Lecture 2: Wetting and dewetting of solids and liquids

Olivier Pierre-Louis

ILM-Lyon, France

28th May 2017
1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaishew construction
   - Thin Films
   - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
1 Static Wetting of liquids and Solids
   - Introduction
     - Wulff-Kaishew construction
     - Thin Films
     - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
Some examples

J.-J. Métois, Au/Graphite
## Differences between liquids and solids

<table>
<thead>
<tr>
<th>Simple Liquids</th>
<th>Crystalline solids</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td><strong>Surface &amp; Interface</strong></td>
</tr>
<tr>
<td>Isotropic</td>
<td>Anisotropic</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
<td><strong>Surface &amp; Interface + Elastic</strong></td>
</tr>
<tr>
<td>Surface &amp; Interface</td>
<td></td>
</tr>
<tr>
<td><strong>Mass Transport</strong></td>
<td><strong>Surface diffusion</strong></td>
</tr>
<tr>
<td>Bulk hydrodynamics</td>
<td></td>
</tr>
</tbody>
</table>

Other cases: Liquid crystals, Non-Newtonian Fluids, amorphous solids, etc.

→ Similar or different behaviors?
1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaishew construction
   - Thin Films
   - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
Equilibrium equations

Free energy

\[ F = \int_{VS} ds \gamma_{VS}(\theta) + \int_{SA} ds \gamma_{SA}(\theta) + \int_{AV} ds \gamma(\theta) \]

Total number of atoms

\[ N = \Omega^{-1} \int \int_A d^2r \]

Vanishing variation

\[ \delta (F - \mu N) = 0 \]

\[ \rightarrow \text{Equilibrium equations} \]
Spreading or not spreading

Spreading coefficient \( S = \gamma_{SV} - \gamma_{SA} - \gamma(0) \)

- **Complete dewetting**
  - \( \gamma_{SV} + \gamma(0) < \gamma_{SA} \)
  - \( S < -2\gamma(0) \)

- **Partial Wetting**
  - \( -\gamma(0) < \gamma_{SV} - \gamma_{SA} < \gamma(0) \)
  - \( -2\gamma(0) < S < 0 \)

- **Total Wetting**
  - \( \gamma_{SV} > \gamma_{SA} + \gamma(0) \)
  - \( S > 0 \)
Facets

Roughening temperature $T_r$

For usual crystals $T_r \sim T_M$

NaCl, Métois et al (620-710°C)
Equilibrium shape, Wulff 1901

Away from the substrate: Wulff Shape

- Discrete with facets

\[ h_i = \frac{\Omega \gamma_i}{\mu} \]

Facet free energy \( \gamma_i \)

- Continuum

\[ \mu = \Omega \tilde{\gamma}(\theta) \kappa \]

Stiffness \( \tilde{\gamma}(\theta) = \gamma(\theta) + \gamma''(\theta) \)

Remarks:

- Wulff construction
- Equivalence discrete - continuum
- Possible coexistence of smooth and facetted parts
Main idea: flat substrate ↔ facet

- Global condition: Truncation

\[ h_s = -\frac{\Omega(\gamma_{VS} - \gamma_{SA})}{\mu} \]

OR

- At the triple line if no facet: Young equation

\[ \gamma_{VS} - \gamma_{SA} = \gamma(\theta_0) \cos(\theta_0) - \gamma'(\theta_0) \sin(\theta_0) \]

Contact angle not a good parameter for facetted crystals!
Isotropic solid or liquid: $\gamma(\theta) = \tilde{\gamma}$

$$\mu = \Omega \tilde{\gamma} \kappa \quad \Leftrightarrow \quad R = \frac{\Omega \tilde{\gamma}}{\mu}$$

$$\tilde{\gamma} \cos(\theta_0) = \gamma_{VS} - \gamma_{SA} \quad \Leftrightarrow \quad h_s = -\frac{\Omega (\gamma_{VS} - \gamma_{SA})}{\mu}$$
Finite size effects

Expansion of the thermodynamic energy in 3D

\[ \mathcal{E} \sim \gamma_3 N + \gamma_2 N^{2/3} + \gamma_1 N^{1/3} + \ldots \]

- \( \gamma_3 \sim \) chemical potential \( N \sim L^3 \)
- \( \gamma_2 \sim \) surface energy \( N^{2/3} \sim L^2 \)
- \( \gamma_1 \sim \) line energy \( N^{1/3} \sim L \)

higher orders are non-trivial!


Edges between facets or Triple line \( \sim L \sim N^{1/3} \)

⇒ corrections to the equilibrium shape.
Contact angle influenced by triple line tension

\( \gamma_{TL} \) positive or negative

3D isotropic with line tension

\[
G = \bar{\gamma} A + (\gamma_{AS} - \gamma_{SV}) A_S + \gamma_{TL} L_{TL} - \mu N
\]

Spherical cap

\[
R = \frac{\Omega \bar{\gamma}}{\mu}
\]

Modified truncation

\[
\bar{\gamma} \frac{h_s}{R} = \gamma_{AS} - \gamma_{SV} + \frac{\gamma_{TL}}{(R^2 - h_s^2)^{1/2}}
\]

Modified contact angle

\[
\bar{\gamma} \cos \theta = \gamma_{SV} - \gamma_{AS} - \frac{\gamma_{TL}}{R \sin \theta}
\]
Non-frozen substrate

C. Herring (1951): Triple-point (triple-line):

\[ \sum_{i=1}^{3} \left( \gamma_i t_i + \gamma'_i n_i \right) = 0 \]

1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaisew construction
   - Thin Films
     - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
**Thin film Wetting potential**

Flat film thickness $h$

**free energy $f(h)$**

- $f(h = 0) = \gamma_{SV}$
- $f(h \to +\infty) = \gamma_{SA} + \gamma(\theta = 0)$

Relation $f \leftrightarrow W$

$$f(h) = \gamma_{SA} + \gamma(0) + W(h)$$

**wetting potential $W(h)$**

- $W(0) = S$
- $W(+\infty) = 0$

**Disjoining Pressure**

$$\Pi = -W'(h)$$
Thin film Wetting potential

Stability

\[ W''(h) > 0 \]

\[ W_{n+1} - 2W_n + W_{n-1} > 0 \]
Thin film Wetting potential

Equilibrium: Double tangent construction

Film Tension

\[ \gamma_{\text{film}}^\text{flat} = f(h) - hf'(h) \]

Equilibrium with substrate

\[ \gamma_{\text{film}} = \gamma_{SV} \]

Film Tension

\[ \gamma_{\text{film}}^+ = f_n - n(f_{n+1} - f_n) \]
\[ \gamma_{\text{film}}^- = f_n - n(f_n - f_{n-1}) \]

Equilibrium with substrate

\[ \gamma_{\text{film}}^+ < \gamma_{SV} < \gamma_{\text{film}}^- \]
Thin film Wetting potential

Wetting Regimes

Small slope free energy

\[ f(h) = \gamma_{SA} + \gamma(0) + W(h) + \frac{\Gamma(h)}{2} (\partial_x h)^2, \]

\[ \Gamma(h) \to \tilde{\gamma}(0) \text{ when } h \to \infty \]

Macroscopic contact angle

\[ \tilde{\gamma}(0) \frac{\theta_0^2}{2} = W(\infty) - W(0) = -S \]

Line tension

\[ \gamma_{TL} = \int_0^{\infty} dh \left\{ \left[ 2\Gamma(h)(W(h) - S) \right]^{1/2} - \left[ 2\tilde{\gamma}(0)(-S) \right]^{1/2} \right\} \]

...Small slope model → lecture notes OPL
Thin film Wetting potential

Bonds and structural effects

<table>
<thead>
<tr>
<th>Type</th>
<th>form</th>
<th>prefactor</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical bonds</td>
<td>$W_0 e^{-h/d_0}$</td>
<td>$W_0 \sim J/a^2$</td>
<td>$d_0 \sim a$</td>
</tr>
<tr>
<td>Layering of Liquids and Polymers</td>
<td>$W_0 \cos(2\pi h/a_0)e^{-h/d_0}$</td>
<td>$W_0 \sim k_B T/a^2$</td>
<td>$d_0 \sim a$</td>
</tr>
<tr>
<td>Structural effects solids $T &lt; T_R$</td>
<td>$W_0 \cos(2\pi h/a_0)$</td>
<td>$W_0 \sim J/a^2, k_B T \ll J$</td>
<td>$(a_0 = a)$</td>
</tr>
</tbody>
</table>


Olivier Pierre-Louis (ILM-Lyon, France)
Thin film Wetting potential

DLVO-like contributions

<table>
<thead>
<tr>
<th>Type</th>
<th>form</th>
<th>prefactor</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic effects</td>
<td>$W_0 e^{-h/\lambda_D}$</td>
<td>$W_0 = 2\frac{\sigma^2 \lambda_D}{\epsilon_0 \epsilon}$</td>
<td>$\lambda_D$</td>
</tr>
<tr>
<td>Van der Waals Interactions</td>
<td>$-\frac{A}{12\pi h^2}$</td>
<td>$A \sim 10^{-20} - 10^{-19}$ J</td>
<td>—</td>
</tr>
</tbody>
</table>

Israelachvili, Intermolecular and surface Forces (1985)
Polymers Layering J. Krawczyk et al EPL 70 726 (2005)
Thin film Wetting potential

... and many other possible contributions!

<table>
<thead>
<tr>
<th>Type</th>
<th>form</th>
<th>prefactor</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic confinement</td>
<td>$\frac{E_{fb}}{h^2} \cos(2k_{fb}h + \phi)$</td>
<td>$E_{fb} = 5.55\text{eV (Ag)}$</td>
<td>osc. $\lambda_f/2$</td>
</tr>
</tbody>
</table>

Yong Han and Da-Jiang Liu PRE 80 155405 (2010)

Debate in the literature: $1/h$ or $1/h^2$?
Electronic Quantum confinement

Free electron model

\[
W_{EC}(h) \approx -\frac{E_{fb}}{(h+2b)^2} \frac{\pi}{36\sqrt{3}} \cos(2k_{fb}h)
\]

\(E_{fb}, k_{fb}\) Fermi energy and wavevec, 
\(b = 3\pi k_{fb}/8\)

(a) Al(111) (purple squares), Ag(111) (blue circles)
(c) Al(111), (d) Ag(111) blue-Stable, red-Unstable
Growth modes

Volmer-Weber  Frank Van der Merve  Stranski-Krastanov

\( \Theta < 1 \text{ ML} \)

1 < \( \Theta < 2 \)

\( \Theta > 2 \)

(a)  (b)  (c)
Pseudo-partial wetting vs ATG

Stranski-Krastanov

Pseudo-partial wetting vs ATG

SiGe MBE growth

Floro et al 1999

recent developments ...

1 Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaischew construction
   - Thin Films
   - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
ATG instability

**Hetero-epitaxial strain** \( \epsilon_0 = (a_f - a_s)/a_s \)

In plane strain \( u_{xx} = u_{yy} = \epsilon_0 \)

**Stress** \( \sigma_0 = -Y\epsilon_0/(1 - \sigma) \)

**Flat film energy**

\[
\mathcal{E}_{el} = -h\epsilon_0\sigma_0 = \frac{Y}{1 - \sigma} h\epsilon_0^2
\]

**Periodic perturbation** \( \delta h, \ell \)

\[
\delta\mathcal{E}_{el} \sim -\delta h\epsilon_0\sigma_0 + C\epsilon_0^2\ell
\]

**Minimize** \( \epsilon \sim \delta h\sigma_0/C\ell \)

**Total perturbation energy**

\[
\delta\mathcal{E} = \frac{\gamma}{2} q^2\delta h^2 - C\epsilon_0^2\delta h^2 q
\]

**Wavelength**

\[
\ell_{ATG} \approx 2\pi \frac{\gamma}{C\epsilon_0^2}.
\]

\( C \sim Y \sim 10^{11}\text{Pa}, \gamma \sim 1\text{Jm}^{-2}, \text{and } \epsilon = n\% \)

\( \rightarrow \ell_{ATG} \sim n^{-2}\mu\text{m} \)

\( (1\mu\text{m for 1\% misfit to }10\text{nm for 10\% misfit}) \)
ATG instability

Almost flat surface: 2D absorbate on flat surface

height \( h \sim \) surface stress \( \sigma = \sigma_0 + \alpha h \)

Local surface forces \( \mathbf{f} \) and elastic energy \( \mathcal{F}_{\text{elas}} \)

\[
\mathbf{f} = -\nabla \sigma = -\nabla \sigma_0 - \alpha \nabla h
\]
\[
\mathcal{F}_{\text{elas}} = \frac{1}{2} \int \mathrm{d}r_1 \int \mathrm{d}r_2 \phi_{12}
\]
\[
\phi_{12} = \frac{1 + \sigma}{\pi E} \left[ (1 - \sigma) \frac{\mathbf{f}_1 \cdot \mathbf{f}_2}{|\mathbf{r}_{12}|} + \sigma \frac{\mathbf{f}_1 \cdot \mathbf{r}_{12} (\mathbf{f}_2 \cdot \mathbf{r}_{12})}{|\mathbf{r}_{12}|^3} \right]
\]

Edges and steps \( \rightarrow \) force lines

\( \mathbf{f}(\mathbf{r}) = \mathbf{f}_0(\mathbf{n}_0(s)) \delta(\mathbf{r} - \mathbf{r}_0(s)) \)
Islands

Contributions to the energy in 3D
Misfit $\epsilon = \Delta a/a$
$G_{isl} = F_{isl} - \mu N$:

$$G_{isl} = +\Gamma_{surf} a^2 N^{2/3} \quad \text{Surface}$$
$$+\gamma_{e1} a N^{1/3} \quad \text{Edge}$$
$$-(\mu + f_1 \lambda \epsilon^2) a^3 N \quad \text{Volume Elastic}$$
$$-\gamma_{e2} f_2 a^{N^{1/3}} \ln[N] \quad \text{Edge Elastic}$$

$\Gamma_{surf}, \gamma_{e1}, \gamma_{e2}$ renormilzed by $\epsilon$

Schukin and Bimberg Rev Mod Phys 1999
### Static Wetting of liquids and Solids
- Introduction
- Wulff-Kaishew construction
- Thin Films
- Elastic effects

### Dynamics of solid wetting
- Dewetting dynamics
  - Surface diffusion model with wetting potential
  - Derivation of the TL Boundary Condition
  - Spinodal dewetting and Accelerated mass shedding
  - Elastic dewetting /ATG
  - KMC study of magic heights
  - Dewetting without a rim
  - Non-conservation of the mass: evaporation and reaction

### Islands on nano-patterns
- Patterns larger than islands
- Patterns smaller than islands
- Islands on nano-pillars
- Solid imbibition in nano-pillars

### Conclusions
Liquid-state Dewetting

Polymer film (PDMS/Si)


FIG. 1. Schematic representation of the experimental setup. A typical shape of the rim, as measured by atomic force microscopy, is shown in the upper right corner. The size of the image is $60 \times 60 \times 0.4 \, \mu m^3$. Note that the lateral scale is about a factor of 100 larger than the vertical scale. In the lower right corner we show an optical micrograph representing the top view corresponding to the scheme. The length of the bar equals 50 $\mu$m.
Dewetting experiments: surface diffusion + anisotropy

Experiments SOI: Si(100)/a-SiO₂

P. Müller et al Cinam Marseille

SOI (Si/SiO₂), AFM

Dornel Barbe Crecy Lacolle Eymery PRB2006
Surface Diffusion Mullins’ Model

Local chemical potential $\mu = \Omega \tilde{\gamma} \kappa$.

Mullins model:

\[
j = -\frac{Dc}{k_B T} \partial_s \mu
\]

\[
v_n = -\Omega \partial_s j
\]

Triple Line
Equilibrium contact angle $\theta = \theta_0$

$v_n \sim \partial_{ss} \kappa$

Relaxation time of island perturbations $t \sim L^4$

Small slope limit

\[
\partial_t h = -B \partial_{xxxx} h
\]

Linear but free boundary
Liquids: viscosity and substrate friction

Viscous dissipation under shear \( \dot{\gamma} = \partial_y v_x + \partial_x v_y \)

\[ dQ \sim \eta \dot{\gamma}^2 dV \]

Continuity of tangential stress \( \text{Navier 1823} \)

\[ \eta \partial_y v|_{wall} = \lambda \Delta v \quad \rightarrow \quad \Delta v = b \partial_y v|_{wall} \]

Slip length

\[ \ell_s = \frac{\eta}{\lambda} \]

\( \ell_s \) is usually small!

Link to wetting: hydrophobic \( \Rightarrow \) depletion \( \Rightarrow \) \( b \) increases

\[ \ell_s \sim (1 + \cos \theta)^{-2} \quad \text{D. M. Huang, et al, Phys. Rev. Lett. 101, 226101 (2008)} \]

at max tens of nm for water on atomically flat hydrophobic surfaces
Hydrodynamics, lubrication Model

*Local* pressure variation $\Delta p = \tilde{\gamma} \kappa$.

Lubrication Model $\partial_x h \ll 1$, viscosity $\eta$, slip length $\ell_s$

$$j = -\frac{1}{\eta \Omega} (h^3/3 + \ell_s h^2) \partial_x \Delta p$$

$$\partial_t h = -\Omega \partial_x j$$

$$\partial_t h = -\frac{\gamma}{\eta} \partial_x [(h^3/3 + \ell_s h^2) \partial_{xxx} h]$$

**Triple Line**

Equilibrium contact angle $\theta = \theta_0$

Linear perturbations $h = h_* + \delta h$

$\partial_t \delta h \sim \partial_{xxxx} \delta h$

Relaxation time of small perturbations $t \sim L^4$
Generalized Model predictions 1D & small slopes

\[ \partial_t h = \partial_x [h^n \partial_{xxx} h] \]

Scaling \( \theta \ll 1 \)

\[ \partial_{xx} h \sim \frac{1}{R} \quad h \sim R\theta^2 \quad x \sim R\theta \]

Triple line velocity

\[ v = \frac{1}{\theta} \partial_t x_0 = \frac{1}{\theta} \partial_x [h^n \partial_x \frac{1}{R}] \sim \frac{\theta^{2n-3}}{R^{3-n}} \]

Mass conservation

\[ \partial_t S = v h^* \quad \rightarrow \quad \theta^3 \partial_t R^2 \sim \frac{\theta^{2n-3}}{R^{3-n}} h^* \]

\[ S \sim hL \sim R^2 \theta^3 \]

Asymptotic scaling

\[ R \sim \theta^{-2(3-n)/(5-n)} h_*^{1/(5-n)} t^{1/(5-n)} \]

\[ x_0 \sim \theta^{(3+n)/(5-n)} h_*^{-(3-n)/(5-n)} t^{2/(5-n)} \]
Multi-scale expansion / Example: \( n = 0 \), solid-state dewetting

Wong, Vorrhees, Miskis, Davis (2000)

small slope limit \( \partial_x h \ll 1 \)

Mullins model

\[
\begin{align*}
\partial_t h &= -\partial_{xxx} h \\
h(x_0(t)) &= 0, & \partial_x h &= \tan \theta = \alpha, & \partial^3_x h(x_0(t)) &= 0, & h(x \to \infty) &= 1.
\end{align*}
\]

normalized variables

\[
X = \alpha(x - x_0(t)), \quad Y = h, \quad T = \alpha^4 t, \quad b = \alpha^{-3} \frac{dx_0}{dt}.
\]

Boundary conditions

\[
Y(X = 0) = 0, \quad \partial_X Y(X = 0) = 1, \quad \partial^3_X Y(X = 0) = 0, \quad Y(X \to \infty) = 1.
\]

Slow dynamics \( Y = Y_0 + Y_1 + Y_2 + \ldots \), with \( Y_{n+1} \ll Y_n \)

\[
\begin{align*}
\partial^4_X Y_0 - b^3 \partial_X Y_0 &= 0 \\
\partial^4_X Y_n - b^3 \partial_X Y_n &= -\partial_T Y_{n-1}
\end{align*}
\]

Solve \( Y_n \) order by order and then impose no-flux condition

\[
x_0(t) = \alpha \left( \frac{5t}{2\alpha} \right)^{2/5} - \frac{5}{4} \left( \frac{5t}{2\alpha} \right)^{1/5} + \ldots.
\]
Example: $n = 0$, solid-state dewetting

Asymptotic scaling

$$R \sim \theta^{-6/5} h_*^{1/5} t^{1/5}$$
$$x_0 \sim \theta^{3/5} h_*^{-3/5} t^{2/5}$$

Mass shedding  
Wong, Vorrhees, Miskis, Davis (2000)
Example: $n = 2, 3$, liquid-state dewetting

Asymptotic scaling $n = 2$

$R \sim t^{1/3}$

$x_0 \sim t^{2/3}$

Asymptotic scaling $n = 3$

$R \sim t^{1/2}$

$x_0 \sim t$

No Mass shedding!

**critical value** $n = 3/2$
Evidences of facets on the rim

**Ni(110)/MgO**


**SOI (Si/SiO₂), LEEM**


**SOI (Si/SiO₂), AFM**

Dornel Barbe Crecy Lacolle Eymery PRB2006

**DEWETTING WITH FACETS?**
Dynamics of solid wetting

Dewetting dynamics

Nucleation barrier

Dynamics limited by peeling or nucleation

Combe, Jensen, Pimpinelli, Phys Rev Lett 2000


Cost: $2\pi \rho \gamma_{\text{step}}$

Gain: $\pi \rho^2 \Delta \mu$ per atom, with $\Delta \mu = \Omega (-S)/h$

Total:

$$G = \gamma_{\text{step}} 2\pi \rho - \frac{-S}{\Omega h} \pi \rho^2$$

$$G_c = \Omega \pi \frac{\gamma_{\text{step}}^2 h}{-S}$$

$$I = \rho_0 \Gamma_c \left( \frac{-a^4 \partial_{ss} G_c}{2\pi T} \right)^{1/2} e^{-G_c/T}$$

Slow relaxation time $t \sim e^{G_c/k_B T} \sim e^h$

Experiments Ice/Pt(111)

Thurmer, Bartelt P.R.L. 2008
Facetted rim dynamics

Surface diffusion on top facet:

\[
\Delta \mu = \Omega \frac{-S}{h_1} \\
h_1 \partial_t x_1 \sim \frac{\Delta \mu}{\ell} \\
\ell(h_1 - h^*) = x_1 h^*
\]

\[h_1 \gg h^* \Rightarrow x_1 \sim t^{1/2} h_1^{-1/2}\]

We recover the previous law:
\[\ell \sim h_1 \Rightarrow h_1^2 \sim x_1 \Rightarrow x_1 \sim t^{2/5}\]

Facetted rim

\[
\partial_t h_1 \sim e^{-G_c} \sim e^{-\Omega \pi \gamma_{\text{step}} h_1 / (-S)} \\
\Rightarrow h_1 \sim \ln t \\
\Rightarrow x_1 \sim t^{1/2} (\ln t)^{-1/2}
\]

Distinguish \(\ln t\) from \(t^{1/5}\) in experiments??
Si/SiO_2 Leroy et al \(x \sim t^{1/3}\) ??
Metal GH Kim et al \(x \sim t^{2/5}\).
SOS KMC model

KMC simulations SOS Hopping rates
A/S: \( r_n = \nu_0 e^{-nJ/T + E_S/T} \)
A/A: \( \nu_n = \nu_0 e^{-nJ/T} \)
\( J \) bong energy; \( E_S \) substrate contact energy
**SOS KMC model**

**KMC simulations SOS** Hopping rates

A/S: \( r_n = \nu_0 e^{-nJ/T + E_S/T} \)

A/A: \( \nu_n = \nu_0 e^{-nJ/T} \)

\( J \) bong energy; \( E_S \) substrate contact energy

**Equilibrium shape** Low temperatures:

\[ h = E_S^{2/3} J^{-2/3} N^{1/3}; \ h/L = E_S/J \]

\( E_S = 1, \ N = 900, \rightarrow h = 8.7, \) simul at \( T/J = 0.35 \)

**Link** \( T \rightarrow O: \)

\[ \gamma(0) = J/2 \]

\[ S = -E_S \]
Facetted rim

OPL, A. Chame, Y. Saito, PRL 2009
Rim instability

\[ \partial_t h = \nabla \cdot [h^n \nabla \Delta h] \]

Transversal direction \( y \), perturbation \( q = 2\pi/\lambda \)
Assuming \( y \sim x \)

\[ \rightarrow q \sim \frac{1}{\theta R} \sim \frac{1}{\theta(n-1)/(5-n) h^{1/(5-n)} t^{1/(5-n)}} \]

\( n = 0 \rightarrow \lambda \sim t^{1/5} \)
\( n = 2 \rightarrow \lambda \sim t^{1/3} \)
\( n = 3 \rightarrow \lambda \sim t^{1/2} \)

OPL 2013, Münch-Wagner 2014

Final finger wavelength?

Kan, Wong J.Appl. Phys. 2005
10 fronts: Metastability?

KMC


Flat Si

SiO₂

Edge Retraction Distance

Si overetch ↑

\[ x = \begin{cases} \frac{t}{2}, & t > 1 \times 10^7 \\ 0, & t < 1 \times 10^7 \end{cases} \]
11 fronts

\[ h = 3, \quad h_1 = 9, \quad T = 0.5, \quad E_S = 1.5, \]

Instability of a facetted rim: Linear Coarsening

- **(110) -rough orientation** $\tilde{\gamma}_1 \approx \gamma$ constant

  Coarsening: $\lambda \sim t^{1/4}(\ln t)^{-1/2}$

  Numerical power-law fit $\lambda \sim t^{0.2}$

---

M. Dufay, OPL, PRL 2011
Instability of a facetted rim: Linear Coarsening

Instability on a - non-steady-state:

- (110) -rough orientation $\tilde{\gamma}_1 \approx \gamma$ constant
  Coarsening: $\lambda \sim t^{1/4} (\ln t)^{-1/2}$
  Numerical power-law fit $\lambda \sim t^{0.2}$

- (100) -vertical (100) facet
  $\tilde{\gamma}_1 = Ta/\beta^2 \approx (T/2a)e^{\gamma h_1/T}/h_1$
  Stable

M. Dufay, OPL, PRL 2011
Dynamics of solid wetting

KMC vs SOI

SOI system LEEM Experiments:
E. Bussman, F. Leroy, F. Cheynis, P. Müller, OPL NJP(2011)
Isotropic

More or less isotropic?

Müller et al LP2MC Marseille

Berbezier et al LP2MC Marseille
Dendritic shapes

More or less dendritic shapes?

Müller et al LP2MC Marseille

[Images of dendritic shapes with measurements]
Dewetting hole of shapes NNN KMC

- Seaweed
  - Isotropic
  - Example: dirty SOI

- Anisotropic Ramified
  - Simple 4-fold
  - Example: SOI

- Dendritic
  - 4-fold with secondary facet
  - Example: GOI
Dewetting of a complete film / Hole nucleation and growth

\( h = 3, \ E_S = 0.7, \ T = 0.5 \)

(a)

(b)

hole radius \( R \sim t^{1/2} \)
hole area \( A \sim R^2 \sim t \)
uncoverage \( \theta \sim t^2 \)

1 Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaischew construction
   - Thin Films
   - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
Continuum model with Wetting potential

Substrate at $h = 0$
Free energy per unit area:

$$\gamma(h) = \gamma_\infty + \mathcal{W}(h)$$

Wetting potential $\mathcal{W}(h) \to 0$ as $h \to \infty$

$$\mu(x) = -\gamma_\infty \partial_{xx} h + \gamma'(h)$$
$$j = -\mathcal{M}(h) \nabla \mu$$
$$\partial_t h = -\nabla \cdot j$$

Far from the substrate: $h \to \infty$
$$\mathcal{M}(h) \to \mathcal{M}_\infty$$
$$\gamma(h) \to \gamma_\infty$$
1 Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaischew construction
   - Thin Films
   - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
Non-equilibrium boundary condition

Equilibrium condition at Triple Line
Young-Dupré
\[ \gamma \cos \theta_{eq} + \gamma_{int} = \gamma_{sub} \]

Liquids
P.G. de Gennes

Grain Boundaries

Solid-state wetting
Wang, Jiang, Bao, Srolovitz (2015)

\[ v = K(\cos \theta - \cos \theta_{eq}) \]

Microscopic origin of the kinetic coefficients:
- Wetting potential?
- Microscopic Kinetic coefficients affected by the vicinity of substrate?

Is this the correct triple line BC?
Derive \( K \) from mesoscopic model?
Matched asymptotic Expansion

- Expand in small parameter $\epsilon \sim h_0$
Matched asymptotic Expansion

- Expand in small parameter $\epsilon \sim h_0$
Matched asymptotic Expansion

- Expand in small parameter $\epsilon \sim h_0$

(a) Film region
\[
\begin{aligned}
  h &\sim O(1) \\
x &\sim O(1)
\end{aligned}
\]

(b) TL region
\[
\begin{aligned}
  h &= \epsilon H(X, t) \\
x &= x_{TL} + \epsilon X
\end{aligned}
\]

(c) Substrate region
\[
\begin{aligned}
  h(x, t) &= \epsilon H(\chi, t) \\
\chi &= x
\end{aligned}
\]
Kinetic Boundary Conditions

To 0th order, Young & no-flux

\[ \theta = \theta_{eq} \]

\[ \frac{\gamma_{\infty}}{2} \theta_{eq}^2 = \gamma_{\infty} - \gamma_{min} \]

\[ J = 0 \]

... To 3rd order, KBC (Linear / Onsager)

\[ \mathcal{L} \begin{bmatrix} v \\ J \end{bmatrix} = \begin{bmatrix} [U] \\ -[\mu] \end{bmatrix} \]
Kinetic Boundary Conditions

To 0th order, Young & no-flux

\[ \theta = \theta_{eq} \quad \frac{\gamma_{\infty}}{2} \theta_{eq}^2 = \gamma_{\infty} - \gamma_{\text{min}} \quad J = 0 \]

... To 3rd order, KBC (Linear / Onsager)

\[ \mathcal{L} \begin{bmatrix} v \\ J \end{bmatrix} = \begin{bmatrix} [U] \\ [\mu] \end{bmatrix} \]

- **Thermodynamic Fluxes** :
  - \( v \) : velocity of triple line
  - \( J \) : mass flux through triple line
Kinetic Boundary Conditions

To 0th order, Young & no-flux

\[ \theta = \theta_{eq}, \quad \frac{\gamma_{\infty}}{2} \theta_{eq}^2 = \gamma_{\infty} - \gamma_{min}, \quad J = 0 \]

... To 3rd order, KBC (Linear / Onsager)

\[ \mathcal{L} \begin{bmatrix} v \\ J \end{bmatrix} = \begin{bmatrix} [U] \\ -[\mu] \end{bmatrix} \]

- **Local Thermodynamic Potentials**:
  \[
  U = -\frac{\gamma_{\infty}}{2} (\partial_x h)^2 + \gamma(h), \\
  \mu = -\gamma_{\infty} \partial_{xx} h + \gamma'(h),
  \]

- **Thermodynamic Fluxes**:
  \[
  v: \text{velocity of triple line} \\
  J: \text{mass flux through triple line}
  \]

- **Thermodynamic Forces**:
  \[
  [U] = (U_+ - U_-) = \gamma_{\infty} (\cos \theta - \cos \theta_{eq}) \\
  [\mu] = (\mu_+ - \mu_-) \propto \gamma_{\infty} \kappa - h \gamma''_{min}
  \]
Kinetic Boundary Conditions

To 0th order, Young & no-flux

\[ \theta = \theta_{eq} \quad \frac{\gamma_{\infty}}{2} \theta_{eq}^2 = \gamma_{\infty} - \gamma_{min} \quad J = 0 \]

... To 3rd order, KBC (Linear / Onsager)

\[ \mathcal{L} \begin{bmatrix} \nu \\ J \end{bmatrix} = \begin{bmatrix} [U] \\ -[\mu] \end{bmatrix} \]

- **Local Thermodynamic Potentials**:
  \[ U = -\frac{\gamma_{\infty}}{2} (\partial_x h)^2 + \gamma(h). \]
  \[ \mu = -\gamma_{\infty} \partial_{xx} h + \gamma'(h), \]

- **Thermodynamic Fluxes**:
  \[ \nu : \text{velocity of triple line} \]
  \[ J : \text{mass flux through triple line} \]

- **Thermodynamic Forces**:
  \[ [U] = (U_+ - U_-) = \gamma_{\infty} (\cos \theta - \cos \theta_{eq}) \]
  \[ [\mu] = (\mu_+ - \mu_-) \propto \gamma_{\infty} \kappa - h \gamma''_{min} \]

- **Kinetic Coefficients**:
  \[ \mathcal{L} = \begin{bmatrix} \mathcal{L}_{2\nu} & \mathcal{L}_{1\nu} \\ \mathcal{L}_{1\nu} & \mathcal{L}_{1J} \end{bmatrix} \]
Kinetic Coefficients

\[ \mathcal{L} \left[ \begin{array}{c} v \\ J \end{array} \right] = \left[ \begin{array}{c} [U] \\ -[\mu] \end{array} \right] \]

Kinetic coefficients

\[ \mathcal{L}_{1J} = \int_{-\infty}^{\infty} dX \left( \frac{1}{M(H_0)} - \frac{\Theta(X)}{M(\infty)} - \frac{\Theta(-X)}{M(0)} \right) \sim \frac{\epsilon}{M} \]

\[ \mathcal{L}_{1v} = \int_{-\infty}^{\infty} dX \left( \frac{H_0}{M(H_0)} - \frac{\Theta(X)}{M(\infty)} X \partial_x h_0(x_{TL}) \right) \sim \frac{\epsilon^2}{M} \]

\[ \mathcal{L}_{2v} = \int_{-\infty}^{\infty} dX \left[ \frac{H_0^2}{M(H_0)} - \frac{\Theta(X)}{M(\infty)} (X \partial_x h_0(x_{TL}))^2 \right] \sim \frac{\epsilon^3}{M} \]

In most cases \( \theta \sim \theta_{eq} \).
Numerical simulations

Wetting potential

Mobility
- case 1 constant mobility
- case 2 reduced mobility in the triple line region
- case 3 asymmetric: lower mobility in the substrate
- case 4 asymmetric: lower mobility in the film
Numerical simulations

(a) $h(x)$

(b) $x_{TL}$

(c) $v_{TL}(x)\times10^{-4}$

(d) $J_{TL}(x)\times10^{-6}$

(e) $[U]_{TL}(x)\times10^{-5}$

(f) $[\mu]_{TL}(x)\times10^{-4}$
Numerical simulations
Numerical simulations

Dynamic contact angle $\theta_D$

$$\eta = \frac{\theta_{eq} - \theta_D}{\theta_{eq}}$$

Dewetting dynamics

Case 1
Case 2
Case 3
Case 4

-9
-6
-3
0
3
$\eta \times 10^{-4}$

10^{-4} 10^{-5} 10^{-6}

$t$

Case 1
Case 2
Case 3
Case 4

$h(x)$

$t=0$
$t=1.2 \times 10^6$
$t=4 \times 10^5$
$t=1.6 \times 10^6$
$t=8 \times 10^5$
$t=2 \times 10^6$
Summary on Kinetic Boundary Condition

- 2 Kinetic Boundary Conditions for $v$ and $J$
- Numerical validation
- Convergence of kinetic coefficients.
  \( W(h) - W(\infty) \sim h^{-n} \), with \( n > 3 \)
  \( M(h) - M(\infty) \sim h^{-m} \), with \( m > 3 \)
  Van der Waals \( n = 2 \) ??
1 Static Wetting of liquids and Solids
- Introduction
- Wulff-Kaischew construction
- Thin Films
- Elastic effects

2 Dynamics of solid wetting
- Dewetting dynamics
- Surface diffusion model with wetting potential
- Derivation of the TL Boundary Condition
- Spinodal dewetting and Accelerated mass shedding
  - Elastic dewetting /ATG
  - KMC study of magic heights
  - Dewetting without a rim
  - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
- Patterns larger than islands
- Patterns smaller than islands
- Islands on nano-pillars
- Solid imbibition in nano-pillars

4 Conclusions
Small thicknesses: spinodal dewetting

Linear stability analysis: \( h = \bar{h} + \delta h \)
\[ \delta h \sim e^{i\omega t + iq} \]

\[ i\omega = \mathcal{M}(\bar{h}) q^2 \left[ -\gamma_\infty q^2 + W''(\bar{h}) \right] \]

Spinodal Instability if \( W''(\bar{h}) \leq 0 \)

\[ \lambda_{LS} = \frac{2^{3/2} \pi \gamma^{1/2}}{W''(\bar{h})^{1/2}} \]

\[ T_{LS} = \frac{4\gamma}{\mathcal{M}W''(\bar{h})^2} \]

Liquids
Embedded Animation

Aswani Tripathi, ILM-Lyon
Mass Shedding

Periodic Mass shedding
\[ \theta_0 = 60^\circ \text{ and } h_0 = 0.1 \]
Small thicknesses: spinodal dewetting

Linear stability analysis: $h = \bar{h} + \delta h$
Spinodal Instablility if $W''(\bar{h}) \leq 0$

$$T_c^{WV} = \frac{\bar{h}^4}{\bar{M}^{\gamma} \theta_0^4}$$

$$T_{LS} = \frac{4\bar{\gamma}}{\bar{M} W'''(\bar{h})^2}$$
1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaischew construction
   - Thin Films
   - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - **Elastic dewetting /ATG**
     - KMC study of magic heights
     - Dewetting without a rim
     - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
Continuum model with Wetting potential

Substrate at \( h = 0 \)

Free energy per unit area:

\[
\begin{align*}
\gamma(h) & = \gamma_\infty + \mathcal{W}(h) + \mathcal{E}_{el} \\
\mu(x) & = -\gamma_\infty \partial_{xx} h + \gamma'(h) + C e_0^2 \mathcal{H}(\partial_x h) \\
j & = -M \nabla \mu \\
\partial_t h & = -\nabla \cdot j
\end{align*}
\]

\[
\mathcal{H}[\partial_x h] = \mathcal{F}^{-1}\{|q|\mathcal{F}[h]\}
\]
Stabilizing exponential $W(h)$ and Anisotropy

FIG. 1 (color online). AFM images of a 5-nm-thin Si$_{0.70}$Ge$_{0.30}$ layer (a) as grown (Fourier transform in inset), (b) after 18-h annealing, and (c) after 54-h annealing at 550 °C. (d) Image of a 8-nm film after 18-h annealing. The [110] direction is horizontal. (The scan area is 3 x 3 $\mu$m$^2$, and the vertical scale is 32 nm.)

FIG. 2 (color online). Numerical resolution of the diffusion equation (1) for a strained anisotropic film for (a) a 5-nm film and $t = 0$ (Fourier transform in inset), (b) 18 h (240$\tau_{0}$), (c) 54 h (720$\tau_{0}$), and (d) an 8-nm film and $t = 18$ h (240$\tau_{0}$). [The scan area is 1.2 x 1.2 $\mu$m$^2$ (=$\sqrt{264}\tau_{0}$), and the vertical scale is 31 nm.]

Aqua, Gouye, Ronda, Frisch, Berbezier, PRL 2013
1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaishew construction
   - Thin Films
   - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - **KMC study of magic heights**
     - Dewetting without a rim
     - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
Electronic Quantum confinement

Free electron model

\[ W_{EC}(h) \approx -\frac{E_{fb}}{(h + 2b)^2} \frac{\pi}{36\sqrt{3}} \cos(2k_{fb}h) \]

- \( E_{fb}, k_{fb} \) Fermi energy and wavevector,
- \( b = \frac{3\pi k_{fb}}{8} \)

(a) Al(111) (purple squares), Ag(111) (blue circles)
(b) Al(111), (d) Ag(111) blue-Stable, red-Unstable
Magic heights and labyrinthine patterns

Metals/semicon or insulator: Electronic confinement → Magic thickness


Experiments Ag/Si(111)
SOS KMC model with magic height

KMC simulations SOS

\[ z \neq 1 \text{ and } z \neq h_* \]
\[ z = 1 \]
\[ z = h_* \]

\[ \nu_n = \nu e^{-(nJ+J_0)/T} \]
\[ r_n = \nu e^{-(nJ+J_0-E_S)/T} \]
\[ r_n^* = \nu e^{-(nJ+J_0-E_*)/T} \]
KMC simulations with magic height

\[ \lambda \sim 30 \text{nm} \]

Semi-quantitative agreement with experiments
Magic-height rim

\[ 800 \times 800, \ T = 0.4, \ h = 3, \ E_S = 0.4, \ h^* = 7, \ E = -0.5 \]

Induced nucleation and incomplete closure

A. Chame, OPL, Phys Rev B 2014
1 Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaischew construction
   - Thin Films
   - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
     - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
Monolayer $\rightarrow$ no rim

$V_{zip} \sim V_{front}$

FIG. 1 (color online). (a)–(c) NC-AFM images of $C_{60}$ islands on CaF$_2$(111) at three different growth temperatures. (d)–(f) Magnified images of single islands: a compact triangle (d), and hexagonal islands with morphologies I (e) and II (f). (g), (h) Height profiles along lines scans shown in (d),(e).

FIG. 2 (color online). (a)–(c) Simulated configurations of the growth model at different temperatures. (d)–(f) Magnified single island structures from the simulations resemble the same morphologies as found in experiments [Figs. 1(d)–1(f)].

P. Maas et al, PRL 2011
1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaishew construction
   - Thin Films
   - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
Dewetting with substrate mediated evaporation

- Constant velocity
- Non-monotonous rim width

A. Chame, OPL, PRE 2013
Interface Reaction in SOI systems: substrate profile

**Experiments**

Sudoh, Naito, JAP 2010.

(2 µm × 2 µm, 1050°)


**Kinetic Monte Carlo**

- Interface: Si+SiO₂ ↔ 2Si+2O
- Interface: O diffusion
- Triple Line: Si+O → SiO(evap)
- Si Surface: Si diffusion

\[ \nu_O = 10/\tau_A, \nu_E = 0.01/\tau_A. \]

**Analytic**

**Reaction-Diffusion**

\[ \partial_t C_O = D \partial_{xx} C_O + K_0 - K_1 C_O^2 \]

\[ \partial_t h_l = K_0 - K_1 C_O^2 \]

\[ \theta_{TL} = \theta_{eq} \]

\[ h = -\pi \frac{D_O^{1/2} K_0^{3/4}}{2^{1/2} K_1^{1/4}} \cosh \frac{x}{x_s} \int_{R_0/x_s}^{x/x_s} \frac{udu}{\sinh u} \]
Interface Reaction: running droplets

Running sild-clusers Sn/Cu(111)

LEEM, 1.5 μm, 290K


Liquid Running oil Droplet

Plate A

Plate B

Sumino, Magome, Hamada, Yshikawa PRL2005
1 Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaishew construction
   - Thin Films
   - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
Guided Self-Organisation vs Healing

Healing length

\[ \xi_{heal} = \left( \frac{\gamma(\bar{h})}{W''(\bar{h})} \right)^{1/2} \]

Guided self-organization

\[ \xi_{heal} = \left( \frac{\gamma(\bar{h})}{-W''(\bar{h})} \right)^{1/2} \]

Ge/Si, 5 x 5\( \mu \)m
Zhong et al PRL 2007
Au/Si
Aqua and Xu PRE 2014
C.V. Thompson
Guided Self-Organisation: Drift Experiments

Controlled positionning of mass in holes

McCarty NanoLetters 2006 Ag/W(110)
Nucleationless motion

Going back to equilibrium height without nucleation on top??

island position \( \sim t^{1/4} \)

M. Dufay, OPL, Phys Rev B, 2010
1. Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaisheew construction
   - Thin Films
   - Elastic effects

2. Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3. Islands on nano-patterns
   - Patterns larger than islands
   - **Patterns smaller than islands**
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4. Conclusions
Three wetting states for liquids on patterns

\[ \chi = \frac{1 + \cos \theta_0}{2} \]

- **Cassie-Baxter**
- **Wenzel**
- **Imbibition**

---

**Bico, Marzolin, Quéré (1999)**


**Seeman et al (2005)**

Polystyrene drops on Silicon

---

*Figure 12. Substrate decorated with posts (the bar indicates 1 \( \mu \)m). If coated with a monolayer of fluorinated silanes, this substrate is found to be super-hydrophobic [37].*
3D KMC Model

3D KMC
Hopping along the surface

\[ \nu = \nu_0 e^{-\left(n_1 J_1 + n_2 J_2 + n_{s1} J_{s1} + n_{s2} J_{s2}\right)/T} \]

\( J \) bond energy, \( n_i \) nb neighbors
\( i = 1, 2 \) NN, NNN adsrobate
\( i = s1, s2 \) NN, NNN substrate
Moves to NN
Allowed when there is NN or NNN

Shape controlled by

\[ \zeta = \frac{J_2}{J_1} = \frac{J_{s2}}{J_{s1}} \]

Wetting controlled by

\[ \chi = \frac{J_{s1}}{J_1} \]

Link \( T \to O \):

\[ 1 - \chi = \frac{-S}{2\gamma(0)} \]

\( \chi \to 0 \): Complete de-wetting
\( \chi \to 1 \): Complete Wetting
ψ parameter

Contact angle not a good parameter for facetted crystals!

\[ \psi = \frac{S_{AV}}{S_{AS}} \]

3D Isotropic crystal \( \gamma(\theta) = \tilde{\gamma} \)

\[ \chi = \frac{1}{2} (1 + \cos \theta_0) = \frac{1}{2} \left( 1 + \frac{\gamma_{SV} - \gamma_{AS}}{\tilde{\gamma}} \right) \]

\[ \psi = \frac{1}{\chi} \]

3D Square crystal \( \gamma_0 \)

\[ \chi = \frac{1}{2} \left( 1 + \frac{\gamma_{SV} - \gamma_{AS}}{\gamma_0} \right) \]

\[ \psi = 5 - 4\chi \]

\( \chi \to 0 \): Complete de-wetting

\( \chi \to 1 \): Complete Wetting (\( \psi = 1 \))
Wetting on a flat substrate

Wetting control parameter

$$\chi = \frac{J_{s1}}{J_1}$$

Cube $\zeta = 0$

$$\psi = 5 - 4\chi$$

KMC:

$N = 11025, \zeta = 0.2, \chi = 0.4, T/J_1 = 0.5$

Error: Energy 1%; $\psi$ 3%.
Parallel nano-grooves

\[ N = 10^4 \]
\[ \lambda = 20 \]
\[ \zeta = 0.2 \]
\[ \chi = 0.4 \]
\[ T/J_1 = 0.5 \]
Parallel grooves:
- Cassie-Baxter state (CB)
- Wenzel state (W)
- Capillary filling (CF)
Wetting parameter

\[ \psi = \frac{S_{AV}}{S_{AS}} \]

neglecting (110) and (111)

\[ \psi_{CB} = 7 - 2\chi \]
\[ \psi_{W} = 2 - 2\chi \]
\[ \psi_{CF} = \frac{1}{3} + \frac{1}{12\nu} \cdot \]

\[ \nu = Na^3/\lambda^3 \]
Hysteresis/Stability

Instability thresholds

\[
\chi_{CB \rightarrow W} = \frac{1}{2},
\]

\[
\chi_{W \rightarrow CB} = \frac{1}{3} - \frac{1}{36v} \left[ 1 + (1 + 30v)^{1/2} \right],
\]

\[
\chi_{W \rightarrow CF} = \frac{2}{3} - \frac{1}{36v} \left[ 1 + (1 + 6v)^{1/2} \right],
\]

\[
\chi_{CF \downarrow} = 1 - \frac{1}{8v}
\]

\[
\chi_{CF \uparrow} = \frac{1}{3} - \frac{1}{24v}
\]

Finite temperature effects \( CF \rightarrow W \)
Migration-induced switching

Nanoswitch controlled by an electron beam
KMC with imposed migration

M. Ignacio, OPL, PRE (2015)
Migration-induced switching

Phase diagram $\bar{F} = FN/(\gamma_{100}\lambda)$

(a1) $h$ $h^*$

$\lambda/4$

(b) $\bar{F}$ $\chi$

(c) $\tau$ $|\bar{F}|$

\[\begin{align*}
F & = FN/(\gamma_{100}\lambda) \\
\tau & = \frac{\gamma_{100}}{\gamma_{110}}
\end{align*}\]
Migration-induced switching

Phase diagram $\tilde{F} = FN/(\gamma_{100}\lambda)$
Static Wetting of liquids and Solids
- Introduction
- Wulff-Kaishev construction
- Thin Films
- Elastic effects

Dynamics of solid wetting
- Dewetting dynamics
- Surface diffusion model with wetting potential
- Derivation of the TL Boundary Condition
- Spinodal dewetting and Accelerated mass shedding
- Elastic dewetting /ATG
- KMC study of magic heights
- Dewetting without a rim
- Non-conservation of the mass: evaporation and reaction

Islands on nano-patterns
- Patterns larger than islands
- Patterns smaller than islands
- Islands on nano-pillars
- Solid imbibition in nano-pillars

Conclusions
Nanocrystals in Cassie-Baxter state

Growth of GaN on Si nano-pillars

Hersee et al. J.A.P. 2005

- Avoiding dislocations?
- Growing without collapse?
- Stability?

\[ \chi = 0.390, \chi = 0.405 \]

Zang et al, APL 2006
Dynamics of the island: 3 Stages

1. Deterministic
2. Collapse
3. Random

$h^*$

$T_{contact}$

$T_{collapse}$

Deterministic collapse

Random walk

13/09/2011

Maxime Ignacio
Elastic islands on nano-pillars

3D KMC with elastic effects

- Extended stability
- Asymmetric CB state
- Partially collapsed state

M. Ignacio, Y. Saito, P. Smereka, OPL, PRL 2014
1 Static Wetting of liquids and Solids
   - Introduction
   - Wulff-Kaishew construction
   - Thin Films
   - Elastic effects

2 Dynamics of solid wetting
   - Dewetting dynamics
   - Surface diffusion model with wetting potential
   - Derivation of the TL Boundary Condition
   - Spinodal dewetting and Accelerated mass shedding
   - Elastic dewetting /ATG
   - KMC study of magic heights
   - Dewetting without a rim
   - Non-conservation of the mass: evaporation and reaction

3 Islands on nano-patterns
   - Patterns larger than islands
   - Patterns smaller than islands
   - Islands on nano-pillars
   - Solid imbibition in nano-pillars

4 Conclusions
Imbibition criterion

\[ 1 > \chi > \chi_{imb} = \frac{1}{2} \left( 1 + \frac{\ell_x^2 - \ell_p^2}{\ell_x^2 + 4h\ell_p - \ell_p^2} \right) \]
Diffusion-limited spreading

\[ \chi = 0.8, \, \ell_x = 6, \, h = 3, \, \ell_p = 4 \]

\[ L \sim t^{1/2}, \text{ and } A \sim t \text{ with log corrections} \]

\[ (V - A_2 h(1 - \phi))(1 - \ln \left( \frac{\frac{(1 - \phi)\pi h}{V}}{\frac{V - A_2 h(1 - \phi)}{\pi^2 \phi(1 - \chi)}} \right)) \]

\[ = \frac{3}{2} \pi \Omega^2 D e q \frac{\gamma}{kdT} \frac{(t_0 - t)}{(1 - \phi)h} \left[ \phi \rho (2\chi - 1) - 2(1 - \chi)(1 - \phi) \right] \]

P. Gaillard, Y. Saito, OPL, Phys Rev Lett 2011
Nucleation-limited imbibition front motion

\[
\chi = 0.8, \ \ell_x = 6, \ h = 3, \ \ell_p = 2
\]

P. Gaillard, Y. Saito, OPL, Phys Rev Lett 2011
Summary

- Equilibrium and stability of islands and films
- Dewetting of solid films: Rim facetting, Instability Coarsening and Anisotropy
- Islands on nano-patterns: Multi-stability / Collapse / Elasticity
- Wetting of reactive islands

Other related issues and Perspectives

- Reactive wetting and nanowire growth
- Surface melting
- Non-equilibrium TL condition
- Link to complex fluids (polymers, etc)
- ... nucleation and growth