Nanotechnology

• 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 *

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Nano-electronics
Shrinking electronic components to molecular scale

Surface/statistical issues:
- Interfacial contacts
- Transport in low-D nanowires and thin sheets

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**Nano-electronic Material**

$V_{gs}$ $I_d$

- Gate
- Dielectric

$V_{ds}$

**Surface/statistical issues**:
- Interfacial contacts
- Transport in low-D nanowires and thin sheets

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*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

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

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

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.

\[ G(t) = \int_{q_{\text{min}}}^{2\pi/a} G_q(t) dq \quad q = 2\pi / \lambda \]

• The overall width of the fluctuations is determined by the system size \( L \sim \lambda_{\text{max}} \):

\[ \omega_{eq}^2 = \left\langle (x(t) - \bar{x})^2 \right\rangle = \frac{kTL}{12\beta} \]

-- Jeong&Williams, SSR 34 175 1999
Effective system sizes

- Two step orientations
  - Different $\beta$ 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 $\text{C}_{60}$ rings

By carefully increasing the $\text{C}_{60}$ coverage, we create circular C60 structures

Local motion of C$_{60}$ molecules is evident. Bimodal hops correlate with a C60 “kink” displacement between two favorable underlying Ag sites.

-- 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

\[ r_k(t) = \int_{-\pi}^{\pi} r(\theta, t) \exp(ik\theta) d\theta \quad k \in I \]
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:

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

*Khare & Einstein PRB 54, 11752 1996
Modal Time Correlation Functions

\[ k=2 \]

\[ k=5 \]

Fitting individual curves yields \( A_k \) and \( \tau_k \)

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

\[ z = 4, \text{ conserved noise} \]
\[ z = 2, \text{ non-conserved noise} \]

C\textsubscript{60} Ring Modes

\[ A_k = (0.009 \text{nm})(R/ k^\alpha), \text{ with } \alpha = 1.88 \]

\[ \tau_k = (11.5 \text{nm}^2 \text{s})(R/k)^z, \text{ with } z = 1.85 \]

- \( z = 2 \) ! Non-conserved Noise - not the same as clean Ag (\( z = 4 \))

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C\textsubscript{60}, \( R = 12.4 \text{ nm} \)

Mode 4:
\( (A_4)^{1/2} = 0.08 \text{ nm} \)
\( \tau_4 = 120 \text{ s} \)

Mode 12:
\( (A_{12})^{1/2} = 0.03 \text{ nm} \)
\( \tau_{12} = 12 \text{ s} \)

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$C_60$ and Ag island edge

$C_60$, $R = 12.4$ nm

Mode 4:
$(A_4)^{1/2} = 0.08$ nm
$\Delta_4 = 120$ s

Mode 12:
$(A_{12})^{1/2} = 0.03$ nm
$\Delta_{12} = 12$ s

Clean Ag, $R = 12.4$ nm

Mode 4:
$(A_4)^{1/2} = 0.009$ nm
$\Delta_4 = 0.8$ s

Mode 12:
$(A_{12})^{1/2} = 0.001$ nm
$\Delta_{12} = 0.016$ 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 - >10^6 Hz (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:
  - silver (conserved)
    \[ A_k \left( f_k = 1/\tau_k \right) = \frac{0.10 nm}{R} f_k^{-1/2} \]
  - C60 (non-conserved)
    \[ A_k \left( f_k = 1/\tau_k \right) = \frac{8 \times 10^{-4} nm^3}{R} f_k^{-1} \]
Line Boundaries and Electrical Transport

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

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

$Z_w = -19$ for Ag

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


Weak Force...

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

\[
\left( \frac{\partial}{\partial t} - \frac{\Gamma_4 \beta}{k_B T} \frac{\partial^4}{\partial x^4} - \frac{\Gamma_4 F}{k_B Ta} \left\| \frac{\partial^2}{\partial x^2} \right\| \right) y(x,t) = \eta(x,t)
\]

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

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

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

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

Wind force causes deviations in time correlation of step wandering

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 $\tau_{EM} = 50$s

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 $\tau_{em}$.

Biased sample ($j = 4 \times 10^5 \text{A/cm}^2$)

Unbiased sample ($j = 0$)

**$T = 380K$**

- 35s electromigration time const., $\tau_{em}$
- 80s electromigration time const., $\tau_{em}$

**$T = 325K$**

- $10^2$s electromigration time const., $\tau_{em}$
- $10^{16}$s electromigration time const., $\tau_{em}$
Analysis

\[ F_w^2 = \frac{kT\beta \tau_h}{a \tau_{em}} \]

Calculate step stiffness† using kink energy 0.117 eV*

\[ F = -2.7 \times 10^{-5} \text{ eV/nm} \] for \( J_{\text{nom}} = 4 \times 10^5 \text{A/cm}^2 \)

\[ F = -9.6 \times 10^{-6} \text{ eV/nm} \] for \( J_{\text{nom}} = 1 \times 10^5 \text{A/cm}^2 \)

\[ F_w = z^* eE = z^* e\rho j \]

\( \rho = 1.8 \times 10^{-6} \Omega - \text{cm} \)

\( T = 325 K \)

\( \rho = 2.2 \times 10^{-6} \Omega - \text{cm} \)

\( T = 370 K \)

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


* T. Stasevich et al., PRB 71 245414 (2005)
Electron scattering at steps/kinks

- Geometric blocking of current flow at steps increases scattering $\sim x^2$
  - 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
• Conservation of momentum requires opposing effect on charge carriers, modifying transport characteristics:

\[
\ell_f \frac{\partial \rho_s}{\partial n_k} \leq \frac{-F_w}{e \eta j} = (3 \pm 1.5 \text{nm}^3) \rho_o
\]

\[
\ell_f = \text{film thickness}
\]

\[
n_k = \text{kink density}
\]

\(
\ell_f =\)

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 nm² area

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

STM images of a graphene device

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

Two Dimensional Morphology of Graphene

Non-contact AFM image in UHV

- $\sigma_{\text{oxide}} = 3.1 \text{ Å}$ and $\sigma_{\text{graphene}} = 1.9 \text{ Å}$
- Graphene 60% smoother than SiO$_2$

Origin of Graphene Roughness

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

- Morphology defined by the substrate
- Finite graphene “stiffness”

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

Model 1: Intrinsic morphology

H. Aranda-Espinoza and D. Lavallee
Structure factor of flexible membranes

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

\( \kappa = \) bending modulus (rigidity)

\[ \kappa = \frac{Et^3}{12(1 - \nu^2)} \text{Graphene} \rightarrow 1.1 \times 10^{-19} J \]

\( V = \) quadratic constraining potential

\[ \xi \equiv \left( \frac{\kappa}{V} \right)^{1/4} \]

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

\[ \langle (h(r) - h(0))^2 \rangle \sim r^2 \]

r\(^2\) dependence equivalent to \(2H = 2\).
Experimentally \(2H \sim 1\)

- Van der Waals type interaction - expand potential \(V(h)\) to 2d order around \(h_0\)
Model 2: Substrate-determined morphology

Estimated relative energies appear reasonable:

Hamaker coefficients:
- SiO$_2$: 650 x 10$^{-21}$J
- graphite: 223 x 10$^{-21}$J

$h_0 = 4.2$ Å

Adhesion energy $\sim 14$ meV/Å$^2$

\[
E_{bend} = \frac{Et^3}{24(1 - v^2)} \frac{1}{R^2}
\]

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

$R > 5.5$ 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 fluctuations 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