2015.9
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Crystals in and out of equilibrium

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1.Introduction

Technical innovation often requires new materials.
 Purified Si → Semiconductor Industry, IT
 iPS cells → Regenerative Medicine
 GaN Blue LED → photonic & electronic industry

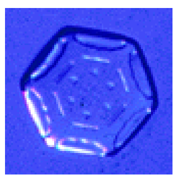
Most of new materials are in solid, crystalline form.
 Growth of high quality crystals is required.

To know how to grow crystals or how crystals grow.
➔ Some basic concepts of crystal growth

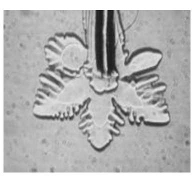
Various crystal shapes


NaCl


Pyrite


snow

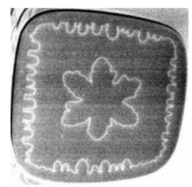

SrCO3

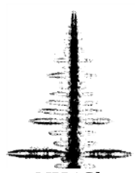

ice


snow


Succininitrile


Polystyrene


Si


NH4Cl


MnO2


Ag

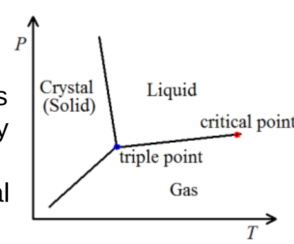
Overview

2. Equilibrium :
 equilibrium crystal shape(ECS)
 minimum of energy, Wulff theorem
 thermal fluctuations → roughening transition
3. Kinetics :
 Birth of crystal nucleus
 ideal growth laws
 Non-ideal laws
  Spiral growth
  2D nucleation growth

2. Equilibrium Properties

2.1 Phase diagram

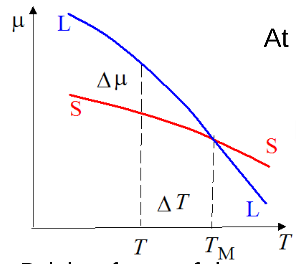
At a given temperature T
 and a pressure P,
one phase is stable which has
 a minimum Gibbs free energy
 G(T,P,N), or
 a minimum chemical potential
 μ(T,P)=G/N.



When two phases have equal μ's, they coexist.

$$\mu(T,P;\text{solid}) = \mu(T,P;\text{liquid, gas})$$

Temperature variation of chemical potentials of liquid and solid at a fixed P.



At the melting temperature T_M(P),

$$\mu_S(T_M, P) = \mu_L(T_M, P)$$

Below T_M(P), solid is stable.

$$\mu_S(T, P) < \mu_L(T, P)$$

Driving force of the crystal growth

$$\Delta\mu = \mu_L(T, P) - \mu_S(T, P)$$

So far for bulk phases.
When crystal is born, surface plays the role.

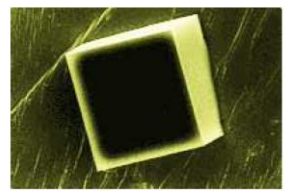
2.2 Equilibrium Crystal Shape (ECS):

2.2.1 Wulff theorem

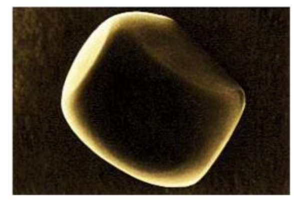
Below T_M crystal is stable, but creation of a crystal nucleus costs interface free energy.

Experiment on ECS:

NaCl by Metois & Heyraud (JCG 84 (1987)503)

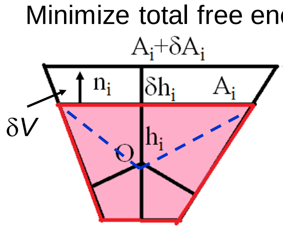


620° C
Polyhedron at low T



710 ° C
Facet connected to curved surface at high T

Minimize total free energy: $G = -\Delta\mu \frac{V}{v_S} + \sum_i \gamma_i A_i$



3D Polyhedral nucleus

A_i; Area of a surface with a normal n_i

γ_i; surface free energy per area

$V = \frac{1}{3}\sum h_i A_i$; Volume

v_S; Molecular solid volume

Height variation δh_i → Area variation δA_i

$$\delta V = \sum A_i \delta h_i = \frac{1}{3}\sum(\delta h_i \cdot A_i + h_i \cdot \delta A_i) = \frac{1}{2}\sum h_i \delta A_i$$

F.e. minimization: $\delta G = \sum_i \left(-\frac{\Delta\mu}{2v_S} h_i + \gamma_i\right)\delta A_i = 0$

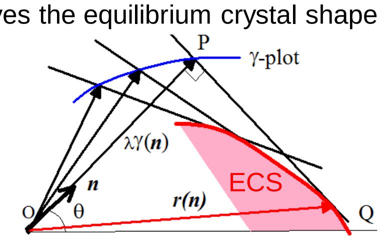
$$\frac{\gamma_i}{h_i} = \frac{\Delta\mu}{2v_S} = \frac{1}{\lambda}$$ Wulff's theorem

Wulff theorem: for a position ***r*** on a surface normal to ***n***

$$h(\boldsymbol{n}) = (\boldsymbol{r} \cdot \boldsymbol{n}) = \lambda\gamma(\boldsymbol{n})$$

Wulff construction; orientation dependent γ → ECS

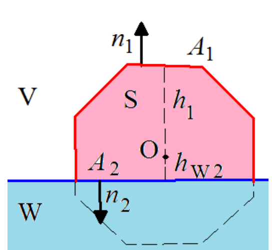
1. Draw a vector OP= $\lambda\gamma$**n** from the origin O.
2. Draw a surface PQ perpendicular to OP.
3. Vary directions n, and take an envelop of PQ (red). It gives the equilibrium crystal shape (ECS).



2.2.2 ECS of an island on an adsorbed wall

Surface normal to n_2 is in contact to a wall W, with an interface area A_2.

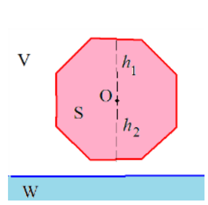
Wall surface with γ_W disappears, and an interface with γ_{W2} is formed.



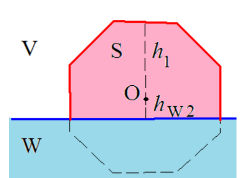
G minimization determines the distance h_{w2} from O to the interface as

$$\frac{\gamma_i}{h_i} = \frac{\gamma_{W2} - \gamma_W}{h_{W2}} = \frac{\Delta\mu}{2v_S} = \frac{1}{\lambda}$$

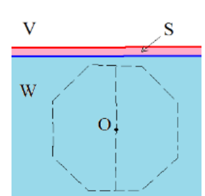
Three types of wetting:



CD:



PW:



CW:

Complete dewetting: $\gamma_2 < \gamma_{W2} - \gamma_W \rightarrow h_2 < h_{W2}$

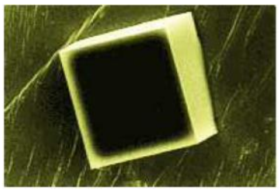
Partial wetting: Bulk ECS cut in the intermediate

$$-\gamma_1 < \gamma_{W2} - \gamma_W < \gamma_2 \rightarrow -h_1 < h_{W2} < h_2$$

Complete wetting: $\gamma_{W2} - \gamma_W < -\gamma_1 \rightarrow h_{W2} < -h_1$

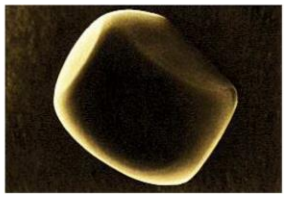
2.2.3 facet size

Experiment on ECS:
NaCl by Metois & Heyraud (JCG 84 (1987)503)



620° C

Polyhedron at low T



710 ° C

Facet connected to curved surface at high T

Facet size?
Facet connected to smooth curve?

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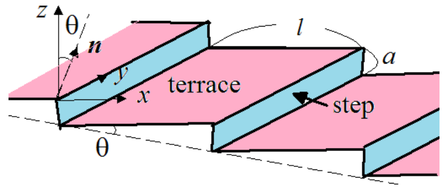
Orientation dependence of surface free energy $\gamma(\theta)$:

If γ is isotropic (indep. of θ), ECS is a sphere.
What determines the anisotropy of γ?

Vicinal surface with a small inclination θ



$$\cos\theta = \ell/\sqrt{\ell^2+a^2}$$
$$\sin\theta = a/\sqrt{\ell^2+a^2}$$
$$\tan\theta = a/\ell$$

Surface free energy of a vicinal surface

$$\gamma(\theta) = \gamma_0|\cos\theta| + (\beta_0/a)|\sin\theta|$$

γ_0: terrace free energy per area
β_0: step free energy per length

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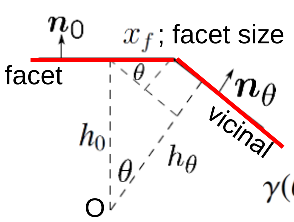
Facet size and the step free energy



x_f; facet size

Wulff theorem

$$\frac{1}{\lambda} = \frac{\gamma_0}{h_0} = \frac{\gamma(\theta)}{h_\theta}$$

$$\gamma(\theta) = \gamma_0|\cos\theta| + (\beta_0/a)|\sin\theta|$$

β_0 ; step energy/length

$$h_\theta = h_0\cos\theta + x_f\sin\theta$$

Height to the facet: $h_0 = \lambda\gamma_0$
Width of the facet: $x_f = \lambda\beta_0/a$

step free energy β_0 ⇔ facet size x_f

Facet size is independent of the neighboring vicinal.

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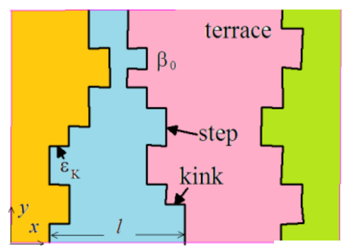
2.2.4 facet connected by curved surface

Step interaction contributes to $\gamma(\theta)$.

On a vicinal surface with an average step separation *l*, steps are thermally fluctuating.

Top view

high



low

β_0 : step energy
ε_K: kink energy

Surface inclination: $\tan\theta = \frac{a}{\ell}$

Step fluctuation induces free energy cost or interaction.

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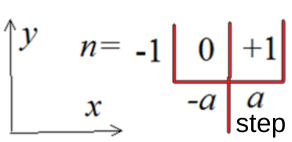
Elementary fluctuation of a step running in y-direction



ε_K: kink energy cost for n=+1 or -1

Probability of kink at finite T; $p_K = \dfrac{e^{-\varepsilon_K/k_BT}}{1+2e^{-\varepsilon_K/k_BT}}$

While a step runs a distance y, it fluctuates laterally as

$$\langle x^2(y)\rangle = \langle\Big(\sum_{i=0}^{y/a} a n_i\Big)^2\rangle = ay\langle n^2\rangle = 2ap_K y$$

Lateral variance is proportional to a step length.

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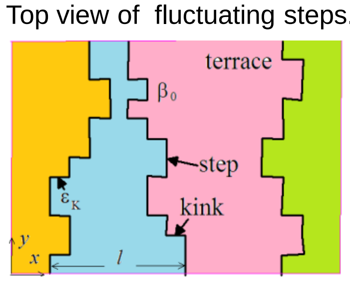
Top view of fluctuating steps.



Step separation l:

β_0: step energy
ε_K: kink energy

When $\langle x^2\rangle = 2ap_K y = \ell^2$, neighboring steps collide.
Since steps cannot cross, entropy decreases and free energy increases by k_BT for each collision.

Step free energy: $\beta_\theta = \beta_0 + \beta_2(a/\ell)^2 = \beta_0 + \beta_2\tan^2\theta$

where $\beta_2 = 2k_BTp_K/a$

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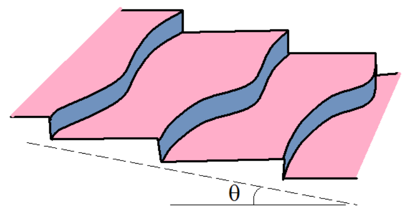
Vicinal surface with fluctuating steps



$$\frac{\gamma(\theta)}{|\cos\theta|} = \gamma_0 + (\beta_0/a)|\tan\theta| + (\beta_2/a)|\tan^3\theta| = f(\theta)$$

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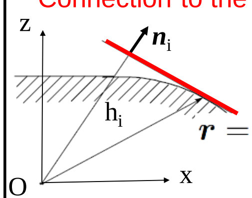
Connection to the smooth surface



Wulff's theorem: $\frac{\gamma_i}{h_i} = \frac{\Delta\mu}{2v_S} = \frac{1}{\lambda}$

$$h_i = \boldsymbol{r}\cdot\boldsymbol{n}_i = \lambda\gamma_i(\boldsymbol{n}_i)$$

$$\boldsymbol{r} = (x, z) \quad \boldsymbol{n}_i = \frac{(-z_x, 1)}{\sqrt{1+z_x^2}}, \; z_x = \frac{\partial z}{\partial x}$$

Then, $-xz_x + z = \lambda\gamma(z_x)\sqrt{1+z_x^2} = \lambda f(z_x)$

or $z = \lambda f(z_x) + xz_x$ → Equilibrium shape

Differentiate by z_x : $x = -\lambda\frac{\partial f(z_x)}{\partial z_x}$

Close to singular surface

$$z_x = -\tan\theta, \; f(z_x) = \frac{\gamma(\theta)}{\cos\theta} = \gamma_0 + \frac{\beta_0}{a}|z_x| + \frac{\beta_2}{a}|z_x|^3$$

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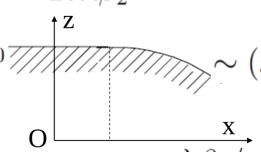
For positive x with a negative slope $z_x \le 0$

$$x = -\lambda\frac{\partial f(z_x)}{\partial z_x} = \frac{\lambda}{a}(\beta_0 + 3\beta_2 z_x^2) = x_f + \frac{3\lambda\beta_2}{a}z_x^2$$

$$z = \lambda f(z_x) + xz_x = \lambda(\gamma_0 - (2\beta_2/a)|z_x|^3)$$

$$= h_0 - \left(\frac{4a}{27\lambda\beta_2}\right)^{1/2}(x - x_f)^{3/2}$$

$h_0 = \lambda\gamma_0$



$\sim (x - x_f)^{3/2}$

$x_f = \lambda\beta_0/a$

Facet size x_f is proportional to the step free energy β0
Facet connects smoothly to round surface.

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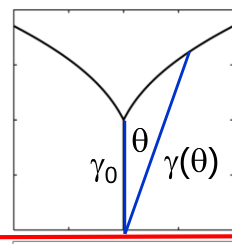
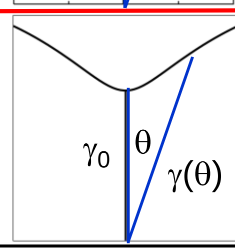
polar plot of γ–θ (γ-plot) with and without singularity



$\gamma(\theta) = \gamma_0|\cos\theta| + (\beta(\theta)/a)|\sin\theta|$

$\beta(\theta) = \beta_0 + \beta_2\tan^2\theta$

Cusp singularity in γ
→ facet with a size ~ β0



Roughening transition

where $\beta_0 = 0$

$\gamma(\theta) = \gamma_0 + \gamma_2\theta^2$

No singularity in γ
→ no facet in ECS

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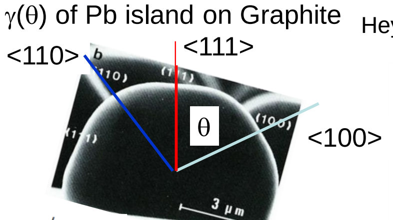
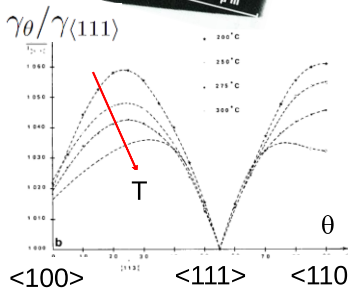
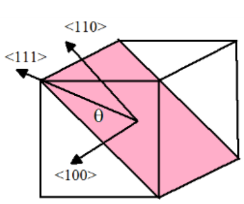
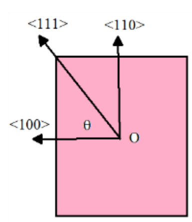
γ(θ) of Pb island on Graphite

Heyraud & Metois, SS (1983)









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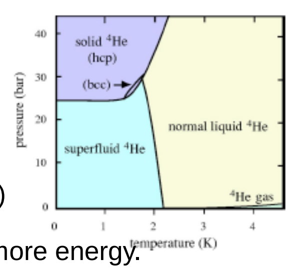
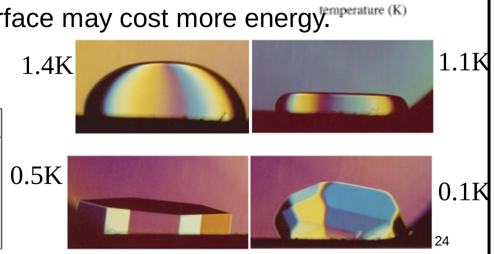
ECS of ^{4}He

Crystal growth from superfluid
Latent heat ~0
Large heat trasnsport
→ Equilibrium shape
(Balibar et al, RMP 2005)



surface may cost more energy.

Face	T_R
(0001)	1.30K
$(10\bar{1}0)$	1.0 K
$(10\bar{1}1)$	0.43K
$(11\bar{2}0)$	0.3 K



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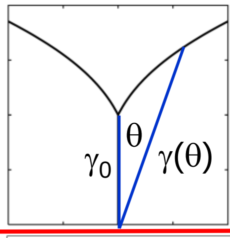
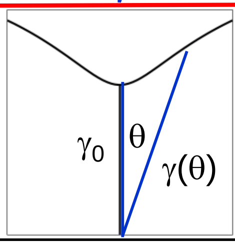
polar plot of γ–θ (γ-plot) with and without singularity



$$\gamma(\theta) = \gamma_0 |\cos\theta| + (\beta(\theta)/a)|\sin\theta|$$

$$\beta(\theta) = \beta_0 + \beta_2 \tan^2\theta$$

Cusp singularity in γ
→ facet with a size ~ β0



Roughening transition

where $\beta_0 = 0$

$$\gamma(\theta) = \gamma_0 + \gamma_2\theta^2$$

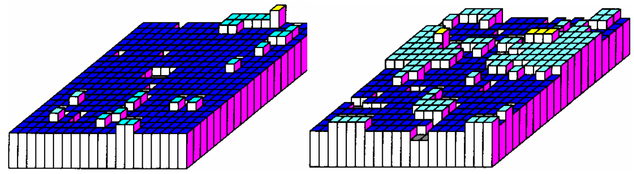
No singularity in γ
→ no facet in ECS

2.3 Surface thermal roughening transition

When will the step free energy vanish?

Singular surface:

Facet has a low surface energy, without entropy gain.
At T>0, rough surface gives contribution to entropy



Low T High T

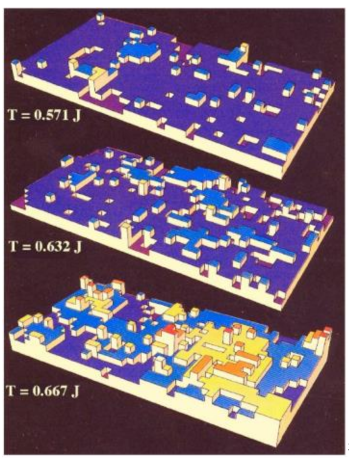
Roughening ~ ad-islands or vacancy islands
~ surrounded by steps

MC simulation of
Solid-on-Solid model
no vacancy,
no overhang

surface ⇔height

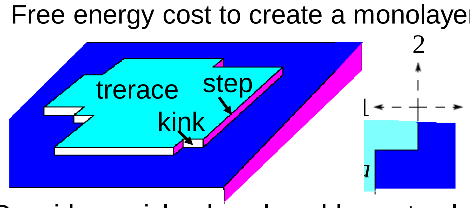
Leamy et al. (1975)

$k_B T_R$=0.632J



2.3.1 roughening transition in a mean field picture

Free energy cost to create a monolayer island



z: coordination number

Consider an island enclosed by a step loop of length L.

Energy cost: $E_s(L) = \frac{J}{2}\frac{L}{a}$ J: NN bond energy

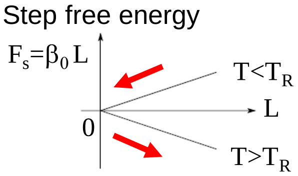
Entropy: $S_s(L) = k_B \ln W, \quad W \sim (z-1)^{L/a}$

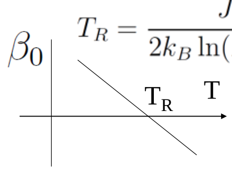
➔ Step free energy:

$$F_s = E_s - TS_s = [\tfrac{1}{2}J - k_B T\ln(z-1)](L/a) = \beta_0(T)L$$

At T=T_R=J/2$k_B$ln(z-1), step free energy vanishes: β0=0.

Step free energy





$$T_R = \frac{J}{2k_B\ln(z-1)}$$

$T < T_R$, $\beta_0 > 0$; F is minimum at L=0, no island, flat

$T > T_R$, $\beta_0 < 0$; F is minimum at L=∞, many islands, rough

Roughening Transition

Close to T_R, many steps interact with each other.

β0 =0 above T_R. Step has a meaning only below T_R.

Surface free energy density

$\gamma(\theta, T) = \gamma_0 + (\beta_0/a)|\theta|$ … T<T_R : Singular

$= \gamma_0 + \gamma_2\theta^2$ … T>T_R : Analytic

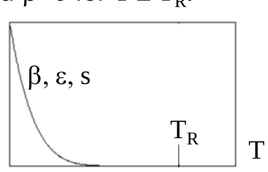
2.3.2 Roughening transition by sophisticated analyses

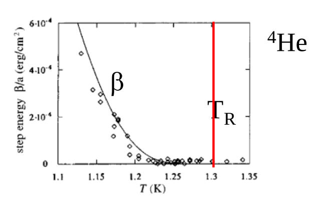
- Kosterlitz-Thouless renormalization group
  "A modern approach to critical phenomena"
  I. Herbut (Cambridge,2007)

Step free energy β has

an essential singularity for T < T_R; $\beta \sim \xi^{-1} \sim e^{-A/\sqrt{T_R - T}}$

and β=0 for T ≥ T_R.





Step energy: $\epsilon(T < T_R) = \partial(\beta/T)/\partial(1/T) \to 0$

entropy: $s(T < T_R) = -\partial\beta/\partial T \to 0$

Height correlation of rough surface

For a rough surface: $z = h(x,y)$

$$F_s = \frac{1}{2}\int d\boldsymbol{r}\tilde{\gamma}(0)(\nabla h(\boldsymbol{r}))^2 = \frac{1}{2}\int \frac{d\boldsymbol{k}}{(2\pi)^2}\tilde{\gamma}k^2|h(\boldsymbol{k})|^2$$

Surface stiffness : $\tilde{\gamma} = \gamma + \gamma''$

finite for analytic γ: $T \geq T_R$

infinite for singular γ: $T < T_R$

The description has meaning only above T_R

height difference fluctuation: $G(\boldsymbol{r}) = \langle (h(\boldsymbol{r}) - h(0))^2 \rangle$

$$G(\boldsymbol{r}) = \int \frac{2d\boldsymbol{k}}{(2\pi)^2}\langle |(h(\boldsymbol{k})|^2\rangle(1-\cos \boldsymbol{k}\cdot\boldsymbol{r}) = \int_{1/r}^{\pi/a}\frac{kdk}{\pi}\frac{k_BT}{\tilde{\gamma}k^2}$$

$$\approx \frac{k_BT}{\pi\tilde{\gamma}}\ln(r/a) + \text{const.}$$ diverges for r → ∞

Rough surface: G(r) diverges at large separation

For an atomically smooth surface?

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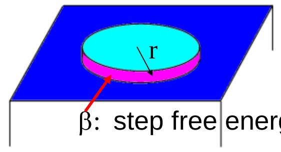
Correlation function below TR



Two-Dimensional Island on a Flat Surface

β: step free energy density

Total free energy: $\Delta F = 2\pi r\beta \leq k_BT$

Small islands $r \leq \xi = k_BT/\beta$ are thermally excited.

Between two points separated by r ≤ ξ, heights behave like on a rough surface: $G(r) \sim \ln r$

For r ≥ξ , every island between two points is closed: G(r) should be saturated. $G(r) = \ln \xi$

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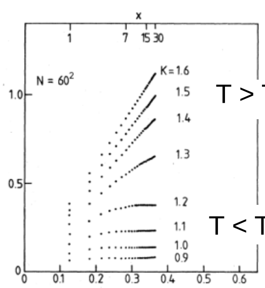
Height correlation function G by MC simulation:

YS. H.M-K, Phys. Rev. B (1981)

G(r)



$T > T_R$, ξ = ∞

$T < T_R$, ξ = finite

~ log r

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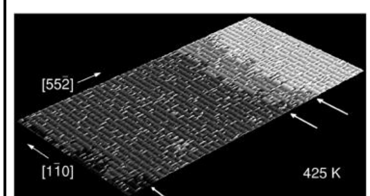
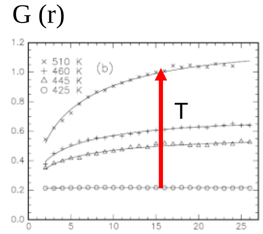
2.3.5. Experiment on height correlation

Ag(115), STM

Hoogeman et al. PRL 82(1999) 1728



G (r)



r (× 7.5A)

$$G(\boldsymbol{r}_{ij}) = \langle (h_i - h_j)^2 \rangle$$
$$= -K(T)\ln[r^{-2} + \xi(T)^{-2}] + C(T)$$

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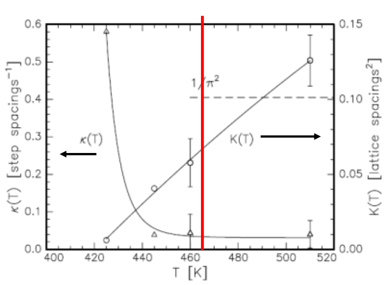
$$G(\boldsymbol{r}_{ij}) = -K(T)\ln[r^{-2} + \kappa(T)^2] + C(T)$$



$T_R = 465\text{K} \pm 25\text{K}$

$$\kappa(T) = \xi(T)^{-1} \sim \beta(T)$$

Universal behavior: $K(T_R) = \frac{1}{\pi^2}$

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Summary of thermal roughening

1. Singular surface undergoes roughening transition at T_R in equilibrium.
2. Below T_R, step creation costs a finite free energy β_0.
3. Above T_R, $\beta_0 = 0$ and step looses meaning.

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2015.9
Porquerolle, France

Crystals in and out of equilibrium

Yukio Saito
Dept. Physics, Keio Univ., Japan

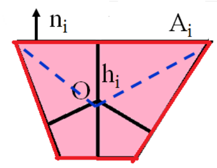
3. Crystals out of Equilibrium; Growth Laws

3.1 Birth of crystal

3.1.1 Homogeneous nucleation

Free energy cost for nucleation

$$G = -\Delta\mu \frac{V}{v_S} + \sum_i \gamma_i A_i$$



A_i; Area of a surface with a normal n_i

γ_i; surface free energy per area

$V = \frac{1}{3}\sum h_i A_i$; Volume, v_S ; Molecular volume

Minimum in shape variation→ Wulff theorem

$$\delta G = 0 \qquad \frac{\gamma_i}{h_i^*} = \frac{\Delta\mu}{2v_S}$$

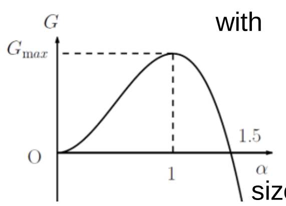
Free energy versus nucleus size

Assume that a nucleus shape is ECS, but size differs.

$$h_i = \alpha h_i^*,\ A_i = \alpha^2 A_i^*,\ V = \alpha^3 V^*$$

where $h_i^* = \frac{2v_S}{\Delta\mu}\gamma_i$

Then, $G = G_{\max}(-2\alpha^3 + 3\alpha^2)$



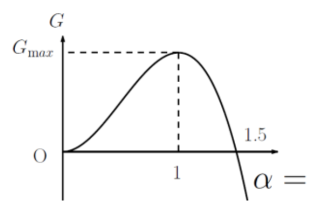
with $G_{\max} = \frac{\Delta\mu}{2v_S}V^* = f\frac{v_S^2\tilde{\gamma}^3}{\Delta\mu^2}$

f ; form factor

$\tilde{\gamma}$; typical surface tension

size scale

G is maximal at a critical volume V^*



$\alpha = (V/V^*)^{1/3}$

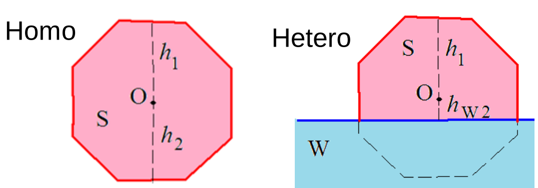
A nucleus with a volume smaller than V* melts back, but if thermal fluctuation allows a volume to exceeds V*, the nucleus grows.

Nucleation rate per unit volume and time

$$J = J_0 e^{-G_{\max}/k_BT} = J_0 \exp\left(-\frac{f v_S^2\tilde{\gamma}^3}{k_BT\Delta\mu^2}\right)$$

3.1.2 Heterogeneous nucleation

If crystal wets wall, nucleus is cut in the middle.
Thus, volume of critical nucleus decreases.



Since the nucleation barrier is proportional to the critical volume, $G_{\max} = \frac{\Delta\mu}{2v_S}V^*$

the nucleation barrier also decreases.

3.2 Ideal Growth

After birth or nucleation, crystal nucleus starts to grow.

We consider a large crystal growing with a flat front.
Then, what is its velocity?
Driving force of crystal growth = chemical potential

$$\mu = \frac{\partial G(T,P,N)}{\partial N}$$

Ideal case with fast surface kinetics (rough surface):
Growth velocity V is proportional to the driving $\Delta\mu$:

$$V = K\Delta\mu = K(\mu_V - \mu_S)$$

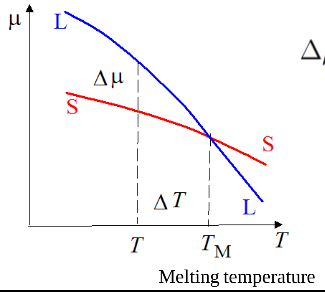
3.2.1 Growth from undercooled melt

$T = T_M : \mu_S(T_M, P) = \mu_L(T_M, P)$ →sol-liq coexist

$T < T_M : \mu_S(T, P) < \mu_L(T, P)$ →crystallization

⇒ driving force: $\Delta\mu = \mu_L - \mu_S$

undercooling: $\Delta T = T_M(P) - T$



$$\Delta\mu = \left(\frac{\partial\mu_L}{\partial T} - \frac{\partial\mu_S}{\partial T}\right)(T - T_M)$$
$$= (-s_L + s_S)(-\Delta T)$$
$$= \frac{\Delta h}{T_M}\Delta T$$

$\Delta h = T_M(s_L - s_S)$: Latent heat

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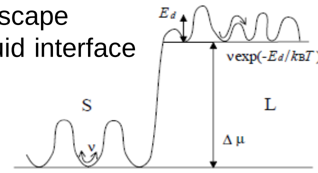
Energy landscape at solid-liquid interface



Solidification: Liquid → Solid:

$$V_+ = a\nu e^{-E_d/k_BT} e^{-\Delta s/k_B}$$

a; Atomic unit

ν; Thermal vibration frequency

E_d; Energy barrier to change position

$\exp(-E_d/k_BT)$; Probability to jump over energy barrier

$W_S/W_L = \exp[-(s_L - s_S)/k_B]$;

Ratio of crystalline configuration

Melting: Solid → Liquid:

$$V_- = V_+ e^{-\Delta\mu/k_BT}$$

$\Delta\mu = \mu_L - \mu_S$;chemical potential difference

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⇒ net growth rate: $V = V_+ - V_- = V_+(1 - e^{-\Delta\mu/k_BT})$

At a small Δμ;

$$V = K\frac{\Delta\mu}{k_BT} = K_T\frac{\Delta T}{T_M}$$ Wilson-Frenkel formula

Kinetic coefficient:

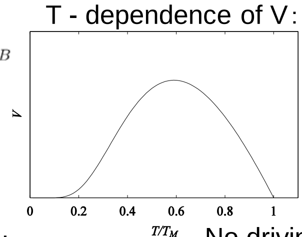
$$K = V_+ = a\nu e^{-E_d/k_BT} e^{-\Delta s/k_B}$$
$$= \frac{k_BT}{\pi a^2\eta} e^{-\Delta s/k_B}$$

η: liquid viscosity coefficient

Stokes-Einstein equation

$$D = \frac{a^2}{6}\nu e^{-E_d/k_BT} = \frac{k_BT}{6\pi\eta a}$$

T - dependence of V:



Large η

No driving $\Delta\mu \to 0$

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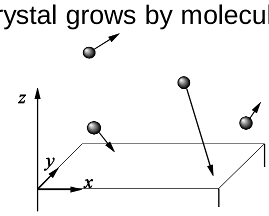
3.2.2 Vapor growth

Crystal grows by molecular deposition from vapor.



Ideal gas at a pressure P and a temperature T

$PV = Nk_BT$

→ density $n = P/k_BT$

Deposition flux per area and time: F(P, T)

Maxwell-Boltzmann distribution:

velocity of a gas molecule ***v***

$$Pr(\boldsymbol{v})d\boldsymbol{v} = \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp\left(-\frac{m\boldsymbol{v}^2}{2k_BT}\right)d\boldsymbol{v}$$

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depositing from above to the surface z=0: $v_z<0$

deposition rate:

$$F(P,T) = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{0} dv_z n|v_z| Pr(\boldsymbol{v})$$
$$= \frac{P}{\sqrt{2\pi m k_BT}}$$

Evaporation flux balances deposition flux at saturation.

$F(P_{eq}(T), T)$ where P_{eq}(T); equilibrium pressure.

Net growth rate: Hertz–Knudsen formula

$$V = a^3[F(P,T) - F(P_{eq}(T),T)] = \frac{v_S(P - P_{eq}(T))}{\sqrt{2\pi m k_BT}}$$

V is proportional to overpressure.

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Chemical potential of an ideal gas:

$$\Delta\mu = \mu_G(T,P) - \mu_G(T,P_{eq}) = k_BT\ln(P/P_{eq})$$

$$\rightarrow V = \frac{v_S P_{eq}(T)}{\sqrt{2\pi m k_BT}}(e^{\Delta\mu/k_BT} - 1)$$

At a small driving force: $V = K\frac{\Delta\mu}{k_BT}$,

Hertz-Knudsen growth law:

with a kinetic coefficient:

$$K = \frac{v_S P_{eq}}{\sqrt{2\pi m k_BT}}$$

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3.2.3 Anisotropic Kinetic coefficient: Growth shape

Ideal growth velocity of a surface normal to n

$$V(\boldsymbol{n}) = K(\boldsymbol{n})\Delta\mu$$

After a time t, neglecting the initial transient,

$$h(\boldsymbol{n}) = (\boldsymbol{r}\cdot\boldsymbol{n}) \approx V(\boldsymbol{n})t = K(\boldsymbol{n})\Delta\mu\, t$$

kinetic Wulff theorem

$$\frac{K(\boldsymbol{n})}{h(\boldsymbol{n})} = \frac{1}{\Delta\mu\, t}$$

~ Wulff theorem of ECS

$$\frac{\gamma(\boldsymbol{n})}{h(\boldsymbol{n})} = \frac{\Delta\mu}{2v_S}$$

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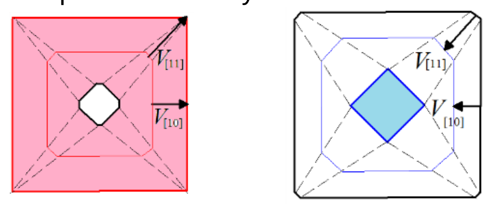
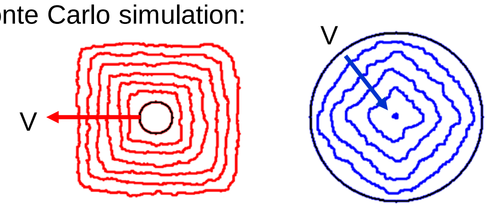
Growth shape is covered by slowest faces:



Melting shape is covered by fastest faces:

Monte Carlo simulation:



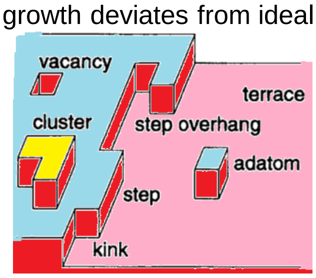
Growing shape: Melting shape:

60

3.3 Non-ideal growth laws

With a flat singular surface,

crystal growth deviates from ideal laws $V = K\Delta\mu$.



An isolated atom adsorbed on a flat surface evaporates easily.

Atoms adsorbed on a flat surface should be incorporated in steps and in kinks.

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How steps and kinks are provided on a flat surface?

There are two main mechanisms;

1) Two-dimensional nucleation and growth
2) Spiral growth

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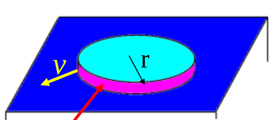
3.3.1 Two-dimensional (2D) nucleation

Below TR, surface is singular and flat.

With a finite driving Δμ, a 2D crystal nucleus is formed.



β: step free energy

Assume an isotropic step free energy β
→ Circular nucleus

Nucleation free energy barrier → nucleation rate?

Step velocity?

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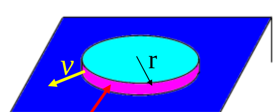
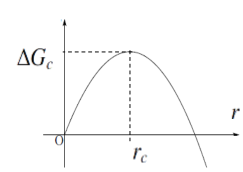
Nucleation rate



β: step free energy



Free energy cost:

$$\Delta G = -\frac{\pi r^2}{\Omega_2}\Delta\mu + 2\pi r\beta \qquad \text{where:} \quad N_2 = \frac{\pi r^2}{\Omega_2}$$

Critical radius: $r_c = \dfrac{\Omega_2 \beta}{\Delta\mu}$

Free energy barrier: $\Delta G_c = \dfrac{\pi\beta^2\Omega_2}{\Delta\mu}$

Nucleation rate per area per time: $J_2 = J_0 e^{-\Delta G_c/k_B T}$

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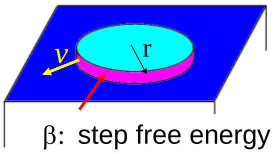
Step velocity



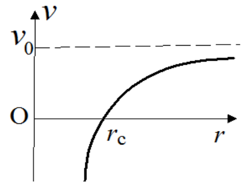
β: step free energy

Free energy cost:

$$\Delta G = -\frac{\pi r^2}{\Omega_2}\Delta\mu + 2\pi r\beta$$

where: $N_2 = \frac{\pi r^2}{\Omega_2}$

Step velocity for a rough step: ideal linear law



$$v_s = -\frac{K_s}{k_B T}\frac{\delta G}{\delta N_2} = v_0\left(1 - \frac{r_c}{r}\right)$$

$v_0 = K_s \frac{\Delta\mu}{k_B T}$; Velocity of a straight step

$r_c = \frac{\Omega_2 \beta}{\Delta\mu}$; Critical radius

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Growth rate by multiple nucleation on a surface area A

Let the time necessary to complete monolayer be τ.

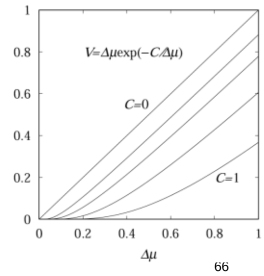
Number of nuclei in an area A in time τ : $N_n = J_2 A\tau$

Area swept : $A = N_n \times \pi(v_0\tau)^2$

➔ $A = J_2 A\tau \times \pi(v_0\tau)^2$ ➔ $\tau = (\pi J_2 v_0^2)^{-1/3}$

Crystal growth rate:

$$V = \frac{a}{\tau} = a(\pi J_2)^{1/3} v_0^{2/3}$$
$$= a(\pi J_0)^{1/3}\left(\frac{K_s\Delta\mu}{k_B T}\right)^{2/3}$$
$$\times \exp\left(-\frac{\pi\beta^2\Omega_2}{3\Delta\mu k_B T}\right)$$
$$= K\Delta\mu e^{-C\beta^2/\Delta\mu}$$



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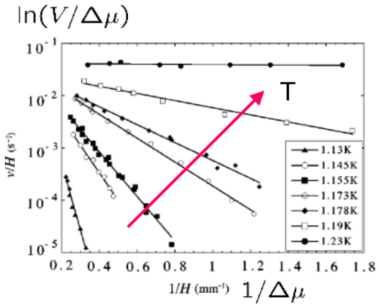
$$V = K\Delta\mu e^{-C\beta^2/\Delta\mu}$$

→ $\ln(V/\Delta\mu) \propto -(\beta^2/\Delta\mu)$

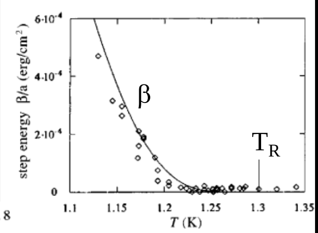
Experiment: 4He

$\ln(V/\Delta\mu)$



$1/\Delta\mu$

Step free energy of 4He



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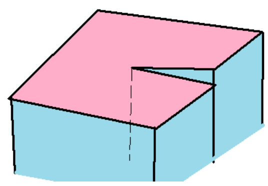
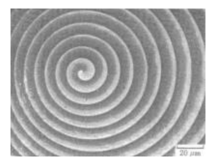
3.3.2 Spiral growth

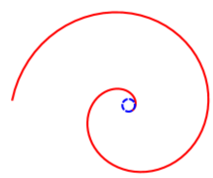
Actual crystals contain defects, as a screw dislocation.



Screw dislocation.



Spiral on SiC (Sunagawa).



Radius of curvature ρ decreases to the center.
ρ should be larger than the critical value rc.

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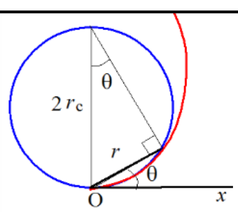
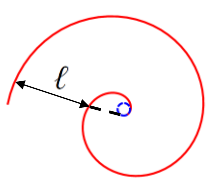


Inner circle with r=rc

$r = 2r_c \sin\theta$

➔ $r_c = \frac{\Omega_2\beta}{\Delta\mu}$



Archimedes Spiral

$r = 2r_c\theta$

Step separation for large θ is $\ell = 4\pi r_c \approx 12.5 r_c$

Step is moving with a step velocity. $v_0 = (K_s/k_B T)\Delta\mu$

Normal growth rate is. $V = \frac{a}{\ell/v_0} = K_s \frac{a}{4\pi k_B T\beta\Omega_2}\Delta\mu^2$

Faster than nucleation and growth.

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3.4 Morphological Instability

Ideal growth. $V = K\frac{\Delta\mu}{k_B T}$

Spiral growth: $V = K_s\frac{\Delta\mu^2}{4\pi k_B T\beta\Omega_2/a}$

Nucleation-growth: $V = V_0\frac{\Delta\mu}{k_B T}\exp\left(-\frac{\pi\beta^2\Omega_2}{3k_B T\Delta\mu}\right)$

Above TR ideal growth is expected,
but there is another effect: Morphological instability.

With a rough surface, surface kinetics is fast, but
transport in the environment matters;
heat conduction, or concentration diffusion

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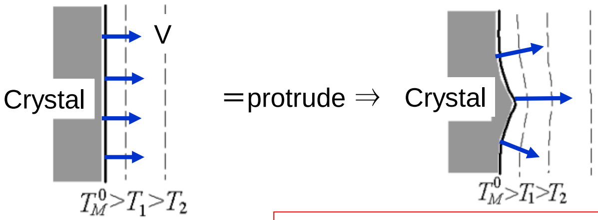
Morphological instability by Mullins-Sekerka

Crystal with a flat front is growing in undercooled melt.
→ Due to latent heat release, interface is warm; Ti> T_∞.
→ Flat interface is unstable to deformation.



Isothermals around a flat front

Near the tip,
large temperature gradient ∇T
⇒ fast heat release $J = -k\nabla T$
⇒ fast growth ⇒ instability

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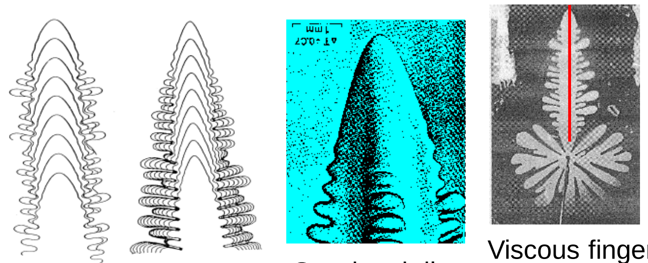
With anisotropy tip is stabilized.
⇒Regular dendrite tip grows in the direction of small interfacial stiffness. (small recovery force)



Simulation NH_4Br Succinonitrile Viscous finger + anisotropy

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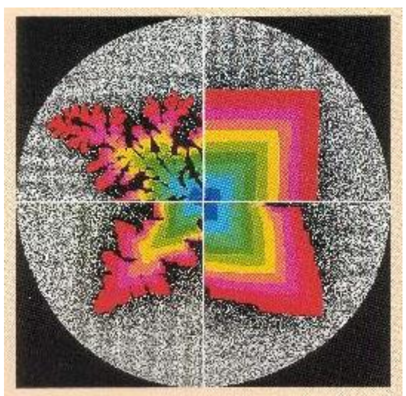
Morphological stability ⇒ Pattern formation

Fractal Dendrite



Polygonal Skeletal

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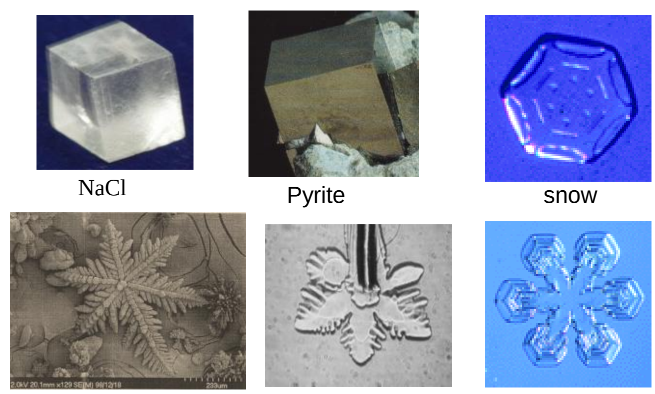
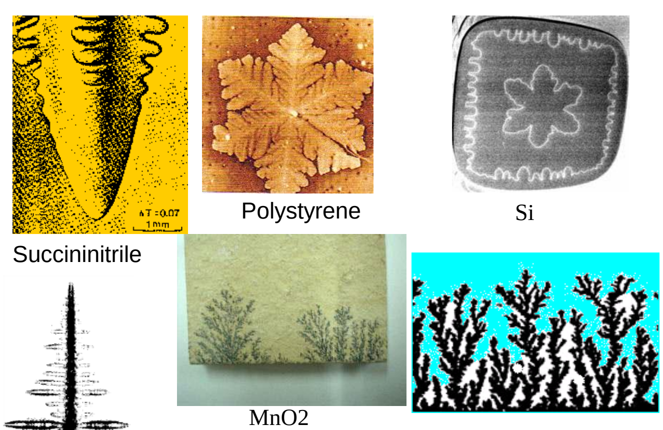
Actual crystal shapes



NaCl Pyrite snow

SrCO3 ice snow

90



Succininitrile Polystyrene Si

NH4Cl MnO2 Ag

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4. Coarsening

4.1 Geometrical selection

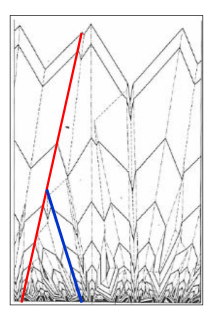
On cold wall, many crystal grains are nucleated. Grains that grow perpendicular to the wall cover tilted grains.

Number of grains N decreases as height h increases.

(1+1)d: $N \sim h^{-1/2}$
(2+1)d: $N \sim h^{-4/5}$

Mean Field Approx.

Thijssen, Knops, Dammer (1992)



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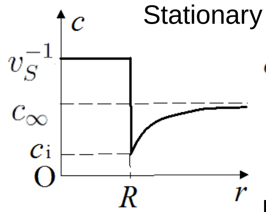
4.2 Ostwald ripening

4.2.1 Evolution of a single spherical nucleus



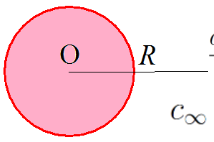
Stationary concentration distrtibution

$$c(r) = c_\infty - (c_\infty - c_i)\frac{R}{r}$$

Local eq. at interface

$$c_i = c_{eq}\left(1 + \frac{2v_S\gamma}{k_B T R}\right)$$

Radial velocity



$$\frac{dR}{dt} = v_S D \frac{\partial c}{\partial r}\Big|_R = \frac{2Dv_S^2 c_{eq}\gamma}{k_B T}\frac{1}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right)$$

Critical radius; $R_c = \frac{2v_S\gamma}{\Delta k_B T}$

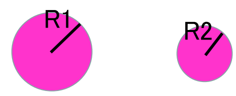
supersaturation; $\Delta = (c_\infty - c_{eq})/c_{eq}$

4.2.2 Ostwald ripening

As many crystals grow in a closed system, average concentration c∞ decreases to ceq, and critical radius Rc(t) increases.

$$\frac{dR}{dt} = \frac{\tilde{D}}{R}\left(\frac{1}{R_c(t)} - \frac{1}{R}\right)$$

If two crystal nucleus with different size R1 > R2 are growing, Δ decreases and Rc increases,



When R1>Rc>R2.

larger crystal grows at the cost of smaller one.

Ostwald ripening.

4.2.3 Lifshitz-Slyozof-Wagner theory

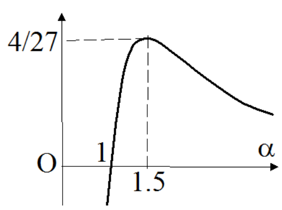
How would the Ostwald ripening proceeds as a function of time?

We assume that the characteristic nucleus size R(t) increases in proportion to Rc(t).

Assume that ratio α=R(t)/Rc(t) remain constant.

$$\frac{dR}{dt} = \tilde{D}\frac{1}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right)$$

$$\rightarrow R_c^2\frac{dR_c}{dt} = \tilde{D}\frac{1}{\alpha^2}\left(1 - \frac{1}{\alpha}\right)$$



Rhs is maximum at α=3/2 with a value 4D/27.

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$$R_c^2\frac{dR_c}{dt} = \frac{4}{27}\tilde{D}$$

The critical radius increases as

$$R_c(t) = (\tfrac{4}{9}\tilde{D}t)^{1/3}$$

And characteristic crystal size increases as R(t)=1.5Rc.

More quantitative and correct analysis is provided in terms of size distribution: p(R,t) by LSW.

Characteristic size is the maximum size.

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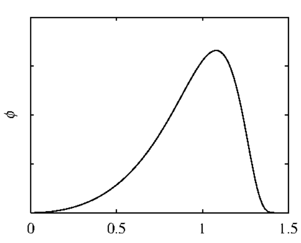
The scaled size distribution for $z = R/R_c(t)$ is

$$\phi(z,t) = R_c(t)^4 p(R,t)$$

$$= \begin{cases} Cz^2(z+3)^{-7/3}(3-2z)^{-11/3}e^{-3/(3-2z)}, & z < 3/2 \\ 0, & z > 3/2 \end{cases}$$



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Thank you very much for your attention!

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