T_m$ \[21\], 2 ns are sufficient to ensure equilibration by diffusion. Following equilibration, we ran a further $5 \times 10^4 \div 10^5$ steps for a good statistical average of thermodynamical quantities, which we now proceed to discuss.

(i) Height fluctuations. The surface height fluctuations were obtained by calculating

$$\delta h^2 = \left\langle \frac{1}{N_S} \sum_i (h_i - \bar{h})^2 \right\rangle$$

where $h_i$ denotes the $z$-coordinates of all surface particles $i$ whose identity and total number $N_S$ are defined at each given configuration, along with the average height $\bar{h} = (1/N_S) \sum_i h_i$. Configurations were chosen at regular time intervals (one every 250 steps for SF, every 500 steps for LF, LH), and $\langle \ldots \rangle$ denotes average over configurations. Surface particles were identified as those not totally or even partially shadowed by other particles, when viewing the surface from the gas and parallel to the $z$ axis, each particle being represented as a sphere of atomic radius $r_o = 0.9\sigma$.

A flat, defect free vibrating crystal surface should be characterized by $\delta h^2 \sim d^2$, where $d$ is the interlayer spacing. Proliferation of surface adatoms/vacancies should give rise to an increase of $\delta h^2$, which for increasing size should tend to a finite value, so long as the surface is
flat, *i.e.* non-rough. Surface roughening should be further signalled by a size-dependent $\delta h^2$ increase, scaling with size as $\log M$. Below roughening and neglecting vibrations, an ideal DOF surface, with its half-occupied topmost layer, should be characterized by $\delta h^2 = (1/4)d^2$. Conversely, a full-layered surface, phase-separated into two DOF domains with a height difference of $d$ between them, would instead exhibit a larger $\delta h^2 \approx (1/2)d^2$.

Fig. 1 shows the behavior obtained for $\delta h^2$. There is a clear and sudden change in the full-surface behavior near a breakdown temperature $\sim 0.83 T_m$. The height fluctuation $\delta h^2$ grows fast for both SF and LF below this temperature; above, it levels off to a value close to that of LH. Moreover, comparison of SF and LF indicates a stronger size-dependence of $\delta h^2$ at the breakdown temperature. Both features, in accordance with previous discussions based on the FCSOS model [20], strongly suggest that *preroughening* is taking place at the breakdown temperature, $T_{PR} \approx 0.83 T_m$. A strong size-dependence of $\delta h^2$ reappears again at higher temperature, compatible with an estimated roughening temperature, $T_R \approx 0.94 T_m$. Both values are in excellent agreement with the experimentally established values of $T_{PR}/T_m \approx 69/84$, obtained from reentrant layering of Ar(111)/graphite [3], and of $T_R/T_m \approx 80/84$, for roughening [4]. This is, to our knowledge, the first determination of these temperatures ever obtained by direct molecular dynamics simulation.

Between $T_{PR}$ and $T_R$, the canonical SF and LF surfaces should really consist, according to the lattice model, of domains made of two kinds of phase-separated DOF regions. The height fluctuations do not show strong evidence for that, because $\delta h^2$ remains close to $(1/4)d^2$ instead of $(1/2)d^2$. We will return to this discrepancy later, when discussing evidence for surface melting.

Next we calculated the layer occupancies, shown in fig. 2, as a crucial indicator of phase separation [20]. Due to phase separation, we would expect that (neglecting vacancies in the second and deeper layers) the concentration of vacancies in the first layer, $n_v$, and of adatoms one layer above, $n_a$, should be $n_v = N_v/M = (1-\sigma)/2, n_a = N_a/M = \sigma/2$, with $\sigma$ the “Ising magnetization” of this problem. In particular we expect $\sigma = 1/2$ for SF, LF, and $\sigma = 0$ for LH, whence $n_v = 1/2, n_a = 0$ for a single DOF phase in LH, but $n_v = n_a = 1/4$ for two phase-separated DOF’s in SF, LF. Hence at the onset of DOF phase separation these concentrations, ordinarily growing with temperature, should stabilize around $1/4$ and roughly stop growing until roughening.

We analyse first the full-layer results, SF and LF. Fig. 2 shows the evolution of the vacancy and adatom concentration with temperature. Beginning with initially small concentrations, the growth rate with temperature has a kink-like feature near $0.83 T_m$. Comparing SF an LF, the kink becomes more pronounced with increasing size, particularly for adatoms. Above the kink, there is a visible tendency to stabilize concentrations at a plateau value which, for both $n_a$ and $n_v$, lies between 0.2 and 0.25, only slightly smaller than the expected phase separation value of $1/4$. A possible reason why $n_a$ and $n_v$ might tend to fall slightly below $1/4$ could possibly be traced to a boundary effect between one DOF domain and the other. At the boundary, two *parallel* steps occur near one another, and parallel step repulsion [13] could be expected to push them apart, thus reducing in the neighborhood both $n_a$ and $n_v$ below $1/4$. At much higher temperatures, $n_v$ nicely tends to $1/4$, while $n_a$ grows again in the neighborhood of $0.94 T_m$, where we believe that roughening is taking place. We conclude that the overall behavior of adatom/vacancy concentration in the full-layer simulations provides a clear evidence for DOF phase separation above the break at $0.83 T_m$. 


Next, we consider the half-layer system LH which, by contrast, shows (Fig. 2) $n_a$ and $n_v$ to remain close to 0 and to 0.5, in full equilibrium, across the whole temperature range, with no particular features throughout. While the presence of two built-in antiparallel steps represents a trivial separation of ordered flat phases at low temperatures, we can conclude from the lack of further evolution of adatom/vacancy concentrations that only the full-layered surfaces show a tendency to spontaneously phase separate above $T_{PR}$, fully consistent with expectations.

It should be possible to identify some of these features by a direct examination of the physical structure of the surfaces generated by the simulation. Fig. 3 shows snapshots of the full- and half-covered surface at the end of runs below and above 0.83 $T_m$. In spite of the fuzziness necessarily present in such snapshots, the following features can be recognized: a) the low-T full surface (top left) is relatively crystalline, although with a large number of adatoms and vacancies (this is about twice the average value in fig. 2); b) the high-T full surface (top right) is now spread on two layers (white and grey), indicating phase separation; c) the low-T half-covered surface (bottom left) is also spread on two layers (gray and black), again indicating phase separation; d) the high-T half-covered surface (bottom right) is very disordered, indicating surface melting.

These results, providing a vivid picture of what the actual surface instantaneously looks like, are in support of the occurrence of PR between the two temperatures. Moreover, they indicate melting of the outermost layer above PR, a result predicted theoretically [16] and independently obtained by Grand Canonical Monte Carlo simulations [19].

As a final piece of evidence, we have calculated the sublattice, or DOF, order parameter, defined as

$$P = \left\langle \frac{1}{N_S} \sum_i e^{i\pi h_i/d} \right\rangle$$

The order parameter is finite for an ordered flat surface; it should drop to zero precisely at $T_{PR}$. Due to a lack of adatom-vacancy symmetry, it should be again finite, but substantially smaller, between $T_{PR}$ and $T_R$. The drop should be either continuous or abrupt, according to whether PR was critical or first order. This quantity has the additional merit of corresponding roughly to the X-ray antiphase scattering amplitude, to be expected for such a surface [21].

As seen in fig. 4, $P$ has a drop, for both SF and LF, more visible for LF, near 0.83 $T_m$. Comparison of the two indicates a weak but nonzero size dependence, suggesting a probable weak first order nature for PR in this surface.

Conversely, the half-layer surface LH exhibits simply a monotonic increase of $P$, roughly up to $T_R$, where results for all three systems, SF, LF, LH eventually merge. When interpreting results for LH below $T_{PR}$ and for SF, LF above $T_{PR}$, we should keep in mind that the order parameter average is not particularly meaningful for a phase-separated surface. We expect that, as a rough approximation, the true grand-canonical surface would show values of $P$ similar to LF for $T < T_{PR}$, with a jump to those of LH for $T > T_{PR}$ (dashed line).

Finally, we wish to return briefly to the open problem of anomalously small height fluctuations found earlier in the DOF separated region of systems SF and LF. It seems possible that an explanation could be found if the top layer did develop a liquid-like character above 0.83 $T_m$. In conjunction with relatively small domain sizes, high surface diffusion would lead to a globally much more homogeneous, and thus flatter, surface than could be
expected on the bare, rigid phase separation picture. The high mobility scenario would apply in particular if, as has been repeatedly suggested, the first surface monolayer, or fraction of monolayer, is in reality solid below $0.83 T_m$ but melted above $T_m$. We qualitatively inspected the diffusivity of our surface atoms and found it indeed to be higher for LH. A fully quantitative investigation, reported separately [19], confirmed the existence of a jump of the top layer lateral diffusion coefficient by more than a factor 2 between LF and LH at $T < T_{PR}$. That result does suggest that the first layer is premelting at the same time as it is preroughening, and indirectly also provides an explanation for the global homogeneity of the DOF phase separated outer surface layers.

In summary, we have found that a canonical, particle conserving MD simulation for an fcc(111) LJ surface contains clear indications for a) preroughening at $T_{PR} = 0.83 T_m$; b) roughening at $T_R = 0.94 T_m$; c) a DOF phase separation between $T_{PR}$ and $T_R$. The latter result is of conceptual relevance, since it shows that the continuous, off-lattice degrees of freedom of the real system do not destroy, with some qualifications, the essence of DOF physics, previously established only in much less realistic lattice models.

Direct experimental observation of DOF phase separation will not be possible on the solid rare gas surfaces, where the very high evaporation rates immediately establish grand canonical equilibrium. In this sense our study is academic for that system, for which we developed separately a grand canonical Monte Carlo approach [18,19]. On the other hand, the DOF phase separation described here could in real life be realized on metals, under conditions where evaporation is irrelevant.

Independently of experimental accessibility, there is an important methodological message to be drawn from the present work, which is very pertinent to the simulation community: surfaces which are likely to undergo a DOF transition should as a rule be simulated grand canonically. Canonical molecular dynamics simulation in particular is very dangerous, as it may inadvertently describe an unphysical state of the surface in the whole temperature interval between preroughening and roughening.

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FIGURES

FIG. 1. Height fluctuations $\delta h^2$ as a function of temperature for the small full (SF, black squares), large full (LF, black circles) and large half-occupied (LH, white circles) sample. Note the gap between LF and LH at low temperature, closing up around $0.83 T_m$. Other features are discussed in the text.

FIG. 2. Layer occupancies as a function of temperature. Symbols are as in fig. 1. Note how the vacancy and adatom and concentrations of the full-layer samples (SF, LF) tend to stabilize in the proximity of $1/4$ between about $0.83 T_m$ and $0.94 T_m$, consistent with the presence of two separated DOF phases in this region.

FIG. 3. Top view of instantaneous snapshots of the three outer layers for systems with initial full- (top) and half-layer (bottom) occupation, at $0.76 T_m$ (left) and $0.85 T_m$ (right). Atoms have been colored in black, grey or white according to the layer they belong to, in turn determined from their $z$ coordinate and the density profile along $z$ of each sample.

FIG. 4. DOF parity order parameter as a function of temperature. Symbols are as in fig. 1. Note the drop around $0.83 T_m$ for the full-layer samples (SF, LF), indicating tendency toward a two-level structure. A hypothetical grand canonical system would approximately follow the dashed line, drastically changing the layer population at $T_{PR}$ in correspondence with a large decrease of the order parameter.
Jayanthi et al., Figure 1
Jayanthi et al., Figure 2
