

## Theory of Tricriticality for Miscut Surfaces

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We propose a theory for the observed tricriticality in the orientational phase diagram of Si(113) misoriented towards [001]. The systems seem to be at or close to a very special point for long range interactions. [S0031-9007(96)00378-X]

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A basic question to all surface studies is the stability of a surface against various processes, e.g., thermal fluctuations, defects, step formation, etc. This question assumes importance especially if the surface is cut, not in a perfect crystallographic direction, but with a slight miscut angle (called misorientation). So far, miscut surfaces have been found to be stable with steps or to reorganize to more complex surface structures [1,2]. An exception to this general rule is the recent observation of a *tricritical* point for a Si(113) surface with a small miscut angle,  $\theta$ , towards [001], point at a temperature  $T_t = 1223$  K. A phase coexistence of a stepped surface with a (113) facet, for  $T < T_t$  was observed in Refs. [3,4]. For  $T > T_t$ , the surface goes continuously to the facet as the misorientation is decreased. In other words, the crystal can be cut at any small angle as one wishes so long as  $T > T_t$  but, for any  $T < T_t$ , there is a minimum miscut angle below which the crystal surface cannot be cut (in thermal equilibrium). This change from a continuous to a first-order transition, as the temperature is varied, takes place at a special point in the  $T$  vs  $\theta$  phase diagram. The special point is also found to be the end point (critical point) of the first-order coexistence curve. This is therefore a tricritical point [5]. The phase coexistence of a reorganized facet and steps can be understood on the basis of two separate free energy curves [1], but a tricritical point demands a more subtle treatment. This discovery of a tricritical point in a two dimensional system is extremely important because it can serve as a fertile ground for recently developed statistical mechanical theories [6–9]. Our aim is to describe the universal aspects of this tricritical point.

The steps run in one direction (“z” axis) without backtracking (no overhang), so that the surface can be characterized by the density of steps,  $\rho$  (number of steps/transverse length) [2]. The misorientation is related to  $\rho$  (see Fig. 1). In the experiment of Refs. [3,4], the coexistence curve [ $\rho \sim (T_t - T)^\beta$ ] was found to have a zero slope at the tricritical point, with  $\beta = 1/2$ , showing utter disrespect to the extent that mean field theory [4,10] predicts  $\beta = 1$ .

The phenomenology of the transition can be discussed in terms of the Legendre transform of the free energy per unit transverse length,  $F(\rho, T)$ ,

$$\mathcal{F}(\mu, T; \rho) = -\mu\rho + F(\rho, T), \quad (1)$$

where  $\mu$  is the chemical potential for steps. The thermodynamic value of  $\rho$  comes from  $\partial\mathcal{F}/\partial\rho = 0$ , or equivalently  $\partial F/\partial\rho = \mu$ . Taking  $f_0$  as the free energy of an isolated step, Eq. (1) can be expressed as

$$\mathcal{F}(\mu, T; \rho) = (f_0 - \mu)\rho + F_{\text{int}}(\rho, T), \quad (2)$$

where  $F_{\text{int}}(\rho, T)$  is the free energy contribution from interactions among the steps. For noninteracting steps,  $F_{\text{int}} = 0$ . Therefore, a first-order transition at  $\mu = f_0$  takes a facet ( $\rho = 0$ ) to a fully stepped surface for  $\mu > f_0$ . For purely repulsive (“fermionic”) steps,  $F_{\text{int}} \sim \rho^3$  leading to the continuous Pokrovsky-Talapov (or “3/2” order) [2,11–13] transition with  $\rho \sim |f_0 - \mu|^{1/2}$ . This has been the rule for almost all systems until the tricriticality in Si(113) was discovered.

The occurrence of a phase separation, as noted in Ref. [4], suggests the existence of attractive interactions among the steps. The steps are generally taken to be nonintersecting. In addition, they are expected to have dipolar or elastic long range  $r^{-2}$  interaction. A long range ( $r^{-2}$ ) attraction for the nonintersecting steps, in a mean field (“Hartree-Fock”) analysis, gives  $F_{\text{int}} \sim (T - T_t)\rho^3 + a\rho^4$ , predicting a tricritical point with a linear phase boundary [10]. With an attractive  $r^{-2}$  interaction, this mean field form of  $F_{\text{int}}$  agrees, in the domain of overlap of parameters, with the exact Bethe ansatz solution [14]. This rules out the possibility of fluctuations causing a zero slope phase boundary in this model with long range attraction.

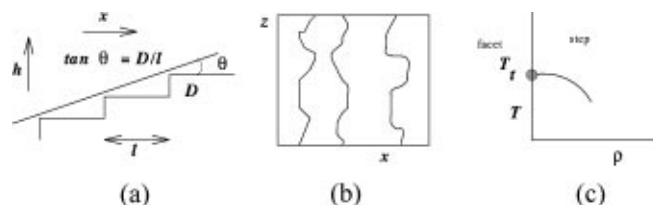


FIG. 1. (a) Schematic diagram of the steps of equal height  $D$ . The misorientation  $\theta$  is related to the density  $\rho$ , as  $\tan\theta = D/l = \rho D$ . (b) The steps viewed from above. (c) Schematic phase diagram.

We therefore consider a completely different scenario. Our proposal is that tricriticality occurs when the steps have a short range attraction. The physical picture we have in mind has strong resemblance to a phase separating polymer solution. In fact taking the steps as directed polymers (DP), the stepped face can be thought of as a DP solution. Our proposal is that in the high temperature phase the steps are repulsive and the phase is dominated by the entropic interaction. As the tricritical point is approached, the attractive part begins to play a role. The steps start colliding and the average separation between collisions determines the correlation length. When this length becomes comparable to the separation of the steps, the tricritical domain is reached. The phase separation takes place in this regime before any bound state can form.

To study the phase separation and the coexistence curve, we use a canonical ensemble approach, and use the analogy with a polymer solution [15]. The phase boundary is identified by equating the “osmotic” pressure of the two coexisting phases. The osmotic pressure in this context would mean the excess pressure generated by the addition of one more step and is obtained from  $\Pi = \rho^2 \partial / \partial \rho (F/\rho)$ , where  $F(\rho)$  is the free energy as a function of density  $\rho$ . Since one phase is a flat surface with zero density, its osmotic pressure is zero. The coexistence curve is therefore obtained from

$$\partial(\rho^{-1}F)/\partial\rho = 0. \quad (3)$$

It is the interaction that determines the shape of the coexistence curve. We, therefore, consider two different possibilities: tricriticality with (i) short range interactions and (ii) long range interactions. It seems that the latter holds the key.

The general approach is to start from a mean field or effective free energy. The renormalization group (RG) approach is then used to incorporate the effects of fluctuations. The RG  $\beta$  functions tell us the effective couplings as the length scales are changed. Integrating the RG equations, one can then obtain the renormalized interactions or coupling constants for the relevant length scale  $\sim \rho^{-1}$ . These renormalized coupling constants can then be used in the mean field free energy to get  $F$  for Eq. (3). This is justified because we are interested not in the details of the tricritical behavior but rather in the phase boundary where all length scales remain finite [15,16]. Furthermore, since we will be using a RG approach, we consider the case of general transverse dimensionality  $d$  which we ultimately set to 1.

To write the Hamiltonian, we note that short range attractions in DP's lead to bound states for two isolated steps. So far as the binding transition is concerned in low dimensions, the universal critical behavior is independent of any further details such as the noncrossing condition of the steps. This is known from exact renormalization group analysis and simple quantum mechanical calcula-

tions [17–19]. Treating the steps as structureless wandering lines, the Hamiltonian in a continuum formulation is taken as

$$H = \int dz \left[ \frac{1}{2} \sum_i \left( \frac{\partial \mathbf{r}_i}{\partial z} \right)^2 + v_2 \sum_{i>j} \delta(\mathbf{r}_{ij}(z)) \right] + H_{\text{int}}, \quad (4a)$$

where  $\mathbf{r}_i(z)$  is the  $d$  dimensional transverse position of the  $i$ th step at a coordinate  $z$  measured along the step from one end,  $\mathbf{r}_{ij}(z) = \mathbf{r}_j(z) - \mathbf{r}_i(z)$  is the separation between two steps  $i$  and  $j$ , and  $v_2 = v_{20}(T - T_t)$  is the effective two step contact (short range) interaction.  $H_{\text{int}}$  is the additional interaction, and two possible choices are

$$H_{\text{int}} = v_3 \int \sum \delta(\mathbf{r}_{ij}(z)) \delta(\mathbf{r}_{ik}(z)) dz, \quad (4b)$$

or

$$H_{\text{int}} = h \sum_{i<j} \int |\mathbf{r}_{ij}(z)|^{-2} dz. \quad (4c)$$

The first form represents a three step contact repulsion while the last form represents a two step long range repulsive interaction. For  $T > T_t$ ,  $v_2 > 0$  and the noncrossing condition is ensured by taking the limit  $v_2 \rightarrow \infty$ . This, however, is not required because it is known from RG that the repulsive case is described for  $d < 2$  by a stable fixed point (FP) (see below).

In a mean field treatment  $\sum \delta(r_{ij})$  in Eq. (4a) can be replaced by  $\rho^2$ . Similarly the three body interaction would generate a  $\rho^3$  term [6–8], and also an  $r^{-2}$  repulsive interaction [10,14] so that the mean field free energy is

$$\mathcal{F}_{\text{int}}(\rho, T) = f_0 \rho + v_{20}(T - T_t) \rho^2 + c \rho^3, \quad (5)$$

where  $c$  depends on  $h$  or  $v_3$  as the case may be. This again gives  $\beta = 1$ , when Eq. (3) is used, though the physics behind this is completely different from that proposed in Refs. [3,4,10].

Let us first consider the short range case, Eq. (4b). A simple dimensional analysis shows that  $v_3$  is marginal in  $d = 1$ . We introduce the dimensionless parameters  $u_2 = v_2 L^{2-d}$  and  $u_3 = v_3 L^{1-d}$  where  $L$  is an arbitrary length scale in the transverse direction. A renormalization procedure would take into account the effects of interactions at scales  $< L$  along the steps, changing the effective interaction felt at length scale  $L$  (“coarse graining”). The details can be found in Refs. [6,7,17]. The running coupling constant for the two step interaction is known exactly [6,7,17] and is given by

$$L \frac{\partial u_2}{\partial L} = (2 - d)u_2 - u_2^2/2\pi. \quad (6)$$

The flow of  $u_2$  is controlled, for  $d < 2$ , by the two fixed points  $u_2^* = 0$  (unstable) and  $u_2^* = 2\pi(2 - d)$  (stable).

The unstable FP corresponds to the transition point for two chains and the tricritical point in the many chain case, while the stable FP describes the repulsive steps acting like fermions in  $d = 1$ . For  $u_2^* = 0$ , the RG equation for  $u_3$  is given by [6,8]

$$L \frac{\partial u_3}{\partial L} = -c_3 u_3^2, \quad (7)$$

with only the fluctuation contribution in the higher order of  $u_3$  at  $d = 1$  [20]. Around the unstable fixed point for  $u_2$ , for small deviations, the effective coupling is given by  $u_2(L) \sim u_2 L$  for  $d = 1$ , so that the renormalized but not rescaled coupling constant is just  $v_2$ . In contrast, the renormalized three step interaction at  $L \sim \rho^{-1}$  gives  $v_3(L) \sim v_3 / \ln \rho$ . Substitution of these changes the  $\rho^3$  term of the free energy of Eq. (5) to  $\rho^3 / \ln \rho$ . The shape of the coexistence curve is then

$$v_2 \sim \rho / \ln \rho, \quad \text{i.e., } \rho \sim |T - T_t| \ln |T - T_t|. \quad (8)$$

We see that fluctuations produce a zero slope coexistence curve, though the coexistence exponent  $\beta$  is still 1, the mean field value [23]. For the high temperature phase, the system is described by the stable FP  $u_2^* = 2 - d$ , and  $v_2(L) \sim u_2^* \rho$  yielding the famous  $\rho^3$  term that produces the Kasteleyn-Pokrovsky-Talapov transition [13,21].

We can also predict the behavior right at the tricritical point. With  $v_2 = 0$ , the analog of the Pokrovsky-Talapov transition would involve only the three body repulsive interaction. The relevant behavior comes from the minimization of the free energy  $F = (f_0 - \mu)\rho + v_3 \rho^3 / \ln \rho$ . Therefore, the step density at tricriticality behaves like  $\rho \sim |\mu - f_0|^{1/2} (\ln |\mu - f_0|)^{1/2}$  with  $f_0 < 0$ . The exponent is the same Pokrovsky-Talapov one but with an additional logarithmic correction (which may be hard to detect).

It is possible to have higher order multicritical points with just  $v_2$  and  $v_m > 0$  involving an  $m$  step repulsive interaction ( $m > 3$ ). An exponent of  $\beta = 1/2$  can be recovered [6] for  $m = 4$  in a mean field way because  $d = 1$  is above the upper critical dimension of  $v_m$ . Such a multicritical point requires  $v_3 = 0$  and with nonintersecting steps, it seems very unlikely that this will happen.

Let us now come to the long range repulsion case, Eq. (4c). Long range (LR) interactions are special by virtue of their singular nature. A renormalization group transformation is analytic in nature and, therefore, can never generate a singular potential. A corollary of this is that the two body LR interaction does not get renormalized but affects the renormalization of the short range (nonsingular) pair potential. Such a renormalization is going to change the exponent of  $\rho$  in the  $v_2$  term of Eq. (5), and, therefore, the nature of the coexistence curve. The RG approach for this case is also available in the literature, and we quote the results [9,24]. Defining  $u(L) = a[v_2(L)L^{2-d} + h(L)A]$ ,  $g(L) = 2K_d A h(L)$ ,

where  $A = 2^{d-1} \pi^{d/2} \Gamma(d/2)$ ,  $K_d$  is the surface area of a unit  $d$ -dimensional sphere, and  $a$  is a (system dependent) constant, the recursion relations from Ref. [9] are

$$L du/dL = -(u - u_s^*)(u - u_u^*) \quad \text{and} \quad dg/dL = 0, \quad (9)$$

where  $u_{s,u}^* = \{2 - d \pm [(d - 2)^2 + 4g]^{1/2}\}$ , with  $d$  being absorbed in the fixed points. Since  $g$  is marginal, and the FP's for  $u$  depend on the long range coupling  $g$ , we find a nonuniversal behavior. The stable fixed point describes the high temperature phase which is different from the free fermion [or the short range (SR)] case. We discuss this case later on. The unstable FP  $u_u^*$  describes the tricritical point, so that linearizing around it, we can determine the effective coupling that goes in the free energy, provided  $g \leq 3/4$ . For two chains with  $g > 3/4$ , the binding transition is first order [9]. We assume that the tricritical point, as an end point of the coexistence curve, has some critical nature [25]. Therefore,  $g \leq 3/4$ . A straightforward analysis then gives  $\Delta u(L \sim \rho^{-1}) \sim |T - T_t| \rho^{1-x}$ , where  $x = u_s^* - u_u^* = [(d - 2)^2 + 4g]^{1/2}$ . The use of this renormalized coupling in Eq. (5) changes the  $\rho^2$  term to  $\rho^{3-x}$  with a coefficient proportional to  $|T - T_t|$ . This gives a coexistence curve  $\rho \sim |T - T_t|^{1/x}$ , where, to repeat,  $x$  is a nonuniversal number. In order to achieve consistency with experiment, one requires  $x \approx 2$ , which in turn requires  $g \approx 3/4$ . The RG analysis of Ref. [9], as already mentioned, also shows  $g = 3/4$  is a very special point, corresponding to an "upper critical dimension" case. Furthermore, for  $g = 3/4$ , with hard core repulsion, log corrections are expected, which are not captured in the simple RG analysis [9,26]. We conclude that if  $h$  of Eq. (4c) happens to be close to  $3/4\pi$ , then the coexistence exponent  $\beta$  will be close to  $1/2$ , and if  $h = 3/4\pi$ ,  $\beta = 1/2$  with additional logarithmic corrections.

In both the SR and LR cases, since the free energy is known, the surface stiffness, an experimentally measurable quantity [4], can also be calculated. We omit the details that can be found in Refs. [4,27]. The steps, with the inherent anisotropy, produce resistance to bending in the step or  $z$  direction and to compression in the transverse direction [27]. These elastic constants can be expressed in terms of the surface tension  $\gamma(\theta)$  which is related to the free energy  $F(\rho, T)$  of Eq. (1) via  $\gamma(\theta) \sim \cos \theta F(\rho, T)$ , with  $\rho D = \tan \theta$  (Fig. 1). In the DP picture, the stiffnesses are  $\tilde{\gamma}_r \sim 1/\tan \theta$ , and  $\tilde{\gamma}_z = \gamma + d^2 \gamma / d\theta^2$ . The scattering experiments measure the geometric mean of these two stiffnesses. We find that at a given  $T > T_t$ , for the short range case, the surface stiffness approaches the free fermion value in a singular fashion  $\sim 1/|\ln \theta / D|$  with the misorientation while for the long range case, the free fermion value is reached from above in a  $\theta$  independent way. The result for the LR case can be derived from the exact results of Sutherland [14]. The basic point to note is that for  $d = 1$ , both the SR and the LR contribute in

the  $\rho^3$  term, leading to an enhancement of the coefficient of this term over and above the free fermion value. The experiments of Ref. [4] seem to conform to this—though this aspect needs to be studied more thoroughly.

To summarize, we considered two different scenarios both of which give a zero curvature coexistence curve. The purely short range interaction, however, gives only a logarithmic correction to the mean field exponent which seems to be far off from the experiment. The long range case predicts a nonuniversal value and the observed exponent seems to suggest that the Si(113) surface with a miscut towards [001] is at or close to a very special point for the long range interaction. It is rather striking that the very first system that showed the tricritical point also corresponds to the very special point for the long range interaction. We are not sure whether it is just an accident or a general rule. If an accident, then other orientational phase diagrams should be studied experimentally to verify the claim of nonuniversality (and may be a simple verification of RG in statistical mechanics). If not an accident, we wonder why nature chooses to be at the threshold.

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