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Equilibrium Stranski-Krastanow and Volmer-Weber models

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Abstract – An equilibrium random surface model in 3d is defined which includes versions of both the Stranski-Krastanow and Volmer-Weber models of crystal surface morphology. In a limiting case, the model reduces to one studied previously in a different context for which exact results are available in part of the phase diagram, including the critical temperature, the associated specific heat singularity and the geometrical character of the transition. Through a connection to the 2d Ising model, there is a natural association with the Schramm-Loewner evolution that has also been observed experimentally in a *nonequilibrium* deposition setting.

Introduction. – In recent times, there has been a renascent interest in surface science promoted partly by experimental methods like Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) [1], which allow direct examination of the surface structure on an atomic length scale. Such structure is of great relevance for understanding the technically significant areas of heterogeneous catalysis and nanotechnology at a fundamental level. At the same time, a systematic theoretical treatment is emerging, in which exact statistical-mechanics results have played a significant role [2]. In this letter, we address the general question of whether equilibrium statistical mechanics can predict the existence of mounds of molecules which are observed experimentally on the substrate in certain systems. The problem is that on naive entropic grounds, the mounds might be expected to dissociate into pieces of monolayer because of the greater available configuration space. But this neglects entirely excluded area effects.

A notable conjecture about surface phase transitions is due to Burton, Cabrera and Frank (BCF) [3]. Consider a classical, low-temperature uni-axial ferromagnet (such as the Ising system, or its lattice-gas analogues) at coexistence. Let both equilibrium phases be present, but organised in a symmetrical way into two different regions of space separated by an interface or domain wall. BCF made the bold conjecture that, because the interfacial region is acted on by equal and opposite and therefore cancelling mean fields, the interface should undergo a transition like the bulk one in 2d, already found by Onsager [4]. Later, using series expansions, Weeks, Gilmer and Leamy [5] gave compelling evidence that there is a phase transition, but not one of 2d Ising type. Rather, in the high-temperature phase the interface manifests large spatial fluctuations which invalidate the customary thermodynamic picture of a sharp interface localised in laboratory-fixed axes. There has never been a proof of a roughening transition in the 3d Ising model, distinct from the usual transition between ferromagnetic and paramagnetic phases. It is known that the transition temperature T_R satisfies the inequality $T_c(3) \geqslant T_R \geqslant T_c(2)$, where $T_c(d)$ is the usual critical temperature in dimension d. This result was established by an ingenious exact association with the 2d Ising magnet [6]. On the other hand, exact results are available for associated Solid-On-Solid (SOS) systems showing both roughening and an essential singularity in the incremental free energy, quite unlike the BCF conjecture [7]. This raises the interesting question of whether the conclusions of the BCF scenario are realised physically in another type of surface phase transition. It is the purpose of the present paper to answer this.

To begin, we need to review three modes of crystal surface growth: firstly, we have the Franck-van der Merwe (FM) mode in which adsorbate is added in complete layers [8]. The analogue at thermodynamic equilibrium is wetting [9]; this is normally characterised by sessile drops, contact angles and the Young rule. Although there are no exact results yet in 3d, the situation for the Ising model in 2d is well understood as is the equivalence of divergent film thickness and vanishing contact angle

(properly defined) [10]. The second growth mode is the Volmer-Weber (VW) one [11]. In this, monolayer islands of adsorbate of finite extent are formed, and then islands grow on top of islands and so on. The natural question is this: are there equilibrium statistical-mechanical models which show these "turreted" configurations, which have indeed been observed experimentally [12]? The third growth mode is due to Stranski and Krastanov (SK) [13]; it is a hybrid of the first two, in which a finite number of layers of FM type are laid down, followed by growth of VW type. A significant property of the turreted crystallites is that they can manifest greatly enhanced chemical activity when compared with the bulk material, a matter of considerable relevance in heterogeneous catalysis.

We now detail the purpose of this paper more closely; we will define a three-dimensional surface model in statistical mechanics which contains cases of the VW and SK scenarios and for which exact results have become available, some of which are in agreement with the BCF predictions. Before our detailed discussion, we point out that our modelling affords another example of the Schramm-Loewner Evolution (SLE) [14–18], a recent mathematical approach to interfaces in 2d systems which is finding increasing relevance [19].

Equilibrium surface model. – We now construct an equilibrium model analogous to the VW and SK growth models first by prescribing allowed configurations, secondly assigning energies to such configurations and thirdly by giving them a Boltzmann weight. The model represents the substrate as a flat plane and inscribes on it a square lattice. Adatoms are physisorbed onto the substrate and, in the spirit of Kossel-Stranski [20,21], they are represented by cubes, the bottom faces of which fit exactly to unit cells of the underlying square lattice. From the outset, we exclude discommensuration and associated elastic phenomena because our theoretical methods appear not to be useful in that case.

Adatoms can occupy neighboring unit squares; such configurations are energetically stabilized by assuming attactive interactions between neighboring adatoms. On energetic grounds, these adatoms tend to assemble into rafts. We assume that there are no holes in the rafts since such configurations would be energetically unstable against filling. Moreover, this restriction is essential for our theoretical analysis.

The energy of a configuration of rafts confined to the first layer can be written as

$$E(\Gamma) = \tau L(\Gamma) + (\tau - \varepsilon_0) A_1(\Gamma). \qquad (1)$$

In the above equation, $A_1(\Gamma)$ is the total area of contact of the rafts with the substrate; by construction this is the same as the area of the upper surface. The term $\tau A_1(\Gamma)$ is the surface energy of the upper surface while $-\varepsilon_0 A_1(\Gamma)$ is the binding energy of the rafts with the substrate. $L(\Gamma)$ is the total length of the curve(s) formed by the intersection of the rafts with the substrate. Γ itself is a collection of simple closed loops, $\Gamma = \{\gamma_1, \ldots \gamma_n\}$. Each γ_j is the intersection with the substrate of plaquettes with the normal parallel to the substrate plane. The term $\tau L(\Gamma)$ is the total surface energy of these plaquettes.

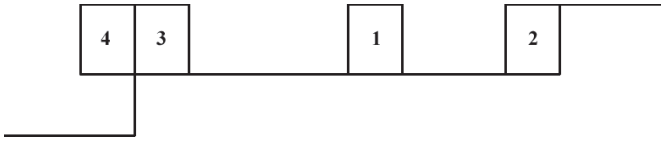

Fig. 1: Side view of four possible locations for adsorption of an adatom on a train of ledges.

At this juncture, the substrate plane is in general partially covered by molecular rafts. We now repeat this process by placing additional rafts strictly on top of those already in place, once again with the exclusion of holes in the added rafts. By "strictly on top", we mean that vertical overhangs are forbidden. Thus the perimeter of any raft in the second layer must be contained within the perimeter of some raft in the first layer. We have departed by this point from the usual lattice gas models of wetting and film thickening which allow internal holes.

The remaining factor to be considered is the energetics which results when elements of the perimeters of different rafts coincide. Ehrlich-Schwoebel [22,23] phenomenology states that an adatom adsorbed on a terrace in a train of ledges is more likely to be adsorbed at the up-going ledge than the down-going one. This is explained by activation energy for the adsorption processes —see fig. 1.

In our model, the placement of a molecule like that numbered 4 in the figure is ruled out entirely, as we have said above, because it is too energetic. Similarly, we regard molecule 3 in the figure as having higher energy than molecule 1, when not only neighboring, but also next-nearest-neighboring interactions are included. This is incorporated into the energetics described by (1) by inserting an additional term:

$$E(\Gamma) = \tau L(\Gamma) + (\tau - \varepsilon_0) A_1(\Gamma) + \varepsilon_1 N(1,1), \qquad (2)$$

where $N(1,1)$ counts the total number of coincident edges and ε_1 is a positive energy. We note that molecule 1 in the figure has higher energy than molecule 2 because of the $\tau L(\Gamma)$ term in (2). The specification of the model then allows further additions of molecular rafts on top of those already laid down. Unfortunately, as far as we know, rather little of substance can be said about this loop gas with configurational energy given by (2). But if we take the limit $\varepsilon_1 \to \infty$, we recapture the Multi-Ziggurat (MZ) model [24], about which there is much useful information [25,26].

At this juncture, it is worth making the following points: firstly, what does our equilibrium statistical mechanical model imply about whether a raft is added on the base plane or on top of other rafts to make multilayered structures? Simple entropic arguments might favor the former, but this matter can only be decided by detailed

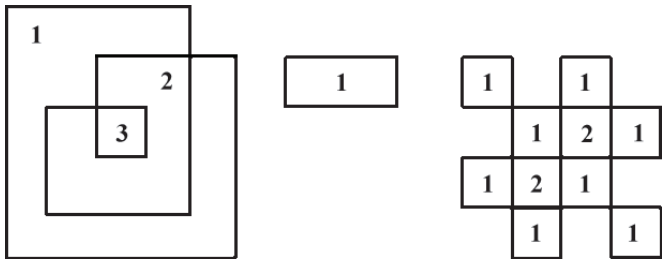

Fig. 2: A typical surface structure having three mounds above the substrate. The left one is a tower, the middle one is a dimer and the right one corresponds to a chessboard pattern of spin values assigned by the Peierls contours. The numbers indicate heights or the regions (or terraces).

investigation. Secondly, there is an entropic repulsion *within* nests of contours describing multilayered structures, that is, *within* individual ziggurats as well as *between* them; this is taken into account implicitly in what follows.

To begin with, in the MZ model, the square lattice underlying the configuration space no longer contains more than singly occupied edges. The configuration space is defined uniquely in terms of the boundaries of the rafts, which are simple closed walks. According to the rules of the model, different walks can meet at corners but they cannot have common edges, because of the assumed limit $\varepsilon_1 \to \infty$ of the ledge-ledge interaction, which has just been stipulated. Thus the configurations are the same as those of the Peierls contours of the two-dimensional Ising ferromagnet with fixed parallel boundary spins, say all plus and their energy will be given by (1). An example is shown in fig. 2.

To make the matter quite definite, take the dual lattice Λ^* of the original square lattice Λ; this has vertices at the centers of the unit cells of Λ. At each such vertex $i \in \Lambda^*$, place a spin $\sigma(i) = \pm 1$, and for $i \in \Lambda^*$, take $\sigma(i) = +1$. In the interaction term $(\tau - \varepsilon_0)A_1(\Gamma)$ for the configuration Γ, the quantity $A_1(\Gamma)$ satisfies

$$A_1(\Gamma) = A(\Lambda^*) - A(\Pi_+(\partial\Lambda^*)), \tag{3}$$

where A denotes the total area and $\Pi_+(\partial\Lambda^*)$ denotes, in the language of Ising percolation theory, the plus cluster of the boundary $\partial\Lambda^*$ of Λ^* [26]. Evidently, we have a rather curious object —namely, a planar Ising model with a magnetic field applied to a set of sites which is random, in that it is generated from the spin configuration.

Note, though, the special case $\varepsilon_0 = \tau$ for which this field vanishes, giving the standard planar Ising model. Finally, an integer-valued height variable $h(i)$ may be assigned to each site i of Λ^*. This height is the least number of Peierls contours crossed in going from i to $\partial\Lambda^*$.

Mounds in the Multi-Ziggurat model. – In the case $\varepsilon_0 = \tau$, it follows from Onsager's seminal work [4] that there is a phase transition with logarithmically divergent specific heat on both sides of the transition. This transition persists for $\varepsilon_0 \geqslant \tau$, since then the substrate is covered with a monolayer [10] thus affording a potential example of the SK scenario. For $\varepsilon_0 = \tau$, there is no monolayer and one has an example of the VW scenario.

A difficulty is to gauge the propensity to form mounds. The probability that the surface at any point, say (0, 0), has at least height k is denoted by $P(h(0,0) \geqslant k)$. It satisfies for $\varepsilon_0 = \tau$, the bound [10],

$$P(h(0,0) \geqslant k) \leqslant (1 - m^*)^k, \tag{4}$$

where m^* is the spontaneous magnetization, given by

$$m^* = \left(1 - (\sinh(\beta\tau))^{-4}\right)^{1/8}. \tag{5}$$

For $\varepsilon_0 > \tau$, because of the monolayer, the height h in (4) should be replaced by $h - 1$. The "droplet" of the origin, denoted D, is defined as the connected cluster of sites r with $h(r) \geqslant 1$ which contains the origin. If $h(0,0) = 0$, then D is the empty set for consistency. Thus, it follows from [24] that for $\varepsilon_0 > \tau$, the mounds, or individual ziggurats, are finite. It has also been shown that in the thermodynamic limit, the height and therefore also the basal area of a typical mound, such as D, diverges as $T \to T_c(2)-$. Consequently, the phase transition implies incorporating a macroscopically thick "film" on the substrate in the high-temperature phase. Nevertheless, the later work in [26] indicates that it is quite inappropriate to think of MZ as a satisfactory model of wetting. Firstly, above the critical temperature, the surface has a "roof" structure, rather than the complete layer-by-layer one associated with equilibrium FM. Secondly, the constancy of the transition temperature is unnatural, as is the logarithmic divergence of the specific heat *on both sides* of criticality; neither of these results corresponds with accepted ideas for wetting derived from RG and MC studies [9].

Our version of the SK and VW scenarios allows us to study the thermal fluctuations of two-dimensional domain walls, both subcritically and at the transition point. In the latter case, their statistics, in the scaling limit of vanishingly small lattice scale, should follow the SLE scheme with the parameter $\kappa = 3$ [14]. SLE(κ) curves are random curves in the plane constructed out of a one-dimensional Brownian motion via conformal mappings. They are essentially the only random curves satisfying both conformal invariance properties and a certain spatial Markov property —for reviews of these and other properties of SLE, see [15,16]. As such, they were identified, based on conformal field theory predictions, as the only possible candidates for scaling limits of interfaces arising in a variety of two-dimensional critical systems. The identification of the parameter κ is aided by the fact that the fractal dimension for $\kappa \leqslant 8$ is $1 + \kappa/8$. In particular the interfaces of the spin clusters in the critical Ising ferromagnet were predicted to have $\kappa = 3$, as verified in [17]. For families of closed loop interfaces as in our level curve-Peierls contour context, the relevant SLE machinery is that of Conformal Loop Ensembles (CLE), as initiated in [18].

Finally, for $0 > (\varepsilon_0 - \tau) > -\tau$, there is also a transition (more strictly speaking at least one) lying somewhere in the region $T \geqslant T_0(\varepsilon_0)$, where $T_0(\varepsilon_0) = T_c(2)(1 - (\varepsilon_0 - \tau)/(4\tau))$ for $0 > \varepsilon_0 - \tau > \tau$ [25]. For T below the transition temperature the mounds are finite. In this case, there is no preliminary covering of the substrate by a monolayer. Thus this affords an example of the equilibrium VW model (as does $\varepsilon_0 = \tau$); the precise location and nature of the transition in the VW regime for $\varepsilon_0 < \tau$ remain to be elucidated. It is thus of more than passing interest that there is recent experimental evidence [27] that the level curves of deposited films of tungsten oxide, WO_3, are consistent with the statistics of SLE(3). This intriguing observation combined with the connection between critical equilibrium surface structure and SLE(3) expounded in this paper raises the interesting question of whether the deposition surface could be well described by an equilibrium model at criticality.

Discussion. – In recent work on deposited films of tungsten oxide, WO_3, Saberi *et al.* [27] have examined the level curves, or ledges in TLK terminology, where the level height is the normal distance from the substrate, by AFM microscopy and have provided evidence that such curves are well described by SLE(3). They have also found similar statistics at large scales in simulations of ballistic deposition models. Their deposition setups are driven dynamical systems and thus an *a priori* precise interpretation of temperature, let alone criticality, is unclear. On the other hand, our exactly solvable model, although admittedly only partially so, since many correlation functions of interest are yet to be obtained, allows us, as an exact result, to associate SLE(3) with the level curves (corresponding to Peierls contours) of the critical equilibrium SK model (and for $\varepsilon_0 = \tau$ the VW model). It would be of considerable interest to investigate experimentally the large-scale statistics of level curves in critical equilibrium surfaces as it would be to relate driven dynamical surfaces to critical equilibrium ones.

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REFERENCES

[1] Williams E. D. and Bartelt N. C., *Science*, **251** (1991) 393.
[2] Abraham D. B., in *Phase Transitions and Critical Phenomena*, edited by Domb C. and Lebowitz J. L., Vol. **10** (Academic, London) 1986.
[3] Burton W. K., Cabrera N. and Frank F. C., *Philos. Trans. R. Soc. London, Ser. A*, **243** (1951) 299.
[4] Onsager L., *Phys. Rev.*, **65** (1944) 117.
[5] Weeks J. D., Gilmer G. H. and Leamy H. J., *Phys. Rev. Lett.*, **31** (1973) 549.
[6] van Beijeren H., *Commun. Math. Phys.*, **40** (1975) 1.
[7] van Beijeren H., *Phys. Rev. Lett.*, **38** (1977) 993.
[8] Frank F. C. and van der Merwe J. H., *Proc. R. Soc. London, Ser. A*, **198** (1949) 205.
[9] Dietrich S., in *Phase Transitions and Critical Phenomena*, edited by Domb C. and Lebowitz J. L., Vol. **12** (Academic, London) 1988.
[10] Abraham D. B., *Phys. Rev. Lett.*, **44** (1980) 1165; Abraham D. B. and Ko L. F., *Phys. Rev. Lett.*, **63** (1989) 275.
[11] Volmer M. and Weber A., *Z. Phys. Chem.*, **119** (1926) 277.
[12] Hartig K., Janssen A. P. and Venables J. A., *Surf. Sci.*, **74** (1978) 69.
[13] Stranski I. N. and Krastanow L., *Akad. Wiss. Wien Math.-Naturwiss. Kl. IIb*, **146** (1939) 797.
[14] Schramm O., *Isr. J. Math.*, **118** (2000) 221.
[15] Werner W., in *Lect. Notes Math.*, Vol. **1840** (Springer, Berlin) 2004, p. 107.
[16] Cardy J. L., *Ann. Phys. (N.Y.)*, **318** (2005) 81.
[17] Smirnov S., in *Proceedings of the International Congress of Mathematicians 2006*, Vol. **2** (European Mathematical Society, Zurich) 2006.
[18] Werner W., *C. R. Acad. Sci. Paris*, **337** (2003) 481.
[19] Cardy J. L., *Nat. Phys.*, **2** (2006) 67.
[20] Kossel W., *Nachr. Akad. Ges. Wiss. Goettingen, Math.-Phys. Kl.* (1927) 135.
[21] Stranski I. N., *Z. Phys. Chem.*, **136** (1928) 259.
[22] Ehrlich G. and Hudda F. C., *J. Chem. Phys.*, **44** (1966) 1039.
[23] Schwoebel R. L., *J. Appl. Phys.*, **40** (1969) 614.
[24] Abraham D. B. and Newman C. M., *Phys. Rev. Lett.*, **61** (1988) 1969; *Commun. Math. Phys.*, **125** (1989) 181.
[25] Abraham D. B. and Newman C. M., *J. Stat. Phys.*, **63** (1991) 1097.
[26] Abraham D. B., Fontes L. R., Newman C. M. and Pisa M. S. T., *Phys. Rev. E*, **52** (1995) R1257.
[27] Saberi A. A., Rajabpour M. A. and Rouhani S., *Phys. Rev. Lett.*, **100** (2008) 044504.