

Physics of Crystal Growth

Alberto Pimpinelli and Jacques Villain

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Physics of Crystal Growth

This text introduces the physical principles of how and why crystals grow.

The first three chapters recall the fundamental properties of crystal surfaces at equilibrium. The next six chapters describe simple models and basic concepts of crystal growth including diffusion, thermal smoothing of a surface, and applications to semiconductors. Following chapters examine more complex topics such as kinetic roughness, growth instabilities, and elastic effects. A brief closing chapter looks back at the crucial contributions of crystal growth in electronics during this century. The book focuses on growth using molecular beam epitaxy. Throughout, the emphasis is on the role played by modern statistical physics. Informative appendices, interesting exercises and an extensive bibliography reinforce the text.

This book will be of interest to graduate students and researchers in statistical physics, materials science, surface physics and solid state physics. It will also be suitable for use as a coursebook at beginning graduate level.

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Physics of Crystal Growth

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Preface

In writing a preface, an author is faced with the question: what is this book of mine? Of course, in the end only the reader will decide what it really is. The scope of this preface, as of all prefaces, is to say what it was intended to be.

This book tries to offer a reasonably complete description of the physical phenomena which make solid materials grow in a certain way, homogeneous or not, rough or smooth. These phenomena belong to chemistry, quantum physics, mechanics, statistical mechanics. However, chemistry, mechanics and quantum physics are essentially the same during growth as they are at equilibrium. The statistical aspects are quite different. For this reason, the authors have insisted on statistical mechanics.

Another reason to emphasize the statistical mechanical concepts is that they will probably survive. The concepts developed many years ago by Frank, or more recently by Kardar, Parisi and Zhang are still valid while, for instance, quantum mechanical calculations of the relevant energy parameters will certainly evolve a lot in the next few years. We have not considered it useful to devote too many pages to them, but we have tried to present the frame in which the data can be inserted, as soon as they are known.

However, although emphasis is on statistical mechanics, other aspects are not ignored, even though they may have been treated somewhat superficially. The reader will find more detailed information in an extensive bibliography, where all titles are given in extenso, thus making its use much easier.

This book is mainly devoted to growth, and therefore to non-equilibrium processes. Nevertheless, we have tried to make it self-contained and to incorporate some elements of equilibrium surface physics, for instance the roughening transition and the equilibrium shape. The reader eager to know more will again find the necessary references in the bibliography.

The authors are theorists and their book is mainly devoted to theory. Few details are given on experimental methods, but many experimental pictures (mostly from scanning tunneling microscopy) show how real materials do behave. In this domain, too, an abundant bibliography is available.

Although the responsibility for all which is written here—good or bad—is completely ours, we owe a lot to all those who contributed to our understanding of the subject. We wish to thank J.M. Bermond, H. Bonzel, J.-P. Bucher, J. Chevrier, G. Comsa, J. Ernst, J. Frenken, M. Hanbücken, J.C. Heyraud, K. Kern, R. Kern, M. Lagally, J. Lapujoulade, J.J. Métois, B. Mutafschiev and E. Williams, whose experimental works revealed to us all the beauty of Surface Physics and Crystal Growth—and often contributed to the iconographic asset of the book. We are also very grateful to D. Wolf, Ph. Nozières, R. Kern again, J. Krug, P. Jensen, J. Langer, C. Misbah, L. Sander, D. Vvedensky and A. Zangwill, who shared with us some of their secrets. Special thanks are due to P. Politi and M. Schroeder, whose untiring reading of preliminary versions has been a source of most valuable suggestions and improvements. A good share of the chapters on elasticity has much profited from the competence of C. Duport, who corrected all our formulae, and even explained some of them to us!

We thank and beg pardon to all who are omitted here either for space or memory limitations. A final thank is due to the people in Cambridge University Press, and most of all to R. Neal, for waiting patiently for the completion of this work.

List of symbols

DLA: *Diffusion limited aggregation (section 11.2)*

MBE: *Molecular beam epitaxy*

ML: *Monolayer*

RHEED: *Reflection high-energy electron diffraction*

a : *lattice constant or atomic distance (usually taken equal to 1 in this book).*

A_x , A_{xy} , A : *kinetic coefficients in sections 13.1 and 13.2*

$A(t)$: *amplitude appearing in section 13.7*

B : *a thermodynamic coefficient in (2.38)*

B_{xy} : *kinetic coefficient in chapter 13*

C : *a constant (section 15.7)*

d : *dimension of the space (usually 3)*

d' : *surface dimension $d - 1$*

$d' = D/D'$, $d'' = D/D''$: *see (6.20)*

d_c^u : *upper critical dimension (section 12.4)*

d_c^l : *lower critical dimension (section 12.4)*

d_f : *fractal dimension of a fractal terrace (section 11.2)*

$\tilde{D}$: *Fick diffusion constant (sections 7.1, 8.4)*

$\tilde{D}_s$, $\tilde{D}$: *surface Fick diffusion constant*

D^* : *tracer diffusion constant (section 7.1)*

D_{int} : *diffusion constant of interstitials*

D_{vac} : *diffusion constant of vacancies in section 7.3.*

D_s^0 : *see eq. (7.13)*

D_0 : *see eq. (11.28)*

D_2 : *diffusion constant of dimers at a surface (sections 7.10 and 11.8)*

D' , D'' : *step kinetic coefficients (section 6.4)*

D_s (D when no ambiguity is possible): *surface diffusion constant of adatoms*

e : *basis of Napierian logarithms*

E : *Young modulus*

E_2 : *binding energy of a dimer (section 11.8)*

- $\delta \mathbf{f}^{\text{ext}}, \delta \mathbf{F}^{\text{ext}}$: elementary external forces (chapter 16)
 F_{α}^{ext} : External force
 F : beam intensity in MBE
 $\mathbf{F}_{\mathbf{R}}$: force acting at point $\mathbf{R}$
 g : gravity (in chapter 1)
 $G(\mathbf{R})$: height-height correlation function at equilibrium, eq. (1.4)
 $G(\mathbf{r}, t)$ height-height correlation function during growth, eq. (12.1)
 h : amplitude of the modulation of a surface, height of a defect
 i^* : critical size of a cluster of adatoms (section 11.2)
 $\mathbf{j}_s$: surface current density of adatoms
 $\mathbf{j}_s^{\text{adat}}$: the current density of adatoms (section 7.5)
 $\mathbf{j}_s^{\text{advac}}$: current density of advacancies (section 7.5)
 $\mathbf{j}_k$: two-dimensional Fourier transform of the surface adatom current density
 $\mathbf{k} = (k_x, k_y)$: a vector of the two-dimensional reciprocal space
 k_B : the Boltzmann constant
 K : bulk modulus (section 16.4)
 K : kinetic coefficient defined by (12.6)
 L_x, L_y : sample sizes in the x and y directions
 L : linear size of a system
 L : wavelength of a modulation (chapter 8)
 m_{xy}, m : force dipole moment, eq. (15.2)
 M : a point at the surface of a solid
 $\mathbf{n}$: unit vector normal to a surface at a point, directed outward
 N : number of particles in a physical system
 N : quantity related to the size of the surface in section 2.6.
 $N(t)$: cluster density (section 11.6)
 p_{xy}, p_0 : stress
 $p_j(\mathbf{r}, t)$: probability that the j -th impurity is at $\mathbf{r}$ at time t (section 7.1)
 $\mathbf{q} = (q_x, q_y)$: a vector of the two-dimensional reciprocal space
 r_1 : characteristic length (chapter 8)
 R : radius of a terrace (section 8.5)
 R : radius of curvature of a line or of a surface (chapter 10)
 $\mathbf{R}, \mathbf{r}$: a point of the two-dimensional (chapter 1) or three-dimensional space
 dS : surface element (chapter 2)
 S : surface of a crystal (chapters 3 and 4)
 t : time
 T : temperature
 T_M : melting temperature.
 T_R : roughening transition temperature
 $\mathbf{u}(\mathbf{r})$: atomic displacement at point $\mathbf{r}$
 $\mathbf{v}, \mathbf{v}(\mathbf{n})$: velocity of the surface of a crystal (chapter 5)
 v : velocity of a step
 $v = V/N$: volume per atom (chapter 2)

- v_g : volume per atom in the vapour (chapter 2)
 v_l : volume per atom in the liquid (chapter 2).
 V : volume
 δV : volume element (section 16.1)
 W : energy or free energy barrier
 W_0 : energy of a kink on a step (section 1.8)
 W_0 : energy barrier (section 15.7)
 w_0 : energy of a chemical bond (section 15.5)
 W_a : adatom creation energy or free energy, see eq. (7.14a)
 W_{adv} : see eq. (7.14b)
 W_1 : energy of a step per bond
 W_{sd} : activation energy for surface diffusion (eq. (7.13) and section 11.8)
 $W_{int}(r)$: interaction energy between defects at distance r (chapter 15)
 W_{coh} : cohesive energy
 x, y, z : coordinates of a point in the three-dimensional space.
 $x_s = \sqrt{D_s \tau_v} = 1/\kappa$: average adatom diffusion length before desorption
 y' : derivative dy/dx
 $\tilde{z}$: dynamical "critical exponent" for the correlation length (eq. 12.14)
 $z_q(t)$: Fourier transform of $z(\mathbf{r}, t)$
 $j_s, D_s, \Lambda_s, \tilde{D}_s$: section 8.4
 α, γ : coordinates x, y or z
 α : kinetic coefficient (eq. 7.8)
 α : critical exponent for the spatial decay of the correlation function (eq. 12.18)
 β : critical exponent for the temporal decay of the correlation function (eq. 12.18)
 $\beta = 1/(k_B T)$
 γ : free energy of a step per unit length or per atom (line tension)
 $\tilde{\gamma} \equiv \gamma(\theta) + d^2\gamma/d\theta^2$: step stiffness (section 2.4)
 γ : exponent defined in section 11.9
 $\Gamma(\mathbf{r} - \mathbf{r}')$: elastic Green function (eq. 15.10)
 Γ : a step, in chapter 10
 δa : misfit (section 15.4)
 $\delta \mathcal{F}, \delta \mu$, etc.: increment of $\mathcal{F}, \mu$, etc. from some reference value
 $\delta \Sigma$: surface element (section 16.1)
 ΔF : "supersaturation" $F - \rho_0/\tau_v$
 Δ' and Δ'' : kinetic coefficients defined in section 6.4
 ϵ : Interaction energy between steps (section 1.7)
 $\epsilon_{\alpha\gamma}(\mathbf{r})$: strain
 $\epsilon(t)$: amplitude of a modulation in eq. (10.14) (called η in eq. (10.7))
 ζ : Poisson ratio (eq. 6.12)
 ζ : in section 10.6, a control parameter
 η : amplitude of a modulation in eq. (10.7) (called ϵ in eq. (10.14))

- θ : value of an angle
 $\kappa = 1/x_s$: inverse evaporation length of an adatom (eq. 6.6)
 λ : capillary length (chapter 1)
 λ : Lamé coefficient (chapters 15 and 6).
 λ : kinetic coefficient in the KPZ equation (13.4)
 λ : a constant (e.g. in section 4.2)
 Λ_s, Λ : surface diffusion constant of advacancies (section 6.5)
 μ : Lamé coefficient (chapters 15 and 16)
 μ : chemical potential (elsewhere)
 $v(t)$: number of sites visited by a diffusing adatom in time t (sections 6.3, 11.4)
 v : kinetic coefficient defined by (12.6)
 $\xi(t)$: correlation length (section 12.6)
 (Π) : tangent plane to the crystal surface (chapter 3)
 $\rho(\mathbf{r}, t), \rho_1, \rho_s$: adatom density (occupied sites/surface sites)
 ρ_n : surface density of clusters of n atoms (section 11.4).
 ρ_0 : equilibrium density of adatoms. (section 6.5)
 $\bar{\rho}$: see section 6.3
 $\rho_{\text{int}}(\mathbf{r}, t)$: concentration of interstitials
 σ_0 : equilibrium density of advacancies (section 6.5)
 $\sigma, \sigma(\mathbf{n})$: free energy of a surface per unit length or per atom (surface tension)
 $\sigma(\mathbf{r})$: density of advacancies
 Σ : Wulff's plot (section 3.2)
 $\tilde{\sigma}$: surface rigidity, formula (2.5)
 $1/\tau_v$: evaporation probability of an adatom per unit time (section 6.1)
 $1/\tau_{\text{nuc}}$: nucleation rate of new terraces (section 11.2)
 $1/\tau_k$: the rate of emission of "gradatoms" (problem 10.6)
 $\phi(z_x, z_y)$: the projected free energy density per unit area (eq. 2.2)
 $\varphi(\{\epsilon(\mathbf{r})\})$: elastic free energy density (section 16.5)
 φ_p : components of an eigenvector of the transfer matrix in Appendix C
 Φ : Gibbs free energy or free enthalpy $\mathcal{F} + PV$ (chapters 2 and 16)
 ω : decay rate of a modulation, see eq. (10.15)
 Ω : atomic area, generally set equal to 1 in this book
 Ω : Grand potential $\mathcal{F} + PV - \mu N$
 $\Omega_{xy}^{\xi\xi}$: elastic constants
 $\tilde{\Omega}_{RR'}^{\alpha\gamma}$: "discretized elastic constants", eq. (16.25)
 ℓ : distance between steps
 ℓ_s : adatom diffusion length before nucleation of a terrace (section 11.1)
 ℓ_s : length on which diffusion is able to heal the surface (chapter 12)
 $d\mathcal{A}$: elementary projected area $dx dy$ (section 16.8)
 $\mathcal{A}$: total projected area $L_x L_y$

$\mathcal{F}$: free energy

$\mathcal{G}$: Gibbs free energy $\mathcal{G} = \mathcal{F} + PV$.

$\mathcal{N}$: number of lattice sites on a surface in section 14.6

$\simeq$: nearly equal to (e.g. $\sin x \simeq x$ for small x)

$\sim$: proportional to (e.g. $10x \sim x$)

$\approx$: of the order of magnitude of (e.g. $10 \approx 1$)

cot: cotangent

z_x, z_α : partial derivative $\partial z / \partial x, \partial z / \partial x_\alpha$

$v_\alpha, j_\alpha, R_\alpha$: the components of the vectors $\mathbf{v}, \mathbf{j}, \mathbf{R}$

$\langle \chi \rangle$: average value of a quantity χ

$|z|$: absolute value of z

$\dot{z}, \dot{\rho}$, etc.: derivative of z, ρ , etc., with respect to time

$(hk\ell)$: orientation of a crystal surface. E.g. the (001) face, the (111) orientation

$[hk\ell]$: orientation of a crystal axis. E.g. [110] steps

$\{hk\ell\}$: set of crystal planes which are crystallographically equivalent. E.g. (cubic crystal): the $\{001\}$ orientations are the (001), (010) and (100) planes.

1

Morphology of a crystal surface

*Je ne me persuade pas aisément
qu'Epicure, Platon et Pythagore nous
aient donné pour argent comptant leurs
Atomes, leurs Idées et leurs Nombres.
Ils étaient trop sages pour établir
leurs articles de foi de choses si in-
certaines et si débattables.*

Montaigne (*Essais*, II, 12)

I can hardly convince myself that
Epicurus, Plato and Pythagoras
have sold us for sound
their Atoms, their Ideas and
their Numbers. They were
too wise to found their belief
on such uncertain and questionable things.

Twenty five centuries after Democritus, we are now able to see individual atoms, or at least small groups of them, through a variety of electron microscopy techniques. The visible atoms are of course those at the surface of a solid. Even motions at atomic scales can be observed.

It is thus possible to identify the fundamental elements of the morphology of a surface: terraces, steps, kinks, adatoms, advacancies.

Despite the fantastic progress in surface experimentation between 1970 and 1995, surface physics relies much on theory. The theory of two-dimensional systems (e.g. surfaces) is fascinating. The transition of a surface at equilibrium from its high-temperature, rough state, to its low-temperature, smooth state, has quite unusual features, e.g. no observable specific heat singularity. The roughness of an equilibrium surface is also extraordinarily weak: a few atomic distances over several centimetres.

1.1 A high-symmetry surface observed with a microscope

In 1986, the Nobel Prize for Physics was awarded to Binnig and Rohrer for the invention of scanning tunneling microscopy (STM). This technique (Binnig & Rohrer 1987) allows the observation of the atomic structure of crystal surfaces.

The observation is easier when the orientation of the surface is close to a high-symmetry direction: (001) or (111) in the case of a cubic crystal. Such orientations are mostly used in technological applications and will generally be considered in this book. For such orientations, the microscope 'sees' (Fig. 1.1) *terraces* separated by *steps* of atomic height. These steps are not straight; they contain straight parts separated by *kinks*. On the terraces one can see surface vacancies (or *advacancies*) resulting from

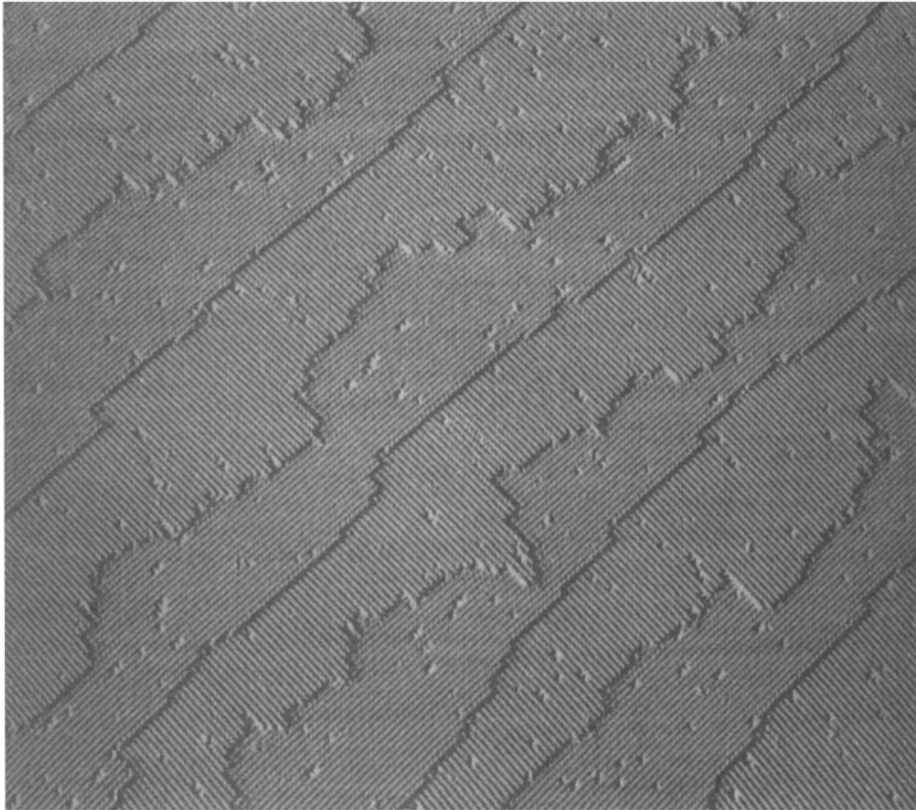


Fig. 1.1. [110] steps on a (001) vicinal silicon face. Terrace width: about 100 Å. Note the alternation of steps of different roughness, which will be explained in chapter 9. Experimental technique: scanning tunneling microscopy (STM) (Lagally *et al.* 1990, with the kind permission of the authors).

missing surface atoms. Certain features (e.g. the alternation of steps with different roughness) are special characteristics of the material which is observed, silicon in this case. They will be discussed in chapter 9.

Technical progress has been fast, and STMs exist that can now be used at very high temperatures (at present, the beginning of 1997, the limiting temperature seems to be around 1500 K). However, varying the temperature without upsetting the instrument is quite a delicate matter, and therefore the STM is not always adequate for the observation of collective motions on a surface. Indeed, the evolution of the morphology of a metal or semiconductor surface at room temperature (still the ideal temperature for most STMs) is very slow, as will be seen in chapter 8. Other methods of electron microscopy, e.g. reflection electron microscopy (REM) (Fig. 1.2) bridge this gap, and also allow the observation of larger scales. Fig. 1.2 is remarkable for the different lengthscales observed in 3 directions: the step height (perpendicular to the surface) is of order a few Ångströms, while the length of the steps in the image amounts to hundreds of Ångströms and the distance between the steps is of the order of one micron. Moreover, several steps can be seen at the same time, because the electron beam makes a very small angle with the surface

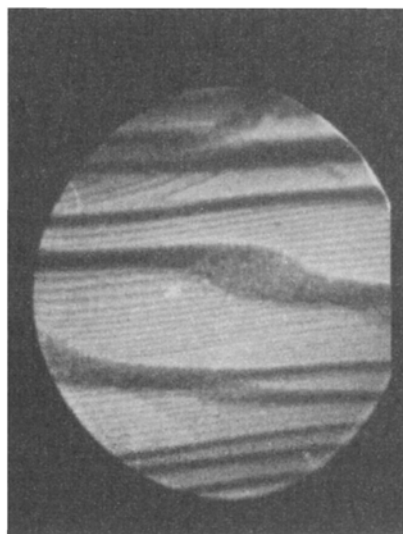


Fig. 1.2. Steps on the silicon (111) face during evaporation by Joule heating. Dark bands are macrosteps or step bunches, while thin lines are monolayer-high steps. The origin of the step bunches is discussed in chapter 9. Width: $1\text{ }\mu\text{m}$ (parallel to the steps). Depth: $35\text{ }\mu\text{m}$ (perpendicular to the steps). Experimental technique: reflection electron microscopy (Alfonso *et al.* 1992, with the kind permission of the authors).

(grazing incidence). The steps are seen to be smoother than on Fig. 1.1. This is partly due to the different scale and surface orientation, but it is also a consequence of the fact that Fig. 1.1 shows the surface of a growing crystal, and a growing surface is far from equilibrium, as will be seen in chapters 11 to 14.

Observation of crystal growth at the atomic scale is not always easy, especially when the crystal grows from the melt or from a solution. Even in growth from the vapour, it is difficult to control the thickness of the deposited atom layer. The type of growth used in the case of Fig. 1.1 was molecular beam epitaxy (MBE). An MBE apparatus is shown in chapter 17. The principle is simple: under ultra-high vacuum conditions, atoms (single or in molecules) are sent onto the surface, where they diffuse until they meet a step where they are incorporated. These diffusing atoms are called *adatoms*. Free adatom diffusion has clearly a meaning only on a high-symmetry terrace (between steps). Adatoms are in general not easily visible by STM, either because their number is too small or because they move too quickly to be resolved by the instrument. Possible instrument-induced perturbations should also be mentioned. A scanning tunneling microscope is essentially a metal tip taken very close to the surface, from which or to which electrons can flow by tunneling. This is a rather disturbing device for the surface, and an isolated atom has a great chance to be strongly perturbed. Isolated atoms can be seen, however, by another technique called field ion microscopy (FIM) (Ehrlich & Hudda 1966, Ehrlich 1977, Wang & Ehrlich 1991). Indeed, field ion microscopy allows the observation of the motion of individual adatoms.

Adatoms are already present at equilibrium. Their equilibrium density (number of occupied sites/number of surface sites) is, according to the Gibbs formula

$$\rho = \exp(-\beta W_a) \quad (1.1)$$

Table 1.1. *Values of some typical energies (in Kelvin) for four fcc metals (Stoltze 1994)*

	Ni	Cu	Ag	Au
Adatom energy $W_a(001)$	8700 K	5900 K	4200 K	3550 K
Step energy $W_1(001)$	2200 K	1450 K	1000 K	750 K
Kink energy W_0	1800 K	1250 K	950 K	800 K
Advacancy energy (001)	8400 K	5500 K	3850 K	2900 K
Adatom energy $W_a(111)$	11650 K	8300 K	6450 K	6600 K
Cohesive energy $-W_{\text{coh}}$	51600 K	40800 K	34400 K	44000 K

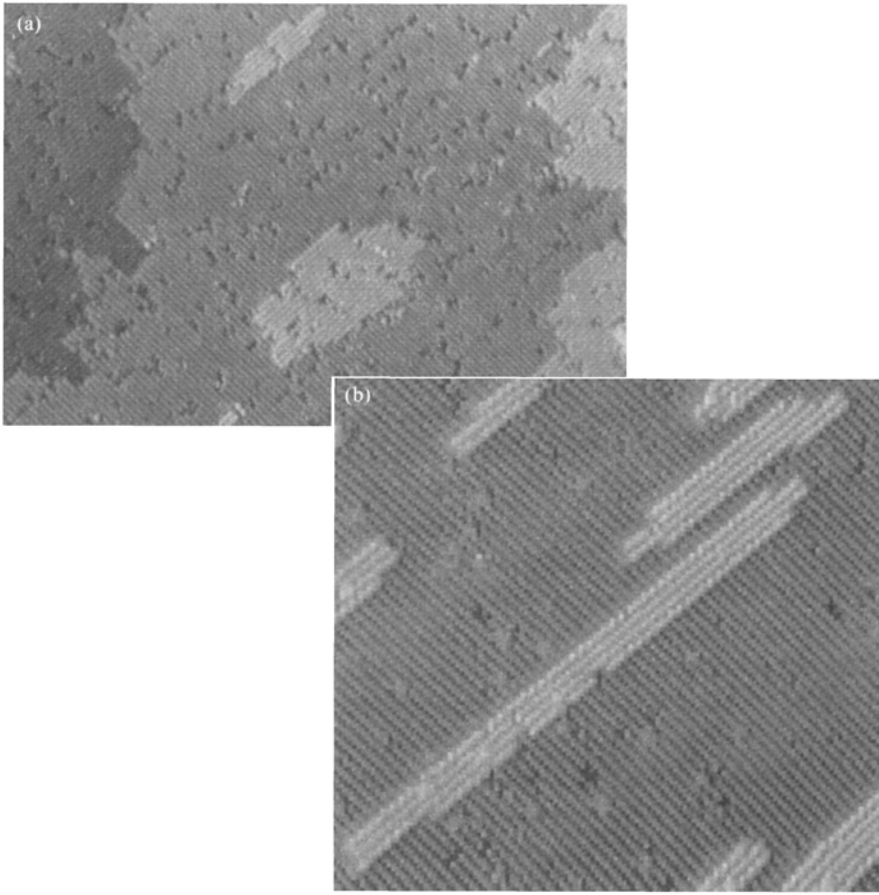


Fig. 1.3. a) The silicon (001) face after MBE growth at room temperature and annealing at 625 K. Note the terraces (or ‘islands’) and the steps. Scale: 800×560 Å. Experimental technique: STM (Lagally *et al.* 1990, with the kind permission of the authors). b) The silicon (001) face after MBE growth at room temperature, but without annealing. The elongated island shape indicates anisotropy in adatom sticking to steps. Scale: 400×400 Å. Experimental technique: STM (Lagally *et al.* 1990, with the kind permission of the authors).

where $1/\beta = k_B T$ and k_B is the Boltzmann constant. W_a is the (free) energy needed to extract an atom from a step and to make it an adatom.

It is one of the many parameters which are required for a quantitative description of surface kinetics. In this book, these parameters will be taken for granted. In principle, they can be obtained from a theory of the electronic structure, which can be *ab initio* (Gross 1990, Ruggerone *et al.* 1997) or make use of simple approximations such as ‘tight binding’, ‘em-

bedded atom', 'effective medium'... The reader will find details in textbooks (Desjonquères & Spanjaard 1993, Lannoo & Friedel 1991, Noguera 1995) and review articles (Stoltze 1994).

Typical values of W_a/k_B according to recent model-potential calculations (Stoltze 1994) are listed in Table 1.1. According to these data, there is at room temperature, on the (111) face of nickel, about one adatom per square centimetre, which is a very low density. On the (001) face of Cu, the proportion of lattice sites occupied by adatoms is about 10^{-9} at room temperature, which is still rather low. This proportion is considerably increased on a growing crystal, as will be seen in chapter 11.

The experimental images displayed in this chapter confirm much older conjectures. We shall not review the twenty five centuries which elapsed between Democritus and the Nobel Prize of 1986, but it is worth mentioning a fundamental article by Burton, Cabrera & Frank (1951) where crystal growth was described as a motion of steps at a time where direct observation of steps (and even less of moving steps) was impossible. This article will be discussed at length in chapter 6.

What happens if the growing crystal is limited by a perfectly oriented high-symmetry surface without steps? The answer is given by Fig. 1.3: new terraces appear, at least temporarily, and therefore steps appear. In practice, a crystal surface always contains steps for two reasons: first, because it is not possible to cut it perfectly straight, and second because a crystal always contains dislocations. A screw dislocation through a

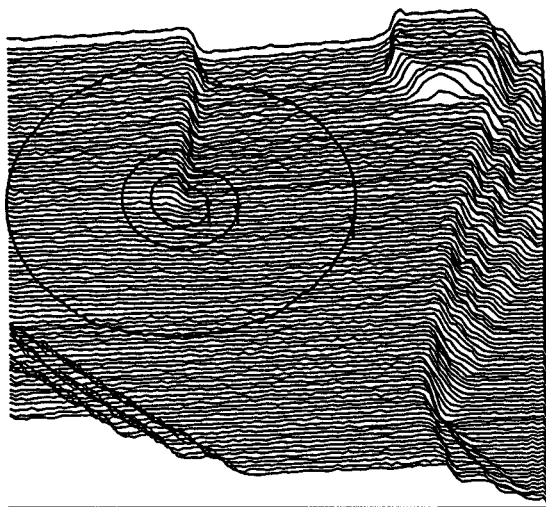


Fig. 1.4. Dislocation and steps on Ag (111) observed by STM (Wolf & Ibach 1991, with the kind permission of the authors.)

surface is necessarily, for geometric reasons, the origin of a step (Fig. 1.4). However, dislocation-free surfaces on macroscopic scales can nowadays be grown for certain materials, e.g. the technologically essential element silicon.

1.2 *In situ* microscopy and diffraction

Now that we have a surface microscope, we would like to look at the surface of a growing crystal as it grows—or, as the jargon demands, *in situ*. It is not that easy, however. On one hand, it is hard to imagine introducing any microscope into a liquid metal or silicon melt! On the other, even though the use of a microscope is in principle easier during vapour phase or ultra-high vacuum growth, each different technique has some specific limitations. Reflection electron microscopy can be used at any temperature, but the images suffer from the strong foreshortening effect seen in Fig. 1.2, which limits the ability of seeing small details. Low-energy electron microscopy (LEEM) does not have this problem, and it has been used for *in situ* studies of growth (see Bauer 1992 for a review), but its resolution is poor (5 to 15 nm) compared to STM. The latter is limited to not-too-high temperatures by technical difficulties which will be certainly overcome in the future, and still suffers from a long—but steadily decreasing—image acquisition time. Some *in situ* observation of growth has started showing up in the literature (Voigtländer & Zinner 1993).

More appropriate for *in situ* observations than microscopy is still diffraction, i.e. scattering of electrons, X-rays or atoms. In a scattering or diffraction experiment (we shall use both words with essentially the same meaning), one measures the scattered radiation as a function of the scattering angle. The analysis as a function of the energy is essential in certain cases, but we shall not care very much about it in this book. The essential difference between microscopy and diffraction is that the diffractionist works in reciprocal space rather than in real space. For a good, three-dimensional crystal, the diffraction spectrum can be interpreted by any student. In the case of a reasonably smooth crystal surface, i.e. a two-dimensional object, the task is already harder. And if the number of imperfections becomes very large, the interpretation is very difficult. On the other hand, pictures from a microscope are understandable (after some image processing, sure...) by the layman, and can in principle be obtained even for a non-crystalline material.

1.3 Step free energy and thermal roughness of a surface

At zero temperature, a surface at equilibrium should contain no step. At low temperature, there are a few adatoms as seen above; there are fewer pairs of adatoms, whose number (or better, whose density) may

be obtained by a Gibbs formula similar to (1.1); and smaller yet is the density of larger clusters. Atom clusters are closed terraces bounded by steps. The step density (total step length per unit surface) increases with temperature.

This increase is not easily seen directly by microscopy. Indeed, most of microscopic methods work best at low temperature, when the surface does not easily attain thermal equilibrium. The atom scattering or X-ray diffraction signal does exhibit a dramatic broadening when temperature is increased (Fig. 1.5). Above some temperature, the lineshape, which is lorentzian at low temperature, undergoes a qualitative change. One can for instance measure the ‘specular’ reflection, i.e. that whose reflection angle almost equals the incidence angle (*speculum* is the Latin for mirror).

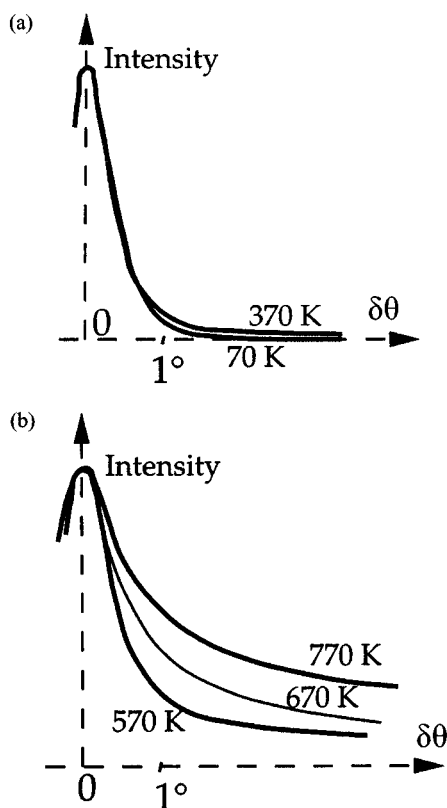


Fig. 1.5. Atom scattering lineshape at temperatures (a) below and (b) above $T_R = 380$ K in Cu(115), after Fabre *et al.* (1987b). The reflected intensity is plotted vs. the deviation $\delta\theta$ with respect to the reflection angle corresponding to the ideally smooth surface.

The specular peak (as well as the Bragg peaks) is narrow for a smooth surface while a rough surface scatters radiation in all directions.

This type of experiment is a quantitative version of everyday observation. Galileo (1632) was perhaps not the first who noticed the importance of surface roughness in light scattering, but he was presumably the first one who realized that light was scattered rather than lost. His problem was to understand the brightness of the moon, which he compared to a wall scattering sunlight:

You see the difference between the reflections occurring on the respective surfaces, that of the wall and that of the mirror: ... Look how the reflection from the wall scatters to all parts of the opposite wall, while that from the mirror goes to a single part, not larger than the mirror itself... If you want to understand all that, you should notice that, for a surface, to be rough means the same thing as to consist of innumerable small surfaces of innumerable orientations, and it necessarily occurs that, among them, many have the appropriate orientation to direct the reflected beams to this place, and many to that place.

The interpretation of diffraction patterns from a hot surface is difficult (Blatter 1984, Levi 1984, Armand & Manson 1988) because the effect of atomic vibrations adds to roughness to broaden the reflected beam. It is however clear, from a quantitative analysis, that the total step length is greatly increased by heating.

The reason is basically the following. Even if the step energy per unit length, W_1 , does not change much, its entropy increases, so that the free energy decreases. In order to calculate it, we consider (Fig. 1.6) on the (001)

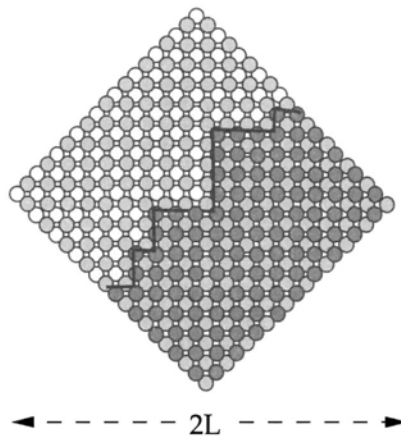


Fig. 1.6. A step on a surface with a square symmetry, e.g. the (001) face of an fcc metal. For this orientation, the line tension is given by (1.2).

face of a cubic crystal a zig-zag step, whose average direction makes an angle of 45° with bond directions. This step orientation is chosen because it allows a simple, though approximate, calculation. The only configurations which will be considered are those which result from random walks going from the left to the right, each step of the random walker being parallel to a lattice bond, and backward steps being forbidden. This definition may be complicated, but what it means is clearly suggested by the figure. If the width of the system in the direction of the walk is uniformly equal to the bond length multiplied by $L\sqrt{2}$, all configurations have the same energy $2LW_1$. Since there are 2^{2L} configurations, the entropy is $2L \ln 2$ and the free energy per bond is

$$\gamma = W_1 - k_B T \ln 2. \quad (1.2)$$

The free energy per unit length γ/a is called the line tension of steps. Since a , the lattice parameter, is generally chosen as the length unit in this book, the term line tension will be often employed for γ itself.

When γ is positive, one has to provide mechanical work to introduce a step into the surface. If the total step free energy $L\gamma$ becomes negative, thermodynamics tells us that one should provide mechanical work to remove steps from the surface. Thus, equation (1.2) tells us that the surface undergoes a transition at a temperature T_R approximately given by

$$T_R \approx \frac{W_1}{k_B \ln 2}. \quad (1.3)$$

This transition is called the roughening transition.

1.4 The roughening transition

As seen above, the roughening transition temperature may be defined as the temperature at which the line tension of steps vanishes. According to the experiment (Fig. 1.7) the line tension does vanish at some temperature. The linear temperature dependence predicted by formula (1.2) is in pretty good agreement with experimental observation, at least far from T_R . Near T_R , the experimental curve bends away from the straight line: one can wonder whether it is an instrumental effect or a fundamental one. As will be seen in the next section, it is a fundamental effect. But before discussing that, we would like to make three remarks.

- 1) The roughening transition temperature depends on the surface orientation, i.e. it is different for a (111) and for a (1,1,19) surface. This point will be addressed in section 1.7.

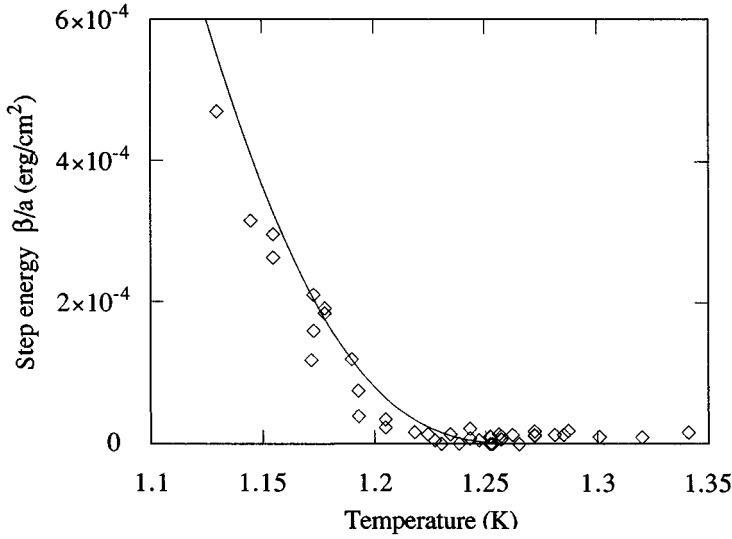


Fig. 1.7. Line tension of a step as a function of temperature, as measured by Gallet *et al.* in helium (Gallet *et al.* 1987, with the kind permission of the authors).

- 2) For a given surface orientation, the step line tension vanishes at the same temperature for all step orientations, so that T_R is independent of the step orientation. This can easily be proved in the case of a square or hexagonal symmetry. If a step of orientation x has a vanishing free energy, the free energy of a step of any orientation y deduced from x by a lattice symmetry operation also vanishes. But then, a step of average orientation ζ may be obtained as a succession of two consecutive steps of orientations x and y , and has therefore a vanishing free energy, apart from the energy of the kink between the two pieces, which is negligible for a long step.
- 3) Formula (1.2) suggests that the step line tension becomes negative for $T > T_R$. Actually, it is not so, if a step is defined in a model-independent way. An appropriate definition is to consider a rectangular sample of sizes L_x and L_y in two orthogonal directions x and y , and to fix the surface height at the two ends of the sample at $z(0)$ and $z(L_x) = z(0) + \delta z$, respectively. The step free energy is the difference between the free energies of the system for $\delta z = 0$ and for $\delta z = 1$ in atomic layer units. With this definition, it can be proved that the line tension is identically zero for $T > T_R$. Actually, the very concept of a step is not very meaningful for $T > T_R$. In this case, if $\delta z = 1$ one can say that there is a step in the system, but if one looks at the surface one cannot say where it is.

1.5 Smooth and rough surfaces

The roughening transition is much more complicated than suggested by the discussion of section 1.3. Indeed, thermally excited steps are not isolated objects as suggested by Fig. 1.6, they are closed loops. In this section, we shall try to give an idea of what a rough surface really is. The reader will find more details about the roughening transition in the monographies by Balibar & Castaing (1985), Van Beijeren & Nolden (1987), Lapujoulade (1994), Nozières (1991) and Weeks (1980).

As seen in the previous section, the concept of step is not useful above T_R . It is therefore appropriate to characterize roughness in an alternative way. Consider an infinite surface of average orientation perpendicular to the z axis. Let (x, y, z) be a point of the surface. The 'height' z will be assumed to be a one-valued function of x and y , so that 'overhangs' are excluded. Let $\mathbf{R} = (x, y)$ be a point of the two-dimensional (x, y) space. We define the *height-height correlation function*

$$G(\mathbf{R}) \equiv \langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle. \quad (1.4)$$

The interest of this function is that it has, if gravity is neglected, two qualitatively different behaviours above and below T_R :

$$\lim_{R \rightarrow \infty} G(R) = \begin{cases} \text{finite value for} & T < T_R \\ \infty & \text{for } T > T_R. \end{cases} \quad (1.5a)$$

$$(1.5b)$$

The finiteness of $G(R)$ at low temperature, in agreement with (1.5a), results from a low-temperature expansion, whose lowest order will be derived below. At very low temperature, the surface is flat, except for very few adatoms, whose density is, as in section 1.2, equal to $\exp(-\beta W_a)$. However, there can be advacancies, whose energy is not very far from W_a in usual metals as seen from Table 1.1. The probability that $z(\mathbf{r})$ or $z(\mathbf{r} + \mathbf{R})$ is 1 or -1 is therefore $2 \exp(-\beta W_a)$. The probability that both $z(\mathbf{r})$ and $z(\mathbf{r} + \mathbf{R})$ are equal to 0 is $1 - 2 \exp(-\beta W_a)$ and the probability that both $z(\mathbf{r})$ and $z(\mathbf{r} + \mathbf{R})$ are different from 0 and ± 1 is negligible. The first term of the low-temperature expansion is therefore

$$G(\mathbf{R}) \equiv \langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle \simeq 2 \exp(-\beta W_a) \quad (R \neq 0). \quad (1.6)$$

Of course, $G(0) = 0$.

Thus, we have proved (1.5a). It is more difficult to prove (1.5b), and only a plausibility argument will be given. It is indeed reasonable to assume that, at sufficiently high temperature, say $k_B T \gg W_1$, the discreteness of the crystal lattice becomes negligible, so that the surface height $z(x, y)$ may be regarded as a differentiable function of x and y , as it is in a liquid. Thus, we just forget that we have a crystal, and we write the surface energy as if it were a liquid. The surface free energy $\mathcal{F}_{\text{surf}}$ of a liquid is

simply proportional to the surface area, and the proportionality coefficient σ is called the surface tension. Writing $z_\alpha = \partial z / \partial x_\alpha$,

$$\mathcal{F}_{\text{surf}} = \sigma \int \int dx dy \sqrt{1 + z_x^2 + z_y^2}$$

or, for small fluctuations,

$$\mathcal{F}_{\text{surf}} = \text{Const} + \frac{\sigma}{2} \int \int dx dy (z_x^2 + z_y^2) . \quad (1.7a)$$

However, in our world subject to gravity, thermal fluctuations of the surface have an additional energy resulting from gravity. The effect of gravity might easily be taken into account in the treatment below T_R and would be found to be irrelevant. It is not so above the transition temperature as will be seen shortly. The energy of a column of matter of cross section $dx dy$, whose ends are at heights z_1 and z , is

$$\rho g dx dy \int_{z_1}^z \zeta d\zeta = \rho g dx dy (z^2 - z_1^2)/2$$

where ρ is the specific mass and g the gravity acceleration. The term containing z_1 is constant and will be omitted. The energy excess associated with surface shape fluctuations and resulting from both gravity and surface tension is

$$\delta \mathcal{F} = -\frac{1}{2} \int \int dx dy \left[\rho g z^2 + \sigma (z_x^2 + z_y^2) \right] . \quad (1.7b)$$

This quadratic form is readily diagonalized if one introduces the Fourier transform of z of wavevector $\mathbf{q} = (q_x, q_y)$:

$$z_q = \frac{1}{L_x L_y} \int dx dy z(x, y) \exp(iq_x x + iq_y y) .$$

One obtains then

$$\delta \mathcal{F} = \frac{1}{2} \sum_q \left[\rho g + \tilde{\sigma}(q_x^2 + q_y^2) \right] |z_q^2| , \quad (1.8)$$

where $\tilde{\sigma} = \sigma$ for a liquid. The notation $\tilde{\sigma}$ has been introduced because, in the case of a crystal, two different quantities appear, as will be seen in chapter 2. The variance of z_q is easily deduced, and the result (the so-called equipartition theorem) is

$$\langle |z_q^2| \rangle = \frac{k_B T}{\rho g + \tilde{\sigma}(q_x^2 + q_y^2)} . \quad (1.9)$$

Inverting the Fourier transform, the correlation function (1.4) is readily obtained as

$$\langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle = 2k_B T \int_0^{1/a} dq_x dq_y \frac{1 - \cos(\mathbf{q} \cdot \mathbf{R})}{\rho g + \tilde{\sigma}(q_x^2 + q_y^2)} . \quad (1.10)$$

An order of magnitude may be obtained if the lower limit of integration is replaced by an appropriate cutoff, below which the numerator is almost zero. This allows us to replace the cosine by its average value 0, and one obtains

$$\langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle \approx \int_{1/R}^{1/a} 2\pi q dq \frac{2k_B T}{\rho g + \tilde{\sigma} q^2} . \quad (1.11)$$

If gravity is neglected, which implies $R \ll \sqrt{\tilde{\sigma}/\rho g}$, (1.11) diverges at large R as:

$$\langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle \approx (4\pi k_B T / \tilde{\sigma}) \ln R . \quad (1.12)$$

This proves (1.5b). A surface is called *rough* if $\langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle$ diverges as in (1.12), and *smooth* if there is no divergence, as in (1.6).

Previously, we defined the roughening transition in terms of the vanishing of the step free energy γ . We should worry about the equivalence of the two definitions. In fact, the proof of (1.12) relies on the use of (1.7b). If the step line tension is positive, equation (1.7b) cannot be true. Indeed, since the number of steps per unit length is given by $|z_x|$, we must add to the surface free energy (1.7b) a contribution of the form

$$\int \int dx dy \gamma |z_x| ,$$

assuming for simplicity that $g = z_y = 0$. The surface free energy is thus non-analytic in contrast with (1.7b). If $\gamma > 0$, the formation of a terrace of size L requires a free energy which diverges with L . Since this is forbidden, the function (1.4) is finite for $R = \infty$. Therefore, the roughening transition can be defined (at least on a high-symmetry surface) either by (1.5) or by the vanishing of γ .

From (1.11), gravity is seen to kill the roughening transition. It is also seen from (1.11) that gravity is negligible if the length $1/q$ of interest is shorter than the *capillary length*

$$\lambda = \sqrt{\tilde{\sigma}/\rho g} . \quad (1.13)$$

The order of magnitude of $\tilde{\sigma}$ is typically the energy of a chemical bond, i.e. 1 eV per atom. The resulting value of λ is a few centimetres, i.e. much larger than the distance over which equilibrium can be reached at a crystal surface. For this reason, gravity will be neglected everywhere else in this book. Note that in the case of water, λ depends on temperature but is of order 0.5 cm as known from everyday life (see next chapter, Fig. 2.1).

1.6 The SOS model and other models

If one wishes to go beyond (1.6) and to determine the next terms of the low-temperature expansion, one has to know, in addition to the energy of a single adatom, the energy of a pair of adatoms, of a triplet, etc. These energies are not known with precision. On the other hand, the qualitative properties of the system should not depend much on those details. Therefore, the theory is often done for simplified models. One of them, called the 'SOS' (solid on solid) model is described in Fig. 1.8. It belongs to the broad class of 'broken bond models'. In such models, atoms are supposed to be hard spheres and the energy (counted from the completely dissociated state) is assumed to be proportional to the number of bonds between nearest neighbours. If the energy per atom is counted from that of the ideal, infinite crystal, then the energy of a particular configuration is proportional to the number of bonds which should be broken to obtain this configuration from the infinite crystal. The proportionality coefficient is $2W_1$ where W_1 is the step energy per atom introduced in section 1.3. The factor 2 appears because, when breaking an atomic layer into two pieces, one makes two steps.

In a broken bond model, the quantities W_a and W_1 introduced previously in this chapter are linked, on the (001) face of a cubic crystal, by the obvious relation

$$W_a = 4W_1. \quad (1.14)$$

According to Stoltze's review article (1994) this relation is satisfied with an accuracy of order 1% by calculated values for Cu and Ni, while the accuracy is not so good for Au. Other predictions of broken bond models

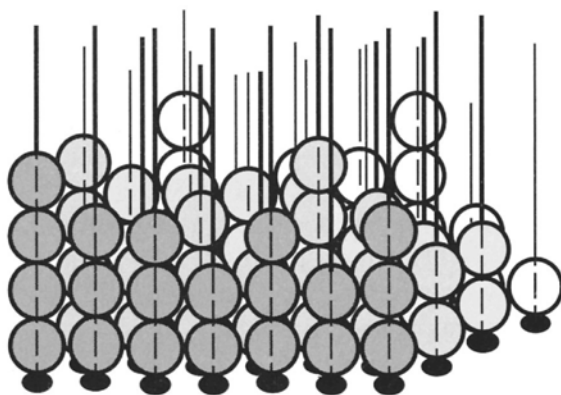


Fig. 1.8. The SOS (solid on solid) model. The adatom positions are fixed on a rigid lattice, and the only degree of freedom is the presence or the absence of an atom, so that there are no overhangs. Each bond has an energy $\epsilon = 2W_1$.

do not fit reality so well. For instance, in the broken bond model of an fcc crystal, the cohesive energy per atom (energy needed to break the material into individual atoms) is 6 times the bond energy $2W_1$, so that its value is $12W_1$ in broken bond models. The actual ratio predicted by more elaborate theories (Stoltze 1994) and to some extent confirmed by experiment, is much larger than 12 (23 for Ni, 28 for Cu, 35 for Ag, 58 for Au). Another prediction of the broken bond model is that the surface energy per atom (1.14) of a (001) face is $4W_1$. More sophisticated approaches (Stoltze 1994) agree with this simple result within 13%: an astonishingly good success for the broken bond model.

As a general rule, the energy of defects (adatoms, advacancies, steps or the surface itself) is much lower than the value expected from the broken bond model. This is due to the fact that the solid has many continuous degrees of freedom which can be used to reduce the energy. This reduction, however, is often spectacular.

The SOS model (Fig. 1.8) is a broken bond model on a simple cubic lattice. A related model is the discrete Gaussian model defined in appendix A.

Another model, generally used for the theoretical treatment of the roughening transition, employs the free energy (1.7b) modified by an additional term $\eta \cos(2\pi z)$ which mimics the crystal periodicity.

1.7 Roughening transition of a vicinal crystal surface

Let us come back to reality and ask the essential question, whether the roughening temperature of a high-symmetry surface occurs below the melting point T_M . If one accepts the crude estimate (1.3) and the theoretical evaluations of Stoltze (1994) the answer is negative for most materials. This means that the roughening temperature occurs when the crystal is in contact with its melt. In the case of semiconductors, the situation may be further complicated by elastic mechanisms, as will be seen in chapter 15. All this makes experimentation difficult for any material except helium, studied by Balibar *et al.* (1993).

However, experimentation is possible on stepped or 'vicinal' surfaces (Fig. 1.9). A *vicinal* (001) surface, for instance, has an orientation in the *vicinity* of the (001) orientation. We can rightfully wonder what is the roughening temperature for such surfaces.

An example are the stepped (11 2n+1) faces of metals: copper has been studied by Fabre *et al.* (1986, 1987a,b) and Ernst *et al.* (1995) using atom diffraction, and using STM by Giesen-Seibert *et al.* (1993) and Girard *et al.* (1994); nickel has been investigated with X-ray diffraction by Robinson *et al.* (1990). These surfaces can be considered as a succession of (001)

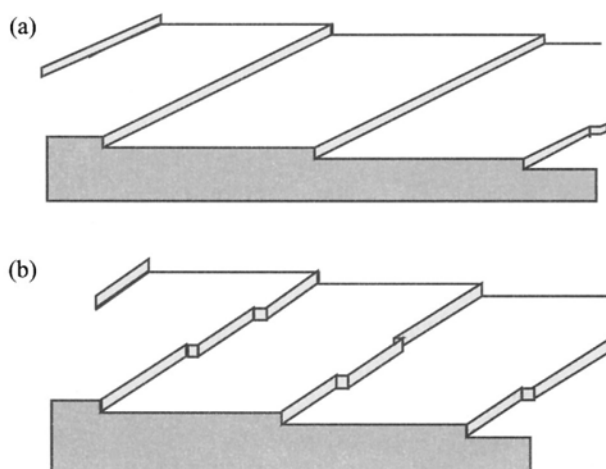


Fig. 1.9. Schematic representation of a stepped (or 'vicinal') surface below (a) and above (b) T_R .

terraces separated by steps (Fig. 1.9). These steps would like to be straight, since each kink costs an energy W_0 . On the other hand, the steps would like to be equidistant. If they are closer or farther than the average by one atomic distance, this costs an energy ϵ for each atom of the step. This energy should be small if the average distance between steps is large. The kink energy W_0 is equal to W_1 in the broken bond model, and actually not very different even within the more sophisticated evaluations of Stoltze's (1994) shown in Table 1.1. On the other hand, it is larger than ϵ .

It will now be shown that, if ϵ is small enough, a vicinal surface is rough at fairly low temperatures $T < T_M$, in contrast with high-symmetry surfaces. The average distance between kinks is about $\exp(\beta W_0)$ atomic distances. In other words, and roughly speaking, the independent elements of a step are not atoms, but step pieces of length $\exp(\beta W_0)$ atomic distances. The interaction energy between these pieces is of order $\epsilon \exp(\beta W_0)$. The roughening transition occurs when this energy is of the same order as the temperature T . The roughening transition temperature is therefore given by

$$k_B T_R \approx \epsilon \exp\left(\frac{W_0}{k_B T_R}\right). \quad (1.15)$$

This hand-waving argument can be confirmed by an exact calculation on a special model (Villain *et al.* 1985).

1.8 The roughening transition: a very weak transition

In fact, thermal roughness is very 'weak' (see problem 1.1). We mean by that that the surface undulation arising from thermal fluctuations is very

shallow in comparison with the waves produced by wind on a pool. This is because the logarithm diverges very slowly in (1.12).

Let us try to imagine people living in a d -dimensional space with d slightly larger than 3. The dimension of a surface would be $d - 1$, in the integrand in (1.11) they would replace $q dq$ by $q^{d-2} dq$, and the integral would no longer diverge! In more than 3 dimensions, there is no phase transition, and d -dimensional scientists would say that a surface at equilibrium is always smooth. On the contrary, in less than 3 dimensions, the divergence of $G(R)$ is faster than a logarithm (see problem 1.2).

It is conceivable that a transition which is absent above 3 dimensions is very weak at the critical dimension 3. We shall see later what this means, but we first want to see how the roughening transition can be studied theoretically. The standard method to study phase transitions is the so-called renormalization group technique. This method was first used by high-energy physicists, and the idea to apply it to phase transitions was rather natural. It was the merit of K.G. Wilson to put this idea into a simple form (Wilson 1983). Wilson's articles generated a cascade of discoveries in the 1970s, and were rewarded by the Nobel prize in 1982. The renormalization group method is outlined in appendix B in the case of the roughening transition, and in appendix J in another instance. In appendix B, we use the equivalence of a model having a roughening transition (the discrete Gaussian model) with a two-dimensional electrolyte. This equivalence (Chui & Weeks 1976) is derived in appendix A. The two-dimensional electrolyte has a transition, whose renormalization group treatment was done for the first time in a celebrated paper by Kosterlitz & Thouless (1973). In appendix B, we present a simpler treatment due to A.P. Young.

We shall only mention two results of the renormalization group treatment:

- i) $G(R)$ diverges at T_R as

$$G(\mathbf{R}) \equiv \langle [z(\mathbf{r}) - z(\mathbf{r} + \mathbf{R})]^2 \rangle \rightarrow \frac{2a^2}{\pi^2} \ln R. \quad (1.16)$$

This is formula (1.12), but with a well-defined value of the prefactor, in which we have explicitated the lattice constant a (usually taken equal to 1 in this book).

- ii) The specific heat does not diverge, and all its derivatives with respect to T are continuous, in contrast with usual transitions (e.g. at the Curie temperature of a ferromagnet). The specific heat has therefore no observable singularity. It has, however a singularity called an essential singularity—a seemingly strange name (coined by mathematicians, probably inspired by philosophic language) for an invisible singularity!