Trends in Nanotribology, Trieste, September 2011

Dynamics of small organic molecules on metallic and graphitic substrates

Bill Allison

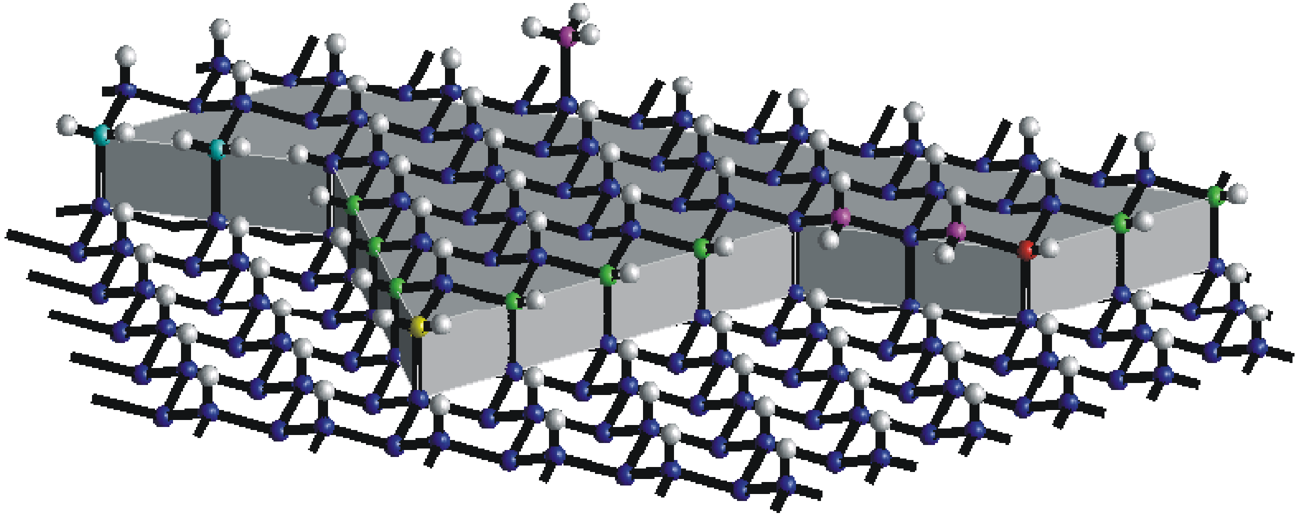
Cavendish Laboratory, University of Cambridge. CB3 0HE, UK

.

- Cambridge : J Ellis, AP Jardine, H Hedgeland, AR Alderwick, D Ward,
  P Kole, BAJ Lechner, F Tuddenham, S Paterson.
- Collaborators:
  G Alexandrowicz (Haifa), P Fouquet (Grenoble),
  M Sacchi, S Jenkins (Chem. Cambridge),
  BJ Hinch (Rutgers), GP Brivio, G Fratesi (Milano)

Modelling and dynamics

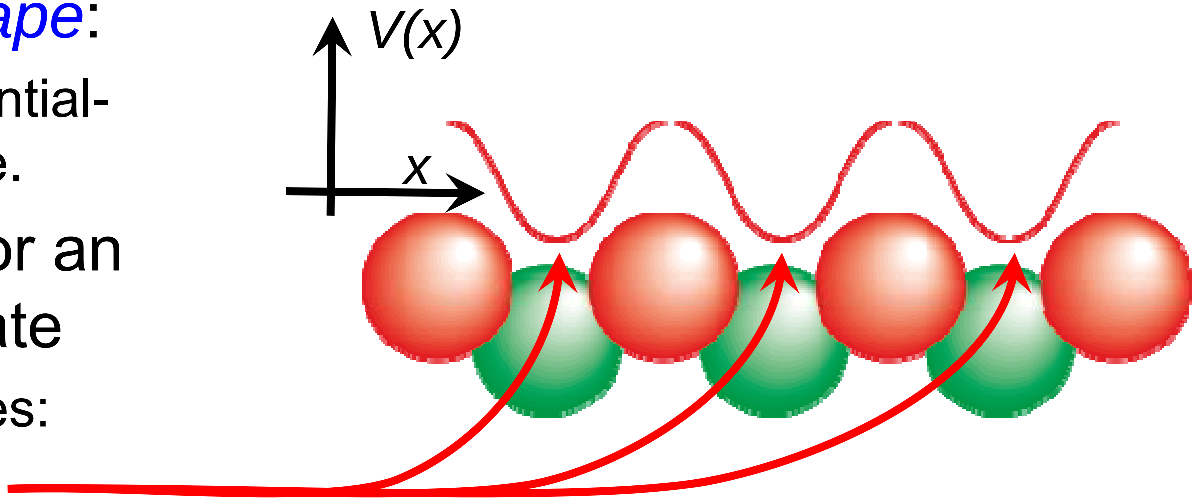
- The “bottom-up” approach to nanoscale- behaviour.



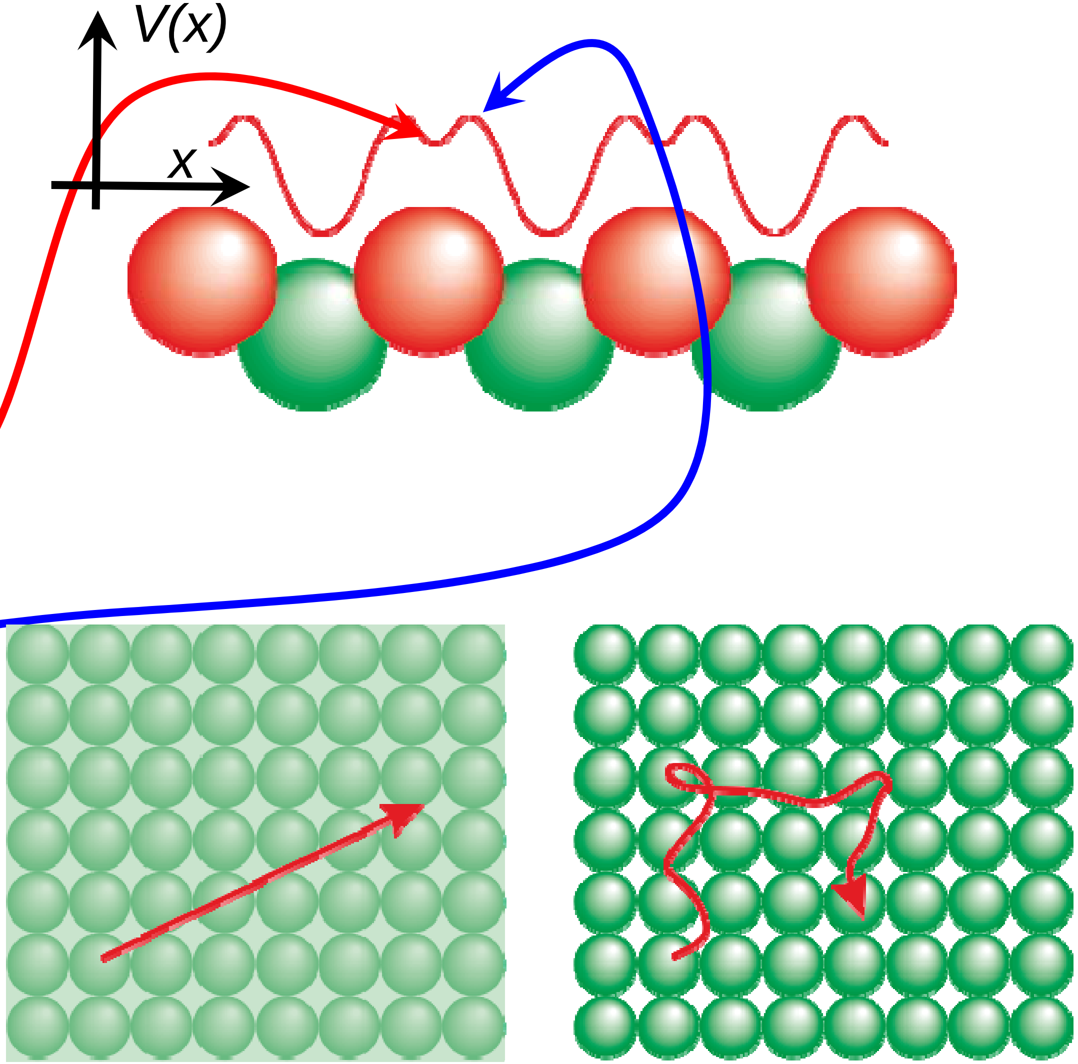
- Identify the important degrees of freedom – usually *slow*.
- Average/combine other processes – usually *fast*.
- Close parallels with our experimental approach

Dynamical framework - I

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



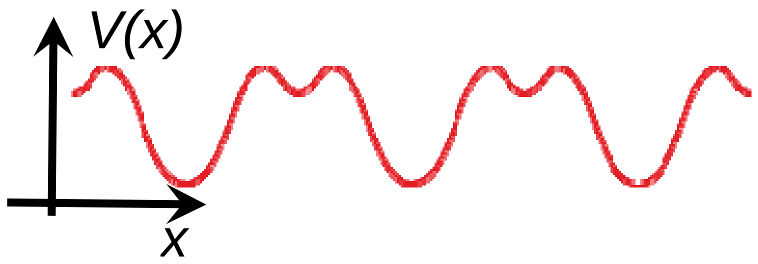
Dynamical framework - I

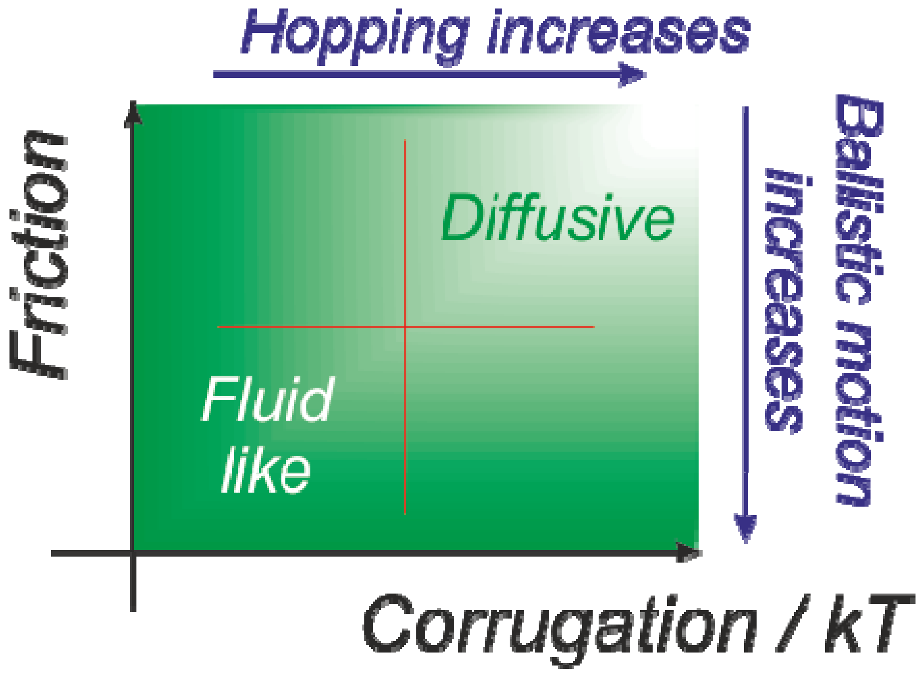


- *Energy landscape*:
  - Adaibatic potential-energy surface.
- Typically 2-D for an atomic adsorbate
  - Adsorption sites:
    - *Structure*.
  - Metastable sites and Transition states:
    - Only evident from *Dynamics*.
- Corrugation has a direct impact on the dynamics.

Dynamical framework - II

- Energy landscape
  - Corrugation
- Inter-adsorbate interactions
  - Attractive / repulsive
  - Pairwise / many-body
- Coupling to the substrate
  - Treated as ohmic friction
- Langevin description

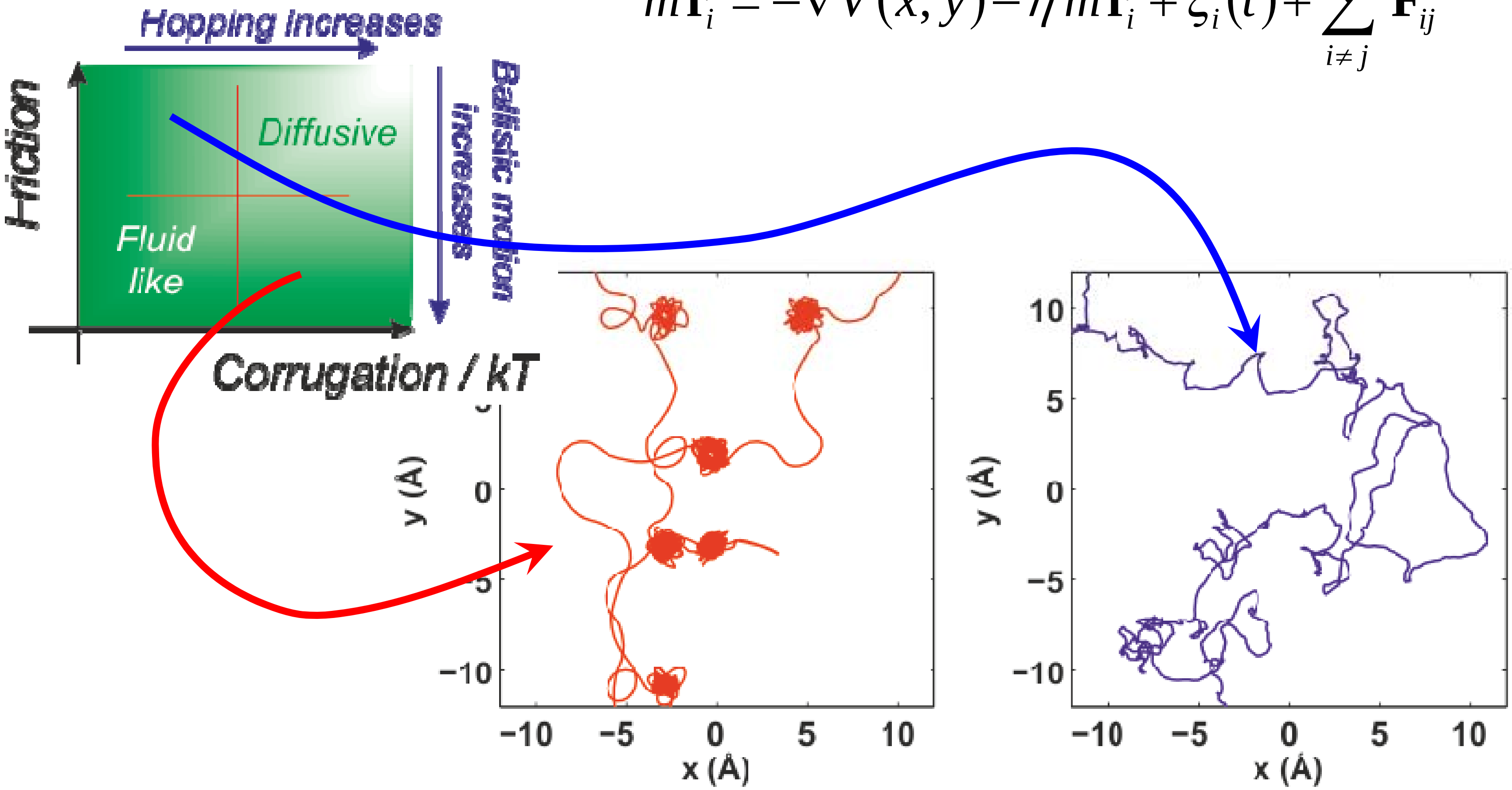




Langevin Equation

- “How to do an experiment by calculation.”

$$m\ddot{\mathbf{r}}_i = -\nabla V(x,y) - \eta\, m\dot{\mathbf{r}}_i + \xi_i(t) + \sum_{i\neq j} \mathbf{F}_{ij}$$



Matching with experiment

- Calculating the scattered intensity:
- *Kinematic theory* (c.f. neutron scattering)

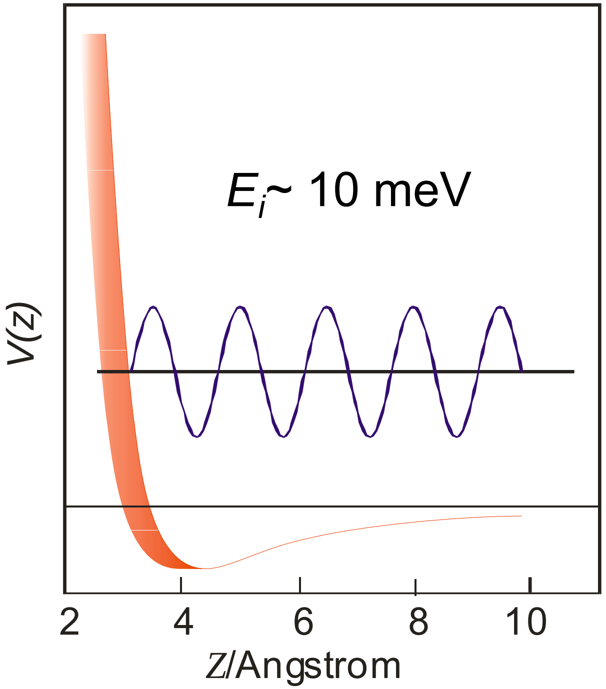
$$A(\underline{\Delta K},t)=\sum_j \exp\left[\underline{\Delta K}.R_j(t)\right] \quad ; \quad I(\underline{\Delta K},t)=AA^*$$

- Intermediate Scattering Function: $I(\underline{\Delta K},t)$.
  - Relation to the dynamics

$$\boxed{I(\underline{\Delta K},t)\overset{spatial}{\underset{F.T.}{\Longleftrightarrow}} G(R,t)}$$

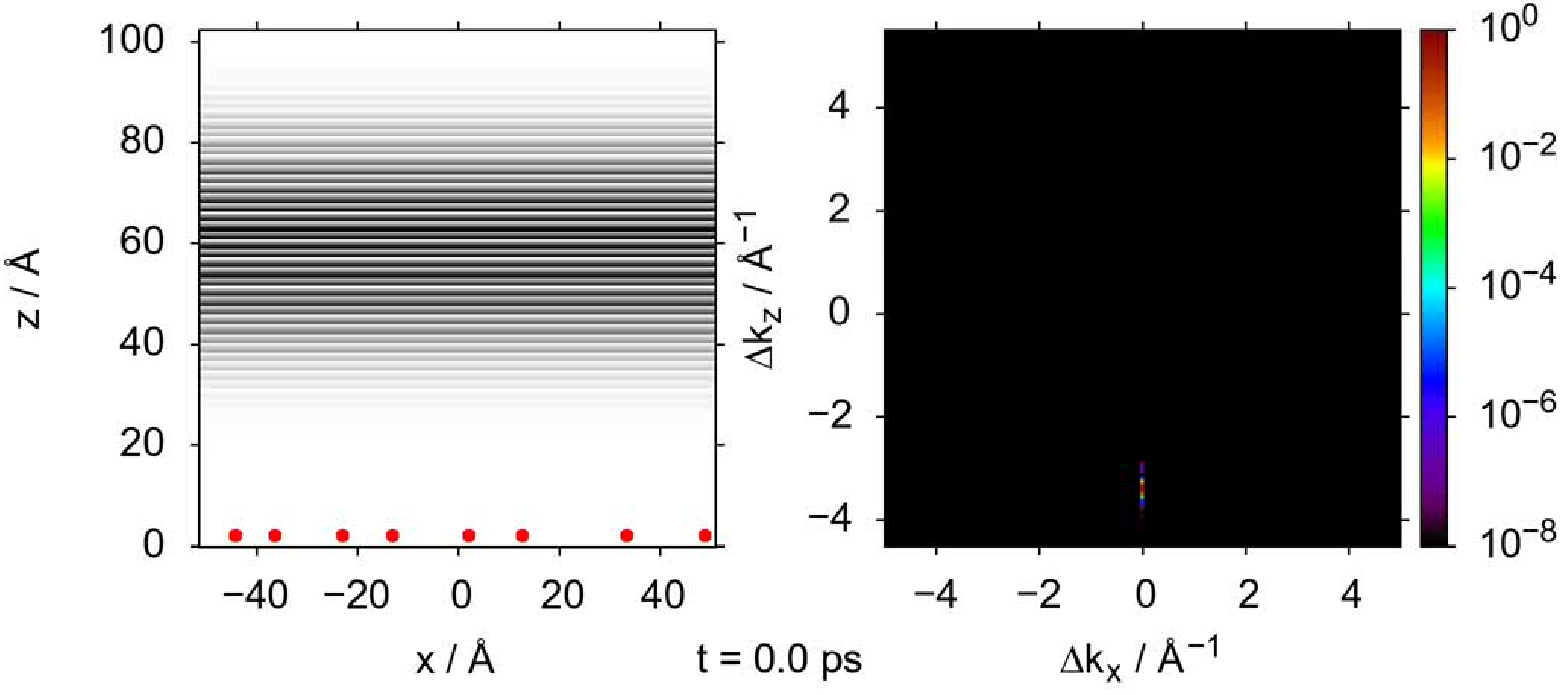
$$S(\underline{\Delta K},\Delta\omega)\overset{temporal}{\underset{F.T.}{\Longleftrightarrow}} I(\underline{\Delta K},t)\overset{spatial}{\underset{F.T.}{\Longleftrightarrow}} G(R,t)$$

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



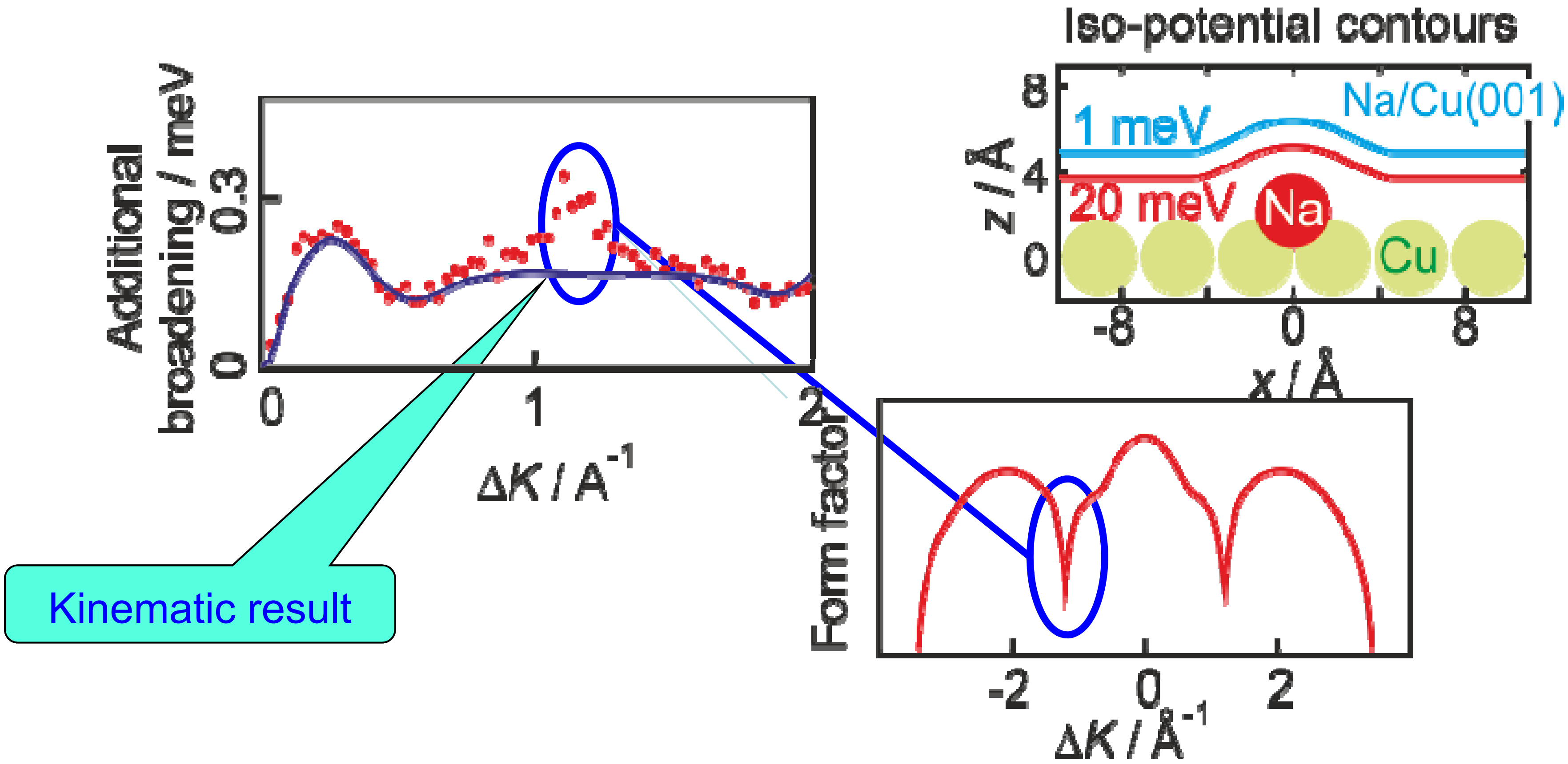
Quasi-elastic scattering

- Surface with several moving atoms



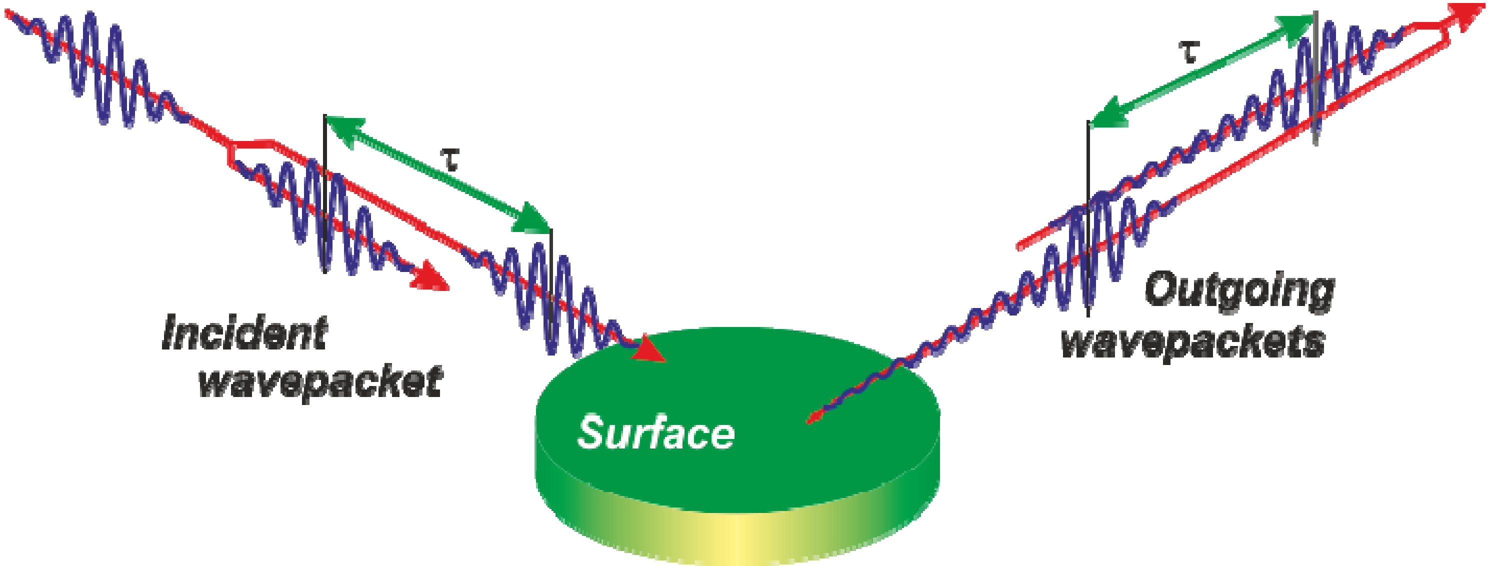
Validity of kinematic theory

- Compare with the full, quantum result.
  - Additional broadening: deconvolute $S(\underline{\Delta K},\Delta\omega)$ 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.



$$A(\underline{\Delta K},t,\tau)=\sum_j\left\{\exp\left[i\underline{\Delta K}.\underline{R}_j(t)\right]+\exp\left[i\underline{\Delta K}.\underline{R}_j(t+\tau)\right]\right\}$$

$$I\propto AA^*\ ;\ P(\Delta K,\tau)=\frac{I_{\max}-I_{\min}}{I_{\max}+I_{\min}}=\frac{\int G(\underline{R},\tau)\exp(i\underline{\Delta K}.\underline{R})d\,\underline{R}}{\int G(\underline{R},0)\exp(i\underline{\Delta K}.\underline{R})d\,\underline{R}}=\frac{I(\underline{\Delta K},\tau)}{I(\underline{\Delta K},0)}$$

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

Science **304** (2004) 1790

Method outline

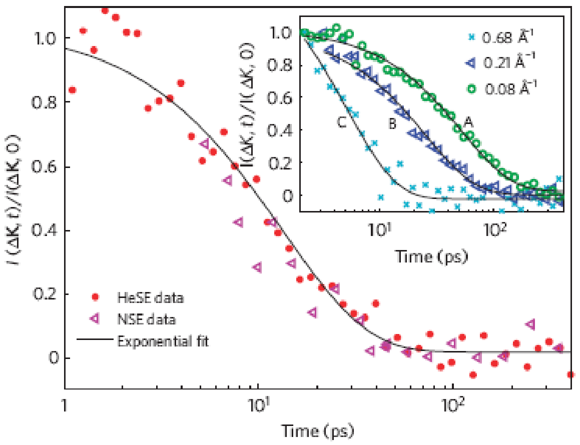
- Intermediate scattering function
  - Measures the time decay of structural correlation at the surface.
    - Temporal correlation is measured directly
    - Spatial correlation measured through the dependence on ΔK.

- Example: Brownian motion:

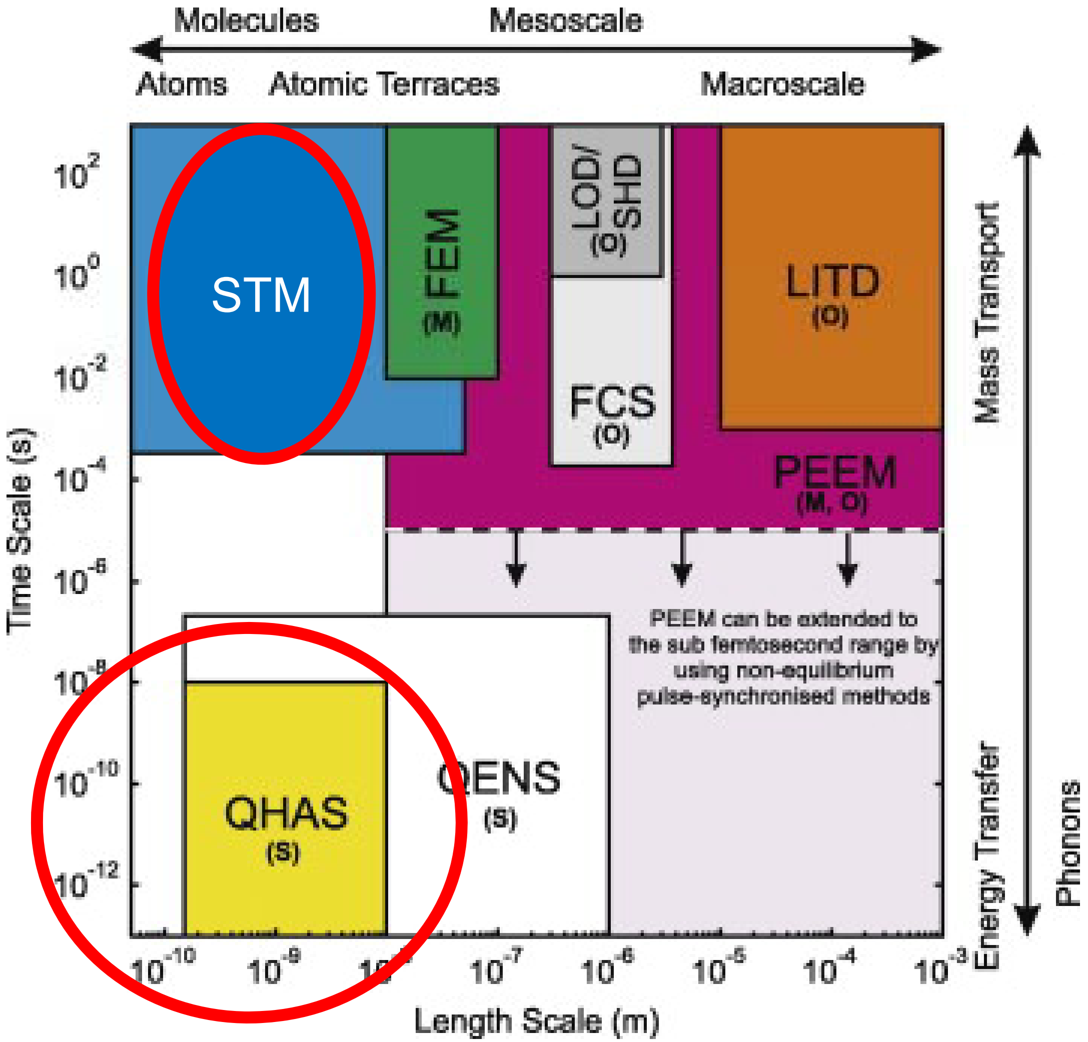
$$I(\Delta K,t)\propto \exp\left(-\overbrace{\Delta K^2 D t}^{\alpha}\right)$$

Dephasing rate

Diffusion const.
Related to *hopping rate*



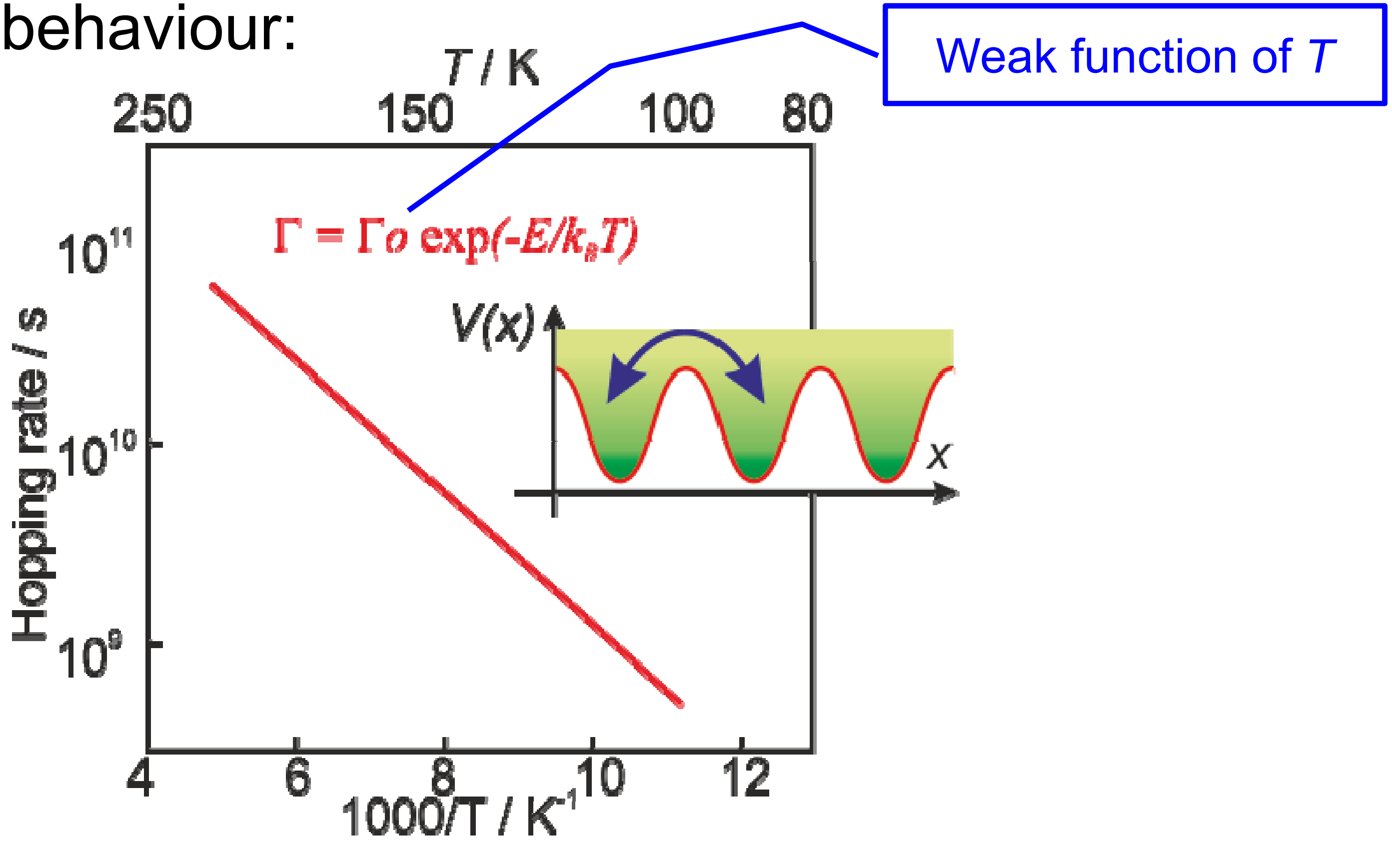
Context for experiment



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

Activated motion

- Arrenhius behaviour:

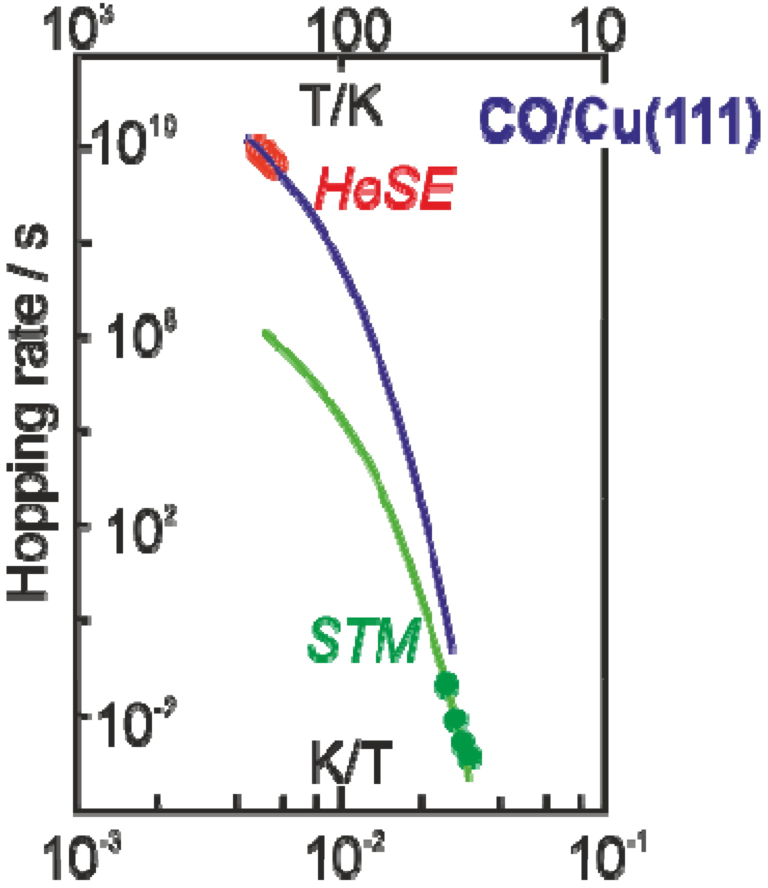

$\Gamma = \Gamma_0 \exp(-E/k_B T)$

Weak function of *T*

- 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):

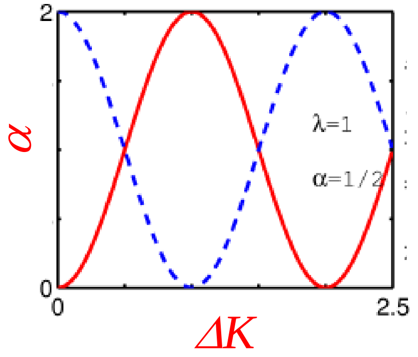


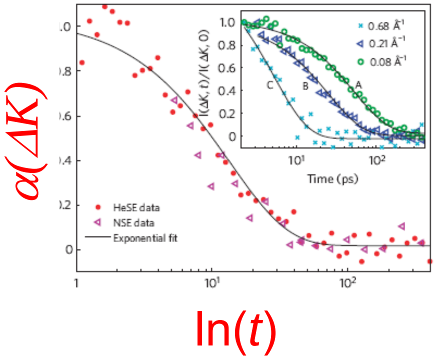
STM: Wong et al J. Chem. Phys. 123, 201102 (2005)

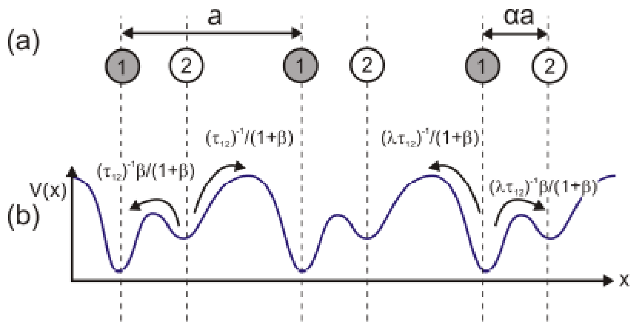
Models for jump dynamics

- Hopping on a *Bravais lattice* (simplest case)
- Single dephasing rate, α, which varies periodically. Period is $2\pi/a$, where a is the jump length.

Chudley and Elliot Proc Roy Soc 77 (1961)

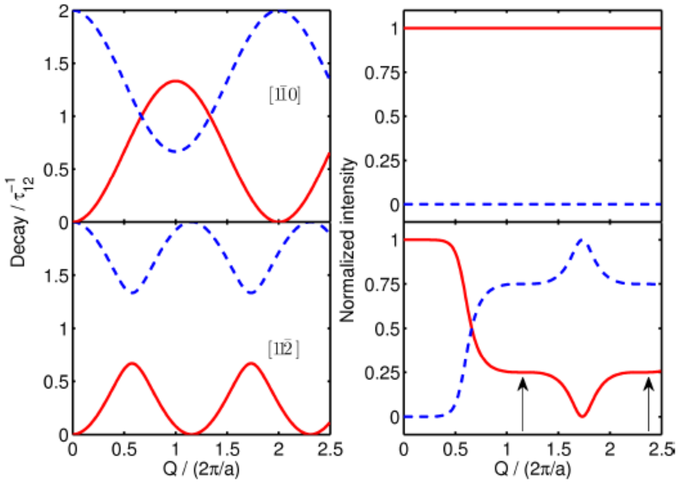






- Hopping on a *non-Bravais lattice*
- Multiple dephasing rates but with a well-defined $\underline{\Delta K}$ dependence.

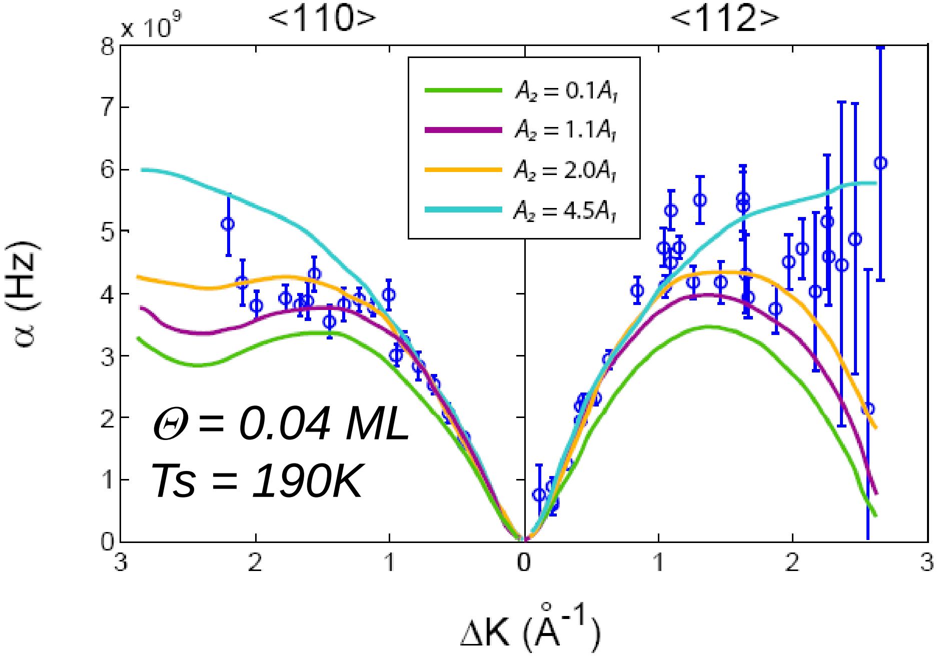
fcc-hcp hopping on (111) surface

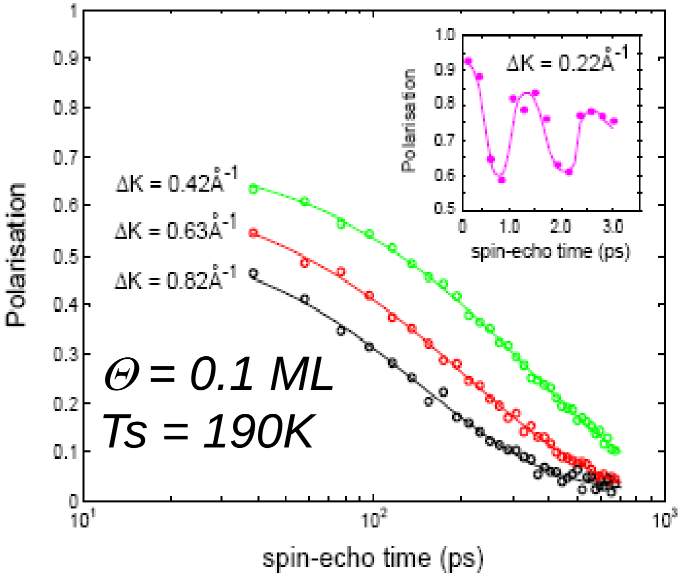


Surf. Sci. **604**, 1459 (2010)

Multiple sites CO/Cu(111)

- Bridge and top sites both involved in the dynamics.





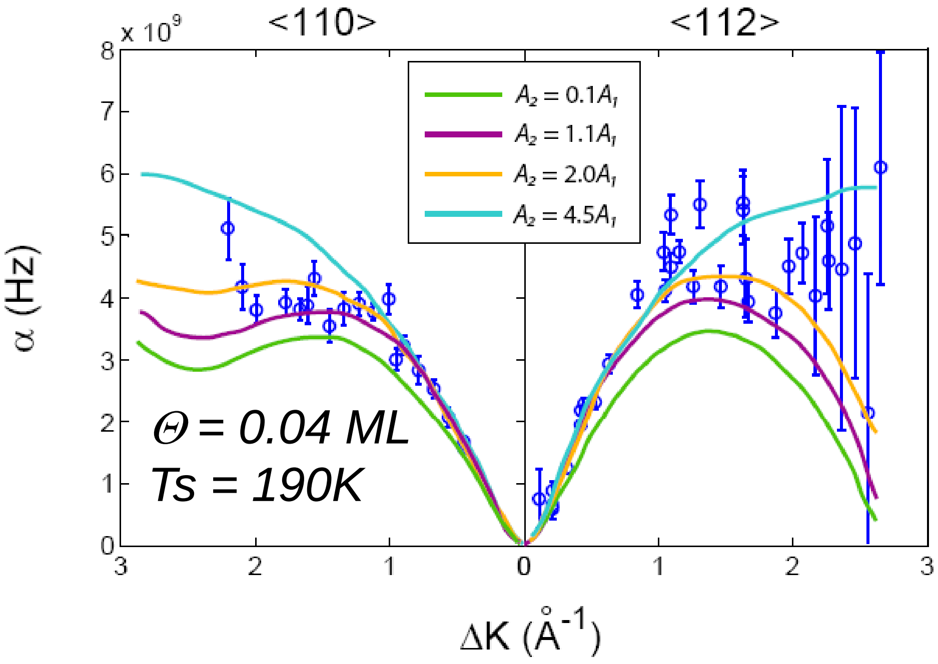
$$U(x,y) = -\sum_{i,n} A_n \cos(n\underline{g}_i - \underline{r}), \quad i = 1,3$$

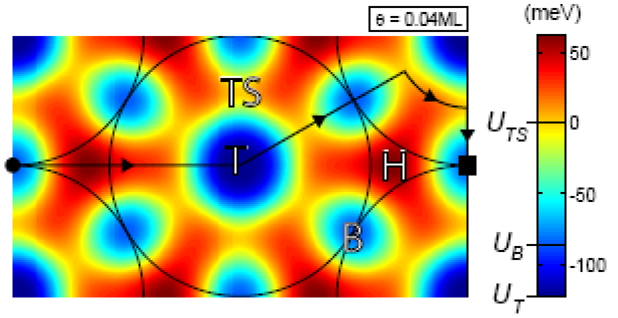
J. Phys. CM, in press (2011)

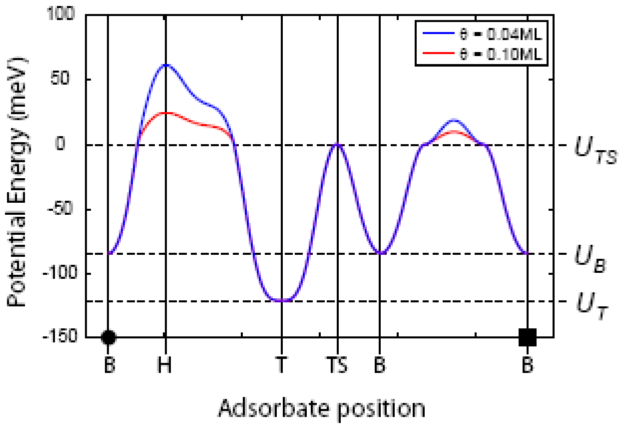
Multiple sites CO/Cu(111)

- Bridge and top sites both involved in the dynamics.

$$U(x,y) = -\sum_{i,n} A_n \cos(n\underline{g}_i - \underline{r}), \quad i = 1,3$$





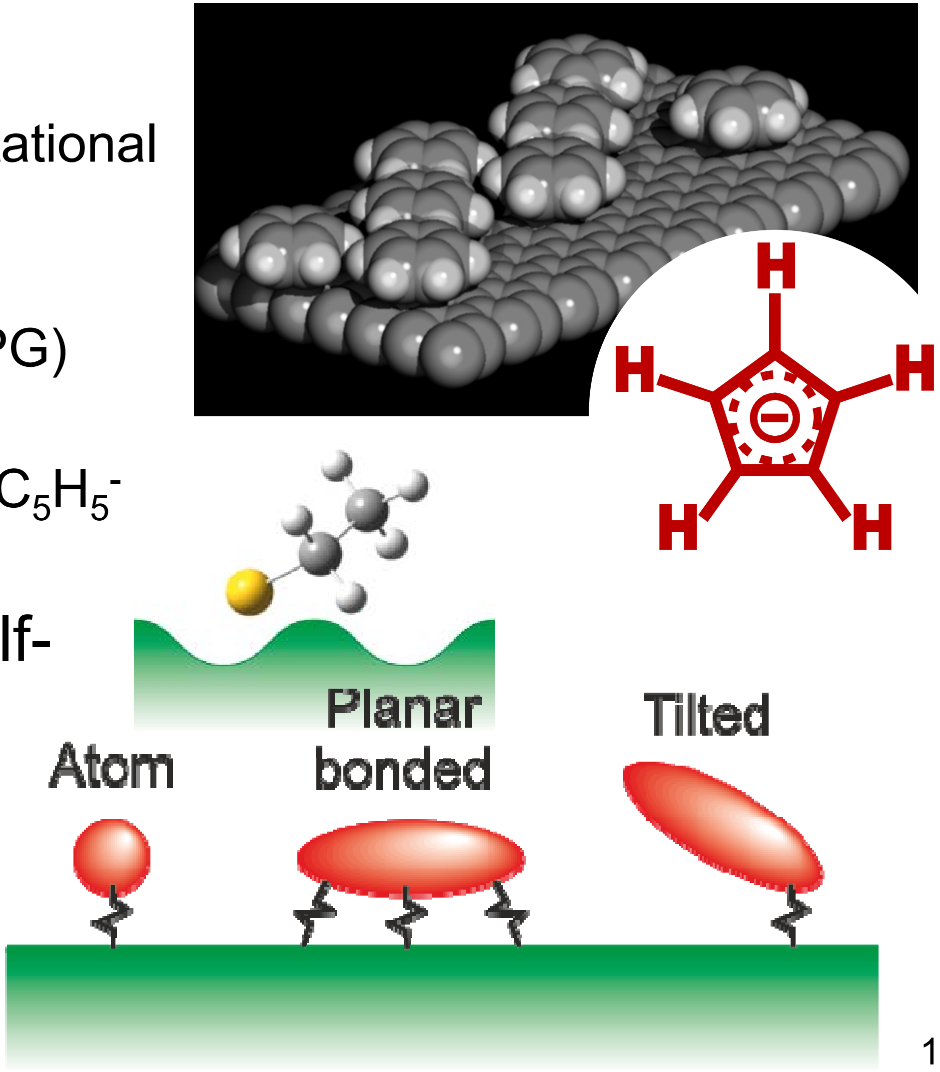


- Changes near the transition state explain coverage dependence.

J. Phys. CM, in press (2011)

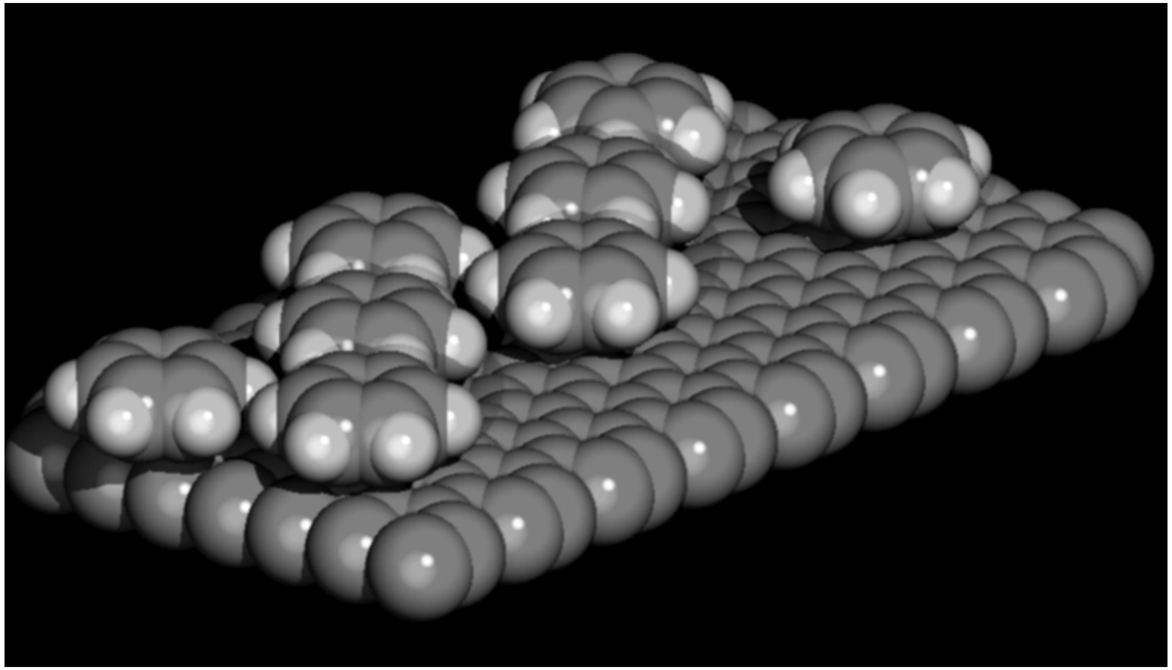
Small organic molecules

- Landscape, forces and dissipation
  - Systems with 5- and 6-fold rotational symmetry
  - Brownian regime: *Benzene*, C_6H_6/graphite (HOPG)
  - Hopping regime: *Cyclopentadienyl* anion (Cp^-) $C_5H_5^-$ /Cu(111)
- Processes necessary for self-assembly:
  - Translation and rotation
  - *Ethanethiolate*/Cu(111)
- Dissipative coupling and molecular size:



C_6H_6/C

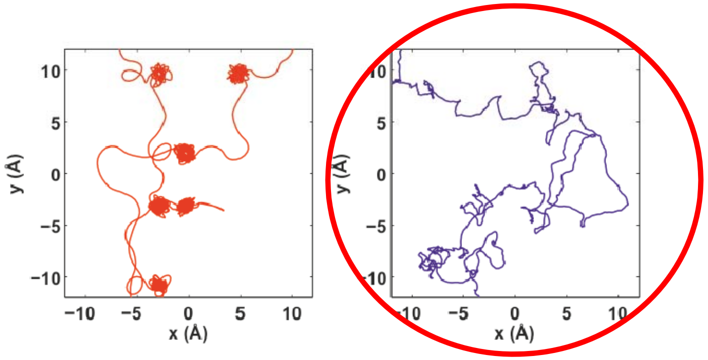
- Benzene-graphite interaction
  - Lattice match - model for graphite/graphene interactions.
  - Motion in thermal equilibrium
  - High surface-area samples allow comparison with neutron spin-echo.



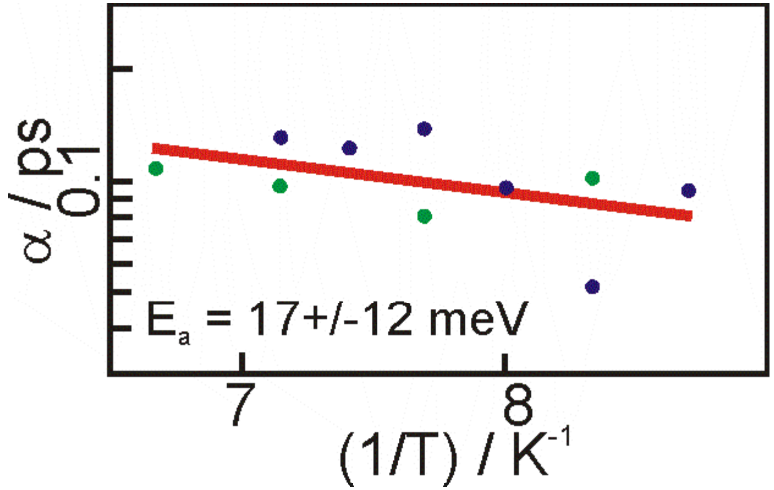
Coverage = 0.5ML
Temperature 140K

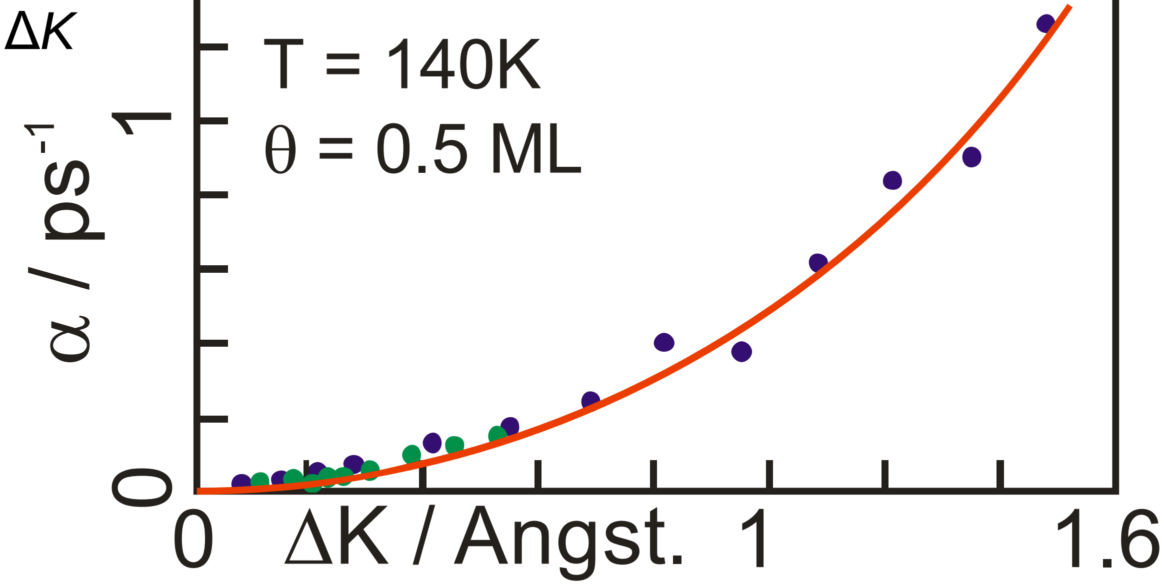
C_6H_6/Graphite

- Brownian motion
  - Lack of activation



  - Quadratic variation with Δ*K*
- Friction:
  - $\eta = 2.8\ \mathrm{ps}^{-1}$
  - Excluding benzene collisions: $\eta = 2.2\ \mathrm{ps}^{-1}$

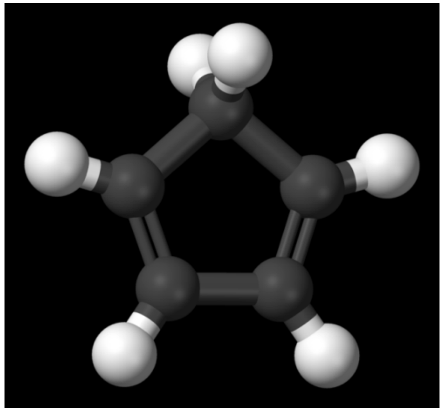




Nature Physics **5**, 561 (2009)

Cyclopentadienyl (anion) / Cu(111)

- Cylcopentadiene C_5H_6
- The molecule adsorbs dissociatively and *ionically*: $C_5H_6 \rightarrow (C_5H_5\text{-})_a$
- Behaviour differs from C_6H_6/graphite

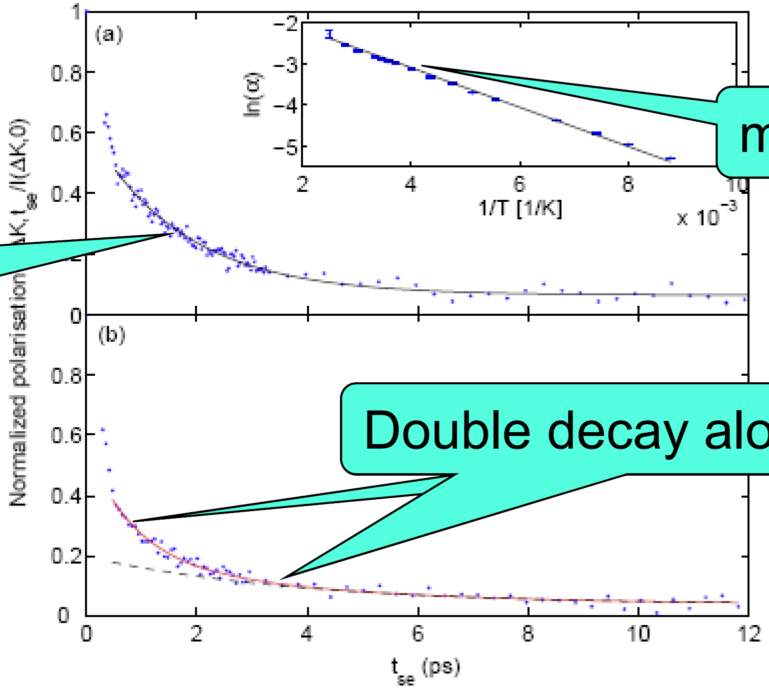


Phys. Rev. Lett. 106, 186101 (2011)

Cyclopentadienyl (anion)/Cu(111)

- Motion does not correspond to hopping on a Bravais lattice
- We have a non-Bravais lattice. In a perfect experiment:

$$I(\Delta K,t)=A_1\exp(-\alpha_1 t) \qquad I(\Delta K,t)=A_1\exp(-\alpha_1 t)+A_2\exp(-\alpha_2 t)$$



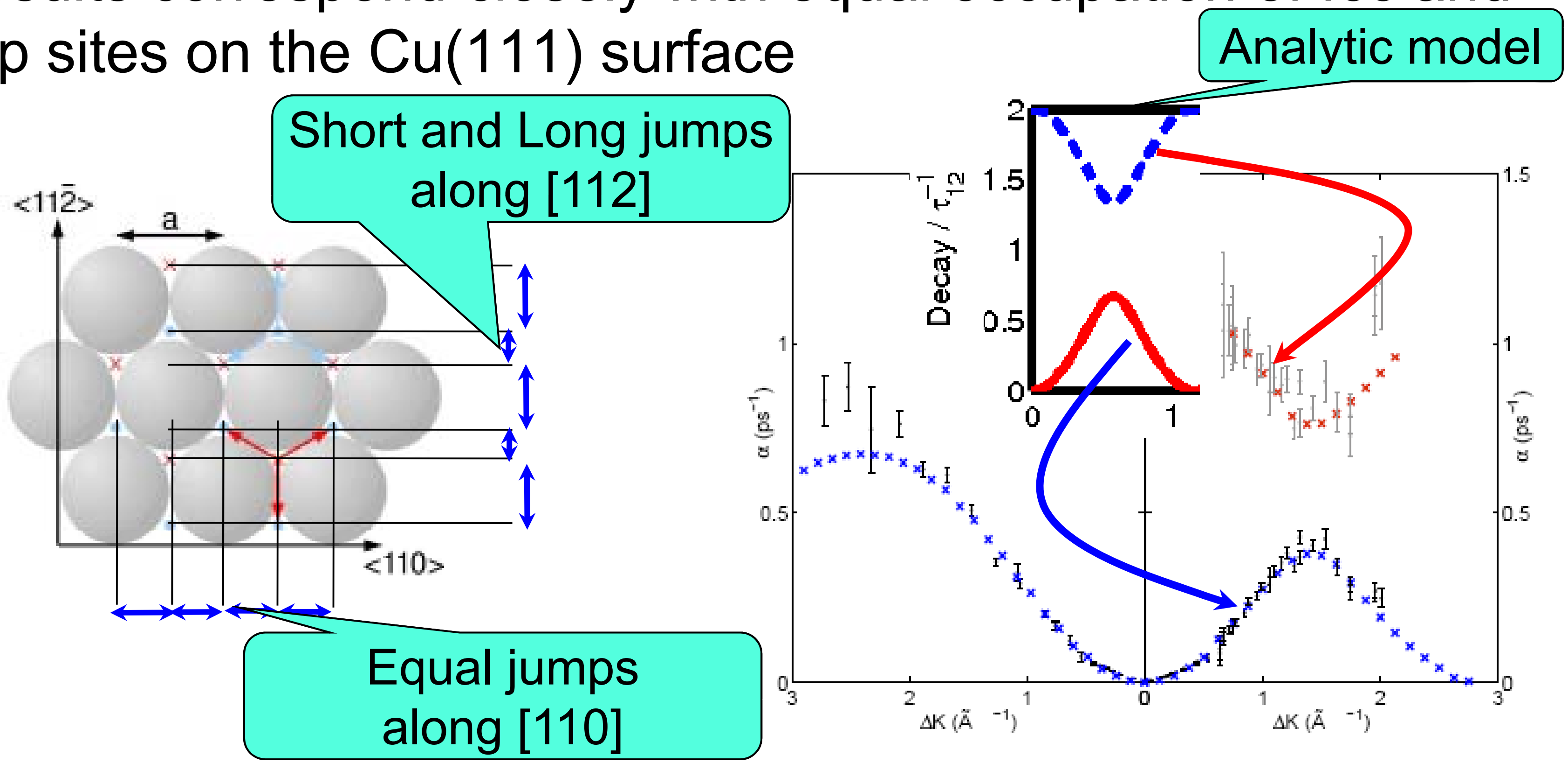
motion strongly activated

Single decay along [110]

Double decay along [112]

Structure from dynamics

- Periodicity in $\alpha(\Delta \mathbf{K})$ 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



Analytic model

Short and Long jumps along [112]

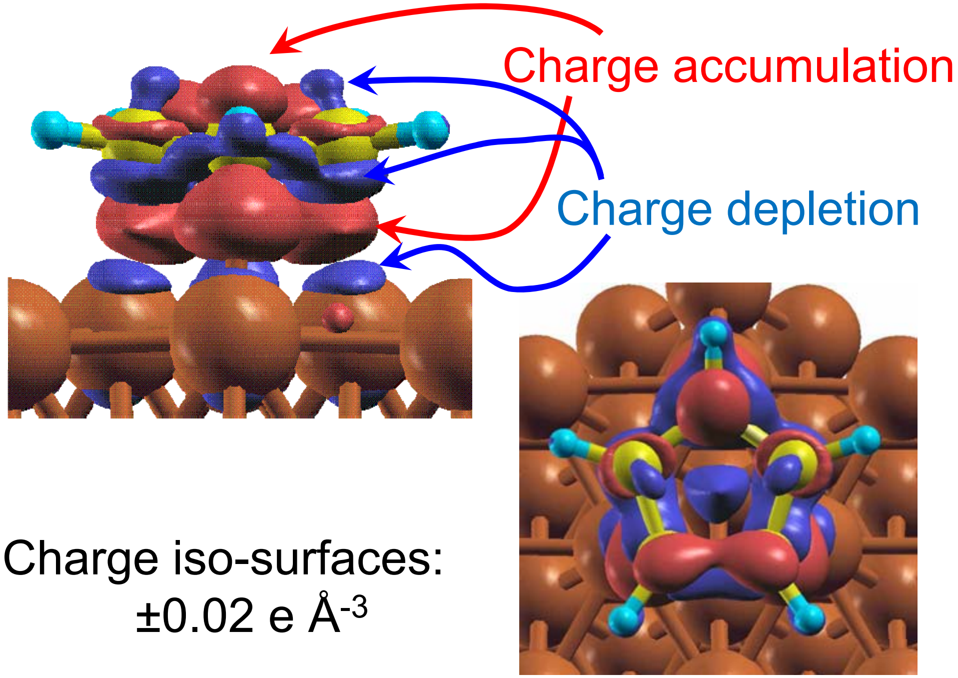
Equal jumps along [110]

Surf. Sci. **604**, 1459-1475 (2010)

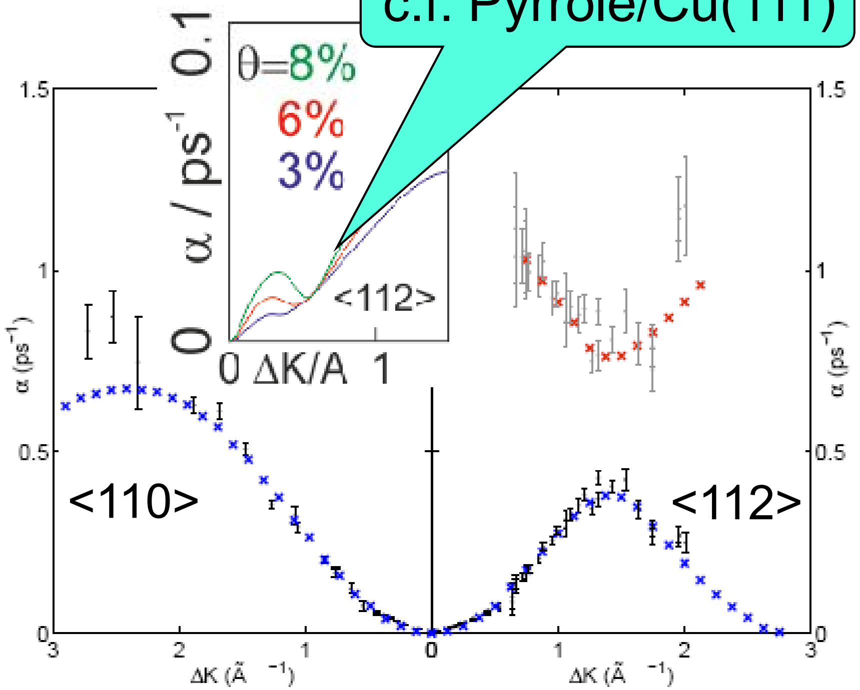
Phys. Rev. Lett. 106, 186101 (2011)

Friction and interactions

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



Charge iso-surfaces:
±0.02 e Å^{-3}

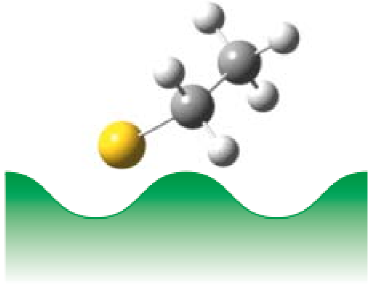


c.f. Pyrrole/Cu(111)

$\eta \sim 2\ \mathrm{ps}^{-1}$, cf $2.2\ \mathrm{ps}^{-1}$ for C_6H_6/ graphite

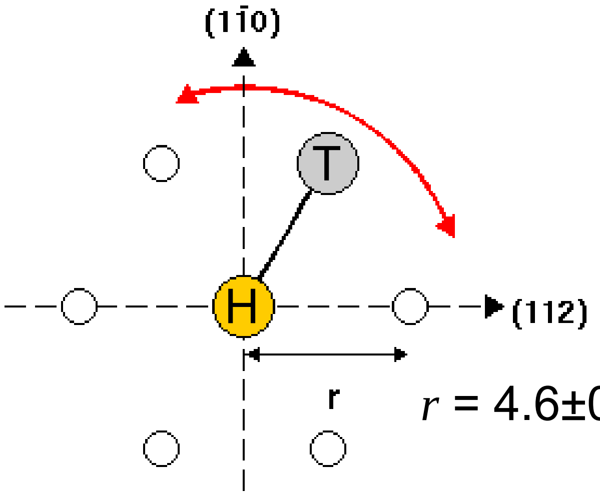
Molecules without a rotation axis

- Observation of diffusional rotation:
  - Dynamics of ethanethiol anion, CH_3CH_2S



Molecular translation and rotation

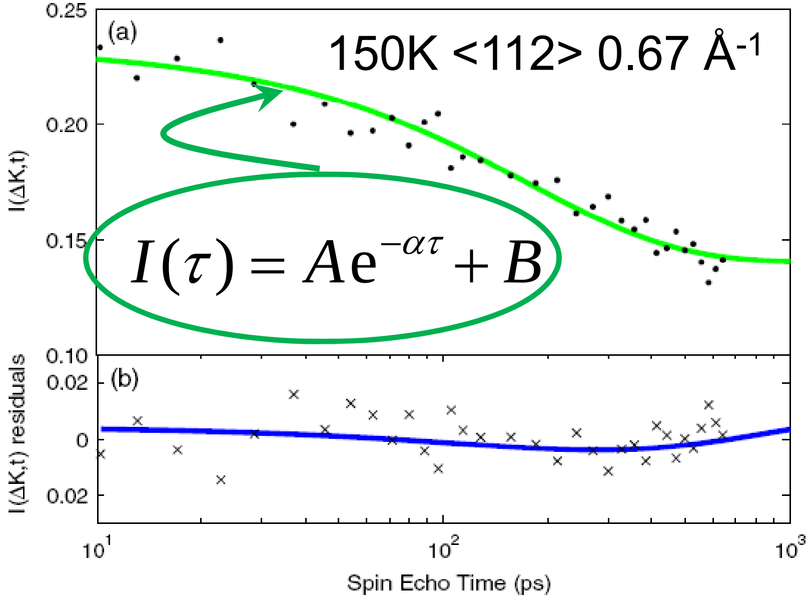
- What is the dynamical signature for rotation?
  - Confined motion (unlike translational diffusion)
    - *Correlation does not go to zero* (in pure rotational hopping)



r = 4.6±0.3Å

$$I_{11\bar{2}}(\underline{\Delta K},\tau)=C_1\,e^{-\beta\tau}+C_2\,e^{-3\beta\tau}+C_3\,e^{-4\beta\tau}+C_4$$

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



150K <112> 0.67 Å^{-1}

$$I(\tau)=Ae^{-\alpha\tau}+B$$

- With uncorrelated translation

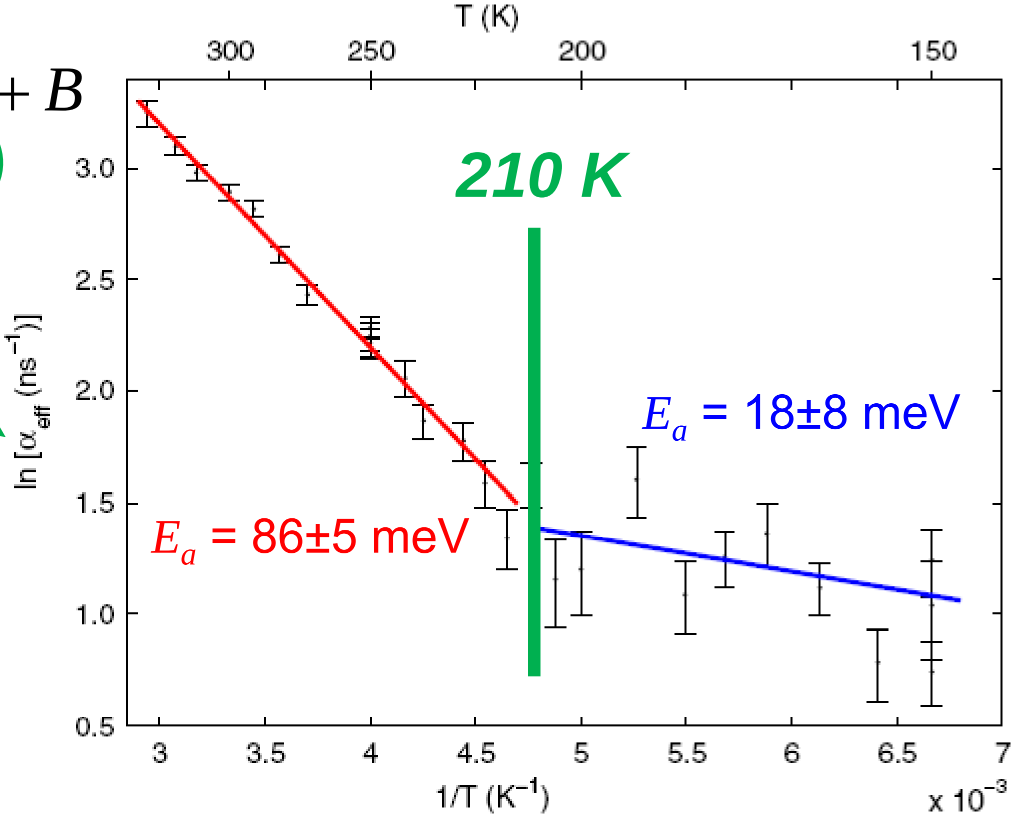
$$I_{Tot}(\underline{\Delta K},\tau)=I_{Rot}(\underline{\Delta K},\tau).I_{Transl}(\underline{\Delta K},\tau)$$

Phys Rev Lett **106**, 256101 (2011)

Temperature dependence

- Temperature dependence of the effective dephasing rate

$$I(\tau) = A\mathrm{e}^{-\alpha\tau} + B$$

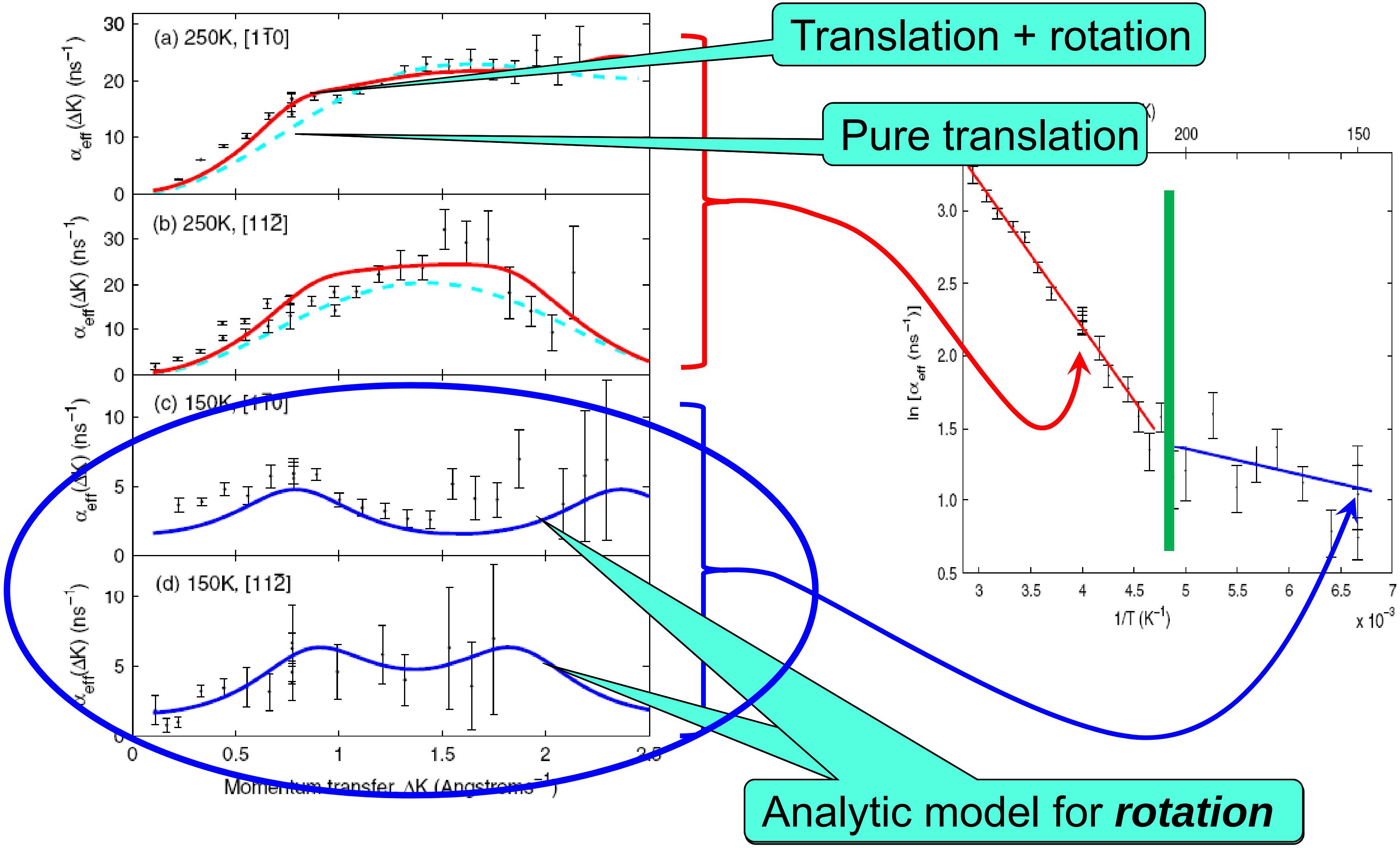


ΔK = 0.47 Å^{-1},
<112>

- Break in slope accompanies a change in ΔK dependence

Dynamical signatures

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



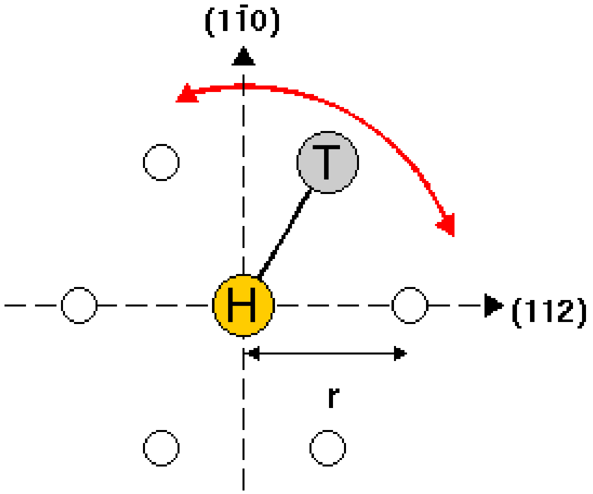
Translation + rotation

Pure translation

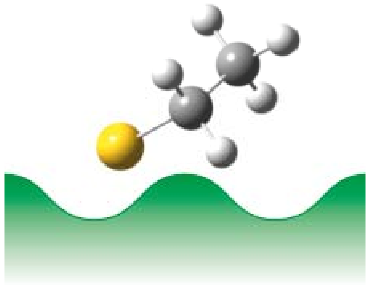
Analytic model for ***rotation***

Ethanethiolate/Cu(111)

- 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*.



r = 4.6±0.3Å

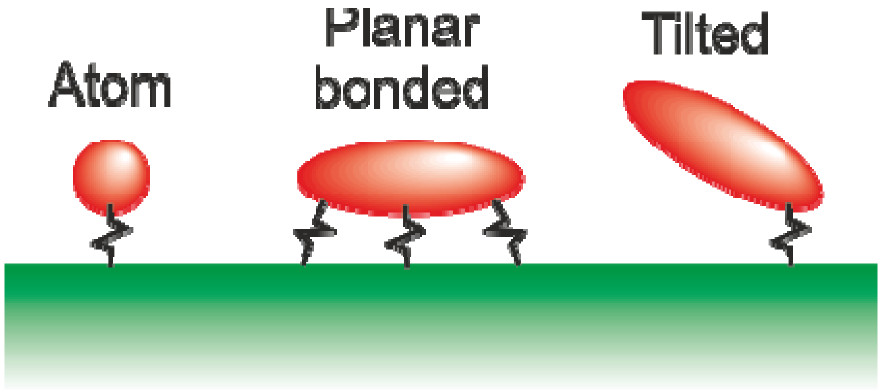


Dissipation in molecular systems

- *Kinetic friction in the Langevin model*.

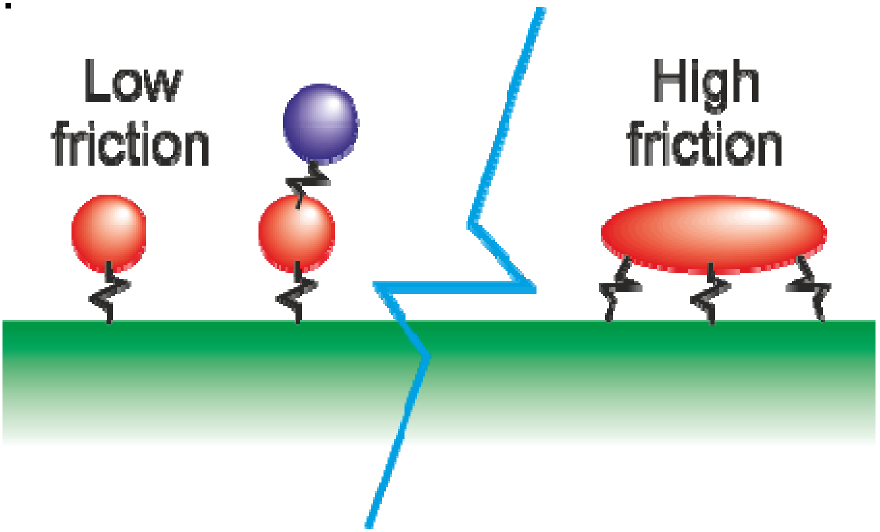
$$m\ddot{\mathbf{r}}_j = -\nabla V(x,y) - \boxed{\eta}\; m\dot{\mathbf{r}}_j + \xi_j(t) + \sum_{i\neq j} F_{i,j}$$

- It measures the disruption to ballistic motion generated by “other coordinates”.
- What factors determine η?
  - Strength of the adsorbate-substrate bond.
  - Magnitude of the corrugation in the energy landscape (static friction).
  - Size/contact area etc.....

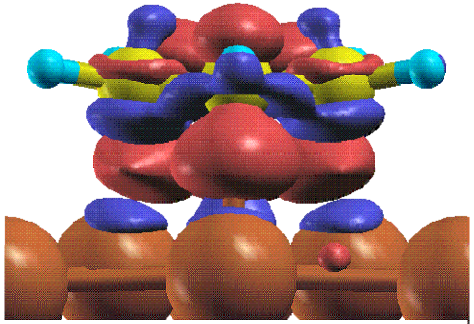


Factors affecting dissipation

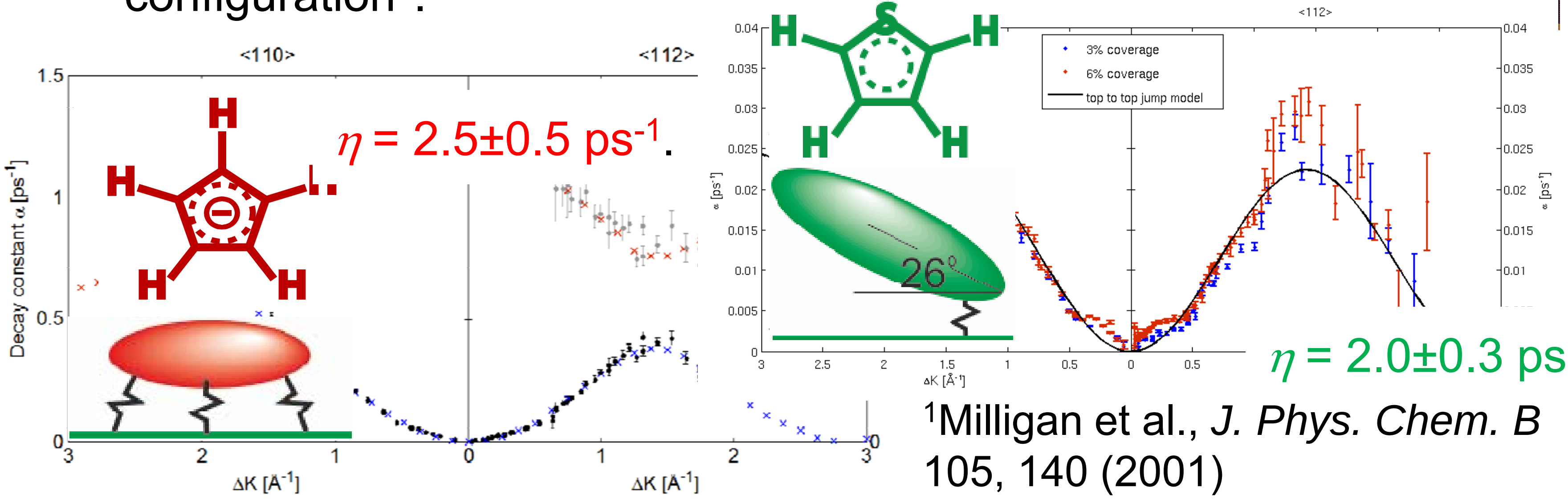
- Atoms and small molecules:
  - eg: Na, CO etc typically have $\eta \leq 0.5$ ps^{-1}.
- Larger molecules: typically have bigger $\eta \sim 2$ ps^{-1}.
  - Substrate properties and adsorbate-substrate bonding seem unimportant
  - c.f. Benzene/Graphite and Cp$^-$/Cu(111), where η is similar but other factors are not.



Thiophene vs cp$^-$ on Cu(111)



- Both 5-fold rings
  - Cp$^-$ in *hollow sites* interacts with several substrate atoms.
  - Thiophene: *top site* adsorption in tilted configuration[1].



η = 2.5±0.5 ps^{-1}.

η = 2.0±0.3 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)

Summary

- 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