Victoria University of Wellington
Te Whare Wānanga o te Ūpoko o te Ika a Māui

The MacDiarmid Institute for Advanced Materials and Nanotechnology

The effective performance of nanostructured surfaces and catalysts

N. Lund[1], X. Y. Zhang[2], D. Schebarchov[1,2], N. Gaston[1,2] and S. C. Hendy[1,2]

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Introduction

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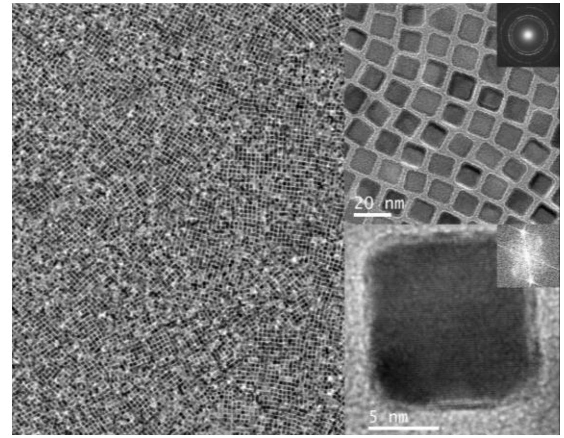

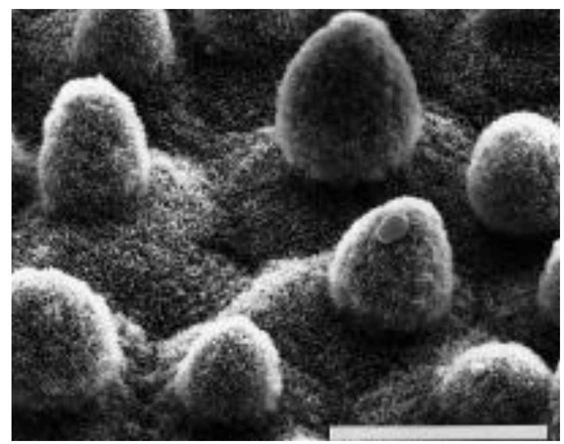

Overview

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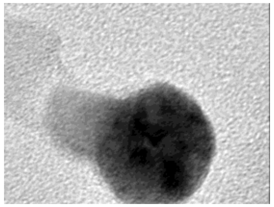
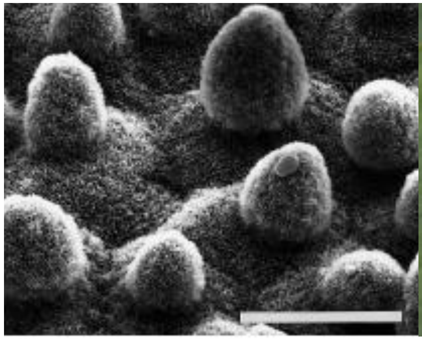
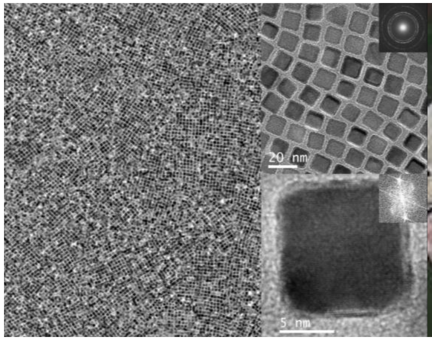
- Nanoscale fluid mechanics



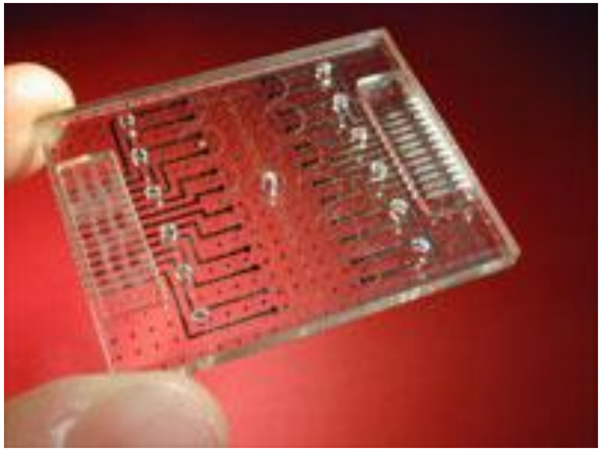

- Flows over nanostructured surfaces

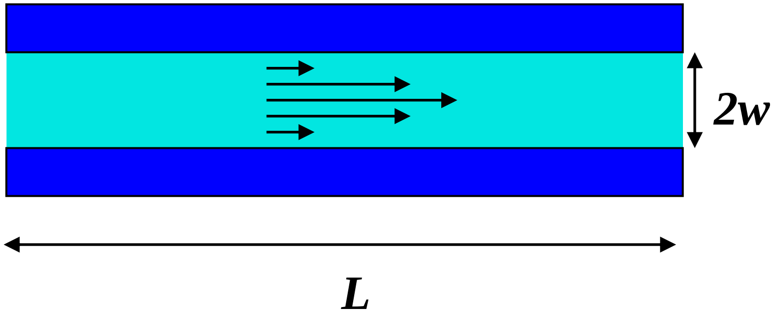



- Performance of nanostructured catalysts



Why is microfluidics hard?





$$\dot{m} \sim \frac{\Delta P}{\mu L} w^4$$

$$\left(\text{c.f. electrons } \; I \sim \frac{\Delta V}{\rho L} w^2 \text{ while } \lambda << w \right)$$

… while nanofluidics is easy?

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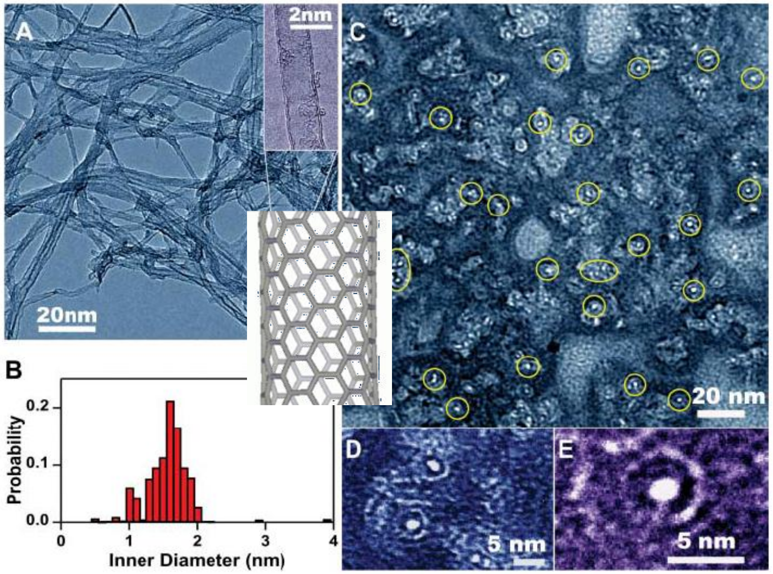
- Holt et al (LLNL)

Fast Mass Transport Through Sub–2-Nanometer Carbon Nanotubes

Jason K. Holt,[1*] Hyung Gyu Park,[1,2*] Yinmin Wang,[1] Michael Stadermann,[1] Alexander B. Artyukhin,[1] Costas P. Grigoropoulos,[2] Aleksandr Noy,[1] Olgica Bakajin[1†]

19 MAY 2006 VOL 312 SCIENCE

$$\dot{m} \sim \frac{\Delta P}{\mu L} w^4$$



Membrane	Pore diameter (nm)	Pore density (cm^{-2})	Thickness (μm)	Enhancement over no-slip, hydrodynamic flow† (minimum)
DWNT 1	1.3 to 2.0	$\leq 0.25 \times 10^{12}$	2.0	1500 to 8400
DWNT 2	1.3 to 2.0	$\leq 0.25 \times 10^{12}$	3.0	680 to 3800
DWNT 3	1.3 to 2.0	$\leq 0.25 \times 10^{12}$	2.8	560 to 3100
Polycarbonate	15	6×10^{8}	6.0	3.7

*From (*18*). †From (*26*). ‡From (*29*).

Metal particles in CNTs

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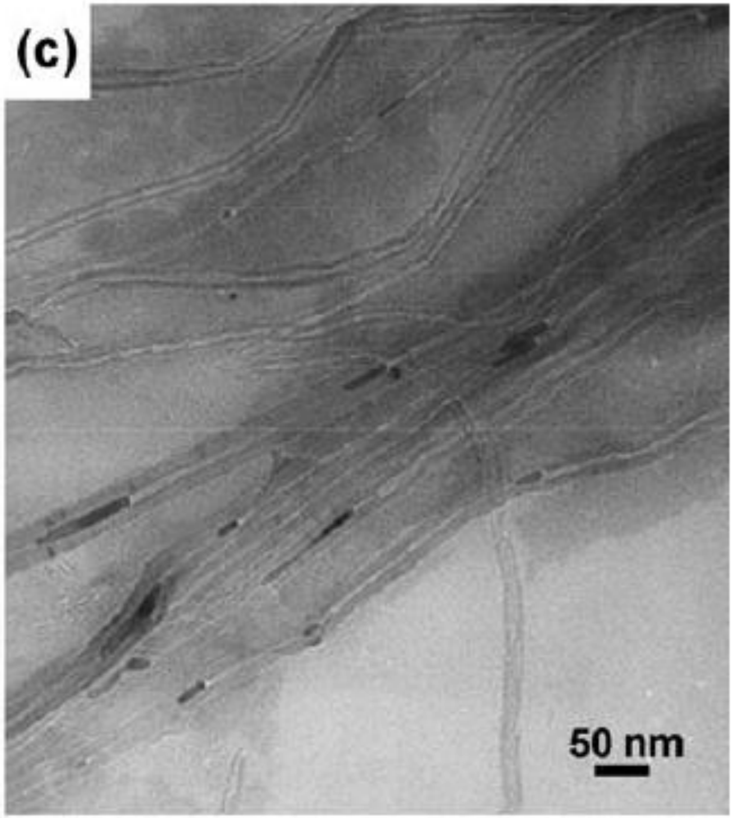
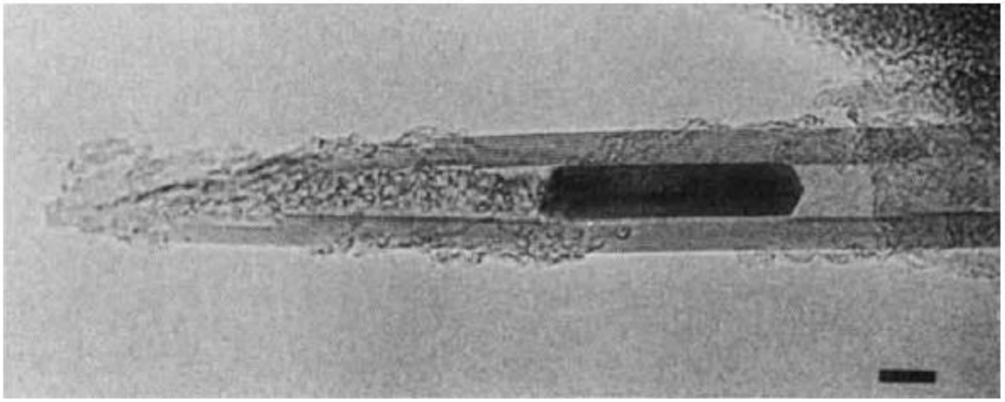


Hsu et al, *Thin Solid Films* **471**, 140 (2005)



Tsang et al, *Nature* **372**, 159 (1994)

Question: How are metal catalyst particles being drawn into carbon nanotubes?

Capillary forces?

Capillary rise

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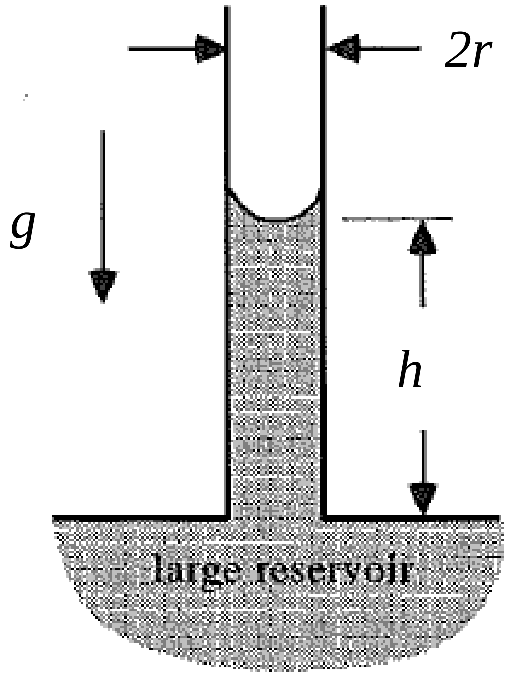
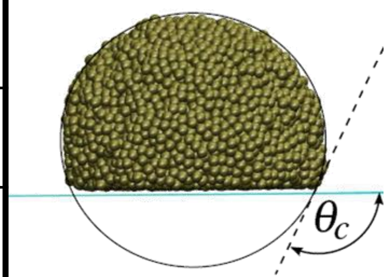
- Balancing gravitational and capillary forces



$$\Delta p = \frac{2\gamma_{lv}}{r}\cos\theta_c - \rho g h$$

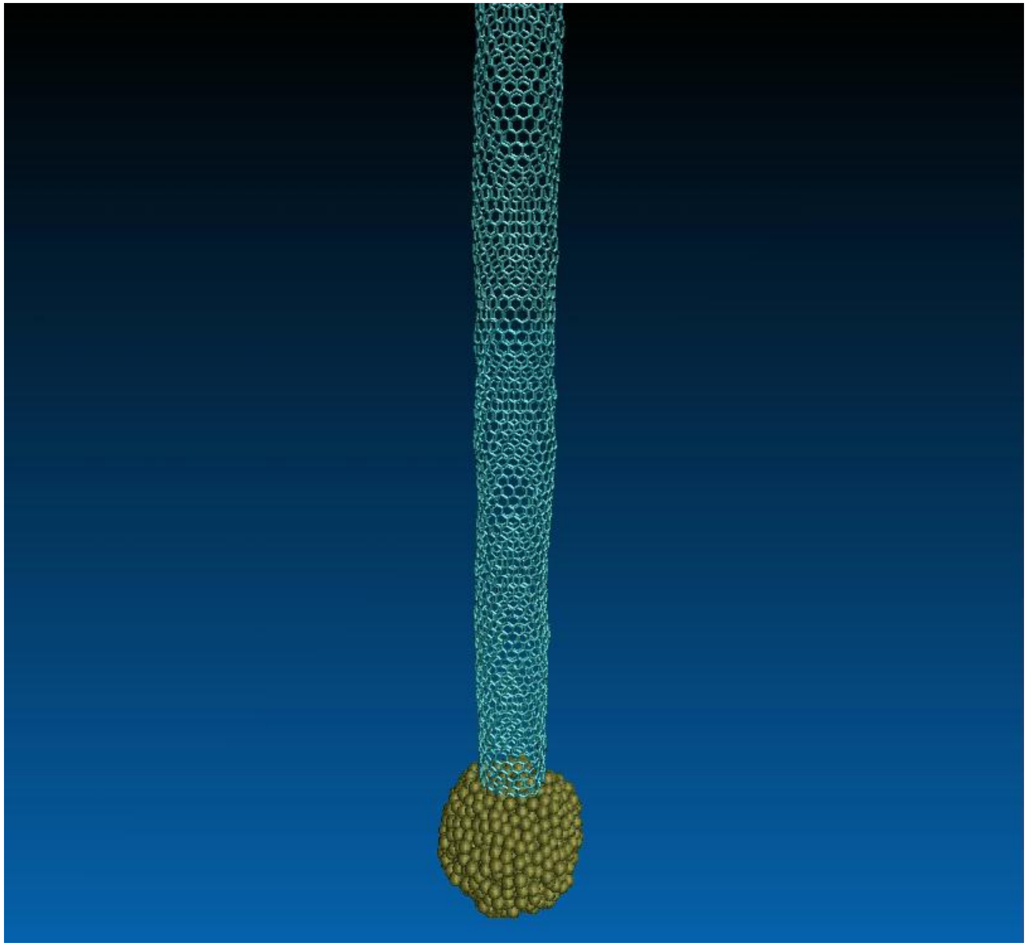
Only get a capillary rise if $\cos\theta_c > 0$

Metal	θ_c
Au	129º
Ag	124º
Ni-C	145º
Fe-C	140º

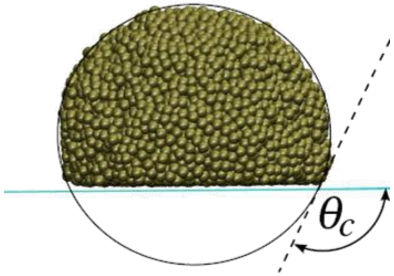


Schebarchov, SH, Erterkin and Grossman *PRL* 107, 185503 (2011)

Absorption of droplets



Simulation shows Pd droplet with θ_c=120º



If the droplets are sufficiently small:

$$0 < \frac{\cos\theta_c}{r_t} + \frac{1}{r}$$

they are be driven in by the Laplace pressure associated with their surface tension.

Nanopipettery

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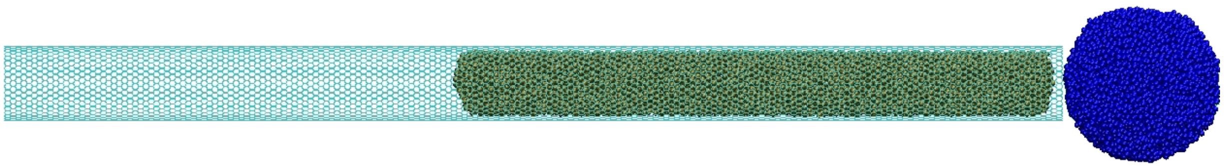
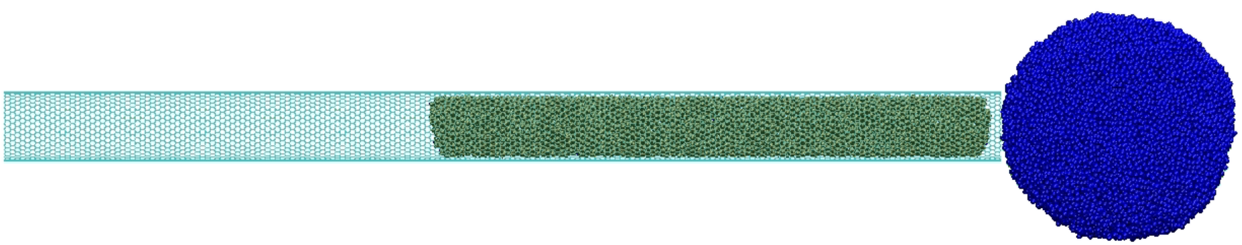
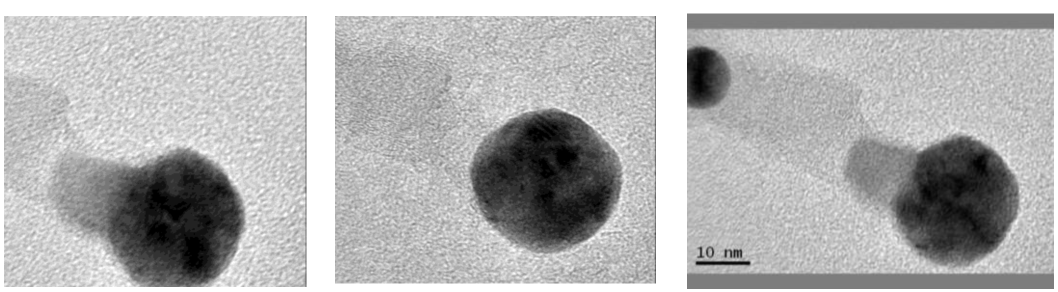
- We can continue to fill tube by adding small droplets:



- We can also evacuate a tube by immersing it in a droplet larger than the critical size threshold





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Edgar, SH, Schebarchov and Tilley, *Small* 7, 737–774 (2011)

Slip or stick?

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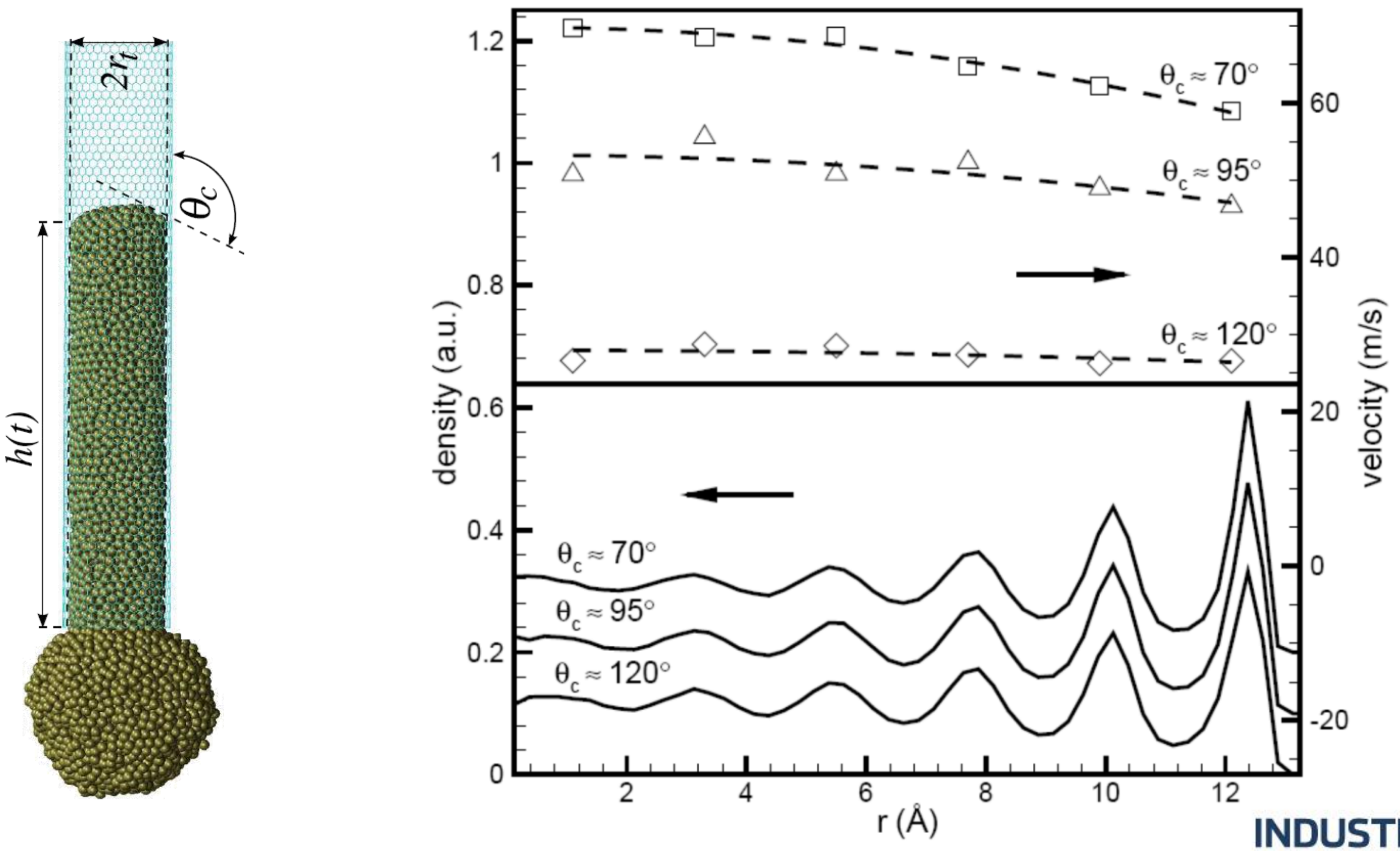
- Slip is occurring at the walls during capillary uptake



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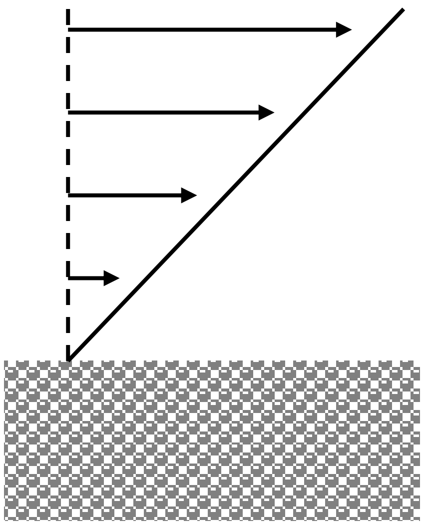
Schebarchov and Hendy, *PRE* 78 046309 (2008)

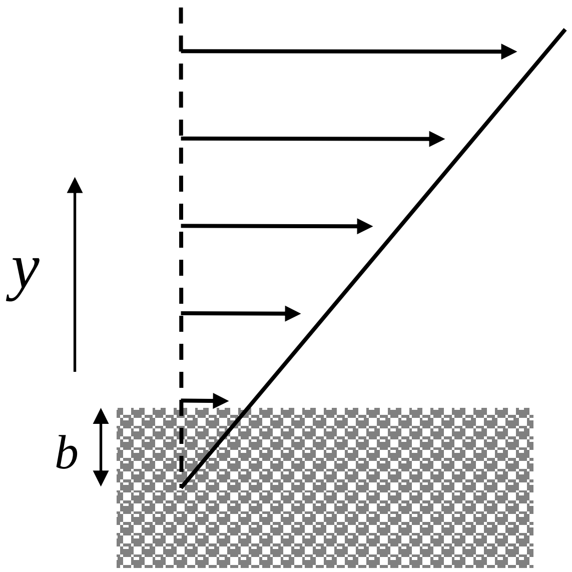
Stick or slip?

No slip



$$u\big|_w = 0$$

Slip



$$k\mathbf{u}\big|_{\mathbf{w}} = b\frac{\partial u}{\partial y}\bigg|_w = \mu\frac{\partial u}{\partial y}\bigg|_w$$

Simulated slip lengths

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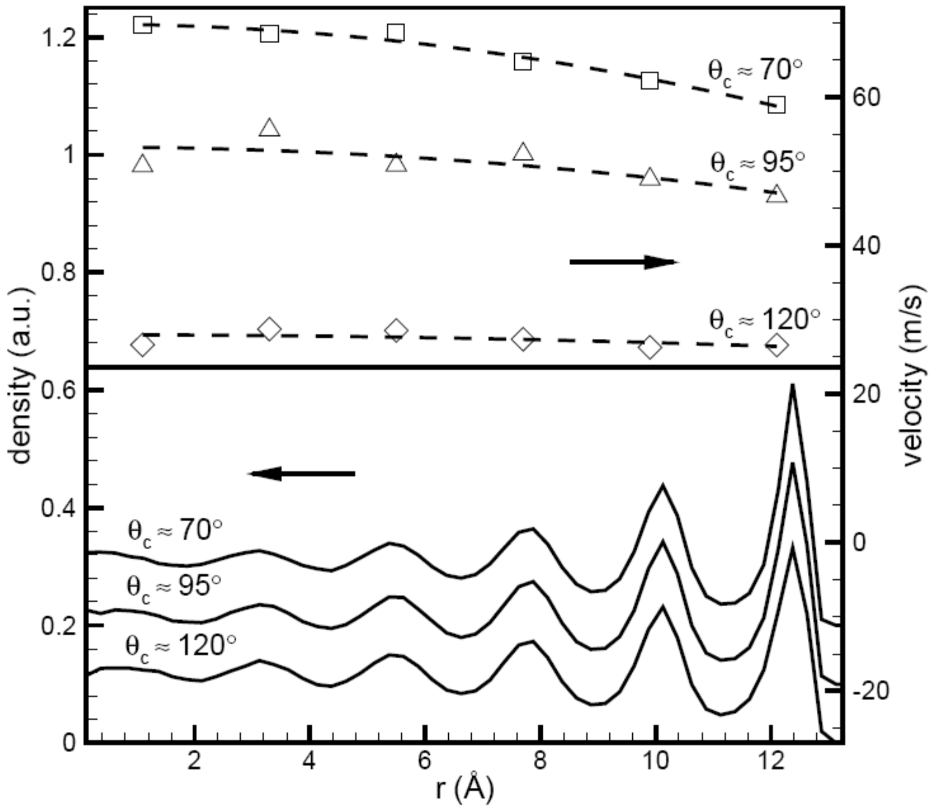
- Our simulations have slip lengths of up to 10 nm



ϵ/ϵ_0	θ_c	$b(\mathring{A})$
1.25	120°	102
1.50	110°	52
1.75	95°	46
2.00	90°	69
2.50	70°	31

Here the tube radius is ~ 3 nm.

Schebarchov and Hendy, *PRE* 78 046309 (2008)

Experimental results

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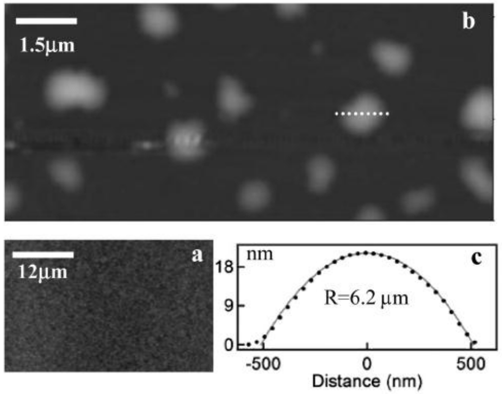
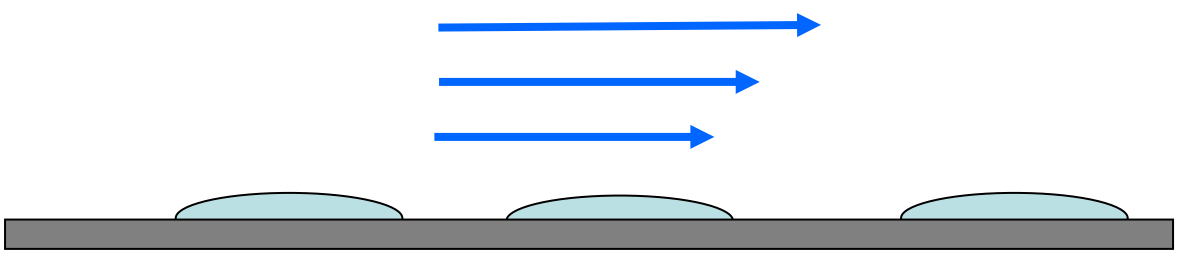
	Surfaces	Liquids	Wetting	Roughness	Shear rates	Slip length	L/NL
Chan [28]	Mica	OMCTS	–	–	$10-10^3$ s^{-1}	no-slip	–
	”	Tetradecane	–	–	”	no-slip	–
	”	Hexadecane	–	–	”	no-slip	–
Israelachvili [77]	Mica	Water	–	–	$10-10^4$ s^{-1}	no-slip	–
	”	Tetradecane	–	–	”	no-slip	–
Horn [72]	Silica	NaCl solutions	45°	5 Å(av)	$10-10^3$ s^{-1}	no-slip	–
Georges [58]	6 surfaces [58]	9 liquids [58]	–	0.2 - 50 nm (pp)	$1-10$ s^{-1}	no-slip	–
Baudry [9]	Cobalt	Glycerol	$20-60$°	1nm (pp)	$1-10^4$ s^{-1}	no-slip	–
	Gold+thiol	”	90°	”	”	40 nm	L
Cottin-Bizonne [39]	Glass	Glycerol	<5°	1nm (pp)	$1-10^4$ s^{-1}	no-slip	–
	Glass+OTS	Glycerol	95°	”	”	$50-200$ nm	L
	”	Water	100°	”	”	$50-200$ nm	L
Zhu [192]	Mica+HDA	Tetradecane	12°	≈ 1 Å (rms)	$10-10^5$ s^{-1}	$0-1$ μm	NL
	Mica +OTE	Tetradecane	44°	”	”	$0-1.5$ μm	NL
	”	Water	110°	”	”	$0-2.5$ μm	NL
Zhu [194]	Mica+OTS	Water	$75-105$°	6 nm (rms)	$10-10^5$ s^{-1}	no-slip	–
	”	Tetradecane	$12-35$°	6 nm (rms)	”	no-slip	–
	Mica+.8 PPO	Water	$85-110$°	3.5 nm (rms)	”	$0-5$ nm	NL
	”	Tetradecane	$21-38$°	3.5 nm (rms)	”	$0-5$ nm	NL
	Mica+.2 PPO	Water	$90-110$°	2 nm (rms)	”	$0-20$ nm	NL
	”	Tetradecane	–	2 nm (rms)	”	$0-20$ nm	NL
	Mica+OTE	Water	110°	0.2 nm (rms)	”	$0-40$ nm	NL
	”	Tetradecane	38°	0.2 nm (rms)	”	$0-40$ nm	NL
Zhu [193]	Mica+PVP/PB	Tetradecane	–	≈ 1 nm (th)	$10-10^5$ s^{-1}	no-slip	–
	Mica+PVA	Water	–	”	$10-10^5$ s^{-1}	$0-80$ nm	NL
Zhu [195]	Mica	n-Alkanes	Complete	–	$10-10^5$ s^{-1}	no-slip	–
	Mica+HDA	Octane	–	–	$10-10^5$ s^{-1}	$0-2$ nm	NL
	”	Dodadecane	–	–	”	$0-10$ nm	NL
	”	Tetradecane	12°	–	”	$0-15$ nm	NL
Cottin-Bizonne [38]	Glass	Dodecane	≈ 0 °	1 nm (pp)	10^2-10^4 s^{-1}	no-slip	–
	”	Water	≈ 0°	”	”	no-slip	–
	Glass+OTS	Dodecane	–	”	”	no-slip	–
	”	Water	105°	”	”	20 nm	L

Experimental results

Cottin-Bizonne et al, Eur. Phys. J. E **9**, 47-53 (2003)

Glass+OTS	Glycerol	95°	”	”	50 – 200 nm
”	Water	100°	”	”	50 – 200 nm

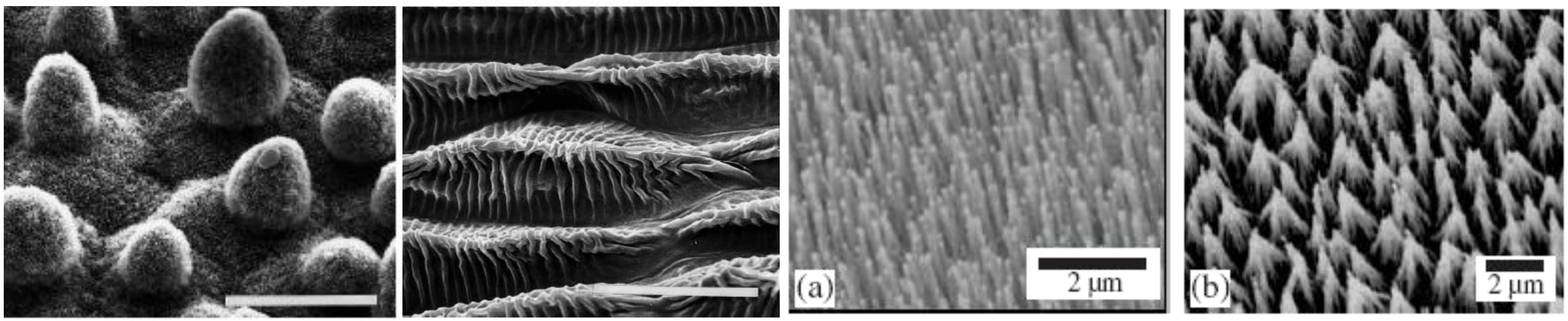




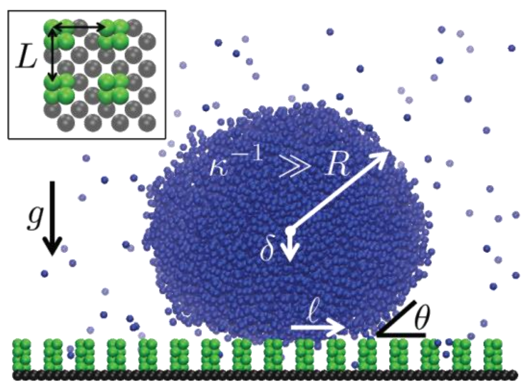
Cottin-Bizonne et al, PRL **94**, 056102 (2005)

Glass+OTS	Dodecane	–	”	”	no-slip
”	Water	105°	”	”	20 nm

Nanostructured surfaces



How can we describe flows over nanostructured surfaces?

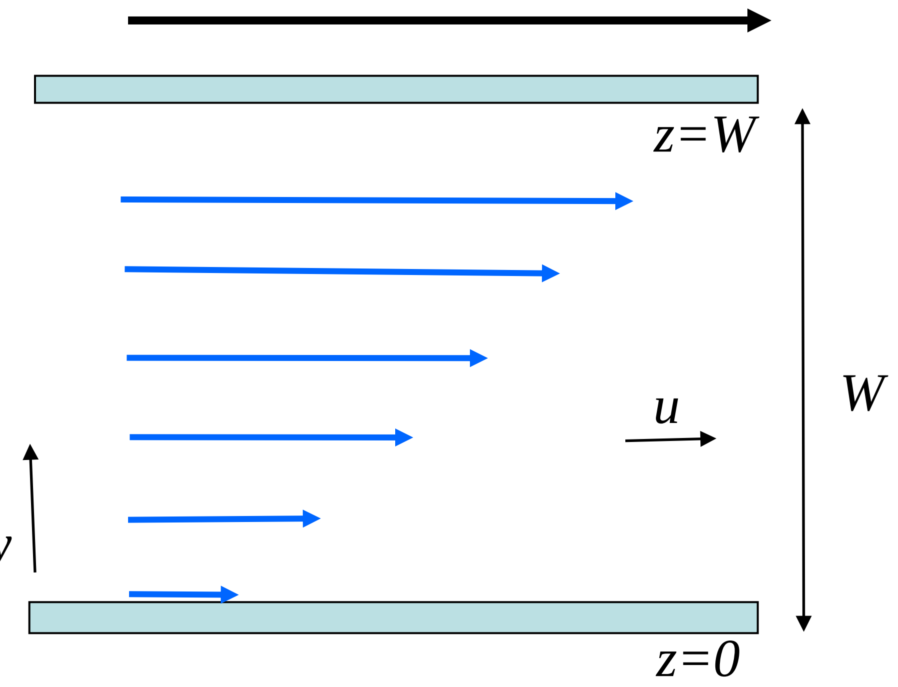


The effective slip problem

$$u\big|_W = u_W$$

$$u(z) = u_W \frac{(z+b)}{W}$$

$$u\big|_0 = b\frac{\partial u}{\partial z}\Big|_0$$

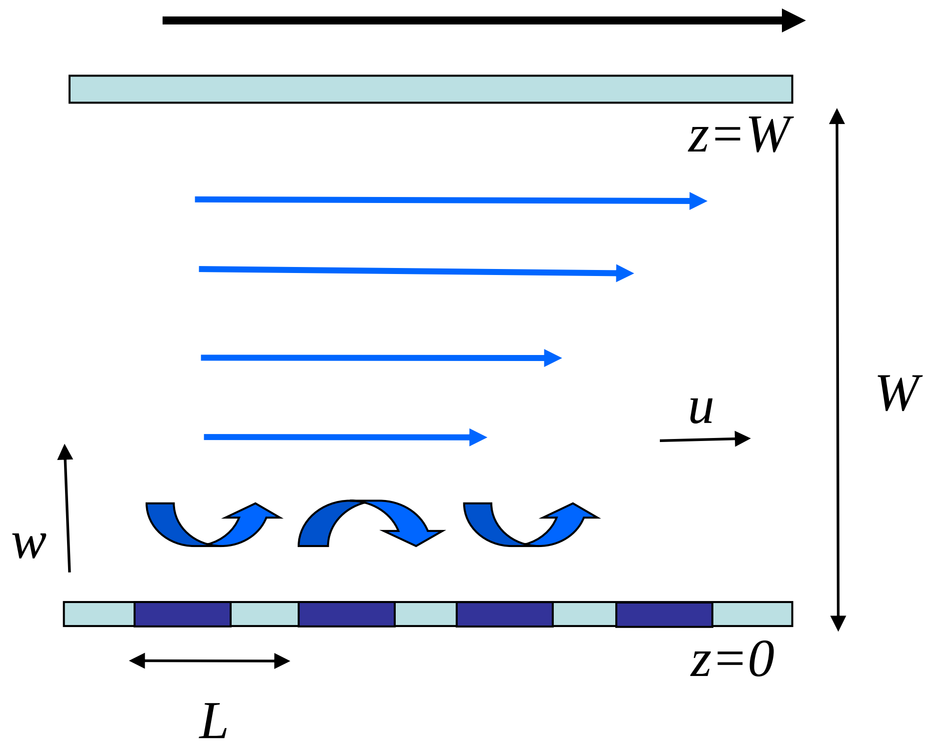


The effective slip problem

$$u\big|_W = u_W$$

$$u(z) \sim u_W \frac{\left(z + b_{eff}\right)}{W}$$

$$u\big|_0 = b(x,y)\frac{\partial u}{\partial z}\bigg|_0$$

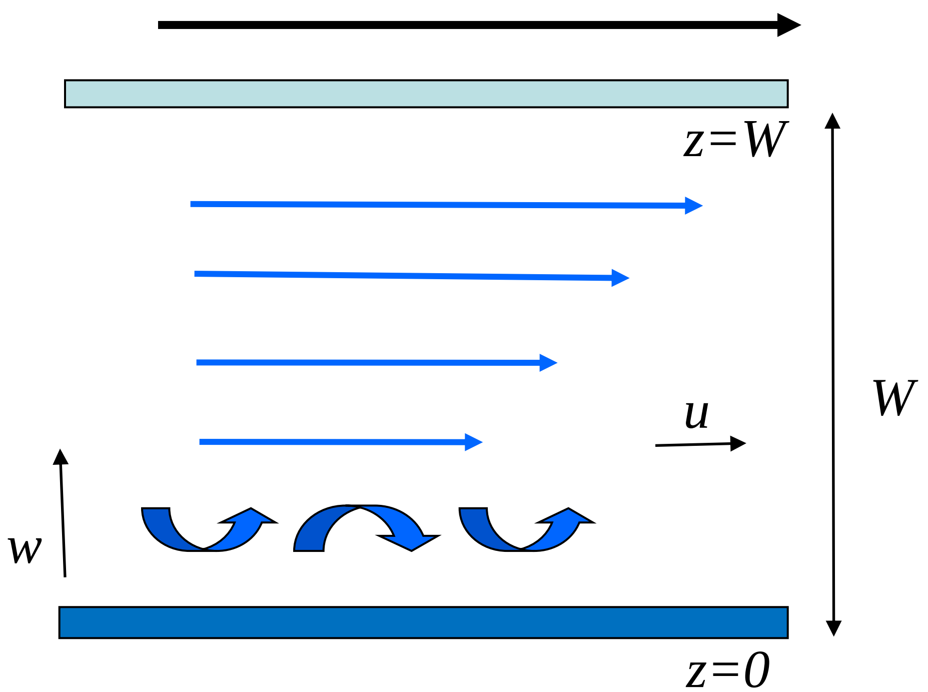


The effective slip problem

$$u\big|_W = u_W$$

$$u(z) \sim u_W \frac{(z + b_{eff})}{W}$$

$$u\big|_0 = b_{eff} \frac{\partial u}{\partial z}\bigg|_0$$

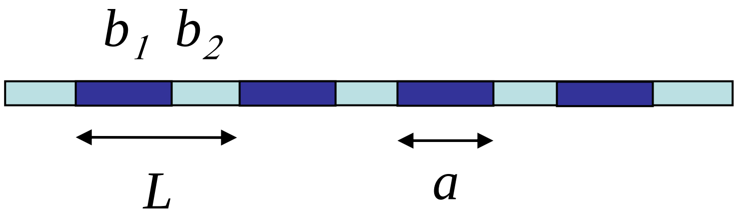


Direct solution approach

- Use an asymptotic expansion of boundary condition and solution of the Stokes equation

e.g. $b_1 << L \qquad b_2 << L$

$$\beta = a / L$$



$$u\big|_{\hat{z}=0} = O\left(\frac{b_1}{L}\right) \qquad 0 < \hat{y} < \beta$$

$$u\big|_{\hat{z}=0} = O\left(\frac{b_2}{L}\right) \qquad \beta < \hat{y} < 1$$

$$\Rightarrow b_{eff} = \langle b \rangle$$

Hendy and Lund, *PRE* **76**, 066313 (2007)

Homogenization approach

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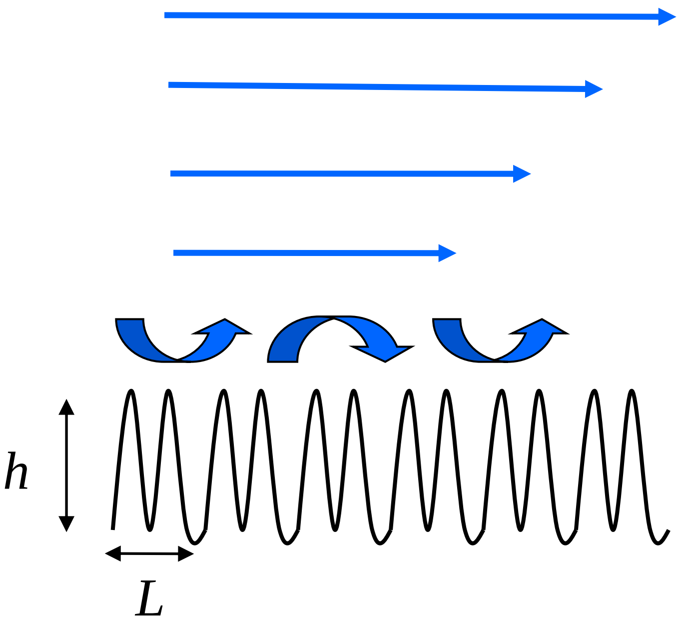
- Use homogenization approach based on weak formulation of Stokes equations:

e.g. $\dfrac{\partial u}{\partial n} = \dfrac{1}{b} u \quad \text{on } \Gamma : z = h(x) = \varepsilon h_0\left(\dfrac{x}{\varepsilon}\right) \geq 0$



$$\int_{\Gamma_\varepsilon} v \frac{1}{b} u \, dxdz \to \int_{\Gamma_0} v \left\langle \frac{\sqrt{1+\left|h_0'\right|^2}}{b} \right\rangle u \, dxdz$$

as $\quad h/W \sim L/W \sim \varepsilon \to 0$

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Zhang, Lund, Mahelona and SCH, *PRE* 86, 046303 (2012)

Summary of main results

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- Small b and small roughness $b(x) << L$

$$b_{eff} = \langle b - h \rangle + O(bh)$$

- Large b and small roughness $b(x) >> L$

$$\frac{1}{b_{eff}} = \left\langle \frac{\sqrt{1+|h'|^2}}{b} \right\rangle$$

Zhang, Lund, Mahelona and SCH, *PRE* 86, 046303 (2012)

Numerical results

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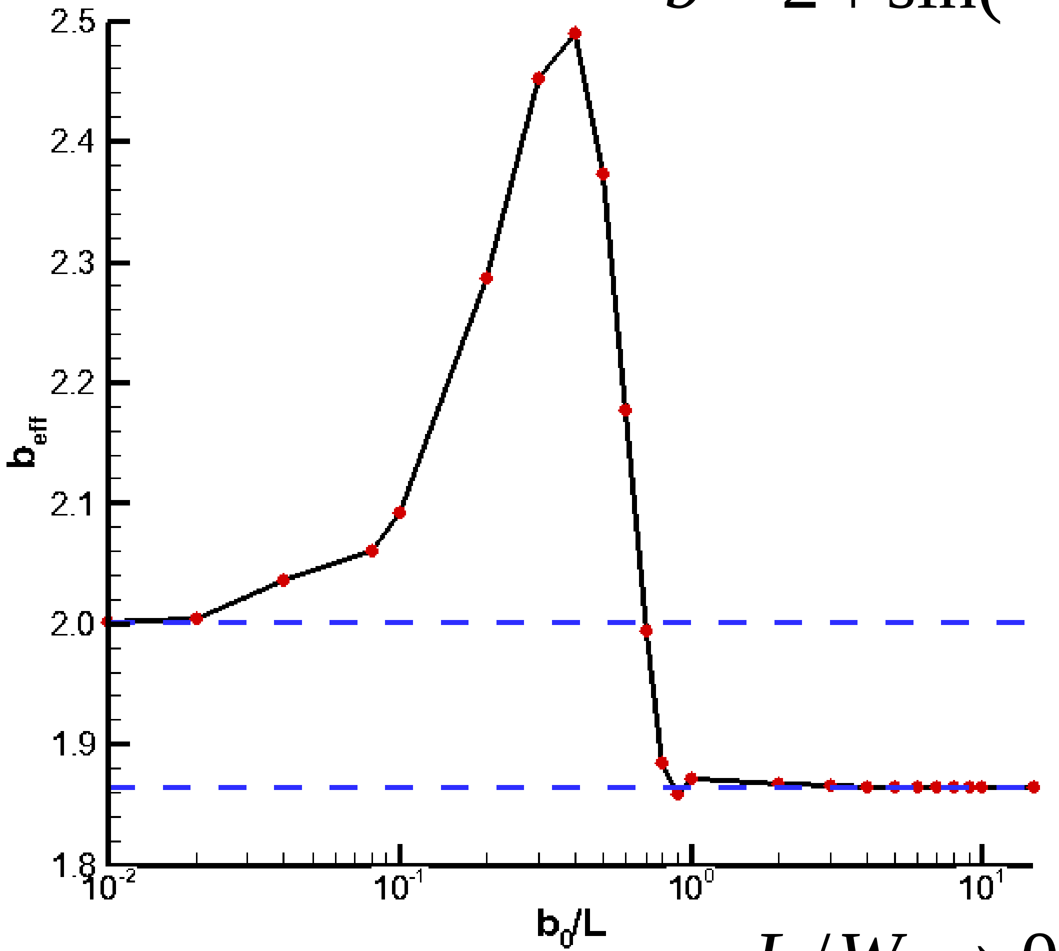
$$b = 2 + \sin(2\pi \, x/L)\sin(2\pi \, y/L)$$

$$b_{eff} = \langle b \rangle$$



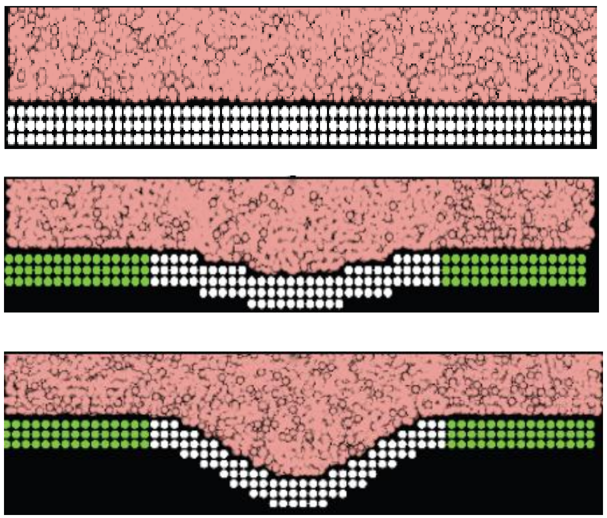
$$b_{eff} = \langle b^{-1} \rangle^{-1}$$

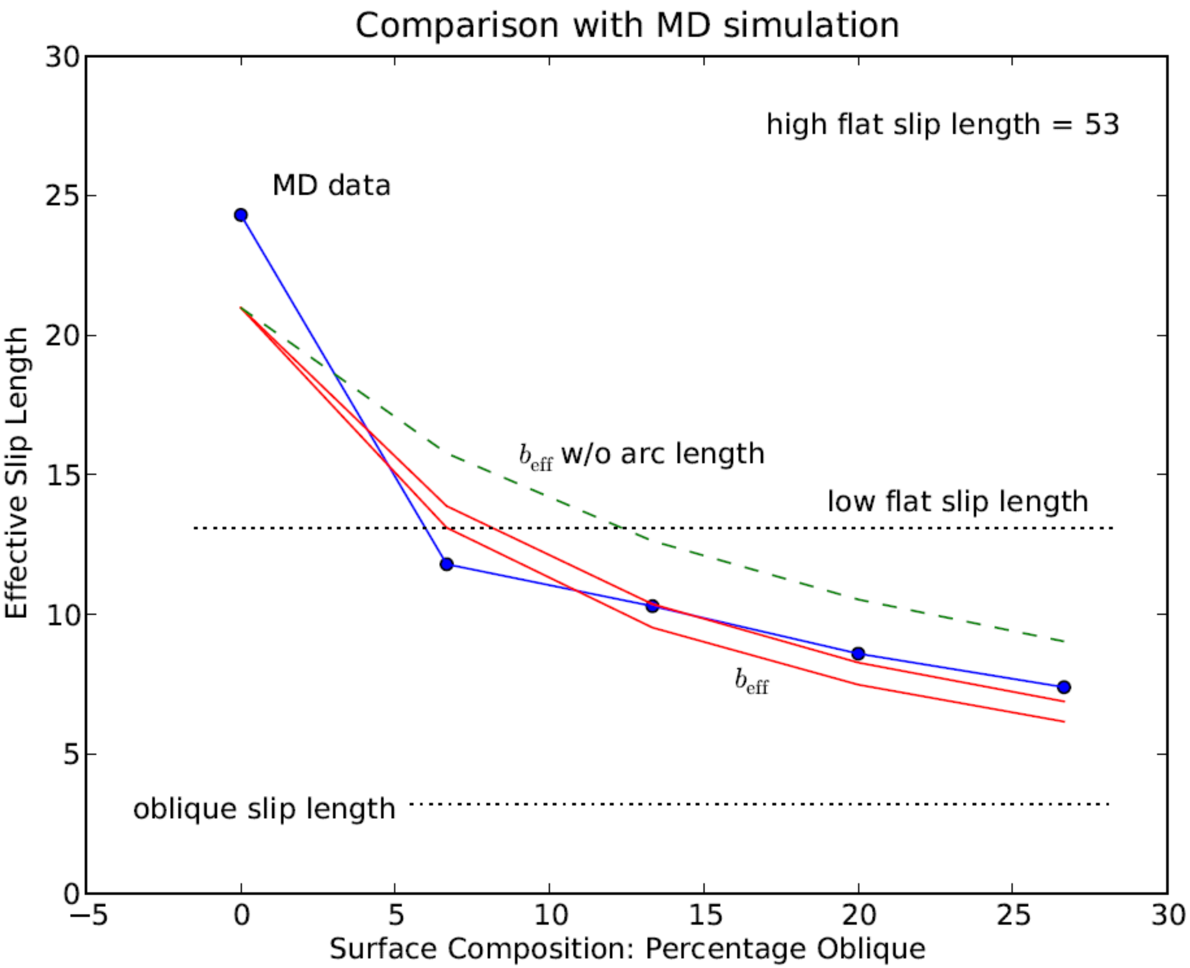
$$L/W \to 0$$

Zhang, Lund, Mahelona and SCH, *PRE* 86, 046303 (2012)

Does it work at the nanoscale?

$$\frac{1}{b_{eff}} = \left\langle \frac{\sqrt{1+|h'|^2}}{b} \right\rangle$$





Zhang, Lund, Mahelona and SCH, *PRE* 86, 046303 (2012)

Nanobubbles

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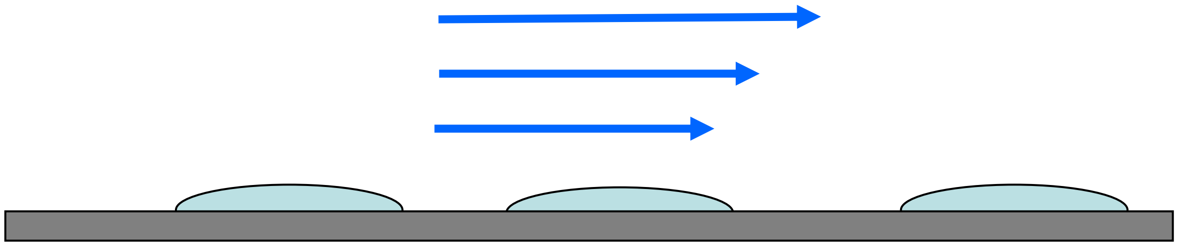
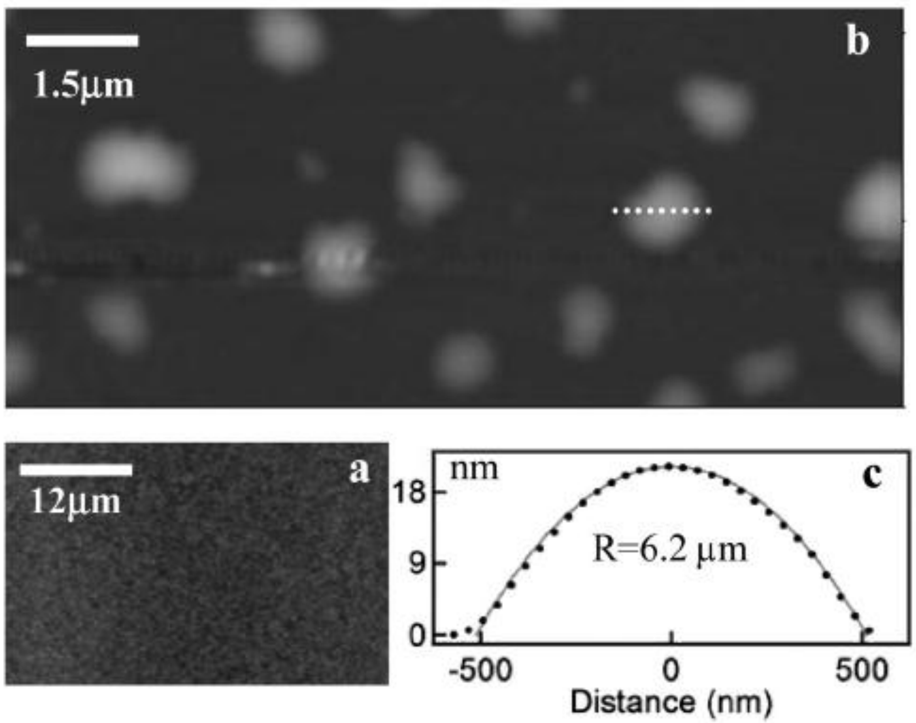


$$b_g \sim (\mu_l / \mu_g) t$$
$$\sim 50\, t$$
$$\sim 1\ \mu\text{m}$$
$$< L$$



t

$$b_{eff} \cong \langle b \rangle = \beta b_1 + (1-\beta) b_2$$
$$= 0.15\, b_g$$
$$= 150\ \text{nm}$$

Hendy and Lund , *J. Phys: Cond. Matt* 21, 144202 (2009)

Experimental results

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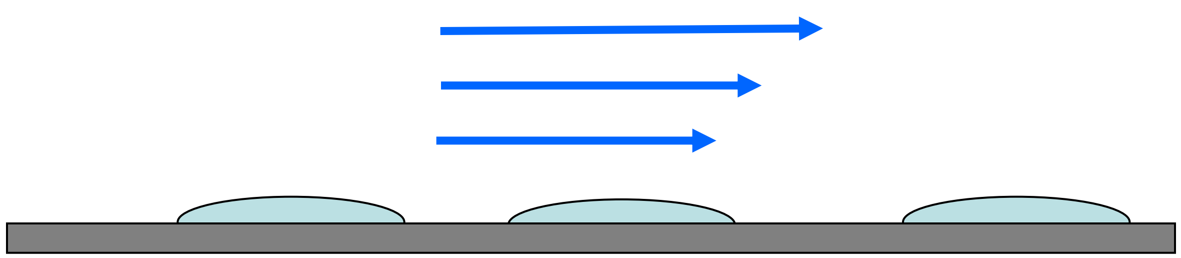
Cottin-Bizonne et al, Eur. Phys. J. E **9**, 47-53 (2003)

Glass	Glycerol	$< 5^\circ$	1nm (pp)	$1 - 10^4$ s^{-1}	no-slip
Glass+OTS	Glycerol	95°	"	"	$50 - 200$ nm
"	Water	100°	"	"	$50 - 200$ nm



Cottin-Bizonne et al, PRL **94**, 056102 (2005)

Glass	Dodecane	$\approx 0^\circ$	1 nm (pp)	$10^2 - 10^4$ s^{-1}	no-slip
"	Water	$\approx 0^\circ$	"	"	no-slip
Glass+OTS	Dodecane	–	"	"	no-slip
"	Water	105°	"	"	20 nm

Precious metal catalysts

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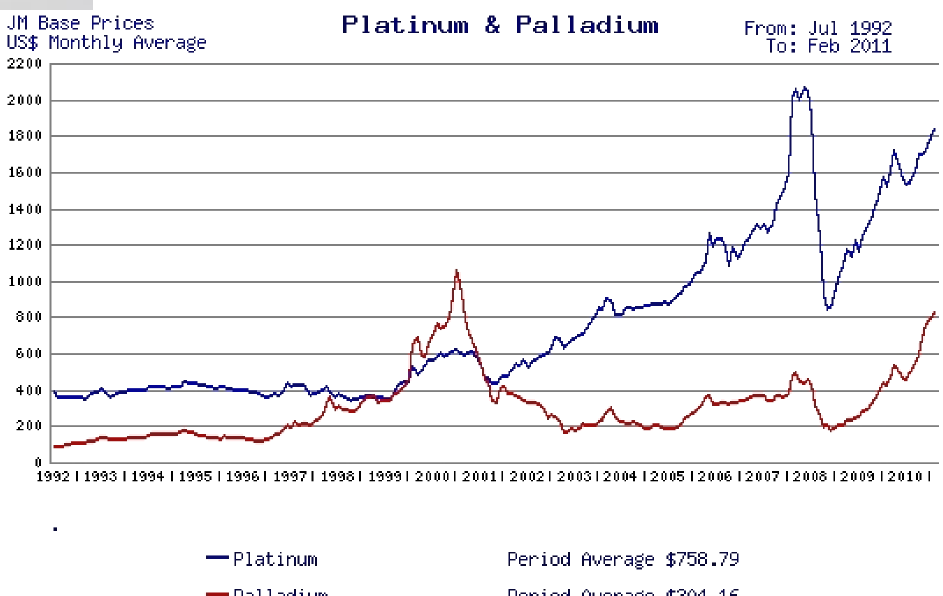
- Precious metal catalysts are used for many applications e.g. platinum and palladium in catalytic converters

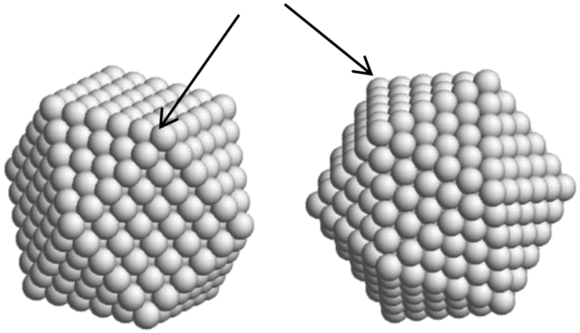
$$CO + 1/2\ O_2 \rightarrow CO_2$$
$$NO_x \rightarrow x/2\ O_2 + 1/2\ N_2$$

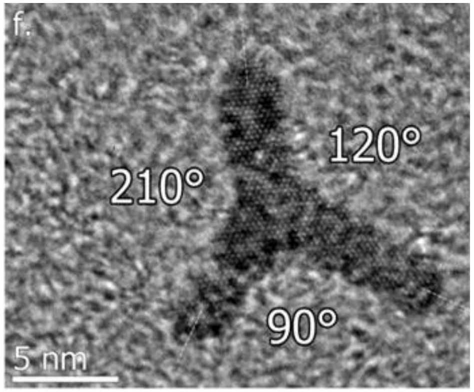


Nanostructured catalysts

- The performance of a catalyst depends on its size & shape

Corners and edges tend to be more reactive





- How might we determine effective performance so that we can optimise shape and size?

Effective catalysis problem

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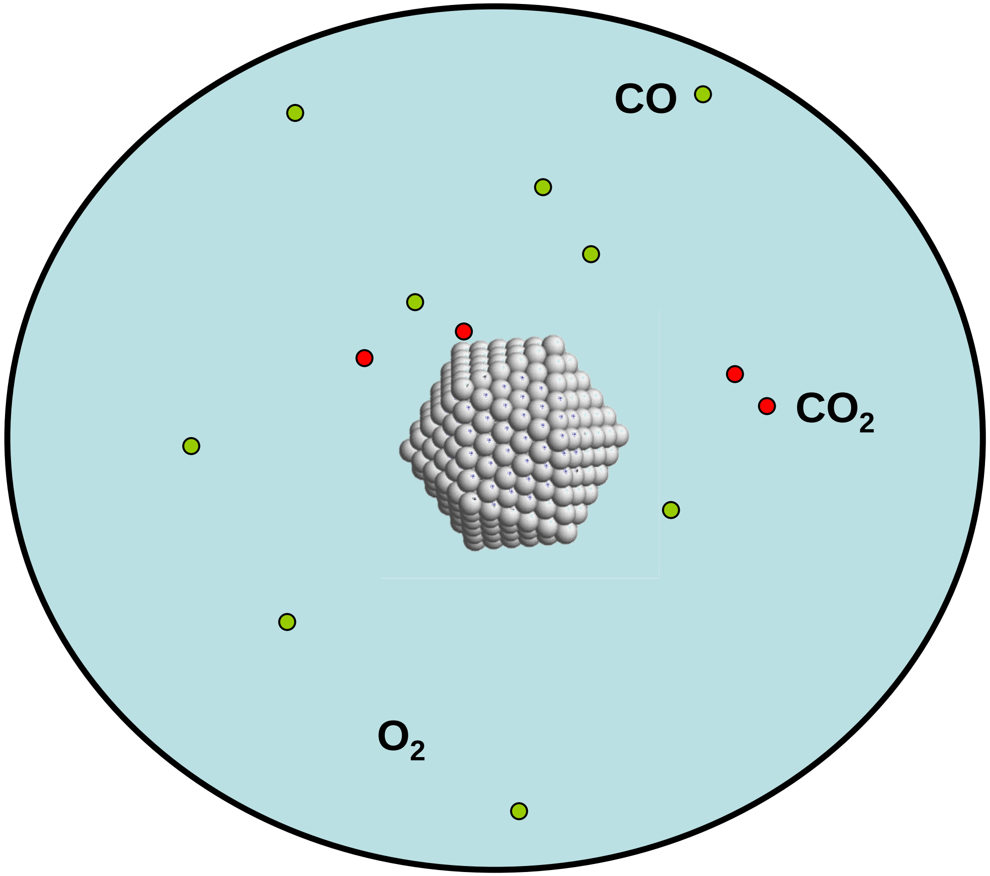
- E.g. oxidation of CO: $CO + 1/2\ O_2 \rightarrow CO_2$



Arrays of nanoparticles

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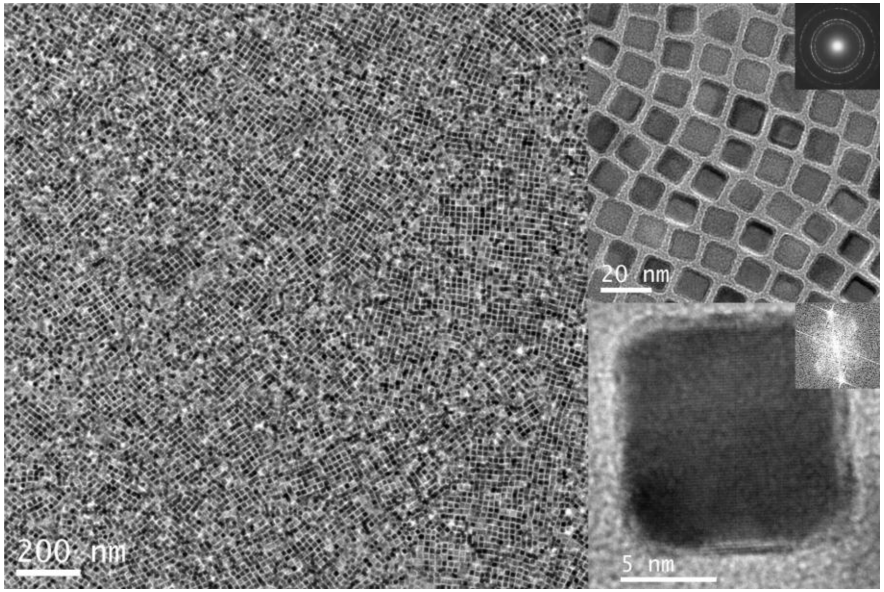
- Consider an array of nanoparticles on a substrate



- How does the effective activity of the particles depend on the arrangement of the particles on the support?

Effective catalysis problem

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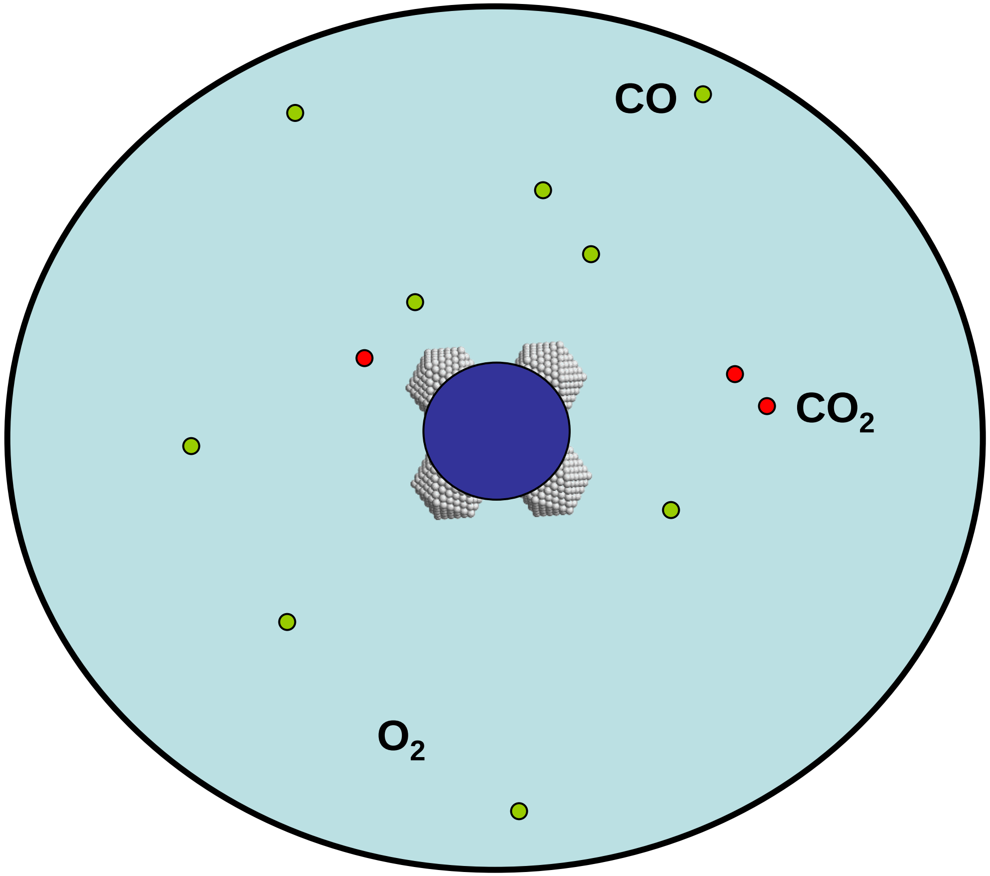
- E.g. oxidation of CO: $CO + 1/2\ O_2 \rightarrow CO_2$



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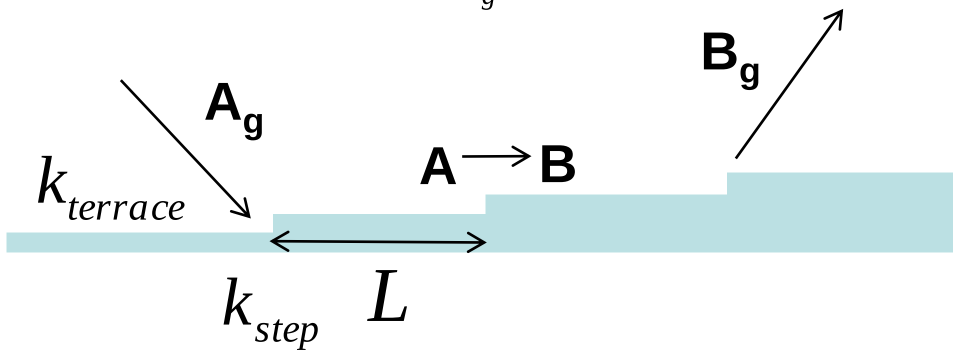
Boundary conditions

- Gas A to B: $\nabla^2 \rho_{A_g} = 0$



$A_g + S_i \rightarrow A$	k_1	$k_1 =$ probability of absorption
$A \rightarrow A_g + S_i$	k_2	$k_2 = 0$
$A \rightarrow B$	k_3	$k_3 << k_4$
$B \rightarrow B_g + S_i$	k_4	

Boundary conditions

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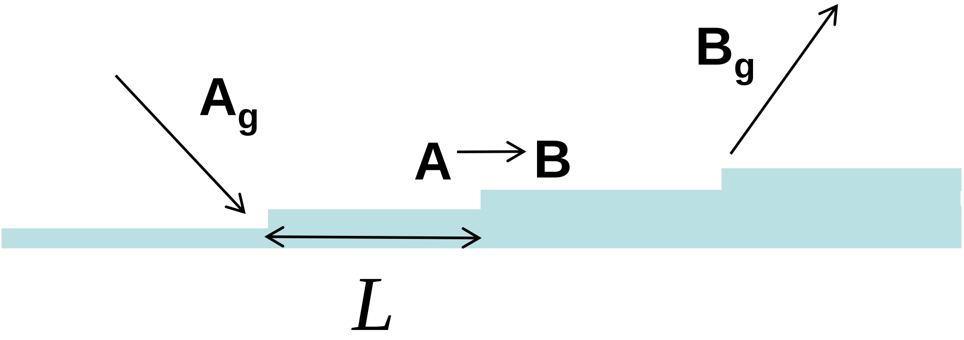


$a_i = \text{area of site } i$

$\theta_i = \text{fractional coverage of site } i$

$Q = \text{collision rate of gas } \mathrm{A_g} \text{ per unit area}$

$$\frac{d[\mathrm{A_g}]_s}{dt} = -k_1(1-\theta_i)Q$$

$$\frac{d[\mathrm{B_g}]_s}{dt} = k_3 \, \theta_i / a_i$$

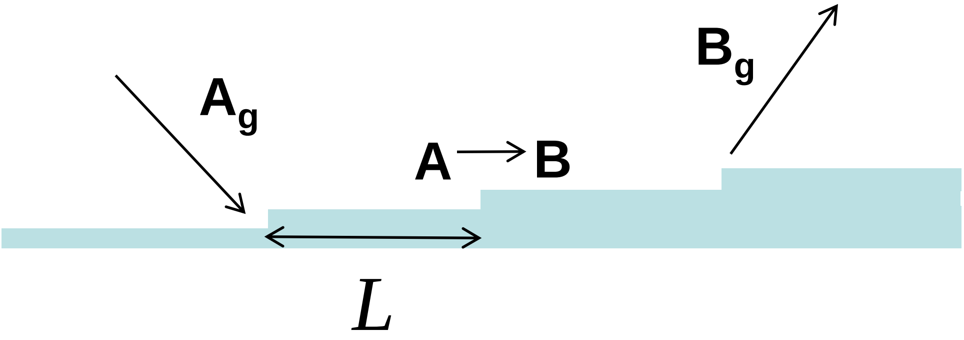
In steady state:

$$-\frac{d[\mathrm{A_g}]_s}{dt} = \frac{d[\mathrm{B_g}]_s}{dt}$$

$$\theta_i = \frac{k_1 Q}{k_1 Q + k_3 / a_i}$$

(Langmuir eqn)

Boundary conditions



a_i = area of site i

θ_i = fractional coverage of site i

Q = collision rate of gas A_g per unit area

$$\frac{d[A_g]_s}{dt} = -k_1(1-\theta_i)Q$$

$$\frac{d[B_g]_s}{dt} = k_3 \theta_i / a_i$$

In steady state:

$$-\frac{d[A_g]_s}{dt} = \frac{d[B_g]_s}{dt}$$

$$\theta_i = \frac{k_1 Q}{k_1 Q + k_3 / a_i}$$

(Langmuir eqn)

Boundary conditions

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- Finally obtain a boundary condition:

$$Dn \cdot \nabla \rho_A \big|_\Gamma = -\frac{k_1 Q}{1 + \frac{k_1 Q a_i}{k_3}}$$

where according to gas kinetic theory $Q = \frac{1}{4}\sqrt{\frac{8k_B T}{\pi m}}\rho_A$

- So for $k_1 Q a_i << k_3$ (i.e. absorption limited)

$$Dn \cdot \nabla \rho_A \big|_\Gamma = -\frac{k_1}{4}\sqrt{\frac{8k_B T}{\pi m}}\rho_A \big|_\Gamma$$

Boundary conditions

- Thus in terms of the length $$b = \frac{D}{k_1}\sqrt{\frac{2\pi m}{k_B T}}$$

$$b n \cdot \nabla \rho_A \big|_\Gamma = -\rho_A \big|_\Gamma$$

- But again, gas kinetic theory has $$D \sim v_g \lambda \sim \sqrt{\frac{k_B T}{m}}\lambda$$

so

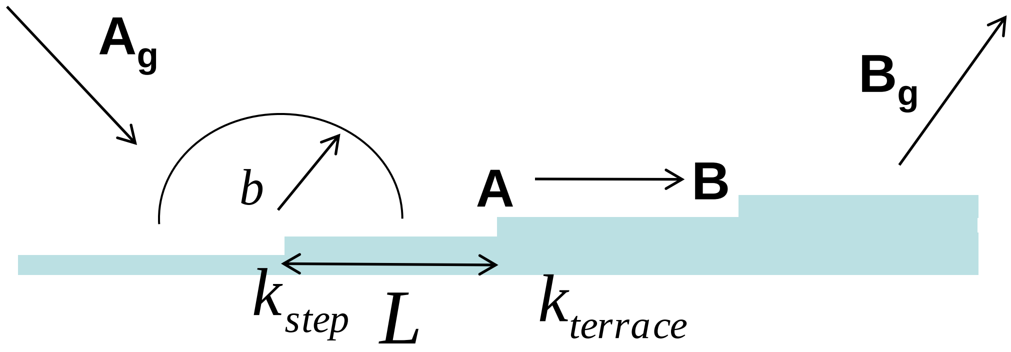
$$b \sim \frac{\lambda}{k_1}$$

where λ is the mean free path of the gas molecule

k_1 is a probability of absorption

Boundary conditions

- So the boundary condition under diffusion limited conditions depends on the length $b \sim \frac{\lambda}{k_1}$



- Mean free path of gas molecule in air at 1 atmosphere is ~ 100 nm, so *b* will be of O(100nm)

Mathematical problem

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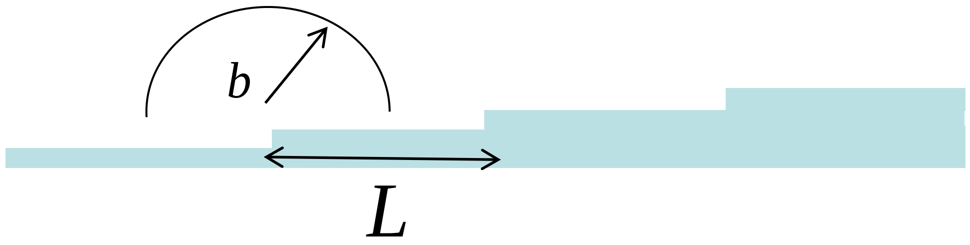
- Now we have a diffusion problem with a heterogeneous mixed boundary condition

$$\nabla^2 \rho_A = 0 \qquad in\ some\ domain\ \ \Omega = \{(x,z)\}$$

$$b(x) n \cdot \nabla \rho_A \big|_\Gamma = -\rho_A \big|_\Gamma \quad on \quad \Gamma : z = h(x)$$

$$\rho_A = \rho_0 \qquad on \quad \partial\Omega / \Gamma$$



- This problem is a simpler version of the earlier homogenization problem

Recall our results

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- Small b and small roughness $b(x) << L$

$$b_{eff} = \langle b - h \rangle + O(bh)$$

- Large b and small roughness $b(x) >> L$

$$\frac{1}{b_{eff}} = \left\langle \frac{\sqrt{1 + |h'|^2}}{b} \right\rangle$$

Effective rate constants

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- Assume two types of rate constant $k_{terrace} << k_{step}$ with spacing L on a flat surface

- Case 1: active sites widely space w.r.t. $b = \lambda / k_{terrace}$

$$L >> \frac{\lambda}{k_{terrace}} \qquad k_{eff} = \left(\left\langle \frac{1}{k_1} \right\rangle \right)^{-1} \approx \frac{k_{terrace}}{1-\beta}$$

- Case 2: active sites closely space w.r.t. $b = \lambda / k_{step}$

$$L << \frac{\lambda}{k_{step}} \qquad k_{eff} = \langle k_1 \rangle = \beta\, k_{step}$$

Effective rate constants

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- At atmospheric pressure, a nanostructured catalyst will likely have

$$L << \frac{\lambda}{k_{active}}$$

so $$k_{eff} = \left\langle \sqrt{1+\left|h'\right|^2} k_1 \right\rangle \approx \beta(1+\alpha)k_{active}$$

where α is the surface roughness

- The activity is dominated by the active sites and enhanced by the roughness

Effective rate constants

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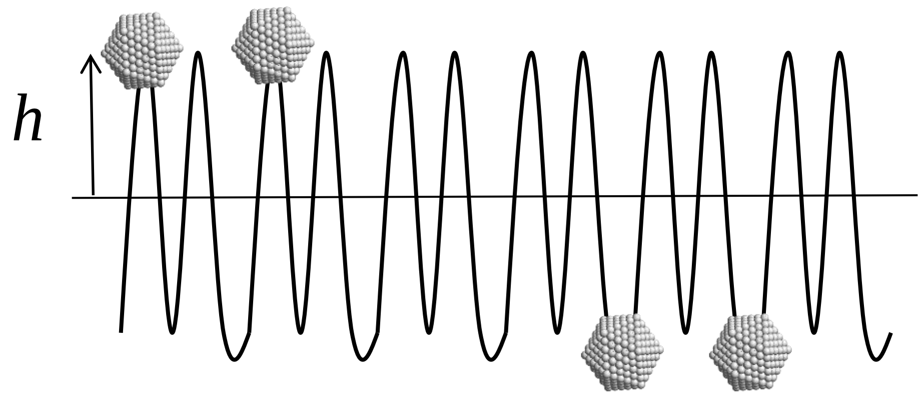
- If however $L >> \dfrac{\lambda}{k_{active}}$ as might occur for an array of particles, then we have

$$k_{eff} \approx \left\langle \frac{\lambda}{k_1} - h \right\rangle + O(\frac{h}{k_1})$$

- Hence, effective activity will depend on the location of the particles



Effective rate constants

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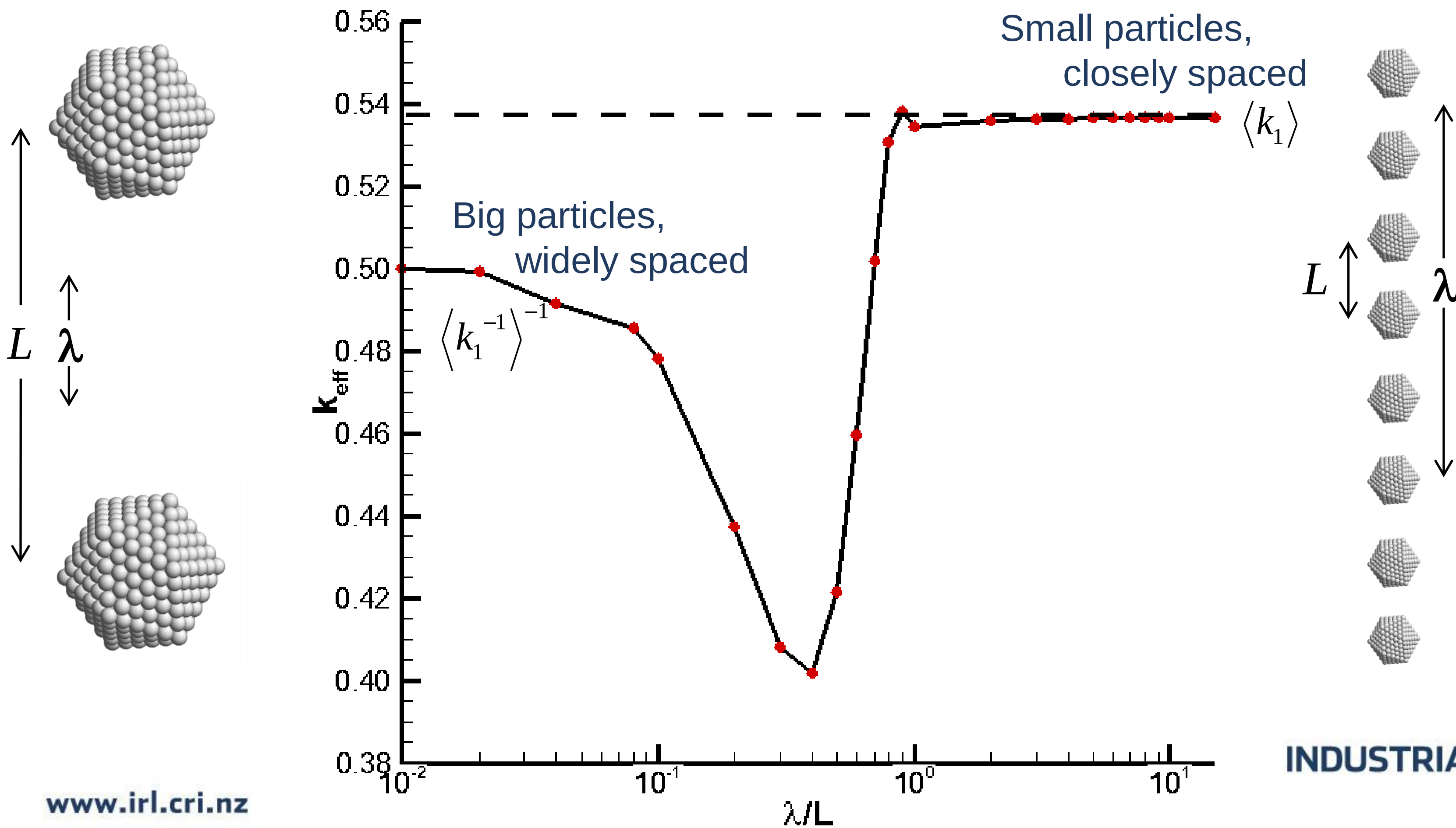
- e.g. $k_1^{-1} = 2 + \sin(2\pi x/L)$ on a flat support, keeping coverage of support by catalyst at 50%



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