Can Liquid Metal Surfaces Have Hexatic Order?

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We propose that extended orientational correlations can appear at the surface of supercooled heavy noble liquid metals, due to the same compressive forces that cause reconstruction of their crystal surfaces. Simulations for liquid Au show a packed surface layer structurally akin to a defected 2D triangular solid. Upon supercooling, the density of unbound disclinations decreases as expected in Nelson-Halperin's theory. It extrapolates to a hexatic transition about 350 K below melting, where a sharp growth of orientational correlation length and time is also found. True hexatic order is preempted by surface-initiated recrystallization. [S0031-9007(97)03001-9]

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Heavy noble metals such as Au, Pt, or Ir have a general tendency to reduce their lateral interatomic distance at the surface, relative to the bulk. This tendency, whose microscopic origin has been traced to a relativistic intra-atomic *s-d* energy shift [1], accounts for the zero-temperature reconstructions of the crystal surfaces. Remarkably, the lateral surface compression does not heal out with temperature. On the contrary, it is seen to persist, and in fact to increase, as temperature rises. For example, the lateral first-layer atomic density of Au(111) and Pt(111) has been found to increase, relative to the bulk layer density, from 1.04 to 1.07, and from 1.0 to 1.05, respectively, between room temperature and 1000 K [2]. Our present rationale for this somewhat surprising behavior is that at high temperatures the substrate periodic potential felt by the first layer atoms is progressively reduced by thermal fluctuations and by a large outwards expansion, so that shrinkage is less hindered by epitaxy.

In the liquid metal surface, which constitutes our present concern, the periodic potential is absent altogether. High lateral densities, now unhindered, can be expected to persist, in conjunction with strong surface layering, at least for temperatures which are not too high. Close to the melting point, x-ray data have revealed very pronounced layering oscillations in the density profiles normal to the surface in liquid metals such as Hg [3] and Ga [4], implying first layer lateral densities larger than the bulk average. Based on simulations, we pointed out some time ago [5] that still larger layering oscillations, and a higher surface lateral density, should be expected for the heavy noble liquid metal surfaces, boosted by the compressive tendencies just discussed. In addition, we found that supercooling makes the effect even stronger, with a nearly 2D-crystalline surface layer. This naturally raised the question, which we resolve in this Letter, of whether it could be possible for hexatic, orientational ordering, or at least for very extended orientational correlations, to appear at the free surface of a heavy noble liquid metal, such as Au, Pt, or Ir, under suitable supercooling conditions.

The original suggestion made by Nelson and Halperin [6] (extending earlier work of Kosterlitz and Thouless [7]), and pursued by Young [8] and others [9], that in 2D an intermediate hexatic phase could appear between the solid and the liquid, led to a wide search in a variety of systems [9]. Beautiful realizations have been achieved such as those in 2D colloidal systems [10], magnetic bubble lattices [11], and vortex lattices [12]. On the other hand, the 2D simulation studies have been exceedingly controversial [9]. An important clue which emerged more recently appears to be the choice of thermodynamic ensemble, with a strong preference of hexatic phenomena to show up in ensembles where density changes are naturally allowed [13]. In grand-canonical conditions, the binding of disclinations taking place at the fluid-hexatic transition is facilitated, since it does not rely on the slow, canonical diffusion of defects. For instance, spontaneous creation of a new disclination near a preexisting one can lead to a much faster appearance of the dislocation bound state.

In the liquid metal surface, atom exchange between layers can be extremely effective, with typical atomic diffusion times of order 100 ps between first and second "layer" for Au at the melting point [14]. This free interchange of particles with the liquid substrate makes the outermost layer of the liquid metal a 2D system which is naturally "grand-canonical" on a very fast, nanosecond time scale. This is fast enough, in particular, that even ordinary, canonical molecular dynamics (MD) simulation should be able to equilibrate orientational correlations without problems.

Moved by these motivations, we conducted very extensive MD simulations of the liquid gold surface. We used a slab geometry with two free surfaces, a thickness of $\simeq 60$ Å and a lateral size of $\simeq 120$ Å, for a total of 50 000 atoms. A second, smaller system with the same thickness but a lateral size of $\simeq 80$ Å was also studied in order to monitor size effects. Periodic boundary conditions were required parallel to the slab. Atoms interacted through the glue model Hamiltonian which is well

documented for this system, providing a good description of many properties of bulk solid and liquid Au, of the melting temperature (T_m = 1320−1350 K, against an experimental value of 1336) of all the main solid surfaces including their detailed energies and reconstructions, and of the liquid surface tension at the melting point [5,15]. Constant-energy runs were used to generate atomic trajectories. Data were taken from 2000 K, well above T_m, to 950 K, well below. Data below T_m clearly refer to a supercooled liquid slab, whose lifetime we nevertheless found to exceed 1 ns down to $T \sim$ 1000 K. Below 1000 K, the lifetime dropped, and it became impossible to equilibrate the liquid, due to (111) recrystallization rapidly nucleating at both slab surfaces. Above 1000 K, where the system remained liquid, we worked at temperature intervals of 50 K up to T_m, then more sparsely. At each temperature, typically 30 000 steps (one time-step $\sim 10^{-14}$ s) were used first for equilibration. Then 20 uncorrelated configurations (40 for the smaller system) were generated from successive 10 000-step runs, and subsequently analyzed.

The first step of the analysis consists in identifying the surface topmost, "first-layer" atoms in each configuration. That was done using a prescription which proved to work well in the past [5]. By representing atoms as spheres of radius R, we define surface atoms as those which remain fully visible, i.e., totally unshadowed from above the slab. The optimal R value, corresponding to atoms in the first density profile peak in Figure 1, was found to be 1.8 Å, reasonably close to the atomic radius. Figure 1 shows a Delaunay triangulation map [16] for the surface atoms, where disclinations (fivefold and sevenfold) are pinpointed. At high temperature there is a high concentration of defects, both bound and free, while the density profile surface peak is relatively weak. Conversely, the peak is very strong at low temperatures, where the map shows large triangular domains, and a reduced density of free disclinations n_f. Theory predicts [6] a behavior of the form

$$n_f \simeq \exp\left[\frac{-2a}{(T - T_i)^{1/2}}\right] \quad (1)$$

as the fluid-hexatic transition temperature T_i is approached. We find that this equation fits very closely our simulation data, with $a \simeq 2.2$ K$^{1/2}$ and $T_i \simeq 974$ K (Fig. 2). This suggests that the liquid Au surface would undergo, in its supercooled metastable state, a genuine fluid-hexatic transition, if one could somehow prevent recrystallization from taking place.

Encouraged by this result, we turned to a comparison of positional and orientational spatial correlations, and of their dynamics, versus temperature. The static orientational correlation function is defined as

$$g_6(r, t = 0) = \langle O_6^{i*}(r, t = 0) O_6^j(0, t = 0) \rangle, \quad (2)$$

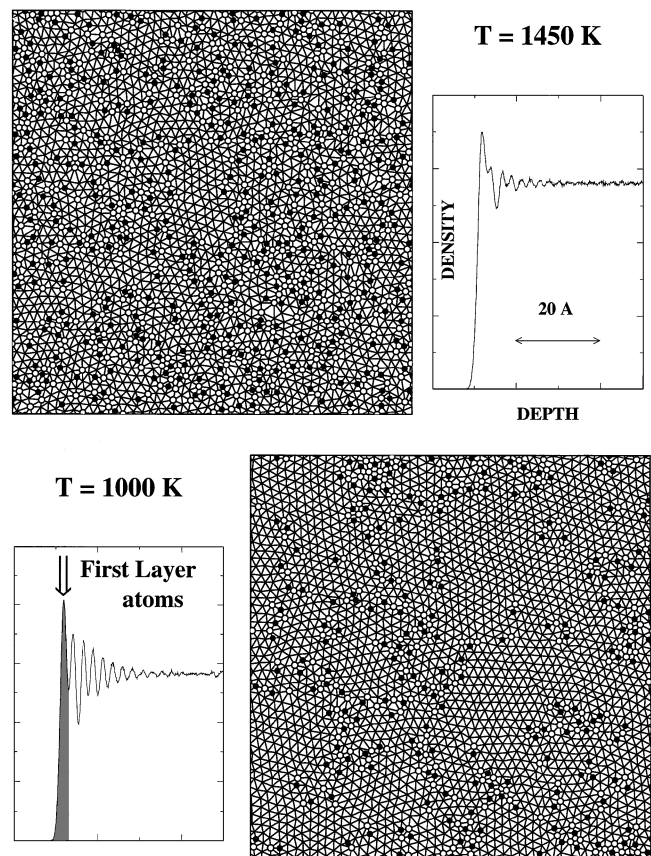where the orientational order parameter O_6 is, at surface

FIG. 1. Delaunay triangulation maps for the surface atoms of simulated liquid Au (larger system) at T = 1450 K (above T_m) and T = 1000 K (supercooled). Fivefold (black) and sevenfold (white) disclinations are pinpointed. The two corresponding density profiles along the surface normal are also shown. The first peak correspond to first layer atoms in the maps.

site i,

$$O_6^i = \frac{1}{N_i} \sum_{j=1}^{N_i} \exp(6i\theta_{ij}). \quad (3)$$

The sum is restricted to the N_i Delaunay surface neighbors of atom i, and θ_{ij} is the angle formed by the ij bond (projected on the xy plane) with the x axis. Positional correlations are defined similarly, using the surface atom local 2D density as the order parameter. Correlation lengths ξ_p and ξ_6 are obtained by fitting the envelope of the computed correlation functions to an exponential decay $g(r) - 1 \sim \exp(-r/\xi_p)$. Figure 3(a) shows that whereas above 1200 K positional and orientational surface correlation lengths are close, and about 5 Å, below this temperature the latter take off while the former do not. A fit of $\xi_6(T)$ to theory, which predicts $\xi_6(T) \simeq \exp[a/(T - T_i)^{1/2}]$ yields reasonable agreement for our larger system, with $a \simeq 15.5$ K$^{1/2}$ and $T_i \simeq 942$ K. There is, however, an alarmingly large discrepancy with the parameter values of the disclination fit. The disagreement turns out to be instructive and is explained by a size effect. By comparing our small and
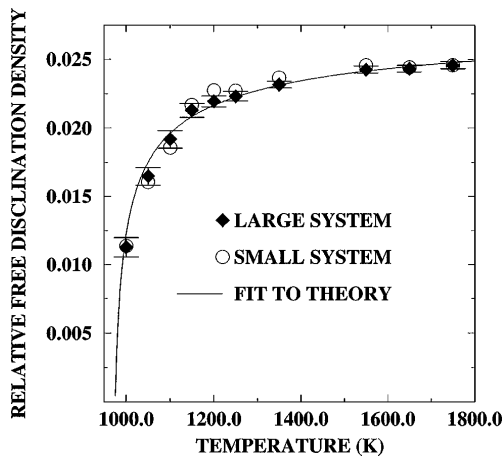
FIG. 2. Density of free disclinations (of both signs) for the liquid metal surface as a function of temperature. Full diamonds, larger system; open circles, smaller system; solid curve, fit to Eq. (1).

large systems, we observe that whereas disclination densities hardly depend on size, the growth of long-ranged orientational correlations is enormously hampered by size. As Fig. 3(a) shows, a decrease of lateral size from 120 to 80 Å is sufficient to damage the rise of ξ_6, reducing it (at 1000 K) from 12.5 to 7.5 Å. This is, we surmise, an independent signature of the Coulomb nature of effective interactions between disclinations in the liquid metal surface. Size effects in two-body correlations are

known to be extremely large in related systems such as the *XY* model [17]. Fortunately (a proper size scaling being presently out of the question), the one-body disclination density is instead well converged (Fig. 1). We conclude that, even though ξ_6 is still far from convergence even in the large system, the disclination fit parameters should safely represent the infinite system.

As theory suggests [18], and as the colloidal experiments have demonstrated [10], the temperature-dependent orientational relaxation times can provide an even stronger dynamical signature of hexatic phenomena. We computed the positional and orientational correlation times τ_p and τ_6 by an exponential time fit of the envelope of the time-dependent 2D structure factor $F(K, t)$, where K is the frustrated reciprocal lattice spacing, and of the time-dependent orientational correlation function $g_6(r = 0, t)$. Figure 3(b) shows the results for the larger system. Below about 1200 K τ_6 is found to rise dramatically (note the log scale) while τ_p does not. There is a clear orientational slowing down, which complements very well the static results, and also suggests that a likely experimental signature to be sought at the liquid metal surface might be dynamical rather than static.

In spite of these growing correlations, true hexatic long-range order appears, in our particular system, to be narrowly preempted by recrystallization. Already at 1000 K, after a lifetime of about 0.5 ns the liquid slab suddenly starts recrystallizing. At 950 K, the liquid lifetime (starting with the 1000 K liquid configuration) drops to less than 0.1 ns. Recrystallization proceeds with two fronts starting simultaneously at the two surfaces. At 1000 K, we analyzed first the metastable liquid surface, and then the moving recrystallization front, monitoring values of ξ_6 and ξ_p in the successive layers as a function of depth [14]. As shown in Fig. 4 the front is split, an orientational ordering front *preceding* a positional ordering, crystalline front. The intermediate region, where orientational correlations are extended, but positional correlations are short, is strongly layered (not shown) and extends for a thickness
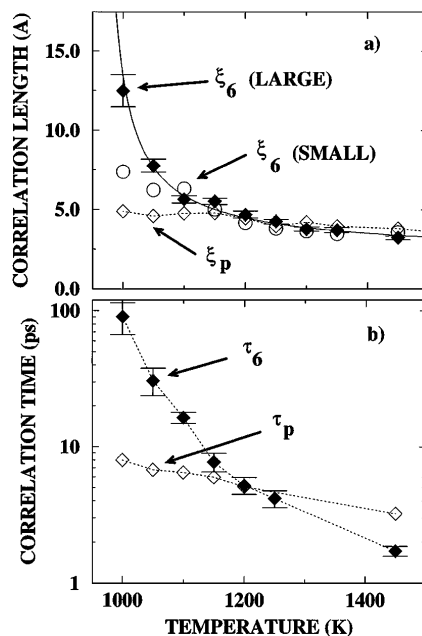

FIG. 3. (a) Orientational (full diamonds) and positional (empty diamonds) correlation lengths. Open circles: Orientational length for the smaller system. The full line is a fit to theory (see text). (b) Orientational (full diamonds) and positional (empty diamonds) correlation times. Dotted lines are guides to the eyes.
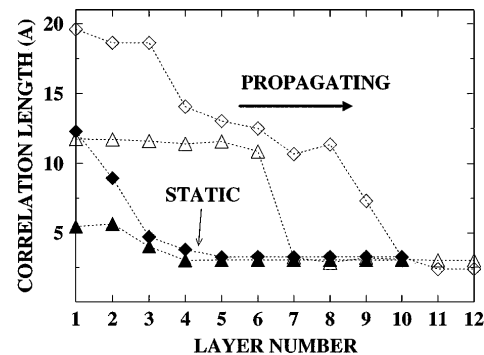

FIG. 4. Orientational (diamonds) and positional (triangles) surface depth profiles. Bottom: Liquid surface, $T = 1000$ K. Top: During recrystallization. Note that the orientational front precedes the positional front.

of about three layers. In fact, layers just below the surface already possess, in the purely liquid slab, long orientational correlations (Fig. 4). This kind of surface wetting by an orientationally ordered film coexists, as we verified directly, with rough, liquidlike height-height static correlations (not shown) and seems an exclusive characteristic of a strongly layered liquid surface. No such orientationally ordered film is found, for example, in a Lennard-Jones system, either at the free liquid surface, or at the crystal-liquid interface [19]. At the liquid metal surface, the presence of the orientationally ordered film seems to provide the required germ for propagation of the crystal phase into the bulk.

In conclusion, the supercooled surface of liquid Au, and most likely also that of other heavy noble metals such as Pt or Ir, is predicted to develop an incipient long-ranged orientational order described by the Nelson-Halperin theory. The order extends a few layers below the surface. Transition to a well defined hexatic phase is preempted by a fast and effective surface-driven recrystallization, where the orientationally ordered film precedes the crystalline front. Our results should motivate future experiments, either structural, to detect the orientationally quasiordered film, or dynamical, addressing the orientational slowing down, or metallurgical, to investigate the nature and depinning of the recrystallization front in these simple but exciting systems.

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