Nanotechnology

"I found my arms and legs were strongly fastened on each side to the ground"

- It's not just a miniature version of the macroscopic world
- Different physical principles result in the new properties of nanotechnology:
  - **Surface-to-volume ratio**
  - **Stochastic behavior**
  - Quantum effects

Fluctuations in Nanoscale Structures *

Ellen D. Williams

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University of Maryland, College Park

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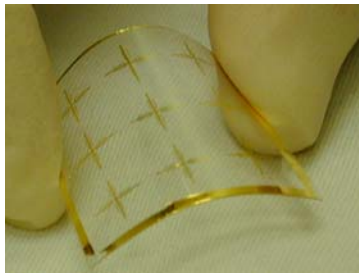
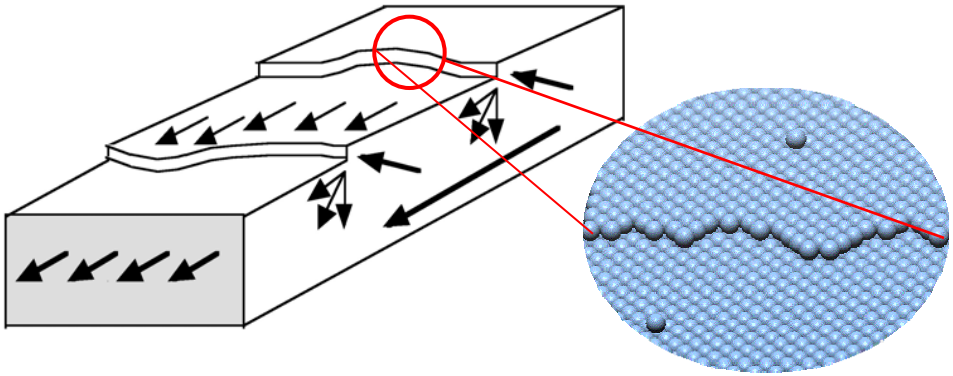
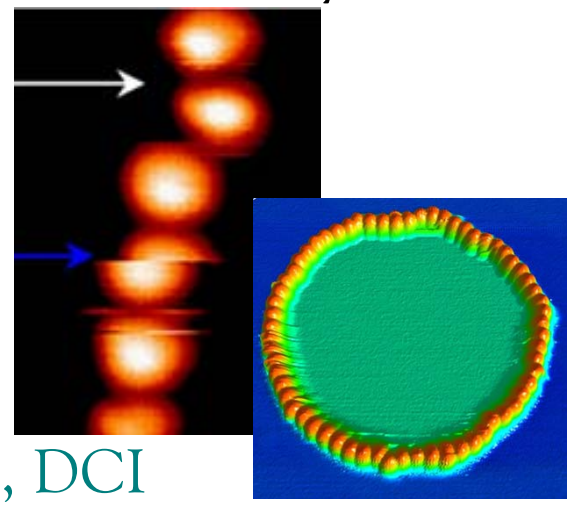


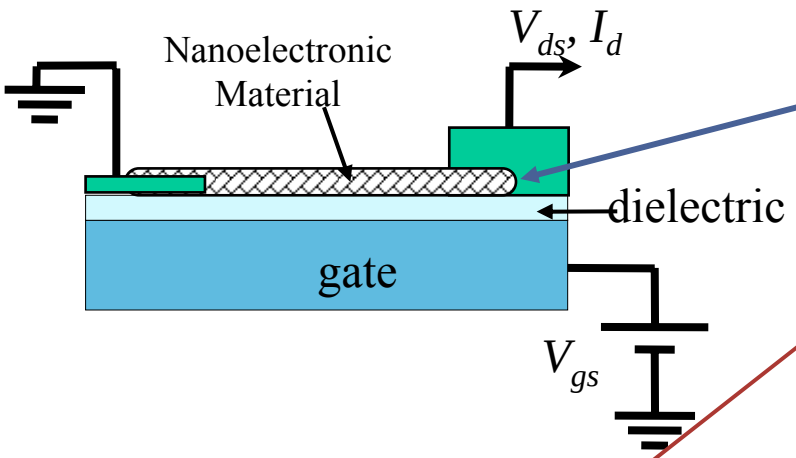




*support: NSF-MRSEC, LPS, DCI

Nano-electronics

Shrinking electronic components to molecular scale



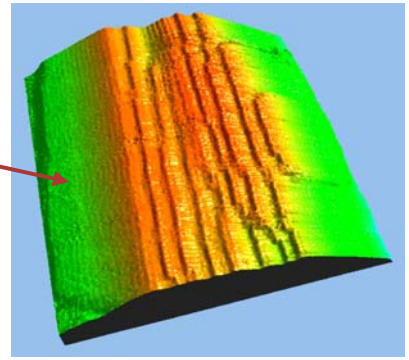
Surface/statistical issues:

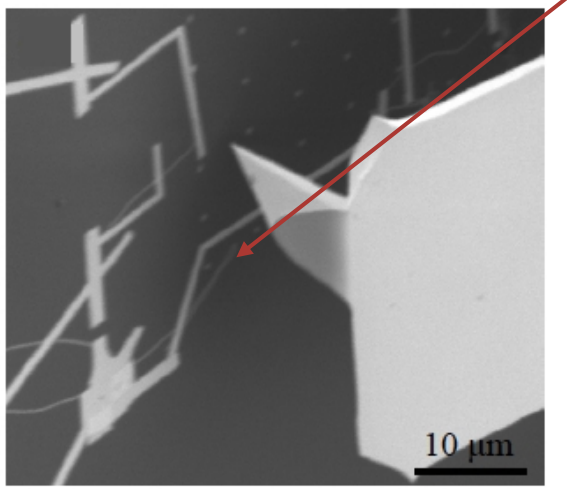
Interfacial contacts

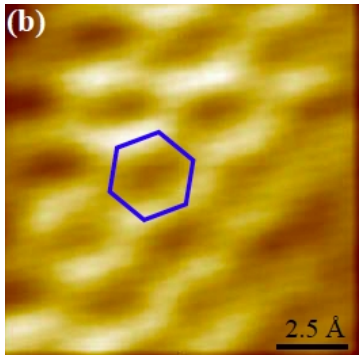
Transport in low-D

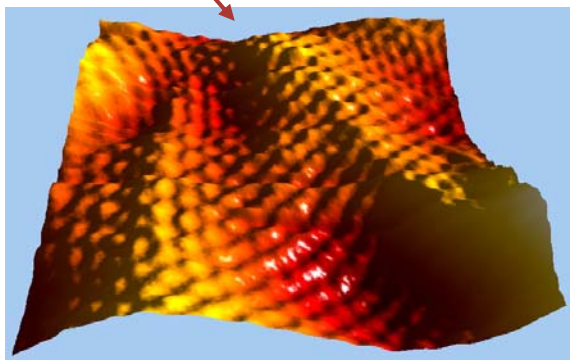
nanowires

thin sheets









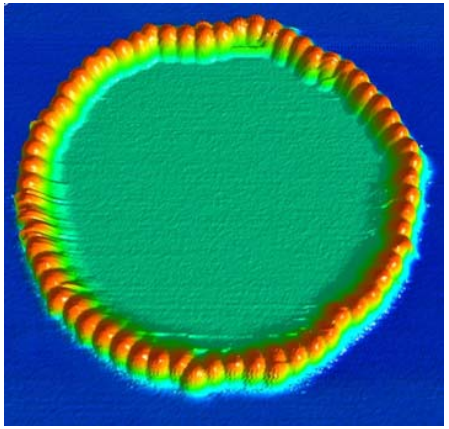
Carbon Nanotube

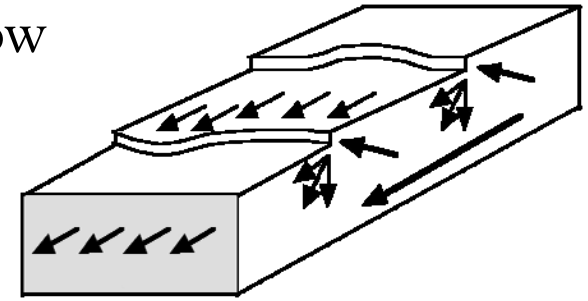
Graphene on SiO_2

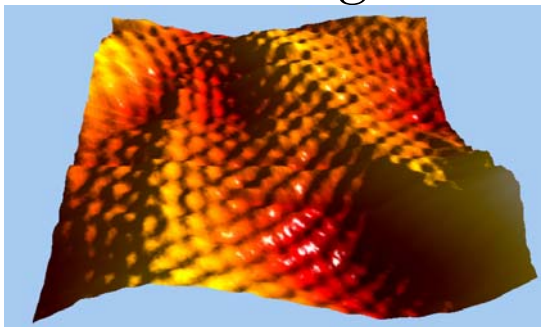
-- Fuhrer/Williams groups collaboration at Maryland, CNT and graphene by M. Ishigami

Outline

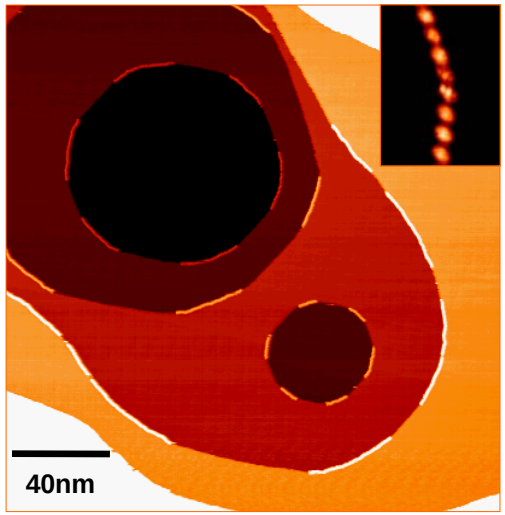
- Three parts…
  - Model metal-molecule interface
    - C60 rings
      - Modal fluctuations
      - Time constants and amplitudes
    - With respect to the metal support
  - Fluctuations and transport
    - Equal and opposite forces: electron scattering
    - Biased step fluctuations under current flow
    - Surface resistivity and transport noise
  - Roughness of a 2-D sheet

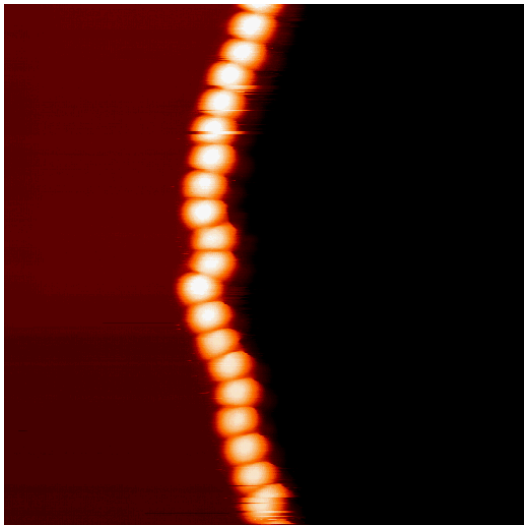






C_{60}/Ag(111)

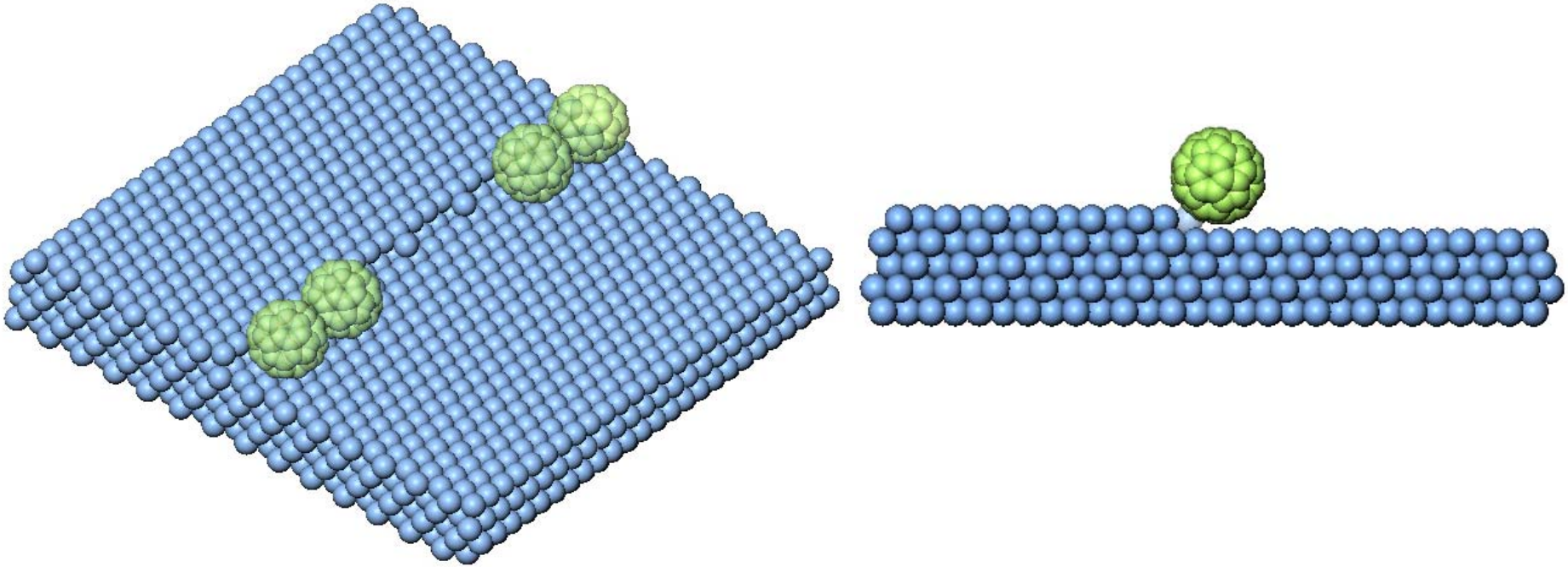




- 400 nm x 400 nm image of clean Ag film
- 200 nm x 200 nm image of partial coverage of C60/Ag/mica at room temperature
- High resolution image: C60 chain decorating a step

*-- C. Tao et al, PRB, **73**, 125436 (2006)*

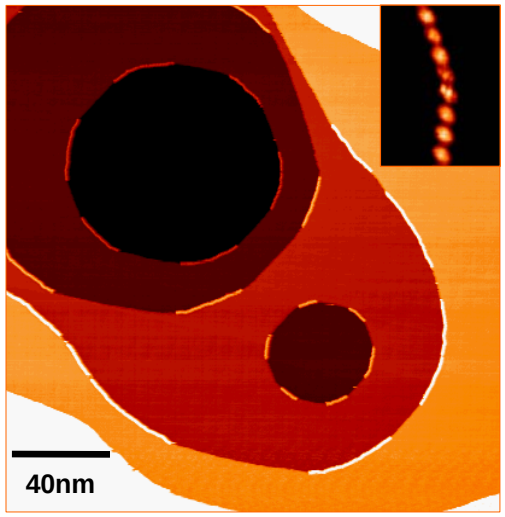
C_{60} and Step Motion

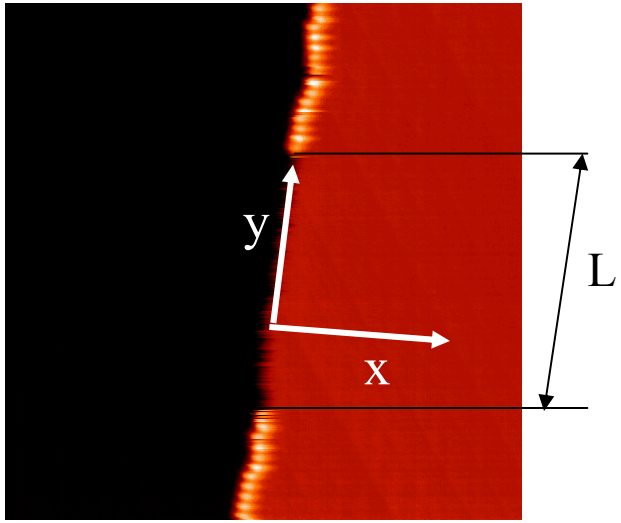


- Silver atomic motion at step edge is fast - time constant of a microsecond
- Individual C_{60} at step edge may be stationary for 100s of seconds
  - Strong charge transfer in C_{60} binding
- If C60 and Ag motion are correlated, C60 will act as pinning site for Ag step fluctuations

*-- C. Tao et al, PRB, **73**, 125436 (2006)*

C_{60}/Ag(111)





Choose different C60 separations and measure the effect on the Ag step edge variations x(t) in between the C60s.

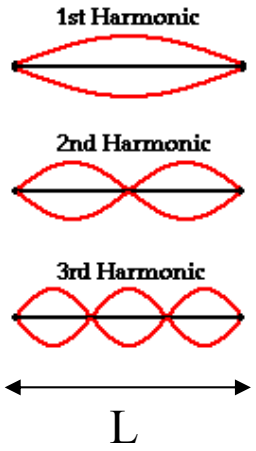
$$G(t) = \left\langle (x(t) - x(0))^2 \right\rangle = \left(\frac{2\Gamma(1-1/n)}{\pi} \right) \left(\frac{kT}{\tilde{\beta}} \right)^{\frac{n-1}{n}} \left(a^{n+1} \frac{t}{\tau} \right)^{1/n}$$

Clean Ag steps (no C60): n=4

Interesting measurement time effects: A. Bondarchuk et al, PRB 71 045426 2005

Fluctuation Modes

- Steps fluctuate like strings - with all wavelengths allowed by the boundary and/or observation conditions.
- The fluctuation correlations we observe are the combination of all the available wavelengths.



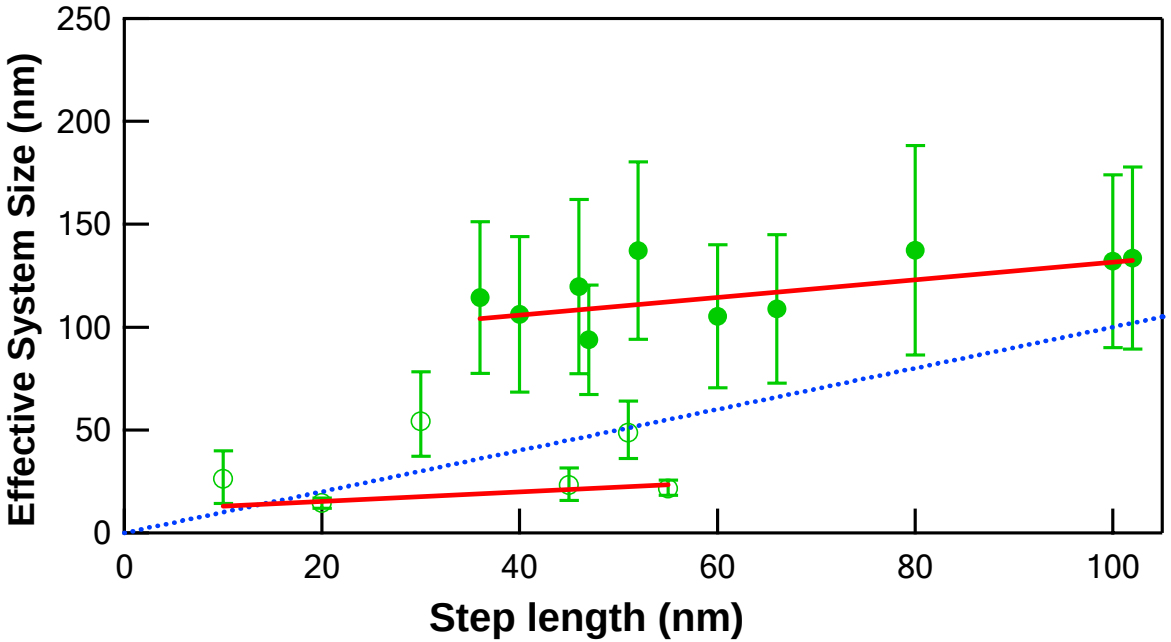
$$G(t) = \int_{q_{\min}}^{2\pi/a} G_q(t)\,dq \qquad q = 2\pi/\lambda$$

- The overall width of the fluctuations is determined by the the system size L ~ λ_{max}:

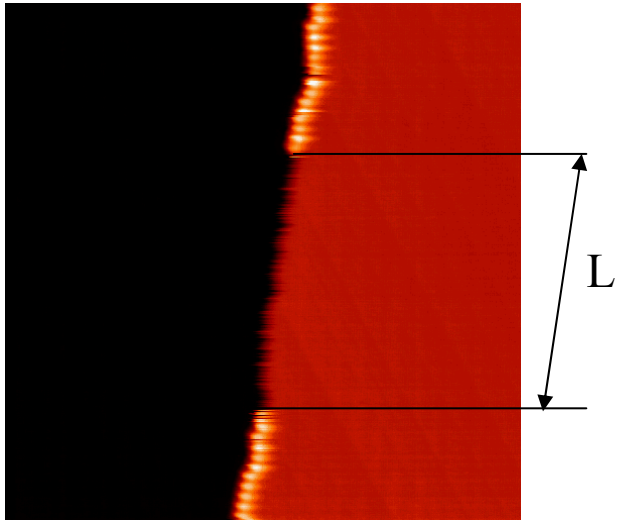
$$w_{eq}^2 = \left\langle \left(x(t) - \bar{x}\right)^2 \right\rangle = \frac{kTL}{12\tilde{\beta}}$$

-- Jeong&Williams, SSR 34 175 1999

Effective system sizes

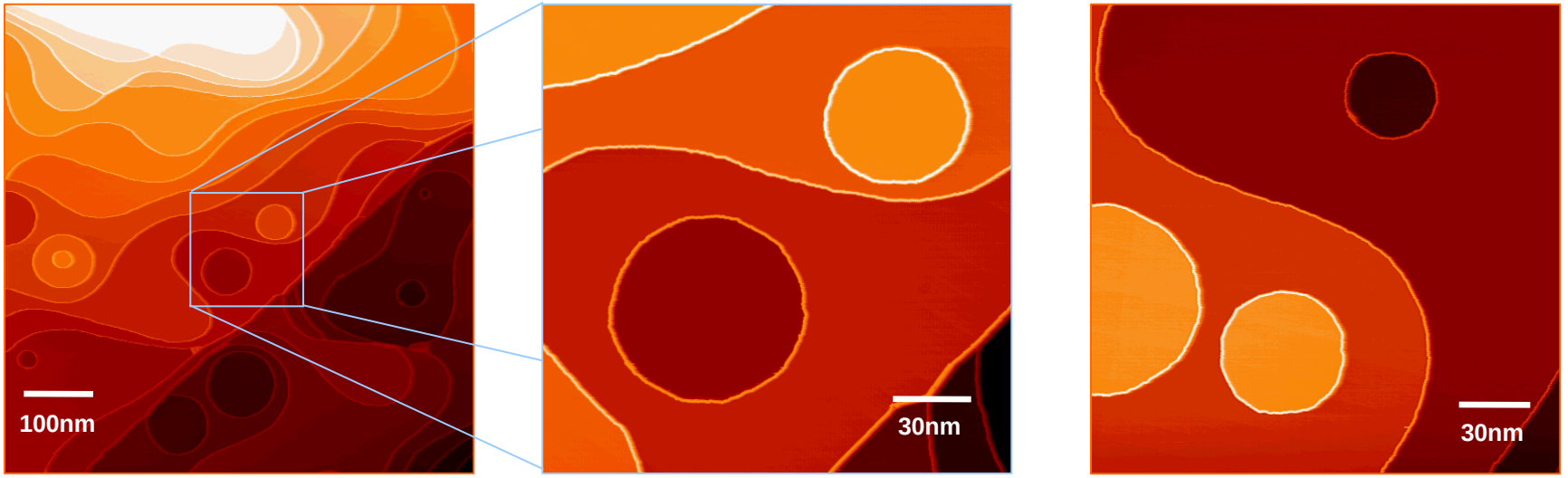


- Two step orientations
  - Different β values
- No significant dependence on C60 separation for either!
- Effective system sizes are the same as for steps on clean Ag



*-- C. Tao et al, PRB, **73**, 125436 (2006)*

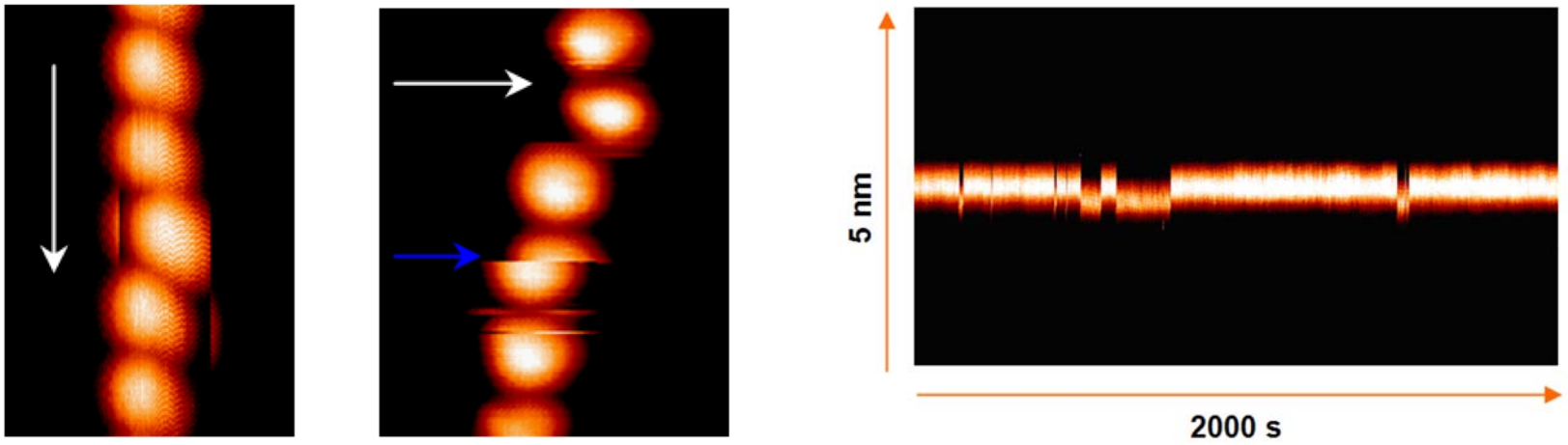
Circular Ag islands decorated by C_{60} rings



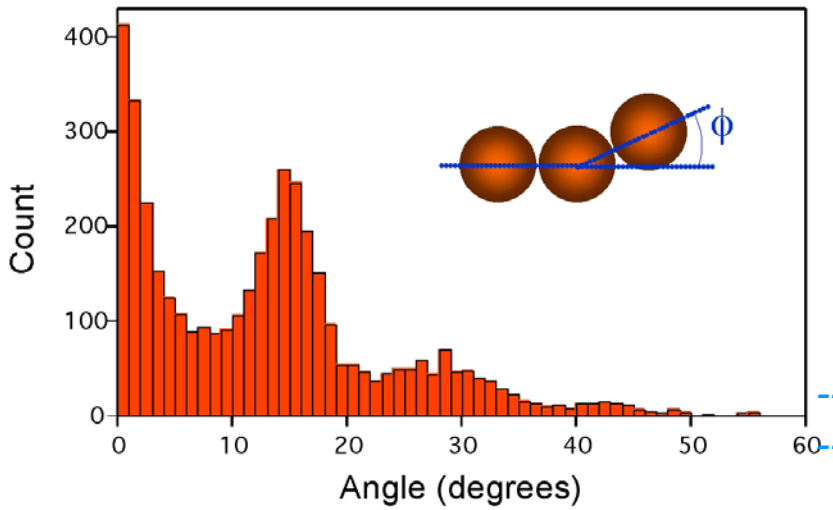
By carefully increasing the C_{60} coverage, we create circular C60 structures

-- C. Tao et al, Nano Letters (2007)

C_{60} Motion with chain

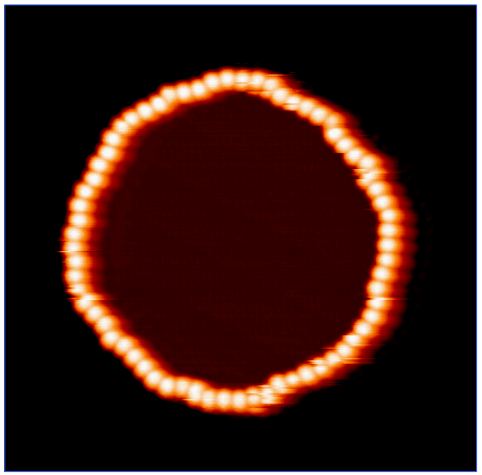


Local motion of C_{60} molecules is evident. Bimodal hops correlate with a C60 "kink" displacement between two favorable underlying Ag sites.

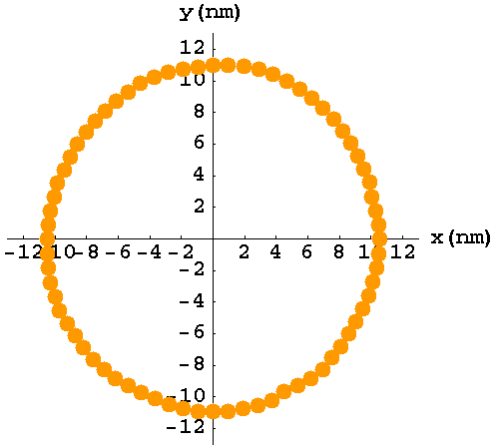


-- C. Tao et al, Nano Letters (2007)
-- T. Stasevich et al., in prep (2007)

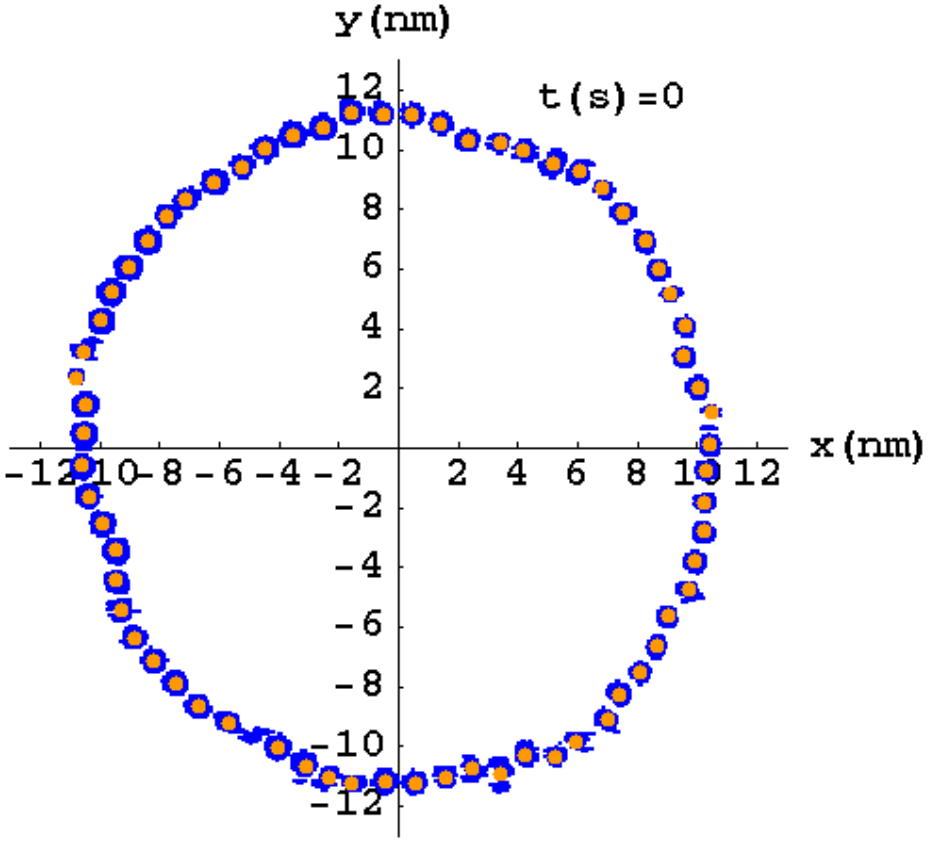
Shape fluctuations



STM image of a Ag island surrounded by a C_{60} ring (line time 0.1 s, 512 lines)



Averaged C_{60} ring shape



Digitized C_{60} rings

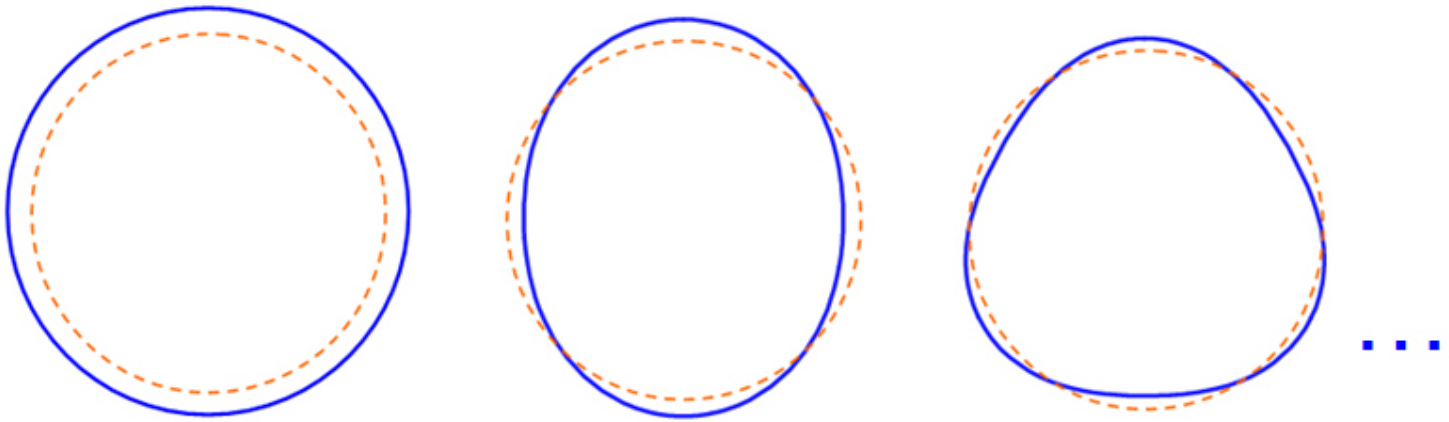
Time per image = 52.4 s

Total time = 3458 s

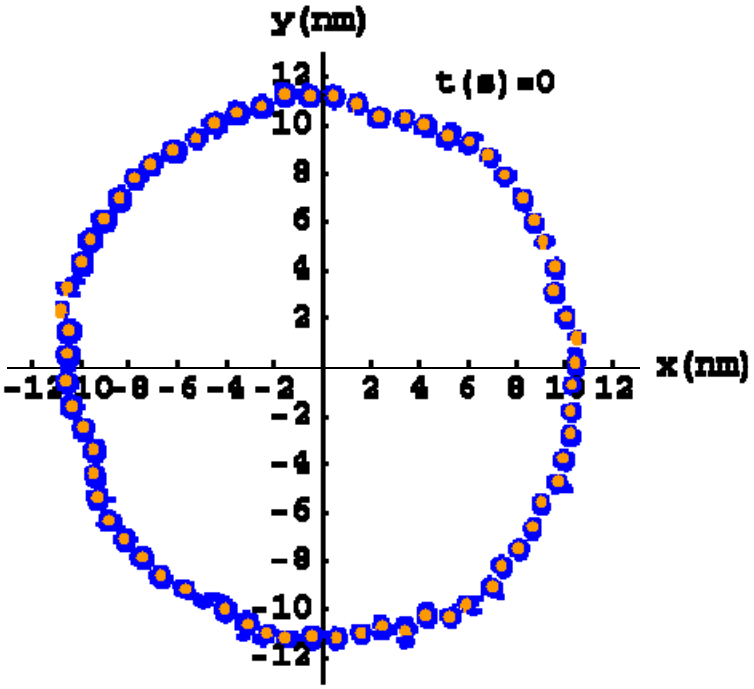
Fluctuation Modes of a Ring

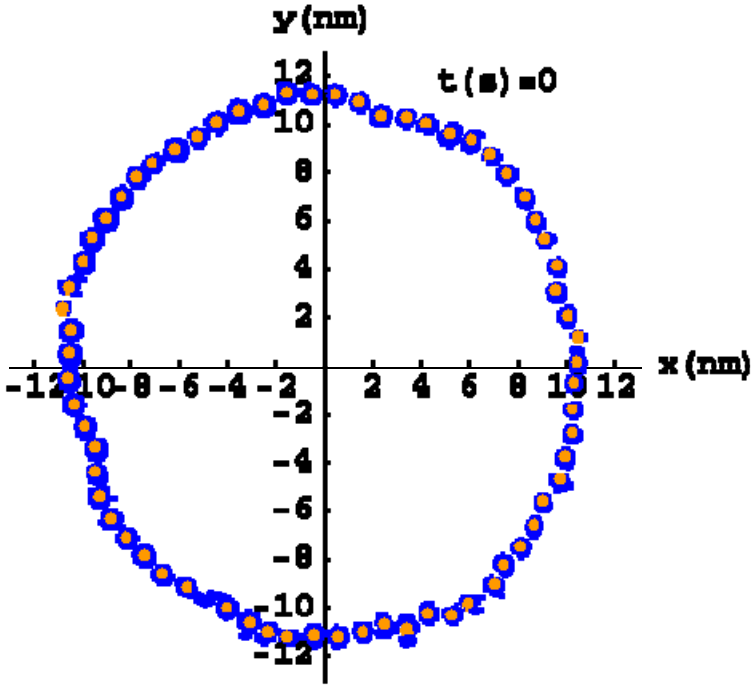
- Analogy to fluctuations of an island bounded by a step
- Define modes of fluctuation

$$r_k(t) = \int_{-\pi}^{\pi} r(\theta,t)\exp(ik\theta)d\theta \qquad k \in I$$



Same movie again…





Digitized C_{60} rings

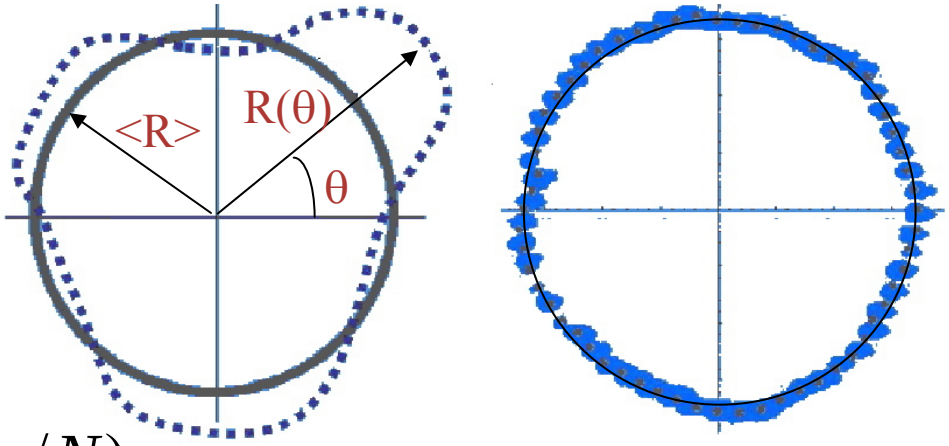
Time per image = 52.4 s,

Total time = 3458 s

Analysis of Island Fluctuations*

Measure radial displacements:

$$g(\theta,t) = R(\theta,t) - \langle R \rangle$$



Angular Fourier transform:

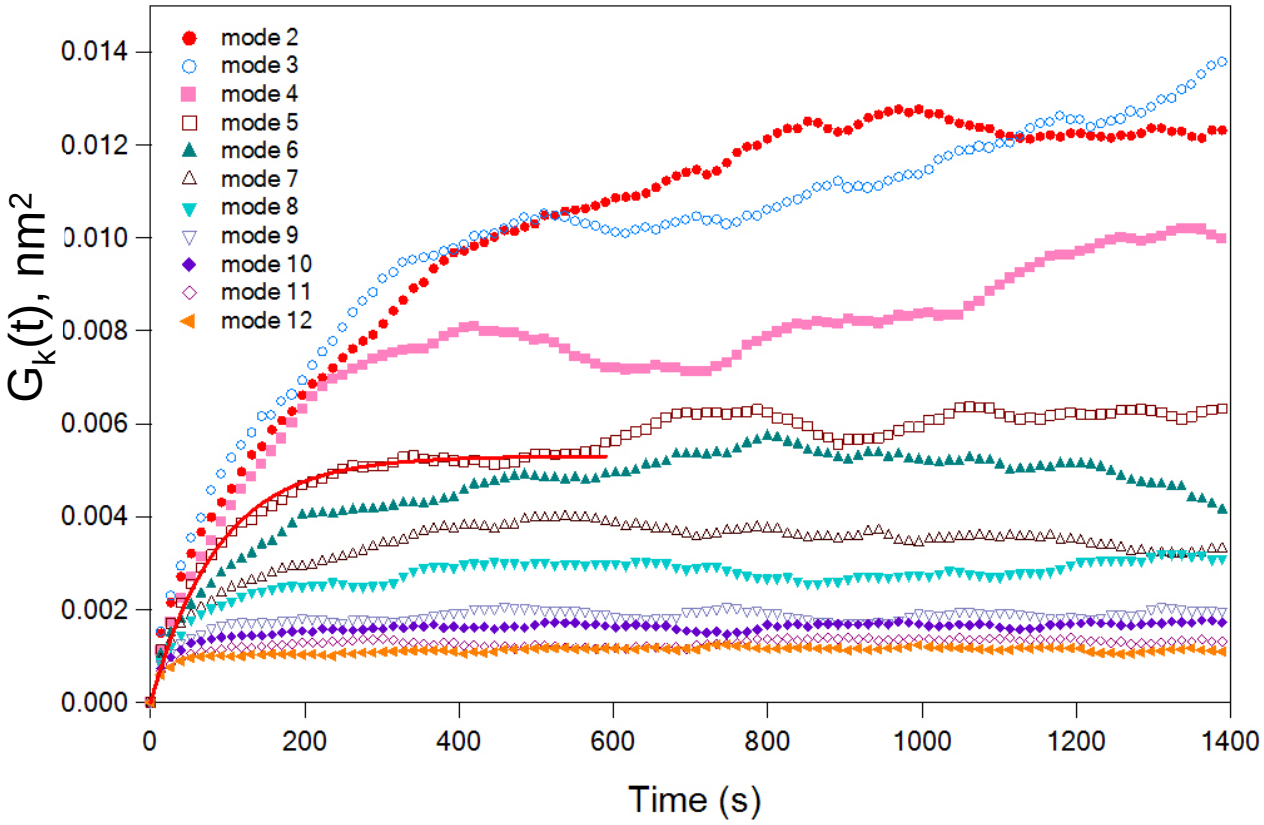
$$g_k = \frac{1}{2N} \sum_{n=N-1}^{N} g(n\pi/N)\exp(kn\pi/N)$$

Modal time-correlation function:

$$\left\langle \left| g_k(t+t_0) - g_k(t_o) \right|^2 \right\rangle = \frac{kTR}{2\pi\tilde{\beta}k^2}\left(1 - e^{-2t/\tau_k}\right)$$

*Khare & Einstein PRB 54, 11752 1996

Modal Time Correlation Functions



k=2

k=5

$$A_k = \frac{kTR}{2\pi\tilde{\beta}k^2}$$

Fitting individual curves yields A_k and τ_k

$$\tau_k = \frac{kT}{\Gamma_z\tilde{\beta}}\left(\frac{R}{k}\right)^z$$

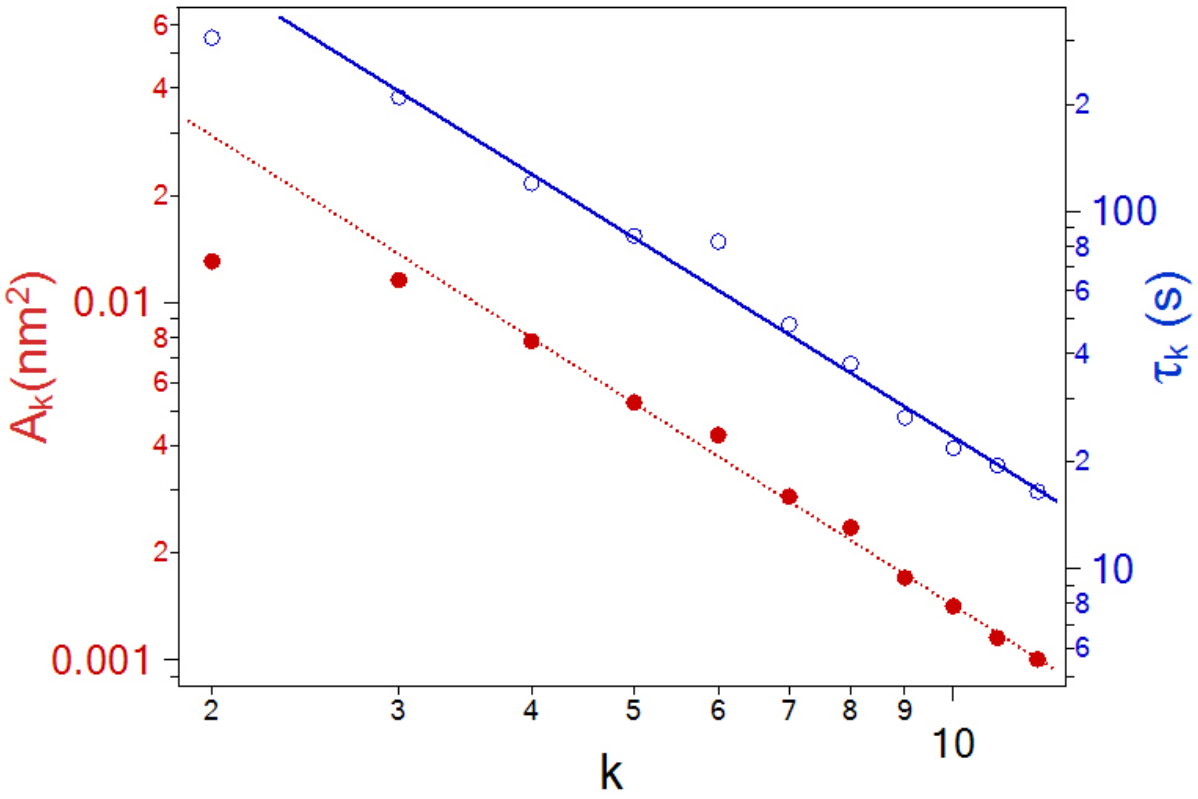
$$\left\langle \left| g_k(t+t_0) - g_k(t_o) \right|^2 \right\rangle = G_k(t) = A_k\left(1 - e^{-2t/\tau_k}\right)$$

z = 4, conserved noise

z = 2, non-conserved noise

-- C. Tao et al, Nano Letters (2007)

C_{60} Ring Modes



C60, R = 12.4 nm

Mode 4:

$(A_4)^{1/2} = 0.08$ nm

$\tau_4 = 120$ s

Mode 12:

$(A_{12})^{1/2} = 0.03$ nm

$\tau_{12} = 12$ s

- $A_k = (0.009\text{nm})(R/k^{\alpha})$, with $\alpha = 1.88$
- $\tau_k = (11.5\text{nm}^{-2}\text{s})(R/k)^z$, with $z = 1.85$
  - $z = 2$! Non-conserved Noise - not the same as clean Ag ($z = 4$)

-- C. Tao et al, Nano Letters (2007)

C_{60} and Ag island edge

C60, R = 12.4 nm

Mode 4:

$(A_4)^{1/2} = 0.08$ nm

$\tau_4 = 120$ s

Mode 12:

$(A_{12})^{1/2} = 0.03$ nm

$\tau_{12} = 12$ s

Clean Ag, R = 12.4 nm

Mode 4:

$(A_4)^{1/2} = 0.009$ nm

$\tau_4 = 0.8$ s

Mode 12:

$(A_{12})^{1/2} = 0.001$ nm

$\tau_{12} = 0.016$ s

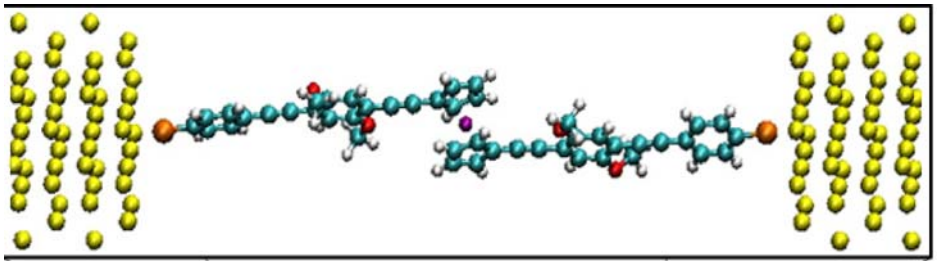
*-- C. Tao et al, PRB, **73**, 125436 (2006)*

_ A. Bondarchuk et al, PRB 71 045426 2005

Impact of Structure Fluctuations

Metal-molecule interface

- Transmission probability across a molecular bridge similar to tunneling - exponential dependence on width of gap + strong dependence on specific metal configuration at contact point



- Motion of individual metal atoms can be fast - >10^6Hz (example Ag)
- Mode fluctuations will be much slower, and large enough in amplitude (0.01 nm) to significantly affect transmission probability
- Conserved and non-conserved noise modes will contribute distinct frequency characteristics:

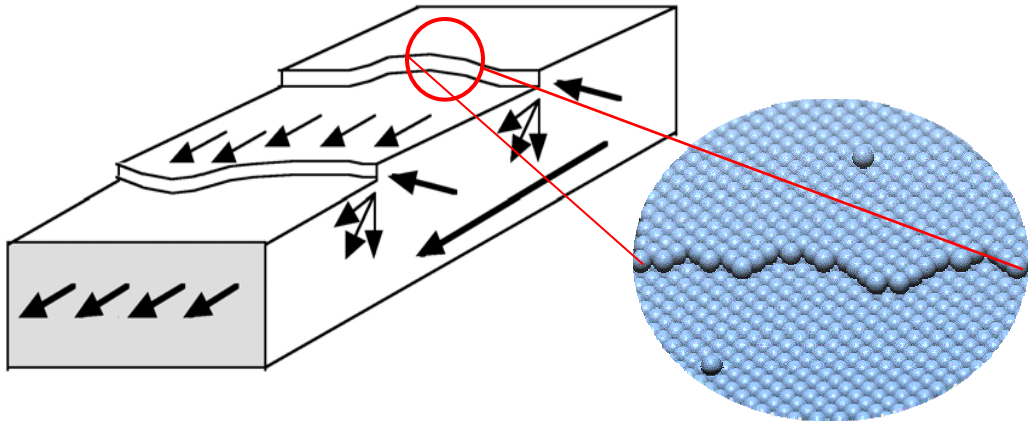
$$A_k(f_k = 1/\tau_k) = \frac{0.10 nm^3}{R} f_k^{-1/2}$$

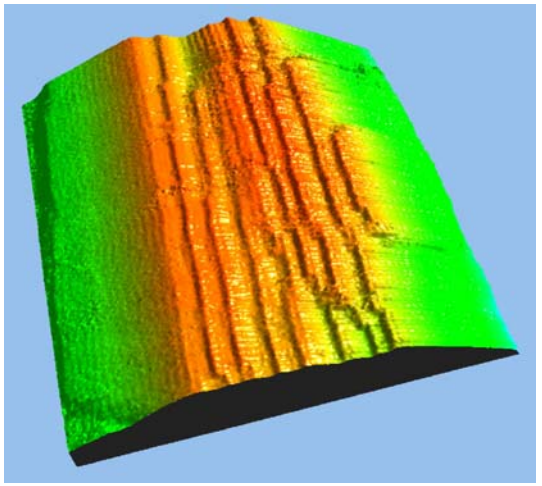
  - silver (conserved)

$$A_k(f_k = 1/\tau_k) = \frac{8x10^{-4} nm^3}{R} f_k^{-1}$$

  - C60 (non-conserved)

Line Boundaries and Electrical Transport





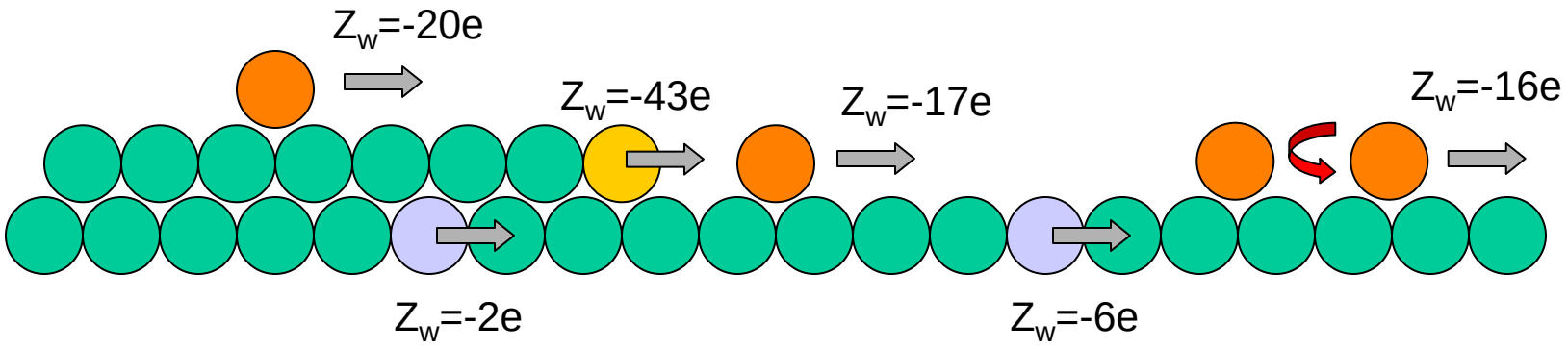
-- 20 nm Ag nanowire
Synthesis - Murphy group USC
STM - Williams group UMD

Fluctuating surface steps affect and are affected by internal scattering of charge carriers from surface/interface

- The effects of interfaces with fluctuations in structure are important when the surface/volume ratio is large or when interfaces are the primarily source of carrier scattering or trapping

Electron-scattering Force

Z_w = -19 for Ag



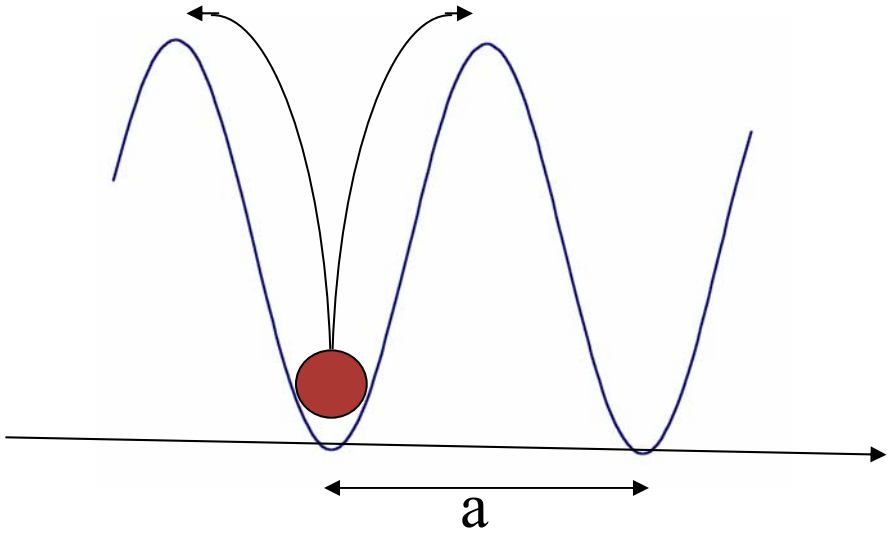
P.J. Rous, "Electromigration force at stepped Al Surfaces," Physical Review B59, 7719, 1999.

- Force on diffusing atom: $F=ez^*E$; E = electric field
- Wind force: $z^*=n_o L\sigma_{tr}$
  - n_o = electron density, ~ 0.1 Å^{-3} (58.5 nm^{-3} for Ag)
  - L = mean free path, ~ 100 Å (~60 nm for Ag)
  - σ_{tr} = transport cross section at E_f; ~ 1 Å^2 (~ha~0.07nm^2 for a step edge)

P.J. Rous et al., Surface Sci. 315, L995, 1994; P.J. Rous, Phys. Rev. B61, 8475 2000

Weak Force…

- For metals (e.g. Ag), resistivity is low
- Fa ~10^{-7}eV/unit cell
- Linear perturbation of Langevin equation for step motion



$$\left(\frac{\partial}{\partial t} - \frac{\Gamma_4 \tilde{\beta}}{k_B T}\frac{\partial^4}{\partial x^4} - \frac{\Gamma_4 F}{k_B T a \parallel a}\frac{\partial^2}{\partial x^2}\right) y(x,t) = \eta(x,t)$$

Measure Effects on step fluctuations, x(t). For Ag, the step fluctuations occur via atomic diffusion along the step edge

- Expect modified fluctuation correlations:

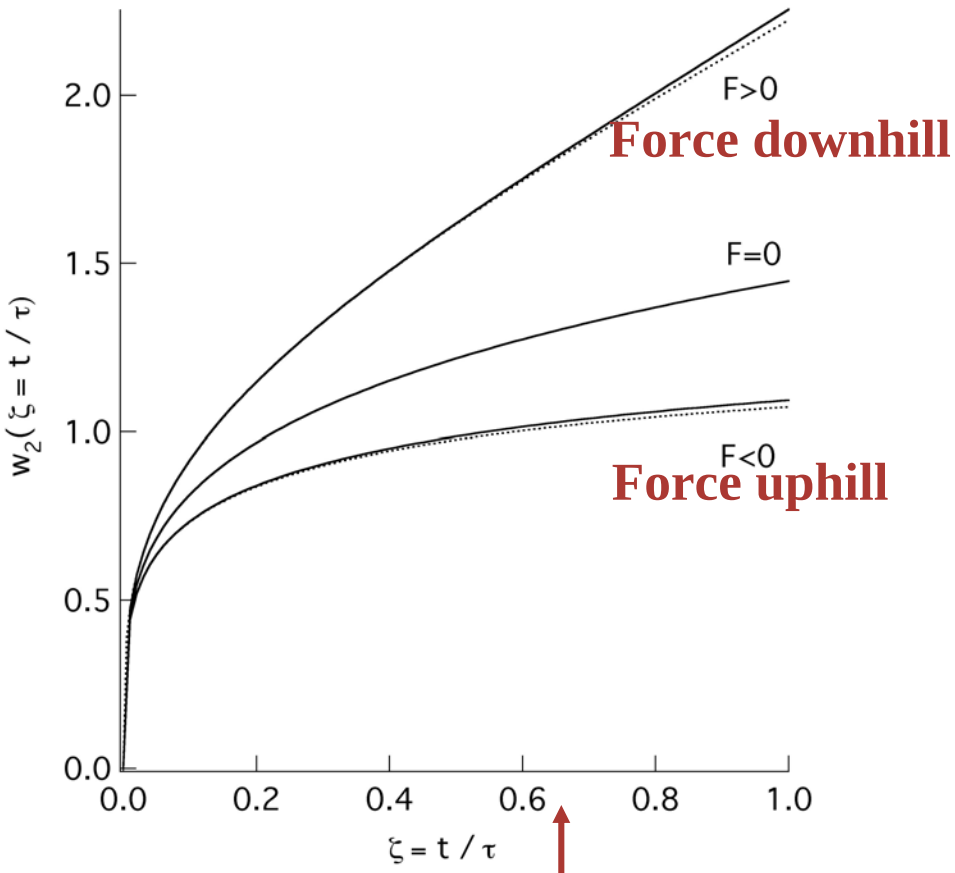
P.Rous et al., in preparation for NJP (2007)

Correlation function with EM - Theory

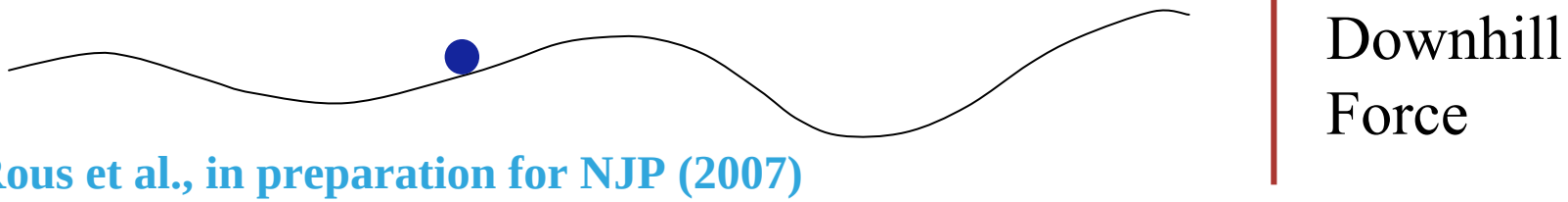
$$G_{eq}(t) = \left(\frac{2\Gamma(3/4)}{\pi}\right)\left(\frac{kT}{\tilde{\beta}}\right)^{3/4}(\Gamma_h t)^{1/4}$$

$$\tau_{EM} = \frac{kT\tilde{\beta}}{(Fa)^2}\tau_h$$

$$G_{EM}(t) \approx G_{eq}(t)\left[1 \pm \left(\frac{t}{\tau_{EM}}\right)^{1/2}\right]^{-1}$$



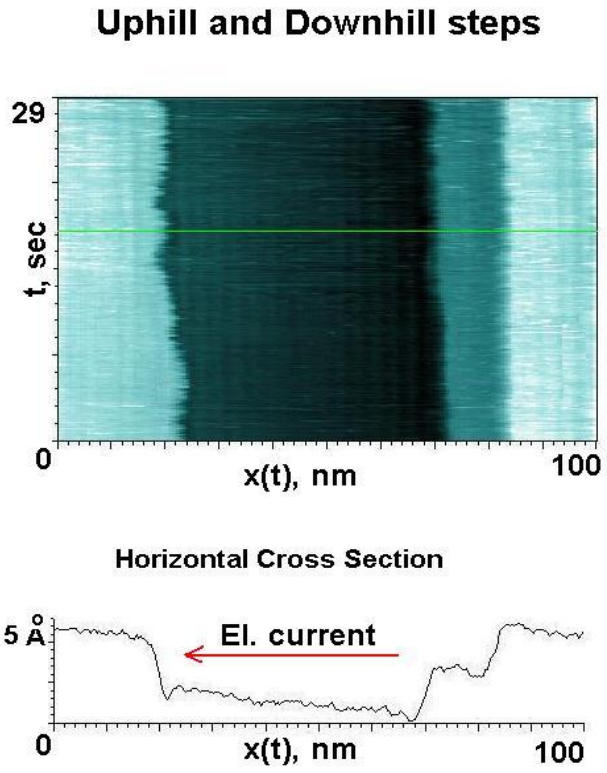
Wind force causes deviations in time correlation of step wandering

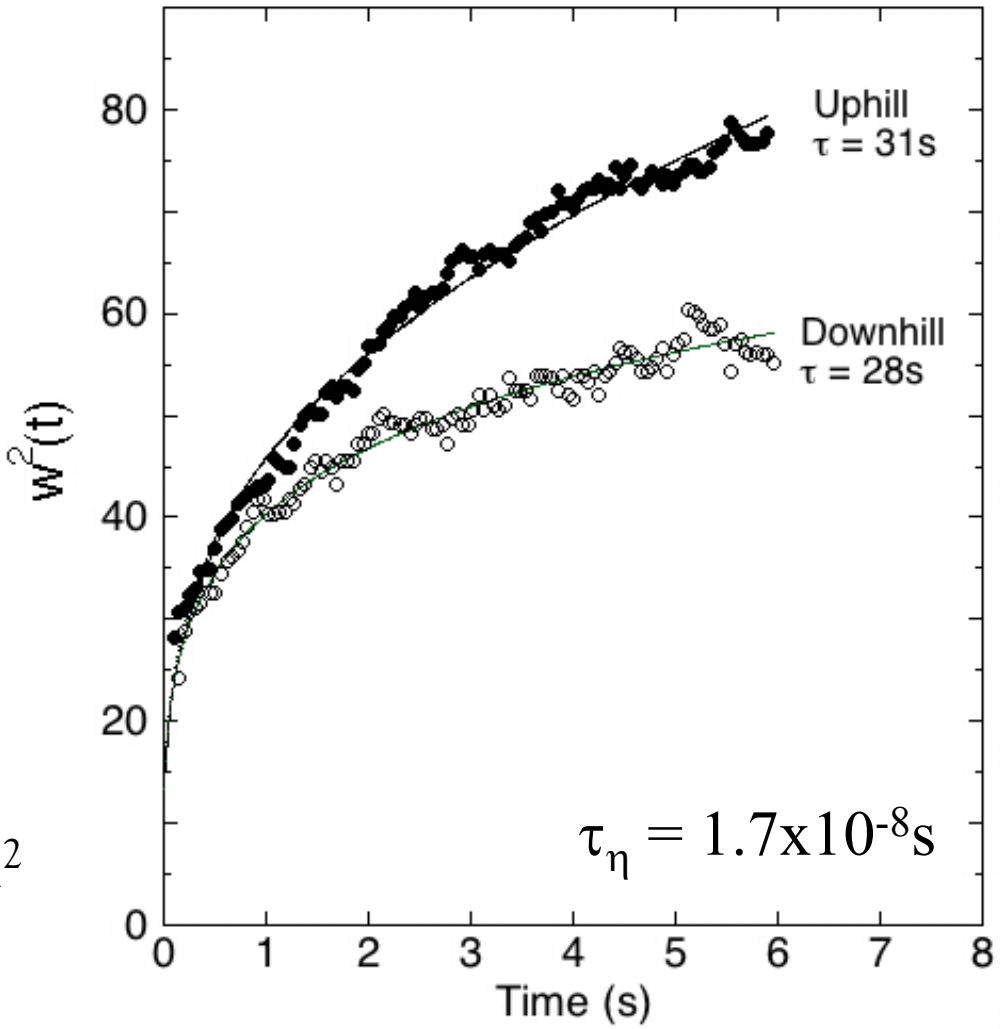


Downhill Force

P.Rous et al., in preparation for NJP (2007)

Ag Thin Film with Bias Current





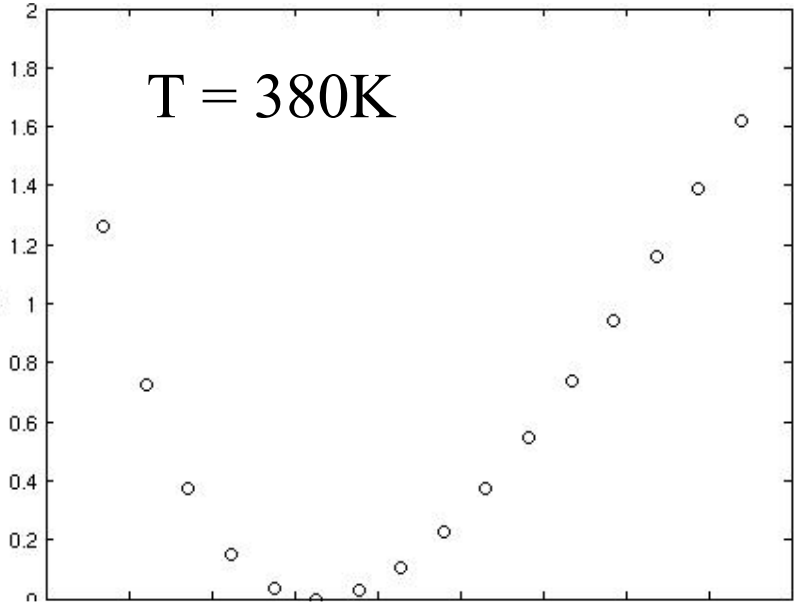
- Current biasing to $>10^5$ A/cm^2
- Fit value is τ_{EM} = 50s

A. Bondarchuk et al., submitted 2007
http://arxiv.org/abs/0704.1852

Comparison with Control

Evaluation of relative chi-squared for fit as a function of the fit parameter τ_{em}.

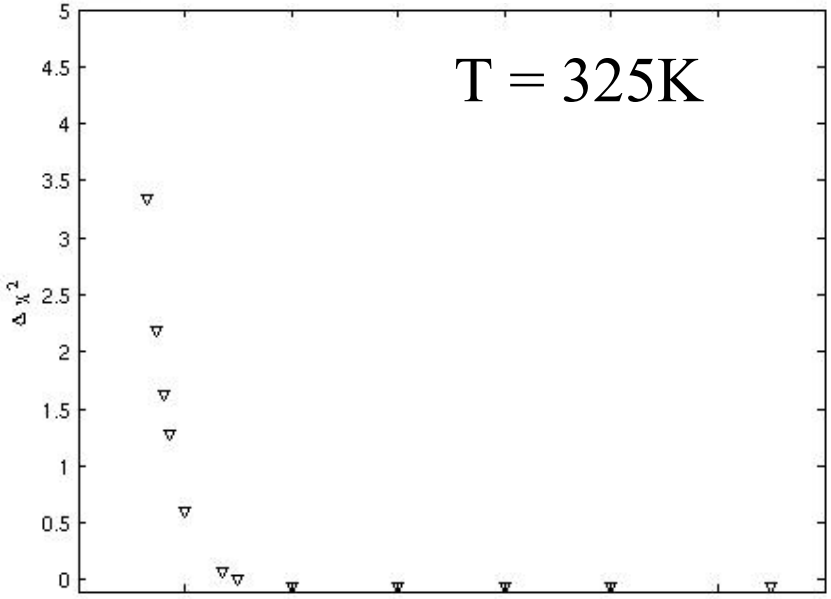
Biased sample (j = 4×10^5 A/cm^2)



35s 80s

electromigration time const., τ_{em}

Unbiased sample (j = 0)



10^2s 10^{16}s

electromigration time const., τ_{em}

Analysis

$$F_w^2 = \frac{kT\tilde{\beta}\tau_h}{a\tau_{em}}$$

Calculate step stiffness† using kink energy 0.117 eV*

$F = -2.7 \times 10^{-5}\ eV/nm$ for $J_{nom} = 4 \times 10^5 A/cm^2$

$F = -9.6 \times 10^{-6}\ eV/nm$ for $J_{nom} = 1 \times 10^5 A/cm^2$

$$F_w = z^* eE = z^* e\rho j$$

$\rho = 1.8 \times 10^{-6}\ \Omega - cm$, $T = 325K$

$\rho = 2.2 \times 10^{-6}\ \Omega - cm$, $T = 370K$

$$100e < |z^*| < 300e$$

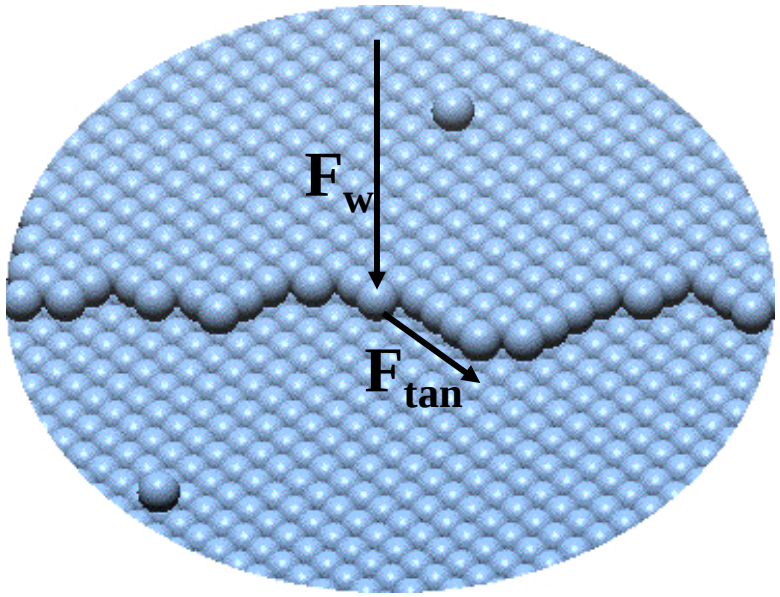
Forces and effective valence substantially larger than calculated value for isolated Ag adatom on a Ag terrace (z* = -19)

† Akustsu&Akustsu J. Phys. Cond. C 11 6635 1999

*T. Stasevich et al., PRB 71 245414 (2005)

† $\left(\frac{\tilde{\beta}a_\perp^2}{kTa_\parallel}\right) = \left(\frac{2}{3}\right)\exp\left(\frac{\varepsilon}{kT}\right)$

Electron scattering at steps/kinks



- Geometric blocking of current flow at steps increases scattering ~x2*
  - Kink sites may enhance geometric blocking
- Only tangential component of force affects step-edge motion
- Kink sites have enhanced charge density†
- Kink sites modify activation barrier for step-edge diffusion‡

*P.J. Rous et al., PRB , 7719, 1999
† T.S. Rahman, SS 600 4501 2006
‡ M. Giesen SS 601 140 2007

Surface Resistivity

- Conservation of momentum requires opposing effect on charge carriers, modifying transport characteristics:

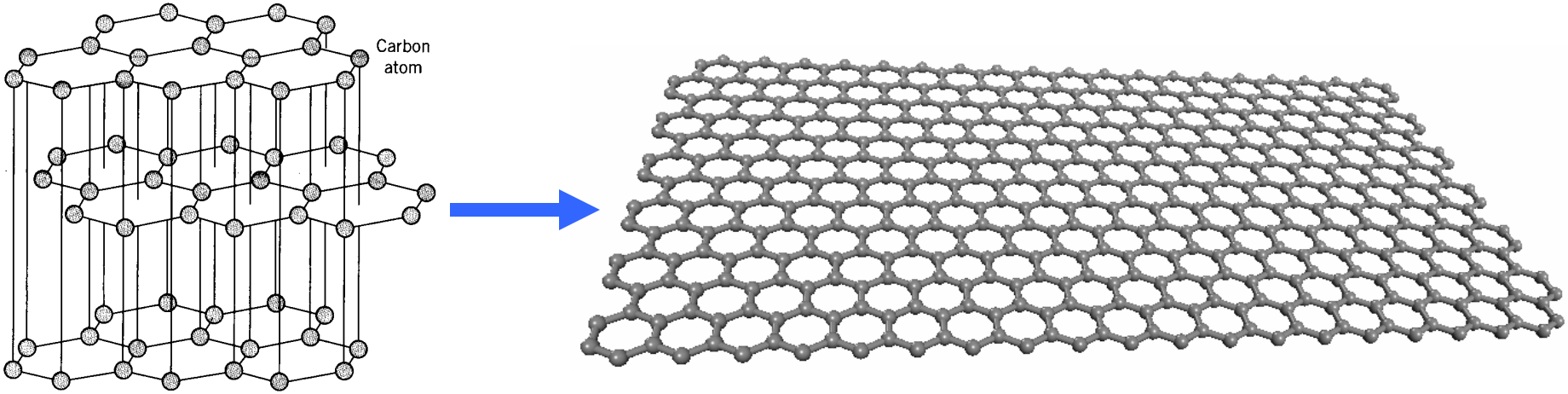
$$\ell_f \frac{\partial \rho_s}{\partial n_k} \leq \frac{-F_w}{e\eta j} = \left(3 \pm 1.5 nm^3\right)\rho_o$$

$\ell_f = film \quad thickness$

$n_k = kink \quad density$

  - For 20 nm scale structures with 1 nm step spacing, $\Delta\rho_s \sim 0.3\rho$
    - Structural fluctuations will affect surface resistivity, creating frequency signature in transport

Atomically thin-sheet: Graphene



Novel electronic properties:

understanding of fundamental mechanisms in flux

trapped charges and morphology both important

Preparation:

Mechanical exfoliation onto SiO2 (Geim, Kim)

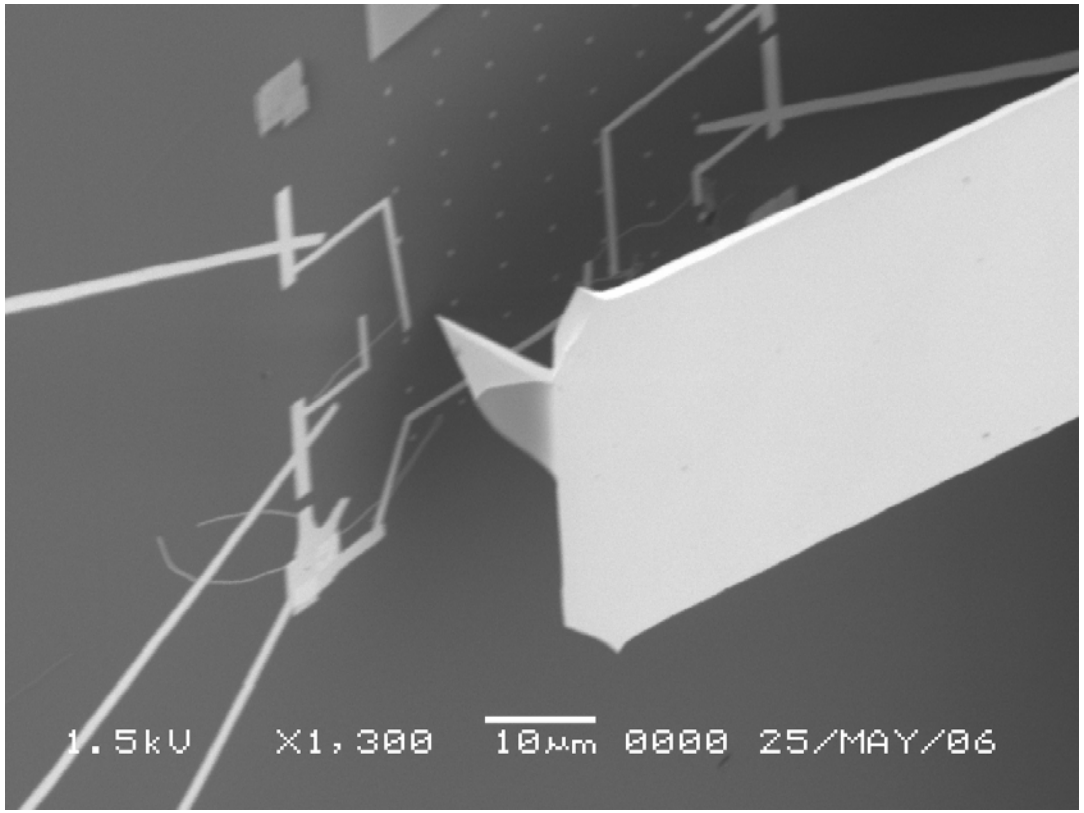
Surface segregation on SiC (de Heer)

Device fabrication:

Lithographic fabrication of electrodes onto graphene

Experimental Issues

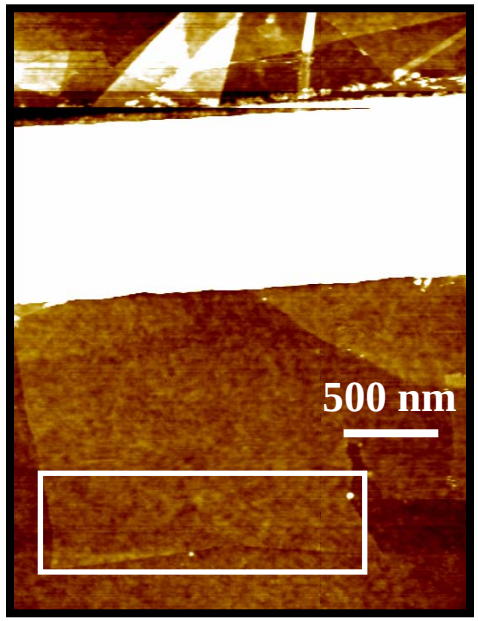
- How to "find" the device
  - Why the device need to "be found"
  - Conducting substrate usually needed
  - Combing SEM, AFM and STM, we can land tip on 1 nm^2 area



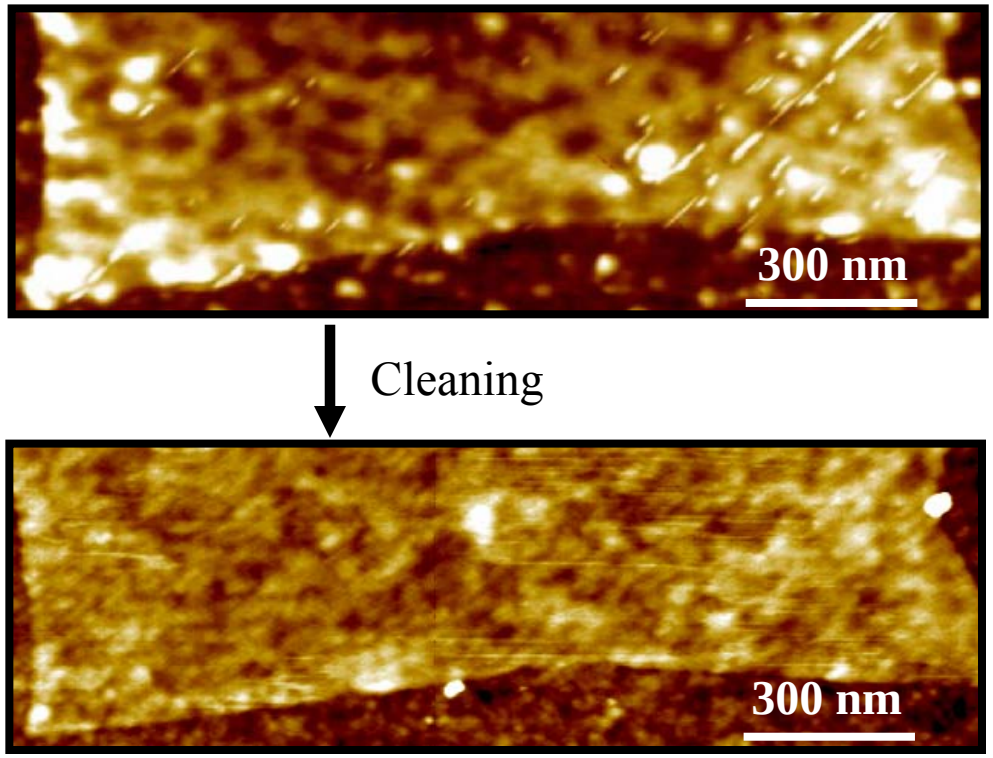
M. Ishigami, J.H. Chen, W.G. Cullen, E.D. Williams, and M.S. Fuhrer, Nanoletters, submitted (2007

Experimental Issues

- How to clean graphene
  - PMMA residue remains on carbon part of the device after lift-off
  - Commercial resist remover doesn't work
  - Special cleaning procedure* can remove PMMA residue
  - STM image show atomically clean graphene device

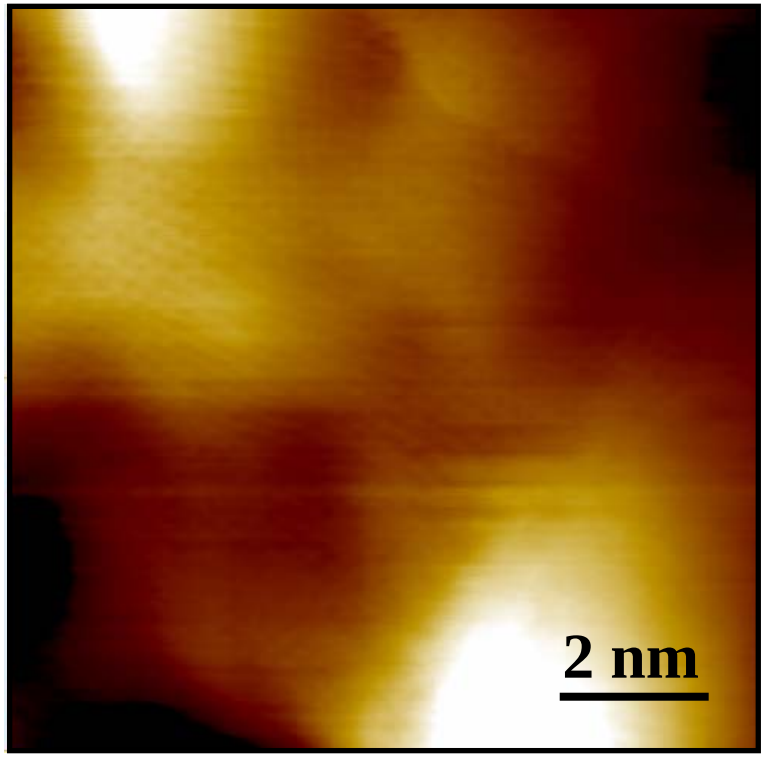


Non-contact AFM image in UHV

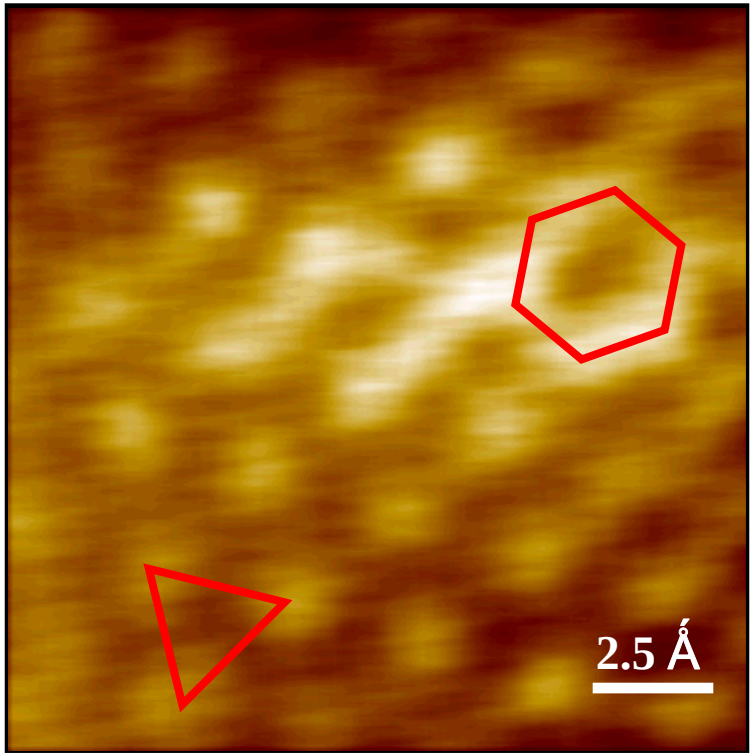


M. Ishigami, J.H. Chen, W.G. Cullen, E.D. Williams, and M.S. Fuhrer, Nanoletters, submitted (2007

STM images of a graphene device



[V_{sample} = 1.1 V and I_{tunnel} = 0.3 nA]



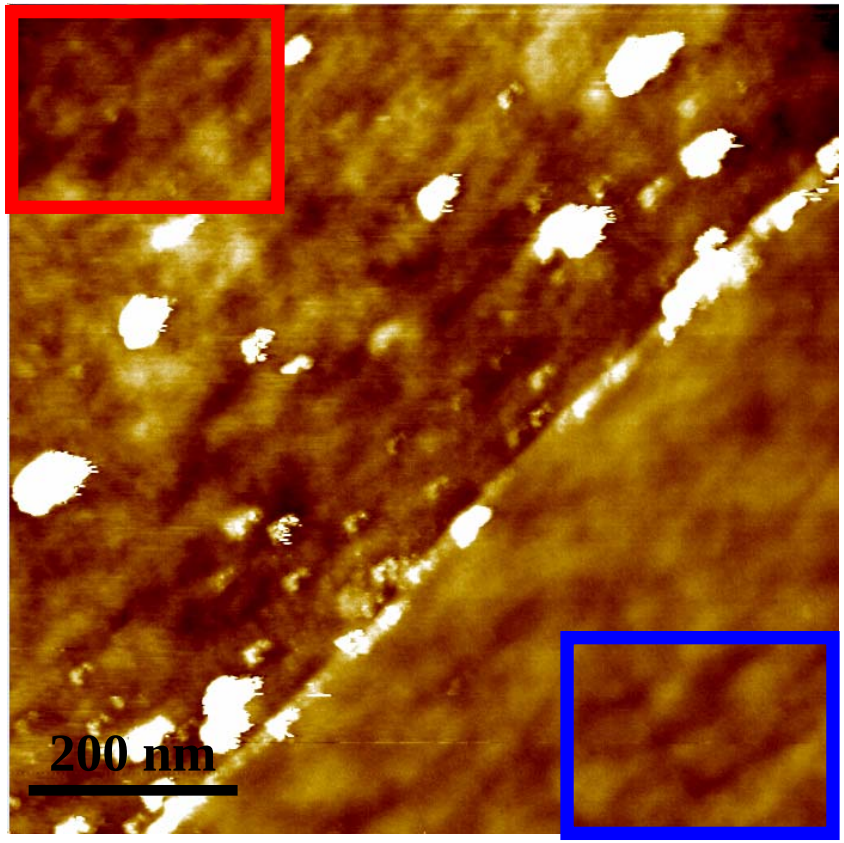
[V_{sample} = 1.0 V and I_{tunnel} = 24 pA]

- Processing residues are completely removed
- Large corrugation
- Hexagonal and triangular patterns apparent

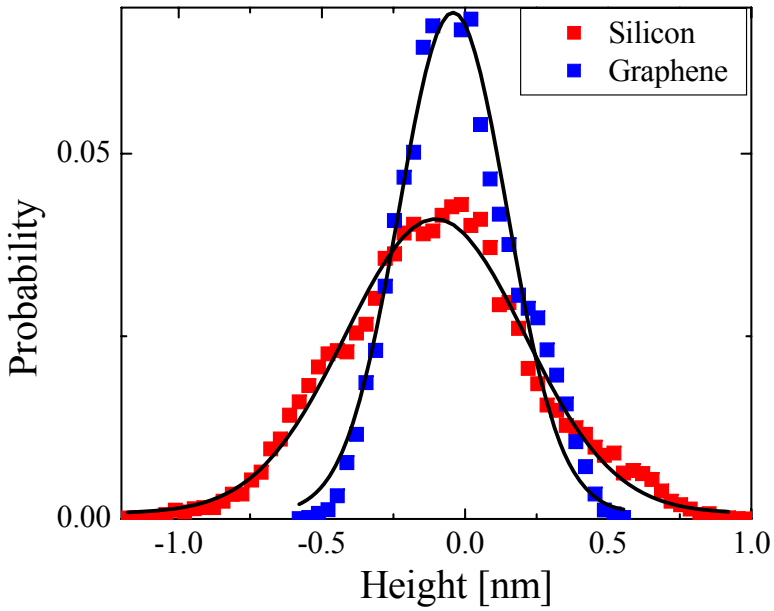
M. Ishigami, J.H. Chen, W.G. Cullen, E.D. Williams, and M.S. Fuhrer, Nanoletters, submitted (2007

Two Dimensional Morphology of Graphene

Non-contact AFM image in UHV



Oxide-graphene boundary

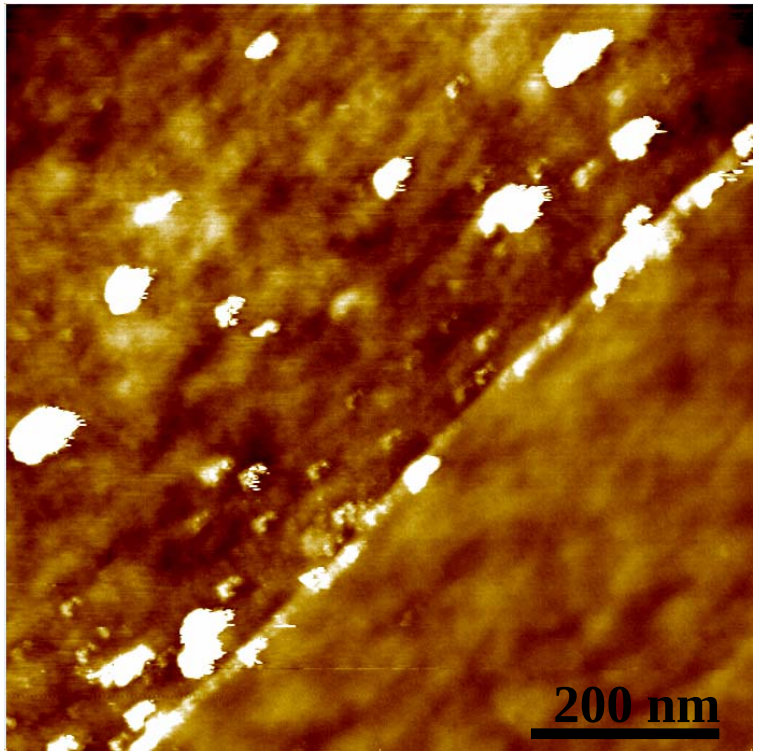


- σ_{oxide} = 3.1 Å and $\sigma_{graphene}$ = 1.9 Å
- Graphene 60% smoother than SiO_2

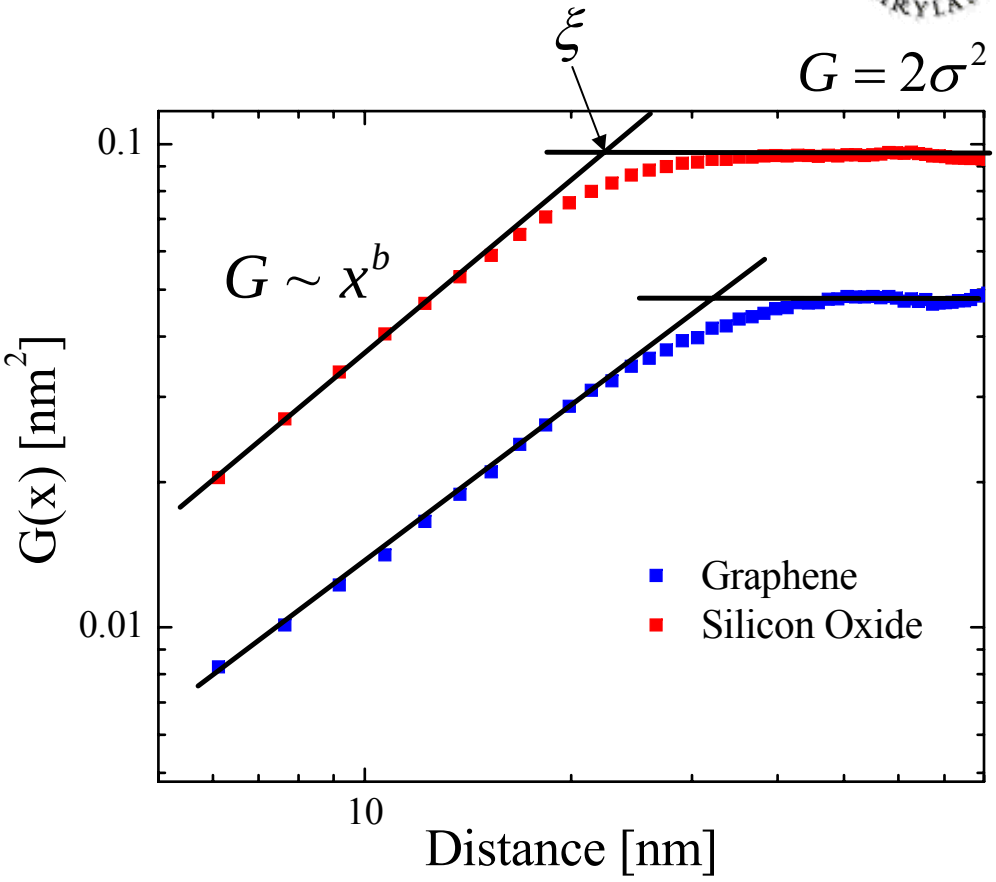
M. Ishigami, J.H. Chen, W.G. Cullen, E.D. Williams, and M.S. Fuhrer, Nanoletters, submitted (2007

Origin of Graphene Roughness

Non-contact AFM image in UHV



Oxide-graphene boundary



- $G(x) = \left\langle (z(x_0 + x) - z(x_0))^2 \right\rangle$
- b_{oxide}=1.2, $b_{graphene}$=1.1
- ξ_{oxide}=23 nm, $\xi_{graphene}$=32 nm

- **Morphology defined by the substrate**
- **Finite graphene "stiffness"**

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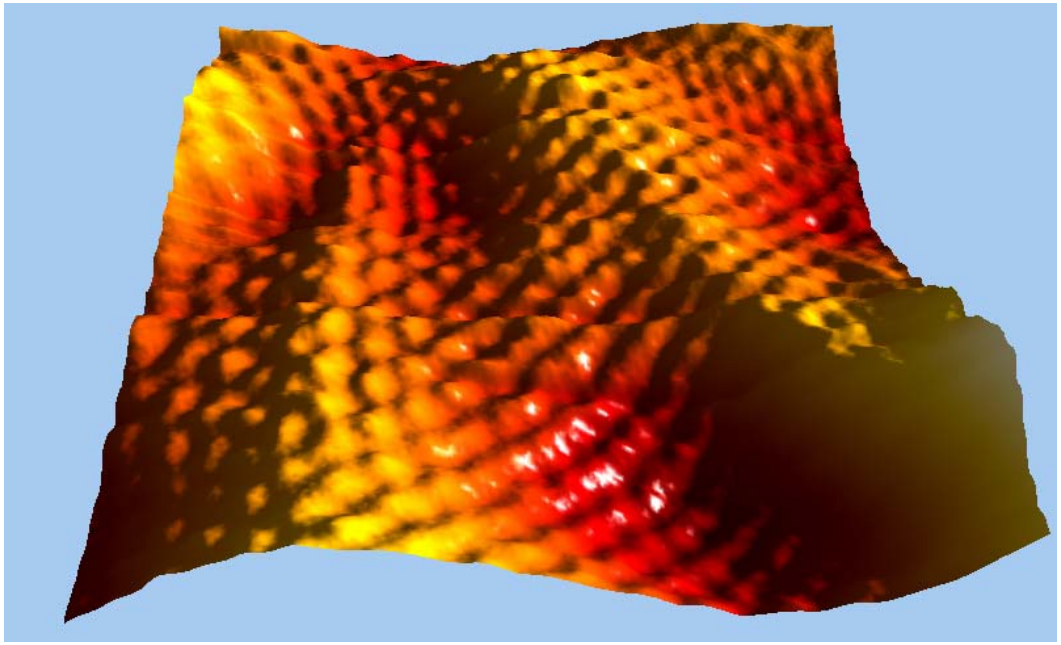
Graphene Corrugation



Physical origins of corrugation:

Model 1:

Intrinsic graphene property constrained via interaction with interface

Model 2:

Corrugations determined by relatively strong interaction with SiO2

M. Ishigami, J.H. Chen, W.G. Cullen, E.D. Williams, and M.S. Fuhrer, Nanoletters, submitted (2007)

Model 1: Intrinsic morphology

H. Aranda-Espinoza and D. Lavallee
Structure factor of flexible membranes
Europhys. Lett, **43** pp. 355-359 (1998)

$$F = \frac{1}{2}\kappa\left[\nabla^2 h(x,y)\right]^2 + \frac{1}{2}Vh^2(x,y)$$

κ = bending modulus (rigidity)

$$\kappa = \frac{Et^3}{12\left(1-\nu^2\right)} \xrightarrow{Graphene} = 1.1x10^{-19}\,J$$

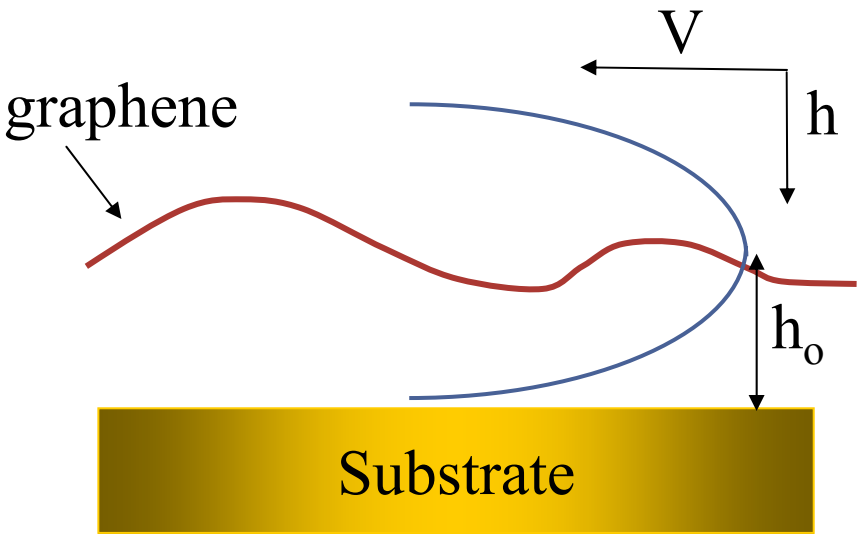
V = quadratic constraining potential

$$\xi \equiv \left(\kappa/V\right)^{1/4}$$

$$\left\langle h(x,y)^2 \right\rangle = \frac{kT}{8\left(\kappa V\right)^{1/2}}$$

$$\left\langle \left(h(r)-h(0)\right)^2 \right\rangle \sim r^2$$

r^2 dependence equivalent to 2H = 2.
Experimentally 2H ~1



- Van der Waals type interaction - expand potential V(h) to 2d order around h_o

Model 2: Substrate-determined morphology

Estimated relative energies appear reasonable:

Hamaker coefficients:

SiO_2: 650 x10^{-21}J

graphite: 223 x10^{-21}J

h_o = 4.2Å

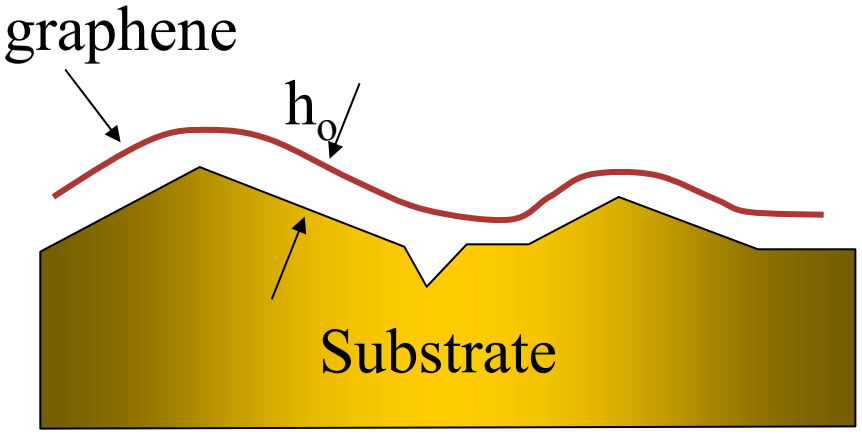
Adhesion energy ~ 14meV/Å^2

$$E_{bend} = \frac{Et^3}{24(1-\nu^2)}\frac{1}{R^2}$$

What is the minimum curvature *R* for which adhesion overcomes bending energy?

$$R > 5.5\text{Å}$$

About the radius of a single walled CNT



- Van der Waals type interaction - constrains graphene to substrate shape except for areas of very sharp curvature

Key Observations

- Interface Fluctuations
  - Collective motion (structural modes) of nanometer structures (~70 C_{60}) observed in 1Hz range with amplitude on the order of 0.1 nm - sufficient to perturb transmission probabilities at electrode interfaces
  - Different mechanisms of mode fluctuation yield different frequency signatures (f^{-1} and $f^{-1/2}$)
- Surface Resistivity
  - Charge carrier scattering off of Ag steps sufficient to bias equilibrium fluctations on time scale of 5 s
  - Surface resistivity due to fluctuating kink structure can be ~10% of bulk resistivity for 10nm nanostructure
- Ultra-thin sheet subject to mechanical constraints (graphene) represents interesting possibilities for coordinating morphology with electrical properties

Experimental Statistical Mechanics at the Nanoscale

Nanoscale structures: fabrication, stability and evolution