2016/03/07 名古屋大学最終講義

結晶成長とパターン形成の物理
― 1973-2016を振り返って―

Physics of Crystal Growth and Pattern Formation

上羽牧夫
Makio Uwaha

名古屋大学理学研究科物理学教室

Background picture by H. Hibino

主な共同研究者

- 後藤芳彦(東北大), 一宮彪彦(名大), E.Williams(Maryland大), C.Thuermer(Maryland大), 宮下哲(富山医科歯科大), 本間芳和(NTT), 日比野浩樹(NTT), 佐藤一雄(名大), 須藤孝一(阪大), 塚本勝男(東北大), 新家寛正(東北大)ほか
- **G. Baym(Illinois大), P. Nozieres(ILL)**, 後藤芳彦(東北大), **齋藤幸夫(慶大)**, 入澤寿美(学習院大), **佐藤正英(名大, 金沢大)**, T. Einstein(Maryland大), **勝野弘康(名大, 立命館大)**, Gosalvez(名大, HUT), 勝野喜以子(学習院大), 三浦均(東北大, 名市大)ほか
- 関進(東北大), 西野賢一朗, 松井裕一, 渡邉克博, 上村英明, 加藤亮, 向井昌紀, 小山克信, 近藤信二, 川口将司ほか

Contents

- 大学院時代(1973-1980)
- 流浪のポスドク時代(1980-1985)
- 助手時代(東北大, ILL; 1985-1992)
- 名大時代(1985-2016)

大学院＋ (1973-1980)

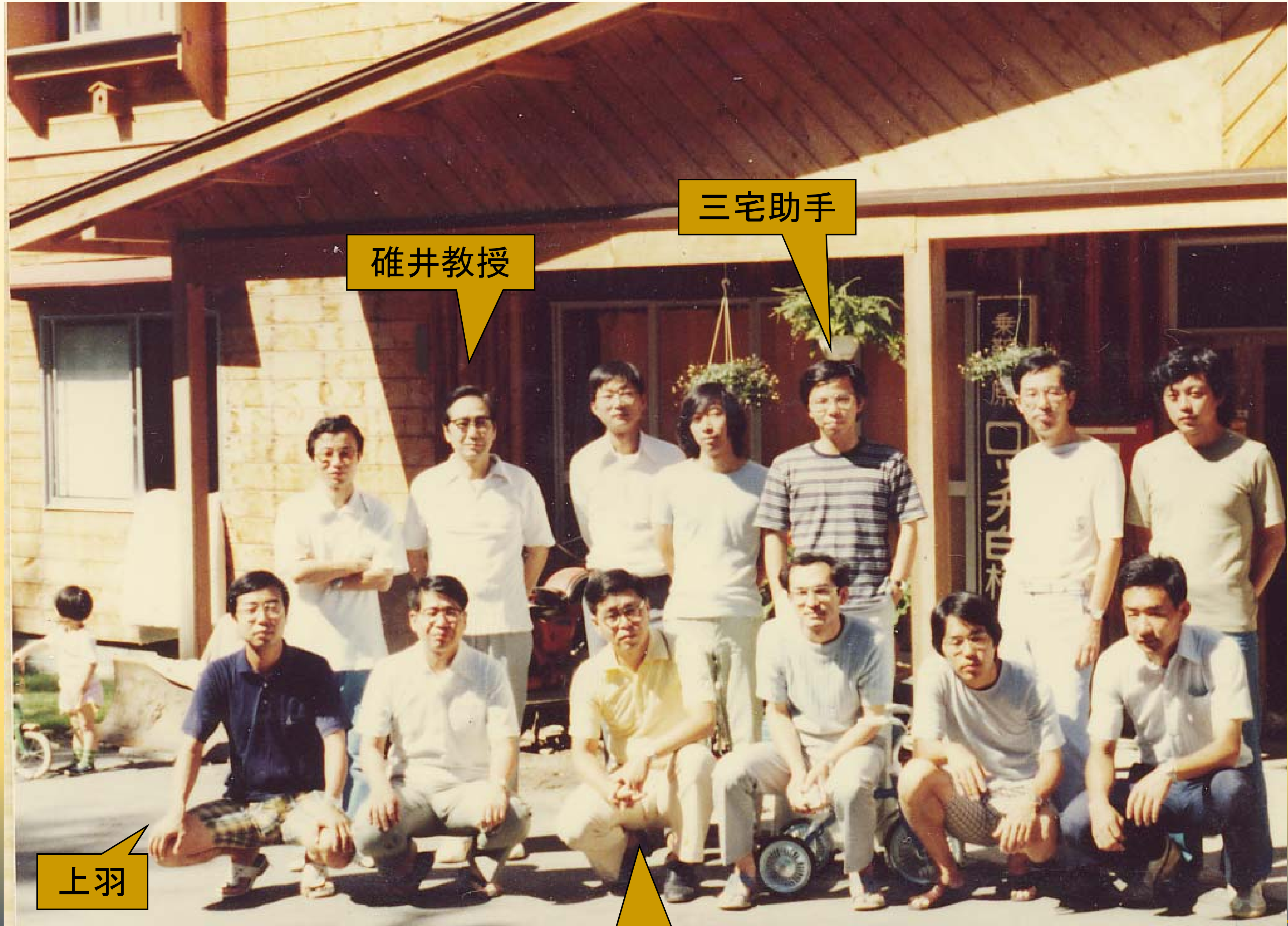
碓井恒丸教授

山田一雄助教授

長岡洋介助教授

40年前の名大物理教室

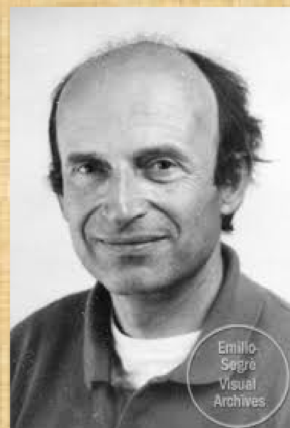
- 物理教室の民主主義
- 自由放任
- 就職難



1979年 S研夏の学校 乗鞍

流浪のポスドク時代 (5年間)
University of Illinois (1980-1982)
Institut Laue-Langevin (1982-1985)

Gordon Baym 教授



Philippe Nozieres 教授

Interface of quantum solid and liquid

名大時代に興味を持った論文

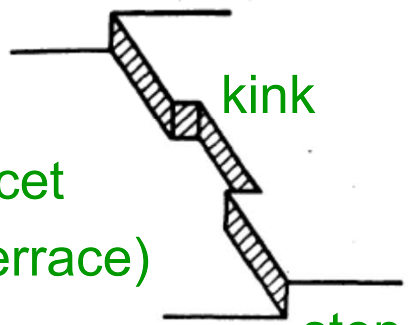
Equilibrium shape and oscillations of the surface of quantum crystals

A. F. Andreev and A. Ya. Parshin

S. I. Vavilov Institute of Physics Problems, Academy of Sciences USSR, Moscow
(Submitted 20 April 1978)
Zh. Eksp. Teor. Fiz. **75**, 1511–1516 (October 1978)

Allowance for the quantum effects is used to explain the experimentally observed absence of faceting of helium crystals. It is shown that weakly damped melting and crystallization waves may be propagated along an He^4–liquid interface. The temperature dependence of the surface tension is found at low temperatures.

PACS numbers: 67.80. – s



kink as quasiparticle

crystallization wave

$$\omega^2 = \left(\alpha + \frac{\partial^2\alpha}{\partial\varphi^2}\right)\frac{\rho_2}{(\rho_1-\rho_2)^2}k^3.$$

kinetic growth coefficient

$$V = K\Delta\mu$$

$$\gamma = \frac{\rho_1\rho_2 k}{2mK(\rho_1-\rho_2)^2}.$$

Interface of quantum solid and liquid

衝撃の論文

Crystallization waves in He^4

K. O. Keshishev, A. Ya. Parshin, and A. B. Babkin

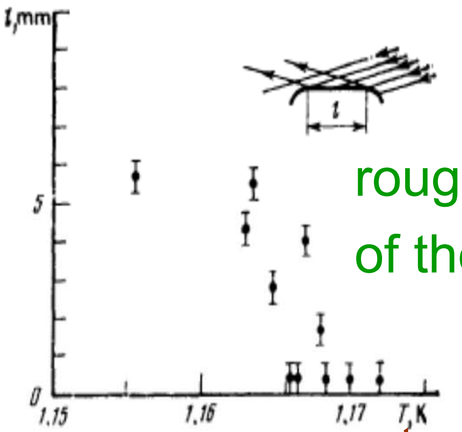
Institute of Physics Problems, USSR Academy of Sciences

(Submitted 16 July 1980)
Zh. Eksp. Teor. Fiz. **80**, 716–728 (February 1981)

The spectrum of crystallization waves in He^4 and the frequency and temperature dependences of their damping are determined. The surface energy on the liquid–crystal interface exhibits a noticeable anisotropy and depends little on temperature in the 0.36–1 K range. It is established that below 1.2 K the equilibrium shape of the He^4 crystal contains both rounded and flat parts.

PACS numbers: 64.70.Dv

facet size

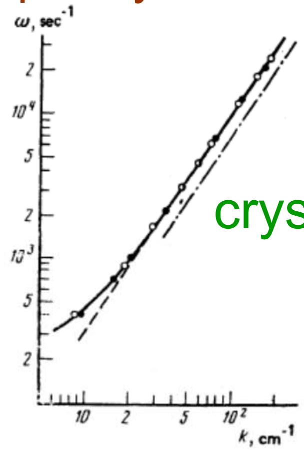


roughening transition
of the (0001) facet

temperature

FIG. 8. Temperature dependence of the size of the flat section.

frequency



crystallization wave

wavelength

FIG. 11. Spectrum of crystallization waves for two samples. Sample No. 1: ●) $T = 0.505$ K, ○) $T = 0.360$ K, $\tilde{\alpha} = 0.21$ erg/cm^2. Sample No. 2—dash-dot line, $\tilde{\alpha} = 0.097$ erg/cm^2.

Interface of quantum solid and liquid

固体表面弾性波との結合

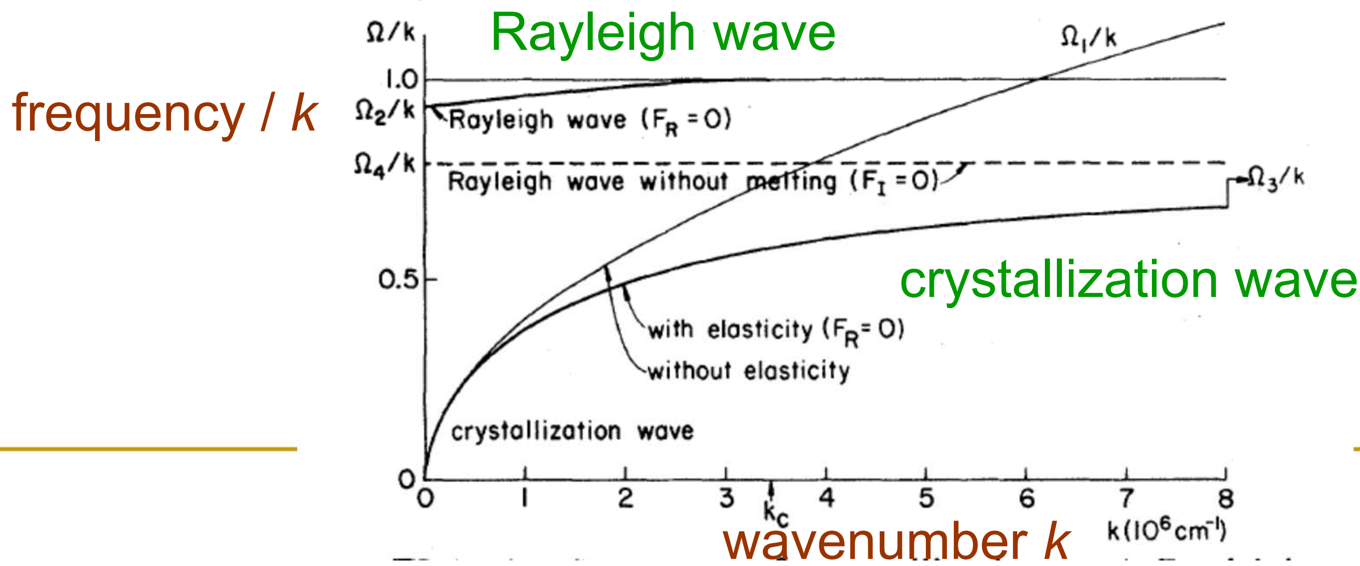
PHYSICAL REVIEW B VOLUME 26, NUMBER 9 1 NOVEMBER 1982

Theory of crystallization waves in ^{4}He at finite frequency

Makio Uwaha and Gordon Baym
Department of Physics and Materials Research Laboratory,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 11 May 1982)

We determine the spectrum of crystallization waves and Rayleigh waves at the interface between superfluid and solid ^{4}He, taking into account the effect of elasticity and the finite-growth coefficient of the crystal. For $k \gtrsim 10^6$ cm^{-1} the coupling between these two modes significantly changes the entire spectrum.



J. Physique **47** (1986) 263-271 FÉVRIER **1986**, PAGE 263

Interface of quantum solid and liquid

Physics Abstracts
67.80 — 67.40 — 68.10 — 47.20

結晶化波の流れによるドップラーシフトと界面不安定

Flow-induced instabilities at the superfluid-solid interface of ^{4}He

M. Uwaha and P. Nozières

Journal of Experimental and Theoretical Physics, Vol. 95, No. 3, 2002, pp. 455–461.
Translated from Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 122, No. 3, 2002, pp. 530–537.

理論の16年後

FLUIDS

The Instability of the Surface of Helium Crystal in a Superfluid Flow

L. A. Maksimov and V. L. Tsymbalenko*
Russian Research Centre Kurchatov Institute, pl. Kurchatova 1, Moscow, 123182 Russia
**e-mail: vlt@isssph.kiae.ru*
Received April 24, 2002

Abstract—The problem on crystal growth under conditions of normal incidence of fluid on the boundary is investigated for stability. The threshold velocity of the emergence of instability is found; at low temperatures, this velocity proves to be much lower than the sound velocity. The stability is examined of the shape of cylindrical crystal in a fluid flow parallel to the crystal axis. The behavior of the atomically rough surface of crystal helium is experimentally investigated in a jet of fluid in the temperature range from 1 to 1.4 K, where the emergence is observed of an instability of the type previously predicted by Kagan, as well as by Nozieres and Uwaha. Observations reveal that, below the roughening transition, the (0001) basal face is stable in a jet of fluid. © *2002 MAIK "Nauka/Interperiodica".*

Change of a crystal shape viewed as moving steps M. Uwaha, P. Nozieres (1985)

Morphology and Growth Unit of Crystals, edited by I. Sunagawa, pp. 17–35.

結晶の平衡形をステップに働く力のバランスとして理解する

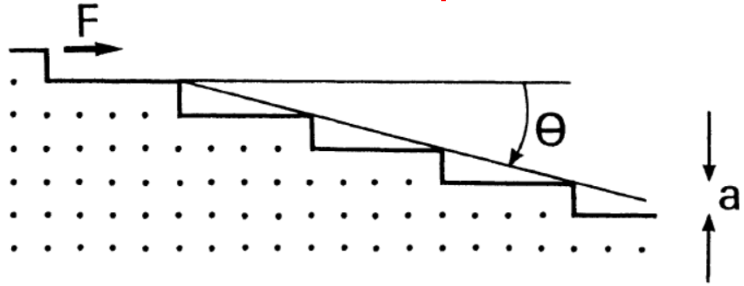
CRYSTAL SHAPES VIEWED AS MECHANICAL EQUILIBRIUM OF STEPS

M. UWAHA[+] and P. NOZIÈRES

Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France

A crystal surface below the roughening temperature T_R tends to develop steps, whose thickness ξ diverges at T_R. For a low angle vicinal surface ($\xi n < 1$, n: step density), the crystal shape is viewed as "mechanical" equilibrium of these steps. We study forces acting on a step and their relation to the crystal shape. Such an approach is extended to describe steady growth shapes under the assumption that bulk processes such as diffusion can be neglected, as is the case for ^{4}He. We study, particularly, the shape and melting rate near the stability threshold of a facet and find different melting laws depending on the step interaction.

external force ← supersaturation



surface energy $\gamma(\theta) = \cos\theta \ E(n)$

step chemical potential $\zeta(n) = \dfrac{\mathrm{d}E}{\mathrm{d}n}$

chemical pot. gradient

$$F' = -\frac{\partial \zeta}{\partial x} = -E''(n)\,\frac{\partial n}{\partial x}$$

force balance

→ equilibrium shape $F' + F = 0$

助手時代 (6年間)
東北大金属材料研究所
(1985-1992)
Institut Laue-Langevin
(1990-1991)


上羽
小松　啓　教授

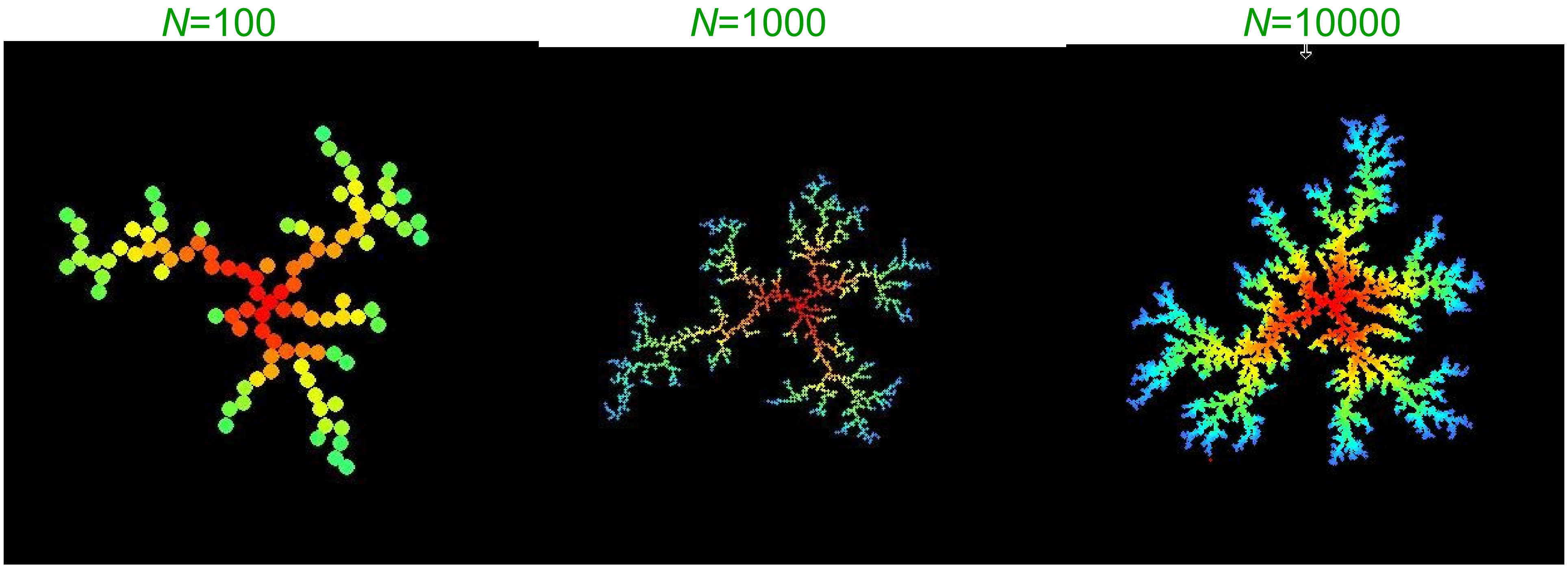
Fractal aggregation in a diffusion field (1988-2005)

拡散律速凝集体 DLA
(diffusion-limited aggregation)

Fractal: 大きいクラスターも小さいクラスターも似た形，
パターンの小さな部分と大きな部分は似た形：
自己相似

10 倍大きなクラスターは 10^{D_f} 倍の粒子をふくむ．

フラクタル次元：D_f $N \sim r^{D_f}$



Growth from a lattice gas: velocity selection via fractal dimension of DLA
M.Uwaha, Y. Saito (1988)

PHYSICAL REVIEW A VOLUME 40, NUMBER 8 OCTOBER 15, 1989

Aggregation growth in a gas of finite density: Velocity selection via fractal dimension of diffusion-limited aggregation

Makio Uwaha
Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980, Japan

Yukio Saito
Department of Physics, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan

(Received 10 February 1989; revised manuscript received 15 June 1989)

The structure and dynamics of an aggregation have been studied when the aggregate grows from a lattice gas with a nonzero gas density n_g. At low n_g and for a short length scale up to ξ, the structure of the aggregation is fractal and similar to the diffusion-limited aggregation (DLA). For a large length scale it is compact and has a nonzero asymptotic density. The steady growth rate V in d-dimensional space is inversely proportional to the characteristic length ξ, and depends on the density as $V \sim \xi^{-1} \sim n_g^{1/(d-D_f)}$, with D_f being the fractal dimension of DLA. Extensive Monte Carlo simulations in two dimensions confirm the above theoretical hypothesis of the velocity selection mechanism with $D_f = 1.71$. The interfacial width w is also found to be compatible with the expectation $w \propto n_g^{-1/2(d-D_f)}$.

$$V \sim n_g^{1/(d-D_f)}$$

齋藤幸夫(慶應大)

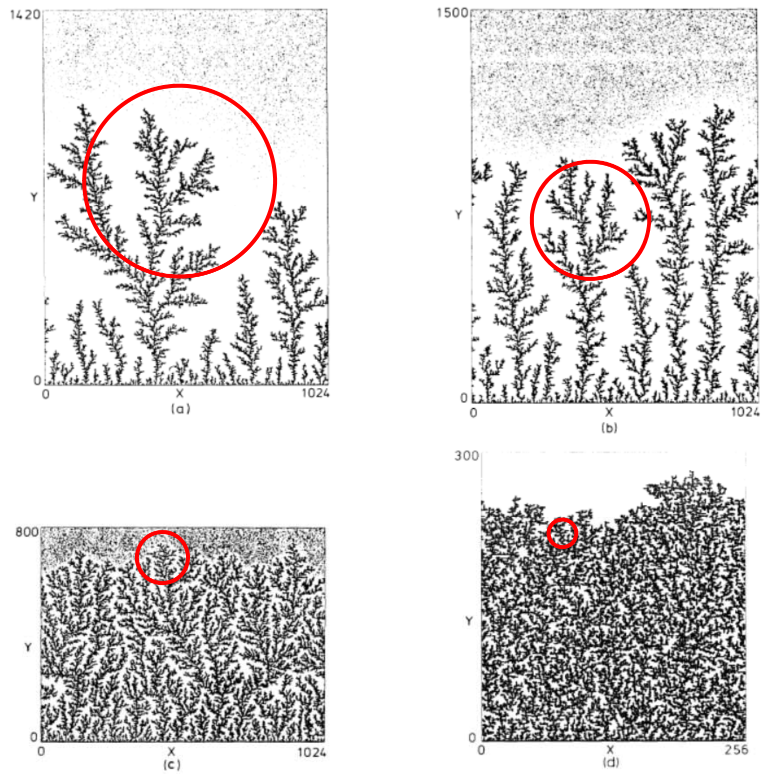
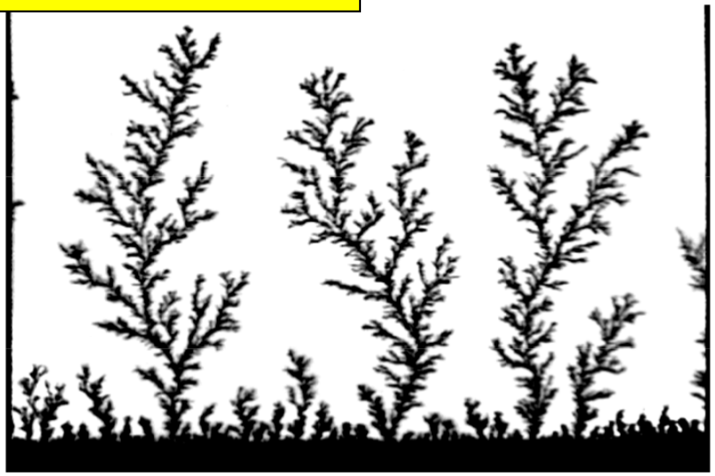


FIG. 2. Aggregations from various gas densities, n_g = (a) 0.08, (b) 0.10, (c) 0.20, (d) 0.40, (e) 0.80, and (f) 1.0. (f) Only solid atoms are shown.

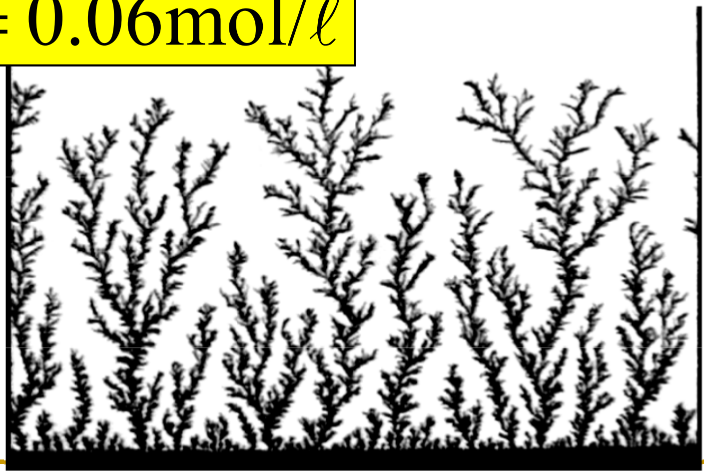
DLAのフラクタル次元が成長則を決める

銀の森の成長

$c = 0.04\mathrm{mol}/\ell$

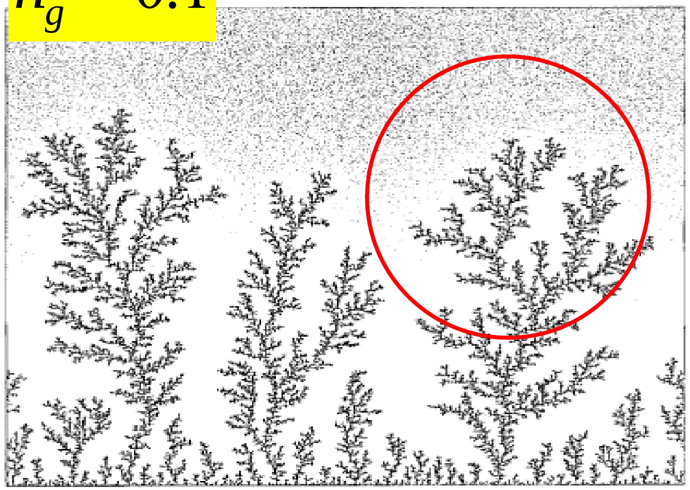


$c = 0.06\mathrm{mol}/\ell$

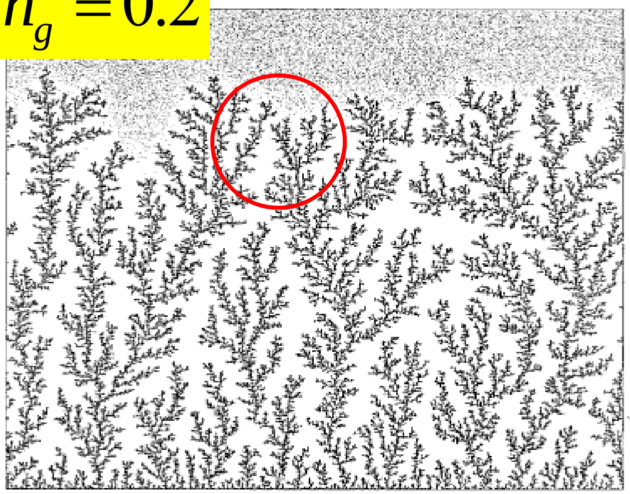


S. Miyashita, Y. Saito and M. Uwaha,
J. Cryst. Growth **283** (2005) 533

$n_g = 0.1$

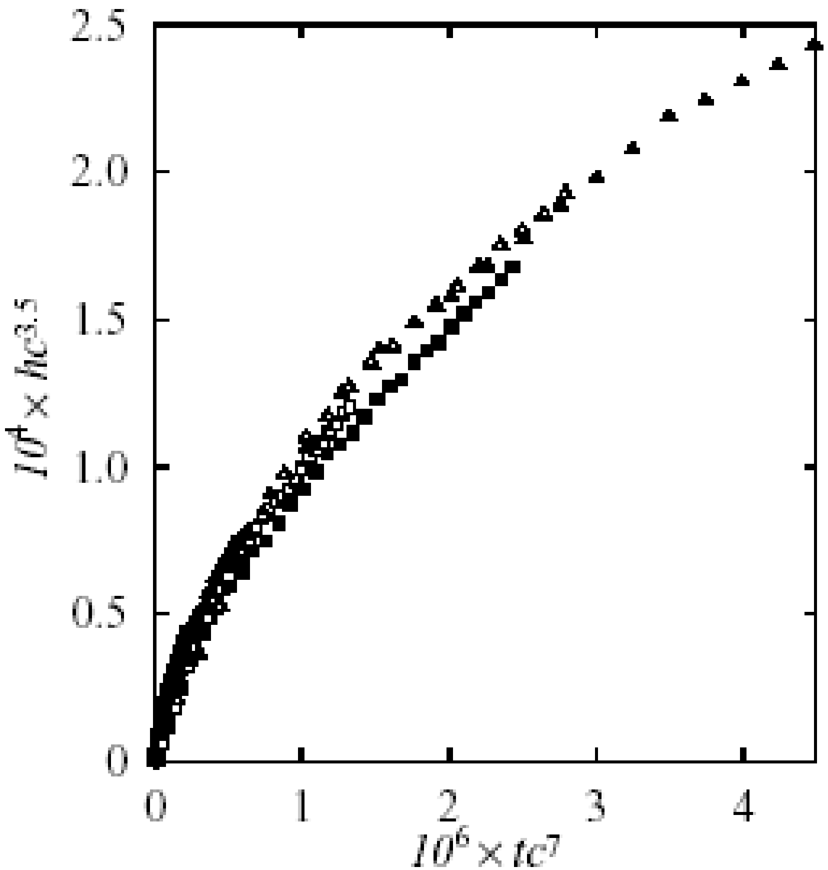


$n_g = 0.2$



M. Uwaha and Y. Saito,
Phys. Rev. A **40** (1989) 4716

理論の予想する濃度-大きさ-時間のスケーリング則



$$h(t)c^{\nu} = f(tc^{2\nu})$$

$$\nu = \frac{1}{d - D_f} = 3.5$$

h: 銀樹の先端までの距離
c: 溶液濃度
d: 空間次元
D_f: 拡散律速凝集体(DLA)の
フラクタル次元

S. Miyashita, Y. Saito and M. Uwaha,
J. Cryst. Growth **283** (2005) 533

Shape relaxation of a small faceted crystal (1988-2001)

結晶の平衡形への緩和

荒れた面に囲まれたファセットのない結晶

τ: relaxation time

R: characteristic size

- 環境相への蒸発と環境相からの凝集

$$\tau \propto R^2$$

- 環境相内でのバルクの拡散（溶液からの成長）

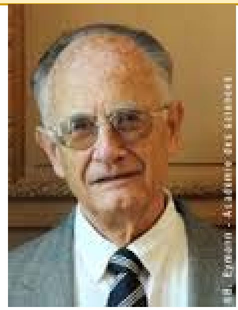
$$\tau \propto R^3$$

- 結晶の表面での拡散(蒸発が無視できるとき)

$$\tau \propto R^4$$

W. W. Mullins, in *Metal Surfaces* (AIME, 1963), p.17

Relaxation of a rough surface by surface diffusion J. Villain (1986)



EUROPHYSICS LETTERS 1 October 1986
Europhys. Lett., **2** (7), pp. 531-537 (1986)

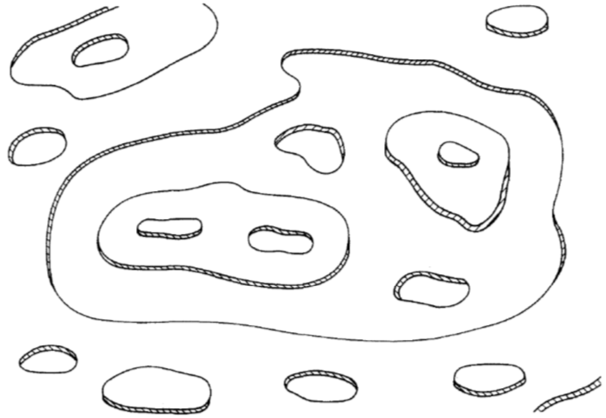
Healing of a Rough Surface at Low Temperature.

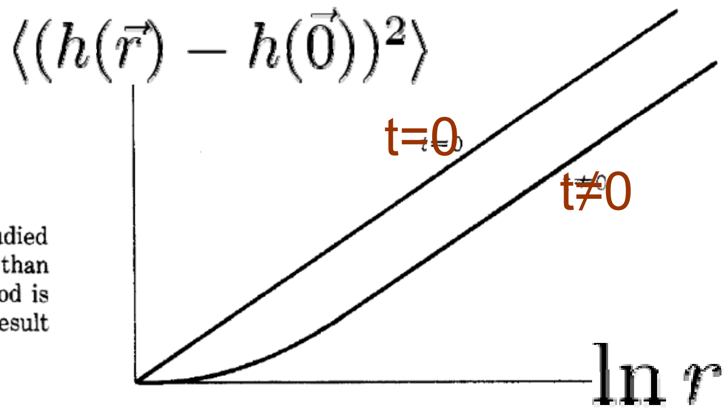
J. VILLAIN
Institut für Festkörperforschung, Kernforschungsanlage Jülich
Postfach 3980, 5170 *Jülich, BRD*

(received 28 April 1986; accepted 12 June 1986)

PACS. 68.20. – Solid surface structure.
PACS. 66.30. – Diffusion in solids.
PACS. 05.40. – Fluctuation phenomena, random processes, and Brownian motion.

Abstract. – The smoothening kinetics of a rough surface due to surface diffusion is studied theoretically. After a long time t, the surface is predicted to be flat on lengthscales smaller than $R(t) \sim t^{1/4}$. At higher lengthscales the roughness is almost the same as at $t = 0$. The method is analogous to the Lifshitz-Slyozov theory of nucleation in a supersaturated solution. Our result $R \sim t^{1/4}$ disagrees with existing theories of smoothening.





Relaxation of crystal shapes caused by step motion
M. Uwaha (1988)

Journal of the Physical Society of Japan
Vol. 57, No. 5, May, 1988, pp. 1681–1686

Relaxation of Crystal Shapes Caused by Step Motion

Makio UWAHA

Institute for Materials Research, Tohoku University,
2-1-1 Katahira, Sendai 980

(Received December 15, 1987)

Shape relaxation of a crystal facet and of vicinal faces is theoretically studied in terms of step movement. When a flat vicinal surface is perturbed, the power of wave number dependence in the relaxation time τ is determined by the bottleneck process, step movement or diffusion, and the proportionality constant depends on the relative angle of the wave vector and the steps. If a small crystal is quenched through a roughening transition, a new equilibrium shape with a facet emerges when the step loops shrink or expand. If diffusion is fast, $D_s \to \infty$, gradual flattening occurs with $\tau \propto R_c^2$ (R_c: radius of the 2D critical nucleus). If the step mobility is large, $\eta_s \to \infty$ and the transport relies on slow diffusion, a small facet appears on the top of the crystal and the facet size expands as $R_f \propto t$

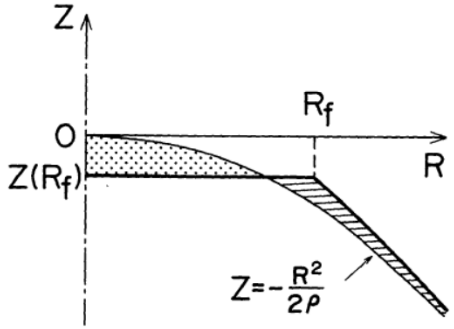


Fig. 2. Since the total mass is conserved, the volume of the initial round shape ($z = -R^2/2\rho$) and that of the faceted shape are the same.

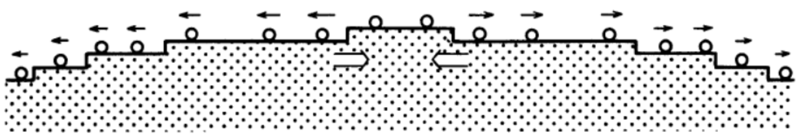


Fig. 1. Because of the outgoing diffusion flow the topmost (inmost) step loop shirinks to disappear, and the flat top (a facet) becomes larger.

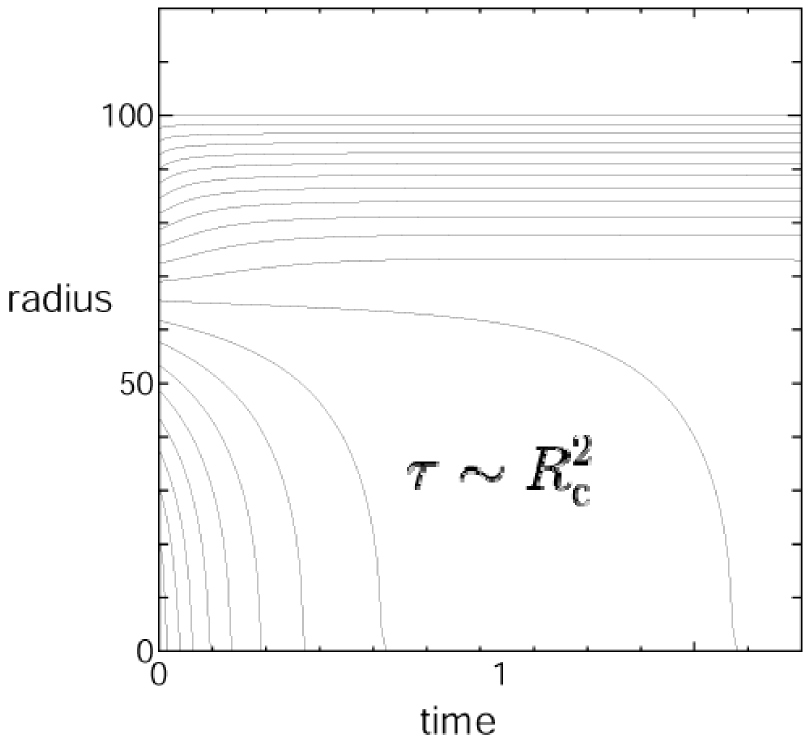
M. Uwaha, J. Phys. Soc. Jpn. **57** (1988) 1681

Emergence of a facet from the high temperature round shape

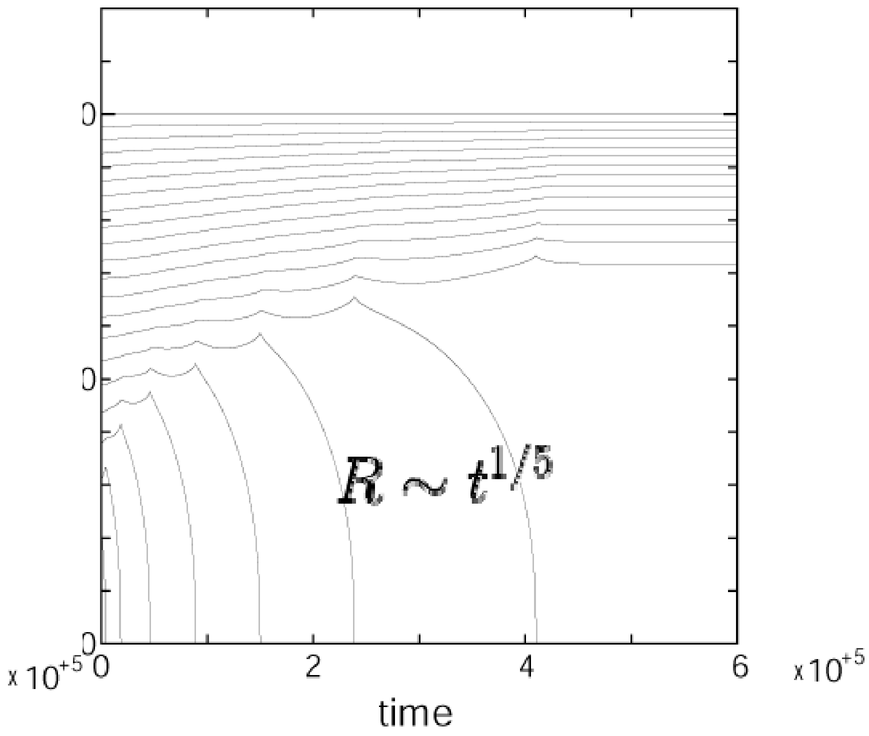
M. Uwaha, J. Phys. Soc. Jpn. **57** (1988) 1681

Change of the radii of steps

condensation and evaporation



surface diffusion



成長機構が緩和の道筋と緩和則を決める

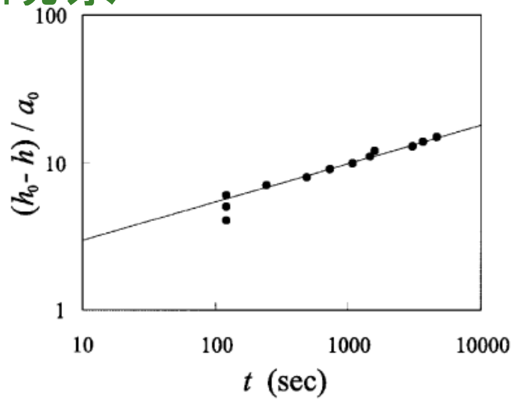
名大時代 (24年間)
教養部助教授 (1992-1993)
理学部助教授 (1993-1996)
理学研究科助教授 (1996-2007)
理学研究科教授 (2007-2016)

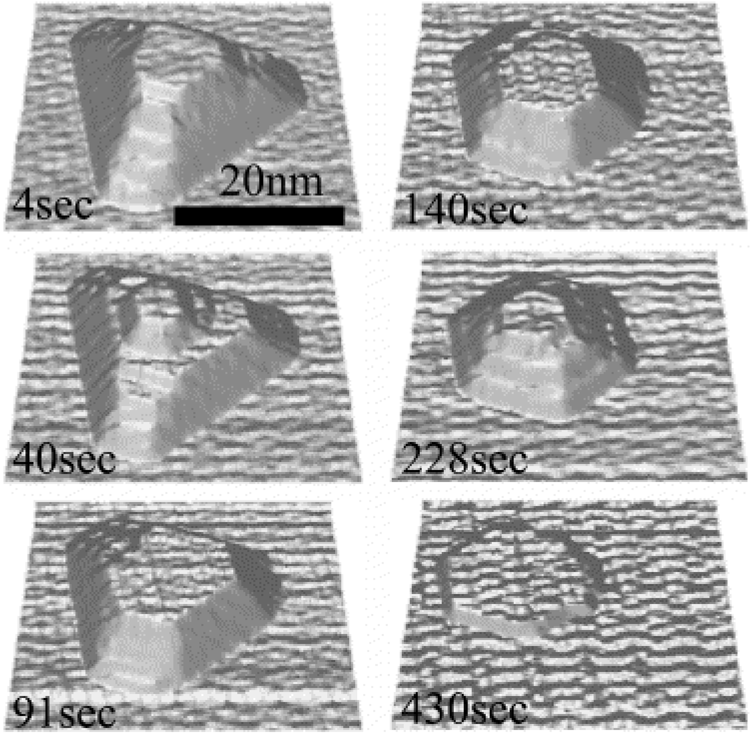

S研夏の学校 1993年7月21日 乗鞍山頂
吉岡 助手
黒田 教授
松浦 教授
三宅 (阪大)
鈴村 助教授
上羽
小林
長岡 (基研)

Si(111)ファセット上の島の崩壊 理論の12年後

ベキ緩和則の検証

- 走査トンネル顕微鏡(STM)探針による島の作成
- 島の崩壊の観察





$$h_0 - h \propto t^{1/4}$$

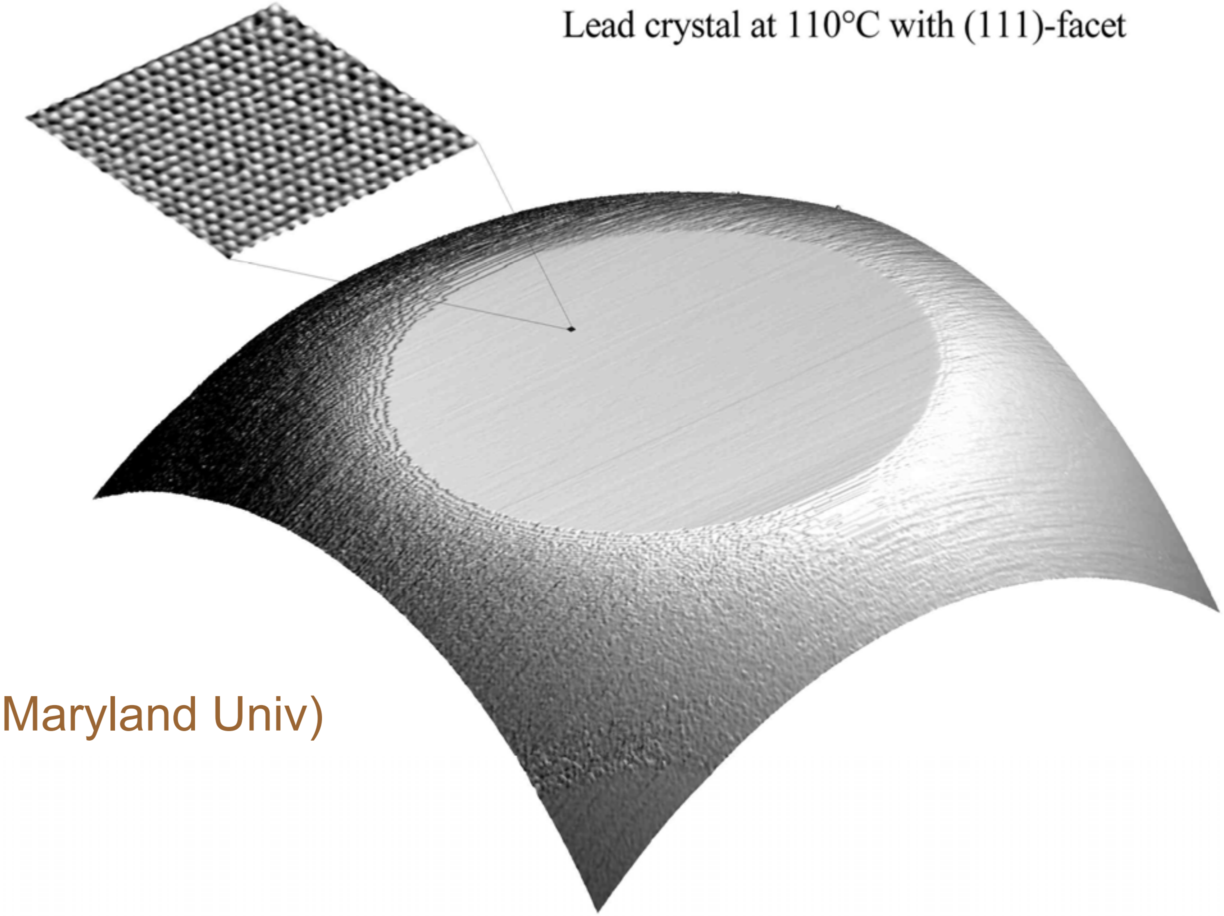
一宮彪彦（名大工）

Ichimiya, Hayashi, Williams, Einstein, Uwaha, Watanabe: Phys. Rev. Lett. 84 (2000) 3662, App. Surf. Sci. **175** (2001) 33

ファセットを持つ鉛結晶の平衡形への緩和

- 高温の平衡形から低温の平衡形へ
  →
  ファセットの拡大

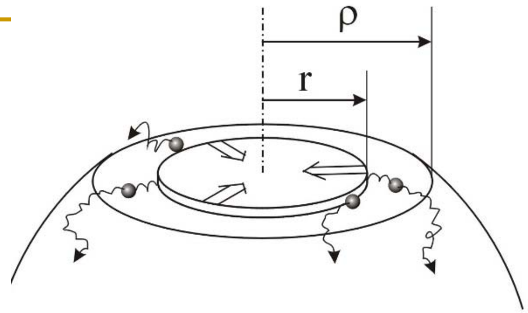
Lead crystal at 110°C with (111)-facet

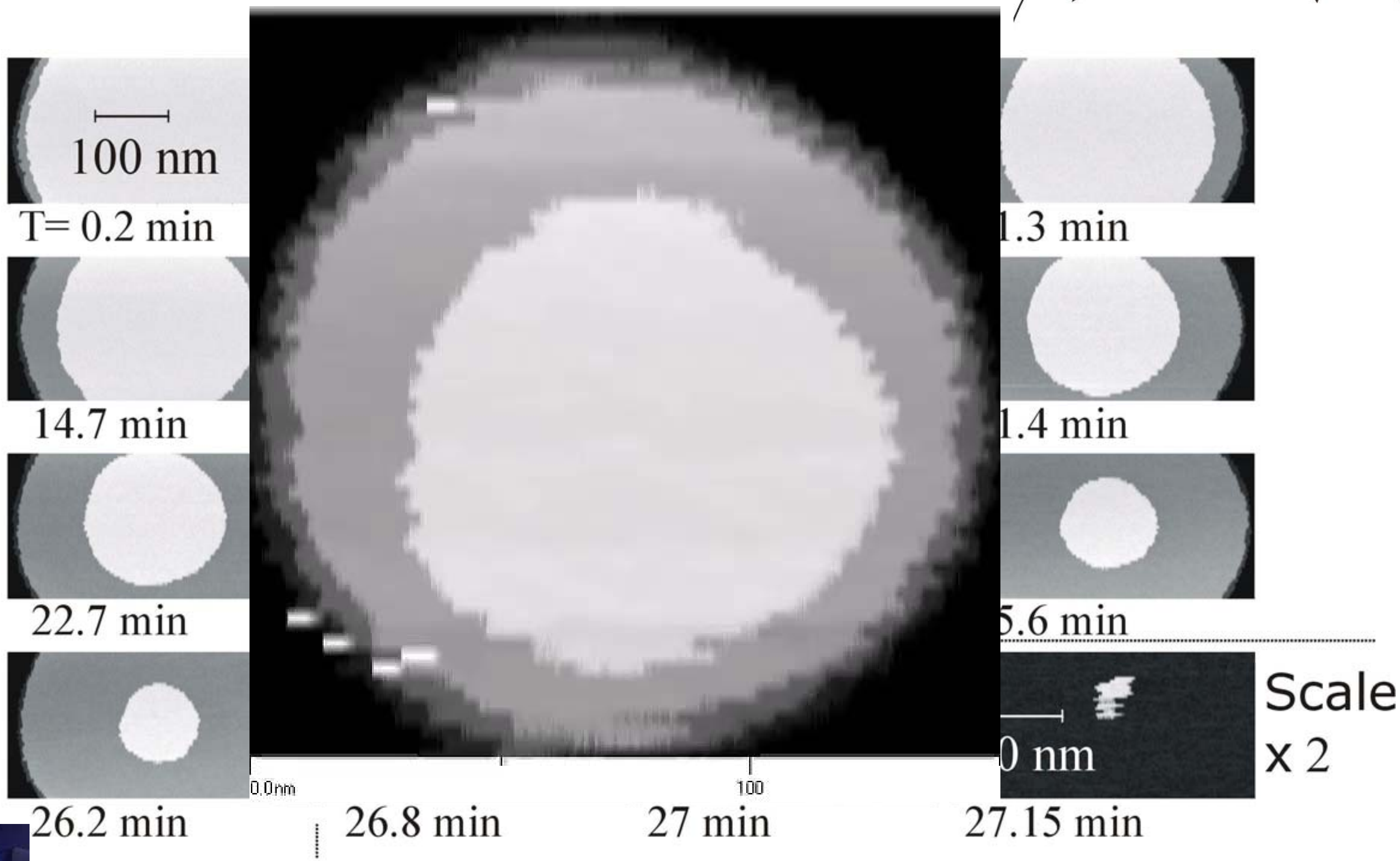


Ellen Williams (Maryland Univ)

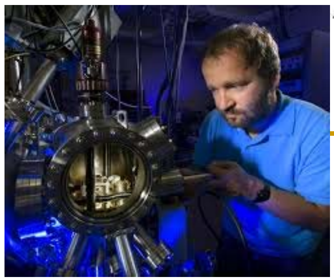
Thuermer, Reutt-Robey, Williams, Uwaha, Emundts, Bonzel: PRL **87** (2001) 186102

ファセット上のテラスの収縮





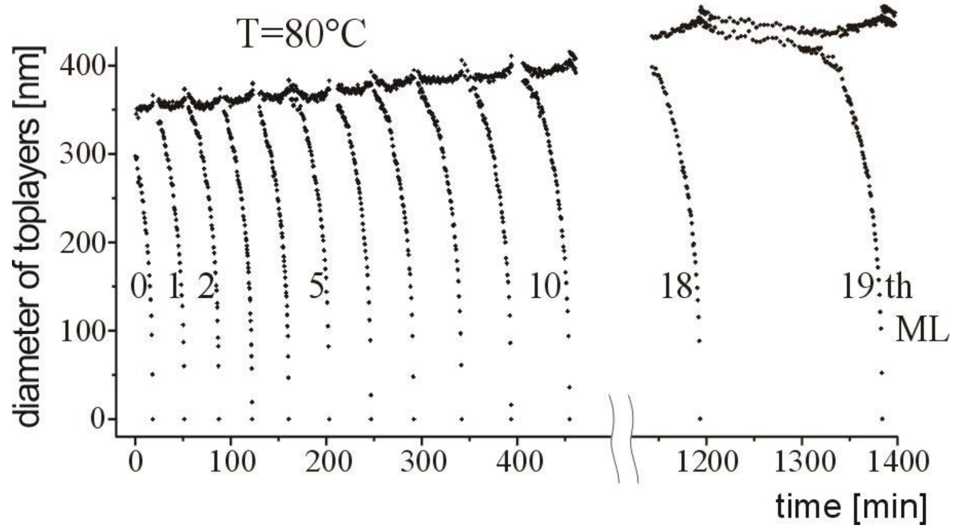
280°C から 80°Cへ急冷後の変化



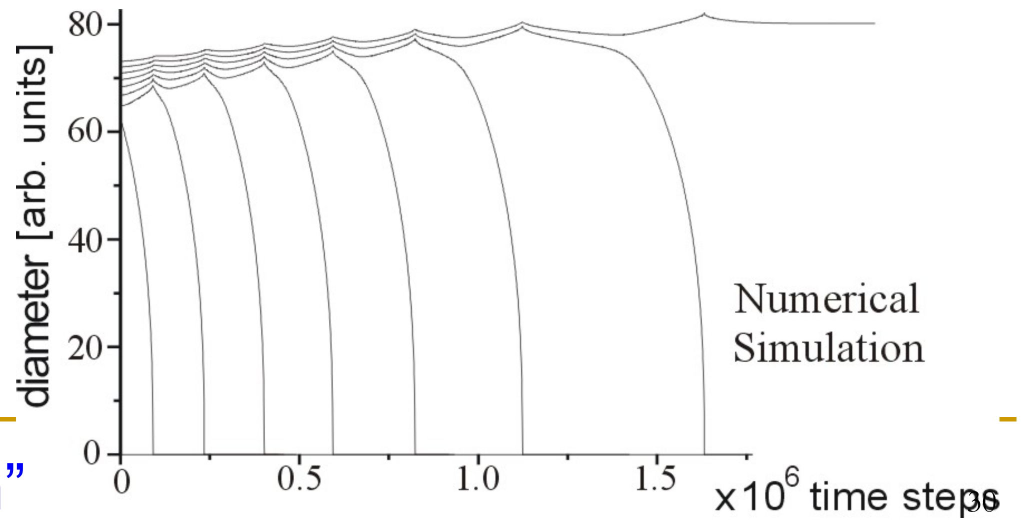
Konrad Thuermer (Maryland Univ)

高温の平衡形からのファセットの拡大

Pbでの実験



数値シミュレーション

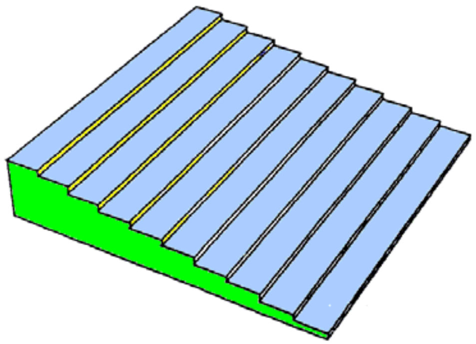


Thuermer, Reutt-Robey, Williams, Uwaha, Emundts, Bonzel: Phys. Rev. Lett. **87** (2001) 186102

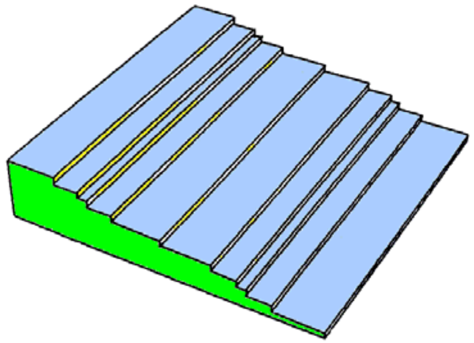
“Critical slowing down”

Wandering of steps in a diffusion field (1992-present)

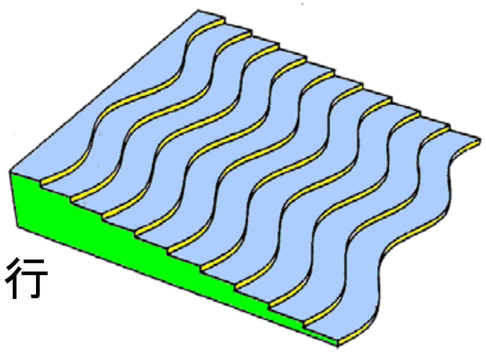
微斜面の不安定パターン



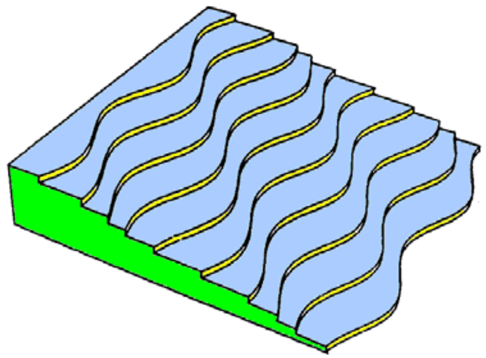
元の微斜面
vicinal face



バンチング
bunching

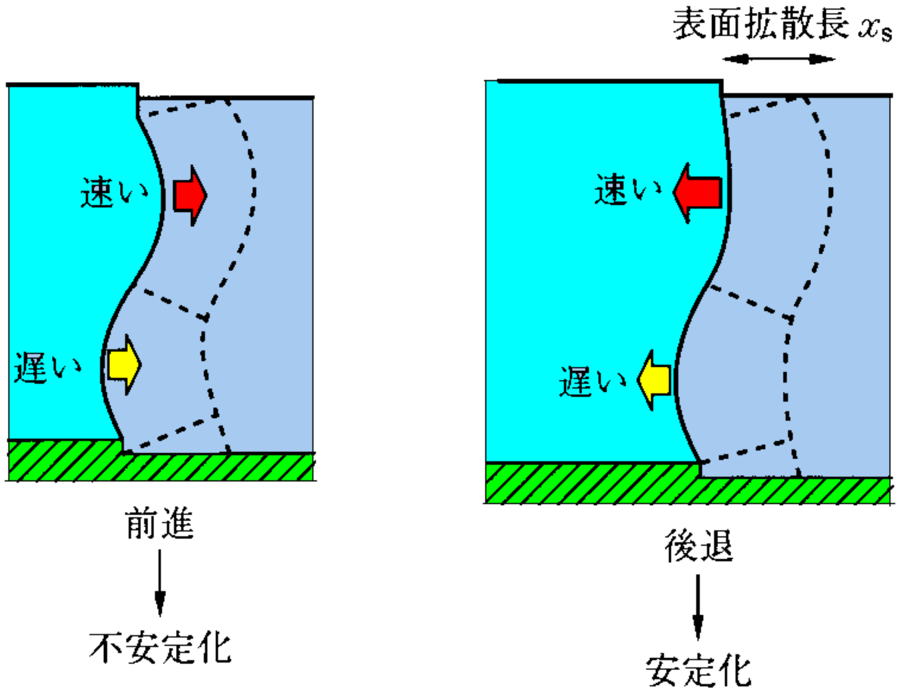


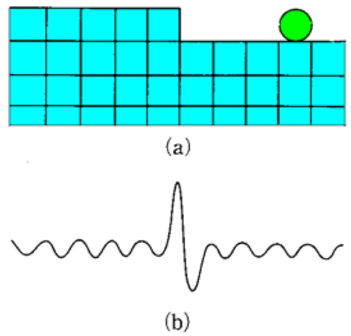
位相のそろった蛇行
inphase wandering



位相のずれた蛇行
bending

ステップの蛇行(step wandering)





ステップの断面(a)と表面原子に対するポテンシャル(b)

ES障壁

PHYSICAL REVIEW B VOLUME 41, NUMBER 9 15 MARCH 1990-II

Morphological instability of a terrace edge during step-flow growth

G. S. Bales and A. Zangwill
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430
(Received 15 November 1989)

We consider the possibility that monoatomic terrace edges undergo a morphological instability during epitaxial *step-flow* growth. A linear stability analysis predicts that such an instability *can* occur, but only when the energy barriers to adatom attachment to steps *differ* for adatoms that approach a step from *opposite* directions. The instability is diffusional in origin and manifests itself as a distinct waviness or meandering of the terrace edges as they propagate across the crystal. Our results, presented in the form of a morphological phase diagram, show that single-crystal growth on a vicinal surface can pass from stable step flow to unstable step flow to two-dimensional island nucleation and spreading as one increases the incident flux in a molecular-beam-epitaxy experiment at elevated temperature. The instability we predict should be readily distinguishable from simple thermal fluctuations.

Reflexion electron microscope observation of Si(111) vicinal face

C.Alfonso, J.M.Bermond, J.C.Heyraud, J.J.Metois (1992)

Surface Science 262 (1992) 371–381
North-Holland

surface science

The meandering of steps and the terrace width distribution on clean Si(111)

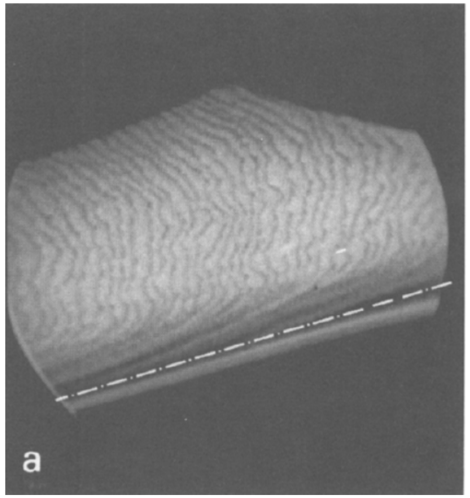
An in-situ experiment using reflection electron microscopy

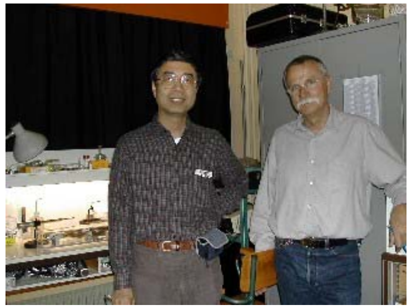
C. Alfonso, J.M. Bermond [1], J.C. Heyraud [2] and J.J. Métois

*CRMC2-CNRS *, Case 913, Campus Luminy, F-13288 Marseille Cedex 9, France*

Received 22 July 1991; accepted for publication 23 September 1991

In situ reflection electron microscopy experiments have been done on steps in thermodynamic equilibrium on clean Si(111) surfaces (900°C). Isolated steps and step trains (mean step separation from 20 to 140 nm) have been studied. From the thermal fluctuations of isolated steps we deduce a value of (roughly) 1×10^{-10} J m^{-1} for the line tension of a step at 900°C. The terrace width distribution has a standard deviation which varies linearly with the mean separation between steps up to mean step distances of 70 nm at least. Over the whole range of step mean separation the distributions are best fitted by a Gaussian law. This is attributed to step interactions decaying as Ax^{-2} (x normal distance to the step edge). The value of A is determined ($A = 4.6 \times 10^{-30}$ J m at 900°C). The nature of these interactions is briefly discussed.

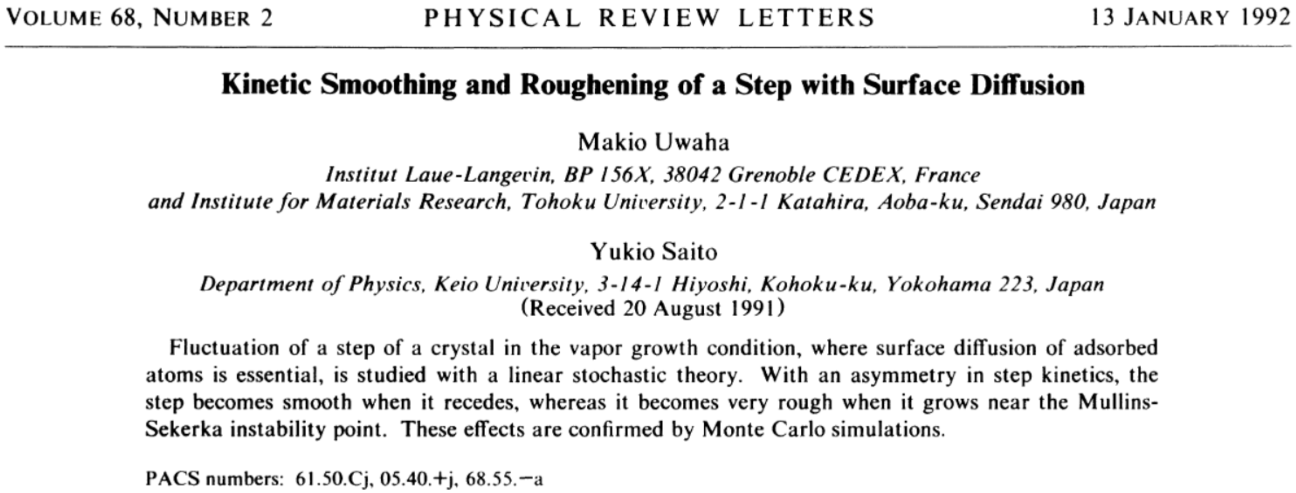




J.J. Metois (CMRC2) Marseille 1990

後退するステップでは揺らぎが小さくなる?

Kinetic smoothing and roughening of a step with surface diffusion
M.Uwaha, Y. Saito (1992)



VOLUME 68, NUMBER 2 PHYSICAL REVIEW LETTERS 13 JANUARY 1992

Kinetic Smoothing and Roughening of a Step with Surface Diffusion

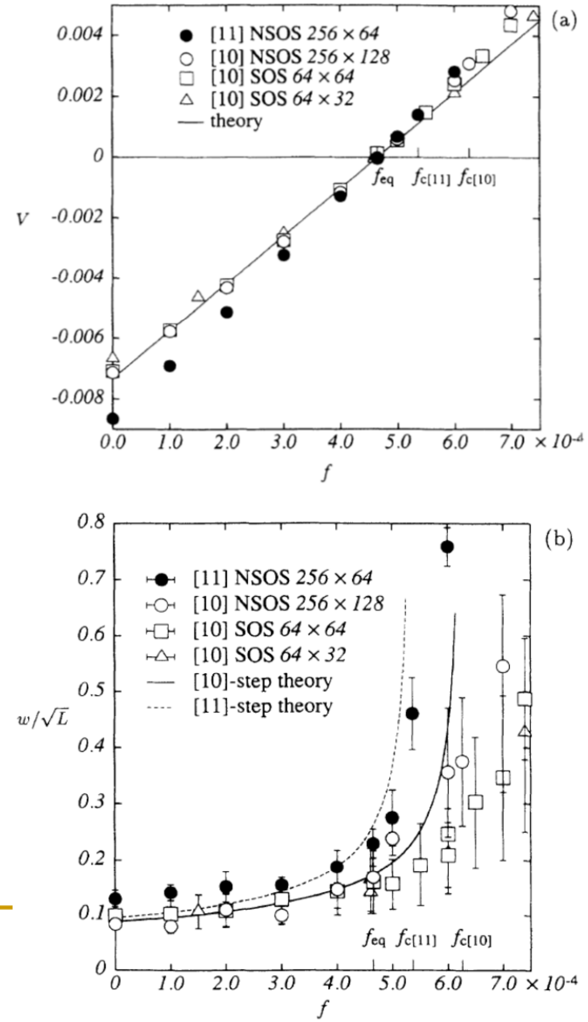
Makio Uwaha
Institut Laue-Langevin, BP 156X, 38042 Grenoble CEDEX, France
and Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980, Japan

Yukio Saito
Department of Physics, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan
(Received 20 August 1991)

Fluctuation of a step of a crystal in the vapor growth condition, where surface diffusion of adsorbed atoms is essential, is studied with a linear stochastic theory. With an asymmetry in step kinetics, the step becomes smooth when it recedes, whereas it becomes very rough when it grows near the Mullins-Sekerka instability point. These effects are confirmed by Monte Carlo simulations.

PACS numbers: 61.50.Cj, 05.40.+j, 68.55.−a

齋藤幸夫(慶大)

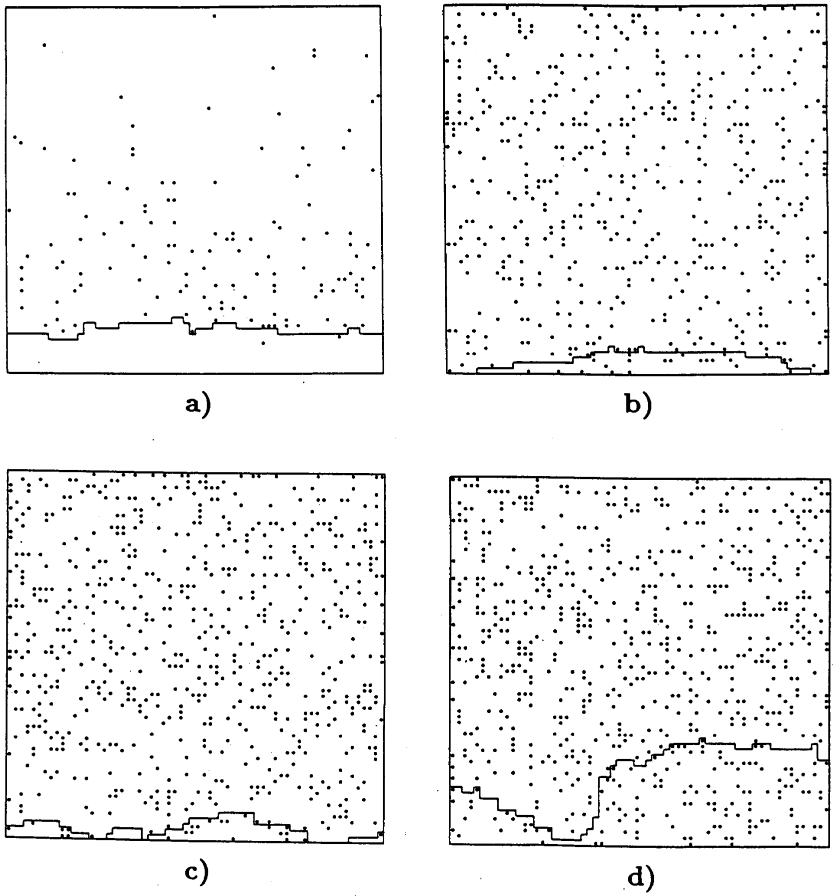


格子モデルのMCシミュレーション

スナップショット

昇華中:
ゆらぎの抑制

平衡状態



成長中:
ゆらぎの増幅

成長中:
蛇行状態

Uwaha, Saito: Surf. Sci. **283** (1993) 366

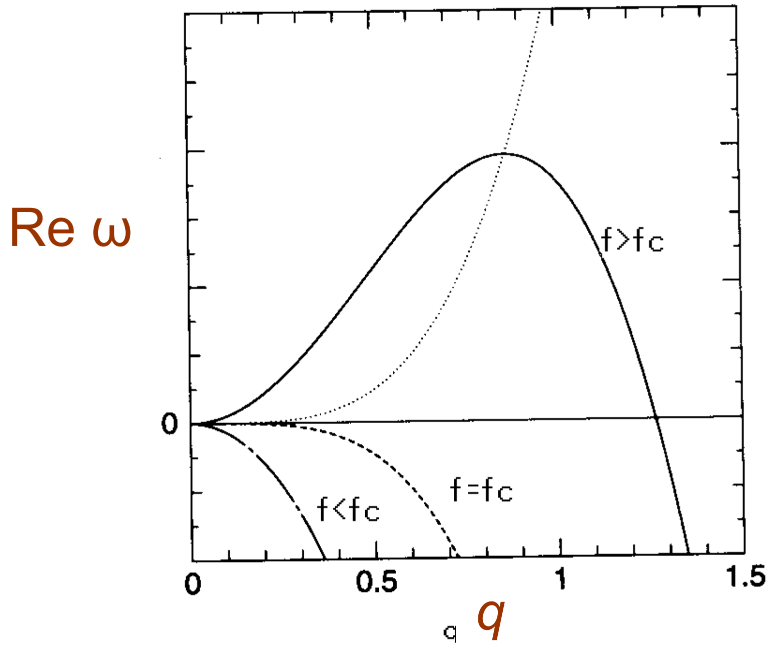
線形安定性解析

- 直線状ステップのゆらぎ

$$y(x,t) = V_0 t + \delta y_q e^{iqx+\omega_q t}$$

- ゆらぎの成長率　　　*f*: 入射頻度

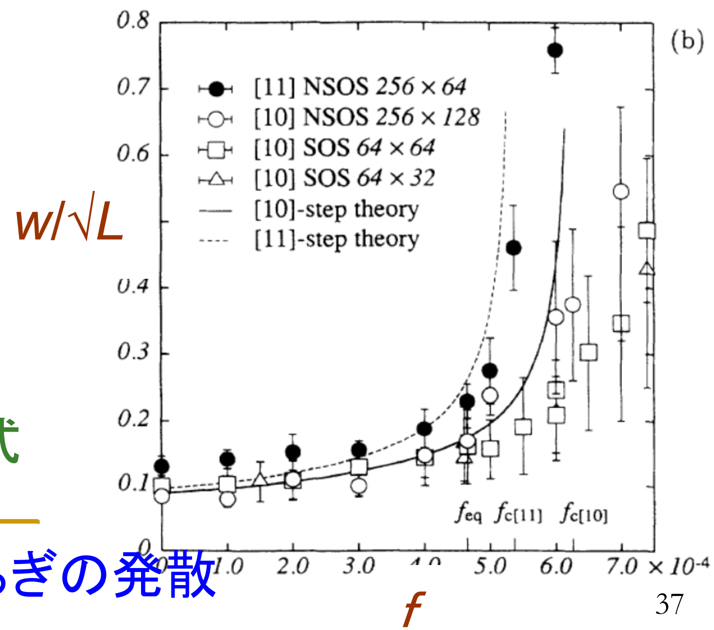
$$\omega_q \propto \varepsilon q^2 - q^4 \qquad \varepsilon \propto f - f_c$$



- 対応する線形方程式

$$\frac{\partial \delta y}{\partial t} = -\varepsilon \frac{\partial^2 \delta y}{\partial x^2} - \frac{\partial^4 \delta y}{\partial x^4}$$

- これにノイズを加えたランジュヴァン方程式



昇華時の揺らぎの抑制と不安定化近傍での揺らぎの発散

Wandering instability and nonlinearity
Y.Saito, M.Uwaha (1994)

PHYSICAL REVIEW B VOLUME 49, NUMBER 15 15 APRIL 1994-I

Fluctuation and instability of steps in a diffusion field

Yukio Saito
Department of Physics, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan

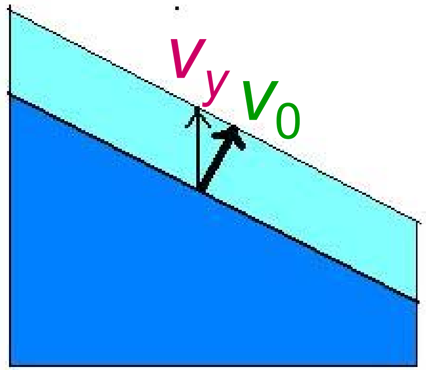
Makio Uwaha*
Department of Physics, College of General Education,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
(Received 23 July 1993; revised manuscript received 10 November 1993)

Fluctuation and morphology of steps growing in a surface diffusion field are studied theoretically and by the Monte Carlo simulation. Owing to the asymmetry in step kinetics (Schwoebel effect), a morphological instability takes place for advancing steps at a critical impingement rate f_c of gas atoms. The fluctuation of a step is reduced for receding steps with $f < f_{eq}$, and enhanced for advancing steps with $f > f_{eq}$. The width of a single step shows critical divergence at f_c. Above the instability $f > f_c$, the step motion exhibits spatiotemporal chaos, in which the crystal anisotropy influences the morphology. For a vicinal face, when the step advancement rate increases, the motion of consecutive steps is strongly correlated and the terrace width becomes stable although the fluctuation of each step is enhanced. When steps recede in sublimation, bunching of the steps is observed, which is analyzed as an instability of antiphase oscillation.

非線形効果

- 前進速度の非線形項(Kardar-Parisi-Zhang term)

$$\frac{\partial y(x,t)}{\partial t} = V_0\sqrt{1+\left(\frac{\partial y}{\partial x}\right)^2} \approx V_0\left(1+\frac{1}{2}\left(\frac{\partial y}{\partial x}\right)^2\right)$$



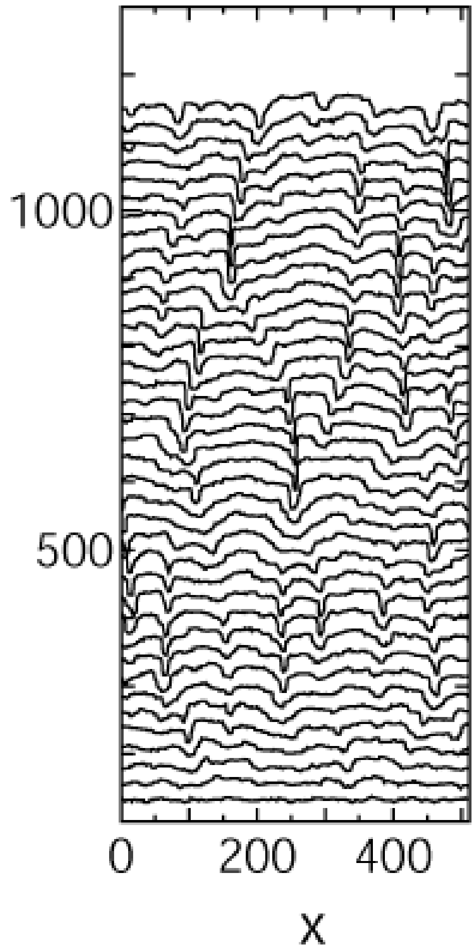
- 蔵本-Sivashinsky(KS)方程式

$$\frac{\partial \delta y}{\partial t} = -\frac{\partial^2 \delta y}{\partial x^2} - \frac{\partial^4 \delta y}{\partial x^4} + \frac{1}{2}\left(\frac{\partial \delta y}{\partial x}\right)^2$$

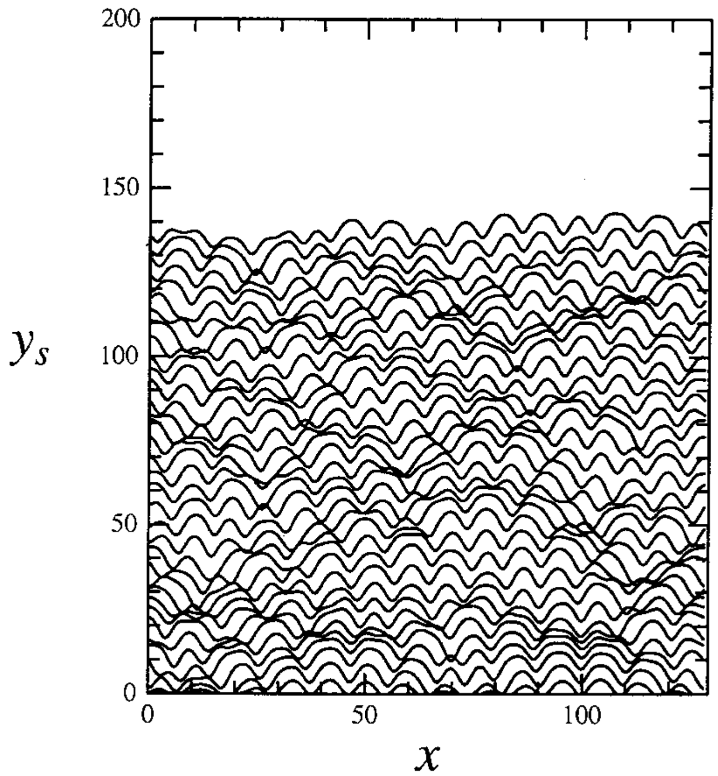
Benna, Misbah, Valance: Phys. Rev. B **47**, 7408 (1993)

KS方程式のカオス解と格子モデルのシミュレーション

格子モデル：
モンテカルロ・
シミュレーション



KS方程式のカオス解:

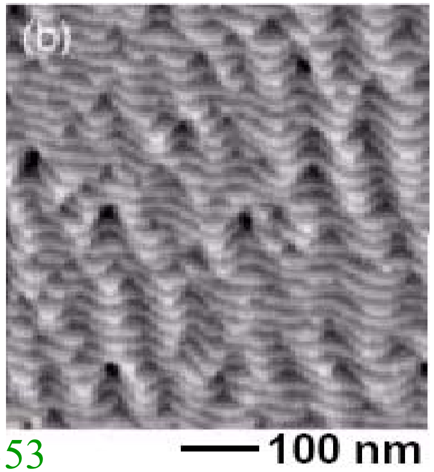


非線形効果によるカオス的振舞い

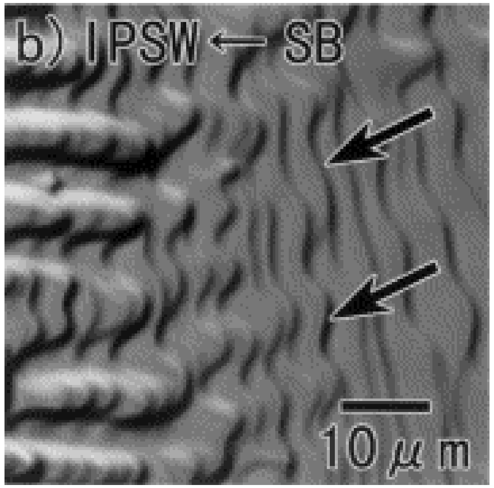
Step wandering instabilities

- Step edge diffusion barrier
- Drift of adatoms by an external field — Sato, Uwaha: J. Phys. Soc. Jpn. **65** (1996) 2146
- Difference of terrace widths in both sides
- Structural difference of terraces

Cu(1,1,17) during growth

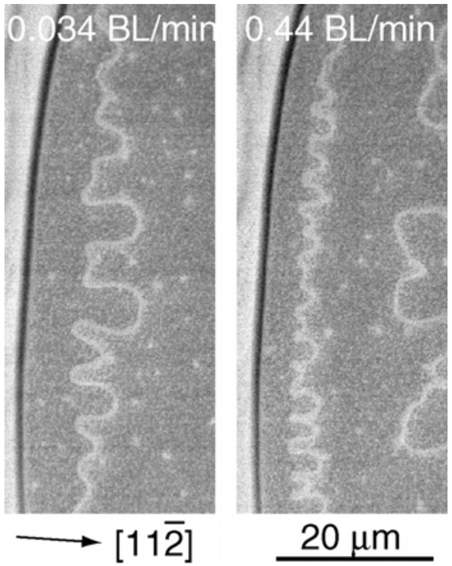


Maroutian, Douillard, Ernst, Phys. Rev. Lett **83** (1999) 4353



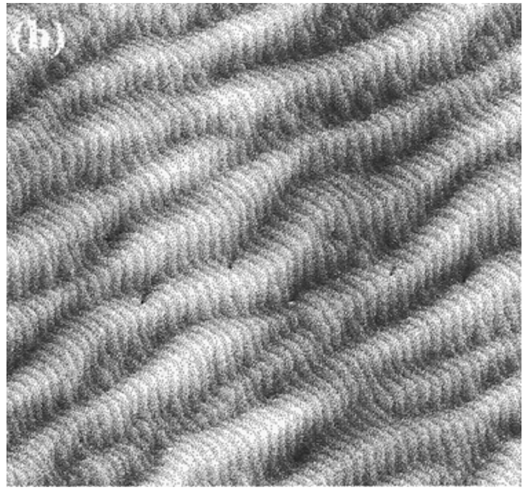
Si(111) at 950℃ with downward DC

Degawa, Nishimura, Tanishiro, Minoda, Yagi Jpn. J. Appl. Phys. 38 L308 (1999)



Si(111) during growth

Homma, Finnie, Uwaha: Surf. Sci. **492** (2001) 125



Si(111) at 860℃ during growth

Hibino, Homma, Uwaha, Ogino, Surf. Sci. **527** (2003) L222

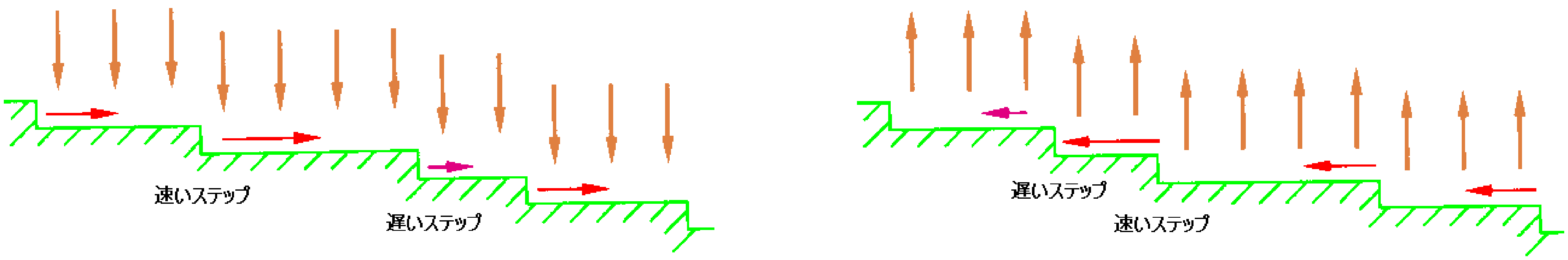
Bunching of steps in a diffusion field (1992-2008)

ステップ･バンチング(step bunching)

ステップバンチングの発生(ES効果の場合)

Schwoebel(1966)

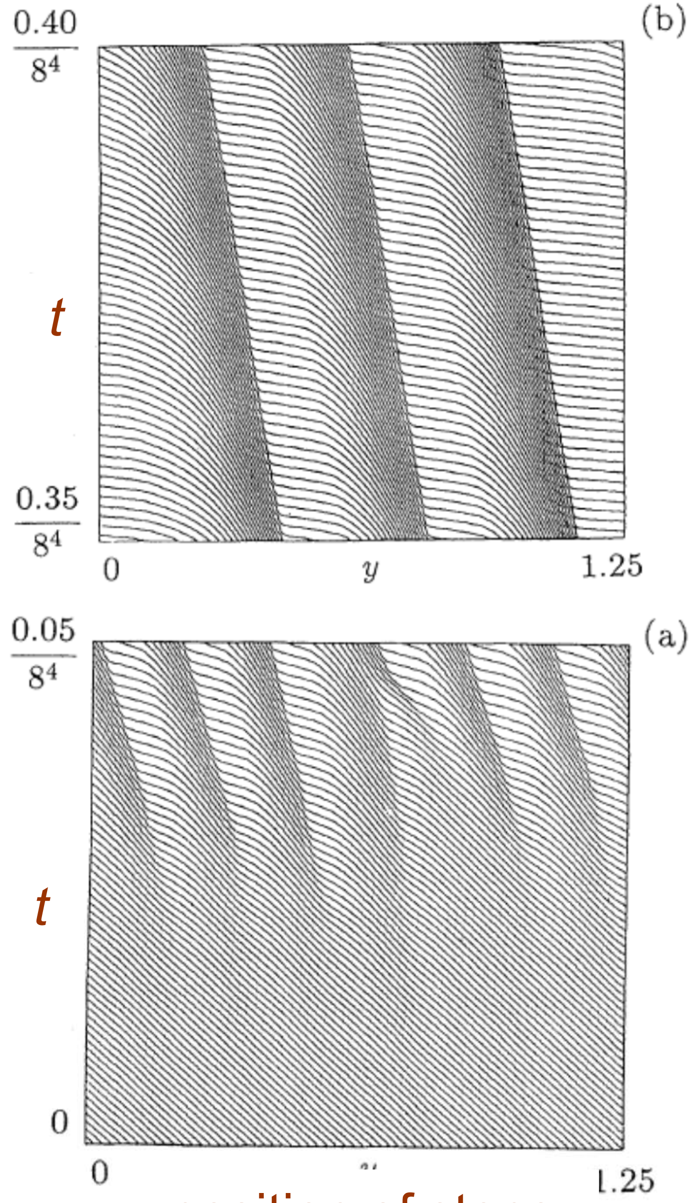
- ステップ速度はテラス幅の関数
- テラス幅が等間隔から外れたときのステップ速度の変化
  → ステップ対形成の有無



(a) (b)

Morphological instability of a vicinal face

M. Sato, M. Uwaha (1995)



PHYSICAL REVIEW B VOLUME 51, NUMBER 16 15 APRIL

Morphological instability caused by asymmetry in step kinetics

Masahide Sato and Makio Uwaha
Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
(Received 25 January 1995)

We study motion of a train of linear repulsive steps in a surface diffusion field. With asymmetric step kinetics (Schwoebel effect) and repulsive step interaction, fluctuations of step density at long wavelengths become unstable if undersaturation exceeds a critical value. This leads to a morphological instability, in which the diffusion takes place along the interface in contrast to the usual Mullins-Sekerka instability. The instability develops a step bunch with a diffuse front and a sharp end.

Pairing instability

↓

＋ Elastic repulsion

↓

Instability of density waves

佐藤正英(名大→金沢大)

ステップバンチングの数学的解析

- 1次元ステップモデルでの時間発展

$$\frac{\partial y_n(t)}{\partial t} = F(\{y_n(t)\})$$

- ステップ密度 ($\rho(x)=1/|y_n-y_{n-1}|$) のゆらぎの時間発展：　Benney方程式

$$\frac{\partial \delta\rho}{\partial t} = -\frac{\partial^2 \delta\rho}{\partial x^2} - \delta\frac{\partial^3 \delta\rho}{\partial x^3} - \frac{\partial^4 \delta\rho}{\partial x^4} - \delta\rho\frac{\partial \delta\rho}{\partial x}$$

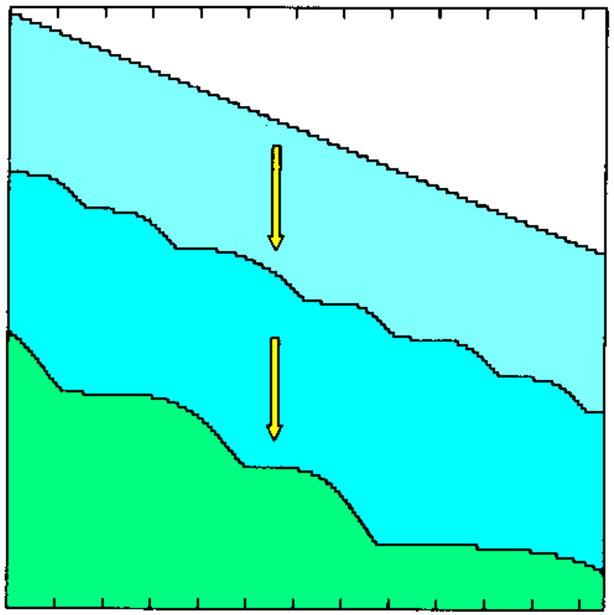
- δ→∞：　KdV方程式　→　ソリトン

$$\frac{\partial \delta\rho}{\partial t} = -\frac{\partial^3 \delta\rho}{\partial x^3} - \delta\rho\frac{\partial \delta\rho}{\partial x}$$

Sato, Uwaha: Europhys. Lett. **32** (1995) 639

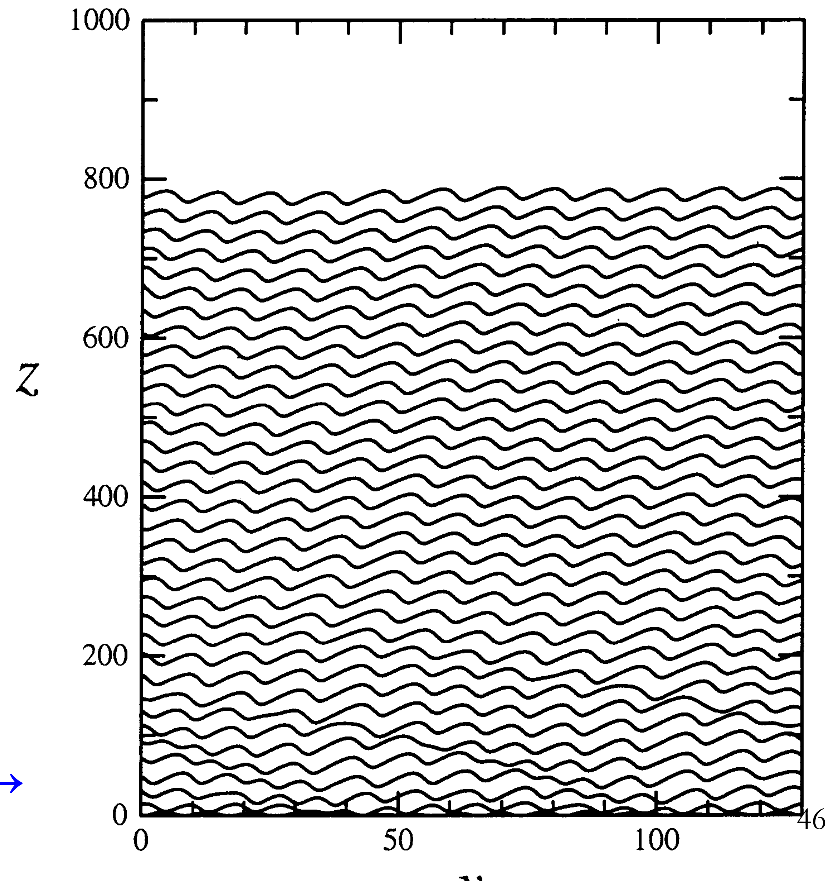
Benny方程式のソリトン列と
1次元ステップモデルのシミュレーション

1次元ステップモデルの
時間発展

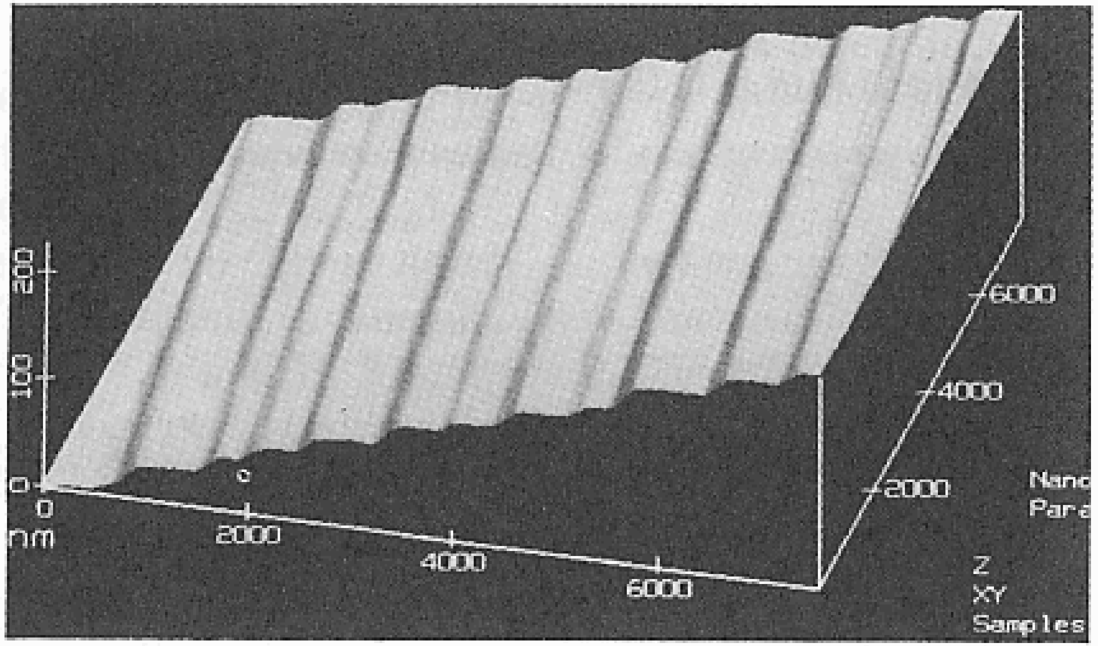


非線形効果によるソリトン列の発生→

Benny方程式のソリトン列



GaAs(111)B面の成長によるステップバンチング



[$\bar{1}\bar{1}0$]方向に 3 度傾いた GaAs(111)B 表面の AFM 像

Ren, Shen, Nishinaga: J. Cryst. Growth **166** (1996) 217

Nonlinear effect and symmetry of the system

- Evolution of fluctuations: Benney equation

  in terms of the surface height (ρ= - dz/dx)

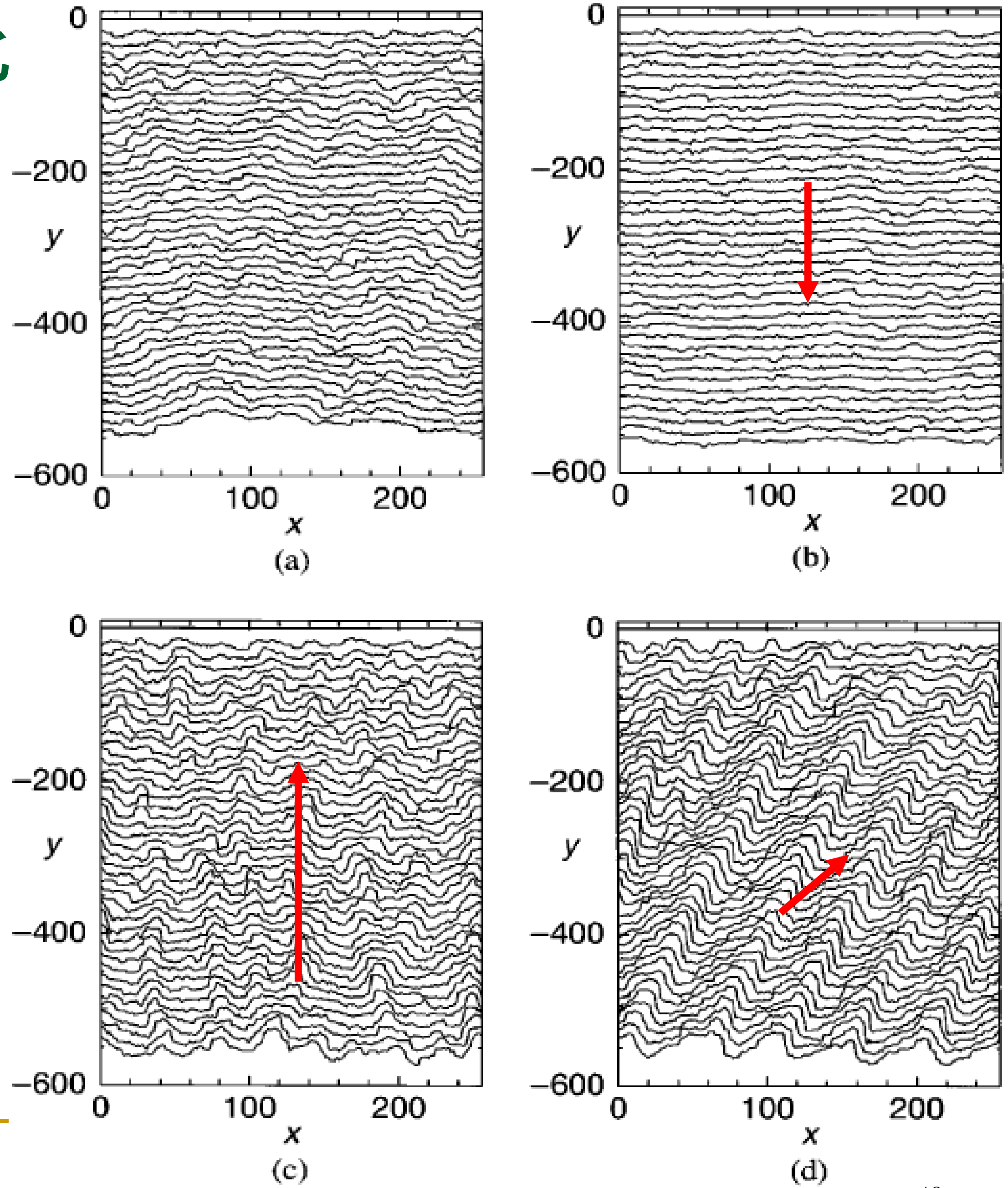
$$\frac{\partial \delta z}{\partial t} = -\frac{\partial^2 \delta z}{\partial x^2} - \delta \frac{\partial^3 \delta z}{\partial x^3} - \frac{\partial^4 \delta z}{\partial x^4} + \frac{1}{2}\left(\frac{\partial \delta z}{\partial x}\right)^2$$

- δ→0 : KS equation → chaos
- δ→∞ : KdV equation → solitons
- Can we control the symmetry of the system by changing the parameter δ ?

系の対称性の変化とパターンの変化

ドリフトによる蛇行：

- ステップが対称軸の方向でドリフトがステップに垂直なら
  - KS方程式→
    - カオス
- ドリフトの向きが斜めなら
  - Benny方程式→
    - 周期パターン



ドリフト流によるパターン制御

Sato, M. Uwaha, Saito: Phys. Rev. Lett. **80** (1998) 4233

ステップによる結晶成長とパターン形成：まとめ

- 成長，緩和機構の違い：
  異なる時間変化，異なる経路をたどる.

- 蛇行やバンチングの原因：
  ステップ前後の拡散場の非対称性(ES効果，ドリフトなど)

- パターンを決めるもの：
  保存則(蒸発の有無)，結晶の対称性，結晶の異方性
  →周期パターン，カオス，粗大化

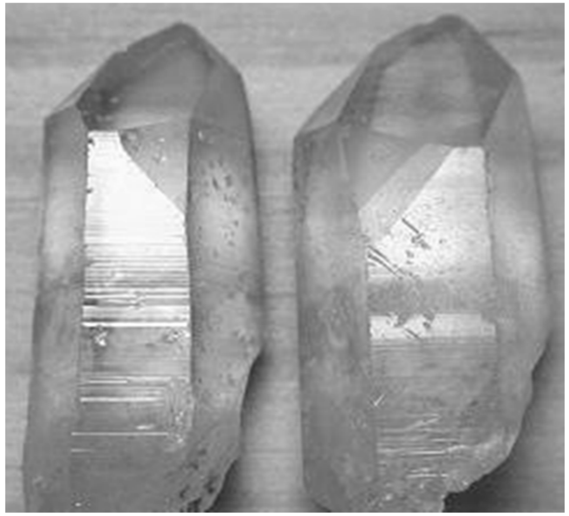
Chirality conversion in crystallization (2004-present)

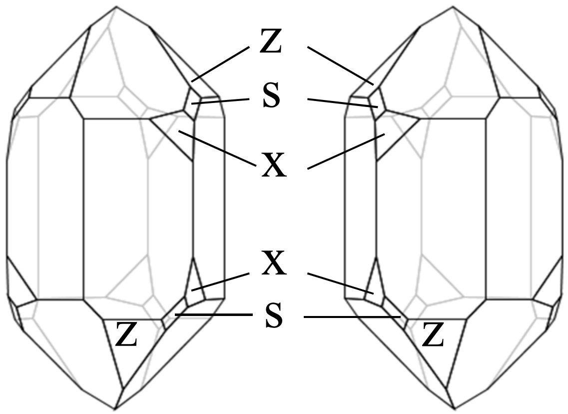
Enantiomorph of crystals

- SiO_2(quartz)

  Low temperature quarts : $P3_121$ and $P3_221$

3 inches synthetic
quartz crystal for wafer
(Fine Crystal Co.)





右水晶
right quartz

左水晶
left quartz

A chiral crystal is made of achiral molecules.

M. Maruyama, K. Tsukamoto:
J. Jpn. Assoc. Cryst. Growth, 35 (2008)

Homochirality of $NaClO_3$ via chirality conversion

- Left-handed(L) and right-handed(D) crystals can be easily distinguished by a polarizer.

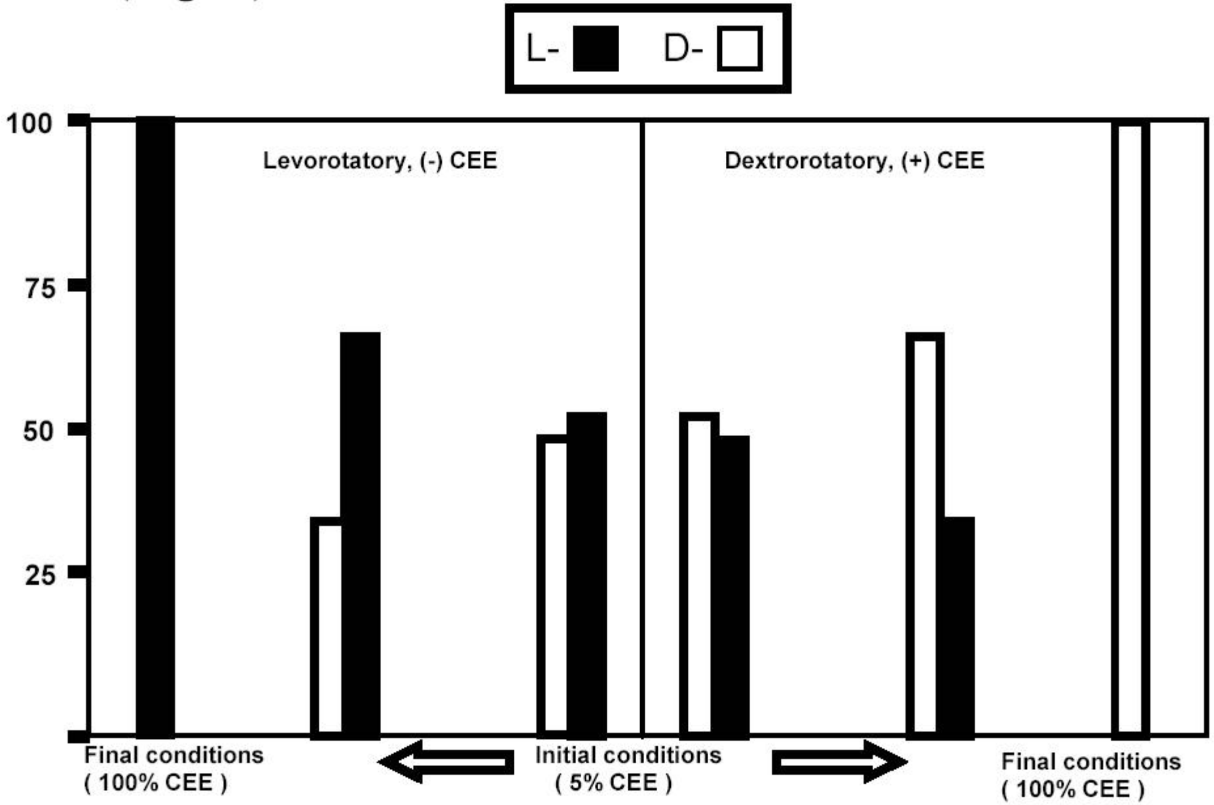
L crystals: blue,
D crystals: white

L crystals: white,
D crystals: blue

C. Viedma: Phys. Rev. Lett. **94,** 065504 (2005)

Homochirality of $NaClO_3$ via chirality conversion

- Change of enantiomeric excess by continuous stirring and abrasion of $NaClO_3$ crystalites in a saturated solution

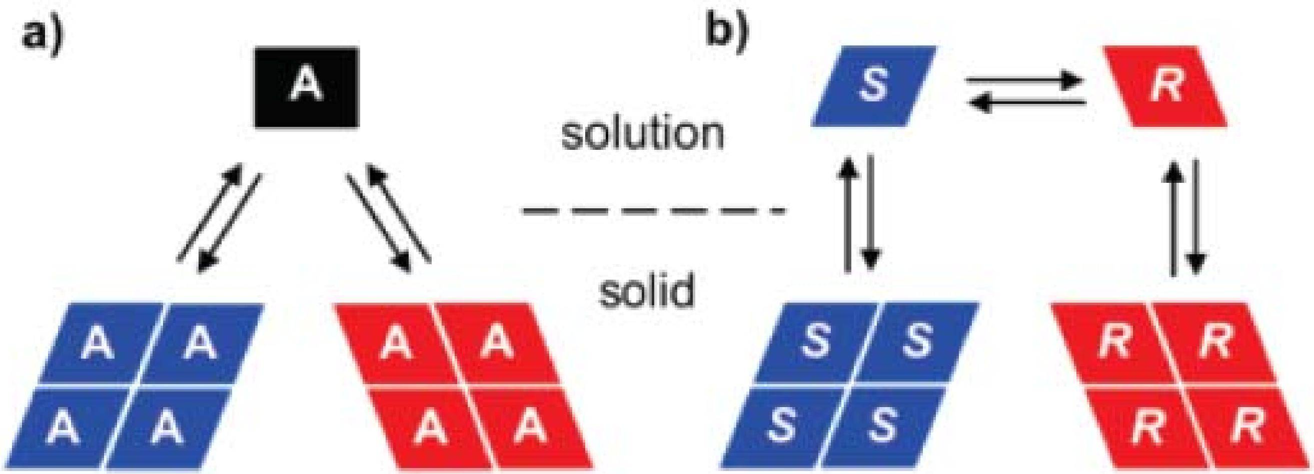


Slight asymmetry results in complete asymmetry.

C. Viedma: Phys. Rev. Lett. **94,** 065504 (2005)

Chirality conversion of an amino acid derivative

The imine of 2-methyl-benzaldehyde and phenylglycinamide racemizes rapidly in solution with added organic base DBU in MeOH.

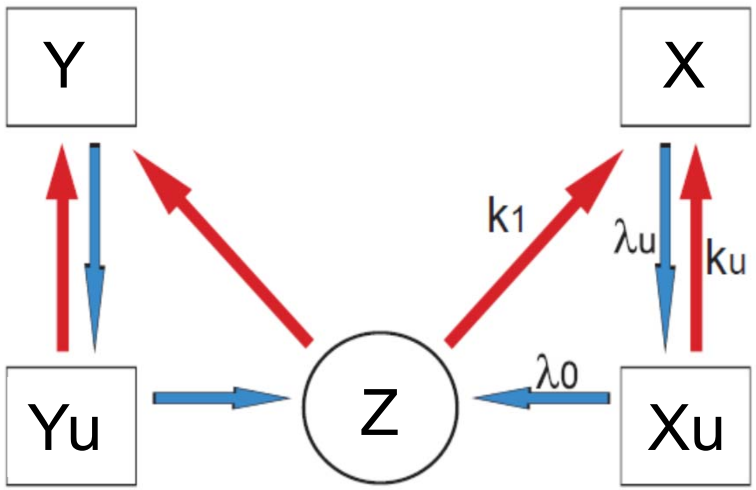


W.L. Noorduin, T. Izumi, A. Millemaggi, M. Leeman, H. Meekes, W.J.P. Van Enckevort, R. M. Kellogg, B. Kaptein, E. Vlieg, D.G. Blackmond:J. Am. Chem. Soc. **130** (2008) 1158

Change of masses of the chiral crystals

- Masses of the right and left crystals: x and y
- Masses of the right and left chiral units(clusters): x_u and y_u
- Mass of achiral molecules: z

$$\frac{dx}{dt} = k_1 zx + k_u x_u x - \lambda_u x,$$
$$\frac{dy}{dt} = k_1 zy + k_u y_u y - \lambda_u y,$$
$$\frac{dx_u}{dt} = k_0 z^2 - k_u x_u x + \lambda_u x - \lambda_0 x_u,$$
$$\frac{dy_u}{dt} = k_0 z^2 - k_u y_u y + \lambda_u y - \lambda_0 y_u,$$
$$\frac{dz}{dt} = -k_1 zx - k_1 zy + \lambda_0 x_u + \lambda_0 y_u.$$



カイラルクラスターによる成長が粉砕撹拌によるカイラリティ転換を実現する

M. Uwaha, J. Phys. Soc. Jpn. **73** (2004) 2601 (McBride and Tully 2008)

Becker-Doering type model with direct crystallization of clusters and grinding

- Dimer as a chiral growth unit
- Growth of crystals with monomers and dimers
- Decay of the largest clusters by grinding

$$A + A \leftrightarrow L_2 \qquad A + A \leftrightarrow R_2$$

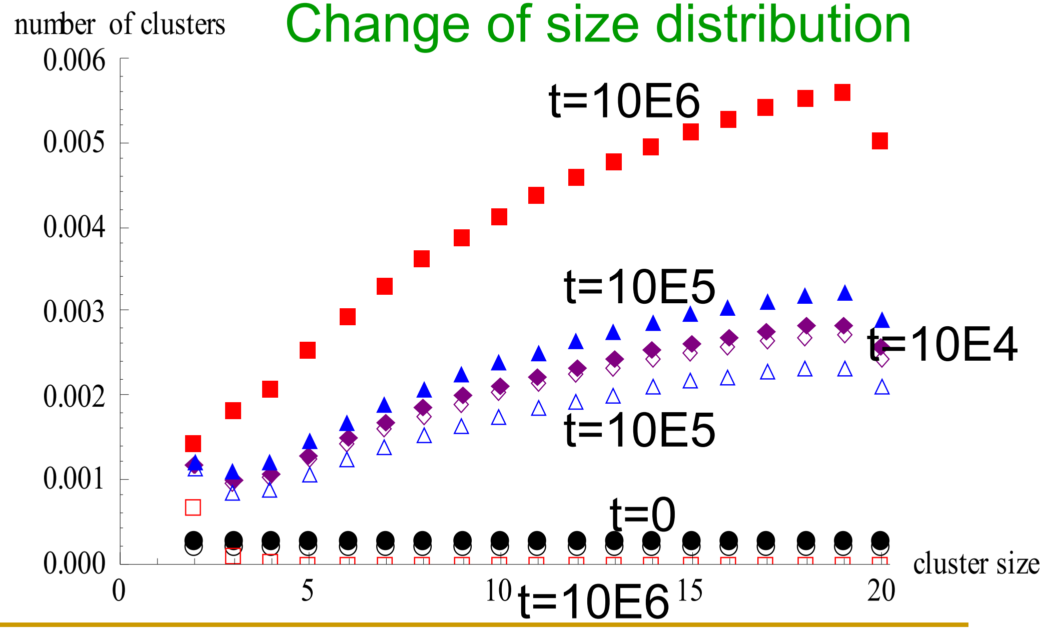
$$A + L_l \leftrightarrow L_{l+1} \qquad A + R_l \leftrightarrow R_{l+1}$$

$$L_2 + L_l \leftrightarrow L_{l+2} \qquad R_2 + R_l \leftrightarrow R_{l+2}$$

$$L_{l_{max}} \to L_2, L_3, \cdots L_{l_{max}-1} \qquad R_{l_{max}} \to R_2, R_3, \cdots R_{l_{max}-1}$$

詳細釣り合いを満たす反応過程でカイラリティ転換が起こる

Change of size distribution



M. Uwaha and H. Katsuno: J. Phys. Soc. Jpn **78** (2009) 023601

Chirality conversion by temperature cycling

Article

Using Programmed Heating-Cooling Cycles with Racemization in Solution for Complete Symmetry Breaking of a Conglomerate Forming System.

Kittisak Suwannasang, Adrian Evan Flood, Celine Rougeot, and Gérard François Coquerel

Cryst. Growth Des., **Just Accepted Manuscript** • DOI: 10.1021/cg400436r • Publication Date (Web): 25 Jun 2013

▲ TP1, ■ TP2, ● TP3 and TP4.

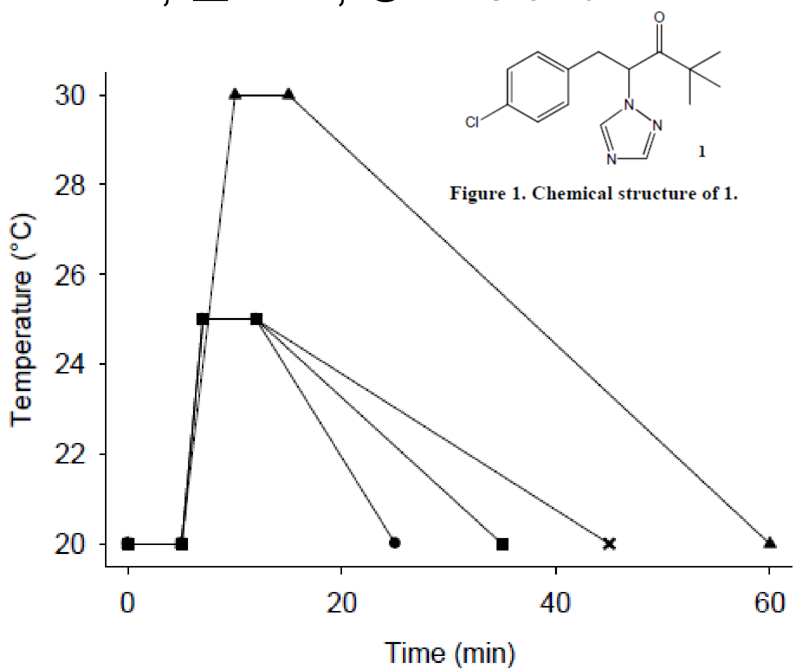
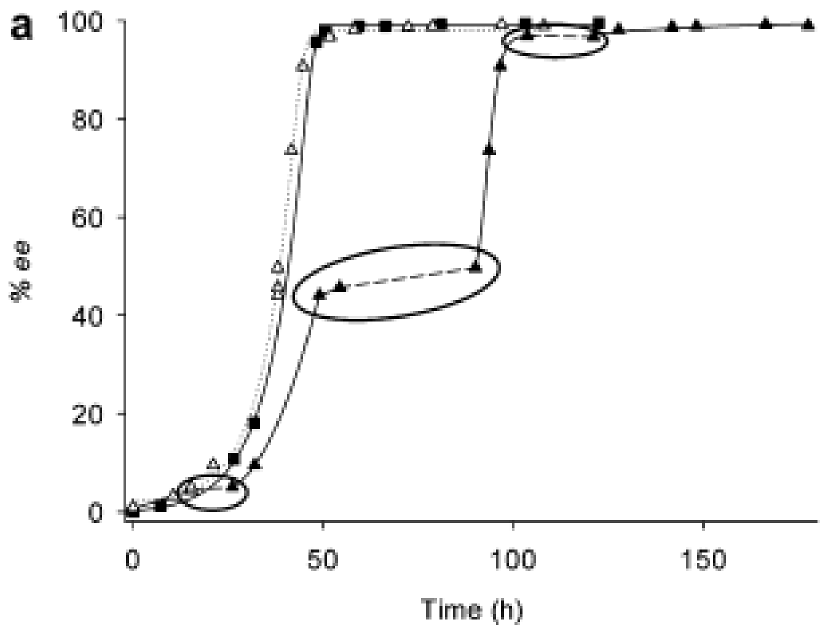


Figure 1. Chemical structure of 1.



Chirality conversion by temperature cycling

温度循環の場合もカイラルクラスター成長で説明可能

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Mechanism of chirality conversion by periodic change of temperature: Role of chiral clusters

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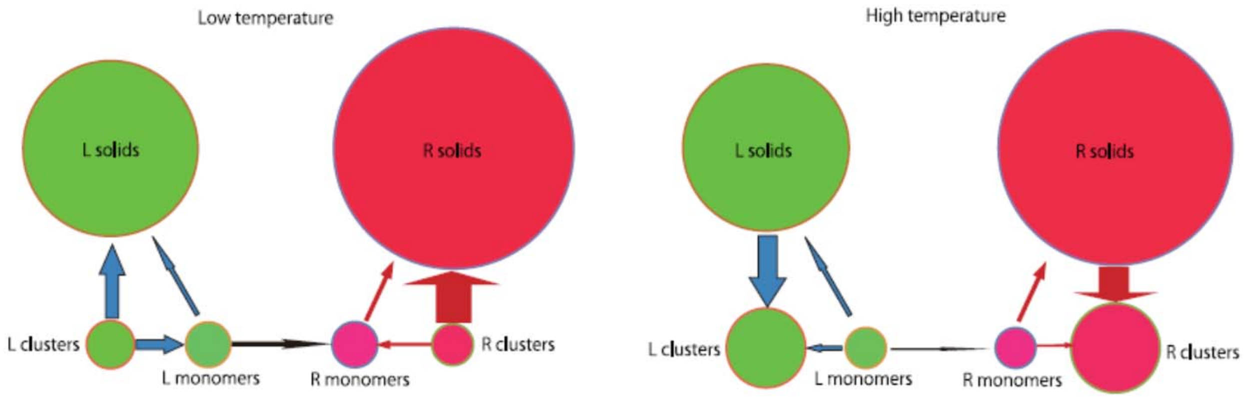
By grinding crystals in a solution, the chirality of crystal structure (and the molecular chirality for the case of chiral molecules as well) can be converted, and the cause of the phenomenon is attributed to crystal growth with chiral clusters. We show that the recently found chirality conversion with a periodic change of temperature can also be explained by crystal growth with chiral clusters. With the use of a generalized Becker-Döring model, which includes enantio-selective incorporation of small chiral clusters to large solid clusters, the change of cluster distribution and the mass flow between clusters are studied. The chiral clusters act as a reservoir to pump out the minority species to the majority, and the exponential amplification of the enantiomeric excess found in the experiment is reproduced in the numerical calculation.

勝野弘康（名大→立命館大）



(a) (b)

FIG. 1. Schematic mass flow at (a) low and (b) high temperatures.

最後に「教訓」的なこと

- テーマの設定が何よりも大切

  自分に合った問題を探す

  人より先に手掛ければ簡単でも意味のある仕事ができる

  (Realあるいはvirtualな)実験の本質をよく考える
- 人との出会いを大切に

- これから (G. Baym's mail)

Baymfest  in Tokyo

The best advice I got about getting old is from David Pines, who said that you should never stop doing what you are doing.