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PREROUGHENING, AND DISORDERED FLAT PHASE SEPARATION IN SURFACE MOLECULAR DYNAMICS SIMULATIONS

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Ordinary molecular dynamics surface simulations are particle-conserving. We have found that, while this restriction may be adequate for a majority of situations, there exists for most surfaces a range of temperatures where that is not the case. The critical temperature range is between preroughening and roughening. There, the surface equilibrium state is disordered and flat (DOF), implying a state of roughly half-filling for the outermost surface layer. A particle-conserving simulation, based initially on a well-defined, usually integer, number of crystalline layers, must phase-separate into two half-layered domains. We discuss evidence, indicating that this kind of phase separation is actually taking place in existing simulations.

1. Introduction

Realistic molecular dynamics (MD) simulations with continuous potentials, initiated in the sixties, are nowadays extremely popular and useful in surface science. A standard setup for one such simulation is the so-called slab geometry. It consists of a certain number of crystalline layers, usually integer and with periodic lateral boundary conditions. The slab has two surfaces, one or both of which represent the physical surface under study. The equations of motion are solved with forces corresponding to some chosen potential, which can be either empirical, or first-principles, and thermal averages (for equilibrium studies) are handled within some convenient ensemble, which is, however, generally *particle-conserving*. For explicit examples, and a review of some recent results obtained by classical surface simulations of metal surfaces, the reader may consult, for example, Ref. 1.

Our main point is to argue that, unexpectedly, the particle-conserving condition may become dangerous for certain crystal surfaces in certain temperature regimes. Specifically, the dangerous situations arise for surfaces which undergo, in full equilibrium, thermal preroughening. Above that temperature, they become disordered and flat (DOF). This state persists up to a higher surface roughening temperature, as first shown in simple models by den Nijs.[2] In the temperature range between surface preroughening and roughening, particle conservation may easily lead — particularly when coupled with insufficiently large sizes and simulation times — to artifacts. The main artifact (if perhaps not the only one) to be expected, and which we will describe below, is a peculiar kind of surface phase separation phenomenon. The surface separates into two types of DOF domains, each with half occupancy, or adatom coverage, in the topmost layer.

2. DOF Phase Separation in Particle-Conserving SOS Models

We have recently shown how, based on a Monte Carlo numerical solution of a lattice model (the so-called FCSOS model[3]), a full-layered surface with strictly conserved particles spontaneously separates in this manner.[4] The main outcome of that study, best

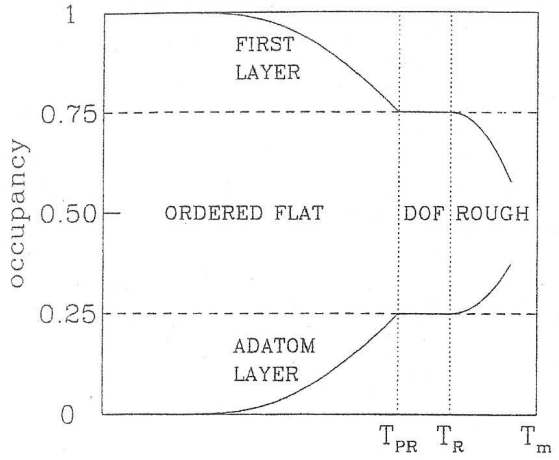

Fig. 1. Schematic behavior of occupancies of the first two layers of an initially full-layered surface as a function of temperature. A characteristic plateau is expected, indicating phase separation into DOF domains between preroughening and roughening (after Ref. 4).

clarified by the temperature evolution of the top layer surface occupancy, and by the corresponding adatom concentration, is summarized by Fig. 1. At low temperatures, well below preroughening, surface adatom-vacancy pairs are rare, their concentration growing in an activated manner. At T_{PR}, both adatoms and first-layer vacancies reach concentration 1/4, and here (neglecting smaller vacancy concentrations in the second and deeper layers) their proliferation suddenly stops. At this temperature, the grand-canonical surface would develop a nonzero DOF order parameter, implying a top layer occupancy of 1/2 (i.e. a half-filled layer). Under canonical, particle-conserving conditions this is however not possible, and a spontaneous phase separation must take place. The separation is into two DOF domains with opposite order parameters, very much as in an Ising system artificially kept at zero total magnetization below T_c. In turn, the separation produces a pinning of first-layer and adlayer occupancies to 3/4 and 1/4 respectively. A plateau at these values is expected, so long as the DOF order parameter remains finite, which is between T_{PR} and T_R.

This scenario is compelling, and we expect that it should be realized quite generally, so long as a well-defined DOF phase is present on a surface. For instance, SOS-type models different from FCSOS, proposed earlier to address general issues such as preroughening versus roughening,[2] as well as special ones such as the interplay of roughening and reconstruction on fcc(110) metal surfaces,[5,6] are expected to predict exactly the same outcome.

However, the full continuous Hamiltonian of a real system is sufficiently different and richer than an SOS model, to suggest careful direct checking of this hypothesized DOF phase separation on a realistic, particle-conserving MD simulation.

3. DOF Phase Separation in Molecular Dynamics Simulations for Metal Surfaces

We can in fact look at the existing simulations first. Very few of the many realistic, good quality MD surface simulations meet the prerequisites. The onset of preroughening and of roughening is in fact extremely difficult to address via MD, because of the very large sizes and long times required. A few among the most recent and extensive studies of high temperature metal surfaces, turn out to provide some useful, even if only partial, clues.

One large size MD simulation has recently been performed at a single high temperature of 1150 K (nominally above T_R) for an EAM model of Cu(110) by the Finnish simulation group.[7] They found layer occupancies 0.96 (second layer), 0.77 (first layer), 0.25 (adatom layer) and 0.025 (second adatom layer). The closeness of the first layer and adatom layer values to the ideal phase-separated DOF values 3/4 and 1/4 is striking. Therefore, either that particular run was in reality still within the DOF region of their effective-medium model of Cu(110), or else the 3/4, 1/4 layer occupancies persist artificially above T_R by virtue of finite size. In the latter case, roughening would then be responsible for the additional 4% of second-layer vacancies and 2.5% second-adlayer occupancies. In either case, we conclude that there is strong evidence for DOF phase separation in this simulation study of Cu(110).

Another more recent simulation, not as large as the one just quoted, was done by F. D. Di Tolla, who, for his thesis in our group, studied the early stages of surface melting on Al(110)[1,8] using a first-principles derived potential.[9] At T/T_m values of 0.946, 0.973 and 0.989, he found top layer occupancies 0.82, 0.85 and 0.82 respectively, with corresponding adatom layer occupancies 0.22, 0.25 and 0.28. While these numbers are not as close to 3/4 and 1/4 as those

for Cu(110), they are again qualitatively suggestive of a DOF phase separation plateau. They also show that vacancies spread substantially to layers deeper than the first. For instance, the occupancies given above imply that on Al(110) at 0.95 T_m the deep vacancies are as many as 10% of a monolayer. At the moment, it is not clear if the deep vacancies are also an artifact associated with the phase separation, or whether they would instead remain under fully grand-canonical conditions. It will be interesting to pursue further this question in future studies.

4. DOF Phase Separation in Molecular Dynamics Simulations for Lennard–Jones Surfaces

If preroughening of metal surfaces is so far speculative, it is on the other hand a very real phenomenon on rare gas surfaces, and in particular for Ar(111) and other rare-gas solid (111) surfaces, where it explains[2,3] the observed re-entrance of layering in the Ar/graphite adsorption isotherms.[10]

Recently, we have performed[11] new extensive MD simulations of the Lennard–Jones (LJ) fcc(111) surface, specifically aimed at understanding whether the DOF phase separation is real. Figure 2 shows the surface height fluctuations 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 $\bar{h} = (1/N_S)\sum_i h_i$. There is a clear and sudden change of behavior near a breakdown temperature $\sim 0.83\ T_m$. δh^2 grows fast for both SF and LF (a small and a large full-layered system) below this temperature; above, it levels off close to that of LH (a large half-layered system). Moreover, comparison of SF and LF indicates a stronger size dependence of δh^2 at the breakdown temperature. Both features, in accordance with previous discussions based on the FCSOS model,[3,4] strongly suggest that *preroughening* is taking place at the breakdown temperature, $T_{\rm PR} \simeq 0.83\ T_m$. A strong size dependence of δh^2 reappears again near $0.94\ T_m$, which is therefore the estimated roughening temperature, $T_{\rm R} \simeq 0.94\ T_m$. Both values are in excellent agreement with the experiment,[10] $T_{\rm PR} \simeq 0.82\ T_m$, $T_{\rm R} \simeq 0.95\ T_m$.

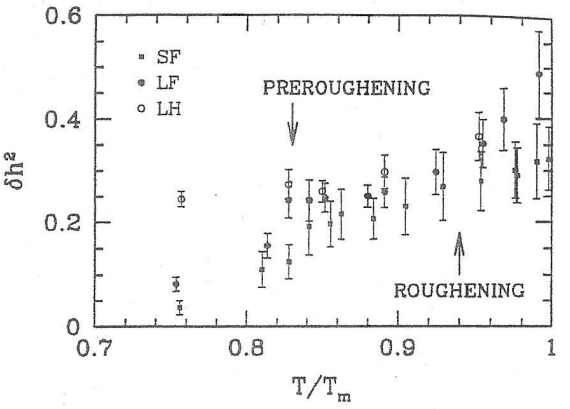

Fig. 2. Height fluctuations δh^2 of a particle-conserving simulated LJ(111) surface as a function of temperature (after Ref. 11). SF (small full), LF (large full) and LH (large half) indicate system sizes and integer or half-integer number of crystalline layers. A break corresponding to preroughening is clearly visible.

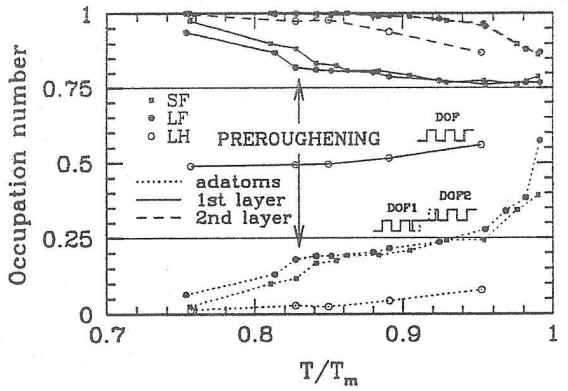

Fig. 3. Layer occupancies of the particle-conserving simulated LJ(111) surface as a function of temperature (after Ref. 11; same notations as in Fig. 2). An approximate plateau is visible, between the preroughening and the roughening temperatures, indicating DOF phase separation.

Coming to layer occupancies (geometry and times are such that the number of atoms lost by evaporation is irrelevant), Fig. 3 shows that the growth of the vacancy and adatom concentration with temperature develops a kinklike feature near $0.83\ T_m$. Moreover, the kink becomes more pronounced with increasing size, particularly for adatoms. There is a visible tendency to form a plateau which lies between 0.2 and

0.25. With provisions made for large fluctuations and corrections induced by finite size, currently being considered, this represents in our view a rather clear piece of evidence for DOF phase separation on the LJ(111) surface between T_{PR} and T_R.

5. Conclusions

Following suggestions, based on an SOS model study, that a particle-conserving surface should spontaneously phase-separate into two kinds of DOF domains in a certain temperature regime, we have considered the impact of such a phenomenon on realistic MD simulations. Preliminary results indicate the presence of DOF phase separation, both for metal and for LJ simulated surfaces. If unnoticed, this phase separation can spoil the validity of the simulation, as the real surface, generally grand-canonical in real life, will be full-layered below T_{PR}, but half-layered above.

Acknowledgments

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