INSTABILITIES AND SCALE INVARIANCE IN THE GROWTH OF NANOSTRUCTURES: MESOSCOPIC DESCRIPTIONS

Rodolfo Cuerno
Departamento de Matemáticas &
Grupo Interdisciplinar de Sistemas Complejos (GISC)
Universidad Carlos III de Madrid

cuerno@math.uc3m.es
http://gisc.uc3m.es/~cuerno
Sketch of the talk

- Introduction

- Example I: Erosion by ion-beam sputtering
  J. M. Albella, C. Ballesteros, A.-L. Barabási, M. Castro, R. Gago,
  M. M. García Hernández, M. Makeev, M. Varela, L. Vázquez
  - Experimental results
  - Discrete approach
  - Continuum approach
  - Discussion

- Example II: Dynamics of steps on vicinal surfaces
  T. Ala-Nissila, M. Castro, I. Koponen, M. Rusanen

- Conclusions
Systems of nanoscopic dimensions feature:

- Fluctuations: thermal origin or externally driven (flux of aggregating units)
- Instabilities $\sim$ pattern formation

Theory of growth has to study the interplay between both trends

Tools: Non-equilibrium Statistical Mechanics

Focus: Coarse-grained description, sensitive to fluctuation effects

Outcome: Universal properties (scaling of fluctuations); also preasymptotic features, relevant to system specifics
Example I: Erosion by ion-beam sputtering

Removal of material from surfaces through the impact of energetic particles

Employed traditionally for

- film fabrication
- surface and depth microanalysis
- surface cleaning and micromachining

Expect “pattern removal”…
Pattern formation

\[ \theta \neq 0 \implies \text{ripples} \]

Habenicht et al., PRB '99: 5 keV Xe\(^+\) graphite

Rusponi et al., PRL '98: 1 keV Ar\(^+\) Cu(110)
\[ \theta \equiv 0 \rightarrow \text{dots} \]

**FACSKO ET AL.,** Science '99: 420 eV Ar$^+$ GaSb

**FACSKO ET AL.,** PRB '02: Ar$^+$ GaSb
Also obtained on Si

GAGO ET AL., APL ‘01: 1.2 keV Ar$^+$ Si

Times: 6 min [(a): $1 \times 1 \, \mu m^2$]; 960 min [(b): $3 \times 3 \, \mu m^2$]

(c), (d): two-dimensional autocorrelation functions over $400 \times 400 \, \mu m^2$ areas
GAGO ET AL, APL ‘01: 1.2 keV Ar⁺ Si
Can also be obtained for rotating targets and $\theta \neq 0$

\textbf{Frost et al.,} PRL ‘00: 500 eV Ar$^+$ InP

Times: 10 s (a); 40 s (b); 9600 s (c)

(d) two-dimensional autocorrelation function
Microscopic approach

Highly complex many-body process

Typical scales in Molecular Dynamics
- Time $\approx 10^{-1} - 10^2$ ps
- Length $\approx 10 - 100$ Å
- Number of atoms $\approx 10^5$

Typical scales in experiments
- Time $\approx 1 - 10^3$ s
- Length $\approx 10 - 100$ nm

Bringa et al., PRB '01: MD simulation 100 keV Xe onto Au
Kinetic Monte Carlo

Trans. probabilities $W(\text{conf} \to \text{conf'} ) = \sum_{a=1}^{N} R_a V^a(\text{conf} \to \text{conf'})$

KOPONEN ET AL, PRB ‘96: 5 keV Ar onto carbon
Typical scales in kinetic Monte Carlo

- Time ≈ 1 μs (≈ 10^6 cascades)
- Length ≈ 30 nm

Koponen et al., PRL ‘97: kMC simulation 5 keV Ar onto carbon
More *coarse-grained* approaches

\[
E(x', y', z') = \frac{\epsilon}{(2\pi)^{3/2} \sigma \mu^2} \exp \left( -\frac{(z' + a)^2}{2\sigma^2} - \frac{x'^2 + y'^2}{2\mu^2} \right)
\]

“Linear cascade” approximation, P. Sigmund, PR (1969)

Erosion probability \( \propto \) Total energy
(a) 3 ML removed
(b) 30 ML
(c) 300 ML
(d) $10^4$ ML

HARTMANN ET AL, PRB ‘02
**Mesoscopic description**

*Goal:* Compute local erosion velocity

\[ v = \frac{\partial h}{\partial t} = \mathcal{V}(\varphi, a, \mu, \sigma, T, J, \ldots) \]

\[ E(x', y', z') = \frac{\epsilon}{(2\pi)^{3/2}\sigma\mu^2} \exp \left( -\frac{(z'+a)^2}{2\sigma^2} - \frac{x'^2+y'^2}{2\mu^2} \right) \]

\[ v = p \int_{\mathcal{R}} \mathrm{d}r \, \Phi(r) \, E(r) \]

Perform expansion for small slopes \(|\nabla h| \ll 1|
Two important facts:

- Surface features are *amplified* \(\sim\) instability
- Effective angle of incidence varies across the surface
\[
\frac{\partial h}{\partial t} = F(h, \nabla h, \ldots) + \eta(r, t)
\]

In general, \( \kappa \) may be anisotropic (metals)

\[\mu \propto \kappa \text{ (curvature)} \sim -\nabla^2 h\]
Full dynamics (Anisotropic, stochastic) Kuramoto-Sivashinsky equation

\[ \frac{\partial h}{\partial t} = \nu_x \partial_x^2 h + \nu_y \partial_y^2 h - D_{xx} \partial_x^4 h - D_{yy} \partial_y^4 h - D_{xy} \partial_x^2 \partial_y^2 h + \lambda_x (\partial_x h)^2 + \lambda_y (\partial_y h)^2 + \eta \]

“surface tension”

“surface diffusion”

lateral growth

Comments

- All coefficients \((\nu_x, D_{xx}, \lambda_x)\) are functions of parameters \(\theta, a, \sigma, \mu, T, J\).

- \(\nu_y < 0 \quad \forall \theta \) (\(\Rightarrow\) instability); \(\nu_x\) changes sign with \(\theta\)

- \(D_{ij} = d_{ij} + K_{ij}\) with

\[ \begin{cases} d_{ij} \propto \epsilon, \text{ indep. of } T \\ K_{ij} \propto \frac{1}{T} \exp(-E_{ij}/k_B T) \end{cases} \]

- For \(\theta = 0\) symmetry is restored in \((x, y)\) plane

\[ \Rightarrow \nu_x = \nu_y; \quad \lambda_x = \lambda_y; \quad d_{xx} = d_{yy}; \quad d_{xy} = 0 \]

- \(\nu_i, D_{ij}, \lambda_k \propto \epsilon\)
Linear theory for $\theta \neq 0$

$$\frac{\partial h}{\partial t} = -|\nu|\nabla^2 h - D\nabla^4 h$$

$$h(k, t) \propto \exp(\omega_k t)$$

$$\omega_k = |\nu|k^2 - Dk^4$$

There exists $k^* \equiv \sqrt{|\nu|/D}$ such that:

- $k > k^*$ stable modes
- $k < k^*$ unstable modes

$k_0 = k^*/\sqrt{2}$ has a maximal growth rate $\omega_{k_0}$

The amplitude of $k_0$ dominates exponentially fast $\Rightarrow$ dot structure

No hexagonal ordering
Linear theory for $\theta \neq 0$ (Bradley & Harper, JVSTA ‘88)

$$h(k, t) \propto \exp \left[ (-\nu_x k_x^2 + |\nu_y| k_y^2 - \mathcal{K} k^4) t \right]$$

Small $\theta$: $\nu_x < \nu_y < 0$

Large $\theta$: $\nu_y < \nu_x$ and $\nu_y < 0$
Effects of anisotropy

COSTANTINI ET AL, JPC ‘01: 1 keV Ar\(^+\) Ag(110)

When surface diffusion is thermally activated \(d_{ij} = 0\), anisotropies \([E_{ij}(T)]\) allow selection of ripple direction by tuning \(T\).
Limitations of BH (linear) theory

The actual surface (rms) roughness saturates with time, rather than diverge exponentially.

**Gago et al., APL ‘02: 1.2 keV Ar, Si**

**Erlebacher et al., JVSTA ‘00: 750 eV Ar, Si**
Limitations of BH (linear) theory

The actual ripple amplitude *coarsens* with time, rather than *stay* constant

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HABENICHT ET AL, PRB ‘02: 30 keV Ga onto Si
Non-linear dynamics ($\theta \neq 0$)

$\lambda_x \lambda_y > 0$

\[ \nu \partial_x h \sim \lambda (\partial_x h)^2 \Rightarrow \nu \frac{W_0}{\ell^2} \sim \lambda \frac{W_0^2}{\ell^2} \Rightarrow W_0 \sim \nu / \lambda \]

\[ W_0 \sim \exp(\nu \tau / \ell^2) \]

\[ \Rightarrow \tau \sim \frac{\kappa}{\nu} \log(\nu / \lambda) \]

PARK ET AL, PRL ‘99

Crossover time $\tau = \text{onset for kinetic roughening}$
Kinetic roughening

\[ K_c \]

GAGO ET AL, APL ‘02: Ar onto Si
HABENICHT ET AL, PRB ‘99: 5 keV Xe\(^+\) graphite

HARTMANN ET AL, PRB ‘02: MD simulations
\( \lambda_x \lambda_y < 0 \) Ripples prevail with *large roughness*: *shadowing* effects may be relevant

PARK ET AL, PRL ‘99

GAGO ET AL, Nanotechnol. ‘02
Non-linear dynamics ($\theta = 0$)

Dots are formed, but not with the proper ordering

Facsko et al. '00

Kahng et al., APL '01
Other sputtered systems might be described by the nKS equation:

Amorphous carbon films (Koponen et al., JAP ‘97)

Ge bombarded at low energy (Chey et al., PRB ‘95)
Other sputtered systems might be described by the nKS equation: 

Si within a magnetron (with M. Castro, M. G. Hernández, L. Vázquez)
Cell (“dot”) coarsening

Dot statistics $\leftrightarrow$ relevance of noise
Continuum description of IBS (a summary)

- Full dynamic equation *cannot* be described out of symmetry arguments:
  
  \[ \partial_t h = |\nu| \partial_x^2 h + \lambda (\partial_x h)^2 + \eta, \text{ Kardar, Parisi, Zhang} \]

- (Qualitative) Agreement in terms of energy and flux dependencies
  (for thermally suppressed diffusion)

- Agreement in terms of pattern formation + stabilization

- Universality class for kinetic roughening? (need extremely long experiments)

- Disagreements:
  - Dot formation: In-plane ordering
  - Ripple formation: Wavelength coarsening

- Mechanisms not considered thus far may play a role
  (viscous flow, shadowing effects, . . .)
Example II: step dynamics on vicinal surfaces

Vicinal surface: orientation close to that of a high symmetry surface \( \rightsquigarrow \) steps

Steps have equilibrium *roughness*, that can be characterized

WANG ET AL. ‘90

TUNG ET AL. ‘90

FIG. 1. Scanning-tunneling-microscope image of a \( \sim 800 \) Å\( \times 200 \) Å region of a stepped Si surface misoriented by 1.2° towards the [1 1 2] direction. Notice that the kink spans one (7\( \times \)7) unit cell.

Under growth conditions, steps move and their roughness evolves

\( \text{d) Si [2 } \bar{1} \bar{1} \text{]; (e) 1 ML; (f) 2 ML} \)
Adatom density $c(r, t)$ on terrace
\[ \frac{\partial c}{\partial t} = D \nabla^2 c - \frac{c}{t} + J - \nabla \cdot q + j \]
$q = \text{fluctuations in diffusion current}$
$j = \text{flucts. adsorption/desorption}$

Attachment/detachment at steps
\[ \pm \mathbf{n} \cdot (D \nabla c - q)|_{\text{step}} = k_{\pm}(c - c_{eq} + j_{\pm}) \]
$+ = \text{at ascending step}$
$- = \text{at descending step}$
$k_{\pm} = \text{kinetic coeffs. for attachment}$

Velocity
\[ \mathbf{v} \cdot \mathbf{n} = \mathbf{n} \cdot (D \nabla c - q)|_{+} - \mathbf{n} \cdot (D \nabla c - q)|_{-} + \left[ \nabla_s^2 \kappa_s \right] \]
**EHRLICH-SCHWOEBEL barrier \Rightarrow instability**

If attachment depends on side of step \((k_+ \neq k_-)\) \Rightarrow *meandering* instability in step profile

![Diagram of meandering steps](image)

**Bales, Zangwill, PRB ‘90**

Protrusions “screen” indentations

Analogous to Mullins-Sekerka instability in solidification (*snowflakes*)

 evolution equation for a single step is the Kuramoto-Sivashinsky equation

\[(\text{Karma, Misbah, Pierre-Louis, ...}, \text{late } 90\text{'s})\]

Can be generalized to trains of steps, no desorption, etc.
Agreement is *not* complete though (wavelength dependence with flux, . . . )

$\Downarrow$ further work is needed
Conclusions

- Tools developed in the study of non-equilibrium systems can be employed for the study of growth systems with nanometer size features (growth, erosion, microfluids)

- Although the formalism is adapted to the study of asymptotic properties (esp. in the case of scale invariance), equations cannot be derived merely from symmetry arguments

- Careful attention must be paid to system specifics

- Still, advantage can be taken from developments on universal or generic models. Specifically, the latter studies can assess parameter regions for pattern formation, or e.g. surface disordering