Dynamics of small organic molecules on metallic and graphitic substrates

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Modelling and dynamics

- The “bottom-up” approach to nanoscale behavior.

- Identify the important degrees of freedom – usually slow.
- Average/combine other processes – usually fast.
- Close parallels with our experimental approach
Dynamical framework - I

- **Energy landscape**:  
  - Adiabatic potential-energy surface.
- Typically 2-D for an atomic adsorbate  
  - Adsorption sites:  
    - *Structure.*
Dynamical framework - I

- **Energy landscape**: Adiabatic potential-energy surface.

- Typically 2-D for an atomic adsorbate
  - Adsorption sites:
    - Structure.
  - Metastable sites and Transition states:
    - Only evident from Dynamics.

- Corrugation has a direct impact on the dynamics.
Dynamical framework - II

- Energy landscape
  - Corrugation

- Inter-adsorbate interactions
  - Attractive / repulsive
  - Pairwise / many-body

- Coupling to the substrate
  - Treated as ohmic friction

- Langevin description
Langevin Equation

“How to do an experiment by calculation.”

\[ m \ddot{r}_i = -\nabla V(x, y) - \eta m \dot{r}_i + \xi_i(t) + \sum_{i \neq j} F_{ij} \]
Calculating the scattered intensity:

Kinematic theory (c.f. neutron scattering)

\[
A(\Delta K, t) = \sum_j \exp[\Delta K \cdot R_j(t)] ; \quad I(\Delta K, t) = AA^*
\]

Intermediate Scattering Function: \( I(\Delta K, t) \).

- Relation to the dynamics

\[
I(\Delta K, t) \leftrightarrow G(R, t)
\]

- Scattering with a realistic potential.
  - Interaction time is a few picoseconds

\( E_f \approx 10 \text{ meV} \)
Quasi-elastic scattering

- Surface with several moving atoms
Validity of kinematic theory

- Compare with the full, quantum result.
  - Additional broadening: deconvolute $S(\Delta K, \Delta \omega)$ given the known, incident energy distribution, as in experiment.
Atom, spin-echo method

Coherent scattering, with nuclear-spin polarisation used as the measure of coherence.

\[
A(\Delta K, t, \tau) = \sum_j \{\exp[i\Delta K \cdot R_j(t)] + \exp[i\Delta K \cdot R_j(t+\tau)]\}
\]

\[
I \propto AA^* ; \quad P(\Delta K, \tau) = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} = \frac{\int G(R, \tau) \exp(i\Delta K \cdot R) dR}{\int G(R,0) \exp(i\Delta K \cdot R) dR} = \frac{I(\Delta K, \tau)}{I(\Delta K,0)}
\]

*Prog. Surf. Sci. 84 (2009) 323*

*Science 304 (2004) 1790*
Method outline

- Intermediate scattering function
  - Measures the time decay of structural correlation at the surface.
  - Temporal correlation is measured directly
  - Spatial correlation measured through the dependence on $\Delta K$.

- Example: Brownian motion:
  \[ I(\Delta K, t) \propto \exp(-\Delta K^2 D t) \]
  - Dephasing rate $\alpha$
  - Diffusion constant
  - Related to hopping rate
Context for experiment

Prog. Surf. Sci. 84 323 (2009)
Activated motion

- Arrenhius behaviour:

- Activation energy – usually recovered accurately.
- Pre-exponential factor – more difficult but more important.
The problem of the pre-exponential

- Recent data for CO moving on Cu(111):

Models for jump dynamics

- Hopping on a Bravais lattice (simplest case)
- Single dephasing rate, $\alpha$, which varies periodically. Period is $2\pi/a$, where $a$ is the jump length.
  
  Chudley and Elliot Proc Roy Soc 77 (1961)

- Hopping on a non-Bravais lattice
- Multiple dephasing rates but with a well-defined $\Delta K$ dependence.

  *fcc-hcp hopping on (111) surface*

Multiple sites CO/Cu(111)

- Bridge and top sites both involved in the dynamics.

\[ \Theta = 0.1 \text{ ML} \]
\[ \Theta = 0.04 \text{ ML} \]
\[ T_s = 190K \]

\[ U(x, y) = - \sum_{i,n} A_n \cos(n g_i - r), \quad i = 1,3 \]

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- \( \Theta = 0.04 \) ML
- \( T_s = 190K \)

- Changes near the transition state explain coverage dependence.

*J. Phys. CM, in press (2011)*
Small organic molecules

- Landscape, forces and dissipation
  - Systems with 5- and 6-fold rotational symmetry
  - Brownian regime: Benzene, C₆H₆/graphite (HOPG)
  - Hopping regime: Cyclopentadienyl anion (C₅H₅⁻) /Cu(111)

- Processes necessary for self-assembly:
  - Translation and rotation
  - Ethanethiolate/Cu(111)

- Dissipative coupling and molecular size:
- Benzene-graphite interaction
  - Lattice match - model for graphite/graphene interactions.
  - Motion in thermal equilibrium
  - High surface-area samples allow comparison with neutron spin-echo.

Coverage = 0.5ML
Temperature 140K
C₆H₆/Graphite

- Brownian motion
  - Lack of activation
  - Quadratic variation with $\Delta K$

- Friction:
  - $\eta = 2.8$ ps⁻¹
  - Excluding benzene collisions: $\eta = 2.2$ ps⁻¹

$T = 140K$
$\theta = 0.5$ ML

$E_a = 17+/−12$ meV

$\frac{\Delta K}{\text{Angst.}}$

$T = 140K$
$\theta = 0.5$ ML

Nature Physics 5, 561 (2009)
Cyclopentadienyl (anion) / Cu(111)

- Cyclopentadiene $C_5H_6$
- The molecule adsorbs dissociatively and ionically: $C_5H_6 \rightarrow (C_5H_5^-)_a$
- Behaviour differs from $C_6H_6$/graphite

Cyclopentadienyl (anion)/Cu(111)

- Motion does not correspond to hopping on a Bravais lattice

- We have a non-Bravais lattice. In a perfect experiment:
  \[ I(\Delta K, t) = A_1 \exp(-\alpha_1 t) \quad I(\Delta K, t) = A_1 \exp(-\alpha_1 t) + A_2 \exp(-\alpha_2 t) \]

- Single decay along [110]

- Double decay along [112]

motion strongly activated
Structure from dynamics

- Periodicity in $\alpha(\Delta K)$ indicates motion on a lattice.
- The double decay indicates a non-bravais lattice.
- Results correspond closely with equal occupation of fcc and hcp sites on the Cu(111) surface.

Friction and interactions

- Energy landscape: Activation energy for hopping 41 meV.
- Strong friction (perfect single jump hopping) $\eta = 2.5 \text{ ps}^{-1}$.
- No signature for repulsive interactions (cf. alkali metals).
- DFT offers some insights into behaviour.

Charge iso-surfaces: ±0.02 e Å$^{-3}$

$\eta \sim 2 \text{ ps}^{-1}$, cf 2.2 ps$^{-1}$ for C$_6$H$_6$/ graphite
Molecules without a rotation axis

Observation of diffusional rotation:
• Dynamics of ethanethiol anion, CH$_3$CH$_2$S
Molecular translation and rotation

What is the dynamical signature for rotation?

- Confined motion (unlike translational diffusion)
- Correlation does not go to zero (in pure rotational hopping)

\[
I_{112} (\Delta K, \tau) = C_1 e^{-\beta \tau} + C_2 e^{-3\beta \tau} + C_3 e^{-4\beta \tau} + C_4
\]

\[
I_{1\bar{1}0} (\Delta K, \tau) = C_5 e^{-\beta \tau} + C_6 e^{-3\beta \tau} + C_7
\]

With uncorrelated translation

\[
I_{Tot} (\Delta K, \tau) = I_{Rot} (\Delta K, \tau). I_{Transl} (\Delta K, \tau)
\]

\[I(\tau) = A e^{-\alpha \tau} + B\]

\[r = 4.6 \pm 0.3\text{Å}\]

Phys Rev Lett 106, 256101 (2011)
Temperature dependence

- Temperature dependence of the effective dephasing rate

\[ I(\tau) = A e^{-\alpha \tau} + B \]

\[ \Delta K = 0.47 \text{ Å}^{-1}, \quad <112> \]

- Break in slope accompanies a change in \( \Delta K \) dependence

\[ E_a = 18\pm8 \text{ meV} \]

\[ E_a = 86\pm5 \text{ meV} \]
Dynamical signatures

Principal dephasing rate \[ I(\tau) = A e^{-\alpha \tau} + B \]

Translation + rotation

Pure translation

Analytic model for rotation
Summary:

- **Low $T$** (<210L): Dominated by weakly activated *rotational diffusion*. The equivalent two-body rotator has a radius 4.6±0.3Å.
- **High $T$** (>210K): Mainly *translation* with high activation barrier.
- Effective diffusion constant (in the high $T$ regime) is significantly faster than for sulphur. Evidently the alkyl chain affects the energy landscape.
- Translational motion well described by single hops so, again, we are in the *high friction regime*. 
Dissipation in molecular systems

- **Kinetic friction in the Langevin model.**

  \[
  m \ddot{r}_j = -\nabla V(x, y) - \eta m \ddot{r}_j + \xi_j(t) + \sum_{i \neq j} F_{i,j}
  \]

- It measures the disruption to ballistic motion generated by “other coordinates”.

- What factors determine \( \eta \)?
  - Strength of the adsorbate-substrate bond.
  - Magnitude of the corrugation in the energy landscape (static friction).
  - Size/contact area etc.....
Factors affecting dissipation

- Atoms and small molecules:
  - eg: Na, CO etc typically have $\eta \leq 0.5$ ps$^{-1}$.

- Larger molecules: typically have bigger $\eta \sim 2$ ps$^{-1}$.
  - Substrate properties and adsorbate-substrate bonding seem unimportant
  - c.f. Benzene/Graphite and Cp$^-$/Cu(111), where $\eta$ is similar but other factors are not.
Thiophene vs \( \text{cp}^- \) on Cu(111)

- Both 5-fold rings
  - \( \text{Cp}^- \) in *hollow sites* interacts with several substrate atoms.
  - Thiophene: *top site* adsorption in tilted configuration\(^1\).

\[ \eta = 2.5 \pm 0.5 \text{ ps}^{-1}. \]

\[ \eta = 2.0 \pm 0.3 \text{ ps}^{-1}. \]

\(^1\)Milligan et al., *J. Phys. Chem. B* 105, 140 (2001)

- Internal degrees-of-freedom appear to dominate the friction of centre of mass motion\(^2,3\).

\(^2\)de Wijn, Fasolino, *JPCM* 21 264002 (2009)  
\(^3\)de Wijn, *Phys Rev* **E84**, 011610 (2011)
The helium spin-echo method:

- Quantitative tool for surface dynamics – with unique attributes.
- Detailed information on static (structure) and dynamic properties.
- Translational and rotational hopping can be observed in the long-time limit of the intermediate scattering function.
- Ballistic motion in the short-time limit remains to be investigated quantitatively.
- Dissipation seems to have both internal and external contributions:
  - Largely independent of the properties of the substrate and the adsorbate-substrate bonding.
  - Internal molecular degrees-of-freedom appear to be important.
THE END