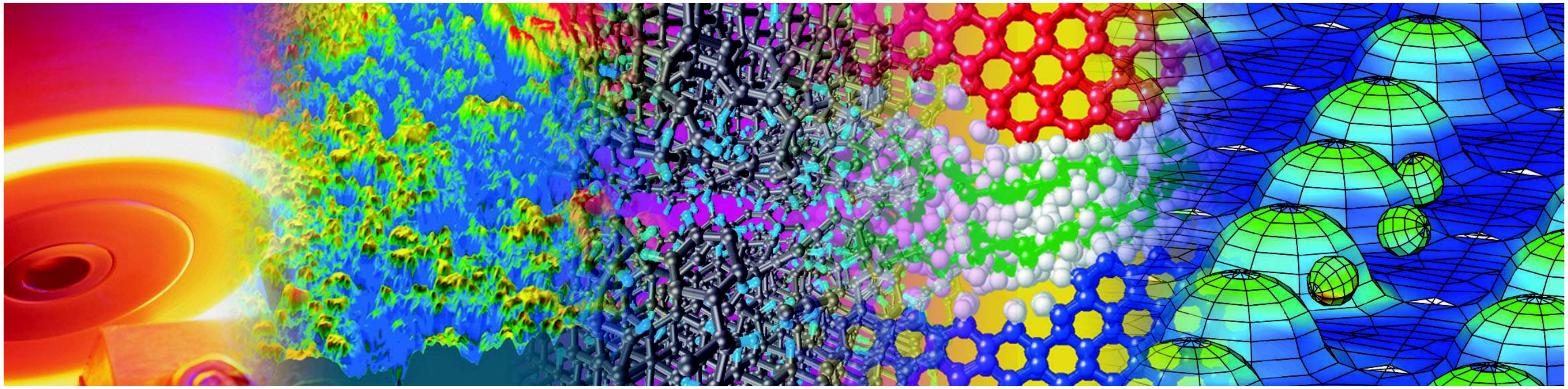
ATOMISTIC/CONTINUUM MULTISCALE COUPLING

Michael Moseler

Multiscale Modelling and Tribosimulation

Fraunhofer Institute for Mechanics of Materials IWM



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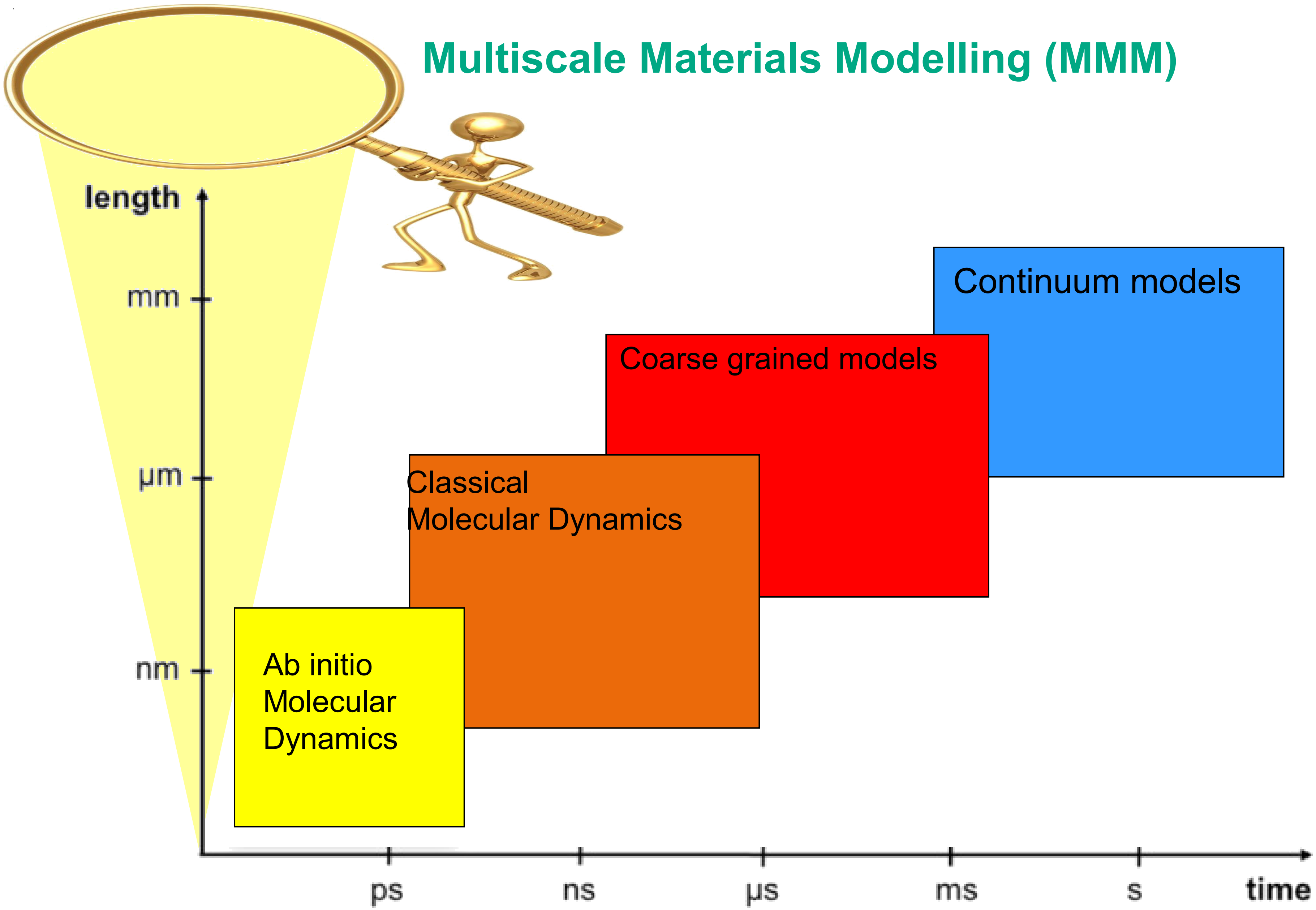
Multiscale Materials Modelling (MMM)



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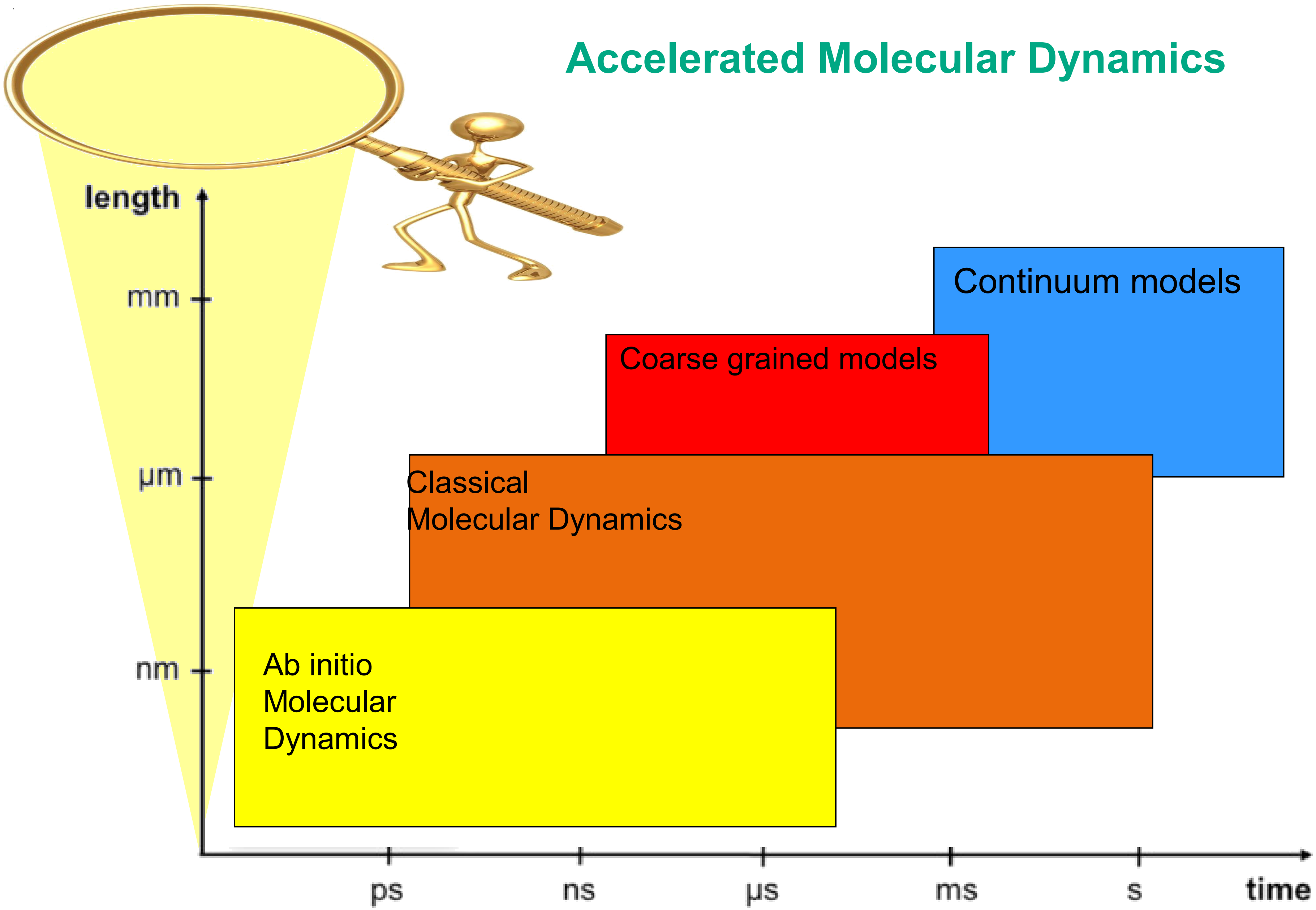
Accelerated Molecular Dynamics



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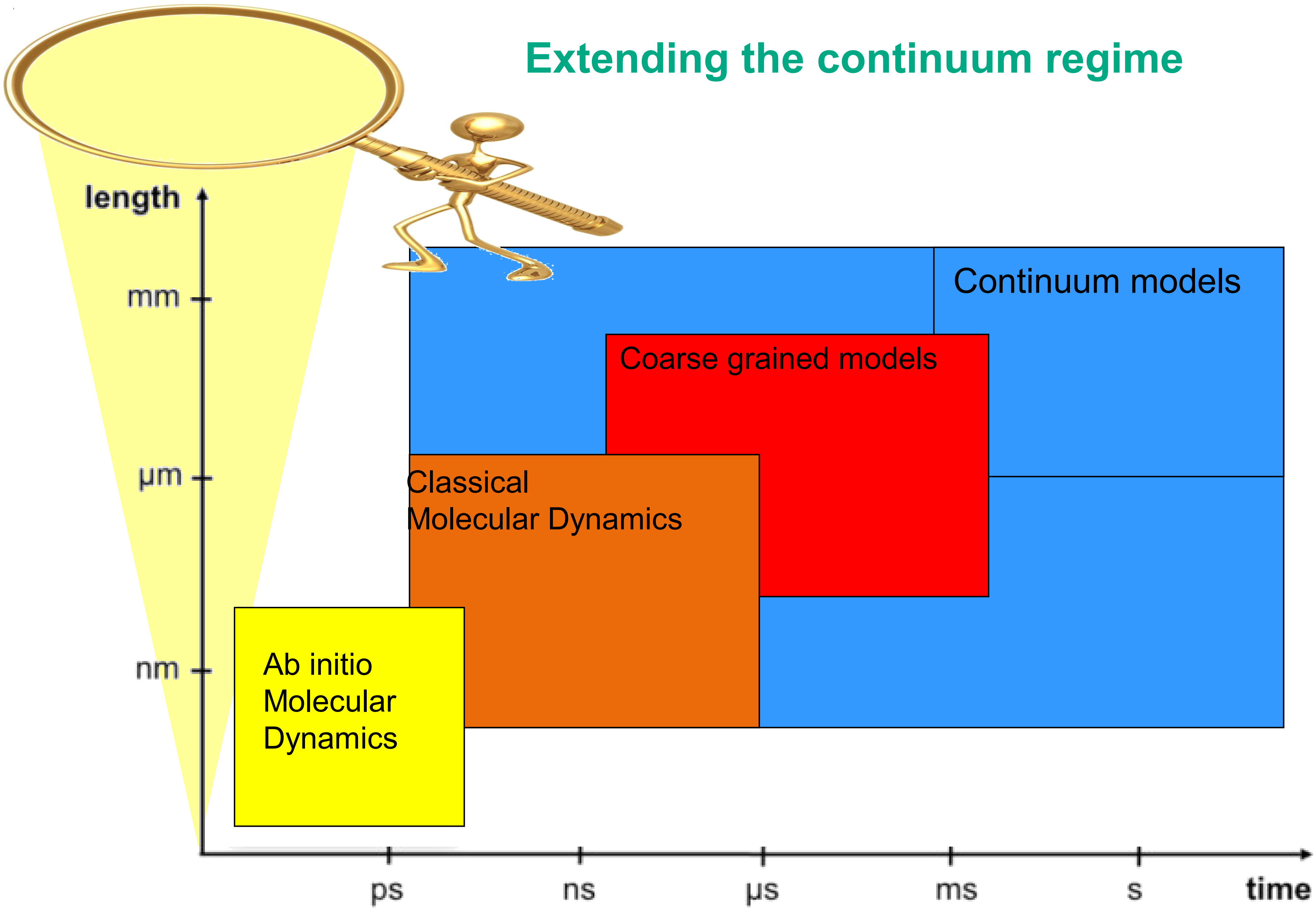
Extending the continuum regime



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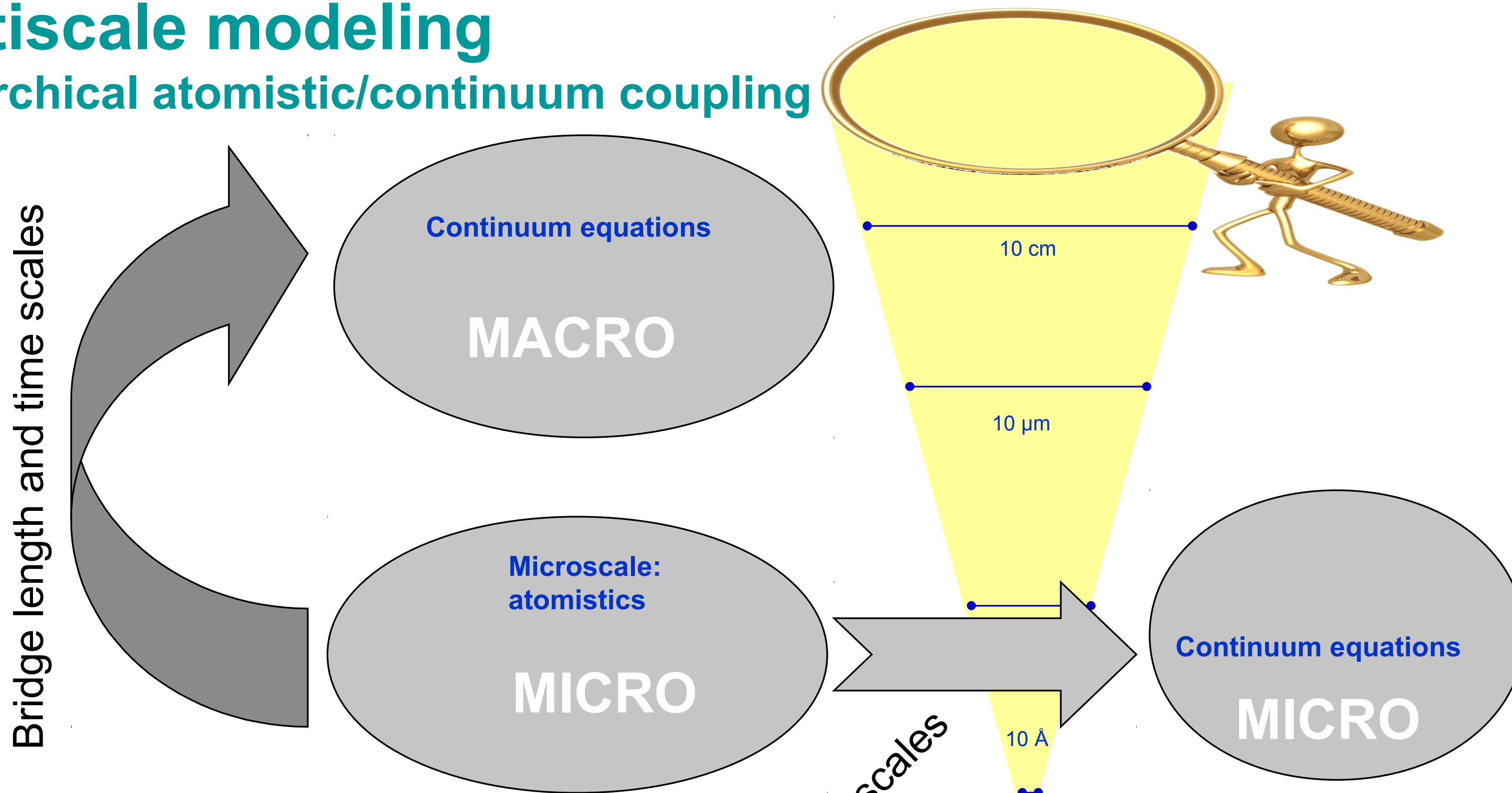
Multiscale modeling

Hierarchical atomistic/continuum coupling



Constitutive equations
Material parameters
Boundary conditions
Corrections (e.g. finite size)
Validation

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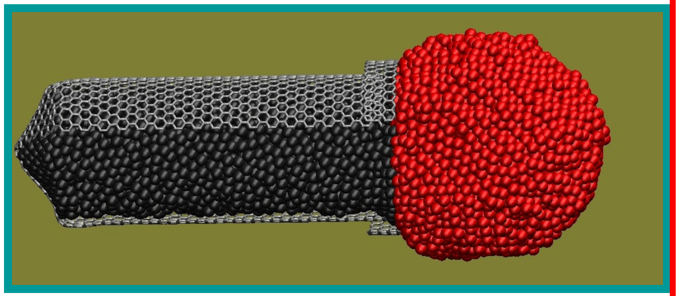
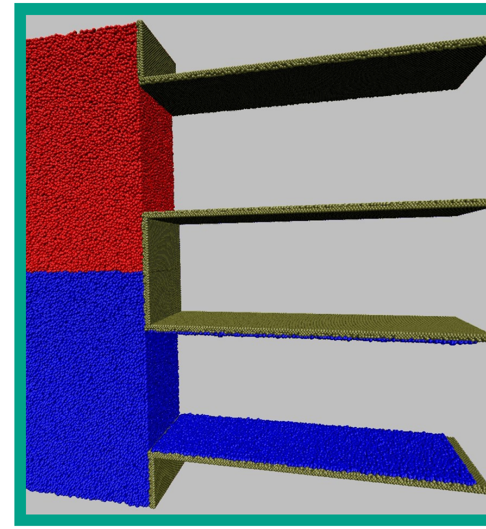
Classical transport and shape evolution in small systems

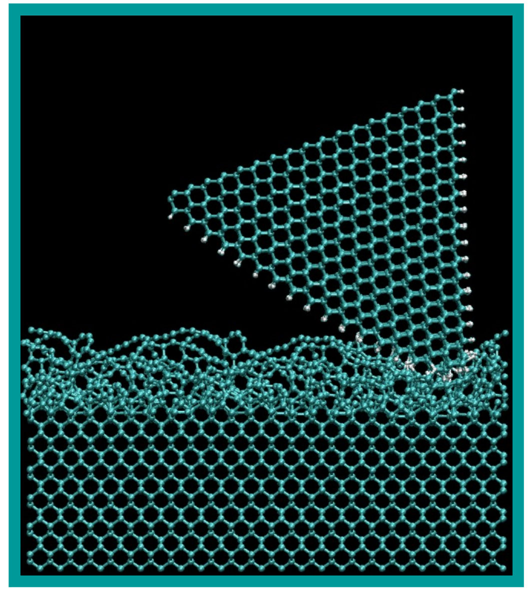
Today



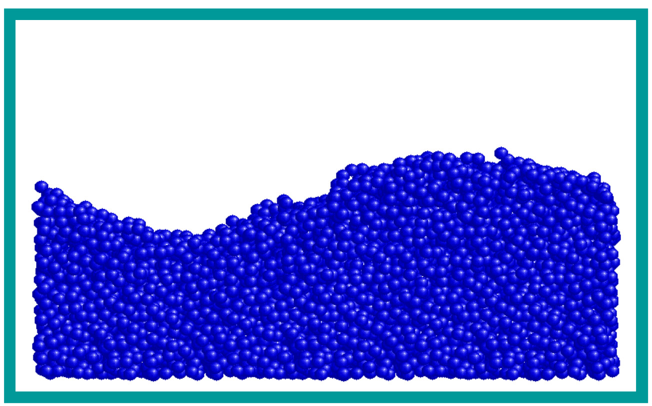
CNT growth:
ACS Nano **5**, 686 (2011)



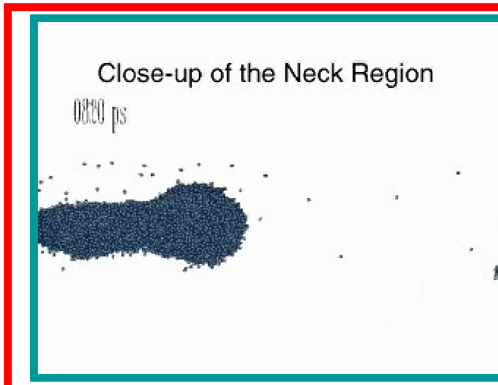
Capillary impregantion:
NJP, 10, 113022 (2008)



Wear of surfaces:
Nature Mat. 10, 34 (2011)



DLC growth:
Science **309**, 1545 (2005)



Rayleigh instability:
Science **289**, 1165 (2000)

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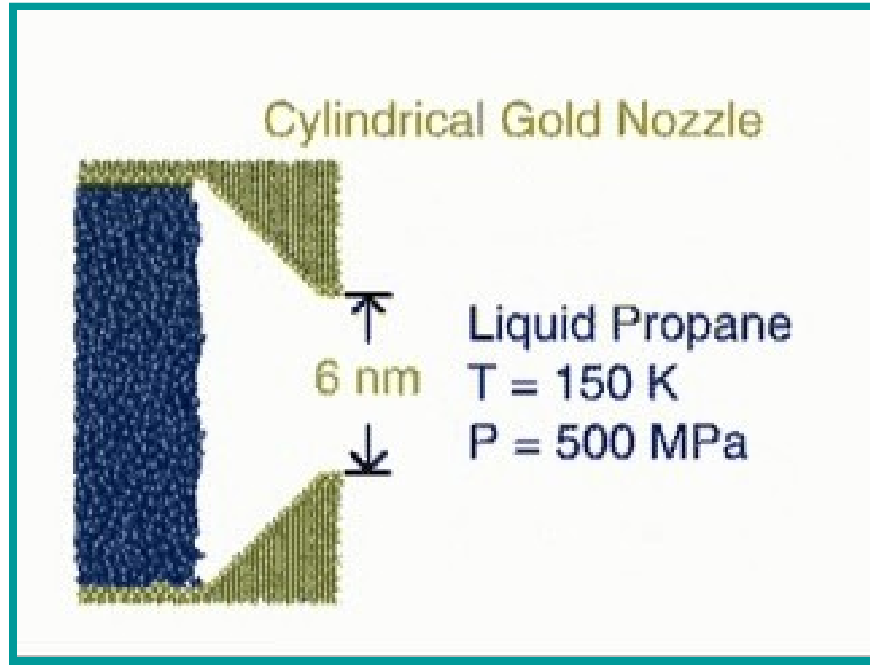
Classical molecular dynamics of nanojet formation and breakup

Nanojets
Moseler & Landman,
Science **289**, 1165 (2000).



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Rayleigh instability and the validity of hydrodynamics on the nanoscale?

Lubrication equations:

$$\partial_t v + v\partial_z v = -\frac{\gamma \partial_z \kappa}{\rho} + 3\nu \frac{\partial_z (h^2 \partial_z v)}{h^2}$$

$$\partial_t h + v\partial_z h = -\frac{h\partial_z v(z,t)}{2}$$

Jens Eggers, Rev. Mod. Phys. **69,** 865,(1997)
J. Eggers, E. Villermaux, Rep. Prog. Phys. **71** , 036601 (2008)

Intrinsic scales:

$$\ell_\nu = \nu^2 \frac{\rho}{\gamma} \qquad t_\nu = \nu^3 \left(\frac{\rho}{\gamma}\right)^2$$

$$\partial_t v + v\partial_z v = -(\partial_z \kappa) + 3\partial_z (h^2 \partial_z v)/h^2$$

Similarity solution :
→ threads

$$h_{\text{neck}} \ll \ell_\nu$$

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Navier-Stokes:

$$\rho(\partial_t v_i(\mathbf{r},t) + v_j(\mathbf{r},t)\partial_j v_i(\mathbf{r},t)) = \partial_j \sigma_{ji}(\mathbf{r},t) \qquad (1)$$

Stress tensor

$$\sigma_{ik}(\mathbf{r},t) = -p(\mathbf{r},t)\delta_{ik} + \eta(\partial_k v_i(\mathbf{r},t) + \partial_i v_k(\mathbf{r},t)) + s_{ik}(\mathbf{r},t)$$

Fluctuation-dissipation theorem

$$\langle s_{ik}(\mathbf{r},t) s_{lm}(\mathbf{r}',t')\rangle = 2k_B T\eta\left(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl} - \frac{2}{3}\delta_{ik}\delta_{lm}\right)\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

Expansion

$$\mathbf{v}(r,z,t) = \sum_{i=0}^{\infty}\int_{-\infty}^{\infty} v^{(2i)}(\bar{z},t)\mathbf{w}^{(2i,\bar{z})}(r,z)d\bar{z}$$

Into divergence-free basis

$$\mathbf{w}^{(2i,\bar{z})}(r,z) = \begin{pmatrix} -\frac{r^{2i+1}}{2i+2}\delta'(z-\bar{z}) \\ r^{2i}\delta(z-\bar{z}) \end{pmatrix}$$

Lubrication approximation

$$\mathbf{v}(\mathbf{r},t)) = \begin{pmatrix} -\frac{x}{2}\partial_z v^{(0)}(z,t) \\ -\frac{y}{2}\partial_z v^{(0)}(z,t) \\ v^{(0)}(z,t) \end{pmatrix}$$

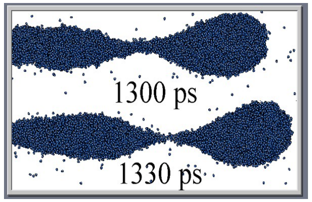
Multiplication of eq. (1) with $\mathbf{w}^{(0,\bar{z})}(\mathbf{r})$

Integration over jet volume $V = \{\mathbf{r} \,|\, \sqrt{x^2+y^2} \leq h(z)\}$

Experimental validation?

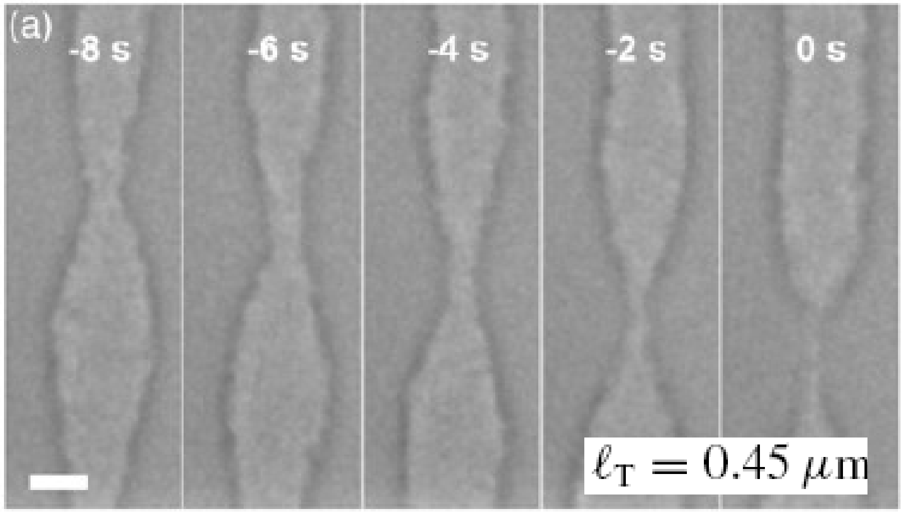
Stochastic terms dominate
on length scales smaller than
Thermal capillary length scales:

$$\ell_{\mathrm{T}} = (k_{\mathrm{B}} T / \gamma)^{1/2}$$



Hennequin, et al., *Phys. Rev. Lett.* **97** 244503 (2006)

Colloidal fluids:



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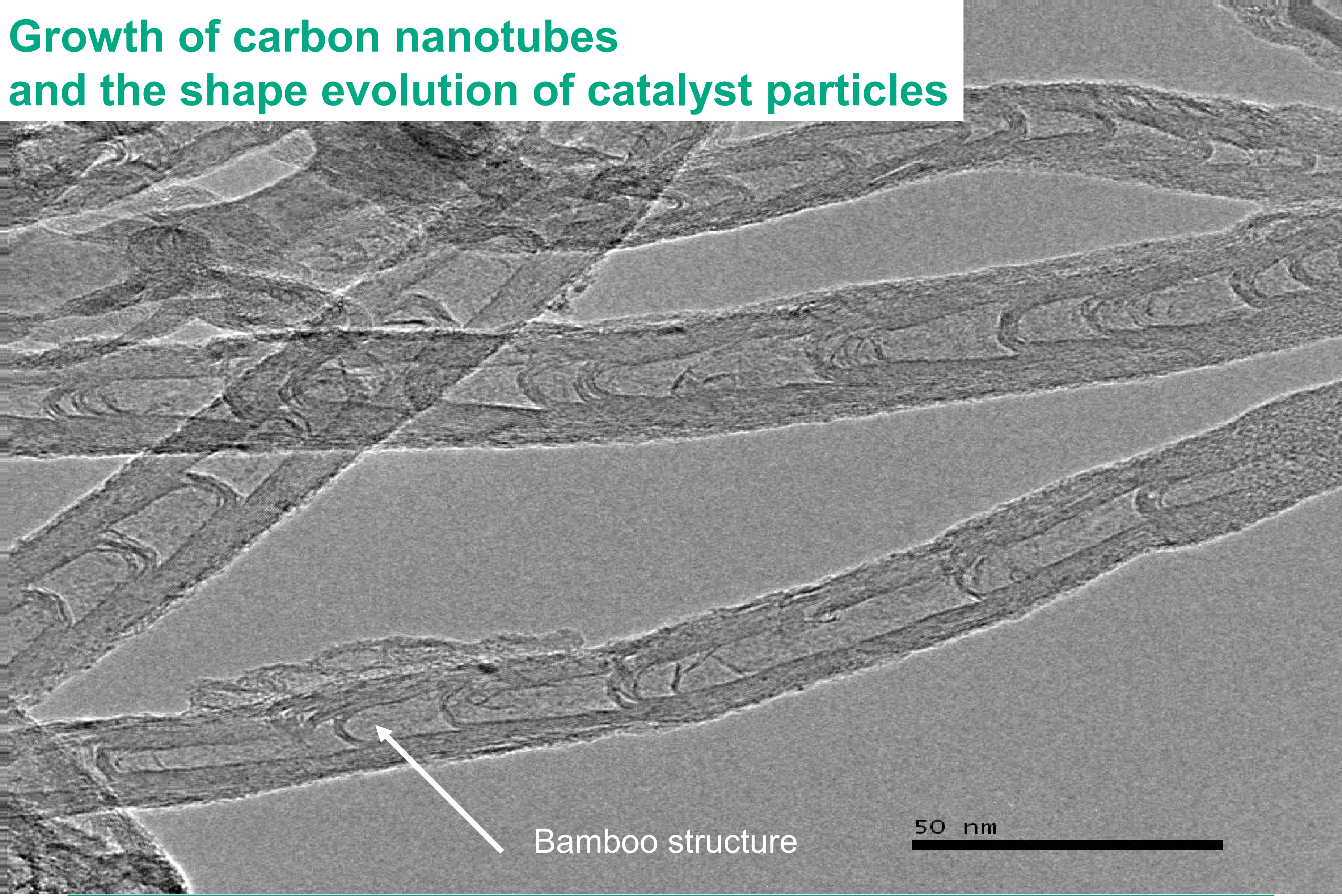
Growth of carbon nanotubes and the shape evolution of catalyst particles



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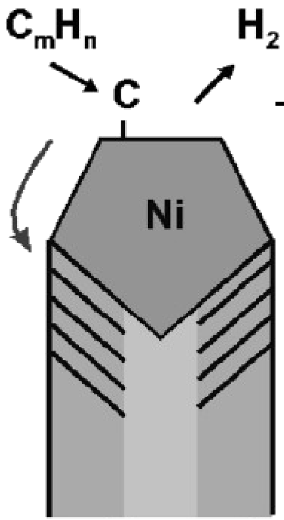
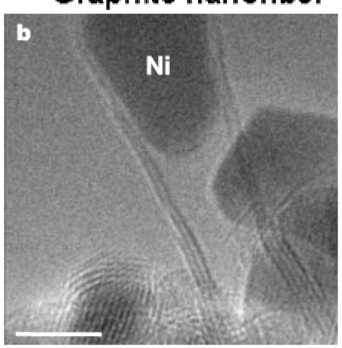
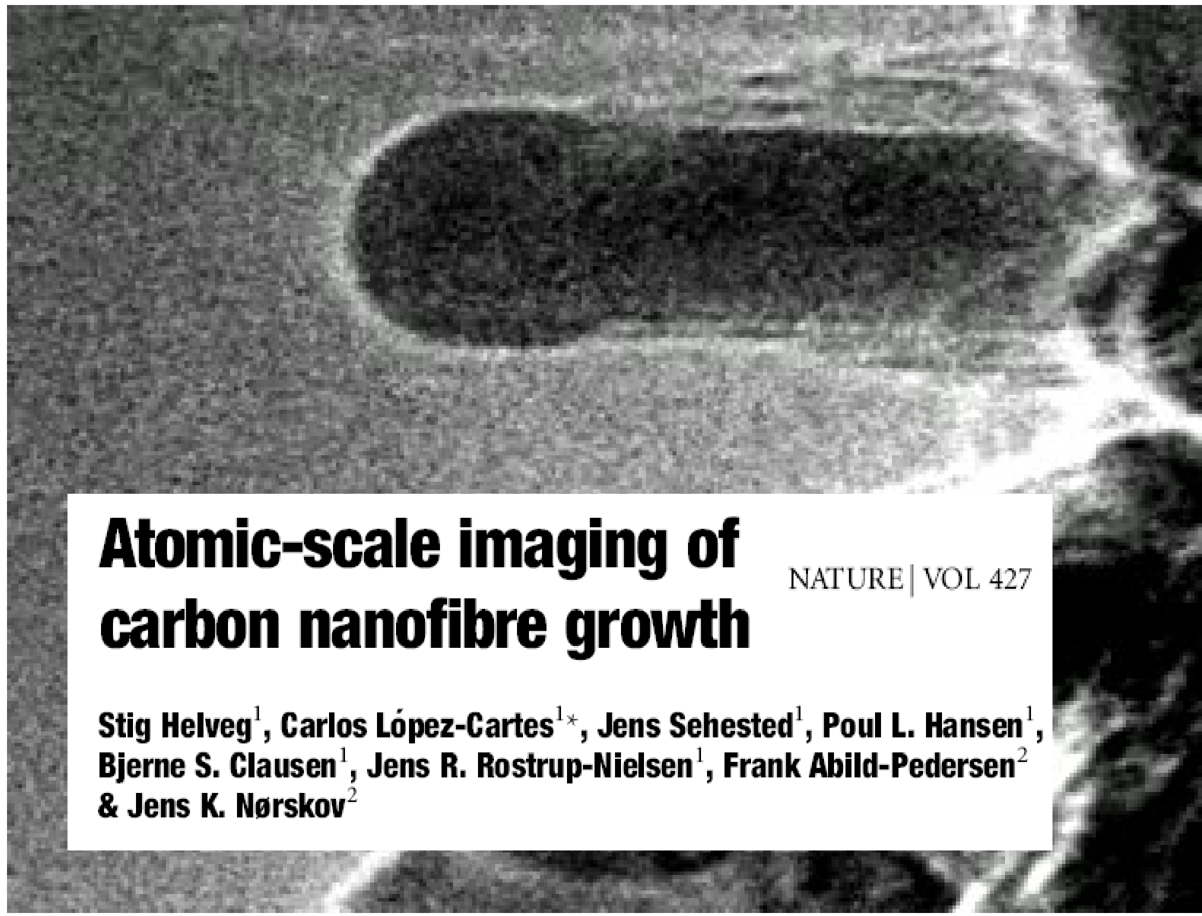
Environmental TEM experiments:
Shape dynamics of Ni catalyst particles



T=750 K

Graphite nanofiber





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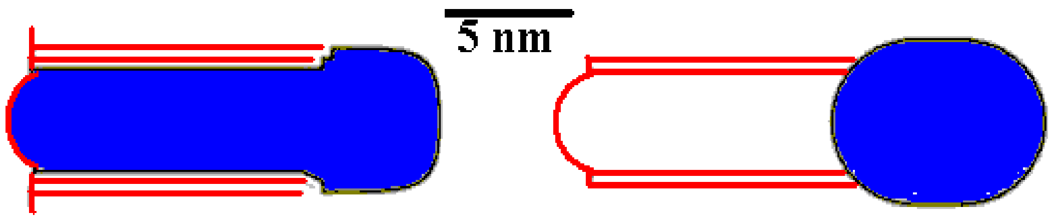
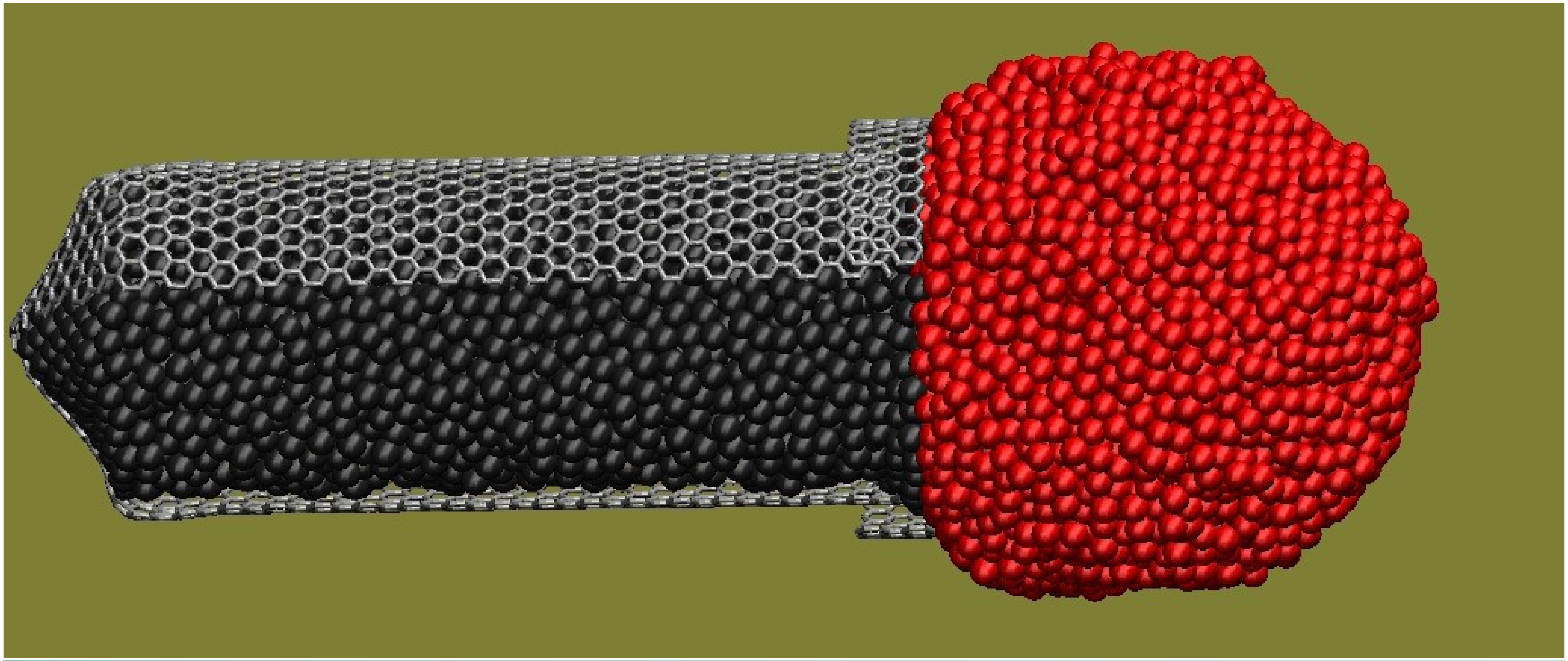
Molecular dynamics of a solid Ni nanoparticle in a double wall carbon nanotube

Moseler et al.,
ACS Nano 5, 686 (2011)

A T=1160 K EAM Ni_{10561} interacting via Morse potentials with a static CNT





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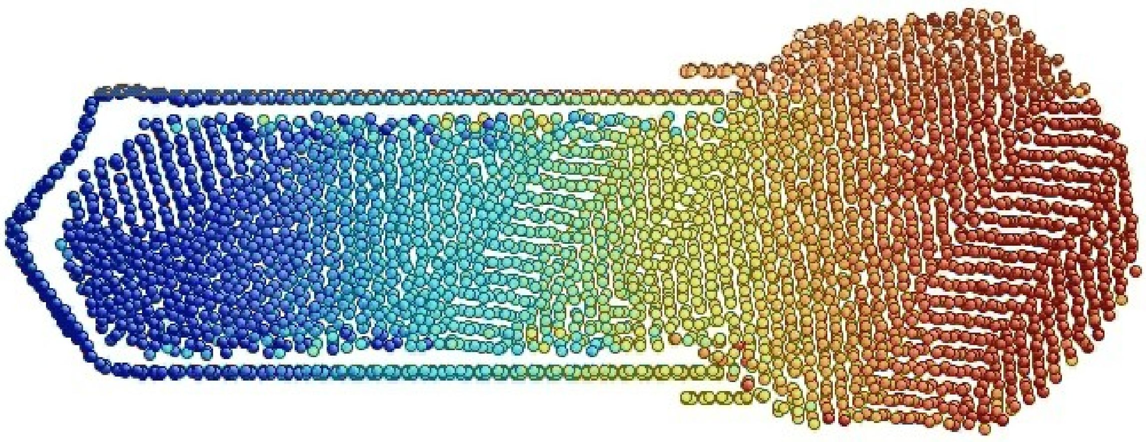
Transport mechanism: surface diffusion



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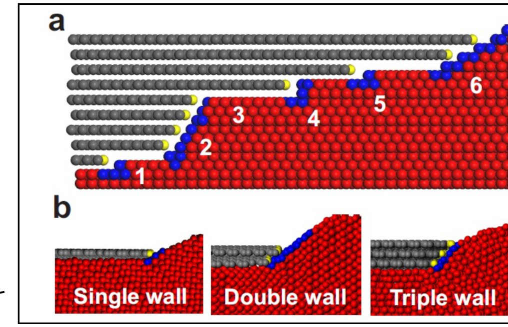
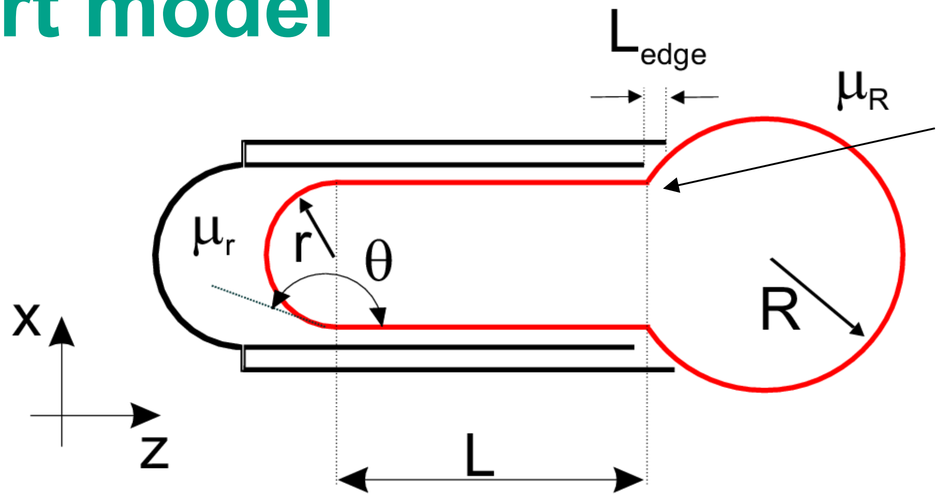
Continuum transport model





Two Reservoirs: $\mu_r = \gamma\Omega \frac{2}{r}$ $\mu_R = \gamma\Omega \frac{2}{R}$

Diffusive particle current:

$$J = -2\pi r \frac{D_s^{edge} \rho_s}{kT} \frac{\partial \mu}{\partial z}$$

Mullins B:

WW Mullins, J.Appl.Phys. 28 333 (1957)

$$\frac{dL}{dt} = -\frac{4B}{L_{edge} r^2}\left[1 - \frac{r}{R(L)}\right]$$

$$B = \frac{\gamma D_s^{edge} \rho_s \Omega^2}{kT}$$

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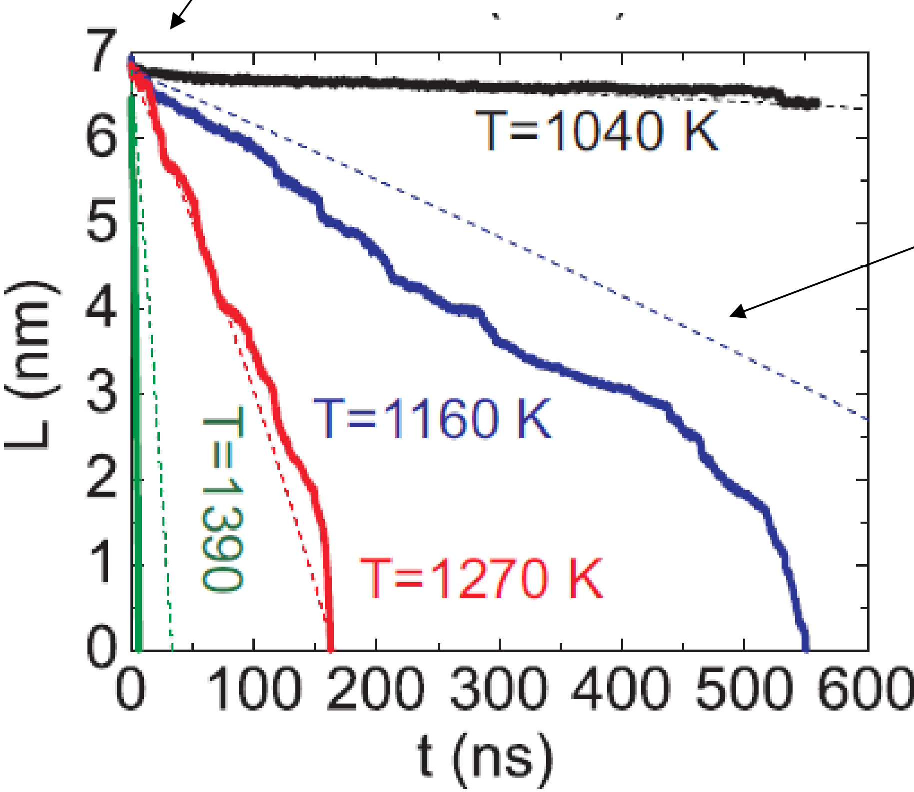
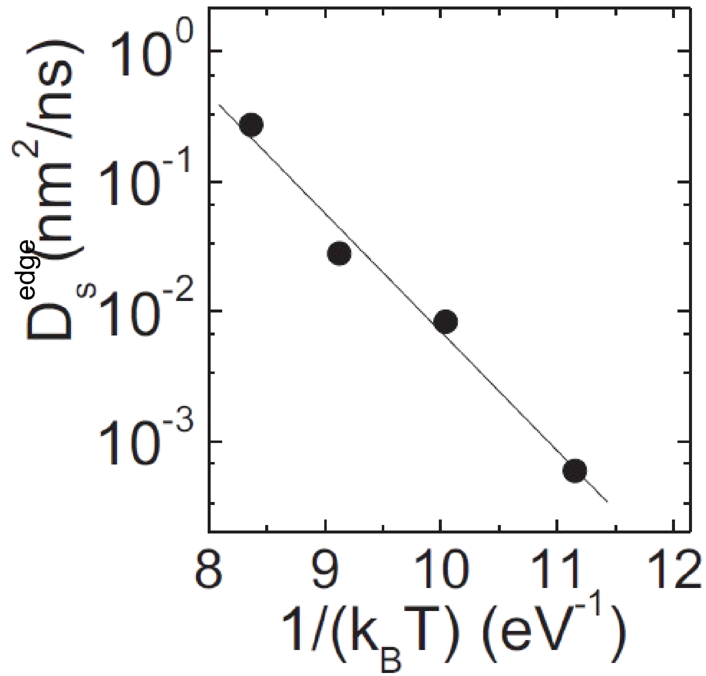
Use $\left.\frac{dL}{dt}\right|_{t=0}$ from MD and solve $\frac{dL}{dt} = -\frac{4B}{L_{edge}\, r^2}\left[1-\frac{r}{R(L)}\right]$ for D_s^{edge}





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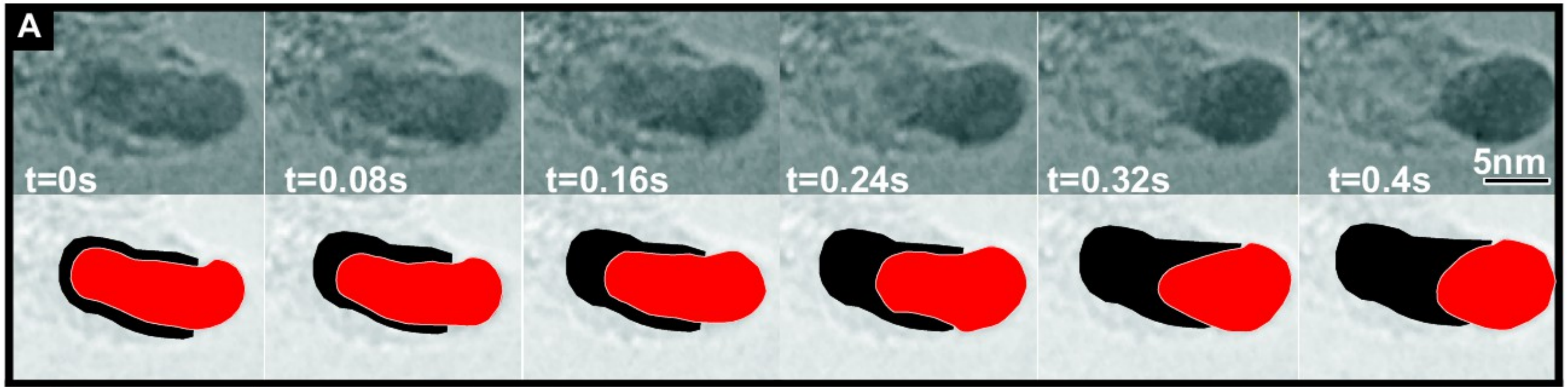
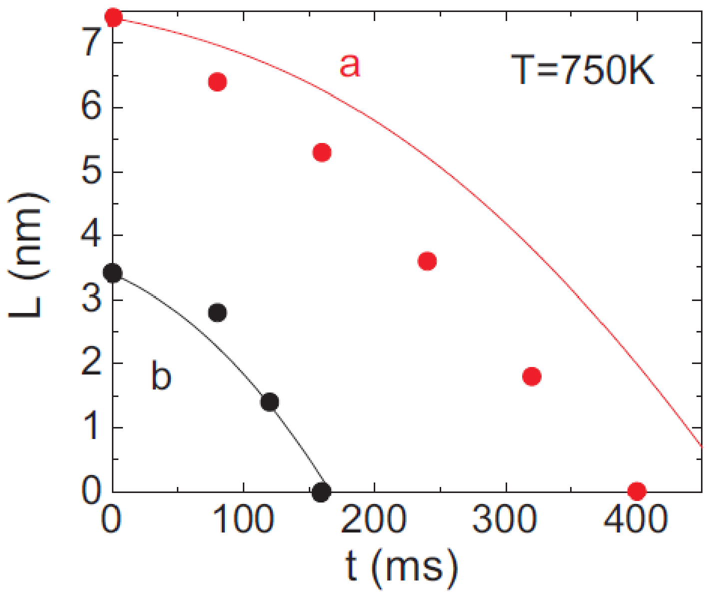
Comparison with experiment





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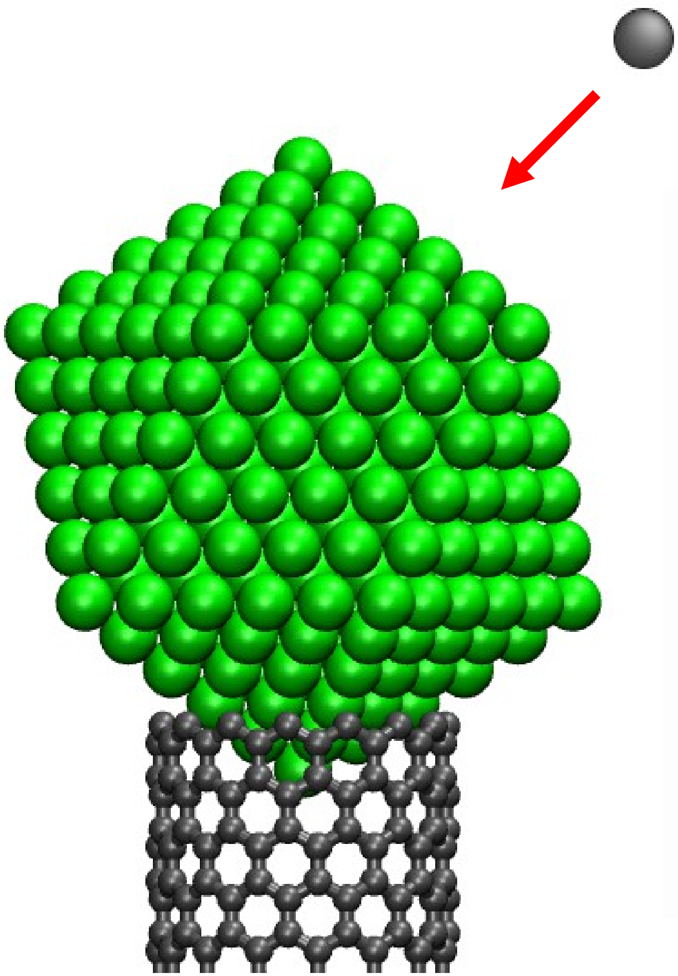
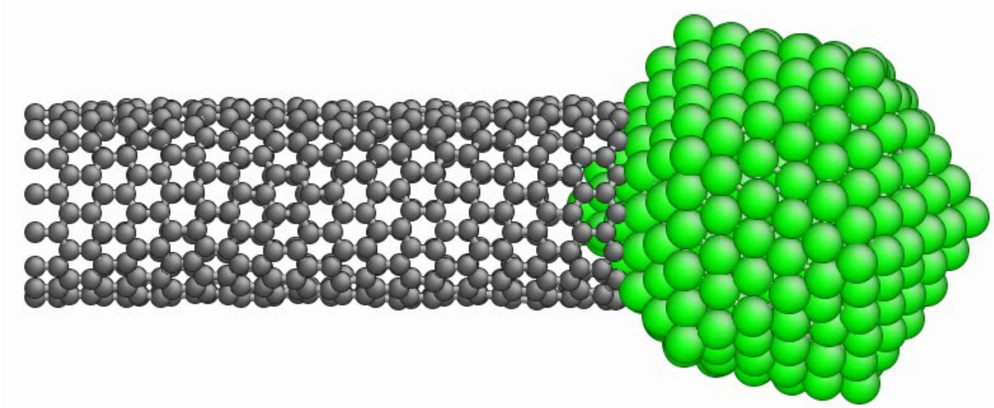
CNT with Fe-Catalyst

Tip growth of (15,0) tube catalysed by Fe_{561}

Molecular dynamics simulation with reactive Bond-Order-Potential (Albe, Nordlund)

Deposition rate $2 \cdot 10^{10}$ C/s





Growth at 600 K

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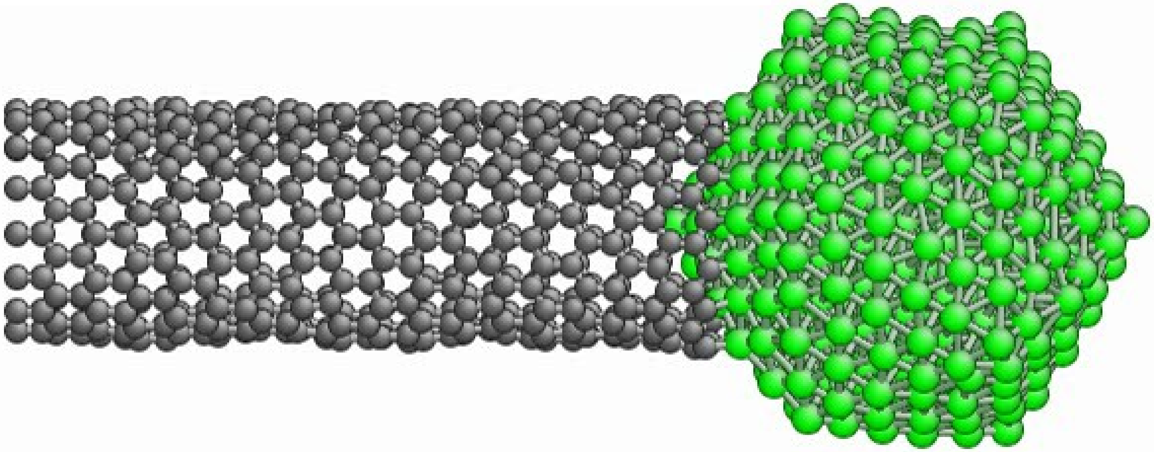
Growth at 1200K



Japanese Journal of Applied Physics
Vol. 43, No. 4A, 2004, pp. L471–L474
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***In Situ* Study of Iron Catalysts for Carbon Nanotube Growth Using X-Ray Diffraction Analysis**

Kenji NISHIMURA[1], Nobuharu OKAZAKI[2], Lujun PAN[1,2] and Yoshikazu NAKAYAMA[1,2,*]

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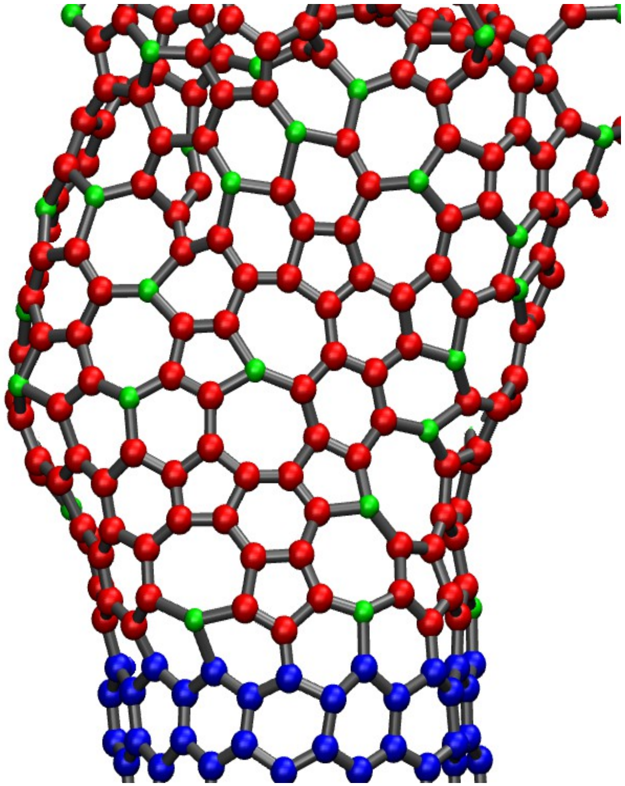
Cross section of the newly grown CNT



Fe (green) is incorporated in CNT-walls

PRL **102**, 126807 (2009) PHYSICAL REVIEW LETTERS week ending 27 MARCH 2009

Embedding Transition-Metal Atoms in Graphene: Structure, Bonding, and Magnetism

A. V. Krasheninnikov,[1,2,*] P. O. Lehtinen,[1] A. S. Foster,[1,3] P. Pyykkö,[4] and R. M. Nieminen[1]

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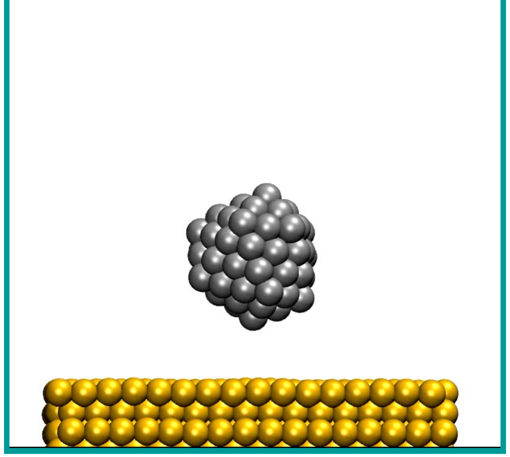
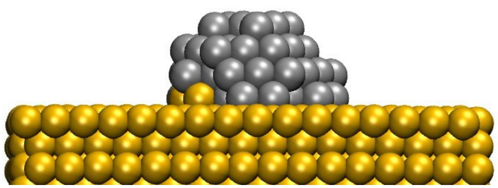
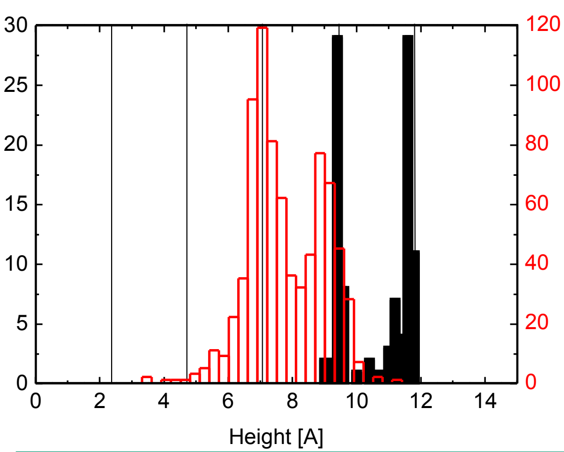
Deposition of Ag_N on Au(111)
Effect of deposition energy

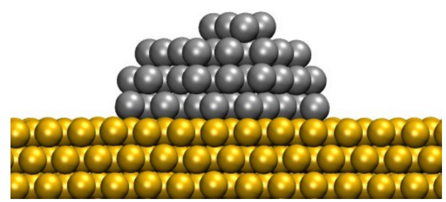


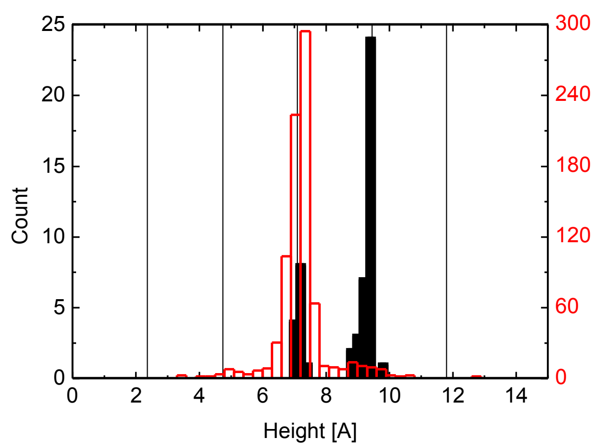
3 eV



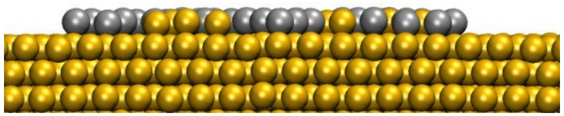


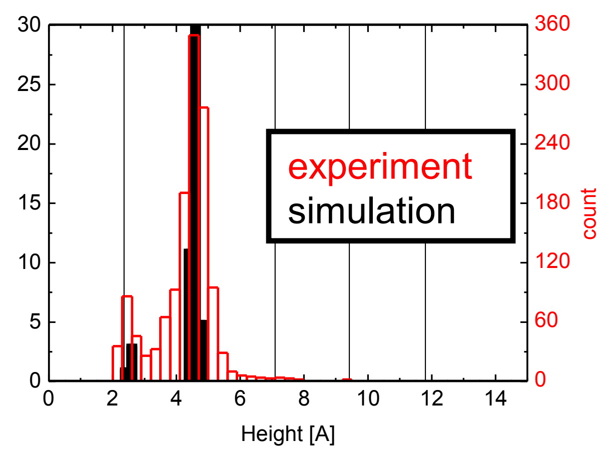
34 eV





340 eV





Grönhagen, Järvi et al., to be published

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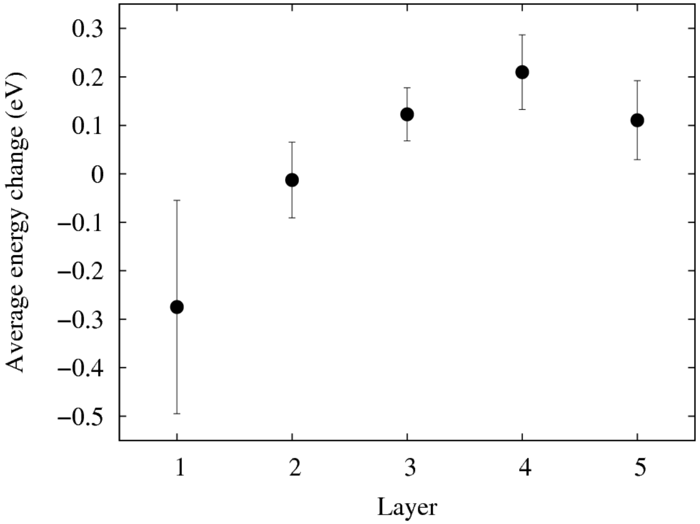
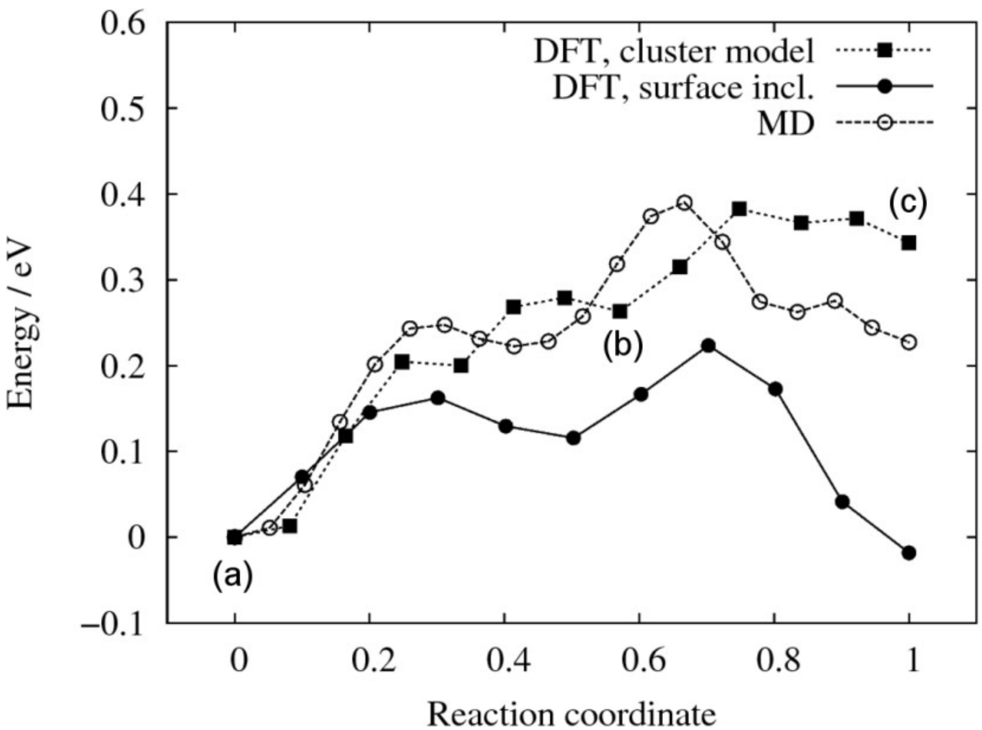
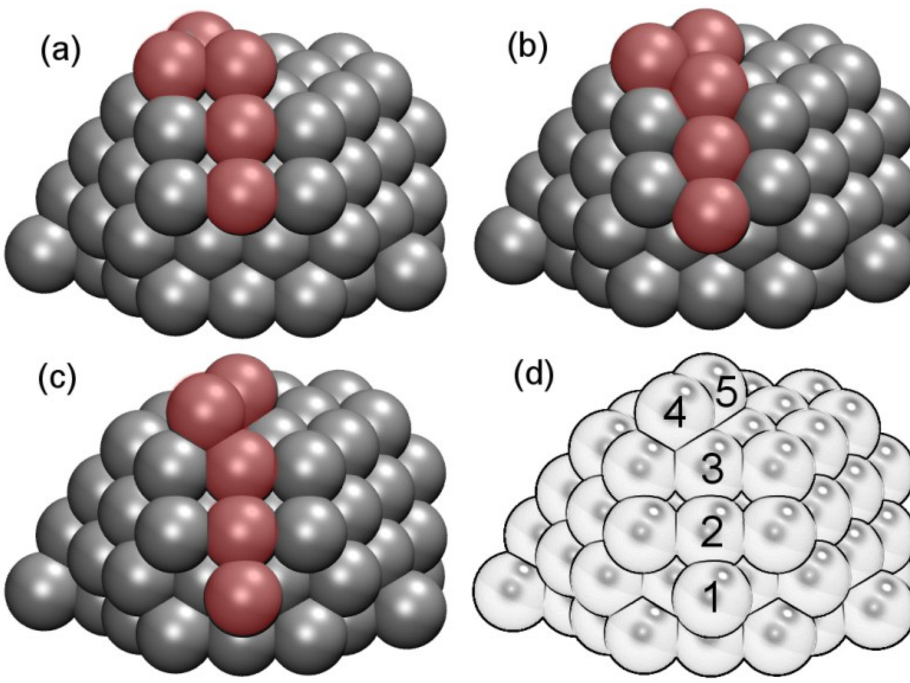
Decay mechanism



- Decay of top monolayer
  - Non-local effect of surface on cluster
    → Barrier from ca. 0.4 to 0.2 eV
- Barrier inferred from experiment at 77 K: ca. 0.25 eV





Summary

A hierarchical atomistic/continuum modelling is quite usefull for a quantitative understanding of complex shape dynamics in nanoscale systems.

Acknowledgement:

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Tommi Järvi, Fraunhofer IWM

Thank you for your attention!

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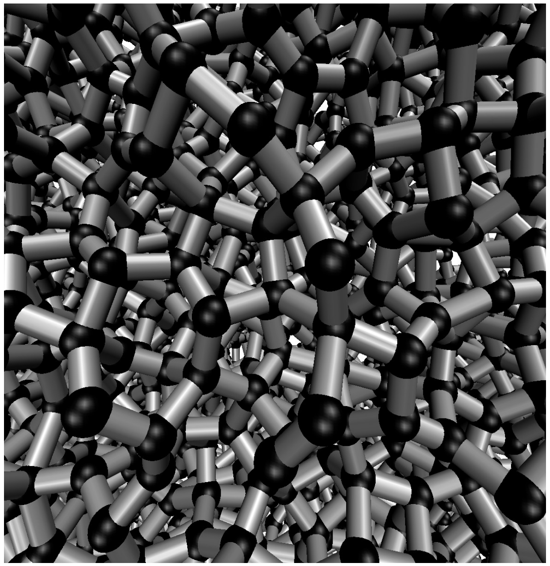
Topography evolution during thin film growth

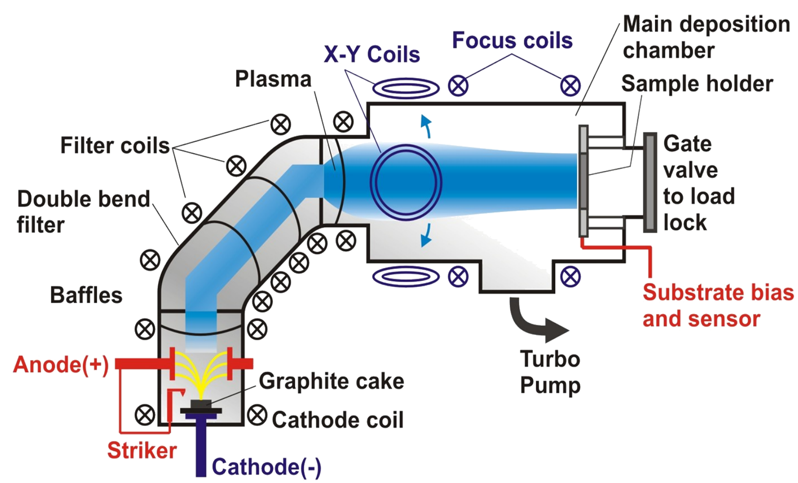


The Ultrasmoothness of Diamond-like Carbon Surfaces

Michael Moseler,[1,2*] Peter Gumbsch,[1,3] Cinzia Casiraghi,[4] Andrea C. Ferrari,[4] John Robertson[4]

The ultrasmoothness of diamond-like carbon coatings is explained by an atomistic/continuum multiscale model. At the atomic scale, carbon ion impacts induce downhill currents in the top layer of a growing film. At the continuum scale, these currents cause a rapid smoothing of initially rough substrates by erosion of hills into neighboring hollows. The predicted surface evolution is in excellent agreement with atomic force microscopy measurements. This mechanism is general, as shown by similar simulations for amorphous silicon. It explains the recently reported smoothing of multilayers and amorphous transition metal oxide films and underlines the general importance of impact-induced downhill currents for ion deposition, polishing, and nanopattering.

www.sciencemag.org SCIENCE VOL 309 2 SEPTEMBER 2005 **1545**



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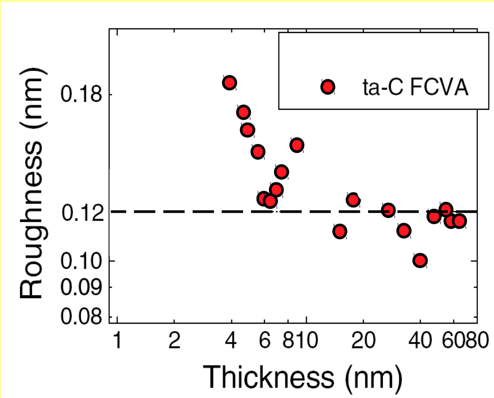
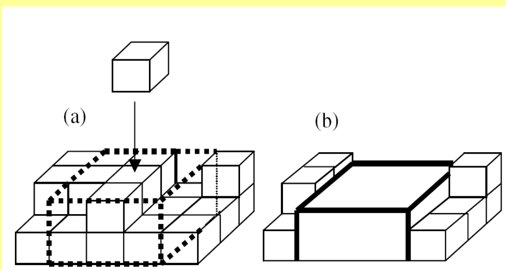
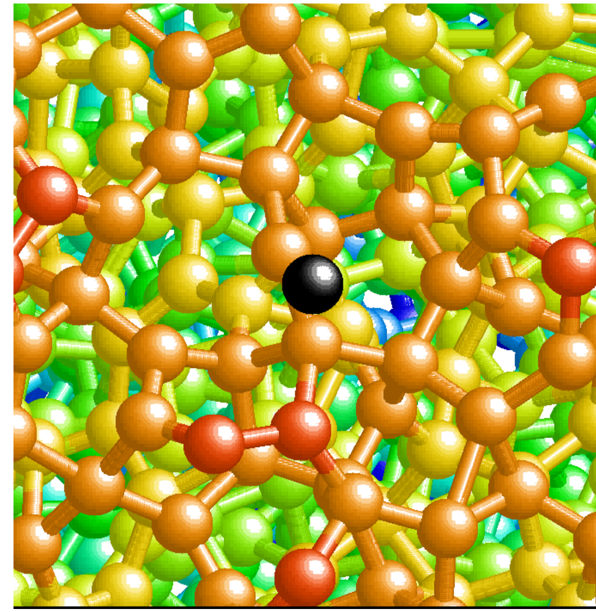
Capillary smoothing?





Casiraghi, Ferrari, Ohr, Flewitt, Chu, Robertson, PRL **91**, 226104 (2003)

C impinges on ta-C with 100 eV



MD with Brenner BOP,
D. W. Brenner, Phys. Rev. B 42, 8458 (1990)

$$E_b = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij})]$$

CAMBRIDGE UNIVERSITY
DEPARTMENT OF ENGINEERING

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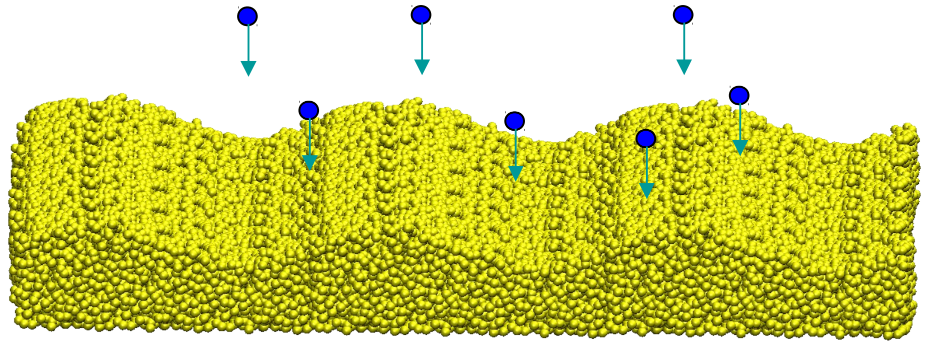
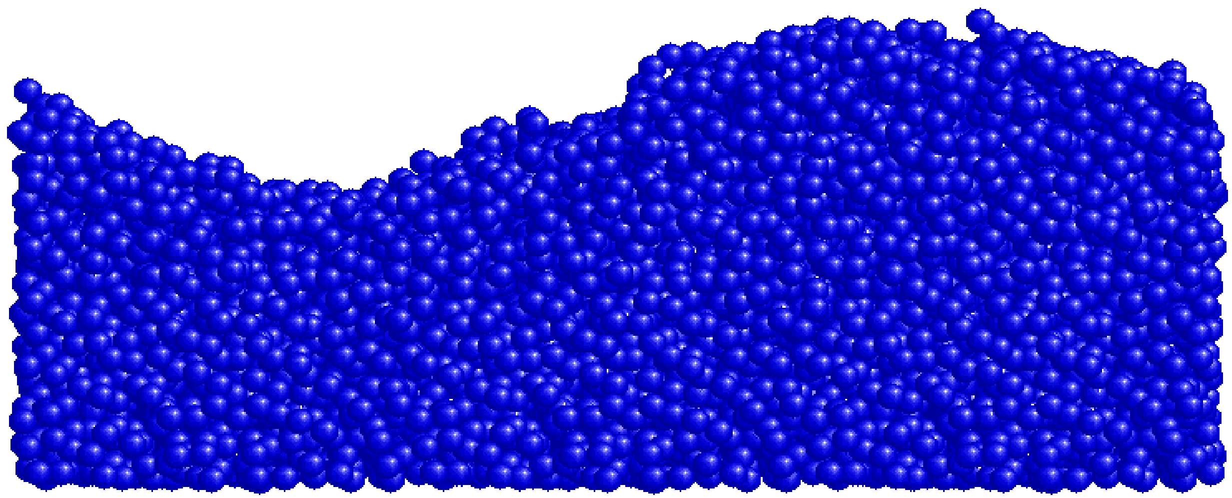
Atomistic simulation of film growth

The smoothing of
a rough DLC film
4000 C-atoms
with 100 eV
hit a film
with an area
7.05nm x 2.35nm





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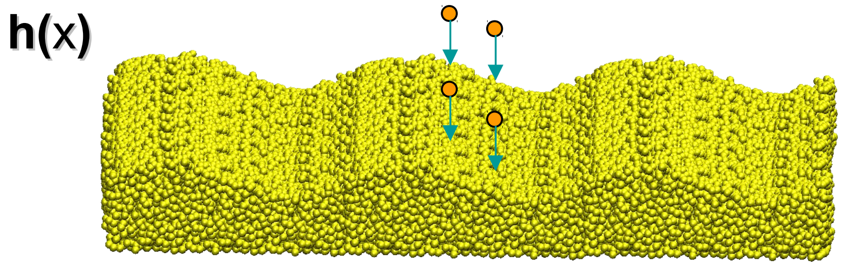
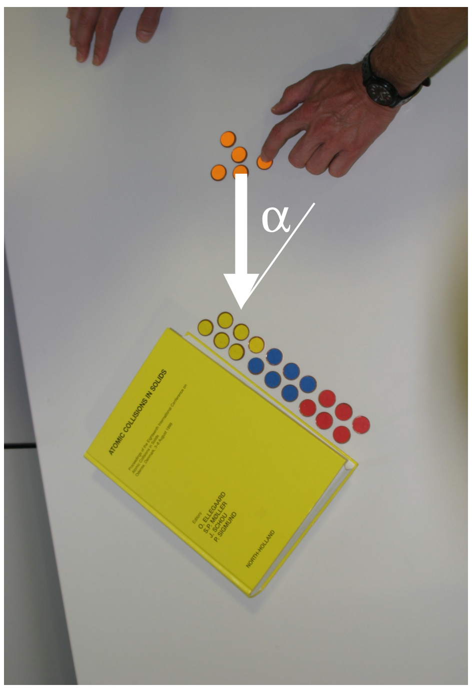
Downhill currents

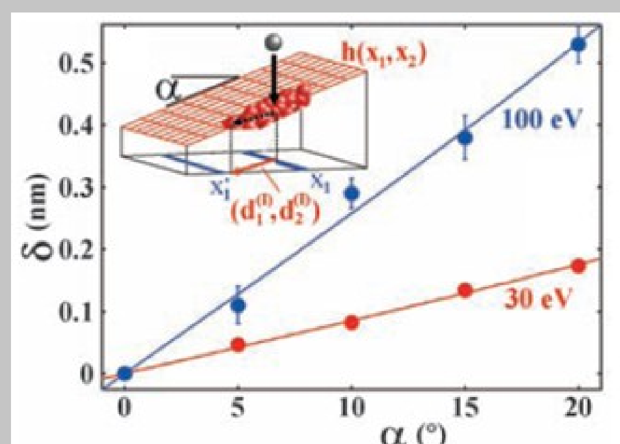
G.Carter, PRB 54, 17647 (1996)
M.Moseler et al. Comp. Mat. Sci. 10, 452 (1998)





Particle current:

$$\mathbf{j}(\mathbf{x}) = -\nu \nabla h(\mathbf{x})$$



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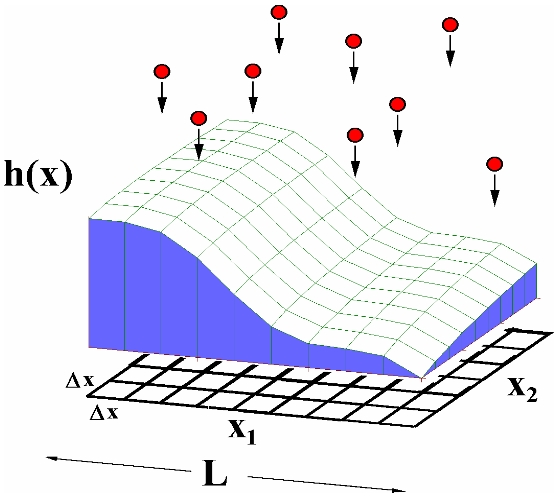
Mesoscale description



Stochastic differential equation of motion

$$\partial h(\mathbf{x},t)/\partial t = -\Omega\nabla\cdot\mathbf{j}(\mathbf{x},t) + \eta(\mathbf{x},t)$$

$$\langle\eta(\mathbf{x},t),\eta(\mathbf{x}',t')\rangle = r\Omega^2\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')$$

$$\mathbf{j}(\mathbf{x},t) = -\nu\nabla h(\mathbf{x},t)$$

r: deposition rate, Ω: average atomic volume

Stanley&Barabasi,
Fractal concepts in Surface Growth

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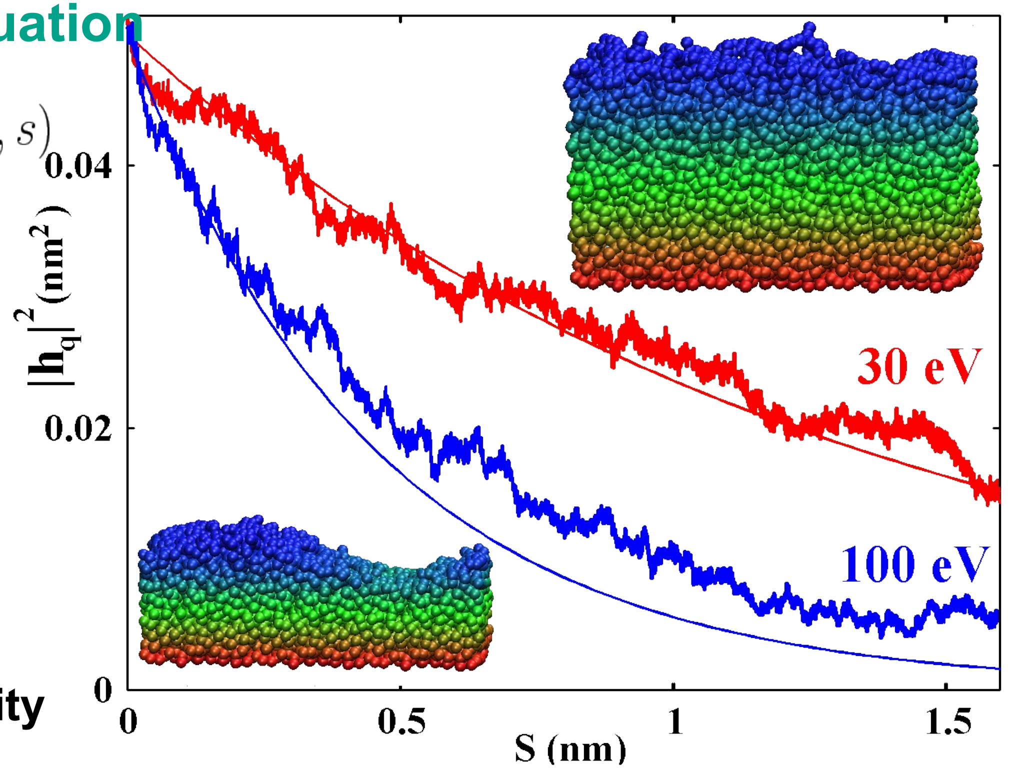
The Edwards-Wilkinson equation

$$\partial h(\mathbf{x}, s)/\partial s = \nu \nabla^2 h(\mathbf{x}, s) + \eta(\mathbf{x}, s)$$

s ~ t

$$h(\mathbf{x}, s) \underset{FT}{\longleftrightarrow} h_k(s)$$



Solution: Power spectral density

$$\langle |h_{\mathbf{k}}(s)|^2 \rangle = e^{-2\nu k^2 s} \langle |h_{\mathbf{k}}(0)|^2 \rangle + \Omega(1 - e^{-2\nu k^2 s})/(2\nu L_1 L_2 k^2)$$

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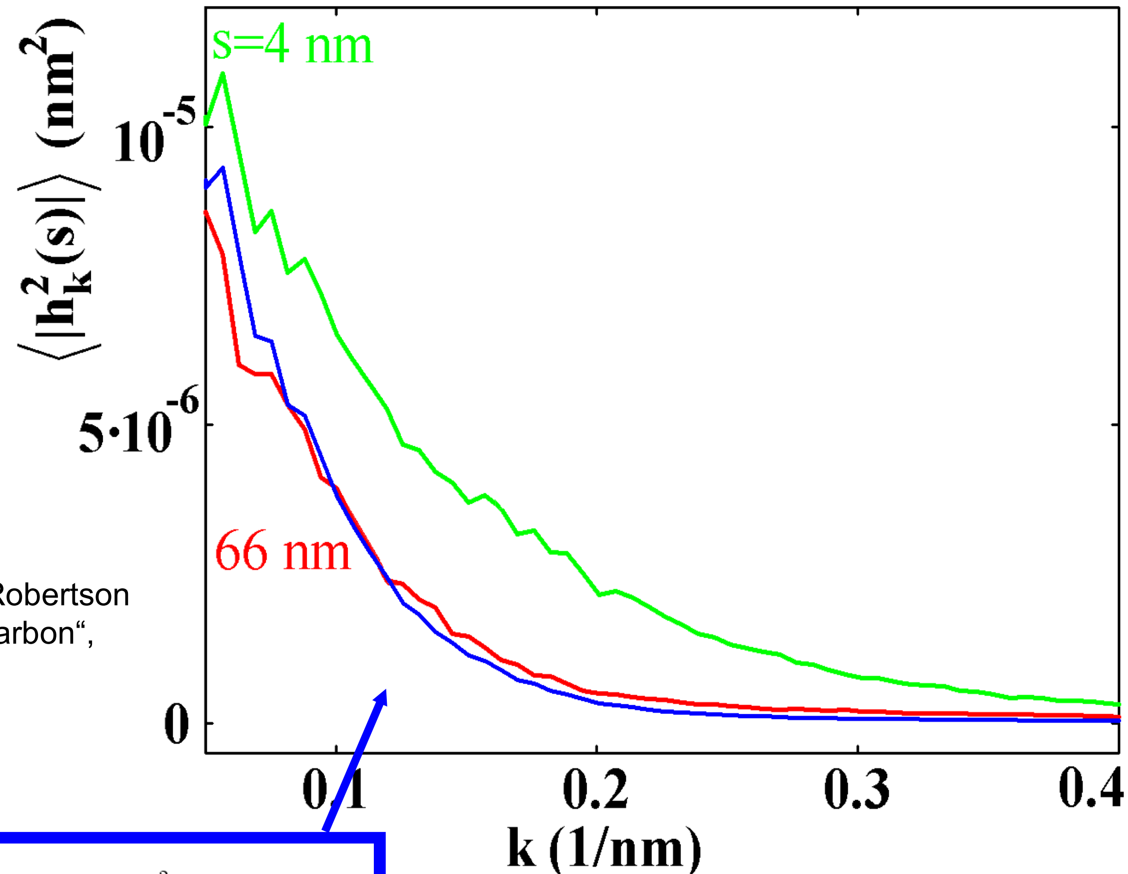
Evolution of the experimental power spectral density



Moseler, Gumbsch, Casiraghi, Ferrari, Robertson
„The ultrasmoothness of diamond-like carbon“,
Science **309**, 1545 (2005)

$$\langle |h_{\mathbf{k}}(s)|^2 \rangle = e^{-2\nu k^2 s} \langle |h_{\mathbf{k}}(0)|^2 \rangle + \Omega (1 - e^{-2\nu k^2 s})/(2\nu L_1 L_2 k^2)$$

CAMBRIDGE UNIVERSITY
DEPARTMENT OF ENGINEERING

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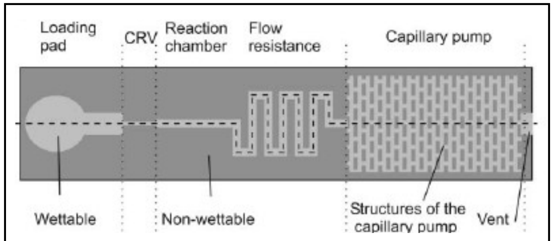
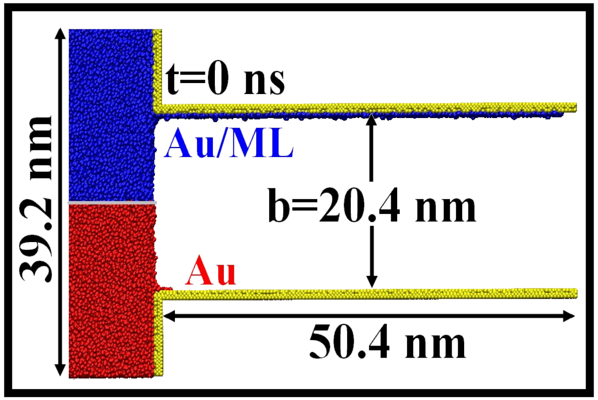
Nanocapillary pumps

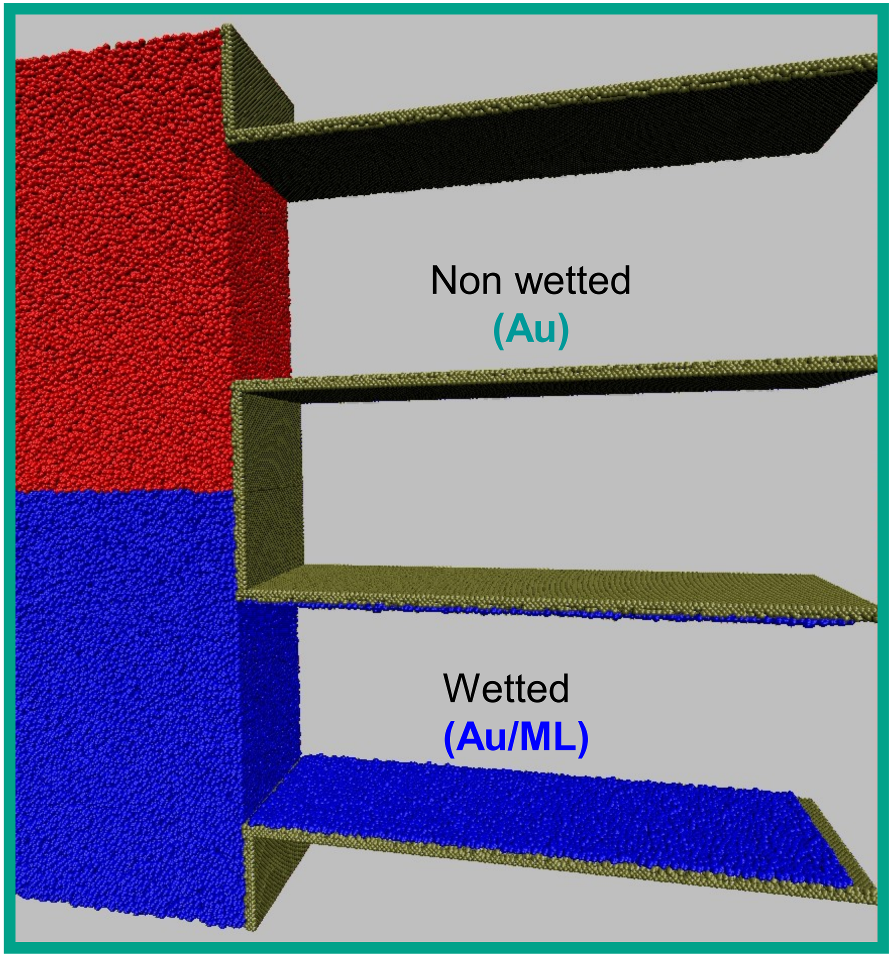
Applications in

- Lab-on-Chips
- Nanotribology
- Printing



Zimmermann et al.,
Lab Chip 7, 119 (2007)





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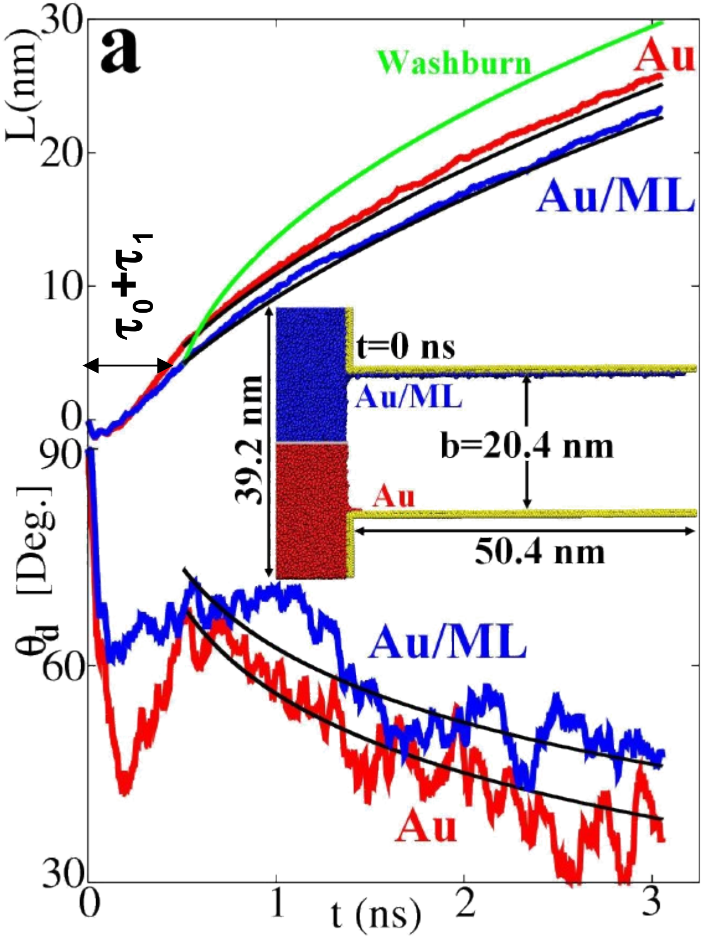

Meniscus relaxation:

$$\tau_0 = \sqrt{\rho(b/2)^3/\gamma}$$

Establisment of Poiseuille flow:

$$\tau_1 = \rho(b/2)^2/\eta$$

D. Quere, Europhys.Lett. 39, 533 (1997).

Washburn‘s law

$$L(t) = \sqrt{\gamma b t \cos\theta_e/(3\eta)}$$

Balance of capillary and Poiseuille pressure:

$$p_c = \gamma\kappa$$

$$p_p = -12\eta L\dot{L}/b^2$$

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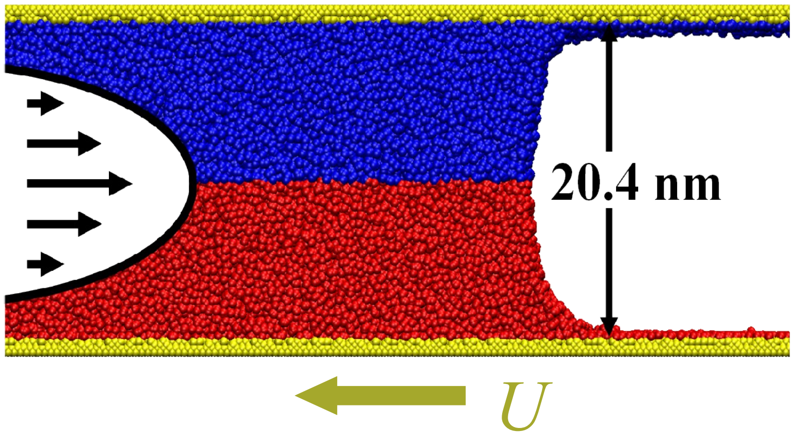
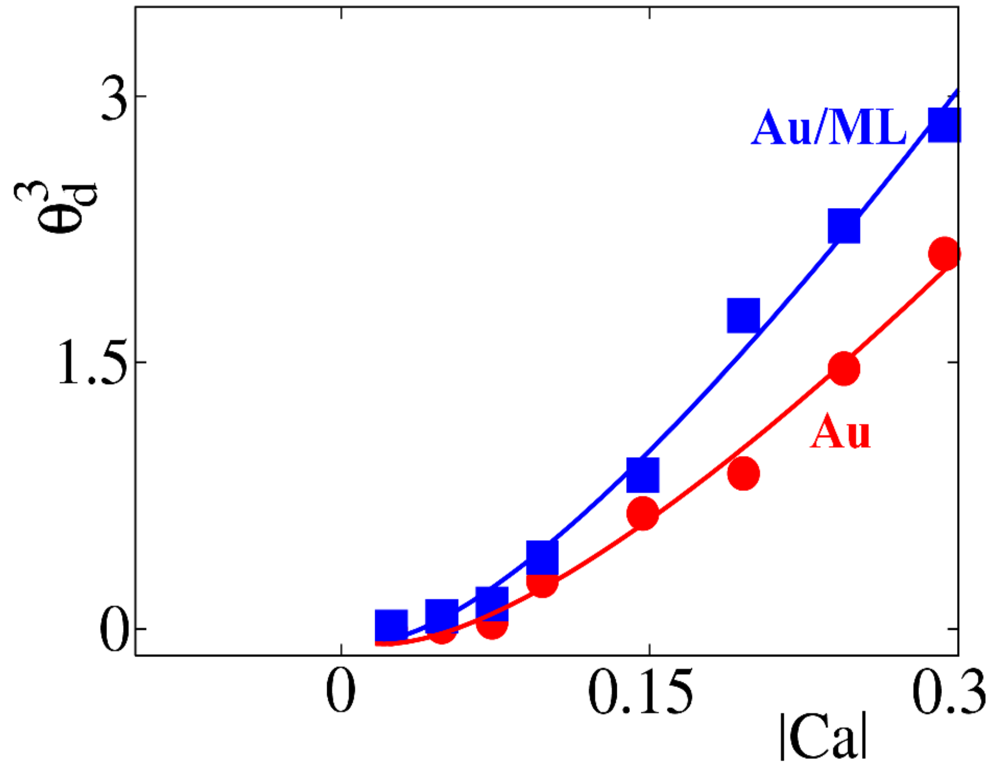
Steady state simulations





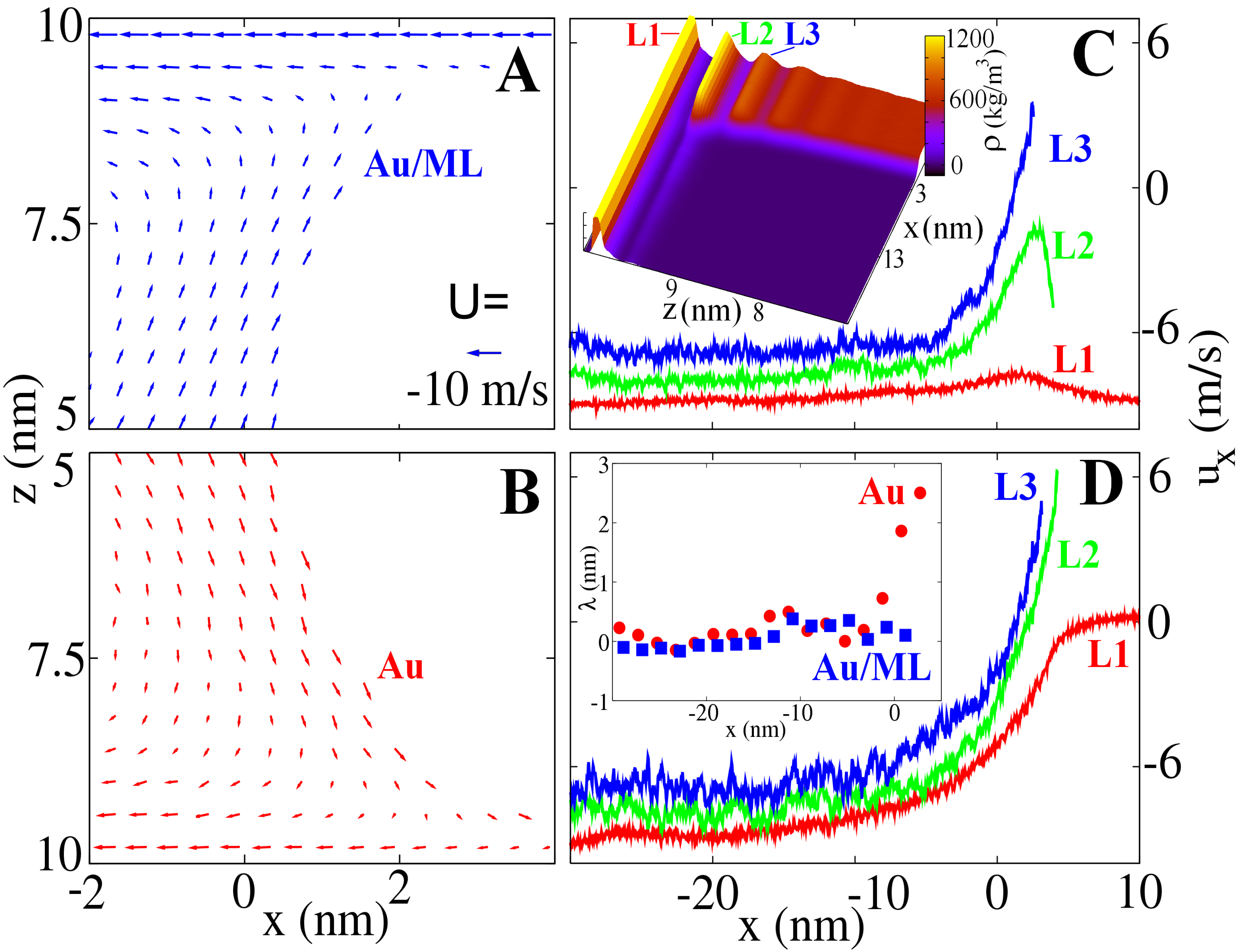
Capillary Number: $Ca = \dfrac{\eta U}{\gamma}$

$$\theta_d^3(\mathrm{Ca}) = 9\mathrm{Ca}\ln(\alpha \mathrm{Ca}^{\beta})$$

Au: $\alpha = 5.97$ and $\beta = 0.55$

Au/ML: $\alpha = 3.78$ and $\beta = 0.46$

J. Eggers, H. A. Stone, J. Fluid Mech. 505, 309 (2004)

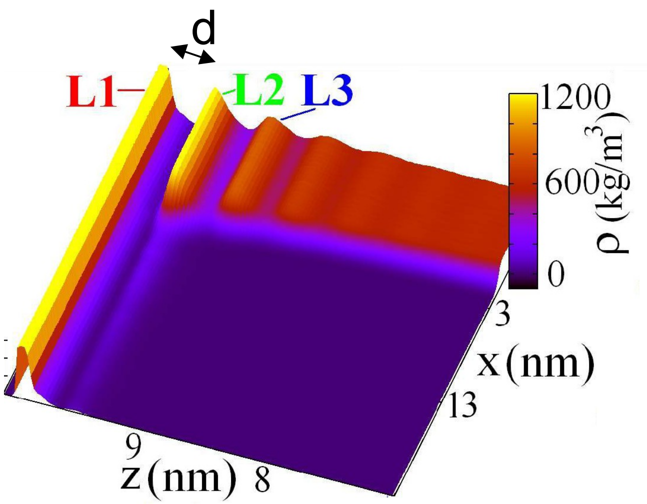


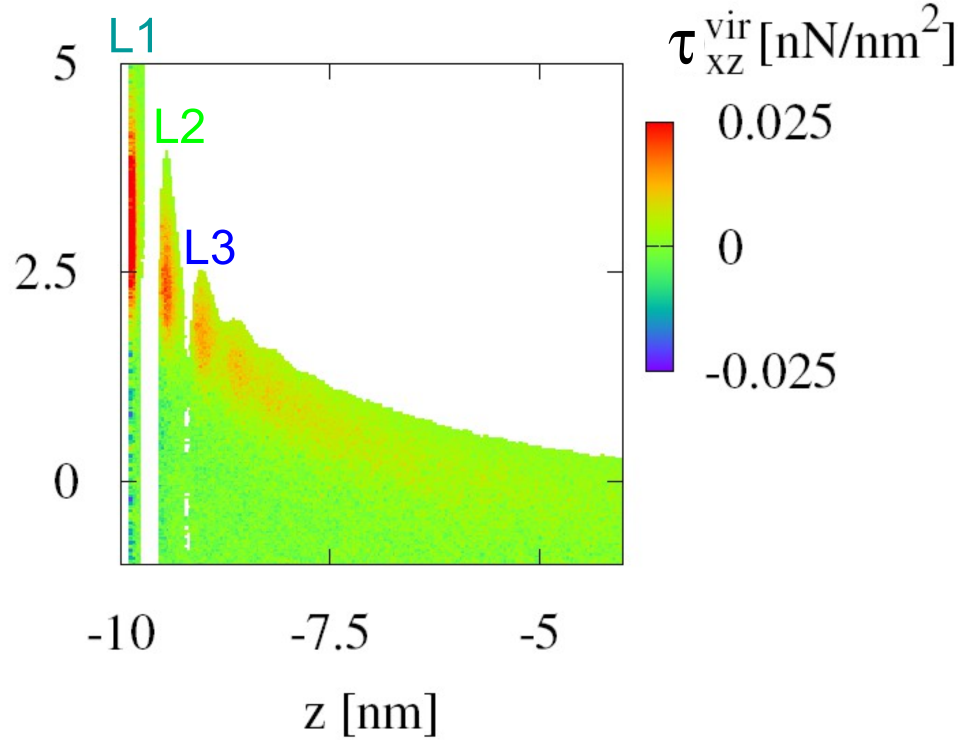
Navier slip law: $u_x(x, z = b/2) - U = \lambda(x)\partial_z u_x(x, z)|_{z=b/2}$

The „stress singularity“:

$$\tau^{vir}_{xz} = \frac{1}{2V_C}\sum_i\sum_{j\neq i} x_{ij}(Fz)_{ij}.$$

$$\eta 2U/d = 0.0144\,\mathrm{nN/nm^2}$$





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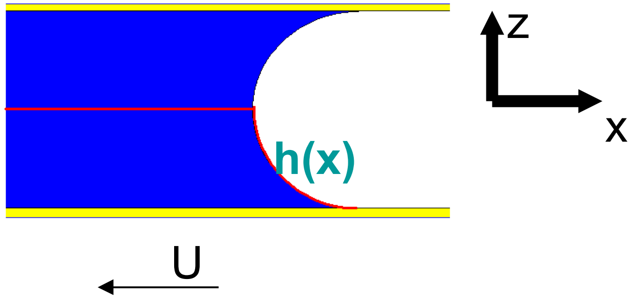
Continuum mechanical modelling



Velocity from lubrication approx.+ BCs

$$u_x(x,z) = U - \left[z^2 + 2h(x)z + 2h\lambda(x)\right]\partial_x p(x)/(2\eta)$$

Mass flux:

$$Q(t) = \int_0^h dz\, u_x = Uh - \partial_x p\left(\frac{h^3}{3} + \lambda h^2\right)/\eta$$

Steady state:

$$Q = (U_{1L}^{wrf} + U)h_{1L}$$

$$3\frac{\mathrm{Ca}(h - h_{1L}) - \mathrm{Ca}_{1L}^{wrf} h_{1L}}{h^3} = \frac{\partial_x p}{\gamma}\left(1 + \frac{3\lambda(x)}{h}\right)$$

$$\mathrm{Ca}_{1L}^{wrf} = \frac{U_{1L}^{wrf}\eta}{\gamma}$$

$$\text{Au/ML:}\mathrm{Ca}_{1L}^{wrf} = 0$$

$$\text{Au:}\mathrm{Ca}_{1L}^{wrf} \approx 0.227$$

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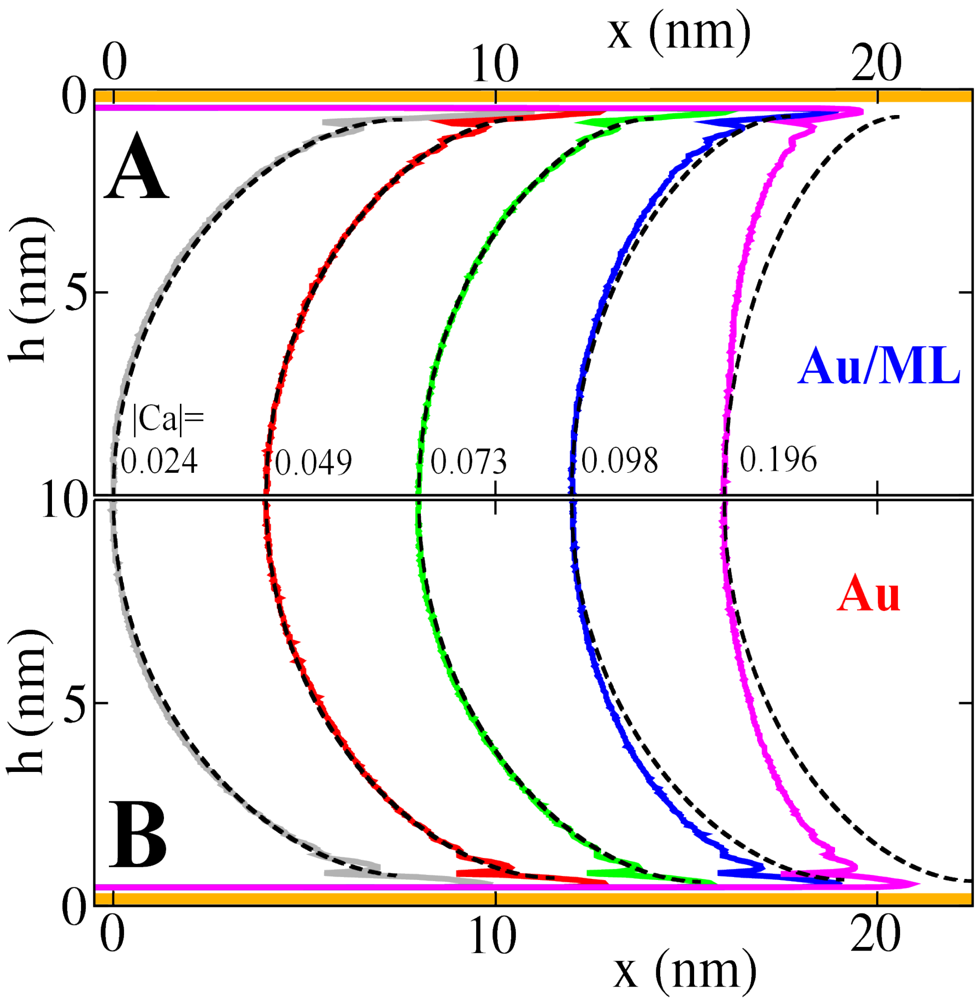

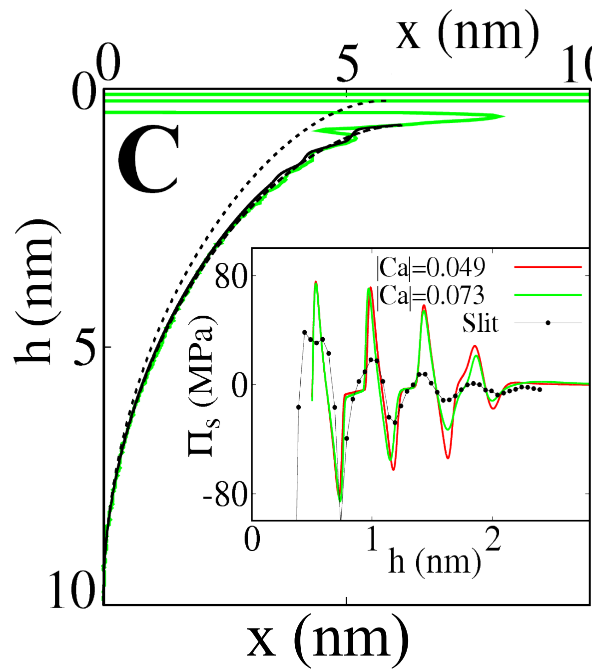

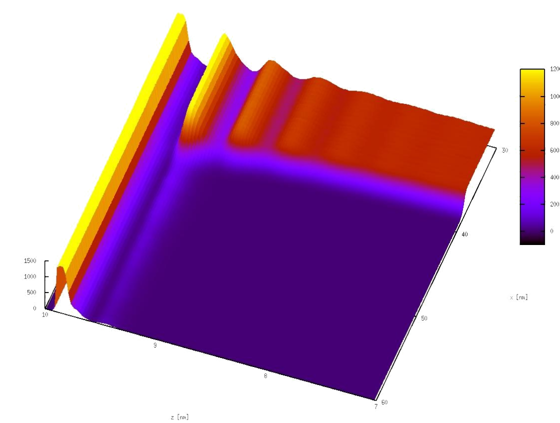

$$\Pi_s(x) = \gamma \left(\int_0^x 3 \frac{\mathsf{Ca}\,(h(\tilde{x}) - h_{1L})}{h^3(\tilde{x})} d\tilde{x} - \kappa \right)$$

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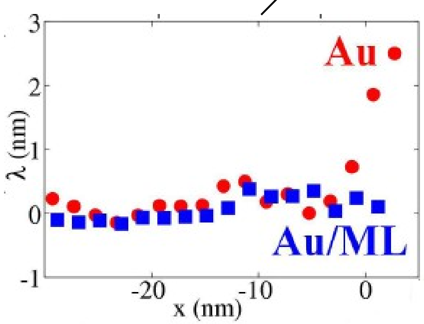
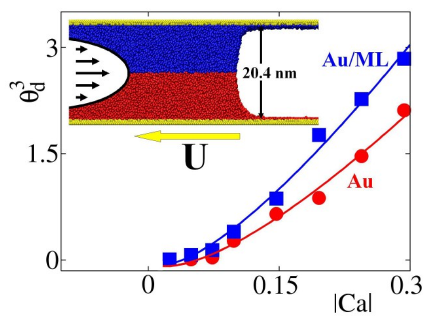
Extended Washburn equation

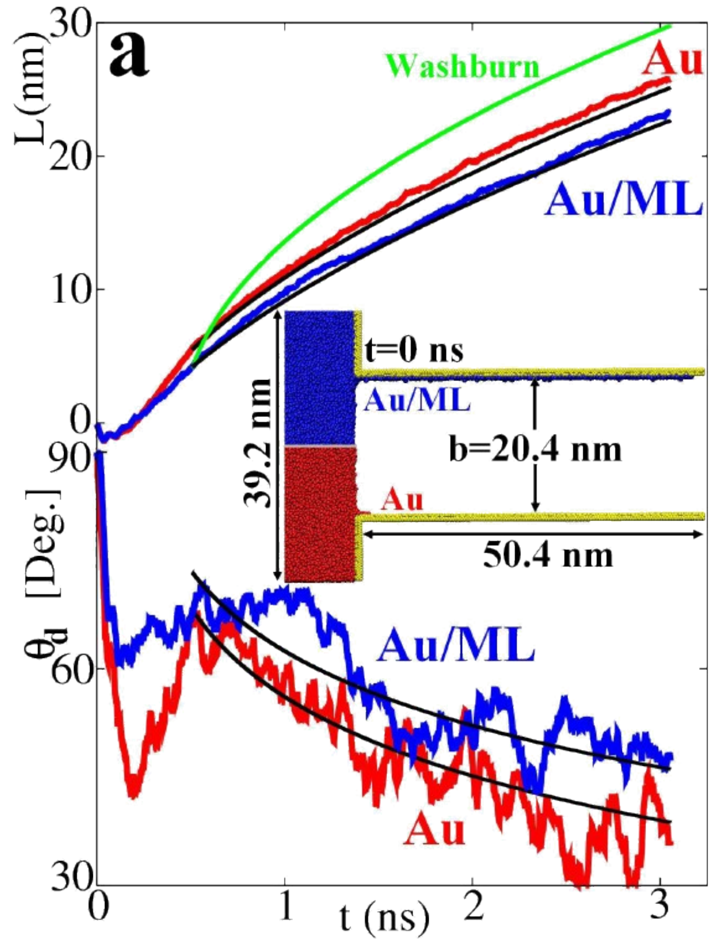
$$Q(t) = \int_0^h dz\, u_x = Uh - \partial_x p \left(\frac{h^3}{3} + \lambda h^2 \right) / \eta$$

$$Q(t) = \dot{L} b/2 \qquad p_c = -2\gamma \cos\theta_d / b$$

$$\dot{L}(t) \int_0^{L(t)} \frac{1}{1 + 6\lambda(x)/b} dx = \frac{\gamma}{6\eta} b \cos\left(\theta_d(\mathrm{Ca}(t))\right)$$







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