Spin-Glass Model of Crystal Surfaces

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We propose and analyze a simple model for the surface of an imperfect crystal in equilibrium with its vapor, below the roughening transition. We show that this system exhibits typical glassy behavior and opens the exciting possibility of experimentally testing recent theoretical ideas originating in spin-glasses.

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Our understanding of spin-glasses has greatly improved following Parisi's solution[1] of the Sherrington-Kirkpatrick model.[2] The picture that emerged is that of a glassy phase, characterized by an infinite number of thermodynamic equilibrium states, for which there exists a natural notion of overlap (or codistance):

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N} m_i^{\alpha} m_i^{\beta},$$

where m_i^{α} is the local magnetization at site i in the state α. Parisi[3] suggested that an appropriate order parameter for the spin-glass transition would be the distribution of overlaps, or more generally the geometric structure of the space of pure states, which in the Sherrington-Kirkpatrick model was in particular shown to be ultrametric: Any triangle in this space has its two largest sides equal, implying that states can be organized in hierarchical clusters.[4] Recent numerical studies[5,6] indicate that ultrametricity could be a universal property of the glassy phase.

The question naturally arises whether such theoretical contentions can actually be tested in the laboratory. With magnetic alloys one would have to reconstruct local magnetizations from neutron-diffraction data,[7] a rather formidable task. In this Letter an alternative will be proposed: I will show how crystal-vapor interfaces, in the presence of screw dislocations, can exhibit glassy behavior (reminiscent of the two-dimensional Ising spin-glass), and provide us with a physical system in which overlaps might be easier to measure (by counting common strings in photographs), and the geometric structure of the space of pure states could, therefore, be experimentally probed. I will propose and analyze a simple model for the low-temperature behavior of this system, by adapting a well-known combinatorial optimization problem. The results are, therefore, also relevant in light of the recent interest in the structure of such problems.[6,8,9]

To draw an analogy between smooth interfaces and spin-glasses, consider the two-level solid-on-solid model[10] of a (100) surface of a perfect cubic lattice at thermal equilibrium with its vapor. The partition function is

$$Z_{\text{perfect}}=\sum_{\text{closed } s} e^{-\beta\sigma L(s)}, \tag{1}$$

where the summation runs over all configurations of nonoverlapping closed strings (or steps) s, of length $L(s)$, on a square lattice, and σ is the energy cost of a step per unit length. Linear defects in the crystal modify this picture by providing sources and sinks for the strings. This is because screw components manifest themselves on the surface[11] as positive or negative[12] topological point defects, such that on making a complete clockwise turn around them, one is found at a level higher or lower than one's starting position. We therefore obtain

$$Z_{\text{imperfect}}=\sum_{\text{matching } s} e^{-\beta\sigma L(s)}, \tag{2}$$

where the summation now runs over all string configurations that "match" a given quenched distribution of dislocations, i.e., such that an open string connects every positive defect to a single negative defect and vice versa.

The reader will no doubt recognize in (1) the two-dimensional Ising ferromagnet, and in (2) a close resemblance to the two-dimensional Ising spin-glass on a square lattice with nearest-neighbor couplings restricted to be $\pm\sigma$.[13] Indeed, to each spin configuration corresponds a configuration of dual-lattice strings traversing all unsatisfied bonds (bonds of nonminimal energy). Frustrated plaquettes have an odd number of such bonds: They are therefore string end points, playing the same role as screw dislocations in crystal surfaces, except that (a) they can act as both a source and a sink, and (b) they have a distribution induced by that of negative couplings, which in particular implies that at low concentrations they tend to be bound in pairs; this need not be the case with screw dislocations.

A little thought should convince one that the important degree of freedom, responsible for the glassy behavior, is the choice of defect matching. We therefore consider a simple model, with N sources and N sinks distributed independently and uniformly over some d-dimensional volume V. Let D_{ij} be the Euclidean, or Manhattan (shortest path on a lattice), distance between the ith source and the jth sink. We define the partition function

$$Z=\sum_{\pi\in S_N} e^{-\beta\mathcal{H}(\pi)}, \tag{3a}$$

where the summation runs over all matchings of sources to sinks, i.e., all permutations π of N objects, and the energy is

$$\mathcal{H}(\pi)=\sigma\sum_{i=1}^{N}D_{i\pi(i)}. \tag{3b}$$

The infinite volume limit is taken by keeping the density $\rho=N/V$ fixed, and thermodynamic variables should be averaged over all quenched distributions of defects.

Let me here warn the reader that model (3a),(3b) is expected to describe only the structure of ground states, or very low-temperature (meta)stable states of a real crystal surface. This is because, in order to isolate the effects of frustration and ground-state degeneracy, I have concentrated on the choice of defect matching, and totally neglected other degrees of freedom such as closed strings and fluctuations of individual open strings, which give rise to surface roughening and render the model inadequate at $kT_{\text{rough}}\sim\sigma$. At lower temperatures, however, their effect can be summarized by a finite renormalization of (a) the distance matrix D_{ij} and (b) concerning nonequilibrium phenomena, the relaxation time scale. The time-scale renormalization is due to the existence of potential barriers separating any two neighboring (i.e., differing by an interchange of two sinks) configurations, since such an interchange must proceed first by deformation of two strings, until they touch and can resettle in their new configuration. Finally note that the approximation of quenched defects is justified, since screw dislocations are anchored in the bulk of the crystal: Their distribution is therefore determined by preparation rather than by thermodynamic equilibrium.

The annealed, rather than quenched, averages are easy to compute. Using for instance Manhattan distances in d dimensions, I obtained the following for the free energy, entropy, and average length per string:

$$F_{\text{ann}}=-\frac{1}{\beta N}\ln\langle Z\rangle=\frac{1}{\beta}+\frac{1}{\beta}\ln\left(\frac{\beta^{d}\sigma^{d}}{\rho}\right),$$

$$S_{\text{ann}}=(d-1)-\ln(\beta^{d}\sigma^{d}/\rho),\quad l_{\text{ann}}=d/\beta\sigma,$$

respectively. At $\beta=0$ there is a nonanalyticity common to all models whose configuration space grows faster than exponentially with the volume. At $\beta_{\text{freezing}}=(\rho^{1/d}/\sigma)\exp(1-1/d)$ the annealed entropy becomes negative, a signal that quenched frustration and freezing become important, rendering the annealed approximation inadequate.[14] This is confirmed by Monte Carlo simulations, which cannot, however, decide on the existence or nonexistence of a sharp phase transition.[15]

The present numerical analysis of the geometry of locally stable states followed closely the corresponding analysis of the traveling salesman problem (TSP) by Kirkpatrick and Toulouse.[6] I studied samples of $N=40$ and 60, in both two and three dimensions, with both Euclidean and Manhattan distances. I found two-optimal configurations (i.e., those stable under a permutation of any two sinks) by first cooling across the freezing temperature, and then searching locally. The overlap of two configurations is defined as the fraction of their common strings,

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}\delta_{\pi_{\alpha}(i),\pi_{\beta}(i)},$$

while their distance is $d_{\alpha\beta}=1-Q_{\alpha\beta}$. Typical overlap distributions (with each two-optimal configuration below some energy cutoff contributing with equal weight) are plotted in Fig. 1. They are sharply peaked near $q=\frac{2}{3}$. I also looked at groups of three configurations; we can represent each group (α,β,γ) by a point inside an equilateral triangle, such that its distances from the three sides are proportional to $d_{\alpha\beta}$, $d_{\beta\gamma}$, and $d_{\gamma\alpha}$.[5] A measure of ultrametricity violation is then defined, and its distribution plotted in Fig. 2.

A comment is in order here concerning the striking resemblance of these results to those obtained by Kirkpatrick and Toulouse for the TSP[6]: In combinatorial optimization finding the ground state of (3b) is known as the bipartite matching problem and, unlike the TSP, is polynomially solvable.[16] We are thus led to conclude that the geometry of locally stable states cannot, by itself, distinguish *NP*-complete[17] from polynomially solvable problems. The former could perhaps be characterized by the possibility of a finite transition temperature (infinite potential barriers in the thermodynamic limit).[18]

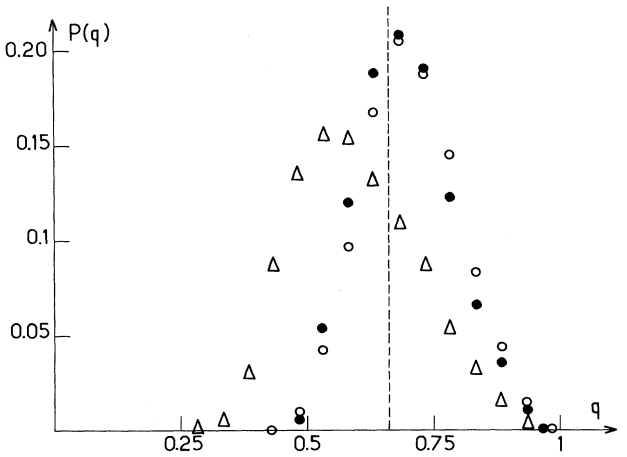

FIG. 1. Typical overlap distributions for three-dimensional Euclidean (black dots), two-dimensional Euclidean (white dots), and two-dimensional Manhattan (triangles) distances. The mean value $q=\frac{2}{3}$ (broken line) follows if one assumes a flat distribution of nonzero occurrence frequencies of strings in two-optimal degenerate configurations (Ref. 20).

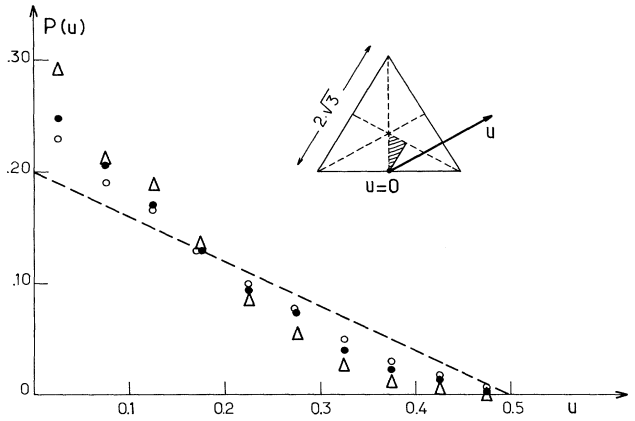

FIG. 2. Typical distributions of triplets of two-optimal states for three-dimensional Euclidan (black dots), and two-dimensional Euclidean (white dots) and Manhattan (triangles) distances. Each triplet corresponds to a point inside an equilateral triangle: by projecting it along the normal bisector one obtains its coordinate u (upper right corner). The little shaded triangle is the accessible region after ordering the overlaps and taking triangular inequalities into account (Ref. 5). A uniform distribution inside this region gives the broken line for $P(u)$. Perfect ultrametricity gives a δ function at $u=0$.

I conclude with some remarks on the prospects of a real experiment: As in spin-glasses, one could explore different free-energy valleys by repeatedly heating and cooling the surface, or by applying a vapor pressure (in some sense the analog of a magnetic field) to induce crystal growth and then letting the system relax to a new equilibrium. The main difficulty that I anticipate is the following: As has already been noted, the energy landscape of model (3a),(3b) is in reality decorated with small bumps, of the order of the energy needed to deform a typical frozen string ($\simeq \sigma\rho^{-1/2}$). Below the roughening transition this leads to a renormalization of atomic relaxation times by a factor $\simeq \exp(\beta_{\text{rough}}\sigma\rho^{-1/2})$, which risks to be enormous. It could be reduced (a) by using close-packed surfaces of asymmetric lattices (this reduces the cost of coherent string fluctuations relative to roughening or adsorption energies), and (b) by increasing the density ρ of dislocations up to the available resolution limit.[19]

In summary, I have proposed and analyzed a simple glassy model of the low-temperature properties of steps on a crystal surface, in the presence of quenched dislocations. This might open the possibility of experimentally testing recent theoretical ideas in spin-glasses.

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[11]The existence of screw dislocations was first invoked to explain the observed rates of crystal growth, and is now firmly established; see for instance, S. Amelinckx, *The Direct Observation of Dislocations* (Academic, New York, 1964).

[12]The restriction to height variations of a single lattice spacing and to screw dislocations of winding number ± 1 helps keep the present argument simple without changing its essence. And in any case, it is an adequate approximation at lower temperatures, even though it modifies the universality class of the roughening transition [see S. T. Chui and J. D. Weeks, Phys. Rev. B **14**, 4978 (1976)].

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[14]A similar thing happens in the two-dimensional spin-glass, see G. Toulouse and J. Vannimenus, Phys. Rep. **67**, 47 (1980).

[15]The two-dimensional spin-glass analogy would in fact suggest that a sharp transition does not occur down to $T=0$, in which case a geometry of pure states can strictly speaking only be defined there. It corresponds, in practice, to the geometry of metastable states, making their appearance roughly below T_{freezing}, with lifetimes that can be made arbitrarily large as the temperature is lowered.

[16]C. Papadimitriou and K. Steiglitz, *Combinatorial Optimization: Algorithms and Complexity* (Prentice Hall, Englewood Cliffs, 1982).

[17]These are the hardest of all reasonable problems in the following sense: Should an algorithm solving an *NP*-complete problem in time bounded by a polynomial of its size exist, it could be modified to likewise solve any other optimization problem whose cost (energy) functional is polynomially calculable.

[18]See for instance C. Bachas, J. Phys. A **17**, L709 (1984).

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