The role of phonons

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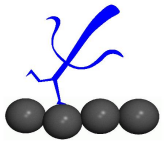
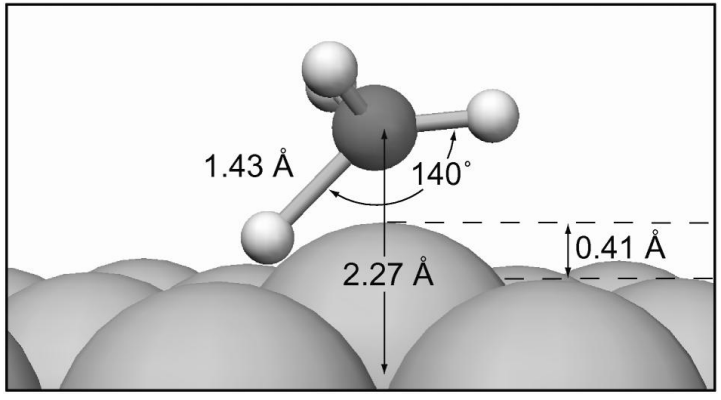
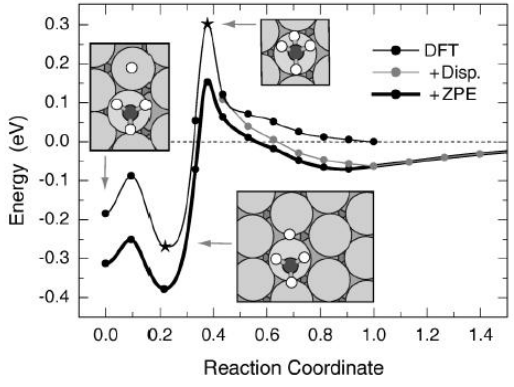
Dynamics of molecule-surface reactions
Universiteit Leiden, Nov 24-25, 2011



"Active" role

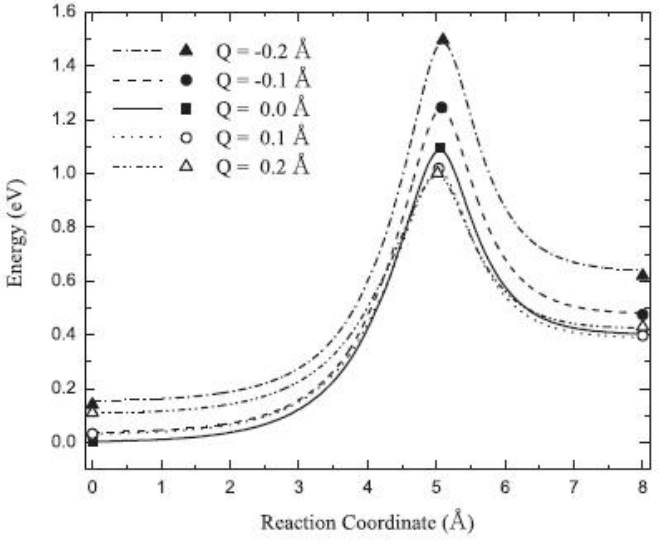
CH_4 on Ir(111)





G. Henkelman and H. Jonsson, *Phys. Rev. Lett.* **86**, 664 (2001)

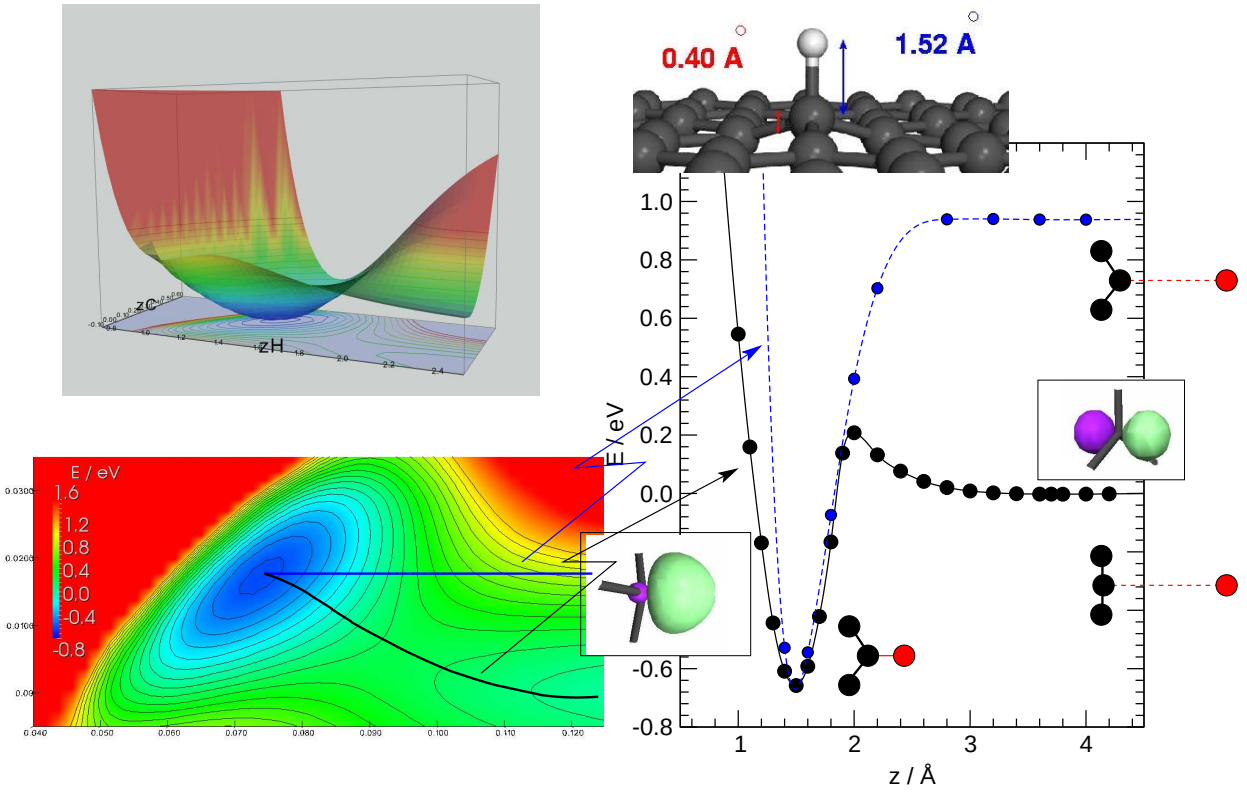
CH_4 on Ni(100)



S. Nave and B. Jackson,
Phys. Rev. Lett. **98**, 173003 (2007)

“Active” role

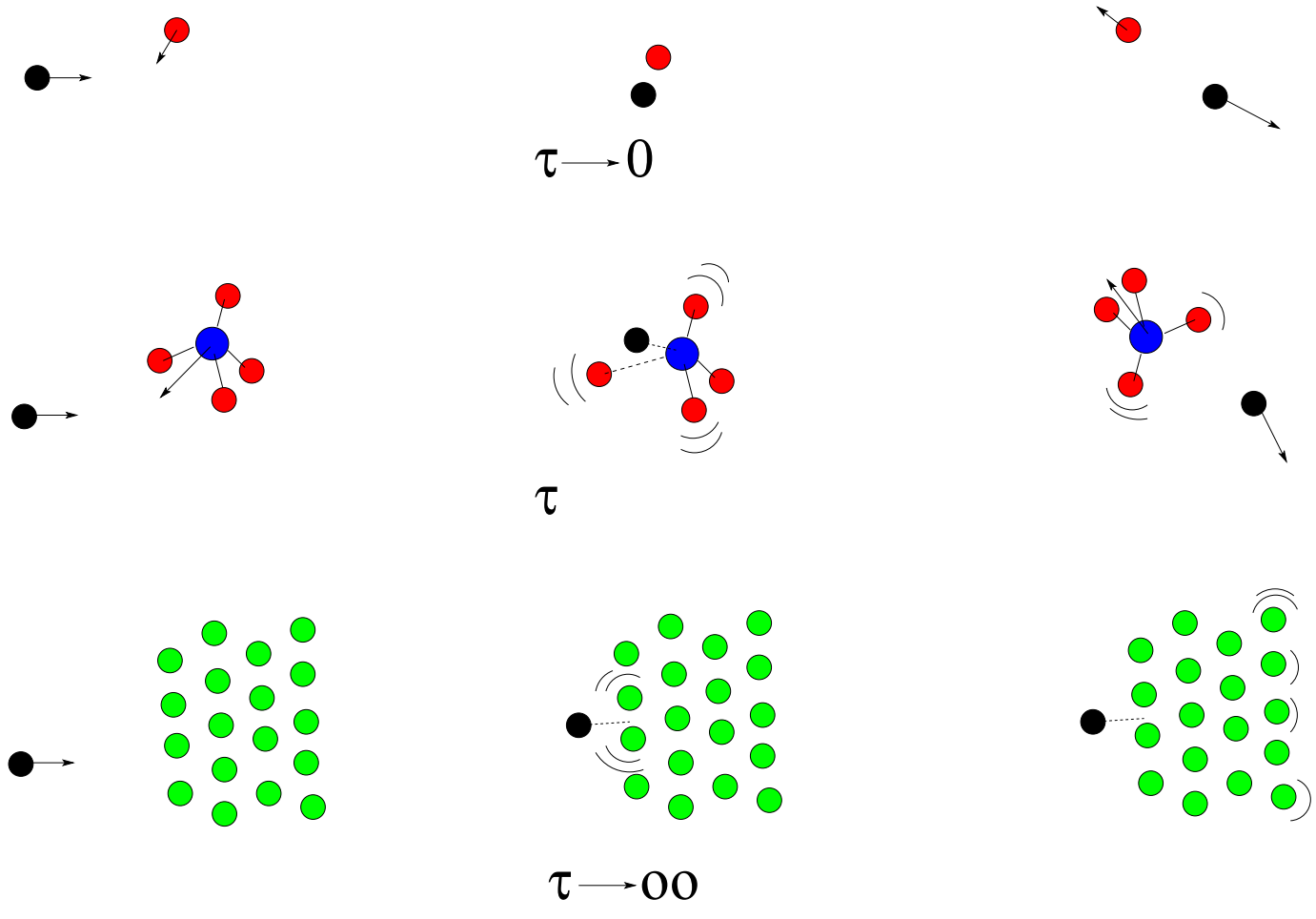
H adsorption on graphene(ite)



L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

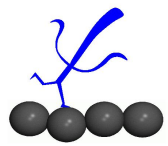
“Passive” role

Sticking of simple atoms



Outline

1. Basics
   - Linear chain model
   - Scattering from real surfaces
2. Reduced dynamical models
   - Traditional models
   - System-bath models
3. Dynamics
   - The methods
   - Examples



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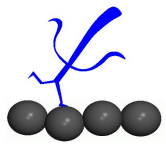

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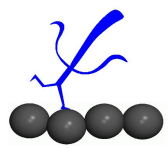

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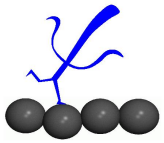
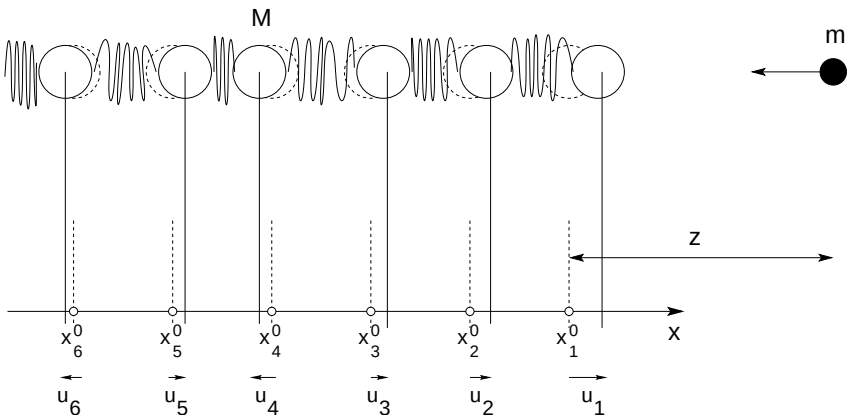
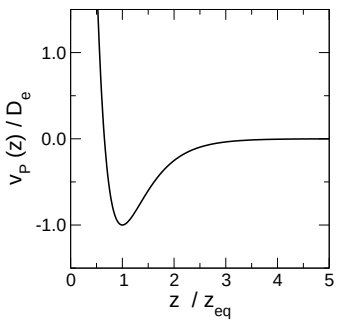


Scattering from a linear chain





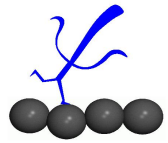
.. a simple model:

$z =$ height of the projectile,
$u_i = x_n - x_n^0 =$ n-th atom displacement

$$H = \frac{p_z^2}{2m} + v_P(z - u_1) + \sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2M} + \frac{M\Omega^2}{2}(u_{n+1} - u_n)^2 \right\}$$

$$\dot{z} = \frac{\partial H}{\partial p_z}, \dot{p_z} = -\frac{\partial H}{\partial z}$$

$$\dot{u_n} = \frac{\partial H}{\partial p_n}, \dot{p_n} = -\frac{\partial H}{\partial u_n}$$



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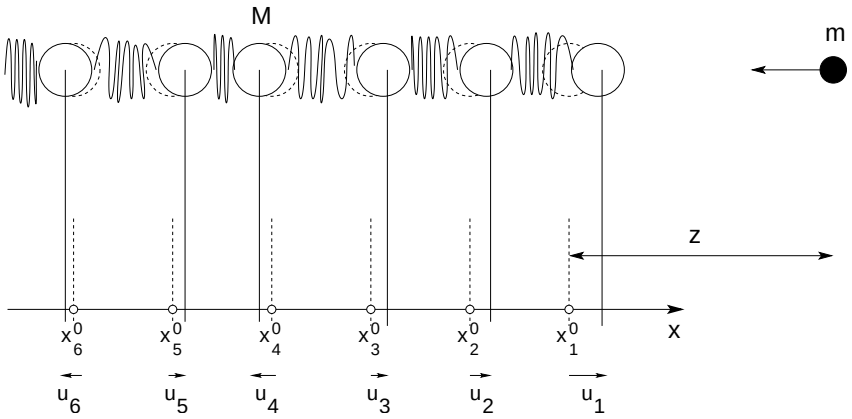
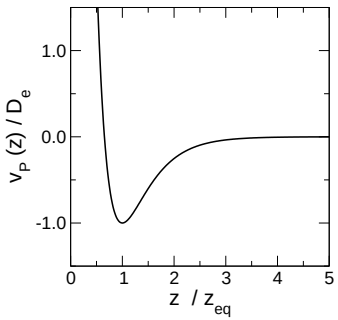
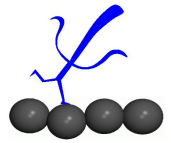




Hamilton's equations read as

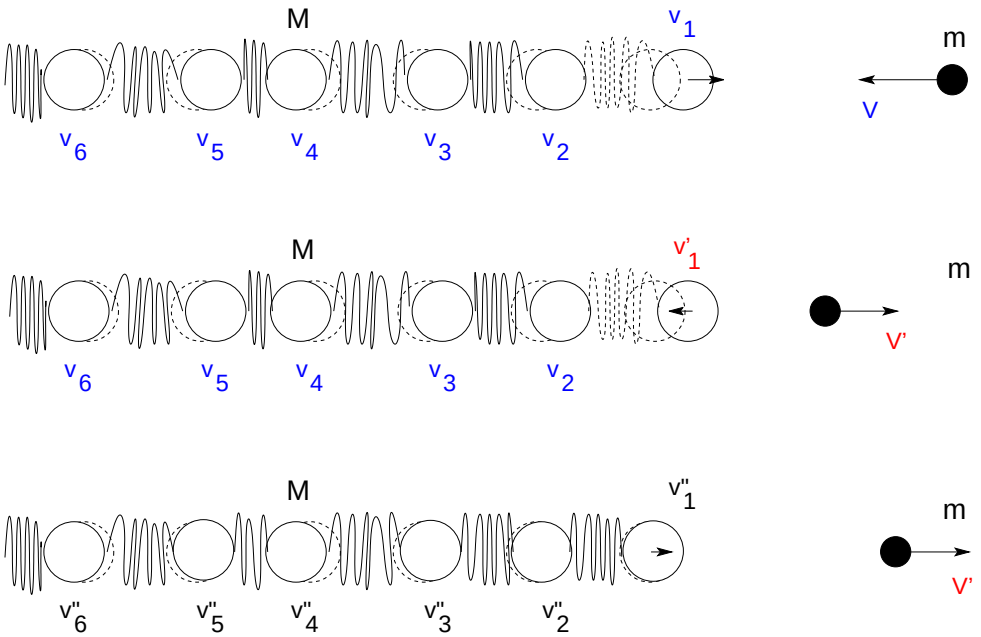
$$
\begin{aligned}
m\ddot{z} &= -\frac{\partial v_P}{\partial z}(z-u_1) \\
M\ddot{u}_1 &= +\frac{\partial v_P}{\partial z}(z-u_1) + M\Omega^2(u_2-u_1) \\
M\ddot{u}_n &= -M\Omega^2(2u_n-u_{n+1}-u_{n-1})
\end{aligned}
$$

..yet too complex to be analytically solved..



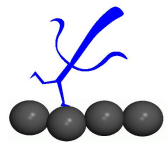
Impulsive limit

"Fast" collision ($\tau \ll \Omega^{-1}$): the projectile leaves the chain unchanged except for an impulse on the outermost atom..



Binary collision..

.. Energy propagation



Energy propagation (outline)

Normal mode (phonon) transformation:

$$H^{chain} = \sum_{n=1}^{\infty} \left\{ \frac{p_n^2}{2M} + \frac{M\Omega^2}{2}(u_{n+1} - u_n)^2 \right\}$$

$$X_k = \sqrt{\frac{2}{\pi}} \sum_{n=1}^{\infty} sin(nk) u_n$$

$$P_k = \sqrt{\frac{2}{\pi}} \sum_{n=1}^{\infty} sin(nk) p_n$$

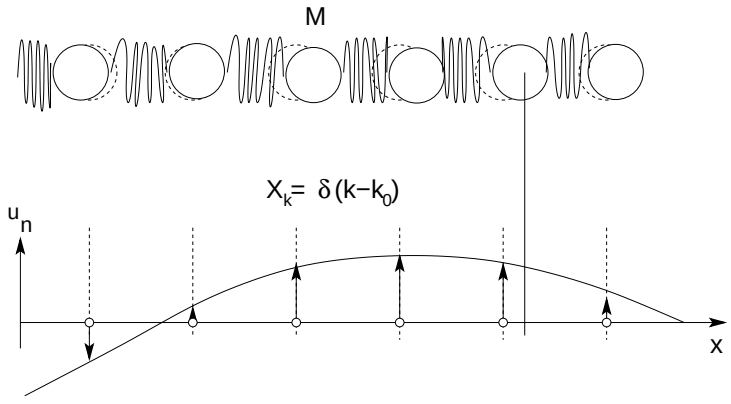
$$\Updownarrow$$

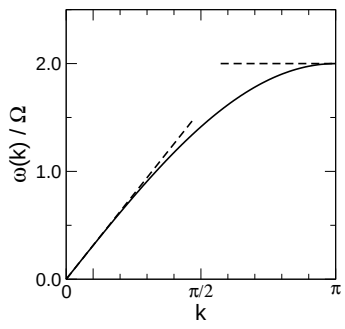
$$H^{chain} = \int_0^{\pi} \left\{ \frac{P_k^2}{2M} + \frac{M\omega(k)^2}{2} X_k^2 \right\}$$

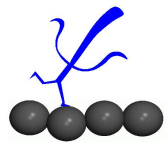
$$\omega(k)^2 = 4\Omega^2 sin^2(k/2)$$

$$u_n = \sqrt{\frac{2}{\pi}} \int_0^{\infty} sin(kn) X_k dk$$

$$p_n = \sqrt{\frac{2}{\pi}} \int_0^{\infty} sin(kn) P_k dk$$







Energy propagation (outline)

Normal modes are independent oscillators:

$$X_k(t) = X_k(0)cos(\omega(k)t) + \frac{P_k(0)}{M\omega(k)} sin(\omega(k)t)$$

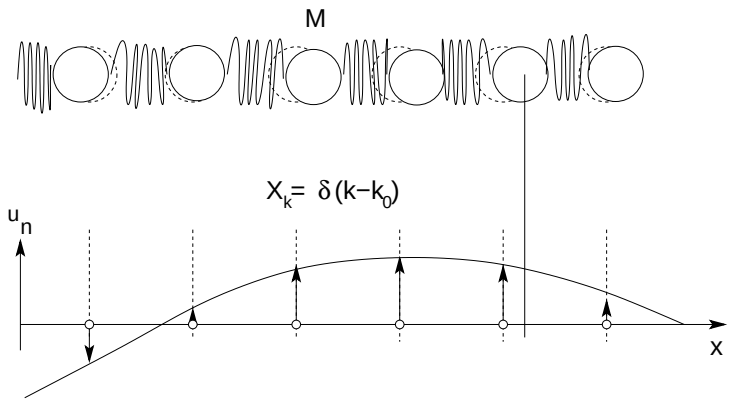
$$u_n(0) \equiv 0 \qquad p_n(0) \equiv \delta_{1n} P$$

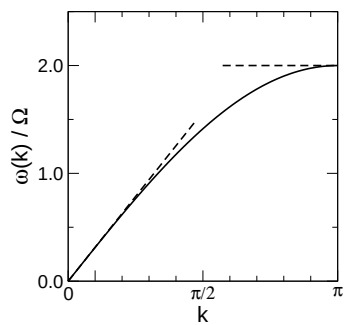
$$\Downarrow$$

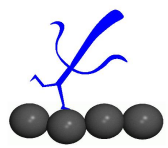
$$X_k(0) = 0 \qquad P_k(0) = \sqrt{\frac{2}{\pi}} sin(k) P$$

$$\Downarrow$$

$$u_n(t) = \frac{2P}{\pi M} \int_0^\infty \frac{sin(kn)sin(k)sin(\omega(k)t)}{\omega(k)} dk$$







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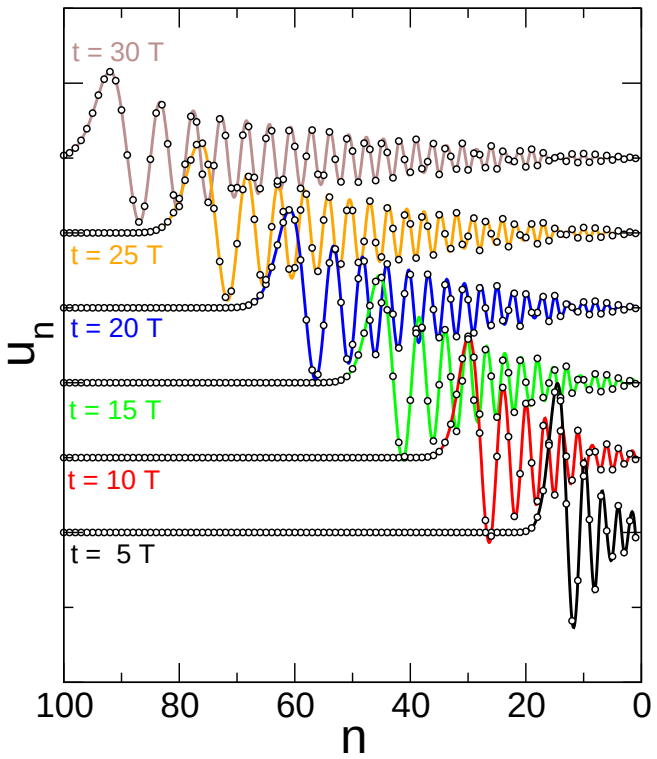
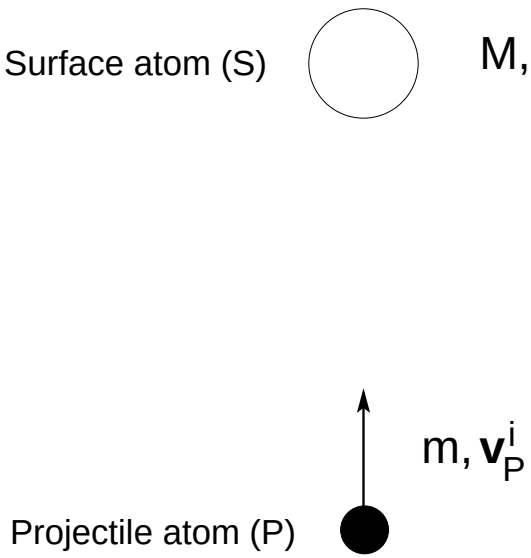


Binary collisions

Energy transfer occurs to the first chain atom only..



$$\boldsymbol{P} = m\boldsymbol{v}_P + M\boldsymbol{v}_S \equiv \boldsymbol{const}$$

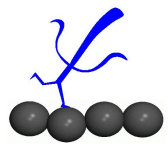
$$E = \frac{\boldsymbol{p}_P^2}{2m} + \frac{\boldsymbol{p}_S^2}{2M} \equiv \frac{\boldsymbol{P}^2}{2(M+m)} + \frac{\boldsymbol{p}^2}{2\mu} \equiv const$$

$$\boldsymbol{p} = \mu(\boldsymbol{v}_P - \boldsymbol{v}_S) \quad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

$\boldsymbol{p}$ = momentum of the relative motion

$$\Downarrow$$

$$p_i = p_f$$



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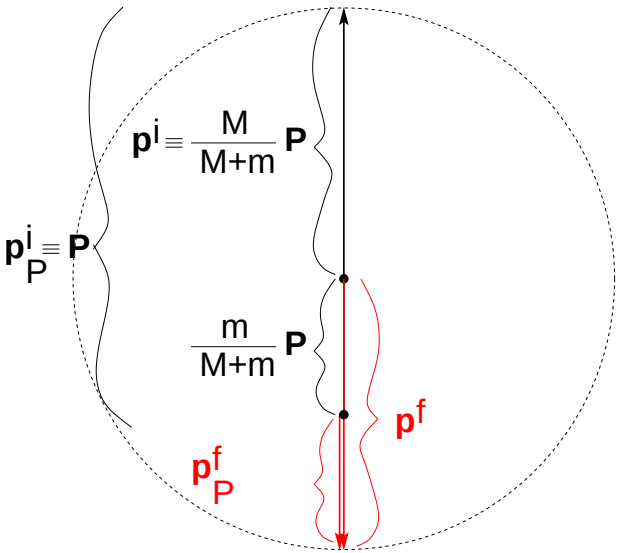
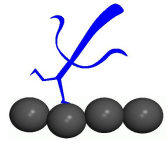


$$\begin{cases} \boldsymbol{P} = & \boldsymbol{p}_P + \boldsymbol{p}_S \\ \boldsymbol{p} = & \mu\left(\frac{\boldsymbol{p}_P}{m} - \frac{\boldsymbol{p}_S}{m}\right) \end{cases} \iff \begin{cases} \boldsymbol{p}_P = & \frac{m}{m+M}\boldsymbol{P} + \boldsymbol{p} \\ \boldsymbol{p}_S = & \frac{M}{m+M}\boldsymbol{P} - \boldsymbol{p} \end{cases}$$

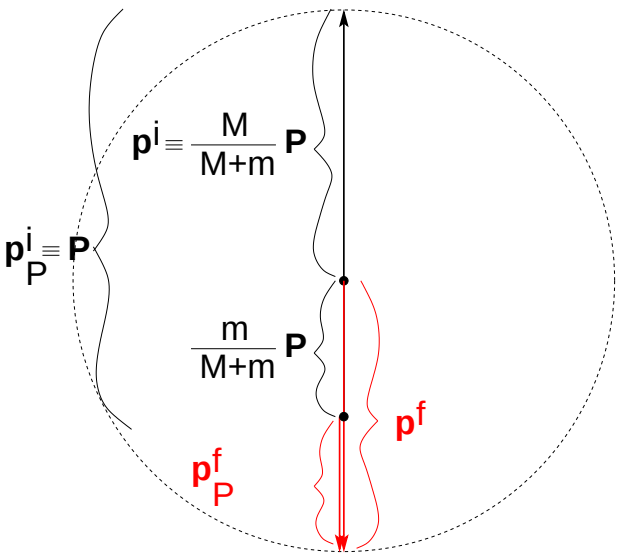
$$\begin{cases} \boldsymbol{p}^i_P = & \frac{m}{m+M}\boldsymbol{P} + \frac{M}{m+M}\boldsymbol{P} \equiv \boldsymbol{P} \\ \boldsymbol{p}^i_S = & \boldsymbol{0} \end{cases} \qquad \begin{cases} \boldsymbol{p}^f_P = & \frac{m-M}{m+M}\boldsymbol{P} \\ \boldsymbol{p}^f_S = & \frac{2M}{m+M}\boldsymbol{P} \end{cases}$$

Initial Final



Binary collisions

$\delta\epsilon_P = \epsilon_P^i - \epsilon_P^f =$ energy transfer to the surface



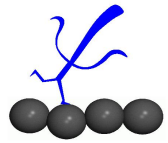
$$\delta\epsilon_P \equiv \epsilon_S^f = \frac{1}{2M}\left(\frac{2M}{M+m}\boldsymbol{P}\right)^2 = \frac{4Mm}{(M+m)^2}\frac{P^2}{2m}$$

$$\epsilon_P^f = \frac{1}{2m}\left(\frac{m-M}{M+m}\boldsymbol{P}\right)^2 = \left(\frac{\alpha-1}{\alpha+1}\right)^2\frac{P^2}{2m}$$

$$\delta\epsilon_P = \frac{4\alpha}{(1+\alpha)^2}\epsilon_P^i$$

$$\epsilon_P^f = \left(\frac{1-\alpha}{1+\alpha}\right)^2\epsilon_P^i$$

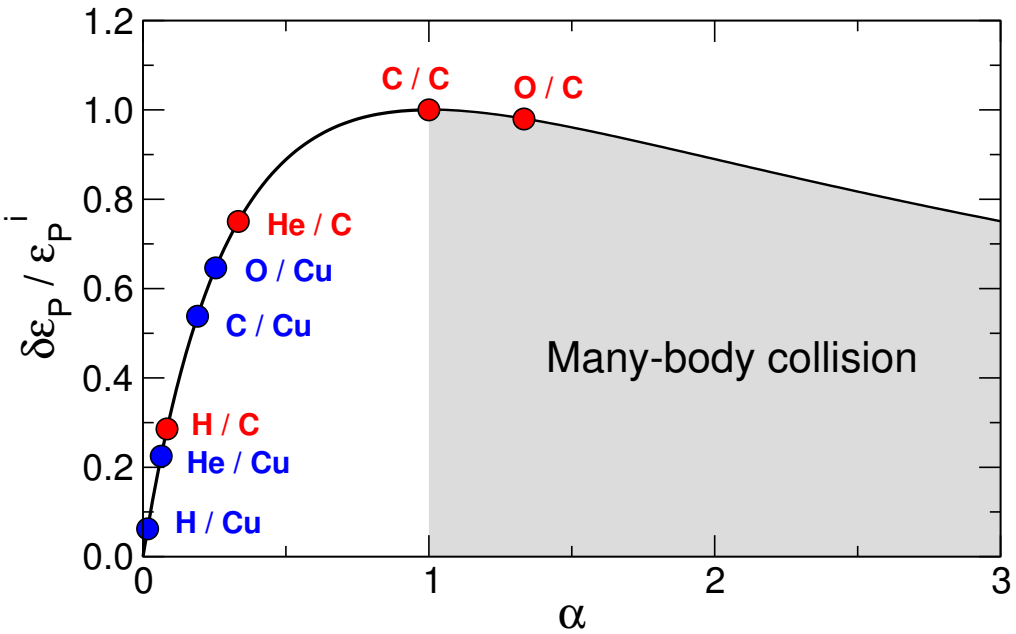
$\alpha = m/M =$ mass ratio
$\epsilon_P^i =$ collision energy

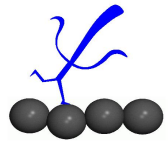


Binary collisions

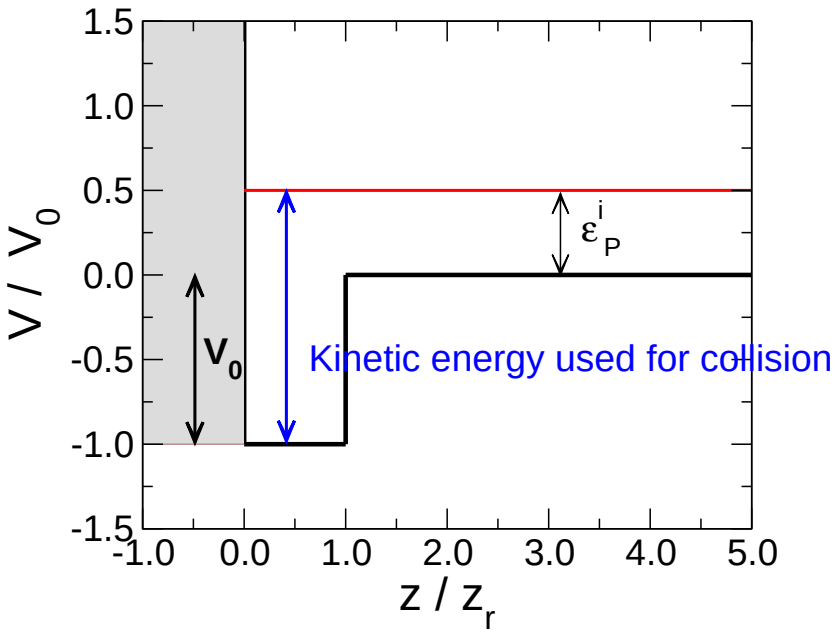
$\delta\epsilon_P$ is maximum for $\alpha \rightarrow 1$

$$\delta\epsilon_P^{max} = \epsilon_P^i$$





Sticking in the impulsive limit



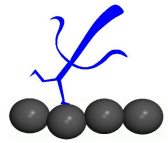
Sticking condition:

$$\epsilon_P^f = \epsilon_P^i - \delta\epsilon_P < 0$$

$$\delta\epsilon_P = \frac{4\alpha}{(1+\alpha)^2}\left(\epsilon_P^i + V_0\right)$$

$$\epsilon_P^i < \frac{4\alpha}{(1-\alpha)^2} V_0 \equiv \epsilon_{th}$$

ϵ_{th} = threshold energy for sticking



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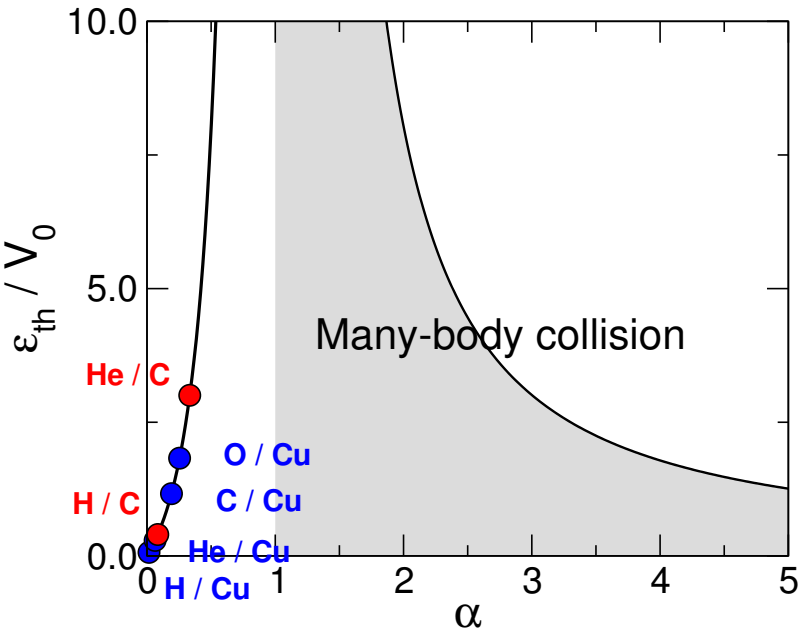

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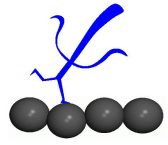
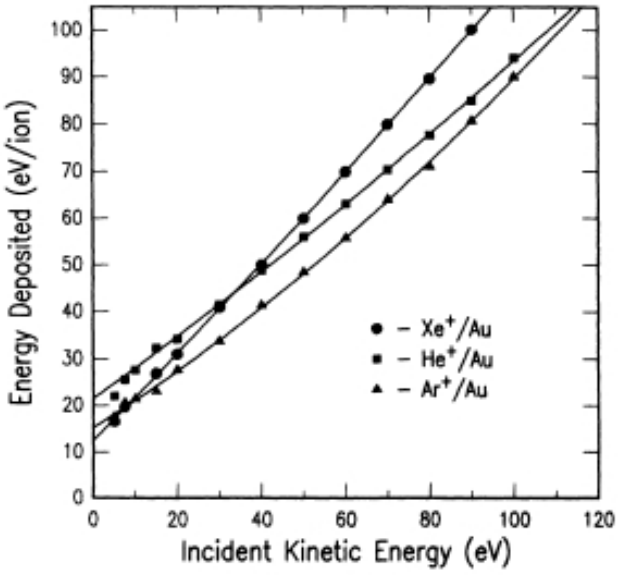
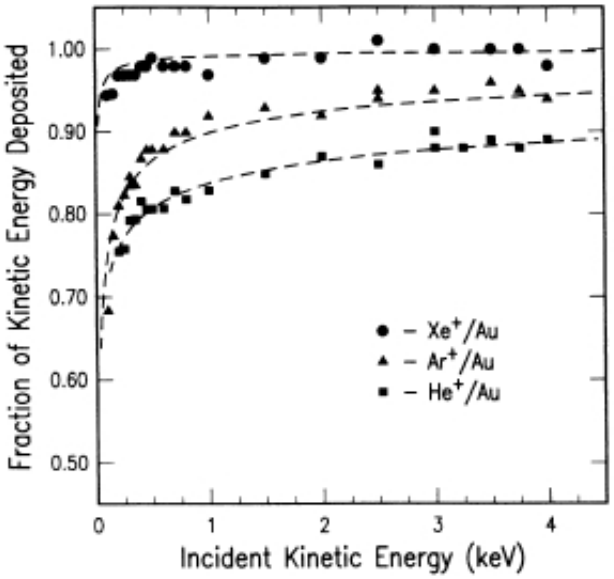


Binary collisions at work

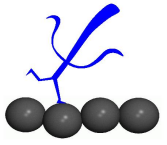




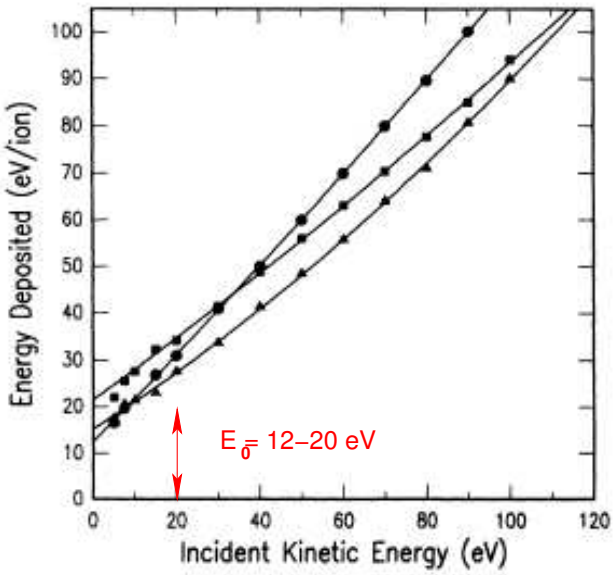
$\delta\epsilon_P = f\epsilon_P^i + E_0$, E_0?

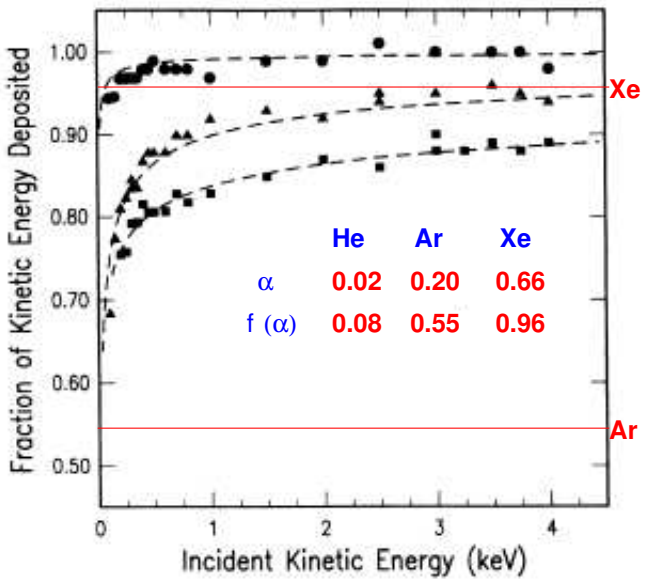
$f = f(\alpha) = \frac{4\alpha}{(1+\alpha)^2}$?

H. F. Winters, H. Coufal, C. T. Rettner and D. S. Bethune, *Phys. Rev. B*, **41** (1990) 6240



Binary collisions at work

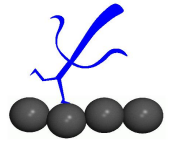




E_0 is related to $R_g^+ + M \rightarrow R_g + M^+$

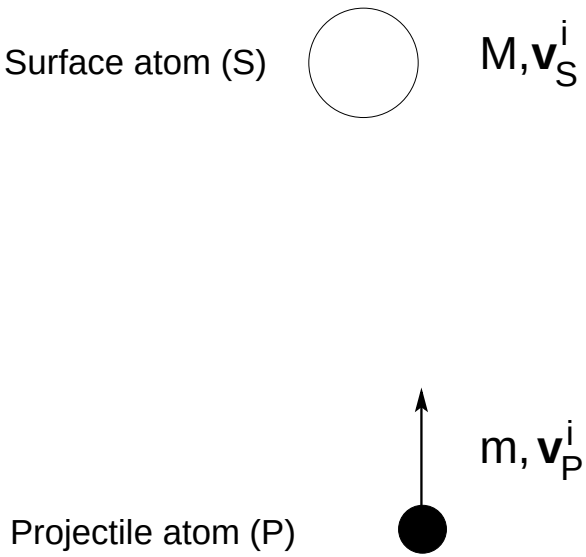
P undergoes multiple collisions with S atoms!!

H. F. Winters, H. Coufal, C. T. Rettner and D. S. Bethune, *Phys. Rev. B*, **41** (1990) 6240



II. Binary collisions: beyond back-scattering

Real surfaces are not linear chains: non-collinear collisions..



$$\boldsymbol{P} = m\boldsymbol{v}_P + M\boldsymbol{v}_S \equiv \boldsymbol{const}$$

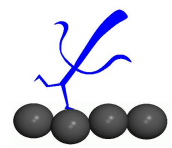
$$E = \frac{\boldsymbol{p}_P^2}{2m} + \frac{\boldsymbol{p}_S^2}{2M} \equiv \frac{\boldsymbol{P}^2}{2(M+m)} + \frac{\boldsymbol{p}^2}{2\mu} \equiv const$$

$$\boldsymbol{p} = \mu(\boldsymbol{v}_P - \boldsymbol{v}_S) \quad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

$\boldsymbol{p}$ = momentum of the relative motion

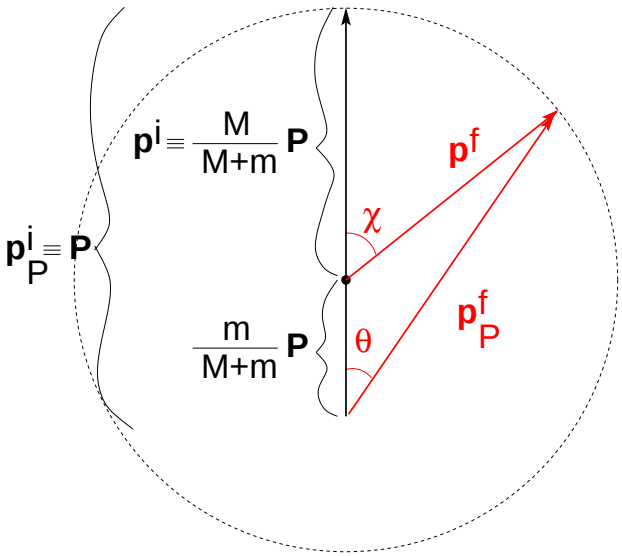
$$\Downarrow$$

$$p_i = p_f$$



II. Binary collisions: beyond back-scattering

Real surfaces are not linear chains: non-collinear collisions..

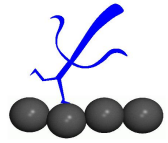


$$\begin{cases} \boldsymbol{P} = & \boldsymbol{p}_P + \boldsymbol{p}_S \\ \boldsymbol{p} = & \mu\left(\frac{\boldsymbol{p}_P}{m} - \frac{\boldsymbol{p}_S}{m}\right) \end{cases} \iff \begin{cases} \boldsymbol{p}_P = & \frac{m}{m+M}\boldsymbol{P} + \boldsymbol{p} \\ \boldsymbol{p}_S = & \frac{M}{m+M}\boldsymbol{P} - \boldsymbol{p} \end{cases}$$

$$\begin{cases} \boldsymbol{p}^i_P = & \frac{m}{m+M}\boldsymbol{P} + \frac{M}{m+M}\boldsymbol{P} \equiv \boldsymbol{P} \\ \boldsymbol{p}^i_S = & \boldsymbol{0} \end{cases} \qquad \begin{cases} \boldsymbol{p}^f_P = & \frac{m}{m+M}\boldsymbol{P} + \boldsymbol{p}^f \\ \boldsymbol{p}^f_S = & \frac{M}{m+M}\boldsymbol{P} - \boldsymbol{p}^f \end{cases}$$

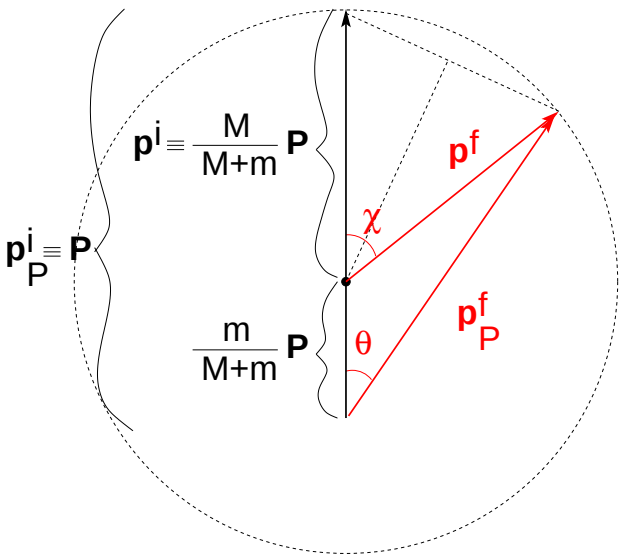
$\chi =$ scattering angle in the c.o.m. reference system

$\theta =$ scattering angle in the lab reference system



II. Binary collisions: beyond back-scattering

$\delta\epsilon_P$ in terms of χ



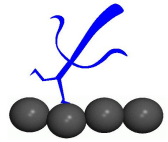
$$\delta\epsilon_P \equiv \epsilon^f_S = \frac{1}{2M}\left(\frac{M}{M+m}\boldsymbol{P} - \boldsymbol{p}_f\right)^2 =$$

$$\frac{1}{2M}\left(\frac{M}{M+m}\right)^2 P^2\left(\hat{\boldsymbol{n}}^i - \hat{\boldsymbol{n}}^f\right)^2 =$$

$$\frac{mM}{(m+M)^2}\frac{P^2}{2m}\left(\hat{\boldsymbol{n}}^i - \hat{\boldsymbol{n}}^f\right)^2$$

$$\delta\epsilon_P = \frac{4\alpha}{(1+\alpha)^2}\epsilon^i_P \sin^2\left(\frac{\chi}{2}\right)$$

$\alpha = m/M =$ mass ratio
$\epsilon^i_P =$ collision energy

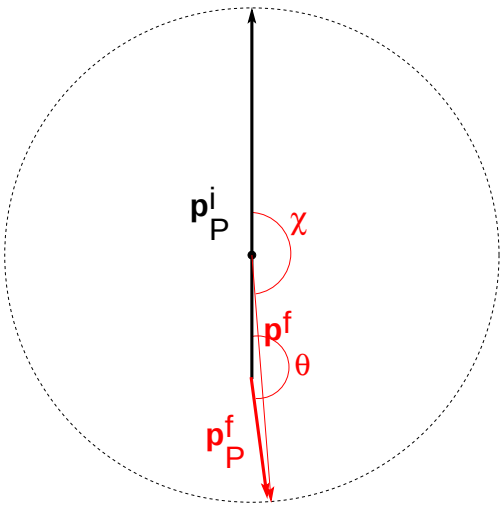


II. Binary collisions: beyond back-scattering

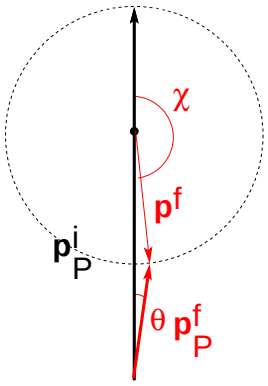
$\delta\epsilon_P$ is maximum for back-scattering (in c.o.m.), *i.e.* $\chi = \pi$, ..

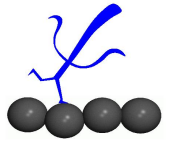
$$\delta\epsilon_P^{max} = 4\alpha/(1+\alpha)^2\epsilon_P^i$$

$\alpha < 1$



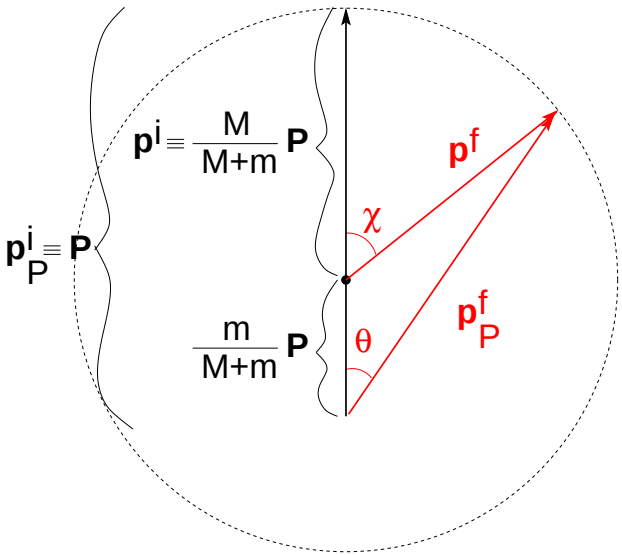
$\alpha > 1$





II. Binary collisions: beyond back-scattering

ϵ_P^f in terms of χ

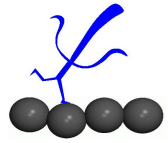


$$\epsilon_P^f = \frac{\boldsymbol{p}_P^f}{2m} = \frac{1}{2m}\left(\frac{m}{M+m}\boldsymbol{P} + \boldsymbol{p}_f\right)^2 =$$

$$\frac{P^2}{2m}\,\frac{M^2+m^2+2mM\cos\chi}{(m+M)^2}$$

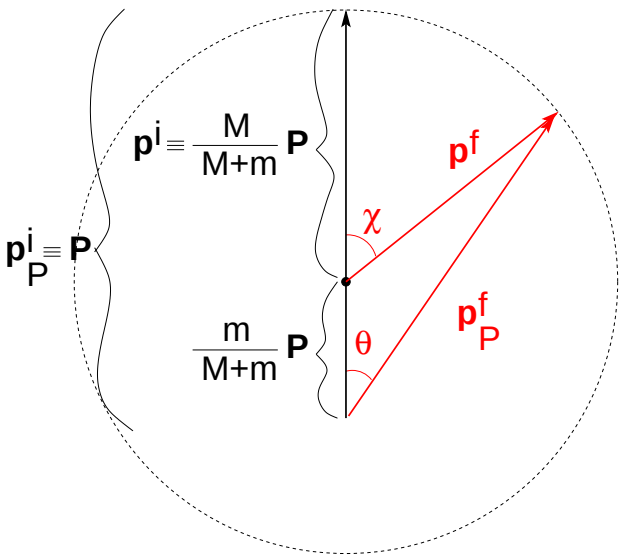
$$\epsilon_P^f = \frac{1+\alpha^2+2\alpha\cos\chi}{(1+\alpha)^2}\epsilon_P^i$$

$\alpha = m/M =$ mass ratio
$\epsilon_P^i =$ collision energy



II. Binary collisions: beyond back-scattering

ϵ_P^f in terms of θ

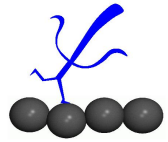


$$\left(\boldsymbol{p}_P^f - \tfrac{m}{m+M}\boldsymbol{P}\right)^2 = p^{f2}$$

$$p_P^f = \tfrac{m}{m+M} P\cos\theta + \tfrac{P}{M+m}\sqrt{M^2 - m^2 sin^2\theta}$$

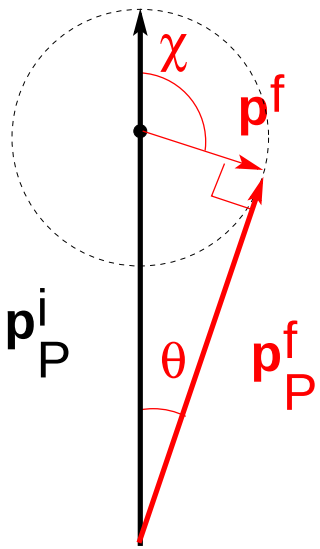
$$\epsilon_P^f = \frac{\left(\alpha\cos\theta + \sqrt{1-\alpha^2\sin^2\theta}\right)^2}{(1+\alpha)^2}\epsilon_P^i$$

$\alpha = m/M =$ mass ratio
$\epsilon_P^i =$ collision energy



II. Binary collisions: beyond back-scattering

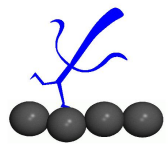
Note: For $\alpha > 1$ there exists a maximum scattering angle



$$\frac{m}{M+m} P \sin\theta_{max} = \frac{M}{M+m} P$$

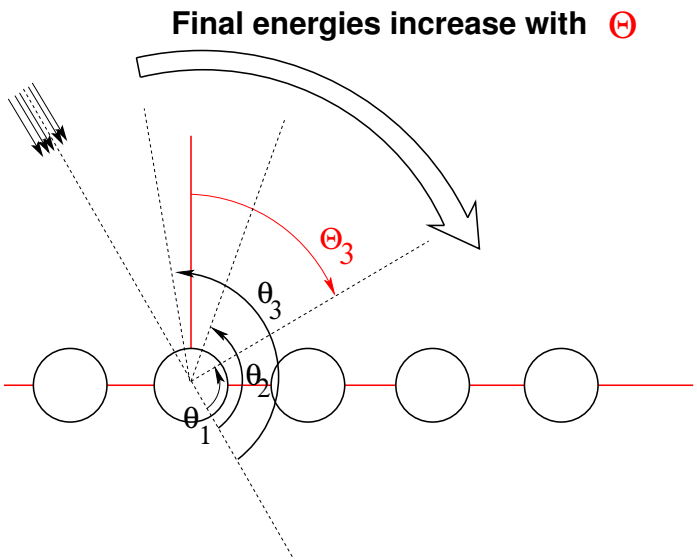
$$\sin\theta_{max} = \frac{1}{\alpha}$$

which only depends on the mass ratio

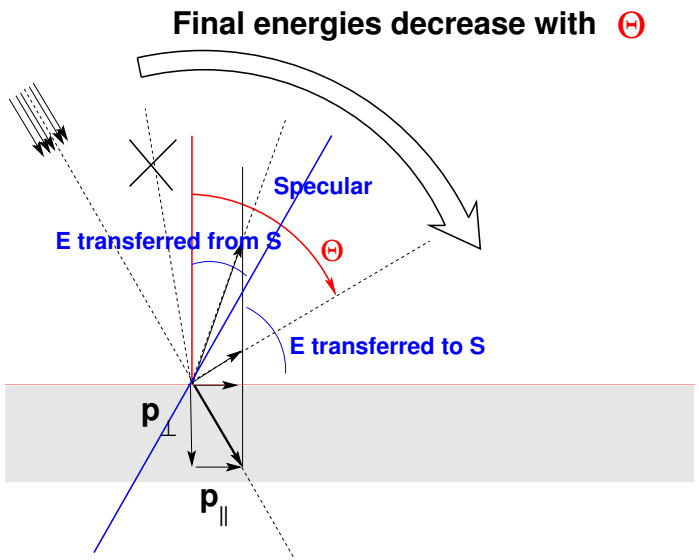


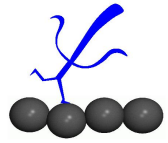
II. Binary collisions: beyond back-scattering

Scattering in the binary limit

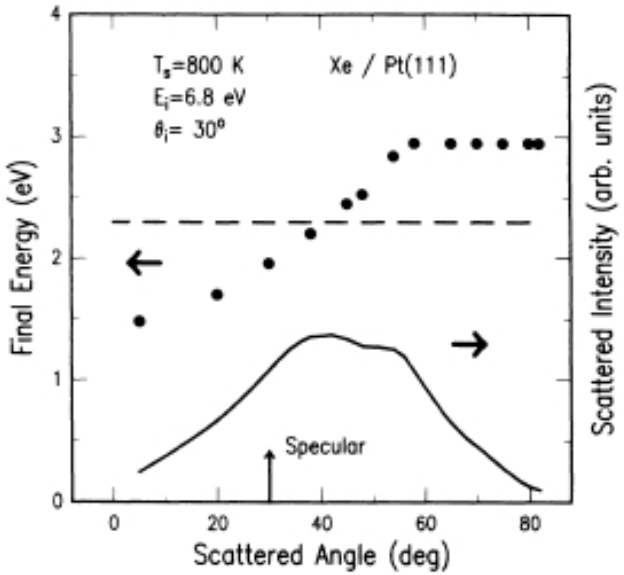


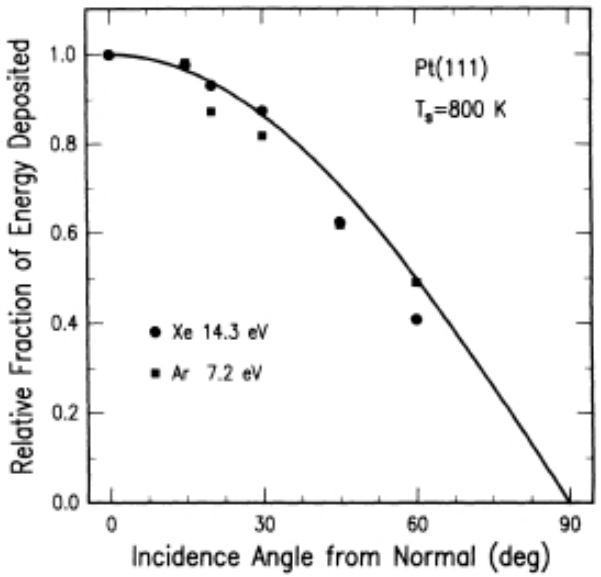
Scattering from a flat surface



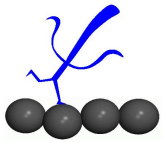


II. Binary collisions: beyond back-scattering





H. F. Winters, H. Coufal, C. T. Rettner and D. S. Bethune, *Phys. Rev. B*, **41** (1990) 6240



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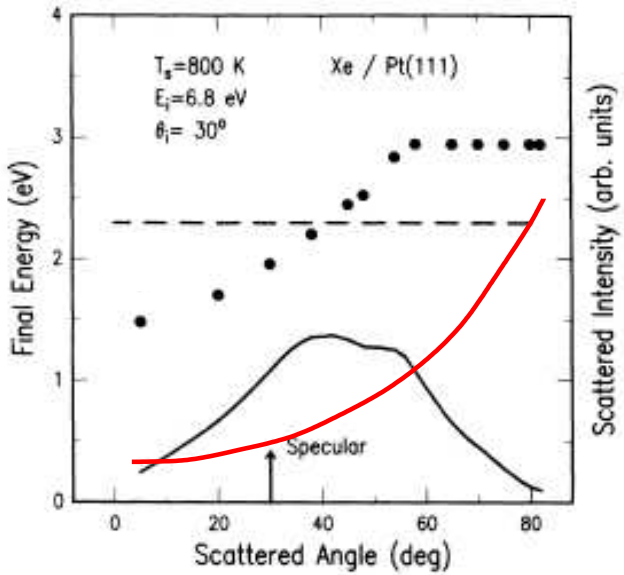
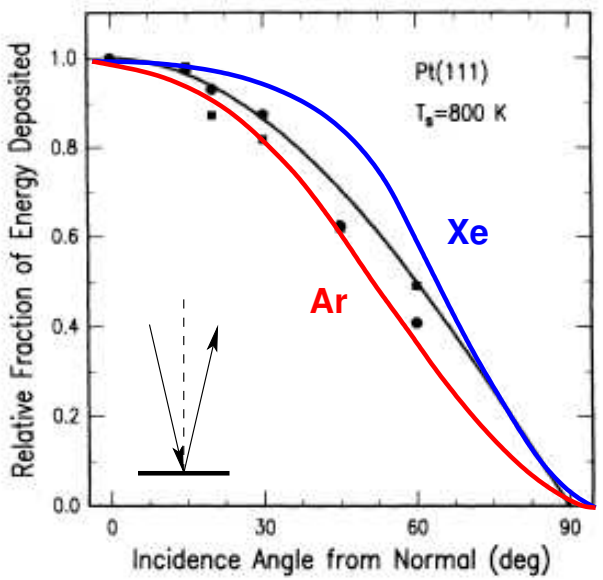
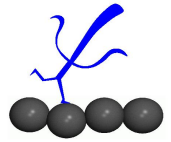


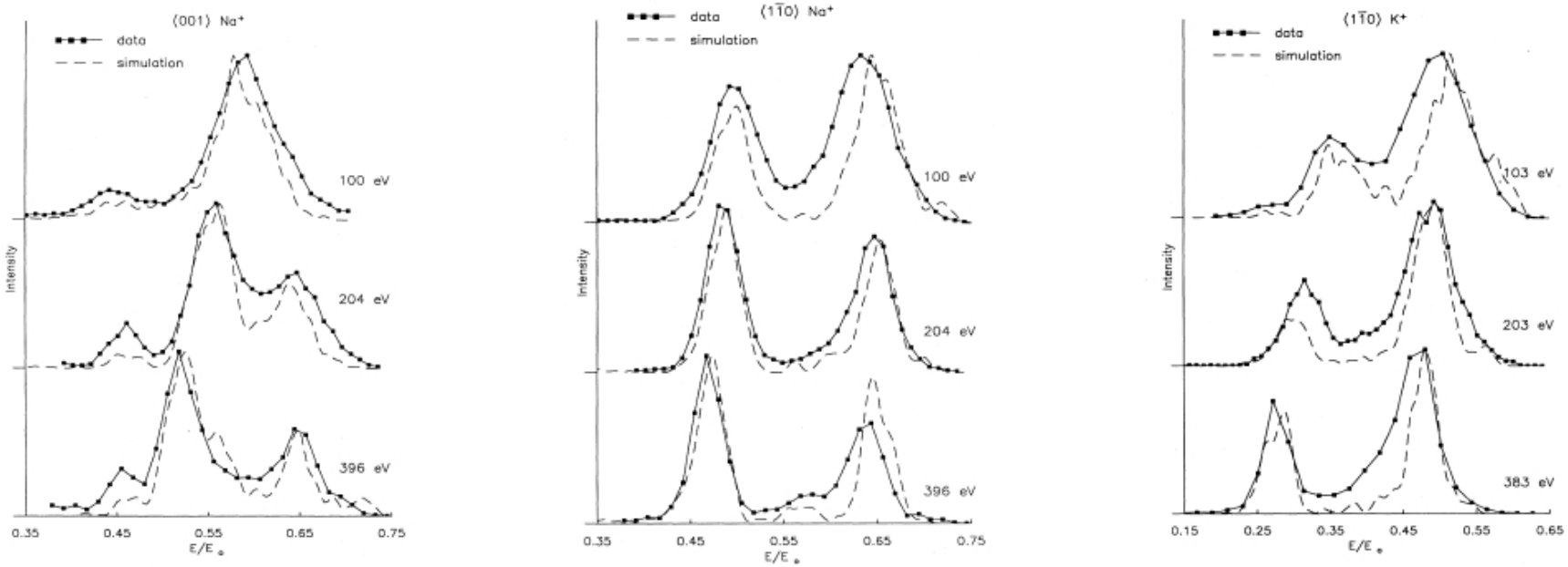


Upon application of $\epsilon_P^f = \left(\alpha \cos\theta + \sqrt{1-\alpha^2 \sin^2\theta}\right)^2 / (1+\alpha)^2 \epsilon_P^i$

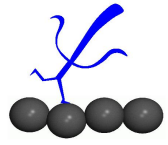
H. F. Winters, H. Coufal, C. T. Rettner and D. S. Bethune, *Phys. Rev. B*, **41** (1990) 6240



II. Binary collisions: beyond back-scattering

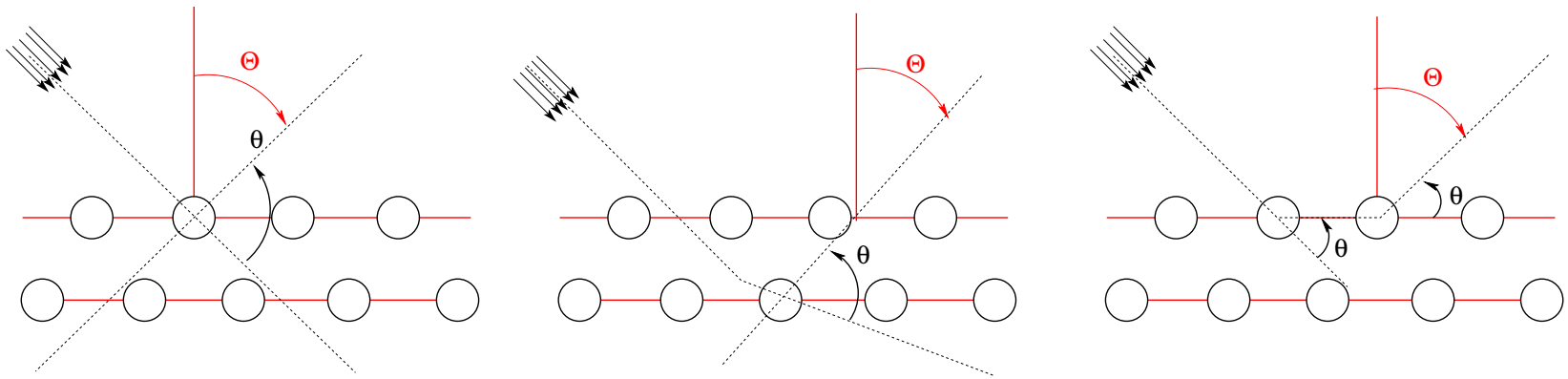


D. M. Goodstein, R. L. McEachern and B. H. Cooper, *Phys. Rev. B*, **39** (1989) 13129



II. Binary collisions: beyond back-scattering

Direct **Focusing** **Indirect**



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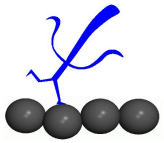
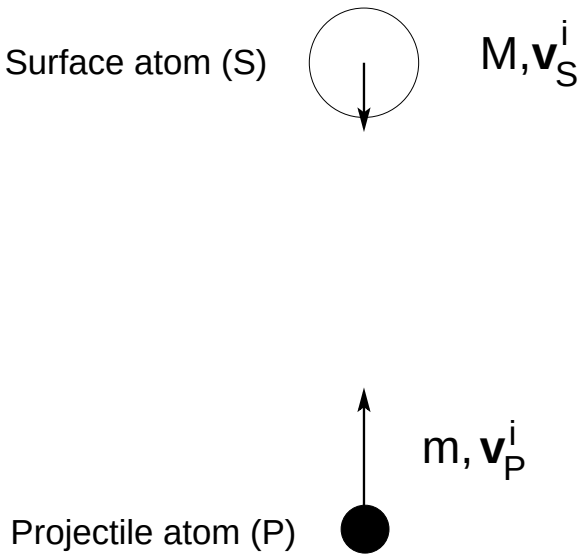


III. Binary collision: surface temperature

Surface atoms are not at rest..



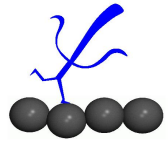
In the frame $\tilde{}$, $\tilde{\boldsymbol{v}}_S^i = 0$
and everything proceeds as before, with..

$$\boldsymbol{v}_P^i = \tilde{\boldsymbol{v}}_P^i + \boldsymbol{v}_S^i$$

$$\epsilon_P^i = \tilde{\epsilon}_P^i + \frac{1}{2} m v_S^i 2 + m \tilde{\boldsymbol{v}}_P^i \boldsymbol{v}_S^i$$

$$\epsilon_P^f = \tilde{\epsilon}_P^f + \frac{1}{2} m v_S^i 2 + m \tilde{\boldsymbol{v}}_P^f \boldsymbol{v}_S^i$$

$$\delta\epsilon_P = \delta\tilde{\epsilon}_P + (\tilde{\boldsymbol{p}}_P^i - \tilde{\boldsymbol{p}}_P^f)\boldsymbol{v}_S^i$$



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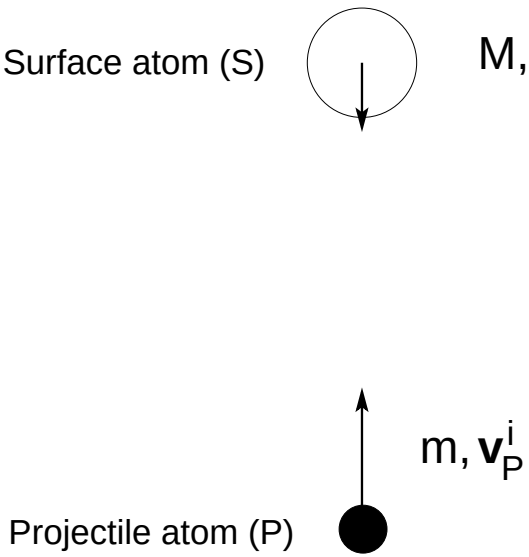


For collinear collisions

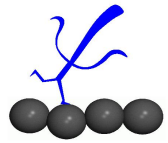
$$\tilde{\boldsymbol{p}}_P^i - \tilde{\boldsymbol{p}}_P^f = \frac{2Mm}{M+m}(v_P^i - v_S^i)$$

$$\delta\tilde{\epsilon}_P = \frac{4\alpha}{(1+\alpha)^2}\frac{m}{2}(v_P^i - v_S^i)^2$$

Upon averaging ($\langle v_P^i v_S^i \rangle = 0$)..

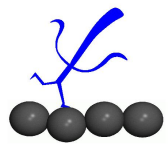
$$\delta\epsilon_P = \frac{4\alpha}{(1+\alpha)^2}(\epsilon_P^i - \langle\epsilon_S^i\rangle)$$

$$\langle\epsilon_S^i\rangle \sim k_B T$$



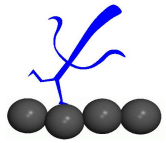
Summary

- Energy transfer is primarly controlled by the mass-ratio $\alpha = \frac{m}{M}$
- Energy transfer is most efficient for back-scattering
- The binary collision model works fine at high energies, provided multiple collisions are included



Outline

1. Basics
   - Linear chain model
   - Scattering from real surfaces
2. Reduced dynamical models
   - Traditional models
   - System-bath models
3. Dynamics
   - The methods
   - Examples



The need of..

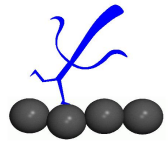
In the impulsive limit $\tau \ll \Omega^{-1}$

- Dynamics is classical (at least for the projectile..)
- Dynamics is decoupled

What about the case $E_{coll} \leq \hbar\Omega$?

- Classical or quantum?
- How to handle infinite numbers of particles?

$\Rightarrow$ Dynamics of (approximate) dynamical models with a limited number of DOFs



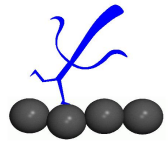
The need of..

Surface atoms may play just a passive role

- Energy dissipation is the main (surface) dynamical issue
- No interest for the dynamics of surface atoms
- Molecular DOFs as accurate as possible (main system)

or an active role

- Some surface atoms must be included in the main system (primary atoms)
- Dissipation is likely of secondary importance..
- Thermal activation of primary atoms may be important



The need of..

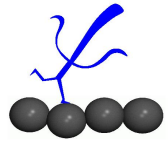
Typically, for scattering processes..

Surface atoms are passive in non-activated processes

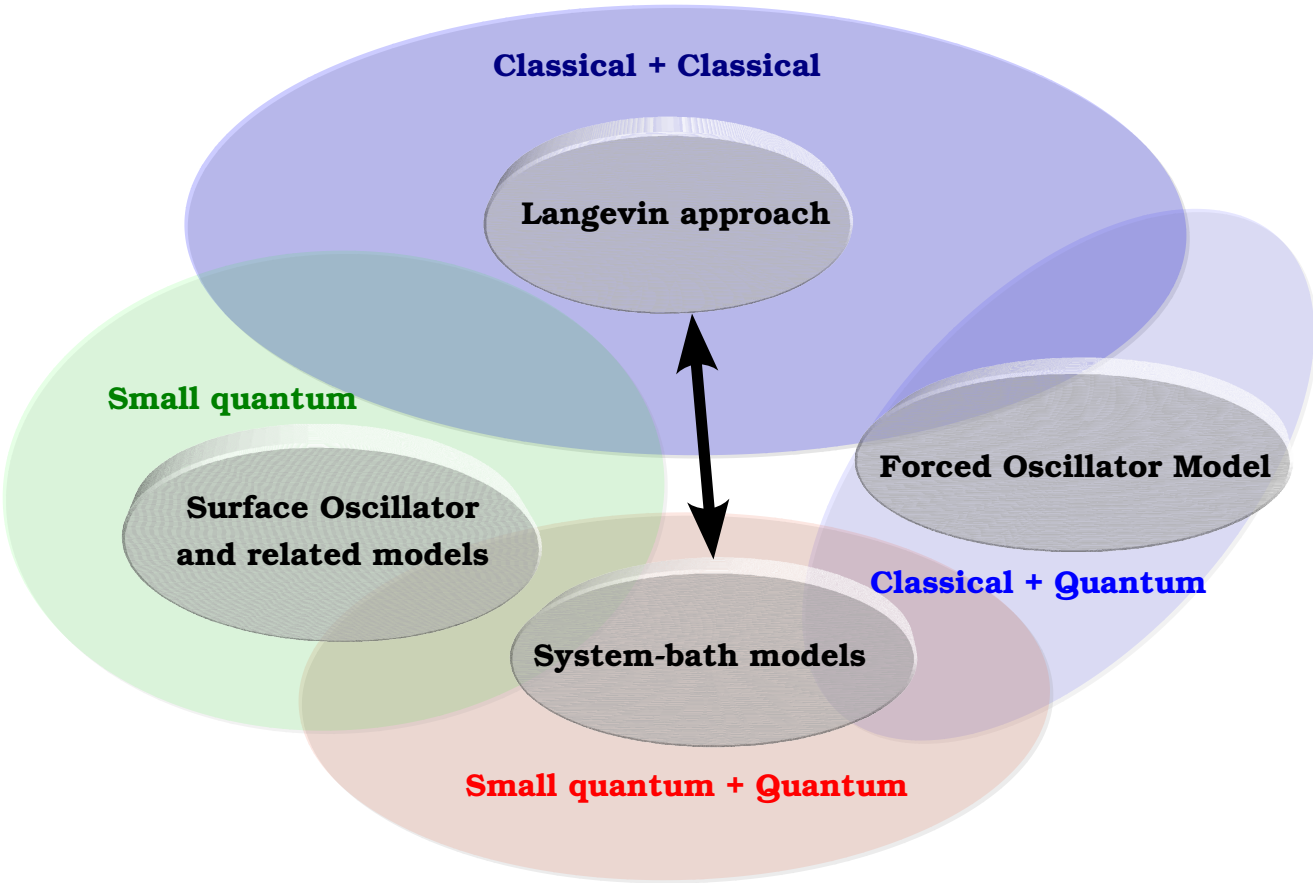
- Energy dissipation is the main (surface) dynamical issue
- No interest for the dynamics of surface atoms
- Molecular DOFs as accurate as possible (main system)

and active in activated processes

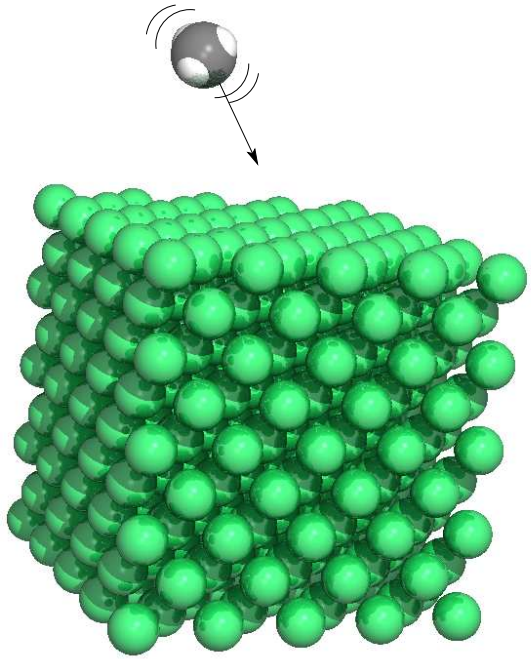
- Some surface atoms must be included in the main system (primary atoms)
- Dissipation is likely of secondary importance..
- Thermal activation of primary atoms may be important



Reduced dynamical models



Langevin

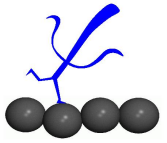


Cluster approach

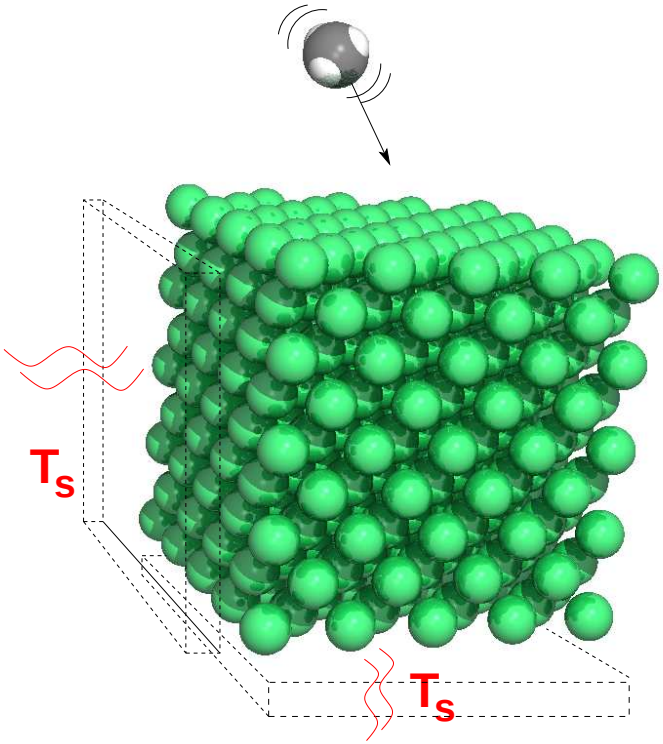
OK for classical systems with a known lattice potential, but..

- How sampling the equilibrium position of S atoms?
- How large the cluster should be?

$\Rightarrow$ Open system



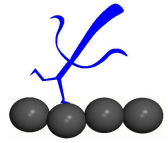
Langevin



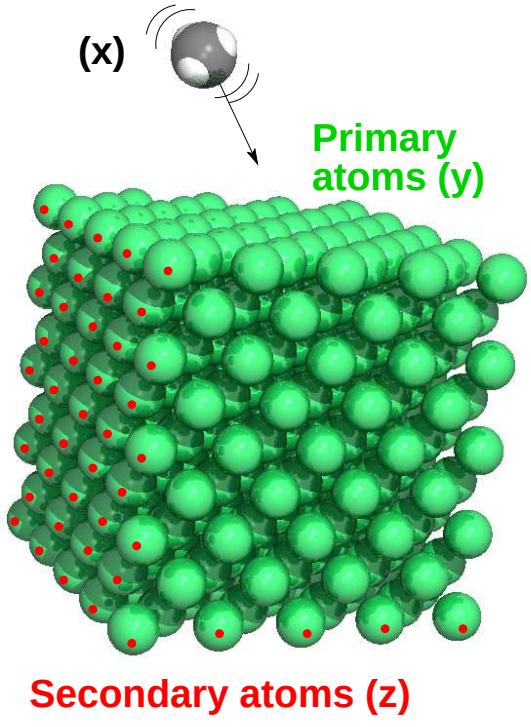
Thermal contacts with a reservoir at T_s

- guarantee E dissipation
- provide E fluctuations

$\Rightarrow$ Possible as long as we are not interested in the whole lattice dynamics



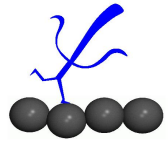
Langevin



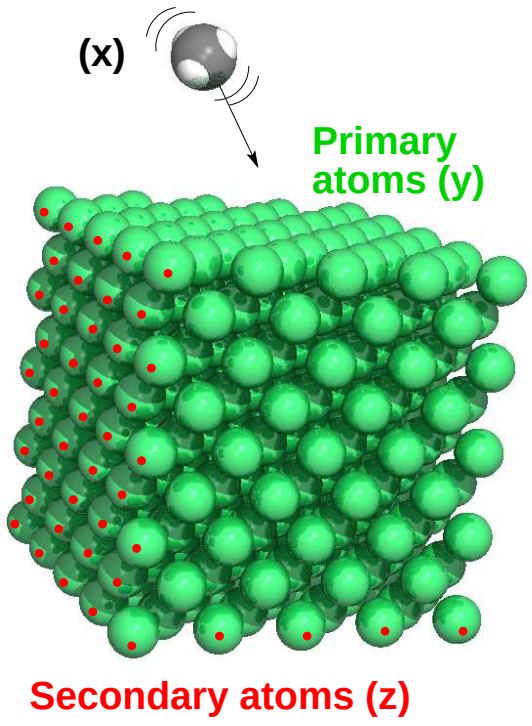
Secondary (edge) atoms are in contact with a reservoir at T_s

$$M\ddot{z} = F(\mathbf{x}, \mathbf{y}, \mathbf{z}) - M\gamma\dot{z} + \xi(t)$$

- F is the deterministic force
- $F_d = -M\gamma\dot{z}$ is the dissipative force
- $\xi(t)$ is the fluctuating force



Langevin



Where is T_s?

For $F = 0$, on the long run the system attains equilibrium

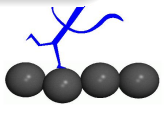
Dissipation $\Longleftrightarrow$ Fluctuation

$$\Downarrow$$

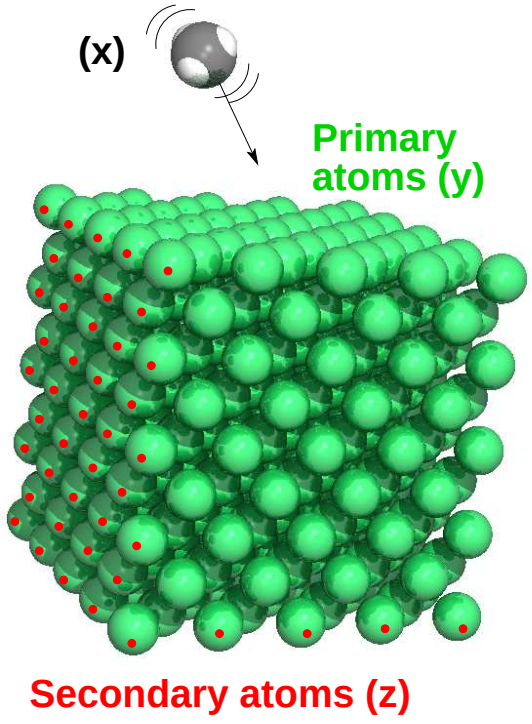
$$\lim_{t\to\infty} \langle v(t)^2 \rangle = k_B T_s / M$$

$$\Downarrow$$

$$\langle \xi(t)\xi(0) \rangle = 2Mk_B T_s \gamma \delta(t)$$



Langevin



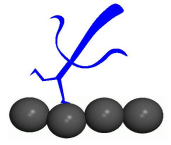
Equations of motion..

$$m\ddot{x} = -\frac{\partial V}{\partial x}(x, y, z)$$

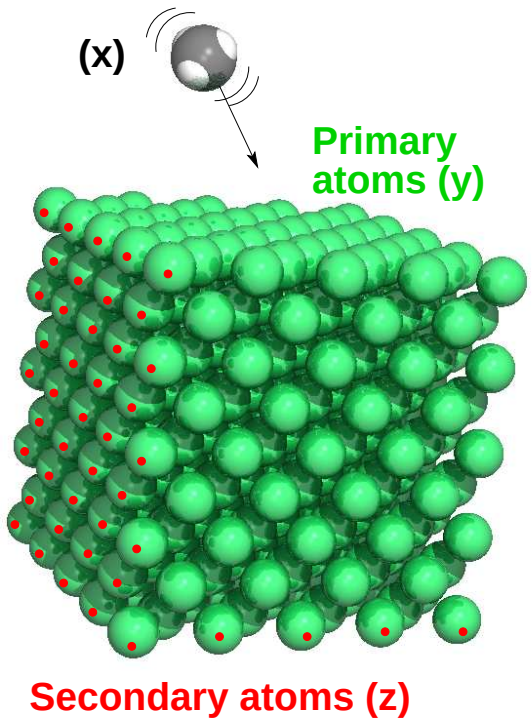
$$M\ddot{y} = -\frac{\partial V}{\partial y}(x, y, z)$$

$$M\ddot{z} = -\frac{\partial V}{\partial z}(x, y, z) - M\gamma\dot{z} + \xi$$

..do not conserve Energy

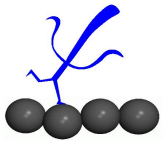


Langevin

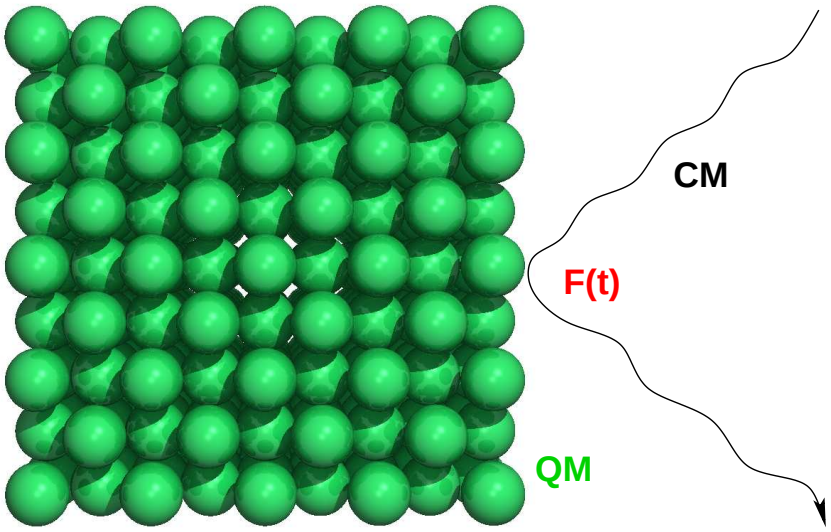


Equations of motion..

- The method can be exact
- the larger is the primary atom zone the better is
- Where to get γ ?



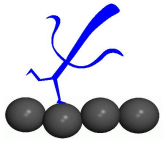
Forced Oscillator Model



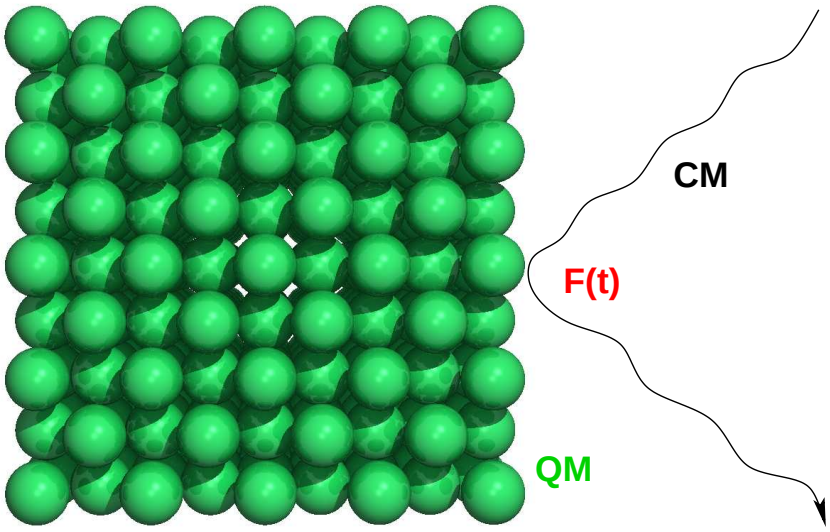
Classical particle on a quantum surface

- Particle's trajectory $\Rightarrow$ $F(t)$ on surface atoms
- Surface is a collection of HOs subjected to $F(t)$

..surface dynamics can be solved!



Forced Oscillator Model



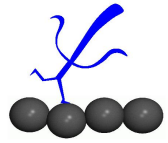
$$H(t) = \frac{p^2}{2M} + \frac{M\omega_0^2 q^2}{2} - qF(t)$$

$$H(t)\,|\psi_t\rangle = i\hbar \frac{d}{dt}\,|\psi_t\rangle$$

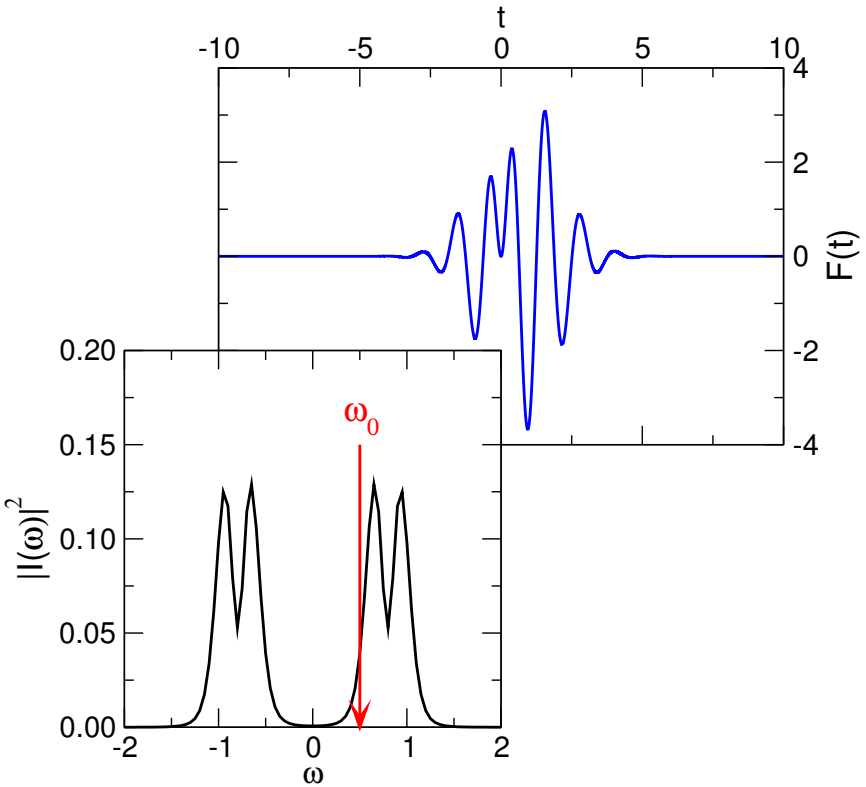
Analytically solvable to give

- Eigenvalues:
  $\epsilon_n(t) = \hbar\omega_0\left(n+\frac{1}{2}\right) - \frac{f^2(t)}{\hbar\omega_0}$
- Transition amplitudes:
  $\phi_{n\to m}(-\infty, +\infty)$

$$f(t) = \sqrt{\frac{\hbar}{2M\omega_0}}\,F(t)$$



Forced Oscillator Model



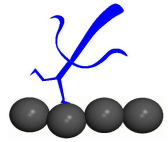
$$\phi^{\infty}_{n\to m} = \langle m|U_I(-\infty,+\infty)|n\rangle$$

$$\phi^{\infty}_{0\to m} = \left(-\frac{i}{\hbar}\right)^m \frac{\tilde{f}(\omega_0)^m}{\sqrt{m!}} e^{-\frac{|\tilde{f}(\omega_0)|^2}{2\hbar^2}}$$

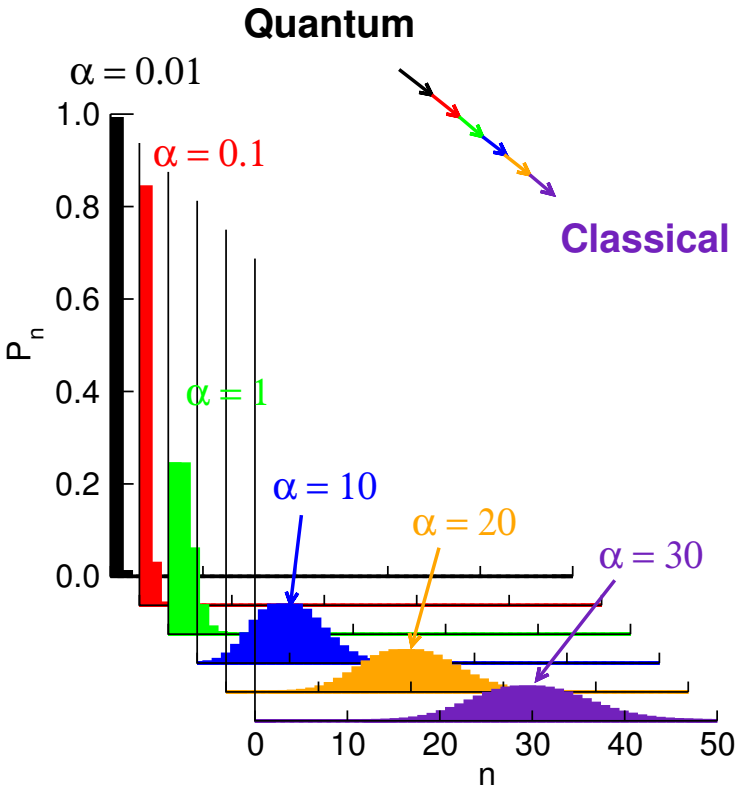
$$\tilde{f}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} f(t) dt$$

Ground-state excitation probability:

$$P^{\infty}_{0\to m} = \left|\frac{\tilde{f}(\omega_0)}{\hbar}\right|^{2m} \frac{e^{-\frac{|\tilde{f}(\omega_0)|^2}{\hbar^2}}}{m!}$$



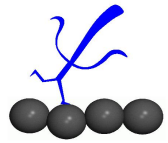
Forced Oscillator Model



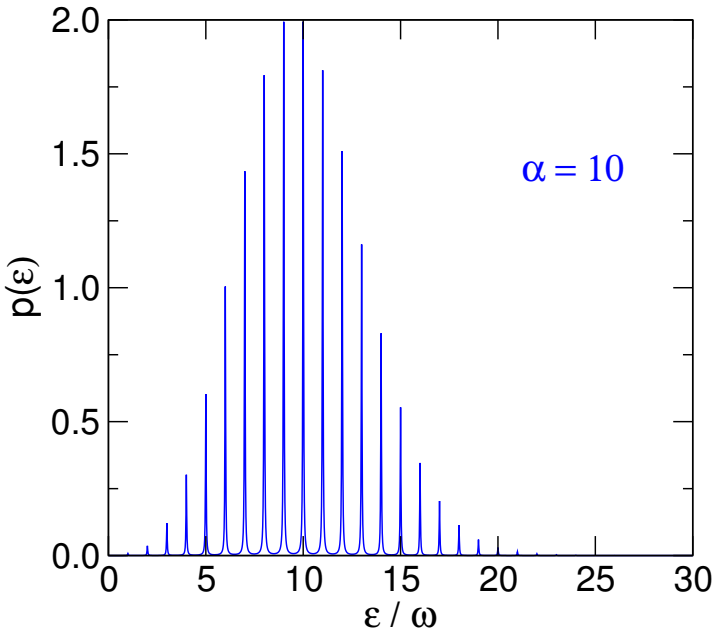
$$P^{\infty}_{0\to n} \equiv P_n = \frac{\alpha^n}{n!} e^{-\alpha}$$

Poisson distribution

- $\langle n \rangle = \alpha = \frac{|\tilde{f}(\omega_0)|^2}{\hbar^2}$
- $\langle n^2 \rangle \equiv \alpha$
- For large n P_n tends to a Gaussian



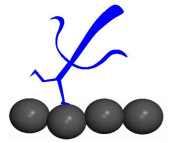
Forced Oscillator Model



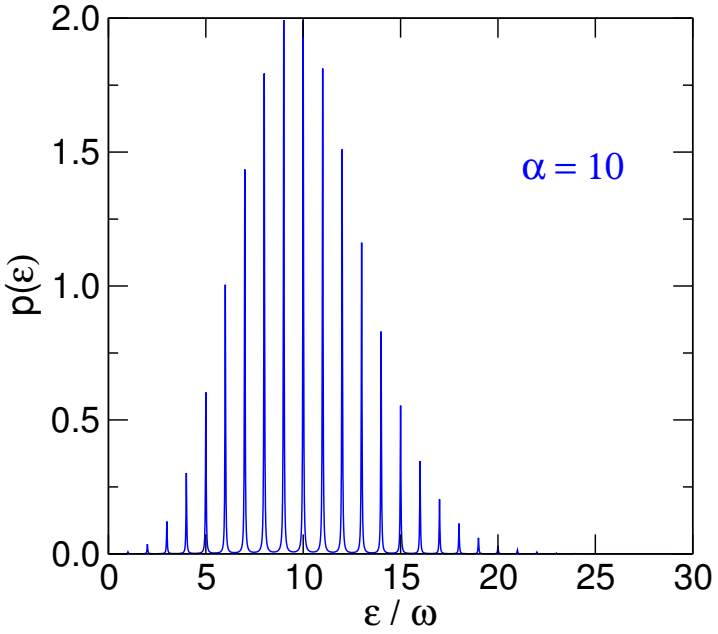
$$p(\epsilon) = \sum_{n=0}^{\infty} \delta(\epsilon - n\hbar\omega_0) P_{0\to n}$$

Probability density that the HO gains energy ϵ
$\equiv$ E-transfer probability density

- $I(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} F(t) dt$
- $\delta\epsilon_{av} = \int \epsilon p(\epsilon) = \alpha\hbar\omega_0 \equiv \frac{|I(\omega_0)|^2}{2M}$
- $\sigma_\epsilon^2 = \frac{|I(\omega_0)|^2}{2M}\hbar\omega_0$



Forced Oscillator Model



$$p(\epsilon) = \sum_{n=0}^{\infty} \delta(\epsilon - n\hbar\omega_0) P_{0\to n}$$

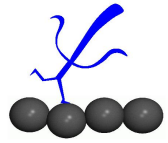
In the impulsive limit..

$$F(t) \approx I_0 \delta(t - \bar{t})$$

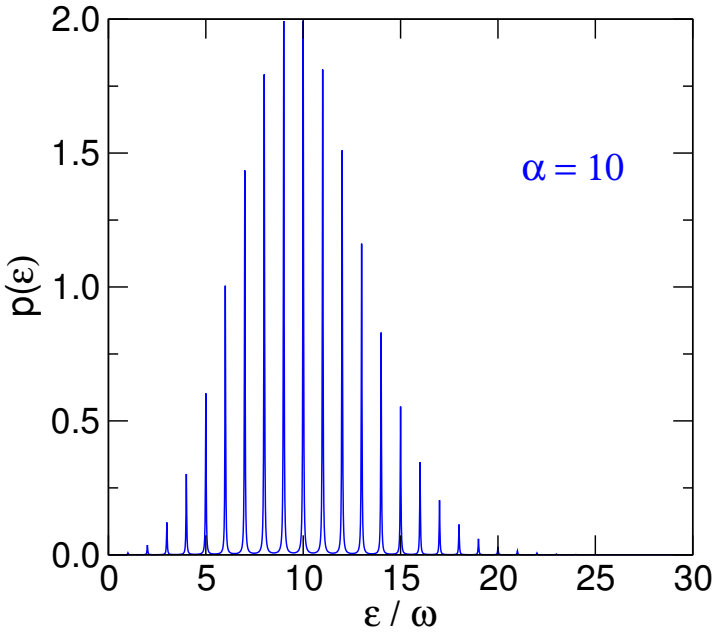
$|I(\omega)| = I_0$ is the impulse

$$\delta\epsilon_{av} \approx \frac{I_0^2}{2M}$$

$$I_0 = \frac{2m}{M+m} P \Rightarrow \delta\epsilon_{av} \approx \frac{4(m/M)}{(1+m/M)^2} \epsilon_P^i$$



Forced Oscillator Model



$$p(\epsilon) = \sum_{n=0}^{\infty} \delta(\epsilon - n\hbar\omega_0) P_{0\to n}$$

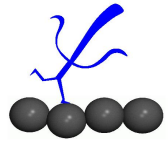
For P to attain the impulsive limit

$$\tau \ll \omega_0^{-1}$$

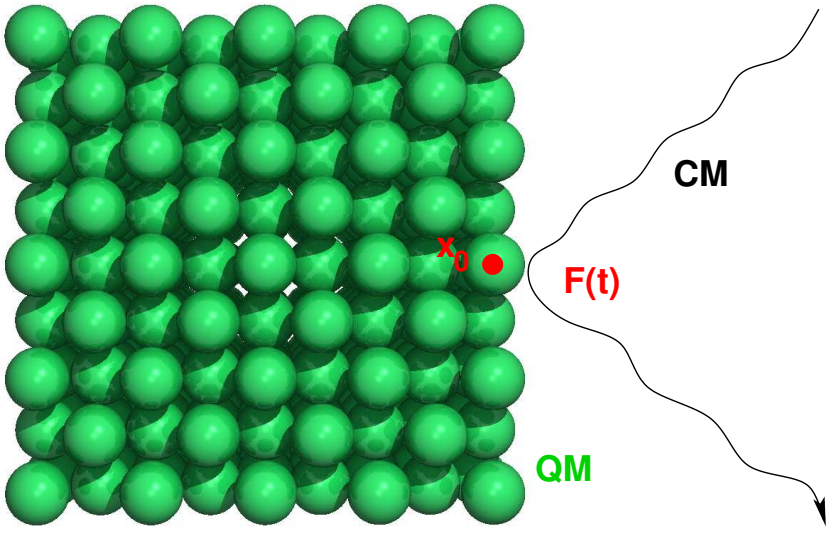
$$\delta\epsilon_{av} \gg \hbar\omega_0$$

$$\alpha \gg 1$$

Classical limit for the HO, too!



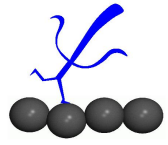
Forced Oscillator Model



$$H(t) = \sum_k \frac{p_k^2}{2} + \frac{\omega_k^2 q_k^2}{2} - x_0 F(t)$$
$$x_0 = \sum_k u_k q_k$$

sum of independent HO Hamiltonian

- u_k: coupling coefficients
- $p_k(\epsilon)$: p-density for the $k-th$ HO to gain ϵ
- $P(\epsilon)$: p-density for the surface to gain ϵ



Forced Oscillator Model

ϵ_k : independent random variables

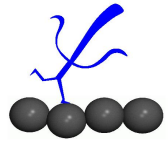
$$\epsilon = \sum_k \epsilon_k$$

$$\{p_k(\epsilon_k)\}_k \Rightarrow P(\epsilon)$$

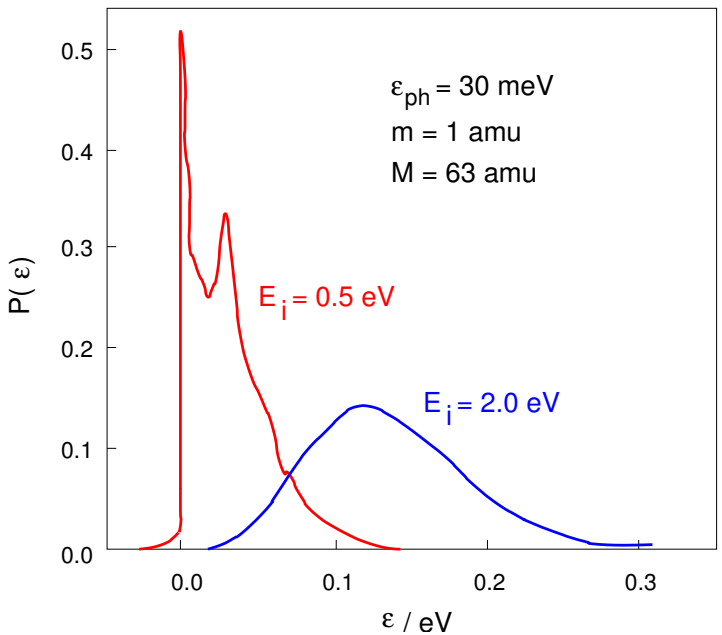
$$P(\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau e^{-i\tau\epsilon + \sum_k (e^{i\hbar\omega_k} - 1) \frac{u_k^2}{2\hbar\omega_k} |I(\omega_k)|^2}$$

density of phonon modes "in x_0":

$$\rho(\epsilon) = \sum_k |u_k|^2 \delta(\epsilon - \epsilon_k)$$



Forced Oscillator Model



H on Cu. Adapted from:
G. R. Darling and S. Holloway, *Rep. Prog. Phys.*, **58** (1995) 1595

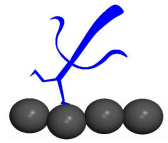
$$\sum_k (e^{i\hbar\omega_k} - 1)\frac{u_k^2}{2\hbar\omega_k}|I(\omega_k)|^2 \equiv \int (e^{i\hbar\omega} - 1)P_1(\epsilon)$$

One-phonon probability density:

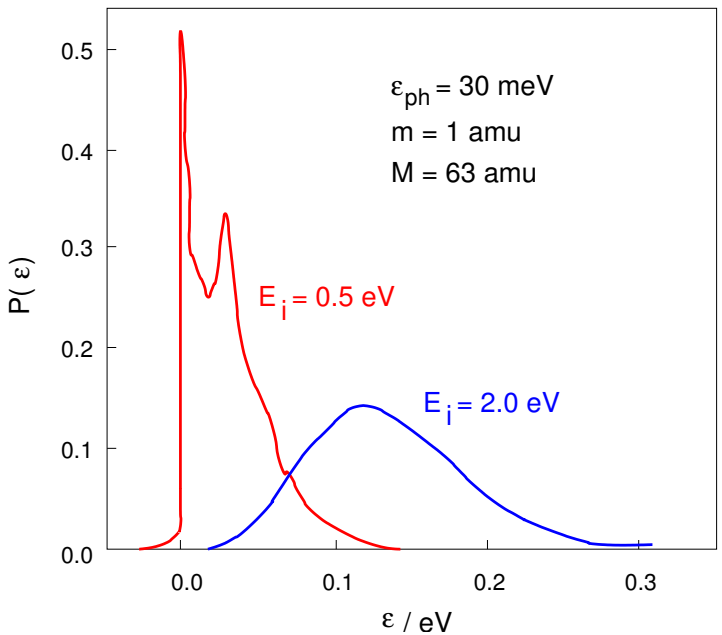
$$P_1(\epsilon) = \frac{|I(\epsilon/\hbar)|^2}{2\epsilon}\rho(\epsilon)$$

For small $I(\omega)$ ($\delta\epsilon_{av} \ll \hbar\Delta_{ph}$)

$$(\epsilon > 0) \quad P(\epsilon) \approx P_1(\epsilon)$$



Forced Oscillator Model



H on Cu. Adapted from:
G. R. Darling and S. Holloway, *Rep. Prog. Phys.*, **58** (1995) 1595

For small $I(\omega)$ $(\delta\epsilon_{av} \ll \hbar\Delta_{ph})$

$$(\epsilon \approx 0) \quad P(\epsilon) \approx \delta(\epsilon) P^{el}$$

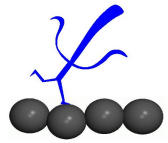
Elastic probability:

$$P^{el} \equiv e^{-\sum_k \frac{u_k^2}{2\hbar\omega_k} |I(\omega_k)|^2} := e^{-2W}$$

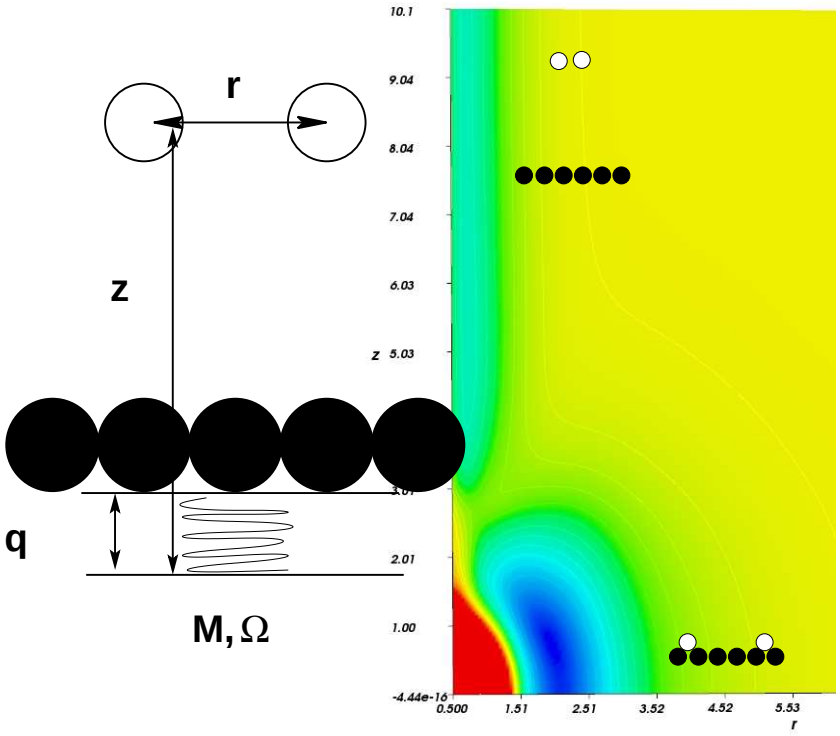
$$(|I(\omega)| \approx I_0) \quad 2W \approx \frac{|I_0|^2 \langle x_0^2 \rangle}{\hbar^2}$$

Elastic scattering for

- light species
- low T_s



Surface Oscillator Model



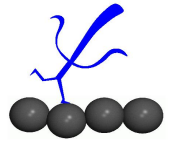
To include a single active phonon mode, *e.g.*

$$H = \frac{P_z^2}{2m} + \frac{p_r^2}{2\mu} + V(r, z)$$

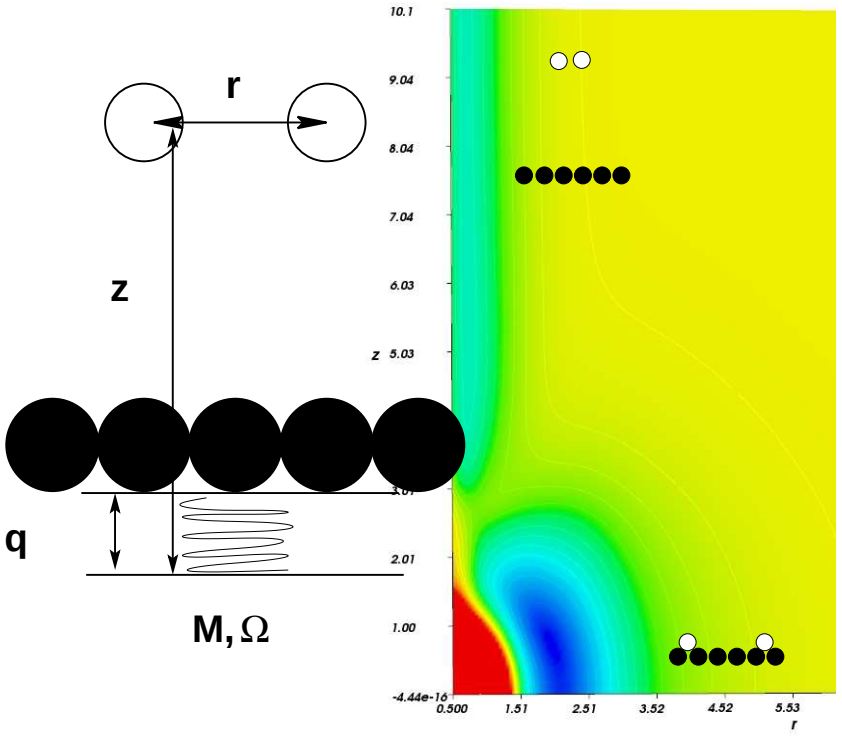
$$\Downarrow$$

$$H = \frac{P_z^2}{2m} + \frac{p_r^2}{2\mu} + \frac{p_q^2}{2M} + \frac{M\Omega^2 q^2}{2} + V(r, z - q)$$

From nD to $(n+1)D$ model



Surface Oscillator Model



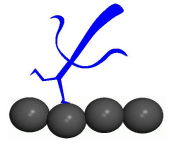
Effect of surface temperature on $S_\nu(E)$, *e.g.*

$$S_\nu(E) \Rightarrow S_\nu(E, n)$$

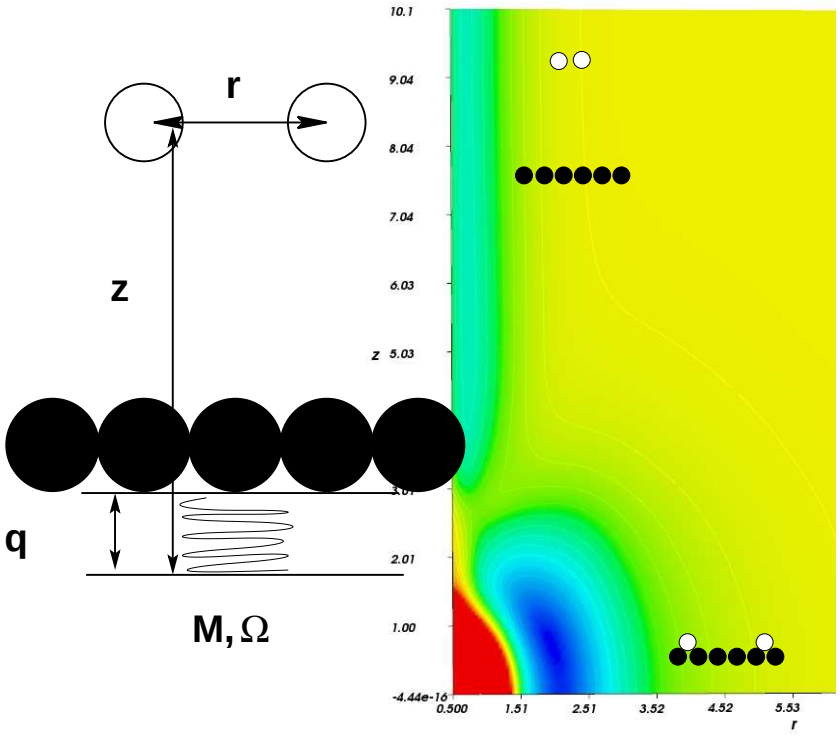
$$\Downarrow$$

$$S_\nu(E, T_s) = \sum_n S_\nu(E, n) P_n(T_s)$$

$$P_n(T_s) = \frac{e^{-\frac{\epsilon_n}{k_B T_s}}}{\sum_m e^{-\frac{\epsilon_m}{k_B T_s}}}$$



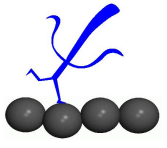
Surface Oscillator Model



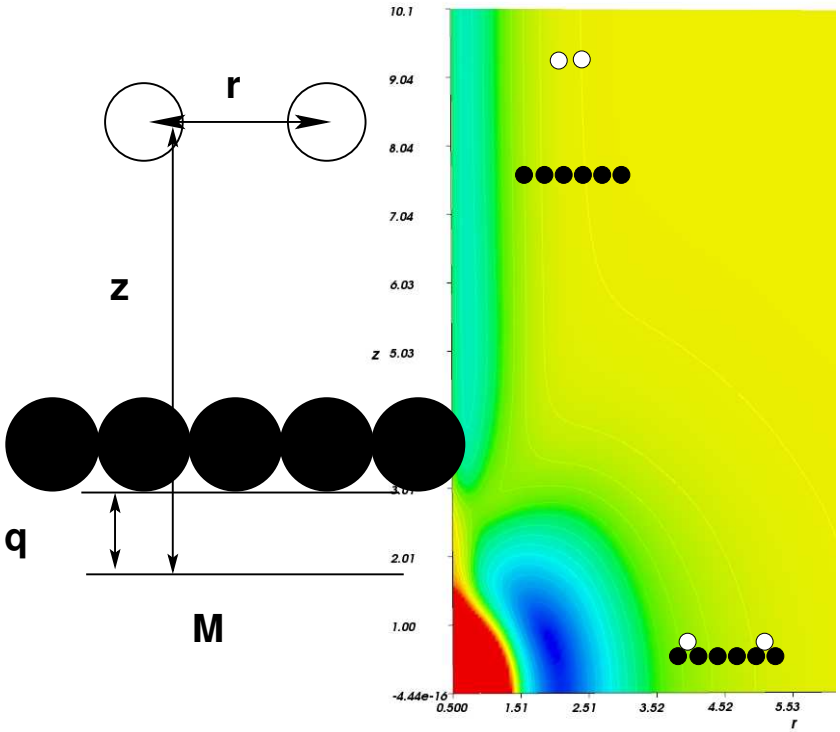
What about the Ω dependence?

- $\Omega \to \infty$: rigid surface model
- $\Omega \to 0$: surface mass model

Actually, results are almost insesitive to Ω,
provided Ω is not too large...



Surface Mass Model



$\Omega = 0$: recoil effect may be enough

$$H = \frac{P_z^2}{2m} + \frac{p_r^2}{2\mu} + \frac{p_q^2}{2M} + V(r, z-q)$$

$$\Downarrow$$

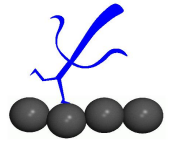
$$H = \frac{P_z'^2}{2\mu_S} + \frac{p_r^2}{2\mu} + V(r, z')$$

$$S_\nu(E) \Rightarrow S_\nu(E_{rel})$$

$$\Downarrow$$

$$E_{rel} = \frac{1}{2}\mu_S v'^2 = E_{rel}(E, E_q) \quad v' = v_z - v_q$$

$$S_\nu(E, T_s) = \int S_\nu(E_{rel}) P(v_q) dv_q$$



System-bath models

A simple model ...

$$H = \frac{p^2}{2M} + V(z) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(x_k - \frac{c_k z}{\omega_k^2} \right)^2 \right\}$$

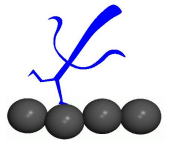
$$H \equiv H^{\text{sys}} + \Delta V(z) + H^{\text{int}} + H^{\text{bath}}$$

$H^{\text{sys}} = \frac{p^2}{2M} + V(z)$: system Hamiltonian (with $z = 0$ equilibrium position)

$\Delta V(z) = \frac{1}{2} \left(\sum_k \frac{c_k^2}{\omega_k^2} \right) z^2$: "renormalization" potential

$H^{\text{int}} = -\sum_k c_k x_k z$: interaction term

$H^{\text{bath}} = \sum_k \frac{p_k^2}{2} + \frac{\omega_k^2}{2} x_k^2$: "bath " Hamiltonian



System-bath models

Classical (or Heisenberg quantum) equations of motions

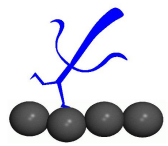
$$\ddot{z} = -\frac{\partial V}{\partial z} - \frac{\partial \Delta V}{\partial z} + \sum_k c_k x_k$$

$$\ddot{x}_k = -\omega_k^2 x_k + c_k z$$

$F_{\text{ren}}^{\text{env}} = \sum_k c_k x_k$: force exterted by the bath on the system

$c_k z$: "external" force felt by the k-th mode

$\Rightarrow$ Each $k-th$ HO is a forced Harmonic oscillator



System-bath models

Formally solving for $x_k(t)$ ...

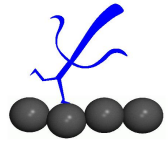
$$x_k(t) = x(t_0)\cos(\omega_k t) + \frac{\dot{x}_k(t_0)}{\omega_k}\sin(\omega_k t) + \int_{t_0}^{+\infty} \Theta(t-t')\frac{\sin(\omega_k(t-t'))}{\omega_k} c_k z(t')\, dt'$$

$\Downarrow$ $\Downarrow$

"free solution" "response"

$x_k^0(t)$: free solution of the HO with initial conditions $x_k(t_0)$, $\dot{x}_k(t_0)$

$\delta x_k(t)$: response of the HO to the external perturbation



System-bath models

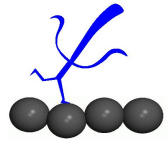
(FLUCTUATION) (DISSIPATION)

$$F_{\text{ren}}^{\text{env}} = \sum_k c_k x_k^0(t) - M\delta\Omega^2 z + \sum_k c_k^2 \int_{t_0}^{+\infty} \Theta(t-t') \frac{\sin(\omega_k(t-t'))}{\omega_k} z(t')\, dt'$$

$\Downarrow$ $\Downarrow$

Free evolution of the bath

Response of the bath to the z-motion



System-bath models

Upon rearranging (integration by parts)

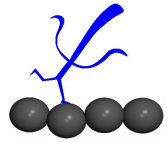
$$F^{\mathrm{env}} = \xi(t) - M \int_{t_0}^{+\infty} \gamma(t - t') \dot{z}(t')\, dt'$$

where

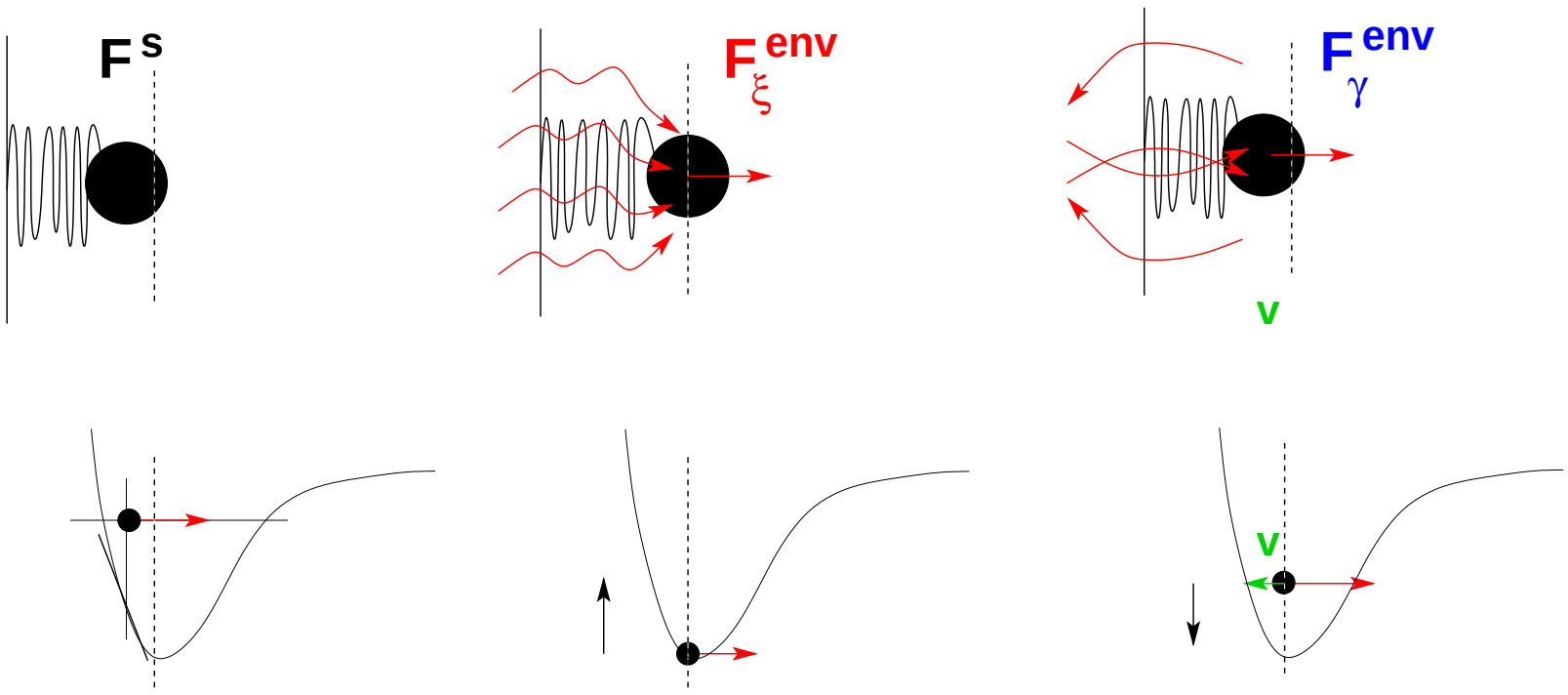
$$M\kappa(t) = \sum_k \frac{c_k^2}{\omega_k^2} \cos(\omega_k t)$$

$$\gamma(t) = \Theta(t)\kappa(t)$$

$$\xi(t) = \sum_k \left\{ \left[x_k(t_0) - \frac{c_k}{\omega_k^2} z(t_0) \right] \cos(\omega_k t) + \frac{\dot{x}_k(t_0)}{\omega_k} \sin(\omega_k t) \right\} c_k$$



System-bath models

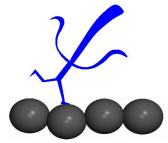


System-bath models

$$F^{\text{env}} = \xi(t) - M \int_{t_0}^{+\infty} \gamma(t - t') \dot{z}(t')\, dt'$$

$\gamma(t)$ is a proper dissipative kernel (with memory)

$\xi(t)$ is a "random" force, with $\{x_k(t_0),\ \dot{x}_k(t_0)\}$ to be extracted from the equilibrium distribution at time t_0



System-bath models

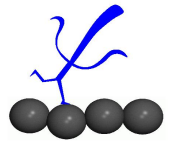
$$F^{\text{env}} = \xi(t) - M \int_{t_0}^{+\infty} \gamma(t - t')\dot{z}(t')\, dt'$$

$$\rho(x_1, x_2, \dots\ p_1, p_2, \dots) = \frac{1}{Z} e^{-\beta H_{z_0}^{\text{env}}}$$

$$H_{z_0}^{\text{env}} = \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(x_k - \frac{c_k z(t_0)}{\omega_k^2} \right)^2 \right\}$$

$$< \xi(t) >= 0$$

$$< \xi(t)\xi(0) >= \frac{k_B T}{M} \kappa(t)$$



System-bath models

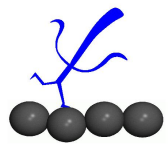
Conversely, for a given GLE with memory kernel $\gamma(t)$,

$$\gamma(t) \longrightarrow \tilde{\gamma}(\omega) = \int_{-\infty}^{+\infty} \mathrm{e}^{i\omega t}\gamma(t)\,dt$$

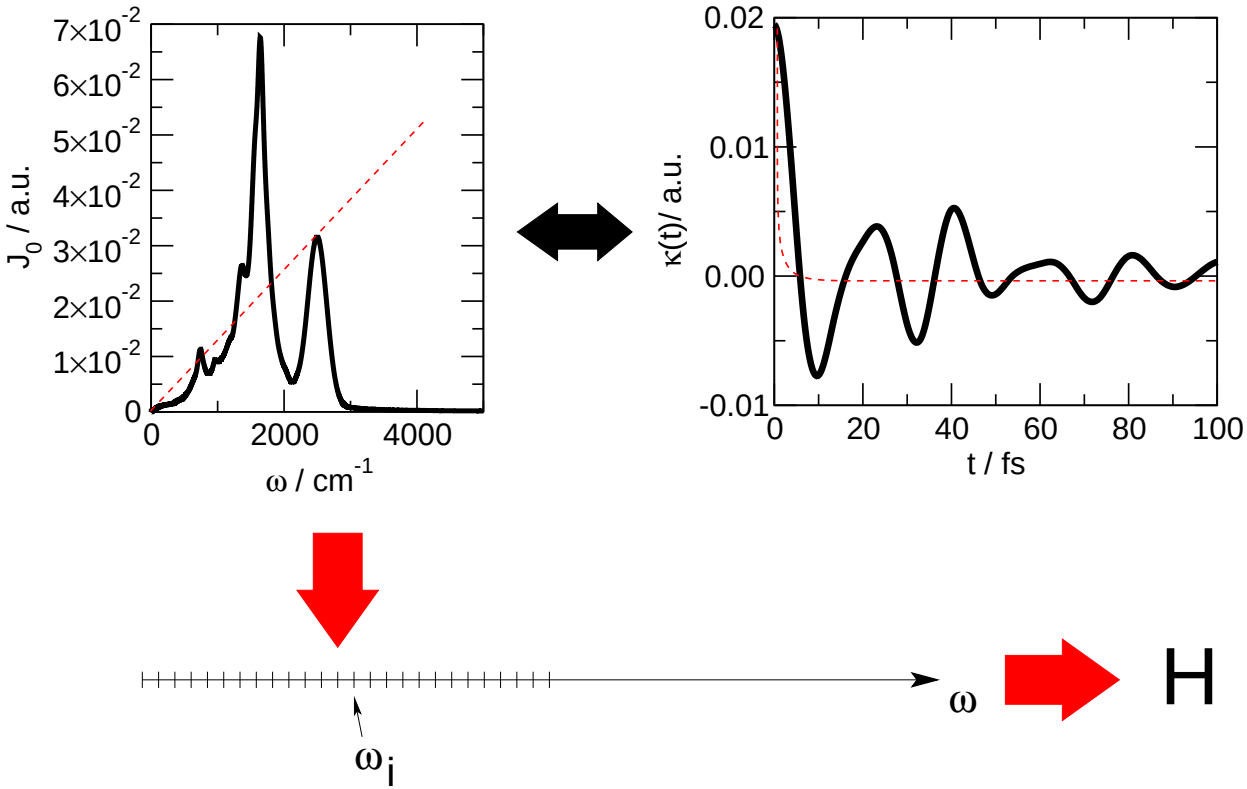
$$J(\omega) = M\,\omega\tilde{\gamma}'(\omega)$$

$$k = 1, \ldots N \qquad \omega_k = k\Delta\omega \qquad c_k = \sqrt{\frac{2\omega_k \Delta\omega J(\omega_k)}{\pi}}$$

provides a discretized model which is equivalent to the GLE in the limit $N \to \infty$



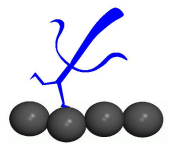
System-bath models



System-bath models

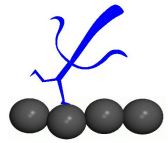
$$H = \frac{p^2}{2M} + V(z) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(x_k - \frac{c_k z}{\omega_k^2} \right)^2 \right\}$$

- dissipative dynamics for $t < T_{\rm rec} = \frac{2\pi}{\Delta\omega}$
- the bath can be obtained from small amplitude expansion of the exact Hamiltonian..
- or used to model phenomenological $J(\omega)$
- the Hamiltonian can be quantized to describe quantum dissipation



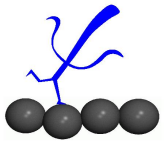
Summary

- Reduced models are necessary for many reasons
- Choice of the model requires physical insight into the process, *e.g.*
- does the surface play an active or passive role?
- is dynamics classical or quantum?

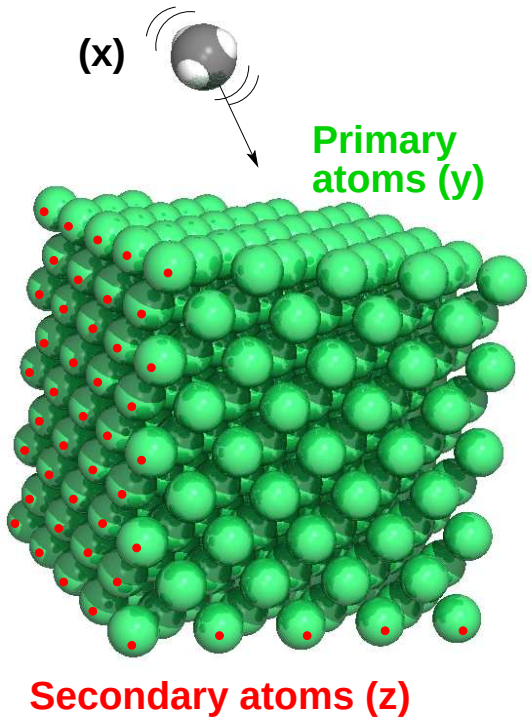


Outline

1. Basics
   - Linear chain model
   - Scattering from real surfaces
2. Reduced dynamical models
   - Traditional models
   - System-bath models
3. Dynamics
   - The methods
   - Examples



Classical dynamics with Langevin atoms



Straightforward ... just integrate

$$m\ddot{x}_i = F_x(\mathbf{x}, \mathbf{y}, \mathbf{z})$$
$$M\ddot{y}_i = F_y(\mathbf{x}, \mathbf{y}, \mathbf{z})$$
$$M\ddot{z}_i = F_z(\mathbf{x}, \mathbf{y}, \mathbf{z}) - M\gamma\dot{z}_i + \xi_i$$

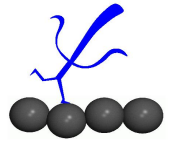
where

$$F_q = -\frac{\partial U}{\partial q}(\mathbf{x}\ \mathbf{y}\ \mathbf{z}) \quad q = x_i, y_i, z_i$$

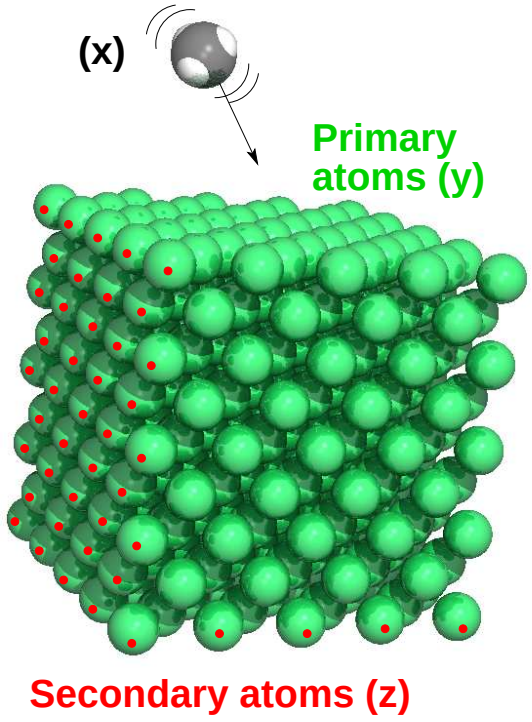
U : many-body potential including

- molecule-surface interaction
- lattice potential

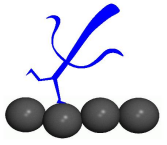
γ, ξ : Langevin terms,"consistent" with the lattice



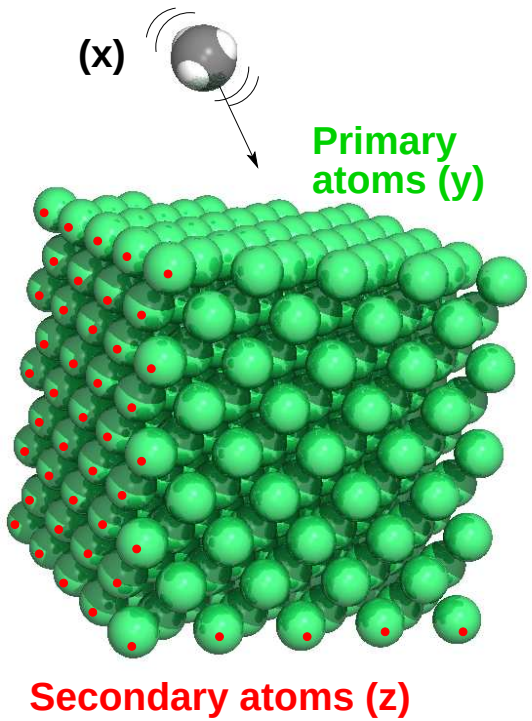
Classical dynamics with Langevin atoms



- Periodic Boundary Conditions || to the surface
- Minimum Image Convention
- ξ_i is a Gaussian random variable
- $\xi_i(t + \Delta t)$ is statistically independent from $\xi_i(t)$



Classical dynamics with Langevin atoms



Sampling intial conditions

Molecule: $(v, j, m_j) \rightarrow \{r, p_r, \theta, j, \phi, j_z\}$

Z_{cm} "large", X_{cm}, Y_{cm}

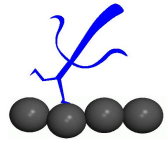
$V_{x,cm}$, $V_{y,cm}$, $V_{z,cm}$

Surface:

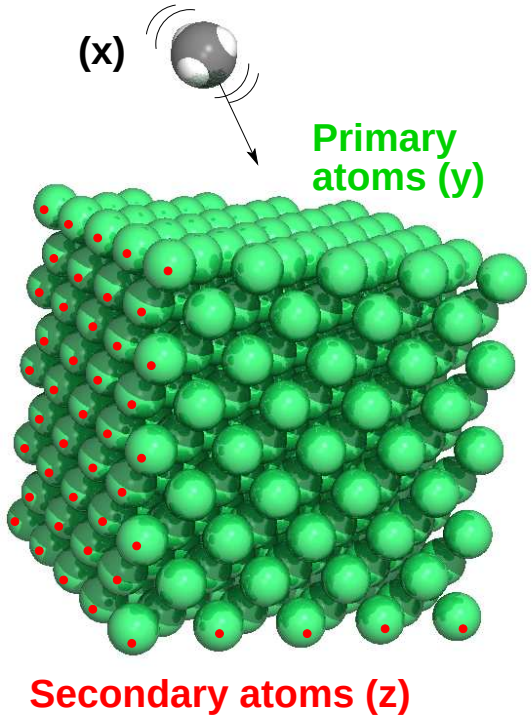
$$T_s \rightarrow \{q_i, v_i\}_{i=1}^{N}$$

$$p(v_i) = \left(\frac{M\beta}{2\pi}\right)^{1/2} e^{-\beta \frac{Mv_i^2}{2}}$$

$$p(q_1, .q_i, ..) = \frac{e^{-\beta V(q_1, q_2, \ldots, q_N)}}{\int e^{-\beta V}\, d^N\mathbf{q}}$$



Classical dynamics with Langevin atoms

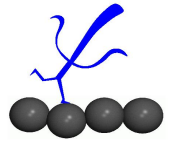


How to get $p(\ldots q_i \ldots)$?

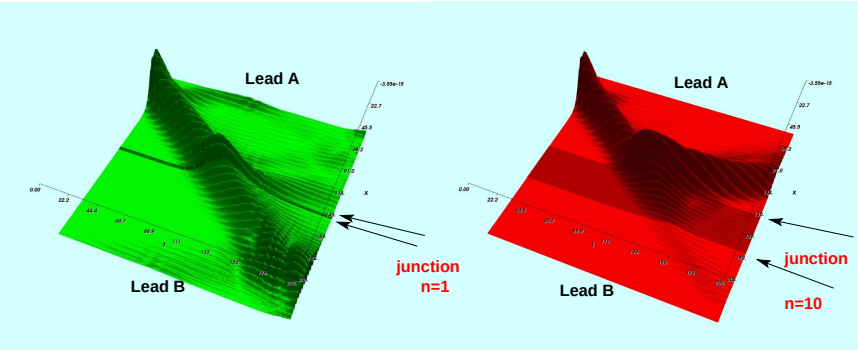
- Set $T_{kin} = \langle \frac{1}{2} M v_i^2 \rangle = 2 T_S$, i.e. sample v_i for $T = 2 T_S$
- Find $\{\bar{q}_i\}$, equilibrium configuration
- Start Langevin dynamics at temperature T_S

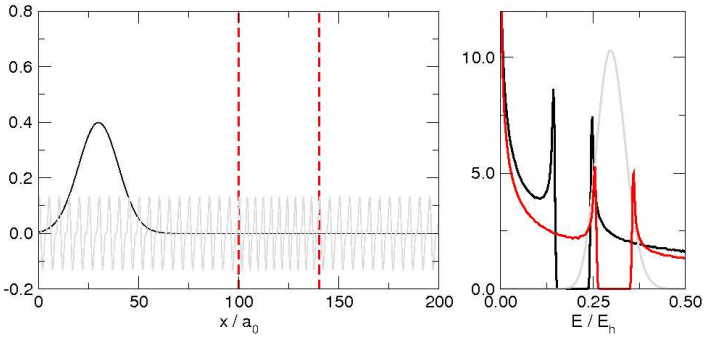
$\Rightarrow$ The system quicky relaxes towards the equilibrium state at T_S

$\Rightarrow$ Extract $\{q_i\}_1$, $\{q_i\}_2$, $\ldots$



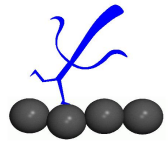
Quantum dynamics (small systems)





$$H\psi = i\hbar\frac{\partial\psi}{\partial t}$$

- Represent
  $\psi(x)$, $\psi(x) \rightarrow \psi_i$
- Represent operators
  O, $O \rightarrow O_{i,j}$
- Evolve
  ψ, $\psi_i(t=0) \rightarrow \psi_i(t)$
- Analyze $\psi(t) \rightarrow P(E)$ at all times



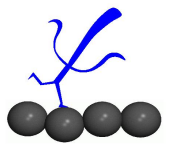
Quantum dynamics (large systems)

Multi Configurational Time-Dependent Hartree

$$\Psi(x_1, x_2, .., x_N) = \sum_{i_1, i_2, \ldots i_N} c_{i_1, i_2, \ldots i_N} \, \phi^{(1)}_{i_1}(x_1) \phi^{(2)}_{i_2}(x_2) \ldots \phi^{(N)}_{i_N}(x_N)$$

- $c_{i_1, i_2, \ldots i_N} = c_{i_1, i_2, \ldots i_N}(t)$ are time-evolving amplitudes for the configurations
- $\phi^{(k)}_i(x) = \phi^{(k)}_i(x, t)$ are time-evolving single-particle functions
- $\langle \phi^{(k)}_i | \phi^{(k)}_j \rangle = \delta_{ij}$ for any $k = 1, ..N$

Equations of motion?



Quantum dynamics (large systems)

Dirac Frenkel variational principle

$$\langle \delta\Psi | i\hbar\partial_t - H|\Psi\rangle = 0$$

- $i\hbar\dot{C} = HC$
- $i\hbar(1-P^k)\frac{d}{dt}|m^{(k)}\rangle = (1-P^k)\sum_{j,l=1}^{n_k}\left[\left(\rho^{(k)}\right)^{-1}\right]_{mj} H_{jl}^{(k)}|l^{(k)}\rangle$

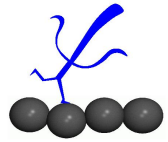
where

$$H_{IJ} = \langle\Phi_I|H|\Phi_J\rangle \quad |\Phi_I\rangle = |\phi_{i_1}^1\rangle \ldots |\phi_{i_N}^N\rangle$$

$$P_k = \sum_{j=1}^{n_k} |j^{(k)}\rangle\langle j^{(k)}| \quad |j^{(k)}\rangle \equiv |\phi_j^{(k)}\rangle$$

$$H_{jl}^{(k)} = \langle\Psi_j^{(k)}|H|\Psi_l^{(k)}\rangle \quad , \quad |\Psi_j^{(k)}\rangle = a_j^{(k)}|\Psi\rangle$$

$$\rho_{jm}^{(k)} = \langle\Psi_j^{(k)}|\Psi_m^{(k)}\rangle$$



Quantum dynamics (large systems)

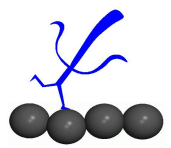
Close-Coupling Wave Packet

$$\Psi(..,x_i,..,z_i,..) = \sum_{\mathbf{n}} \psi_{\mathbf{n}}(x_1,x_2,..)\phi^{(1)}_{n_1}(z_1)\phi^{(2)}_{n_2}(z_2)\ldots\phi^{(N)}_{n_N}(z_N)$$

- $\psi_{\mathbf{n}}(x_1,x_2,..)$ are time-evolving channel wavepackets (*e.g.* molecular WPs)
- $\phi^{(k)}_n(x)$ are stationary single-particle functions (*e.g.* HOs eigenstates)

$$i\hbar\frac{\partial\psi_{\mathbf{n}}}{\partial t}(x_1,x_2,..) = \sum_{\mathbf{m}} H_{\mathbf{nm}}(x_1,x_2,..)\psi_{\mathbf{m}}(x_1,x_2,..)$$

$$H_{\mathbf{nm}}(x_1,x_2,..) = \langle\phi^{(1)}_{n_1}\phi^{(2)}_{n_2}\ldots\phi^{(N)}_{n_N}|H|\phi^{(1)}_{m_1}\phi^{(2)}_{m_2}\ldots\phi^{(N)}_{m_N}\rangle$$



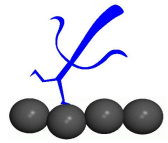
Quantum dynamics (large systems)

Time-Dependent Self-Consistent Field

$$\Psi(x_1, x_2, .., x_N) = c_t\, \phi^{(1)}(x_1)\phi^{(2)}(x_2)\ldots\phi^{(N)}(x_N)$$

- $c(t) = e^{-iS(t)}$ phase-factor
- $\phi^{(k)}(x) = \phi^{(k)}(x,t)$ are time-evolving single-particle functions..
- ..one spf for each DOF

$$i\hbar\frac{\partial\phi^{(i)}}{\partial t}(x_i) = H^{(i)}(x_i)\phi^{(i)}(x_i)$$
$$H^{(i)}(x_i) = \langle\ldots\phi^{(i-1)}\phi^{(i+1)\ldots}|H|\ldots\phi^{(i-1)}\phi^{(i+1)\ldots}\rangle$$
$$\Rightarrow i-th \text{ mean-field}$$



Quantum-classical dynamics (large systems)

Time-Dependent Self-Consistent Field with Gaussians

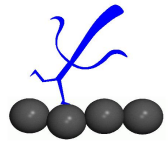
$$\Psi(..,x_i,..,z_i..) = \psi(..,x_i,..)\phi^{(1)}(z_1)\ldots\phi^{(N)}(z_N)$$

- $\phi^{(k)}(x) = g^{(k)}(x,t)$ are Gaussian wavepackets centered in $\{z_k(t), p_k(t)\}$

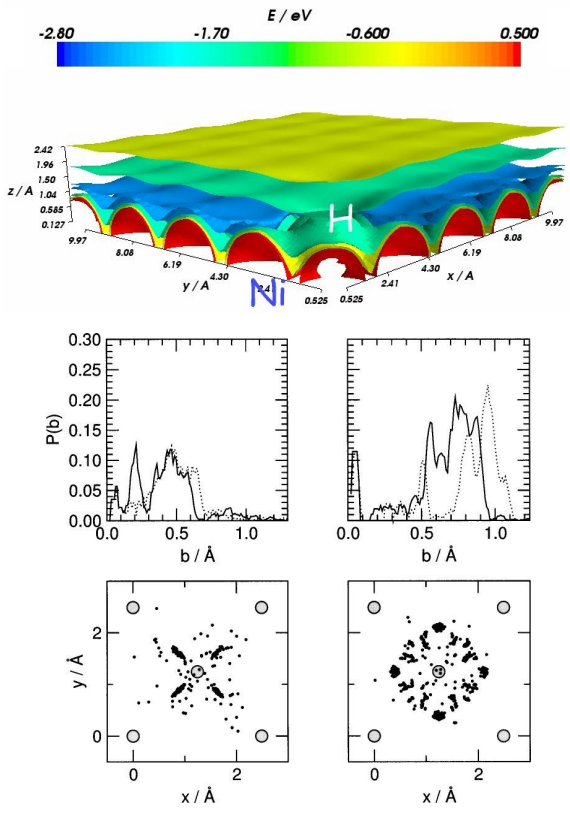
$$i\hbar\frac{\partial\psi}{\partial t}(..,x_i,..) = H(t)\psi(..,x_i,..)$$

$H(t)$ is the quantum Hamiltonian averaged over the classical DOFs

$\{z_k(t), p_k(t)\}$ evolve classically on a mean-field Hamiltonian

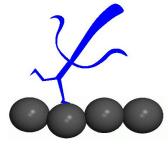


Langevin

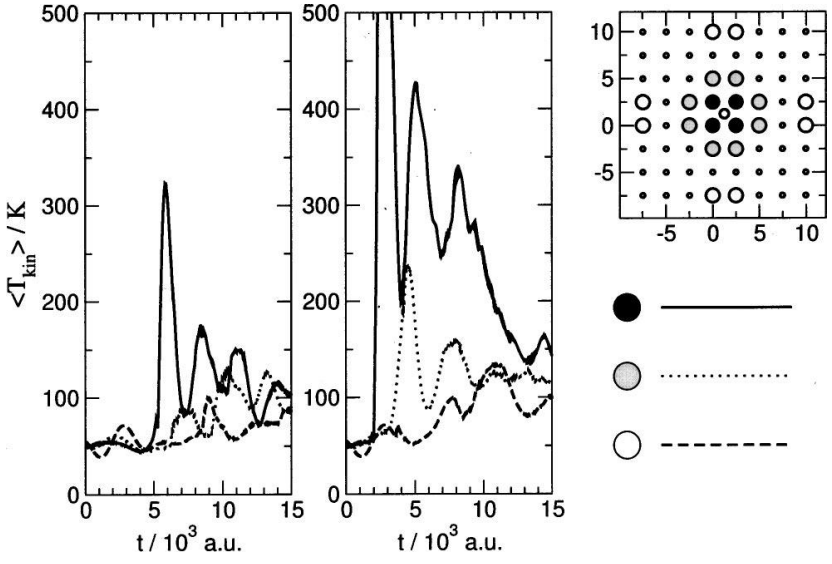


- H atom on H adsorbed on Ni(100)
- Classical dynamics with a 9x9x11 slab
- Thermal contacts with a reservoir at $T_s = 120 - 300K$
- Eley-Rideal H_2 formation *vs.* Hot-atom species

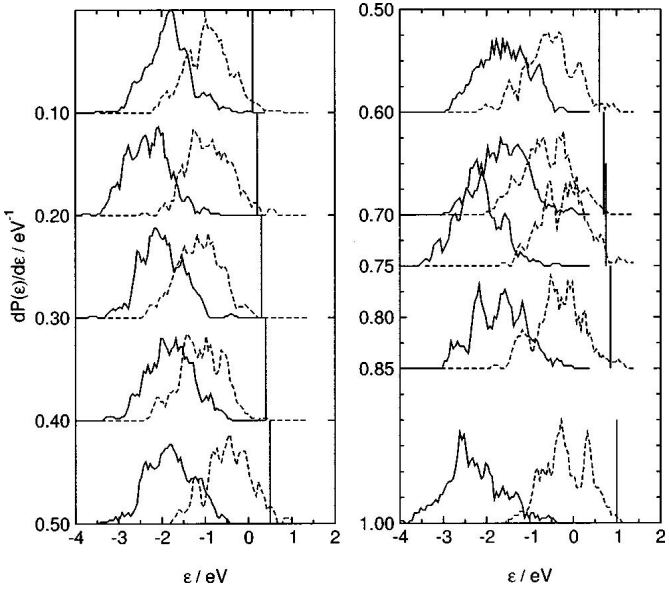
R. Martinazzo, S. Assoni, G. Marinoni, G.F. Tantardini, *J. Chem. Phys.*, **120** (2004) 8761



Langevin

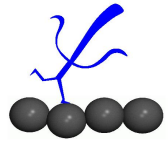


Thermal shock-wave

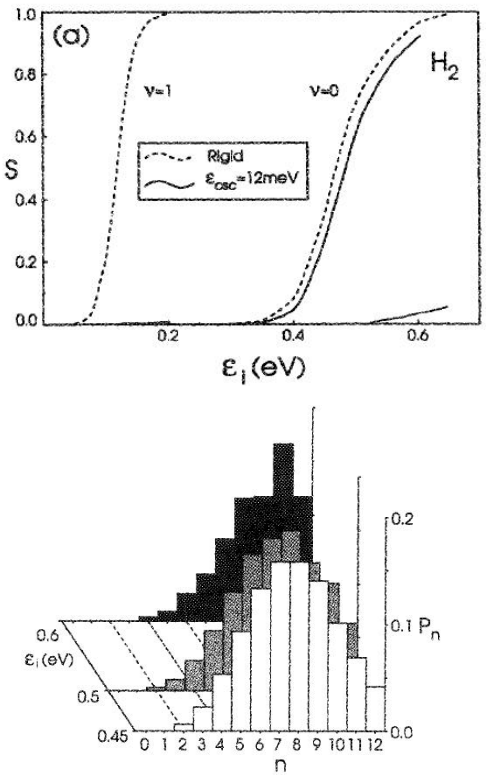


Hot species

R. Martinazzo, S. Assoni, G. Marinoni, G.F. Tantardini, *J. Chem. Phys.*, **120** (2004) 8761

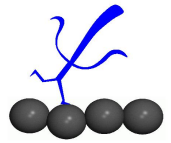


Surface Oscillator Model

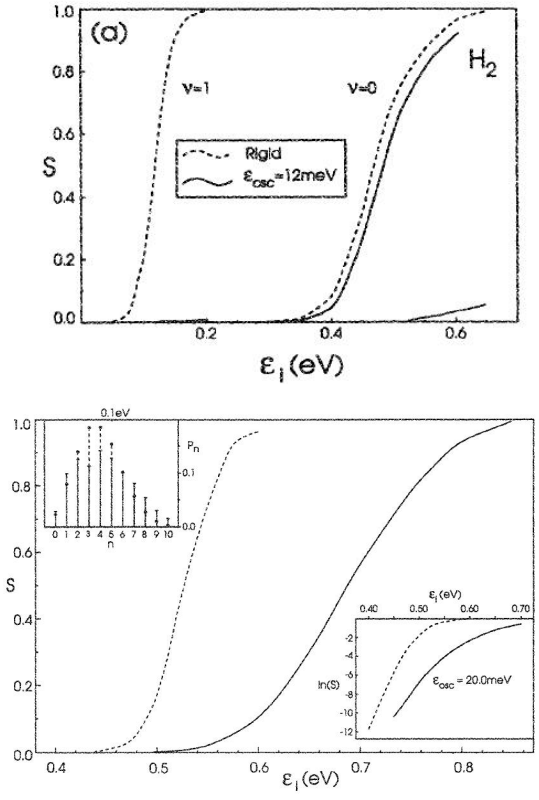


- Minimal model for dissociative sticking of diatomics (z, r, q)
- 3D Quantum dynamics with wave packets
- Recoil effects in surface dissociation

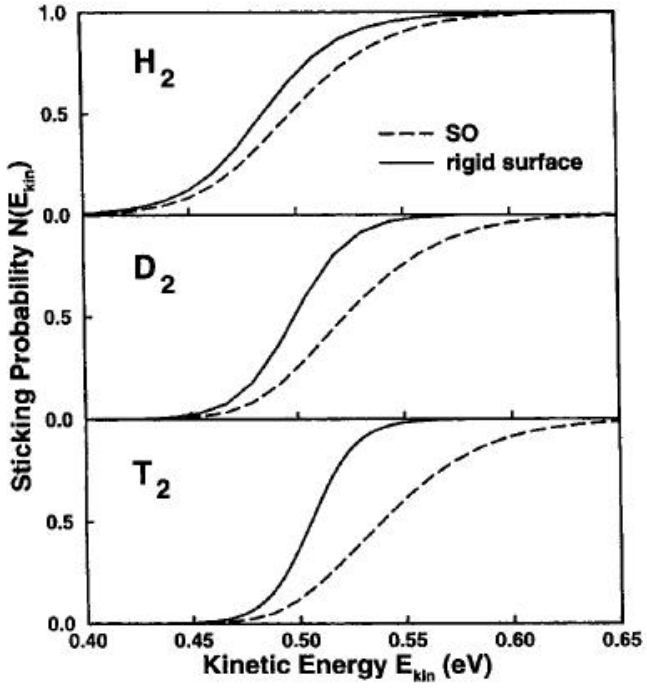
M. Hand and J. Harris, *J. Chem. Phys.*, **92** (1990) 7610



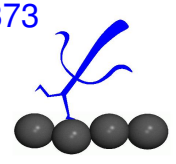
Surface Oscillator Model



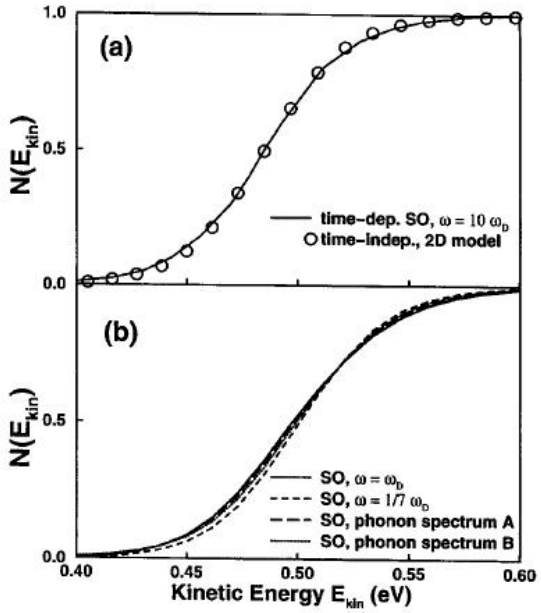
M. Hand and J. Harris, *J. Chem. Phys.*, **92** (1990) 7610



M. Dohle and P. Saalfrank, *Surf. Sci.*, **95** (1997) 373



Surface and Mass Oscillator Models



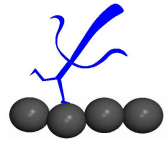
- Results do not depend on Ω
- The shift is mainly due to the $E \rightarrow E_{rel}$ transformation

For q initially at rest

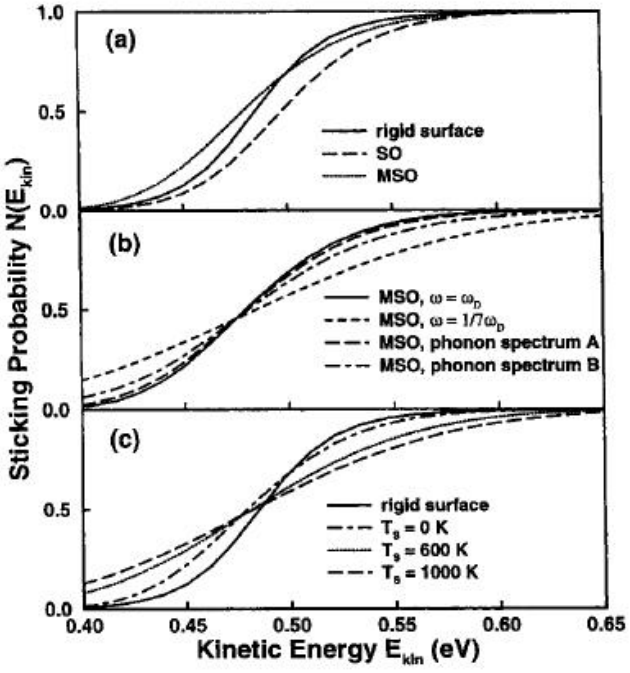
$$p = \frac{M}{M+m} P$$

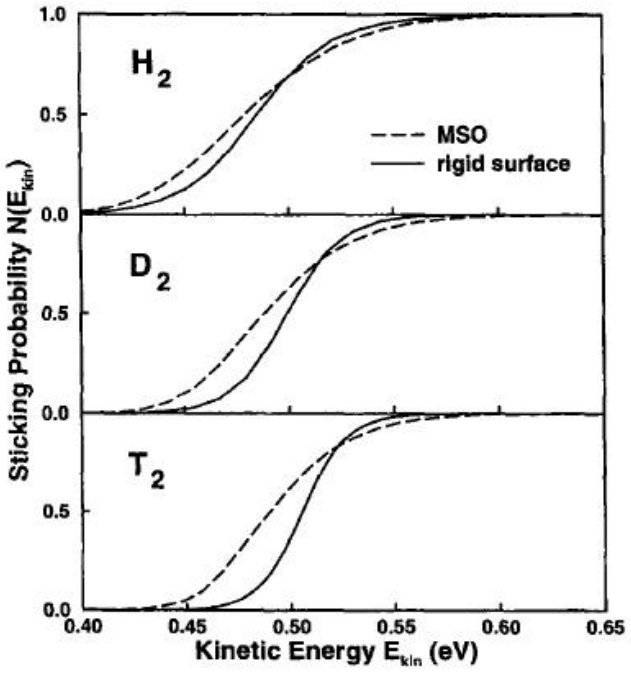
$$E_{rel} = \frac{p^2}{2\mu} = E \frac{M}{M+m}$$

M. Dohle and P. Saalfrank, *Surf. Sci.*, **95** (1997) 373

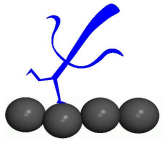


Modified SO Model

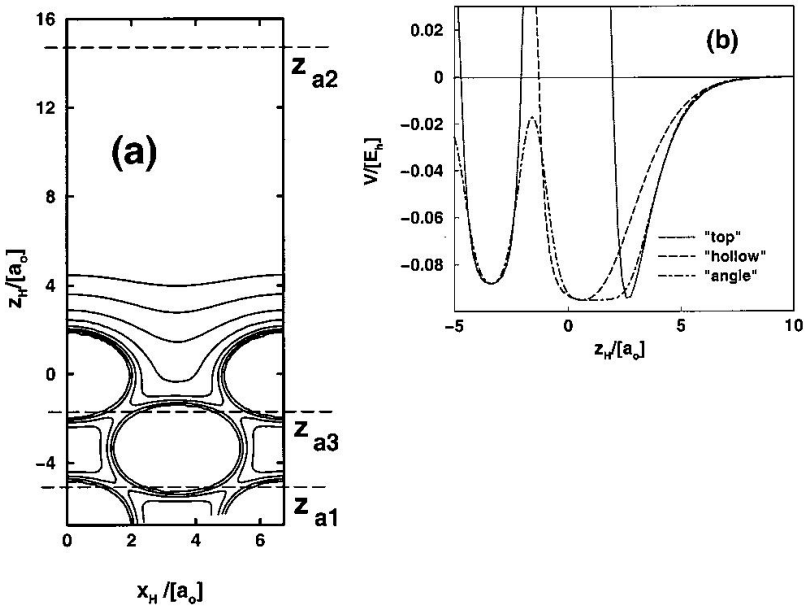




M. Dohle and P. Saalfrank, *Surf. Sci.*, **95** (1997) 373

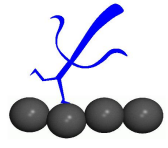


Quantum dynamics: approximate methods

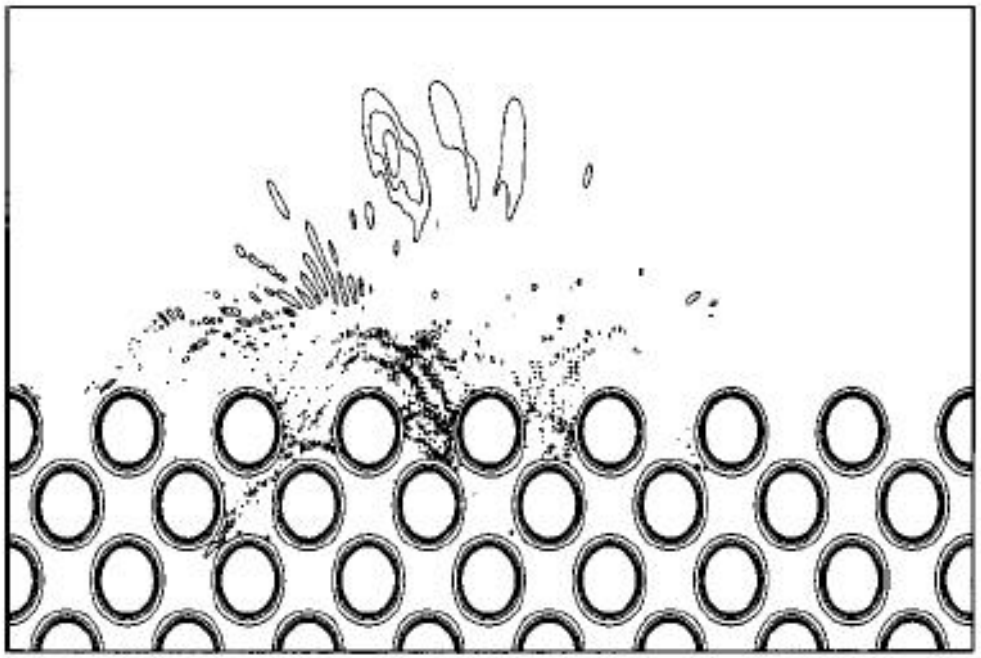


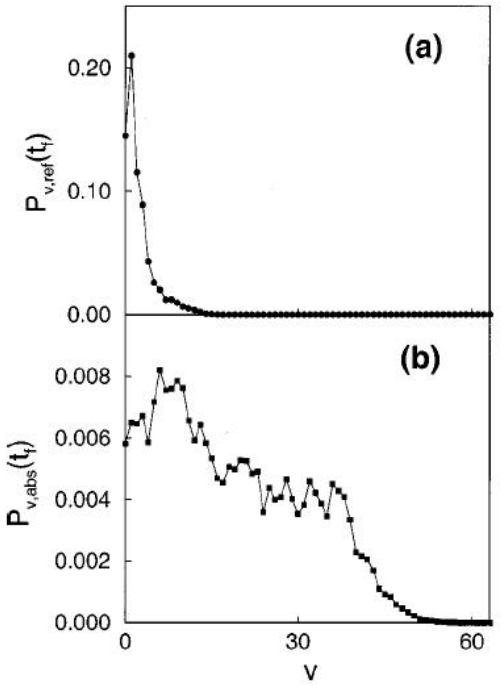
- Different models and different methods
- Failure of the mean-field approximations
- Classical can be better than mixed quantum/classical

T. Klamroth and P. Saalfrank,
J. Chem. Phys., **112** (2000) 10571

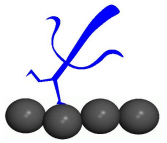


Quantum dynamics: approximate methods

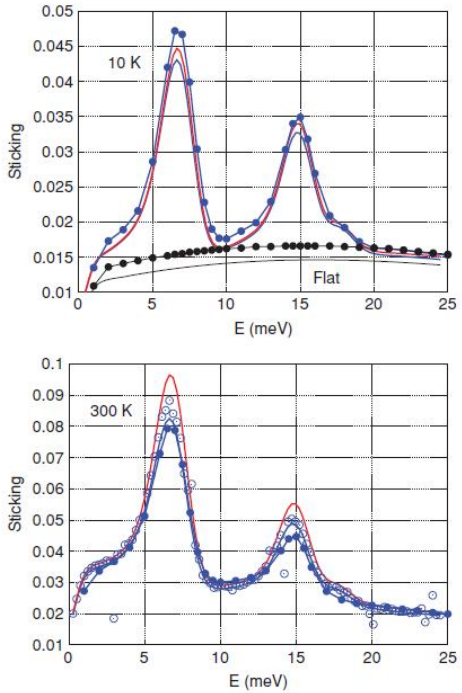




T. Klamroth and P. Saalfrank, *J. Chem. Phys.*, **112** (2000) 10571

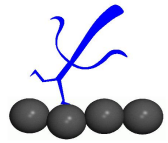


Quantum dynamics (large systems)

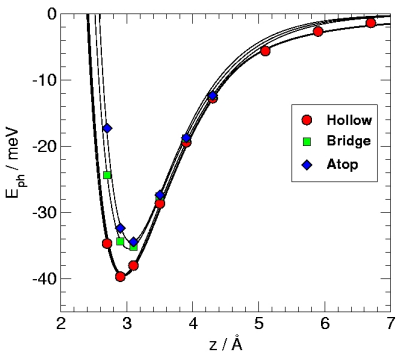


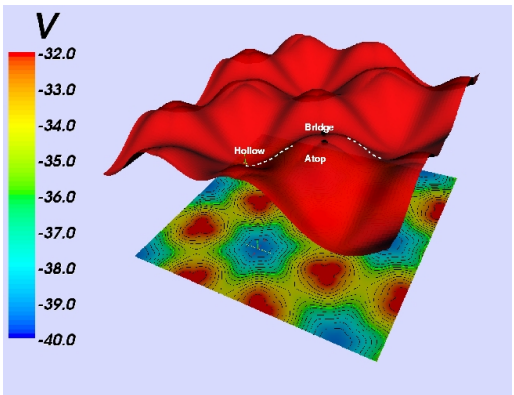
- Accurate rigid-surface PES
- Coupling to the lattice phonons leads to a system-bath-like Hamiltonian
- Full quantum dynamics with CCWP and other methods
- One-phonon approximation works fine

B. Lepetit, D. Lemoine, Z. Medina and B. Jackson, *J. Chem. Phys.*, **134** (2011) 114705



Quantum dynamics (large systems)





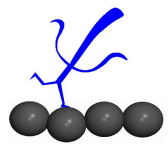
The adopted CCWP correctly handles PES corrugation

$$\Psi(\mathbf{r}, q_1, q_2, .., t) = \sum_{i,n} c_{i,n}(t)\phi_i(\mathbf{r})\Phi_n(q_1, q_2, ..q_N)$$

$$H_{3D}\phi_i = \epsilon_i\phi_i$$

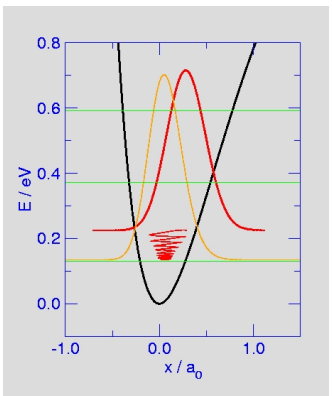
$$|\Phi_n\rangle = |0_1, 0_2, ..0_{n-1}1_n0_{n+1}..0_N\rangle$$

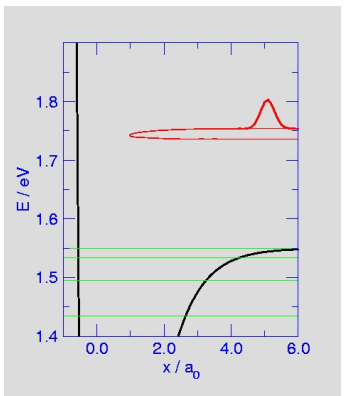
$\Rightarrow$ Selective adsorption resonances



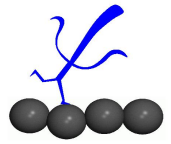
Quantum dynamics (large systems)

$$H = \frac{p^2}{2M} + V(s) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(x_k - \frac{c_k f(s)}{\omega_k^2} \right)^2 \right\}$$





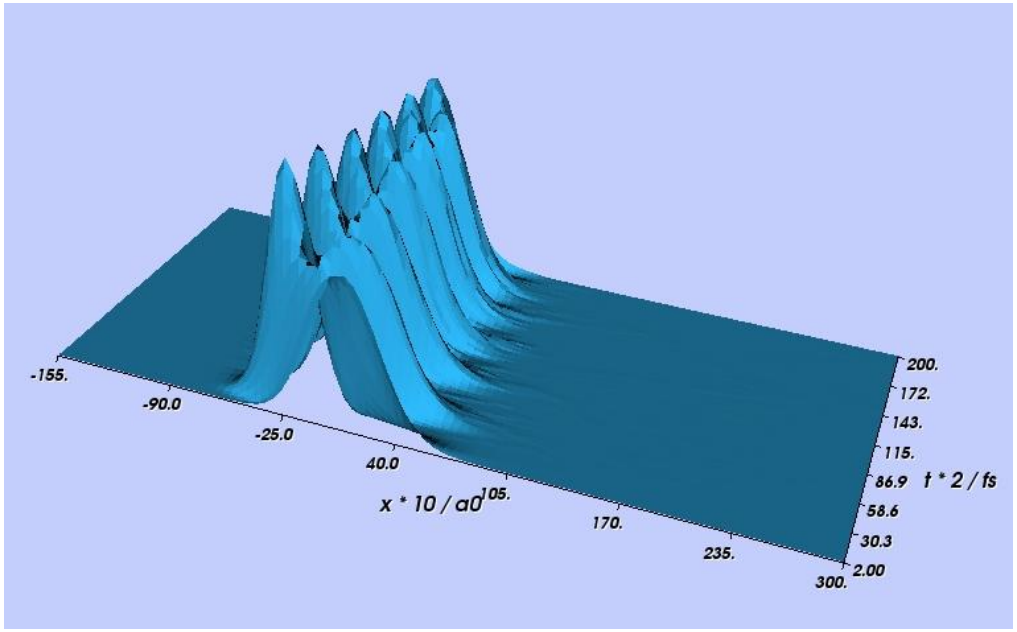
- $f(s) = \frac{1-e^{-\alpha s}}{\alpha} \longrightarrow s$ for $s \longrightarrow 0$
- $V(s) = D_e e^{-\alpha s}(e^{-\alpha s} - 2)$, with $D_e = 1.55eV$
- $M = m_H$
- Several $J(\omega)$s



Quantum dynamics (large systems)

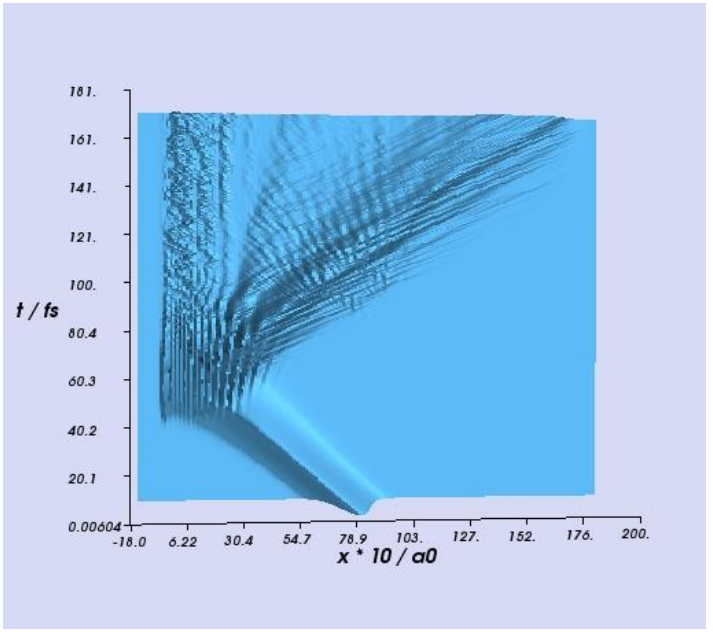
Vibrational relaxation

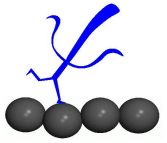
$\rho_t(s|s)$



Sticking

$\rho_t(s|s)$

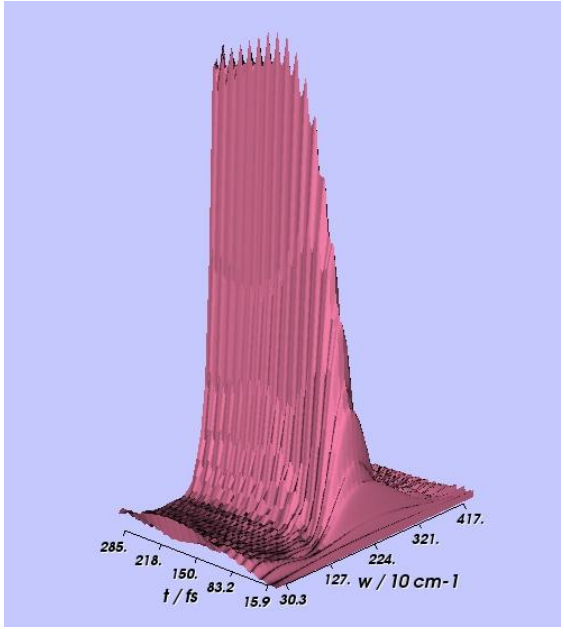




Quantum dynamics (large systems)

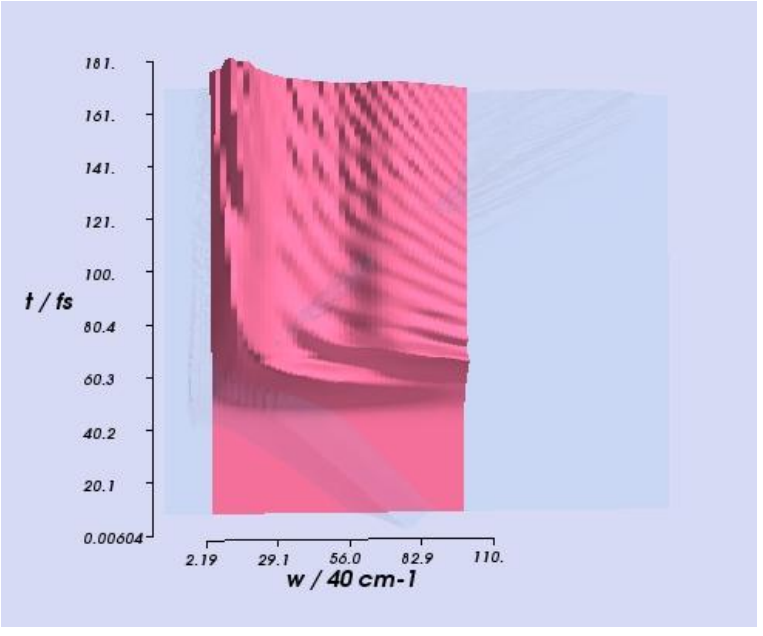
Vibrational relaxation

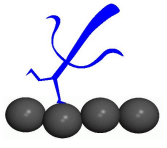
$\langle a_\omega^\dagger a_\omega \rangle_t$



Sticking

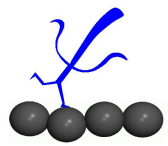
$\langle a_\omega^\dagger a_\omega \rangle_t$





Summary

- Surface atoms may be directly involved in activated process, *i.e.* their motion exponentially influences the rates
- Surface atoms are responsible for energy dissipation
- Approximations are always needed, no recipe works for any situation



Acknowledgements

Thank you for your attention!