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Friction measurements in the single-molecule limit

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Friction measurements in the single-molecule limit

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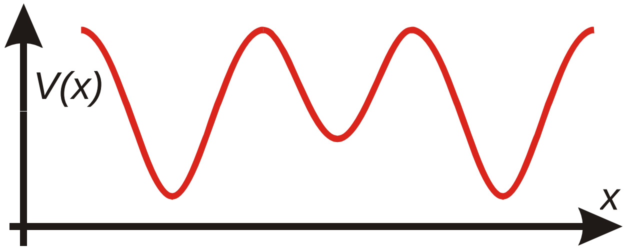
Co-workers:

- Cambridge (Expt/simulation): J Ellis, AP Jardine, H Hedgeland, AR Alderwick, D Ward, B Lechner, F Tuddenham.
- Tel Aviv (Expt): G Alexandrowicz
- Grenoble (Neutron spin-echo): P Fouquet
- Milano (Calculation): GP Brivio, G Fratesi (Alkali adsorption)
- Genova (Theory): R Ferrando (CO/Pt(111))
- Rutgers (Expt): BJ Hinch (Cp^-/Cu(111))

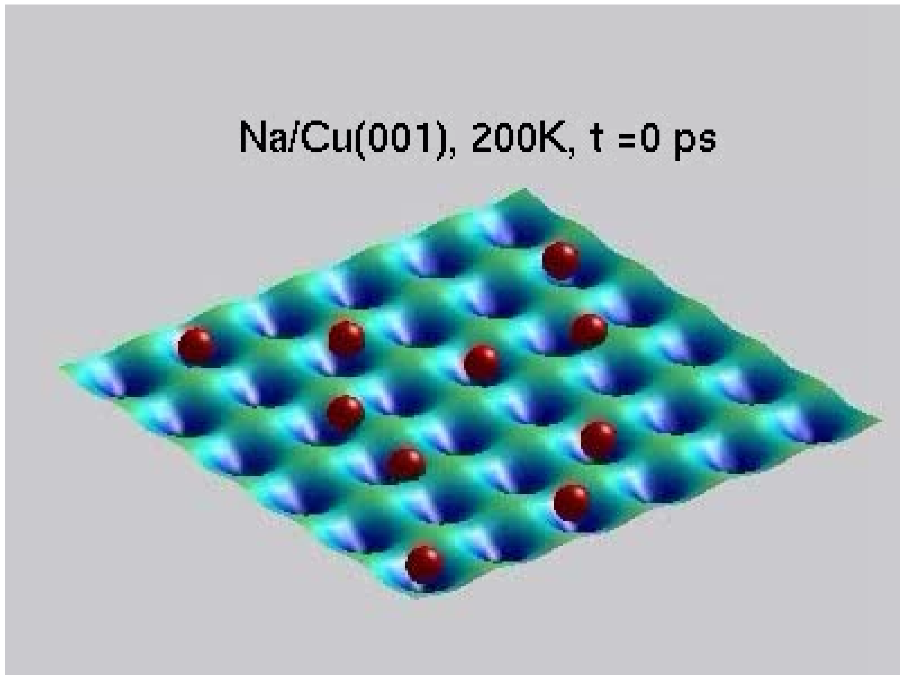
Friction from adsorbate dynamics

- Motion induced by thermal excitation
  - Modelled as “Adsorbate plus heat bath”
  - Langevin equation:

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

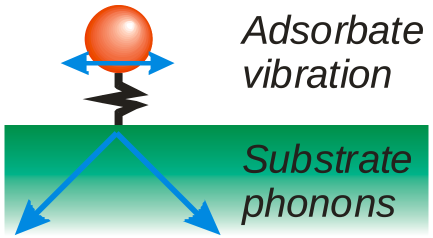


- Three aspects to the motion:
  - Energy Landscape
    - *STATIC FRICTION*.
  - Atomic scale friction
    - *KINETIC FRICTION*.
  - Interactions
    - *Co-operative effects*.



Landscape and kinetic friction

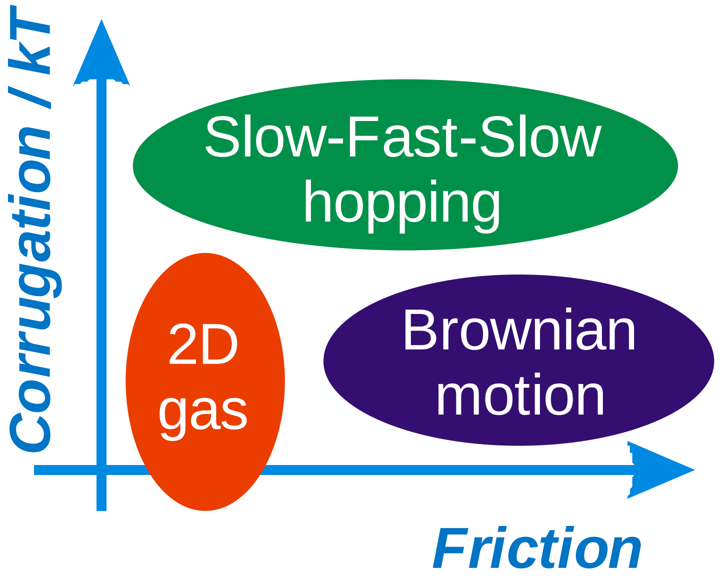
- Connection through frustrated translation.
  - Vibrational damping[1].

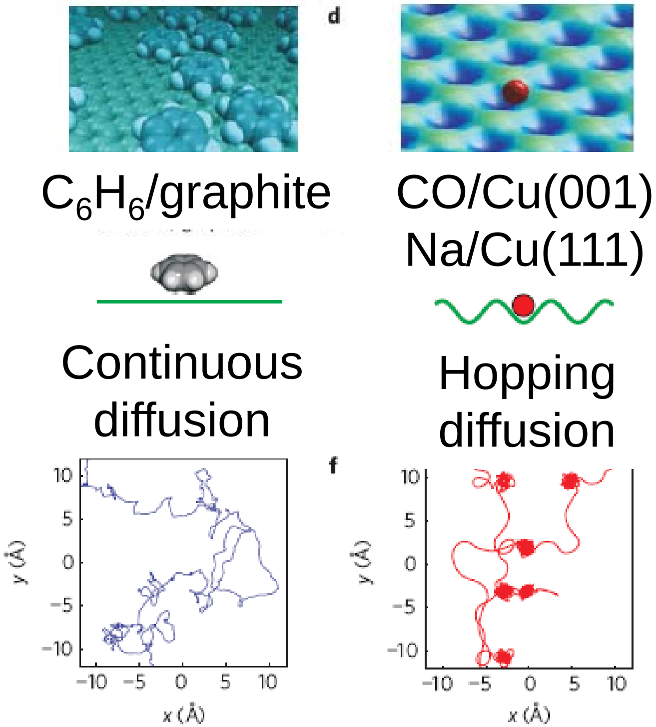


$$\eta = \kappa \frac{\omega_o^4}{c_T^3}$$

[1]Persson, Tosatti, Fuhrmann, Witte, Wöll PRB **59** 11777 (1999)

- Dynamic regimes:



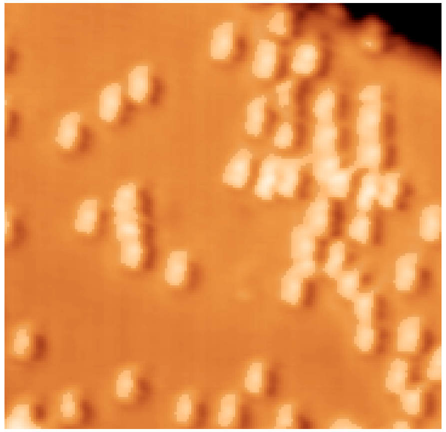


Measurements

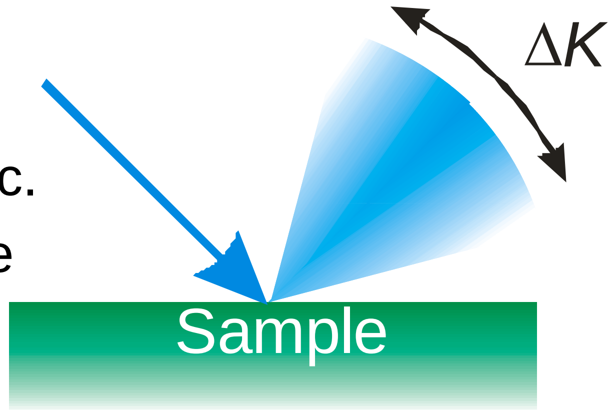
- Response
  - Microscopy – ***snapshots***.
    - Typically long time-scales
      > ~1 msec

CO/Cu(111)

Bartels et al. JCP **123** 201102 (2005)

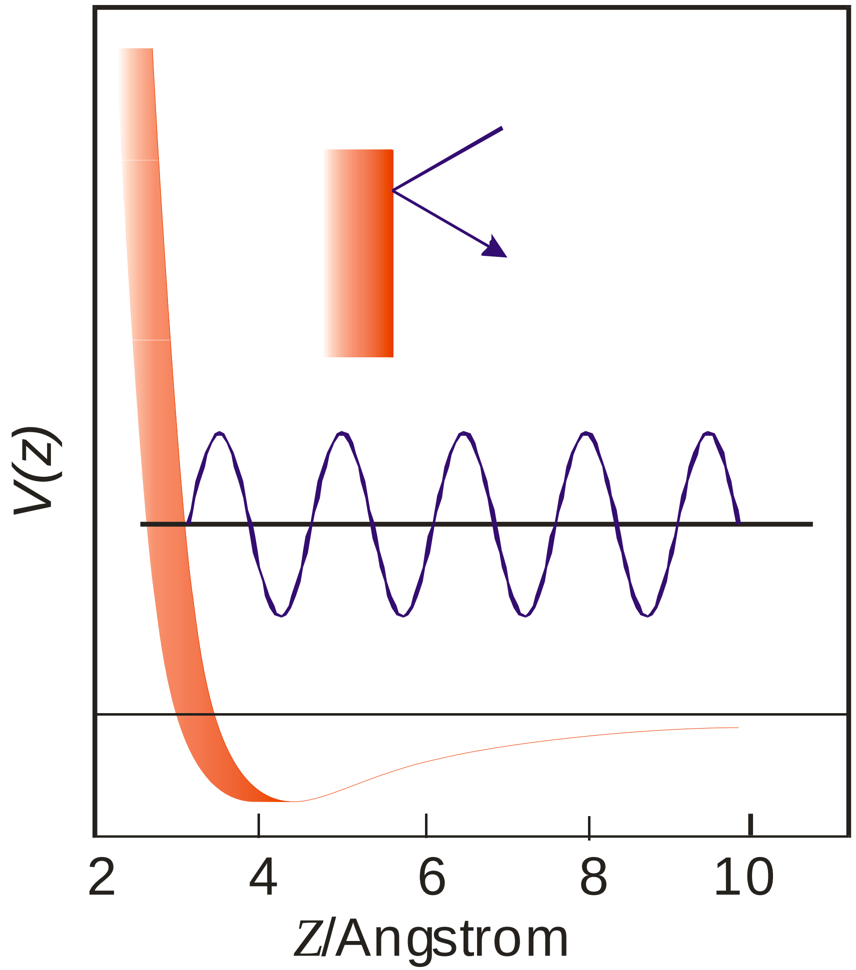


  - Scattering – ***correlations***.
    - *TIME :* Spin-echo method gives access between pico-sec and nano-sec.
    - *SPACE:* Through angular dependence of scattering, typically >~ 1Å



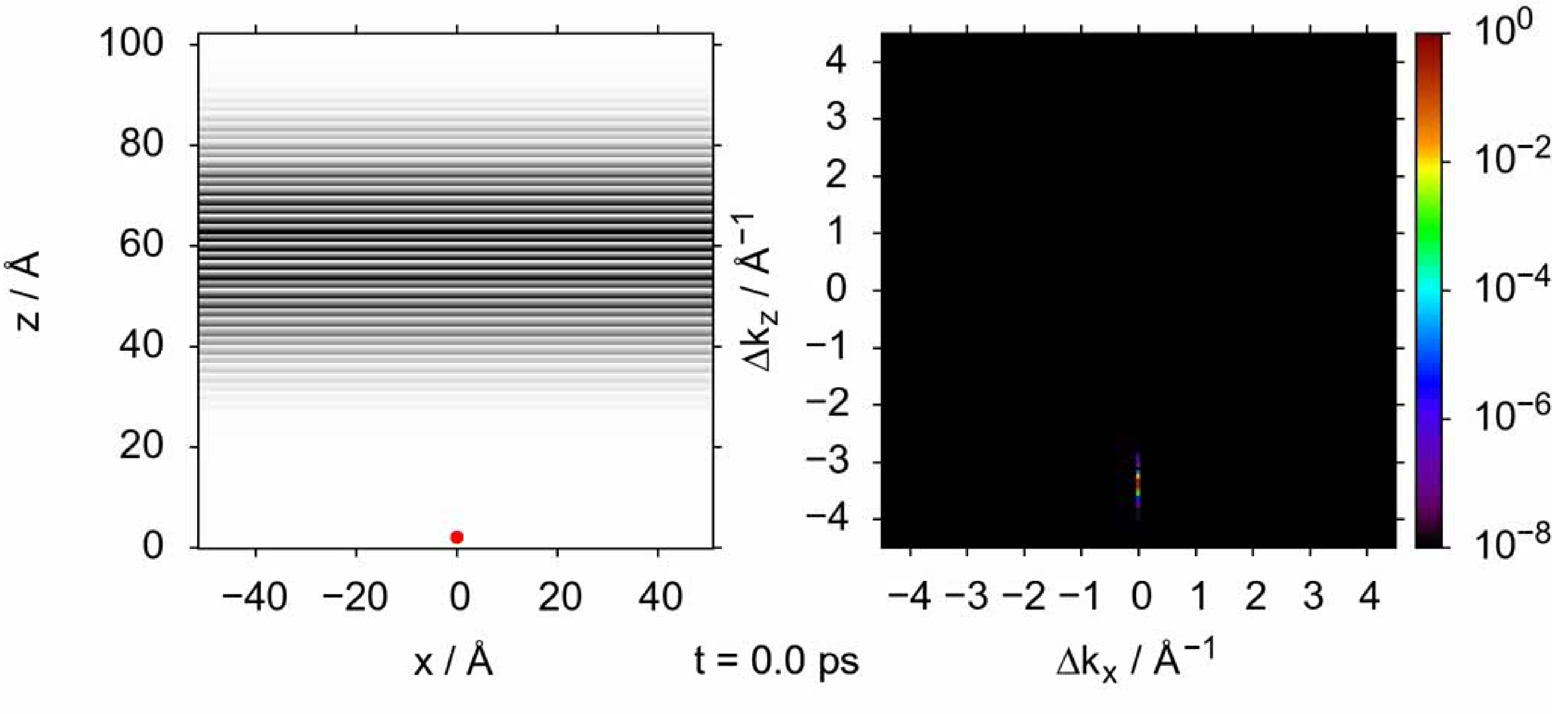
Interaction at thermal energies

- Helium-surface interaction
  - Classic *van der Waals* form
  - Well-depth <10meV
  - Incident energy <50meV
- Collision time
  - ~ a few pico-seconds



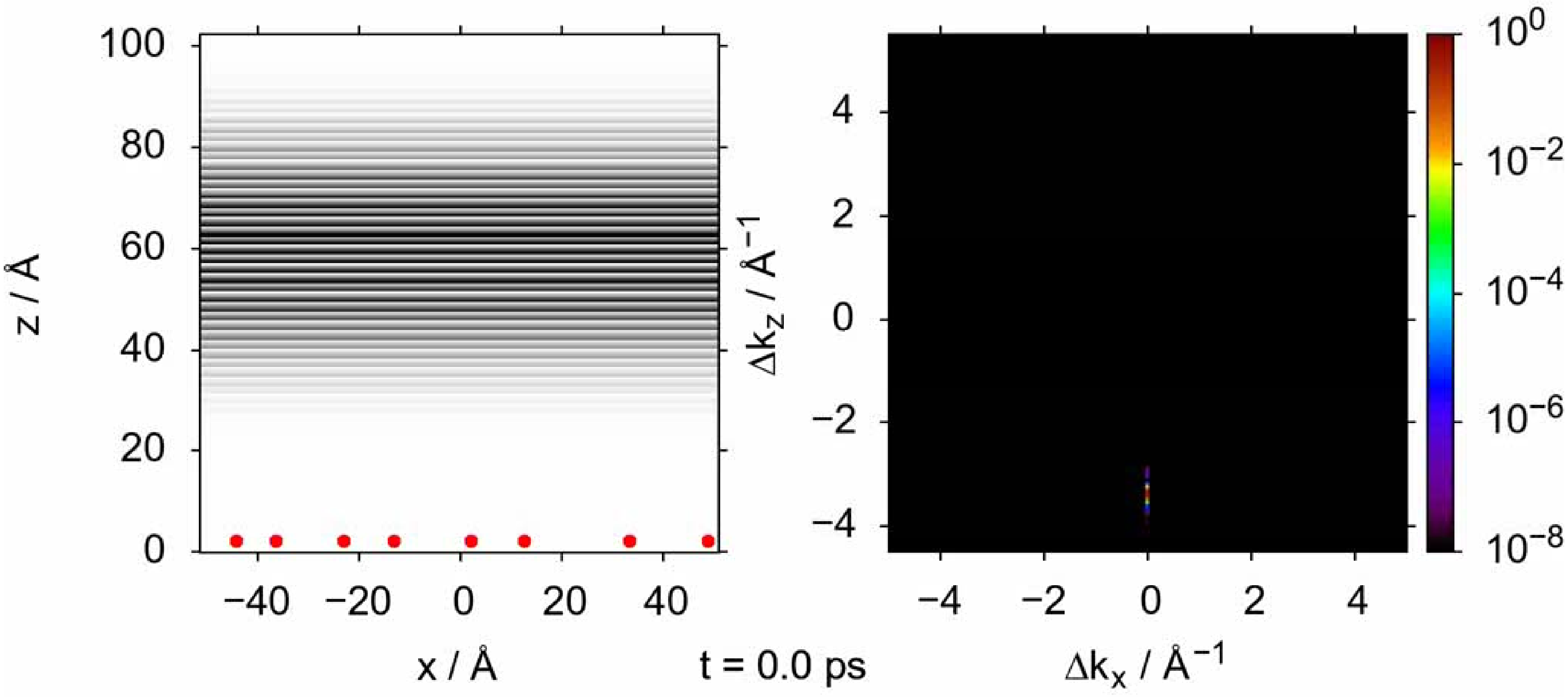
Elastic scattering

- Static target with a single adsorbate



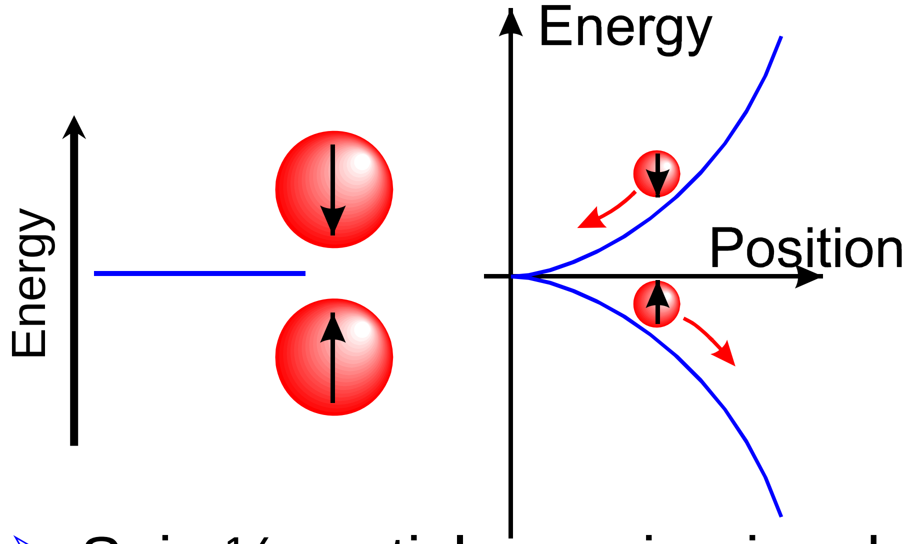
Quasi-elastic scattering

- Surface with several moving atoms

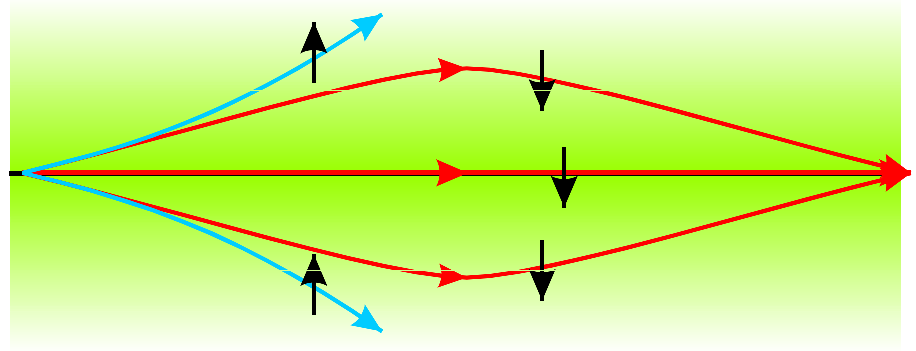


Spin-echo experiment

- Spin ½ particle in an inhomogenous magnetic field.

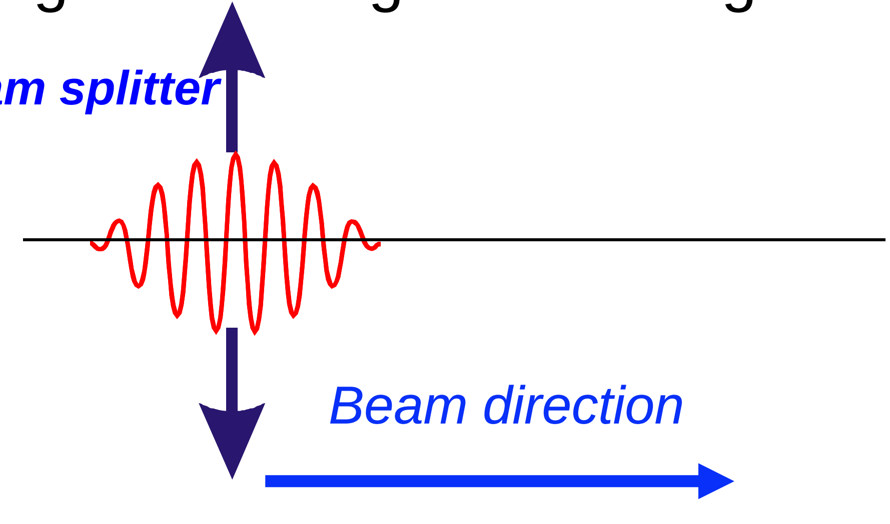


A polariser and atom-lens



- Spin ½ particle moving in a homogeneous magnetic field.

A time-shifting, beam splitter



Rev Sci Inst.
76 053109 (2005)
75 1963 (2004)
72 3834 (2001)

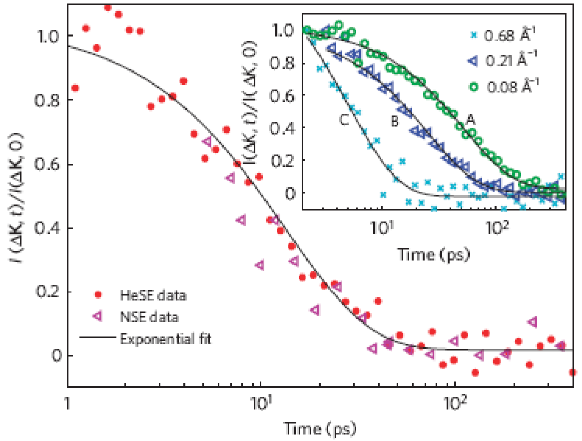
Intermediate scattering function

- The spin-echo method gives the ISF
  - It is a measure of decay, with time, of the structural correlation at the surface.
    - Temporal correlation is measured directly
    - Spatial correlation measured (indirectly) through the dependence on ΔK.
- For Brownian motion:

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

Single exponential

Diffusion const

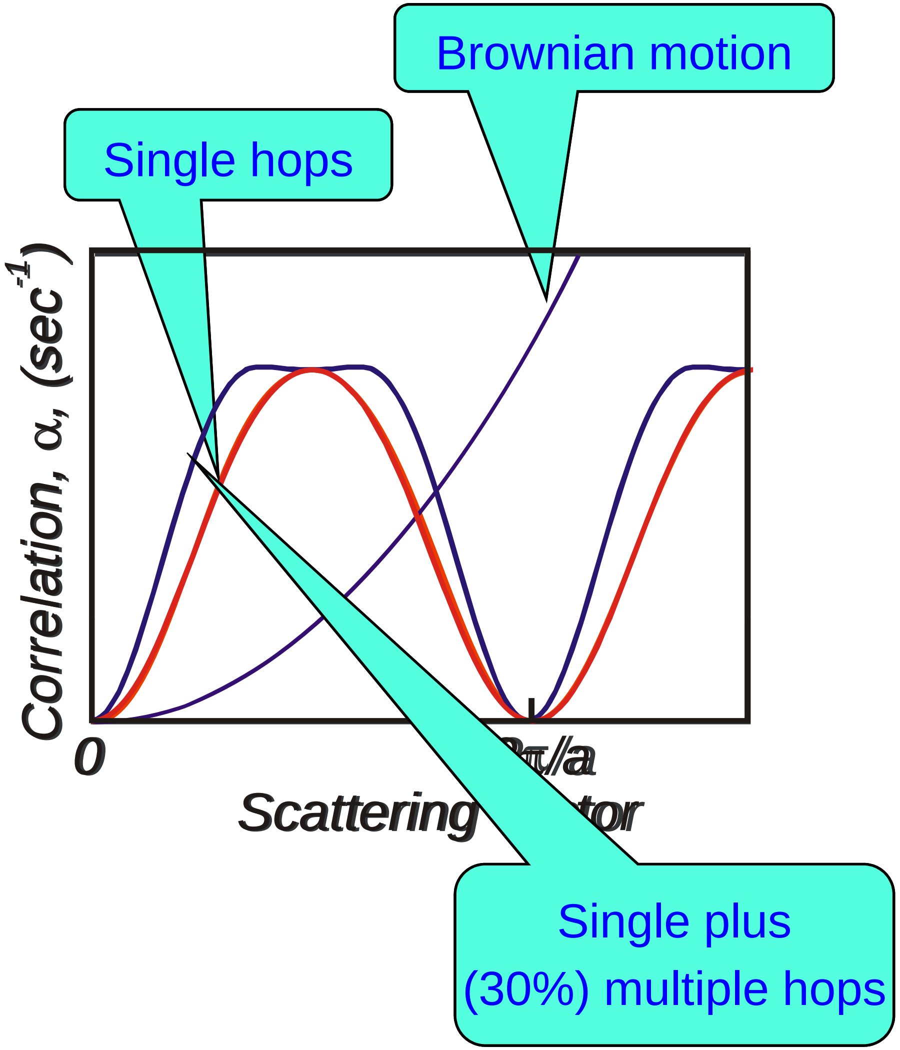


Analytic models - jump dynamics

- Decay rate of the correlation has an analytic form for simple dynamics.

$$\alpha(\mathbf{K}) \propto \nu \sum P_j \sin^2\left(\frac{\mathbf{K}.\mathbf{r}_j}{2}\right)$$

- Such behaviour is only observed for independent particles (typically at low coverage).
- The “shape” changes drastically, with coverage, if cooperative motion occurs (eg: repulsive, pairwise forces)



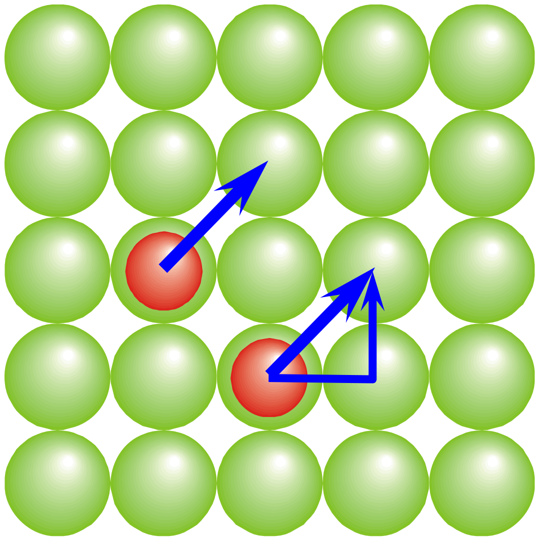
Chudley and Elliot Proc Roy Soc 77 (1961)

Case studies

- Landscape (static friction)
  - CO/Cu(001) at low coverage.
- Intermolecular forces
  - Do repulsive interactions inevitably result in pairwise forces?
  - Comparison of Na/Cu(001) and CO/Pt(111).
- Kinetic friction
  - Friction in weak and strongly chemisorbed molecular systems;
  - Comparison of C_6H_6/Graphite and $C_5H_5^-$/Cu(111).

Landscape (Static friction)

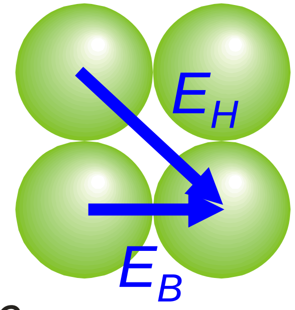
- CO/Cu(001):
  an early measurement to determine the energy landscape

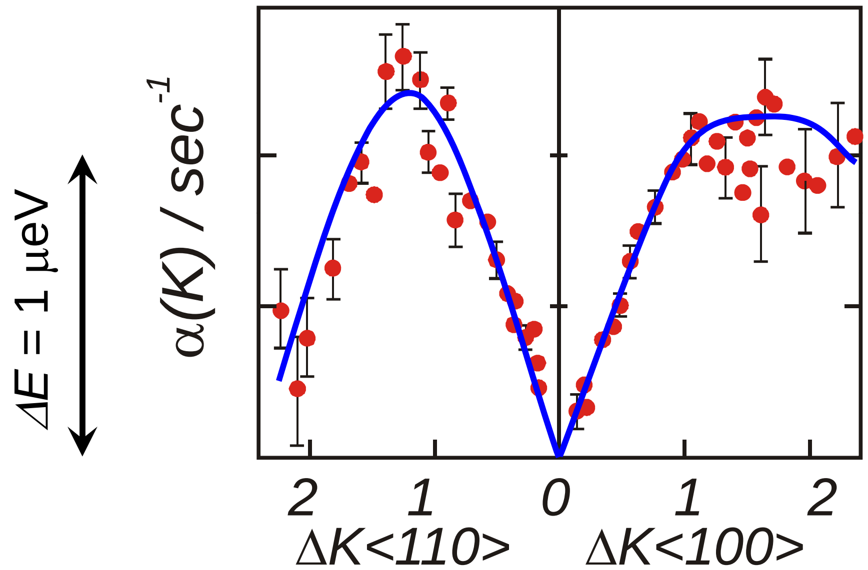


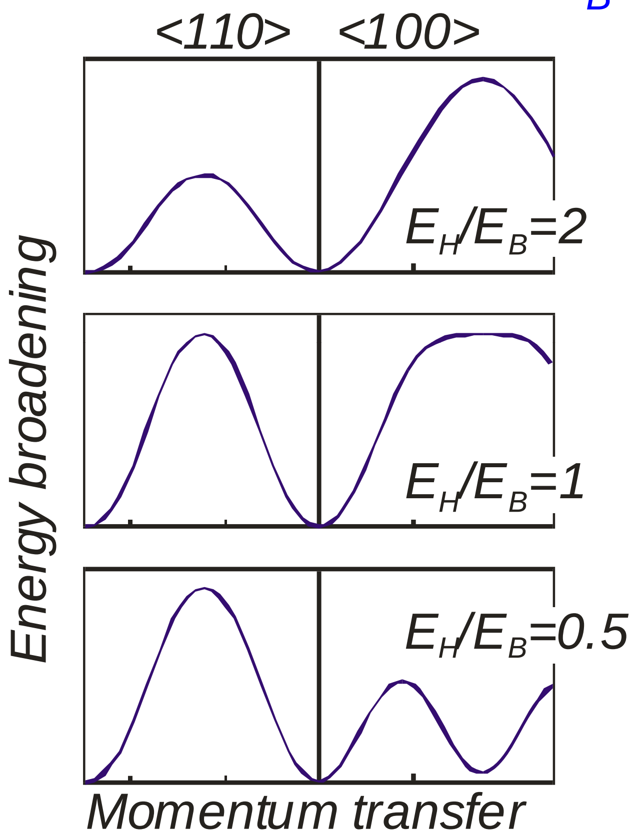
Science **<u>304</u> 1790** (2004)

Energy Landscape – CO / Cu(001)

- Similar broadening along <110> and <100>.
- Analytic picture gives similar barriers.
- Confirmed by full MD-simulation.



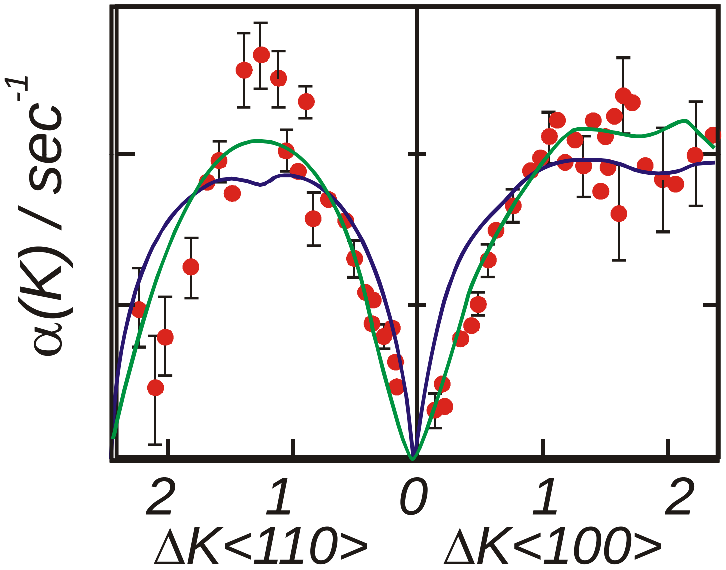




Phys. Rev. Lett. **93** **156103** (2004)

Friction / dimensionality

- Full MD simulations confirm the landscape
- Friction:
  - Best “fit” to hopping rate has kinetic friction η = (1/2) ps^{-1} (Scaling needed)
  - Best “fit” allowing friction to vary: $\eta = 1/(\ldots)$ = (1/13) ps^{-1}.



- Fewer long jumps observed.

- Either:
  - Friction is position dependent,

    OR
  - Molecular degrees of freedom are involved in the dynamics.

η = (1/8) ps^{-1} from the T-mode linewidth. (Graham et al *JCP* **104** (1996) 5311)

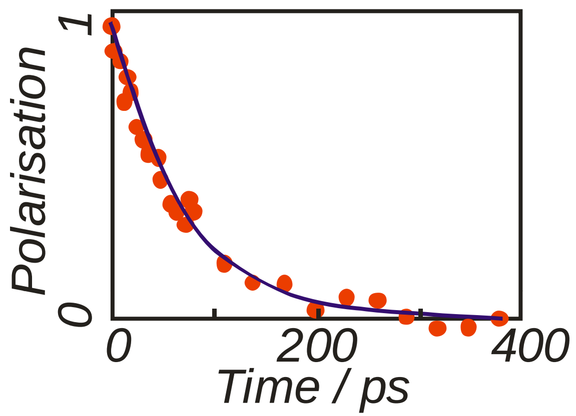
Adsorbate interactions

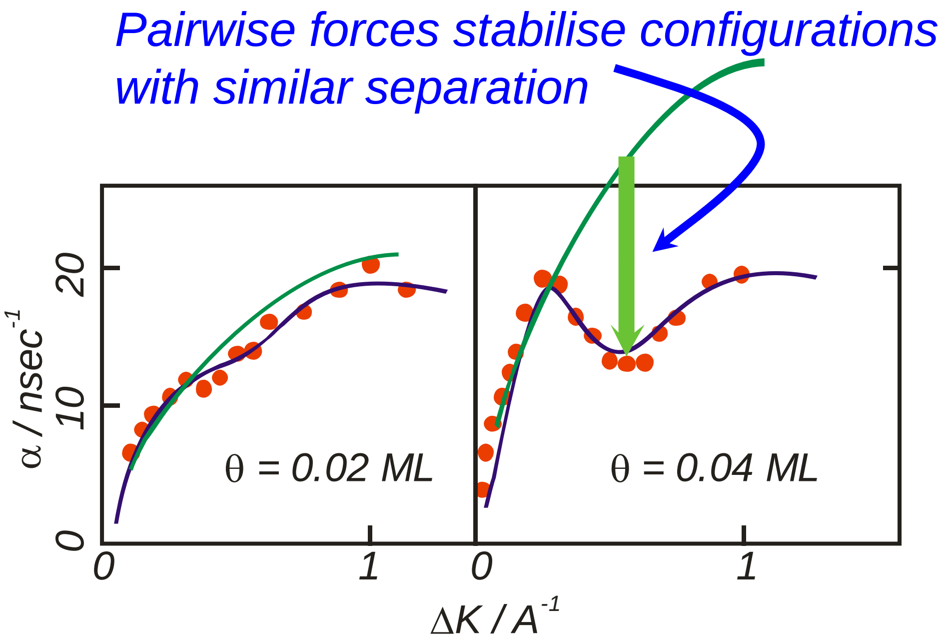
- Pairwise forces

Na/Cu(001)	CO/Pt(111)
Heat of adsorption very strongly coverage dependent.	Heat of adsorption decreases strongly with coverage.
Strong dipole repulsion.	Attributed to pairwise forces (Consensus on the origin or magnitude of these forces is absent)

Alkali metal dynamics: Na/Cu(001)

- Low coverage data gives the landscape, as before.
- Medium coverage data shows the effect of interactions.
- Typically the polarisation follows an exponential decay at low and moderate coverage (but not at high coverage)

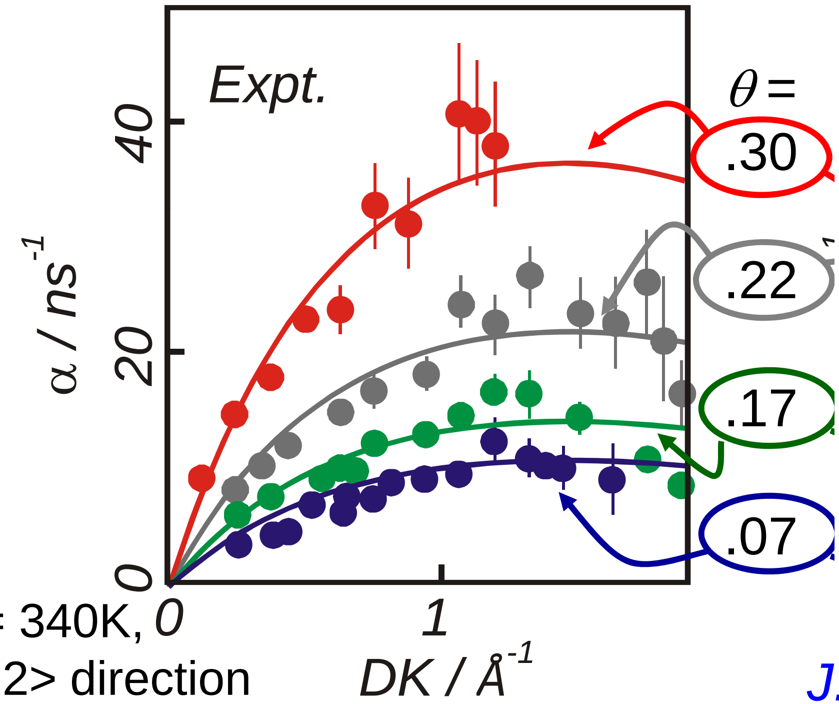




Phys. Rev. Lett. **97** 156103 (2006)

CO interactions: CO/Pt(111)

- *Uncorrelated motion* with strongly interacting adsorbates *!*
  - Hopping rate increases with coverage, but with fixed K-dependence.
- No force law (eg ~1/r^3) can simultaneously explain heat of adsorption and the dynamics. See simulation
  - Pairwise interactions ~1/10 of the expected magnitude.



T_s = 340K,
<112> direction

J. Am. Chem. Soc. **130** (2008) 6789

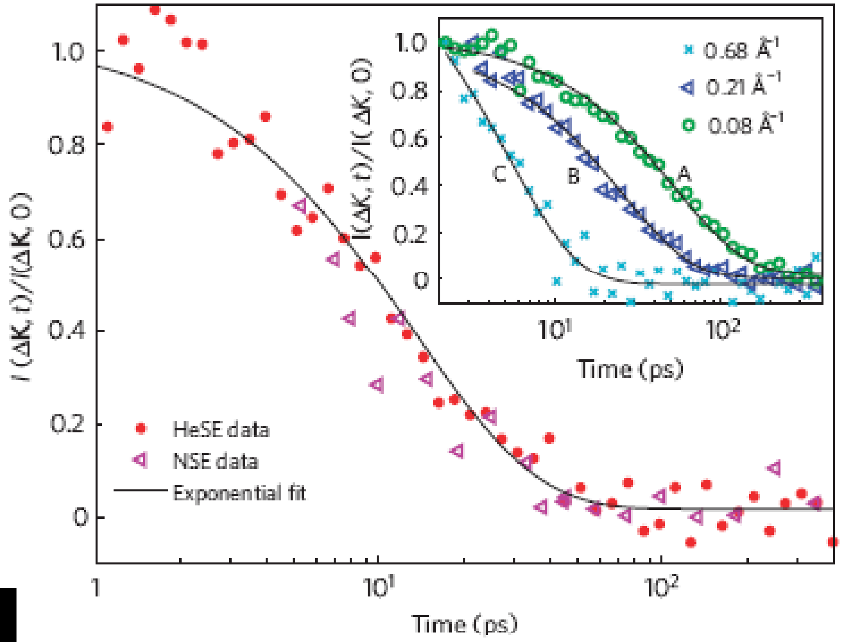
Kinetic friction

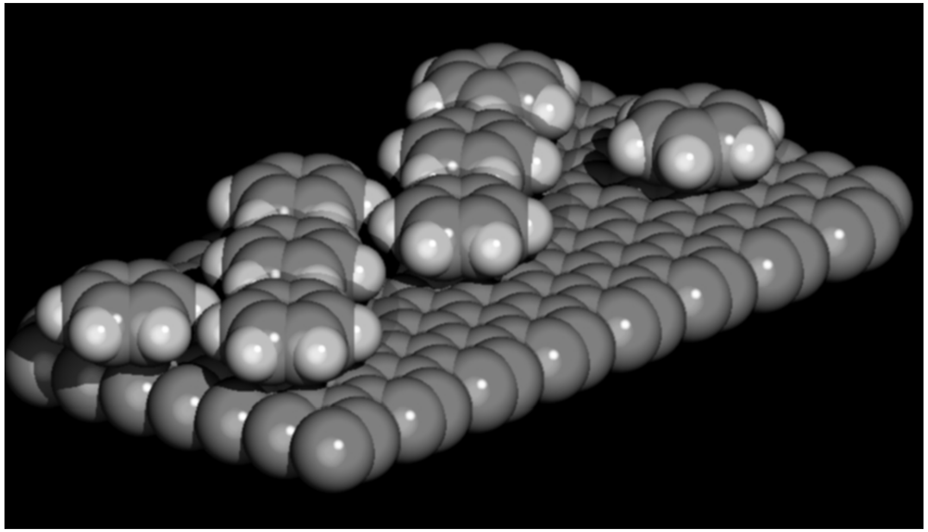
- *Kinetic friction in molecular systems*.

- What factors determine the kinetic friction?
  - Strength of the adsorbate-substrate bond.
  - Magnitude of the corrugation in the energy landscape (static friction)

Nano-scale friction

- Single-molecule friction
  - Benzene on graphite
- Special features
  - Negligible corrugation
    - Arrenhius plot
  - Strong friction
    - Brownian motion





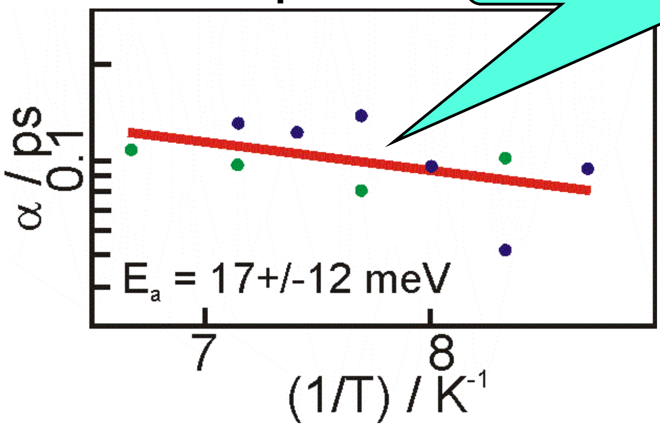
Coverage = 0.5ML
Temperature 140K

Nature. Phys. (2009)
doi: 10.1038/NPHYS1335

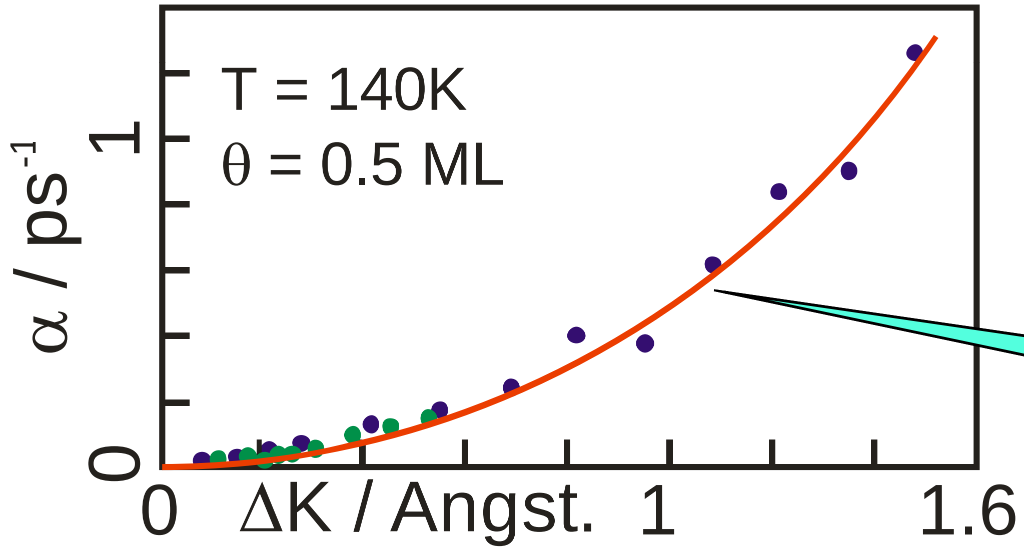
Benzene on graphite

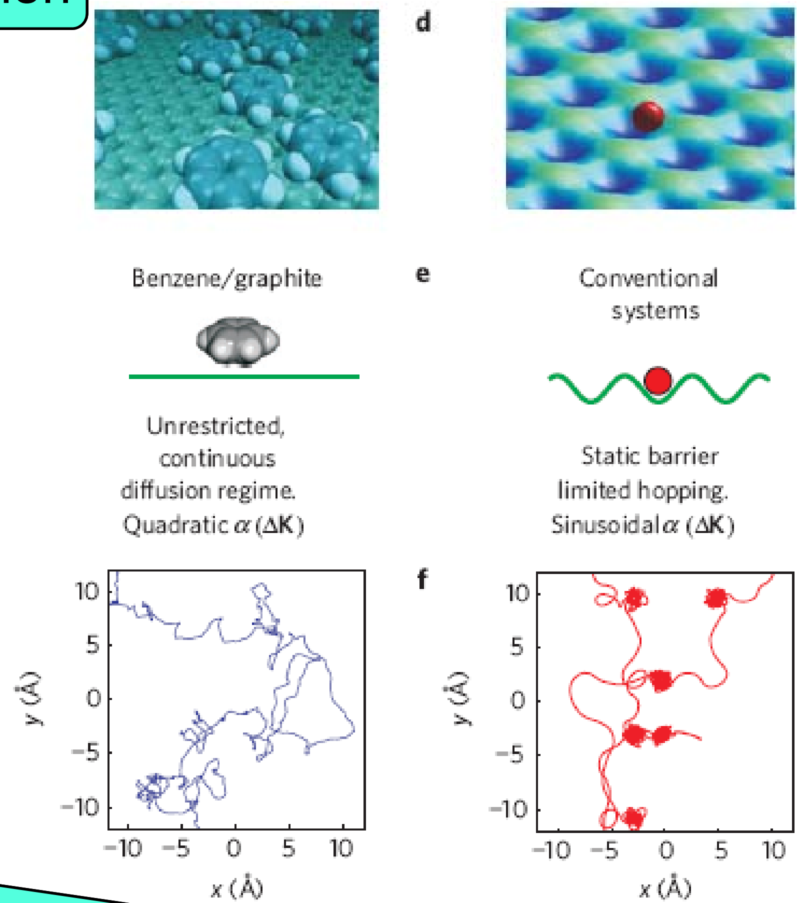
- Arrenhius plot

motion lacks activation



- Perfect Brownian motion $\alpha = \Delta K^2$.





η = 2.8 ps^{-1} with collisions
η = 2.2 ps^{-1} without collisions

Summary

- The helium spin-echo method:
  - Uniquely sensitive to surface motion for pico-sec to nano-sec regime.
  - Static and dynamic effects in simple, well characterised systems can be measured precisely.
  - Pairwise forces between adsorbates are not necessarily obvious.
  - Strong friction seen in an weakly adsorbed, un-corrugated system:
    - C_6H_6/graphite.
  - Similar friction in a strongly adsorbed, corrugated system:
    - C_5H_5-/Cu(111).

Recent perspective article:
PCCP. **11** (2009) 3355

- Open questions:
  - Molecular origin of friction – white noise approximation
  - Role of internal, molecular, degrees of freedom (CO/Cu(001))
  - etc................

THE END