Second Order Classical Perturbation Theory For The Sticking Probability Of Heavy Atoms Scattered On Surfaces[1]

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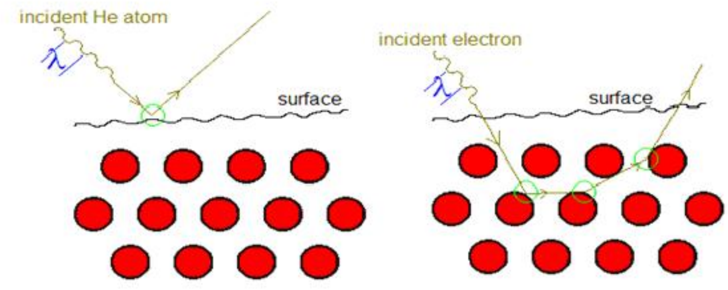
[1] T. Sahoo and E. Pollak, J. Chem. Phys. **143**, 064706 (2015)

Introduction

Importance

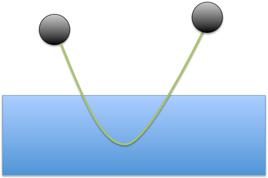
- Atom - surface scattering is a surface analysis technique used in materials science.
- It provides information about the surface structure and lattice dynamics of a material by measuring the diffracted atoms from a monochromatic helium beam incident on the sample.

Difference between Atom and electron scattering



Trapping of atom on metal surface

A)



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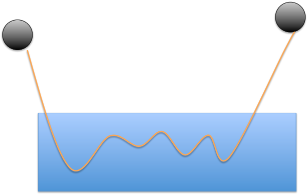

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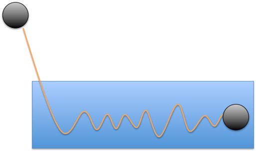
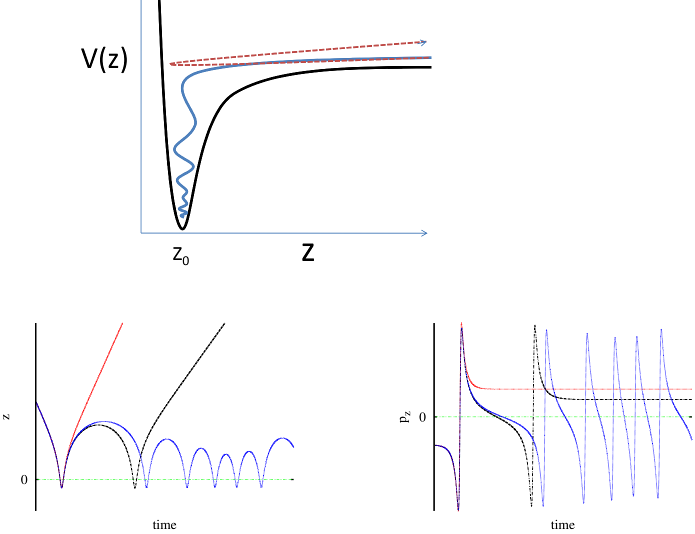


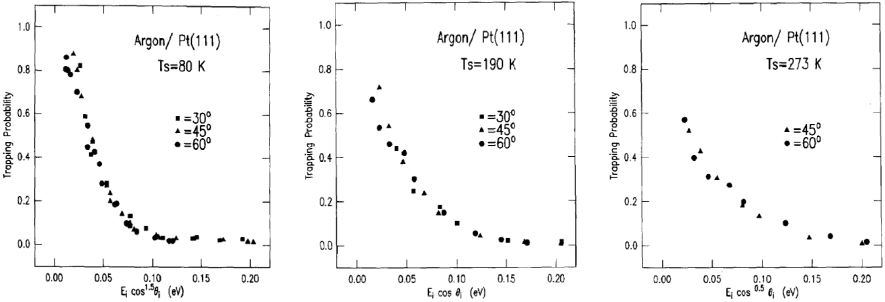
Trapping of atom on metal surface



- A trajectory which undergoes $2K-1, K \geq 1$ sign changes before exiting to the asymptotic region will have undergone K traversals over the attractive well.

Some experimental observations

- Experimental observation by Mullins *et al.* (Chem. Phys. Lett. 163, 111 (1989).)



- This probability decreases with increasing incident kinetic energy of Ar atom, E_i, in a manner that depends on both θ_i, and T_s.

Theoretical study

- For many years these phenomena have been considered theoretically in the framework of the "washboard model" [J. C. Tully, Surf. Sci. 111, 461 (1981)] in which the interaction of the incident particle with the surface is described in terms of hard wall potentials.
- Hubbard and Miller [J. Chem. Phys. 80, 5827 (1984)] have applied a semiclassical perturbation (SCP) approximation to calculate the sticking probability for the He-W(110) and Ne-W(110) systems.
- Challenges - To explain surface temperature effects, phonon bath effects on sticking and energy transfer processes
- Our main tool - the classical perturbation theory for the atom - surface scattering derived by Eli Pollak and his group[2].

[2] E. Pollak, J. Phys. Chem. A **115**, 7189 (2011), Y. Zhou, E. Pollak and S. Miret-Artes, J. Chem. Phys. **140**, 024709 (2014)

The model Hamiltonian

- We assume that the Hamiltonian has the following structure:

$$H = \frac{p_z^2}{2M} + V(z) + \frac{1}{2}\sum_{j=1}^{N}\left(p_j^2 + \omega_j^2\left[x_j - \frac{c_j}{\sqrt{M}\omega_j^2}V'(z)\right]^2\right) = H_0 + H_I.$$

- The zero-th order Hamiltonian is written as

$$H_0 = H_S + H_B, \quad \texttt{with} \quad H_S = \frac{p_z^2}{2M} + V(z) \quad \texttt{and} \quad H_B = \frac{1}{2}\sum_{j=1}^{N}\left(p_j^2 + \omega_j^2 x_j^2\right).$$

- The initial conditions for the bath phase space variables are are taken from the canonical distribution $\exp(-\beta H_B)/Z_B$, with $\beta = 1/k_B T$.
- The time dependent system and bath phase space variables are expanded in powers of the coupling coefficients c_j:

$$\begin{aligned} z_t &= \sum_{l=0}^{\infty} z_{t,l}, & x_{j_t} &= \sum_{l=0}^{\infty} x_{j_t,l}, \quad j = 1, ..., N \\ p_{z_t} &= \sum_{l=0}^{\infty} p_{z_t,l}, & p_{j_t} &= \sum_{l=0}^{\infty} p_{j_t,l}, \quad j = 1, ..., N. \end{aligned}$$

Law of Energy Conservation

- The energy gained by the bath $=$ The energy lost by the particle.
- The initial energy of the bath is

$$E_B(-t_0) = \frac{1}{2}\sum_{j=1}^{N}(p_{j,-t_0}^2 + \omega_j^2 x_{j,-t_0}^2).$$

- To second order, the final energy of the bath after the collision is:

$$\begin{aligned}
E_B(t_0) \equiv E_B(-t_0) \quad &+ \quad \sum_{j=1}^{N}[p_{j_{t_0},0}(p_{j_{t_0},1} + p_{j_{t_0},2})] + \omega_j^2 x_{j_{t_0},0}(x_{j_{t_0},1} + x_{j_{t_0},2})] \\
&+ \quad \frac{1}{2}\sum_{j=1}^{N}(p_{j_{t_0},1}^2 + \omega_j^2 x_{j_{t_0},1}^2), \\
E_B(t_0) - E_B(-t_0) \quad &\equiv \quad \delta E_{B,1} + \delta E_{B,2} + \langle \Delta E_B \rangle.
\end{aligned}$$

- $\langle \Delta E_B \rangle$ is the average energy gained by the bath when its temperature vanishes.

The First and Second Order Components of Energy Loss

- The fluctuational energy loss to the bath has two components:

$$\langle \delta E_{B,1} \rangle = 0, \qquad \text{and} \qquad \langle \delta E_{B,1}^2 \rangle = \frac{2}{\beta} \langle \Delta E_B \rangle.$$

- For Ohmic friction

$$\gamma(t) = 2\gamma\delta(t).$$

- The First and Second Order Components of Energy Loss are:

$$\langle \triangle E_B \rangle_{OHM} = \frac{\gamma}{M} \int_{-\infty}^{\infty} dt\, V''(z_{t,0})^2 \dot{z}_{t,0}^2, \qquad \langle \delta E_{B,2} \rangle_{OHM} = -\frac{\gamma}{M^2\beta} \int_{-\infty}^{\infty} dt V''(z_{t,0})^2.$$

The final momentum distribution

- The final momentum distribution averaged over the thermal bath is defined to be:

$$\begin{aligned} P(p_{z_f}) &= \int_{-\infty}^{\infty} \prod_{j=1}^{N} dp_{j,-t_0} dx_{j,-t_0} \frac{\beta\omega_j}{2\pi} \exp\left(-\frac{\beta}{2} \sum_{j=1}^{N} [p_{j,-t_0}^2 + \omega_j^2 x_{j,-t_0}^2] \right) \\ &\times \quad \delta(p_{z_f} + p_{z_i} - p_{z_{t_0},1} - p_{z_{t_0},2}) \end{aligned} \tag{1}$$

The Final Energy Distribution

- The final energy distribution is Gaussian distributed through the fluctuational term $\delta E_{B,1}$.

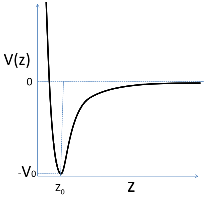
$$P_1(E_f|E_i) = \left(\frac{\beta}{4\pi\langle\triangle E_B\rangle}\right)^{\frac{1}{2}} \exp\left(-\frac{\beta(E_f - E_i + \langle\Delta E_B\rangle + \langle\delta E_{B,2}\rangle)^2}{4\langle\triangle E_B\rangle}\right).$$

- We note that this distribution is normalized by allowing the final energy to range between $-\infty$ and ∞:

$$\int_{-\infty}^{\infty} dE_f \, P_1(E_f|E_i) = 1$$

and has the correct average energy loss:

$$\int_{-\infty}^{\infty} dE_f \, P_1(E_f|E_i)(E_i - E_f) = \langle\triangle E_B\rangle + \langle\delta E_{B,2}\rangle.$$



The Trapping Probabilty

- To obtain the sticking probability, we follow the multiple collision theory of Fan and Manson[3].
- The probability T_1 that the particle escapes after this first traversal is:

$$T_1 = \int_0^\infty dE_f P_1(E_f|E_i) = \frac{1}{2}\mathrm{erfc}\left(\frac{\sqrt{\beta}\left(\langle\Delta E_B\rangle + \langle\delta E_{B,2}\rangle - E_i\right)}{2\sqrt{\langle\Delta E_B\rangle}}\right).$$

- Iterating, we find that the final energy distribution for a particle undergoing K traversals is

$$P_K(E_f|E_i) = \int_{-\infty}^0 dE P_1(E_f|E)P_{K-1}(E|E_i).$$

- The fraction that escapes after the K-th traversal is:

$$T_K = \int_0^\infty dE_f P_K(E_f|E_i).$$

- The fraction of particles which remain in the well after K traversals is:

$$R_K = 1 - \sum_{j=1}^K T_j.$$

- The sticking probability is then:

$$P_{stick} = \lim_{K\to\infty} R_K.$$

[3] Phys. Rev. B **79**, 045424 (2009), J. Chem. Phys. **130**, 064703 (2009)

Morse potential analytical model

$$V(z) = V_0(1 - \exp(-\alpha z))^2 - V_0.$$

- Analytic forms of energy transfer:

$$\frac{\langle \delta E_{B,2} \rangle_{OHM}}{V_0} = -\frac{2\tilde{\gamma}}{\beta V_0}\sqrt{\frac{E_i}{V_0}}\left(5 + \frac{8}{3}\frac{E_i}{V_0} + \Phi\left[4\sqrt{\frac{E_i}{V_0}} + 5\sqrt{\frac{V_0}{E_i}}\right]\right)$$

and

$$\frac{\langle \triangle E_B \rangle_{OHM}}{V_0} \quad = \quad 2\tilde{\gamma}\sqrt{\frac{E_i}{V_0}}\left(3 + 4\frac{E_i}{V_0} + \frac{16}{15}\frac{E_i^2}{V_0^2} + \Phi\sqrt{\frac{V_0}{E_i}}\left[3 + 5\frac{E_i}{V_0} + 2\frac{E_i^2}{V_0^2}\right]\right),$$

where

$$\tilde{\gamma} = \gamma\omega_0^3$$

- Parameters for numerical calculation:
  Well depth, $V_0 = 88$ meV;
  Stiffness parameter, $\alpha = 0.5$ $\mathring{A}^{-1}$;
  Mass of Ar, $M = 39.948$ amu;
  Reduced friction coefficient, $\tilde{\gamma} = 0.00182$.

The population fractions remaining in the well

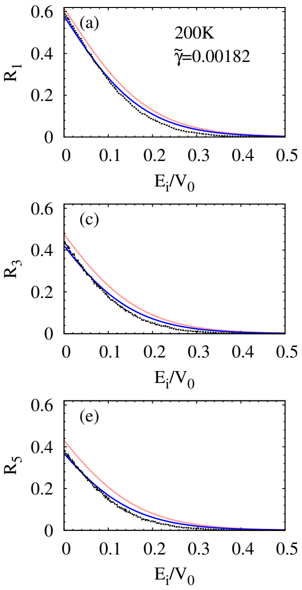


Figure: The population fractions remaining in the well. The fraction remaining after $K = 1 - 5$ traversals is plotted as a function of the reduced incident energy $\frac{E_i}{V_0}$ for a model of the Ar-LiF system at a surface temperature of $T = 200$ K.

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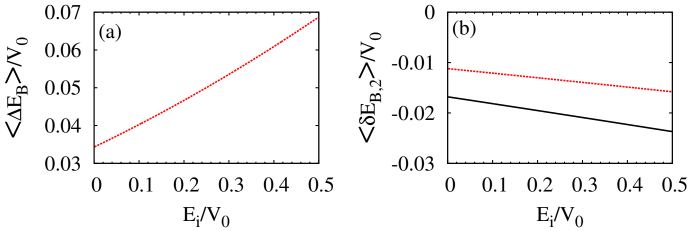
The Energy Loss and Relative Contribution of The Second Order Term



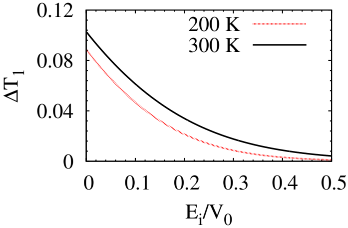
Red line ⇒ 200K;

Black line ⇒ 300K

$$P_1(E_f|E_i) = \left(\frac{\beta}{4\pi\langle\triangle E_B\rangle}\right)^{\frac{1}{2}} \exp\left(-\frac{\beta(E_f-(E_i-\langle\Delta E_B\rangle-\langle\delta E_{B,2}\rangle))^2}{4\langle\triangle E_B\rangle}\right).$$

The relative contribution ΔT_1 of the second order term $\delta E_{B,2}$ to the fraction of particles escaping the interaction region after one traversal of the well.

$$\Delta T_1 = \frac{T_1\left(\delta E_{B,2}\right) - T_1\left(\delta E_{B,2}=0\right)}{T_1\left(\delta E_{B,2}\right)}$$



$$\Delta R_K = R_K - R_{K+1}, \quad K \geq 0$$

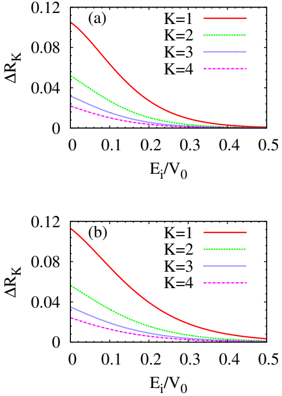


Figure: The fraction of particles remaining in the interaction region after K traversals of the well, ΔR_K as a function of the reduced energy at $T = 200$ K (panel (a)) and $T = 300$ K (panel(b)).

Sticking probability at 200K

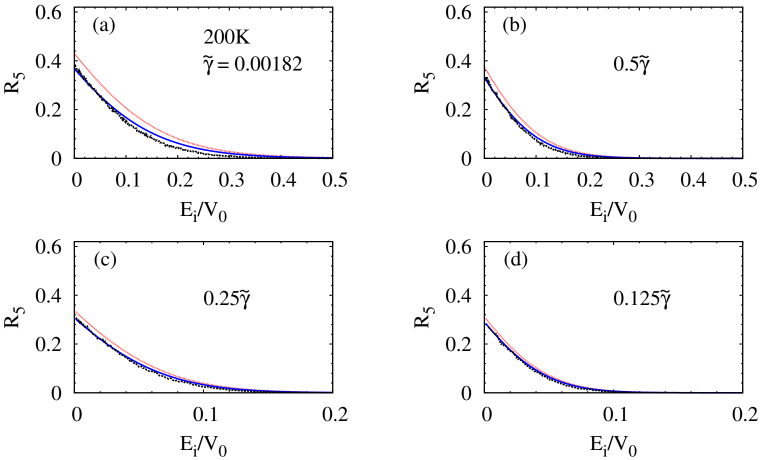


Figure: The sticking probability (assuming convergence after 5 traversals of the well region) is plotted as a function of the (reduced) incident energy for four different values of the friction coefficient at a surface temperature of $T = 200$ K.

Sticking probability at 300K

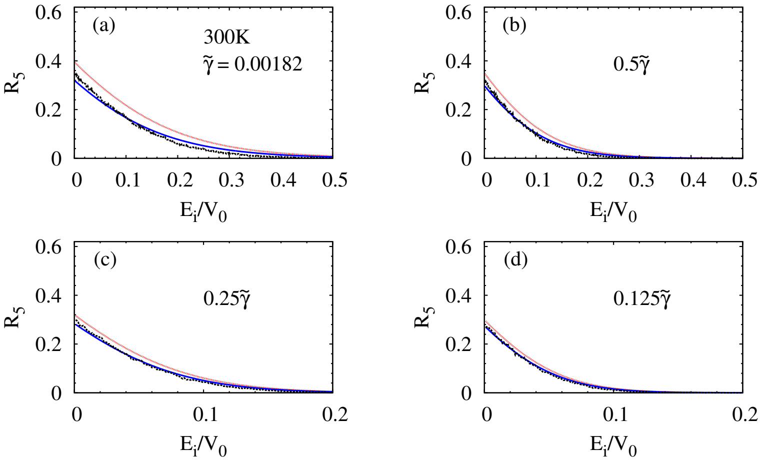


Figure: The sticking probability (assuming convergence after 5 traversals of the well region) is plotted as a function of the (reduced) incident energy for four different values of the friction coefficient at a surface temperature of $T = 300$ K.

Validity of our theory

- We do note that at very low energies the perturbation theory is no longer valid.
- A condition for the first order perturbation theory to be valid is

$$\frac{\langle \Delta E_B \rangle}{E_i} \simeq \left| \left\langle \frac{p_{z_{t_0,1}}}{p_{zi}} \right\rangle \right| \ll 1.$$

In the limit of vanishing incident energy

$$\lim_{E_i \to 0} \frac{\langle \Delta E_B \rangle_{OHM}}{V_0} = 6\pi\tilde{\gamma}$$

implying that the perturbation theory is valid provided that

$$\frac{E_i}{V_0} \gg 6\pi\tilde{\gamma}.$$

Summary

- We have derived an expression for the temperature dependence of the energy loss of a heavy atom scattered on a surface based on second order classical perturbation theory and valid for arbitrary time dependent friction.
- The model used for describing the scattering process on a thermal (uncorrugated) surface was that of a space dependent generalized Langevin equation. The new feature of the present treatment is the inclusion of the thermal surface induced energy transfer to the particle, which reduces the sticking probability.
- Comparison of the theory with numerically exact simulations showed that quantitative agreement between numerics and analytical theory is possible only if one includes the added surface temperature induced term.
- The comparison with the numerical results also justifies the multiple collision theory of Fan and Manson for the sticking probability.
- The present theory can be further developed by applying it also to a corrugated surface, employing the second order perturbation theory used previously with respect to the corrugation height as well as the coupling to the surface phonons.
- Finally, the present second order perturbation theory may also be used in the context of a semiclassical theory of sticking.

Acknowledement

- Professor Eli Pollak
- Deans support of postdoctoral fellowship
- Department of Chemical Physics, Weizmann Institute of Science

The End

- Thank you for your patience
- Quenstions?

Numerical Results of Energy Loss

$$\begin{aligned} \langle \Delta E_B \rangle &= \frac{1}{2M} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' \frac{dV'(z_{t',0})}{dt'} \frac{dV'(z_{t'',0})}{dt''} \gamma(t''-t'), \\ \texttt{where} \quad \gamma(t) &= \sum_{j=1}^{N} \frac{c_j^2}{\omega_j} \cos(\omega_j t). \end{aligned}$$

We do note that at very low energies the perturbation theory is no longer valid.

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