Wetting and adhesion on nano-patterned surfaces,

How geometry couples to physics

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Wetting of solid clusters on nano-patterned surfaces,

How geometry couples to physics

Some examples

- Contact angle
- Lotus effect

Young contact angle

Surface/Interface free Energies

$$\mathcal{F} = \int_{VS} \mathrm{d}s\, \gamma_{VS}(\theta) + \int_{SA} \mathrm{d}s\, \gamma_{SA}(\theta) + \int_{AV} \mathrm{d}s\, \gamma(\theta)$$

Assumptions:
(i) flat substrate
(ii) fixed total volume:

$$\mathcal{N} = \Omega^{-1} \int\int_A \mathrm{d}^2\mathbf{r}$$

Equilibrium:

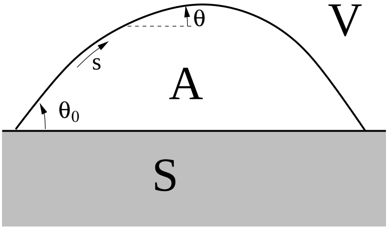
$$\delta(\mathcal{F} - \mu\mathcal{N}) = 0$$

Laplace:

$$\mu = \Omega\gamma_{AV}\kappa$$

Young relation (1805):

$$\gamma_{SA} + \gamma_{AV}\cos\theta_0 = \gamma_{SV}$$



Super-hydro-phobic surfaces: Wenzel and cassie-Baxter states

Bico, Marzolin, Quéré, Europhys. Lett (1999).

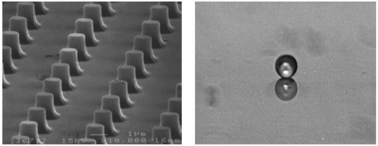
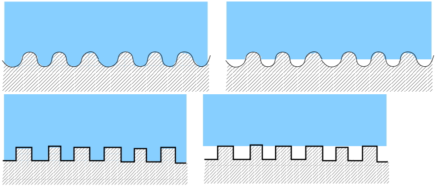


Figure 12. Substrate decorated with posts (the bar indicates 1 μm). If coated with a monolayer of fluorinated silanes, this substrate is found to be super-hydrophobic [37].

Wenzel and Cassie-Baxter states



Effective contact angle:

$$\gamma_{SA}^{eff} + \gamma_{AV} \cos\theta_0 = \gamma_{SV}^{eff}$$

Wenzel (1936)
substrate lengthening $r \geq 1$

$$\cos\theta_W = r\cos\theta_0$$

Cassie-Baxter (1944)
solid-liquid contact fraction ϕ_{AS}
liquid-vapor contact fraction η_{AV}

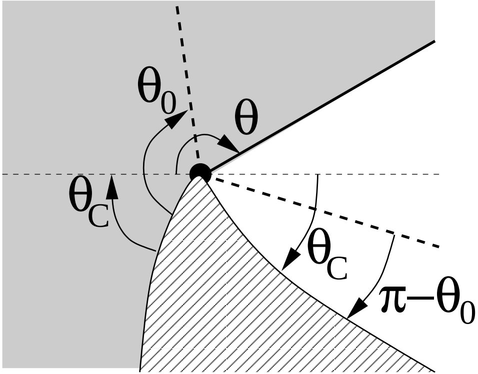
$$\cos\theta_{CB} = \phi_{AS}\cos\theta_0 - \eta_{AV}$$

Pinning

Gibbs Inequality Condition (1906)

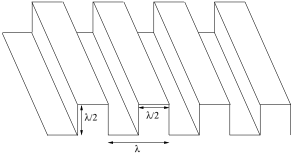
$$\theta_0 - \theta_C \leq \theta \leq \theta_0 + \theta_C$$

$\rightarrow$ Pinning at corners



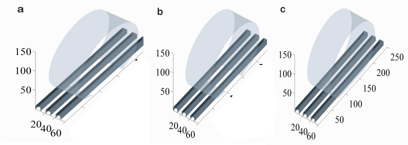
Dynamics of lifting and collapse

Parallel grooves:



Lattice-Boltzmann simulations

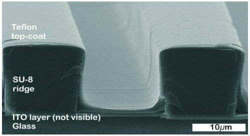
Solve the hydrodynamics

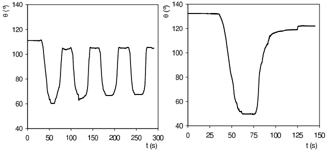


Movies

Electro-wetting experiments

Vary θ_0 continuously with V

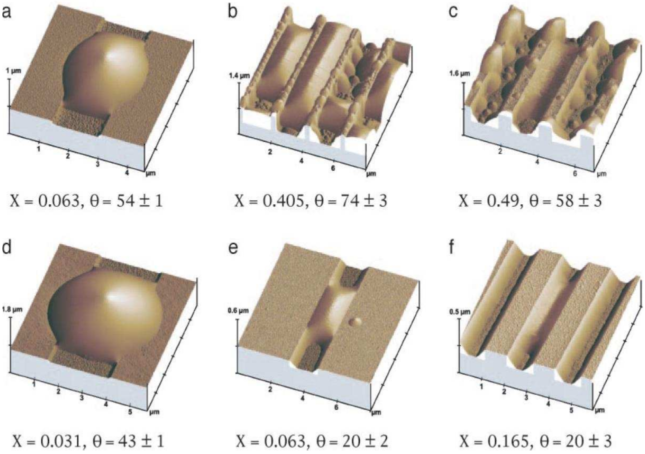




R. J. Vrancken, H. Kusumaatmaja, K. Hermans, A.M. Prenen, O. Pierre Louis, C. W. M. Bastiaansen, D.J. Broer, preprint

Capillary filling

Seeman*et al* (2005)
Polystyrene drops on Silicon



Wetting of solid clusters on nano-patterned surfaces,

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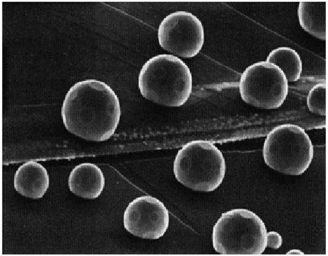
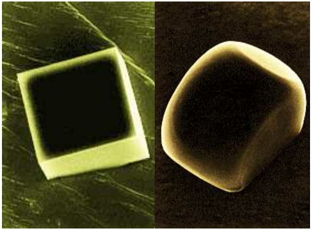
Experimental equilibrium shape

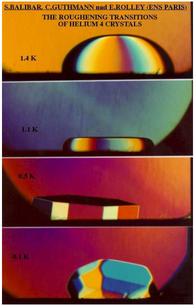
Au/Graphite, Héyraud, Métois, Marseille



NaCl, Métois et al (620-710^{o}C)



He$_4$ crystal, Balibar et al, Paris



Solids vs liquid

- Anisotropy: roughnening transition $\longrightarrow$ facets

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- Energy: elasticity, eletronic energy, etc.

Solids vs liquid

- Anisotropy: roughnening transition $\longrightarrow$ facets
- Energy: elasticity, eletronic energy, etc.
- Mass Transport: diffusion (surface atoms, or bulk vacancies)

The Wulff and Kaishev constructions

Isotropic solid $\gamma(\theta) = \bar{\gamma}$

$$\mu = \Omega\bar{\gamma}\kappa \quad \Rightarrow \quad R = \frac{\Omega\bar{\gamma}}{\mu}$$

$$\bar{\gamma}\cos(\theta_0) = -\gamma_S \quad \Rightarrow \quad h_s = \frac{\Omega\gamma_S}{\mu}$$

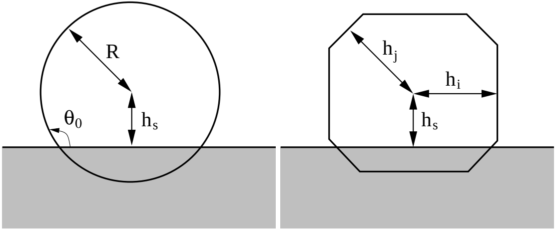
Polygonal shape

$$h_i = \frac{\Omega\gamma_i}{\mu}$$

$$h_s = \frac{\Omega\gamma_S}{\mu}$$

Global geometry

$$\psi = \frac{\mathcal{S}_{AV}}{\mathcal{S}_{AS}}$$



3D KMC Model

3D KMC
Hopping along the surface

$$\nu = \nu_0 \, \mathrm{e}^{-(n_1 J_1 + n_2 J_2 + n_{s1} J_{s1} + n_{s2} J_{s2})/T}$$

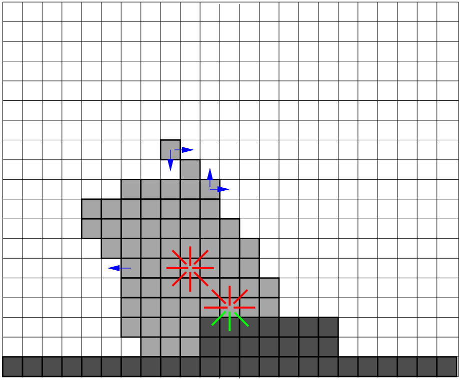
J bond energy, n_i nb neighbors
$i = 1$ NN adsrobate
$i = 2$ NNN adsorbate
$i = s1$ NN substrate
$i = s2$ NNN substrate
Moves to NN/ surface
Shape parameter

$$\zeta = \frac{J_2}{J_1} = \frac{J_{s2}}{J_{s1}}$$

Wetting controlled by

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

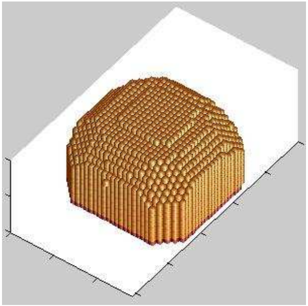
isotropic: $\chi = (1 + \cos\theta_0)/2$

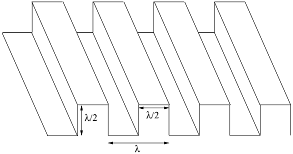


Flat substrate vs parallel nanogrooves

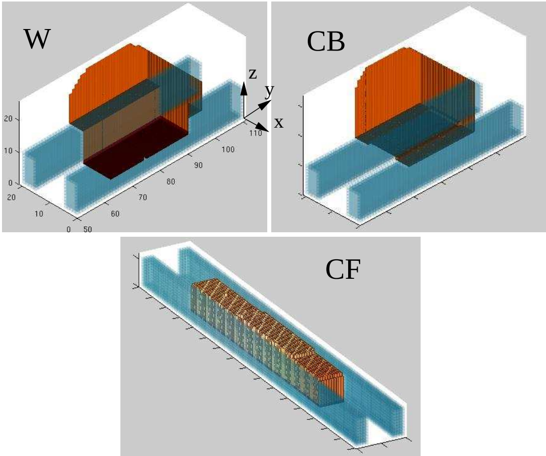
$N = 10^4$, $\lambda = 20$, $\zeta = 0.2$,
$\chi = 0.4$, $T/J_1 = 0.5$

Flat substrate



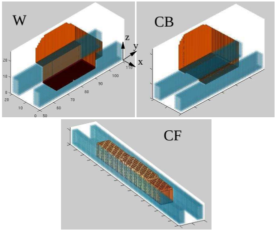


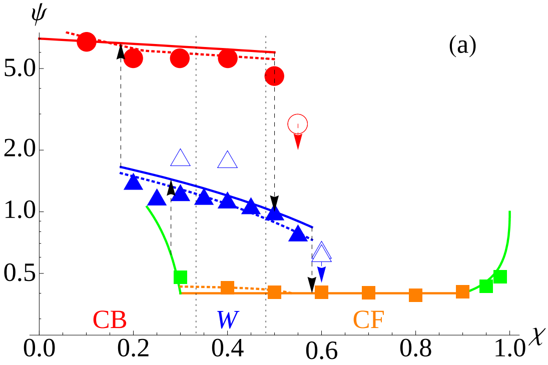
Parallel grooves $\rightarrow$ 3 states
Wenzel, Cassie-Baxter, Capillary Filling



Hysteresis

$$\psi = \frac{\mathcal{S}_{AV}}{\mathcal{S}_{AS}}, \qquad \chi = \frac{J_{s1}}{J_1}$$

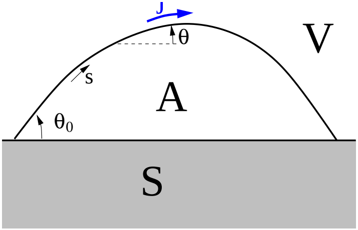




Surface Diffusion

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 $\theta = \theta_0$

Scaling
$v_n \sim \partial_{ss}\kappa$
Relaxation time $t \sim L^4$

Dynamics

Dynamics limited by peeling or nucleation

Combe, Jensen, Pimpinelli, Phys Rev Lett 2000

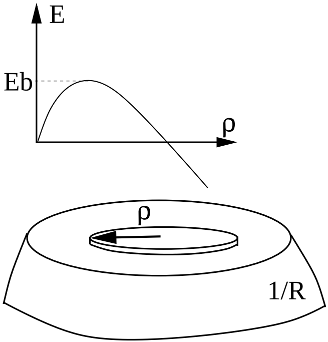
Mullins and Rohrer, J. Am. Ceram. Soc. 2000

Activation energy: $\sim$ lateral size R
Cost: $\gamma_{step} 2\pi\rho$
Gain: $\gamma_{rough}(1/R)$ per atom
Total:

$$E = \gamma_{step} 2\pi\rho - \frac{\gamma_{rough}}{R}\pi\rho^2$$

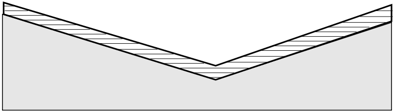
$$E_b = \pi \frac{\gamma_{step}^2}{\gamma_{surf}} R$$

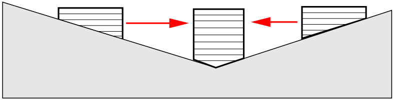
Slow relaxation time $t \sim \mathrm{e}^{E_b/k_B T}$

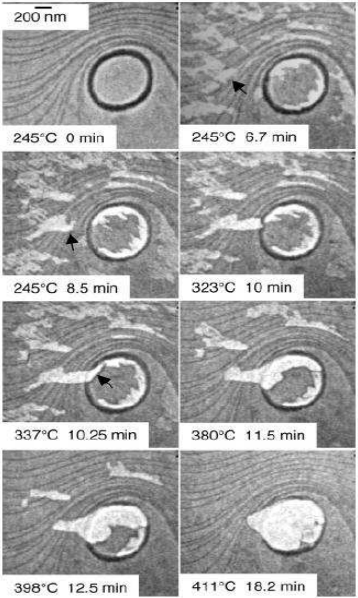


Experiments

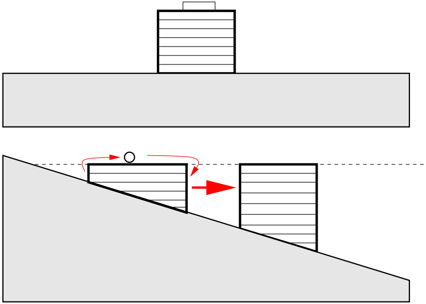
Controlled positionning of mass in holes
Ling *et al* Surf. Sci 2006
McCarty NanoLetters 2006 Ag/W(110)



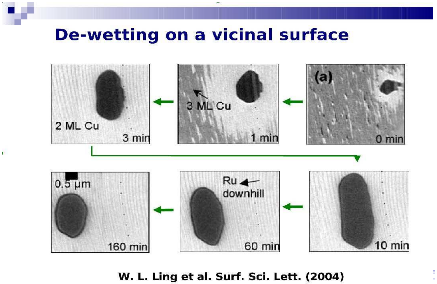




Nucleationless motion



Going back to equilibrium height without nucleation on top??



Model

$\mathcal{X} = (x_U + x_D)/2$, and $\mathcal{H} = \mathcal{X}\tan(\theta)$
$l_T = x_U - x_D$, $l_\perp = y_+ - y_-$

Einstein-like relation

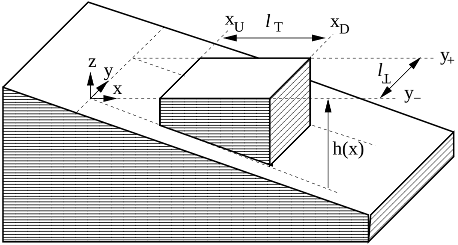
$$\partial_t \mathcal{X} = -\frac{D_C}{k_B T}\partial_{\mathcal{X}} E_T.$$

Diffusion limited dynamics

$$D_C \approx \frac{\Omega^2 D c_{eq}}{\mathcal{H}^2 l_T l_\perp}$$

Khare, Bartelt, Einstein, Phys. Rev. Lett. 1998

OPL, T.L. Einstein, Phys. Rev.B 2000



Interfacial and Wetting energies

Free energy

$$E_I \approx \gamma(h_U + h_D)(l_\perp + l_T) + 2\gamma(1-\chi) l_T l_\perp$$

$\mathcal{X} \gg l_T$

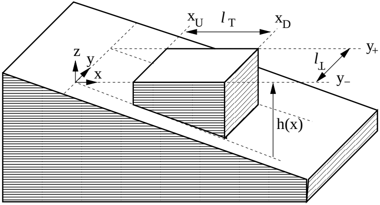
Maximum aspect ratio $r = l_\perp / l_T$

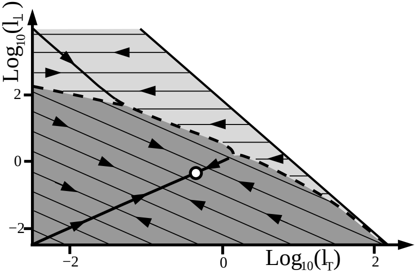
$$r^I_{max} \approx \left(\frac{1-\chi}{\tan\theta}\right)^{1/4} r^{3/2}_{init}$$

Drift dynamics

$$\partial_t \mathcal{X} = \frac{\Omega^2 D c_{eq}}{k_B T} \frac{2\gamma(1-\chi)}{\mathcal{X}^3 \tan^2(\theta)}$$

leading to $\mathcal{X} \sim t^{1/4}$
(also wetting potential $\mathcal{W}(h)$)





Elastic energy

Exp: Tersoff Tromp, 1993 Ag/Si(100)
Exp: Xu et al 2007, Ge/Si(111)

$$E_E \approx \frac{1}{2} \int dr_j \int dr_k \;\; \mathcal{G}_{j,k}\left(\mathbf{r}_j - \mathbf{r}_k\right) \; \mathbf{f}_j(\mathbf{r})\, \mathbf{f}_k(\mathbf{r})$$

Maximum aspect ratio $r = l_\perp / l_T$

$$r^E_{max} = C \frac{V^{1/2}}{\tan(\theta)^{1/2} d_0^{3/2}} \mathrm{e}^{-3(3+\sigma)/8(1-\sigma)}$$

where $C = 0.175...$

Drift dynamics

$$\partial_t \mathcal{X} = \frac{\Omega^2 D c_{eq}}{k_B T} \frac{\alpha^2(1-\sigma^2)}{\pi Y d_0} \mathrm{e}^{-1/(1-\sigma)} \frac{1}{\mathcal{X}}$$

where Y is the Young modulus.
Scaling law $\mathcal{X} \sim t^{1/2}$.

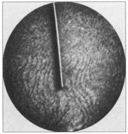
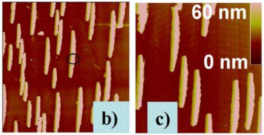
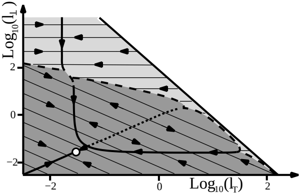


FIG. 3. Portion of a Ag island on Si(001), as seen with LEEM. Field of view is 6 μm. Faint wavy lines are steps on substrate surface.





Other energy

Metallic layers: Electronic confinement energy

Z. Zhang et al, Phys.Rev.Lett.1998,1999

Metals/Semiconductor

1) Quantum confinement of electrons

2) Charge spilling in the substrate

3) Friedel oscillations

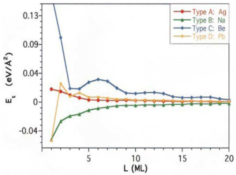
Van der Waals forces

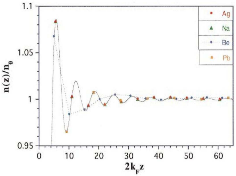
$$U_{VdW} = -\frac{A}{12\pi h^2}$$

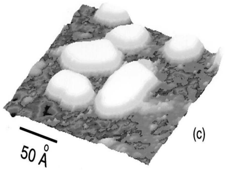
A can be either > 0 or < 0 ?

?? $A \sim 10^{-20}$J

Z. Suo and Z. Zhang, Phys Rev B (1998)







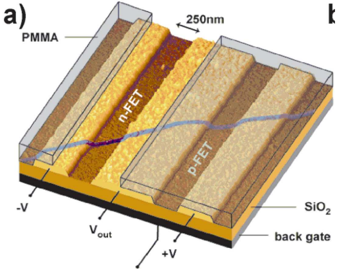
Magic thicknesses (as in metal clusters)

Wetting of solid clusters on nano-patterned surfaces,

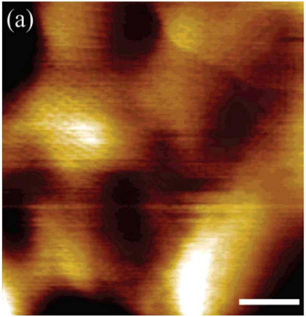
How geometry couples to physics

Carbon nanostructures

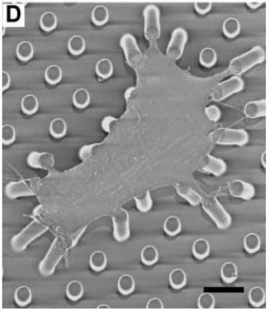
Nanotubes on ripples (or grids)
Derike *et al*, NanoLetters (2001).



Graphene on rough SiO_2
E.D. Williams *et al*, NanoLetters (2007);
scale-bar 2nm.

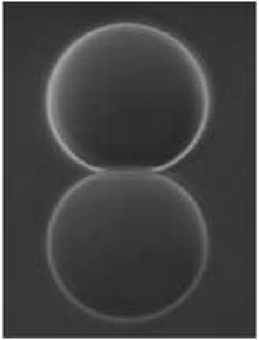


Lipidic membranes



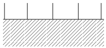
L. Tan *et al* PNAS (2003); scale-bar 10μm

Simple (fluid) lipid membrane on a non-flat surface

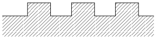


M. Abkarian A. Viallat, Biophys J. (2005); $D = 130\mu$m

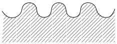
1D model: Filament or membrane on ripples



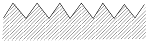
Fakir Carpet



Crenellated



Sinusoidal



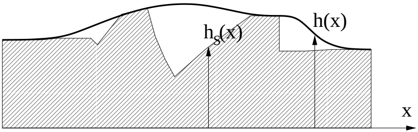
Saw tooth

Wavelength λ
Amplitude ϵ

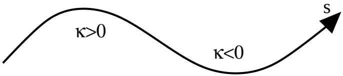
Total energy

$$\mathcal{E} = \int ds \left[\frac{C}{2} \kappa(s)^2 + \sigma + V(\mathbf{r}(s)) \right]$$

outside solid $V = 0$, surface $V = -\gamma$,
inside $V = +\infty$.
i.e. Deformations $\gg \ell_{eq}$
Adhesion energy γ
Bending rigidity C
Tension σ



Equilibrium equations for the Euler elastica with adhesion

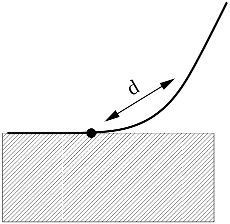


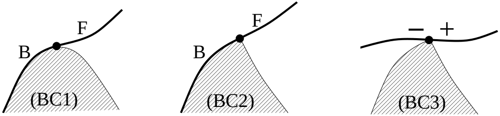
Free parts

$$C\partial_{ss}\kappa + \frac{C}{2}\kappa^3 - \sigma\kappa = 0.$$

Euler-Bernoulli elastica model

Cut-off length $d = (C/\sigma)^{1/2}$





Boundary conditions

BC1

$$\kappa_F = \kappa_B - \kappa_{eq},$$

where $\kappa_{eq} = (2\gamma/C)^{1/2}$

BC2

$$\kappa_B - \kappa_{eq} \leq \kappa_F \leq \kappa_B + \kappa_{eq}.$$

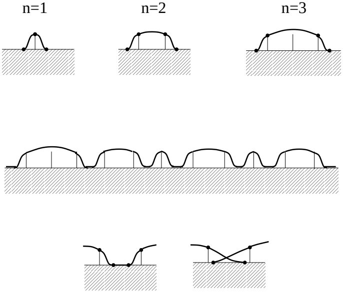
Similar to the Gibbs Inequality Condition for the wetting contact angle

BC3

$$\kappa_+ = \kappa_-, \qquad \text{and} \qquad \partial_s\kappa_+ \leq \partial_s\kappa_-,$$

Patterned substrates: a 1D model

Constructing solutions from *n*-bridges



All possible solutions

Non-overlapping reduces the number of possible states

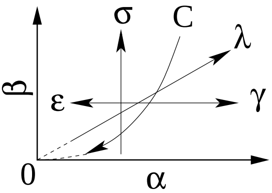
Natural parameters

$$\beta = \frac{\lambda}{d}$$

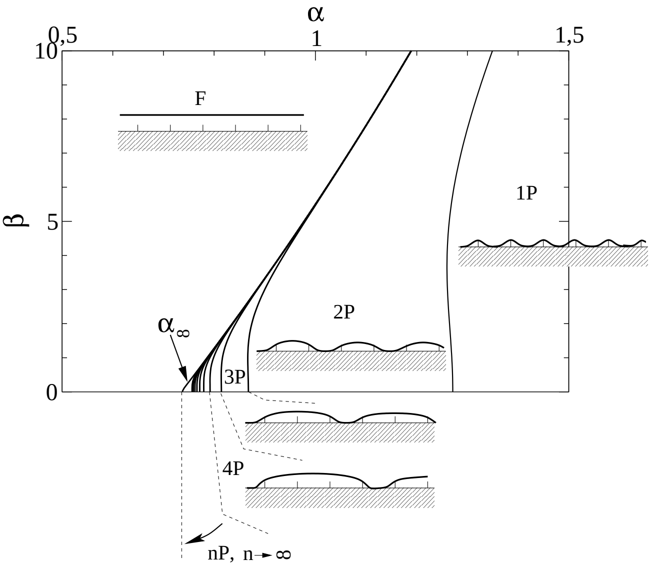
$\beta \gg 1$ tension dominates
$\beta \ll 1$ curvature dominates

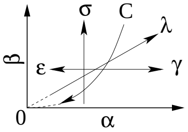
$$\alpha = \left(\frac{\kappa_{eq}}{\kappa_g}\right)^{1/2}$$

geometrical curvature $\kappa_g = 4\pi^2\epsilon/\lambda^2$
$\alpha \ll 1 \rightarrow$ Floating state
$\alpha \gg 1 \rightarrow$ Membrane follows patterns

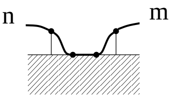


Ground state Transitions

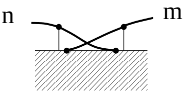




Metastability

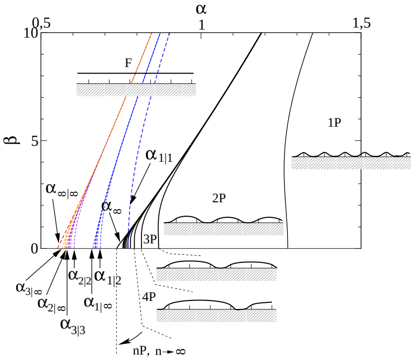


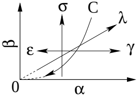
$\alpha > \alpha_{n|m}[\beta]$



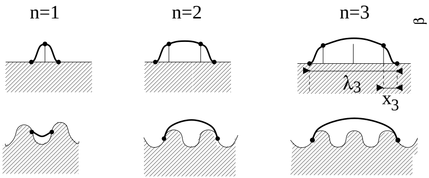
$\alpha < \alpha_{n|m}[\beta]$

$\alpha_{n|m}[\beta] > \alpha_{n|m+1}[\beta]$
$\alpha_{n|m}[\beta] = \alpha_{m|n}[\beta]$
$\rightarrow \alpha_{n|m}[\beta] > \alpha_{n|m+p}[\beta]$
But no "total order",
e.g. $\alpha_{5|5}[0] < \alpha_{4|9}[0]$, and $\alpha_{5|5}[1] > \alpha_{4|9}[1]$
$\rightarrow$ β-dependent decimation order
Non-sticky F ground state at $\alpha < \alpha_{\infty|\infty}[\beta]$

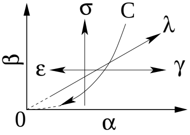




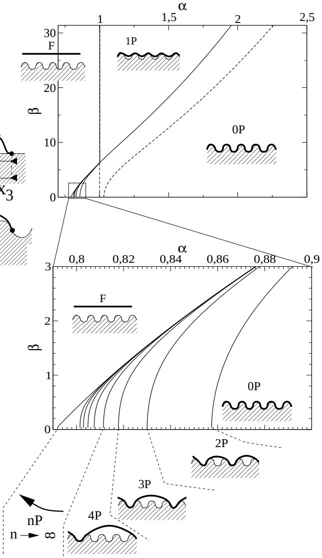
Sinusoidal surfaces



A single family of bridges for: fakir carpet and sinusoidal,
more for other surfaces



Sinusoidal surface



Orders of magnitude

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Graphene

$C = 0.9\mathrm{eV}$, $\gamma \sim 6\mathrm{meV\AA}^{-2}$, $\sigma \approx 0$
$\rightarrow \epsilon\kappa_{eq} \sim 1$.
$\epsilon = 1$nm, and $\lambda = 10$nm, $\Rightarrow \alpha \sim 2$
larger than 100nm follow

A. Incze, A. Pasturel and P. Peyla, Phys.Rev.B (2004)

Oxygen adsorption tunes bending rigidity:
12.5% oxygen $C = 40\mathrm{eV}$ Peyla et al
$\epsilon\kappa_{eq} < 1$.
$\epsilon = 1$nm, and $\lambda = 10$nm, $\Rightarrow \alpha \approx 0.6$.
Oxygen adsorption $\Rightarrow$ scan tranisiton region

Orders of magnitude

lipid membranes(Swain and Andelman)
$C = 1.4 \times 10^{-19}$J, and $\sigma = 1.7 \times 10^{-5}$Jm^{-2}
$\gamma = 5 \times 10^{-6}$Jm^{-2}, $\ell_{eq} = 3$nm
Choosing
$\epsilon \approx 50\mathrm{nm} \gg \ell_{eq}$, $\lambda \approx 500\mathrm{nm} \gg \epsilon$,
we obtain
$\Rightarrow \alpha \approx 1.5$ and $\beta \approx 5$

Nanotubes

$\sigma \approx 0$, $C = 20\mathrm{eV.nm}$, and $\gamma \approx 1\mathrm{eV.nm}^{-1}$
Choosing
$\epsilon = 5$nm, $\lambda = 50$nm
we obtain
$\alpha \approx 2$
(Nevertheless $\epsilon\kappa_{eq} \sim 1$)

Wetting of solid clusters on nano-patterned surfaces,

How geometry couples to physics

Summary

- Liquids on micro-grooves:

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  OPL, Y. Saito, EuroPhys. Lett. 2009
- Drift of solid islands:
  M. Dufay, OPL, preprint
- Membranes and filaments on patterns
  OPL, Phys. Rev. E 2007

Perspectives

- Coupling between physics and morphology

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  OPL, A. Chame, Y. Saito, Phys. Rev. Lett. 2007

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- Dewetting of solid films on flat substrates
  OPL, A. Chame, Y. Saito, Phys. Rev. Lett. 2007
- Nonlinear dynamics, instabilities, and fluctuations of extended fronts
  OPL, Europhys. Lett. 2005; C. Misbah, OPL, Y. Saito, Rev. Mod. Phys. 2009

Elastica: variation of the energy

$s < s_B$ free
$s > s_B$ adhesion

$$\mathcal{E} = \int^{s_B} ds \left[\frac{C}{2}\kappa^2 + \sigma \right] + \int_{s_B} ds \left[\frac{C}{2}\kappa^2 + \sigma - \gamma \right].$$

$$\mathbf{t}_{s_B^-} = \mathbf{t}_{s_B^+},$$

Variation $\delta\mathbf{r}(s)$
with $\delta\mathbf{r}(s) = 0$ for $s > s_B$.

$$\begin{aligned} \delta\mathcal{E} &= \int^{s_B} ds(\delta\mathbf{r}\cdot\mathbf{n}) \left[C\partial_{ss}\kappa + \frac{C}{2}\kappa^3 - \sigma\kappa \right] \\ &+ [-(\delta\mathbf{r}\cdot\mathbf{n})C\partial_s\kappa + (\partial_s\delta\mathbf{r}\cdot\mathbf{n})C\kappa]\,|_{s_B^-} \\ &+ ds_B \left[\left(\frac{C}{2}\kappa^2 + \sigma \right)|_{s_B^-} - \left(\frac{C}{2}\kappa^2 + \sigma - \gamma \right)|_{s_B^+} \right] \end{aligned}$$