

# Second Order Classical Perturbation Theory For The Sticking Probability Of Heavy Atoms Scattered On Surfaces<sup>1</sup>

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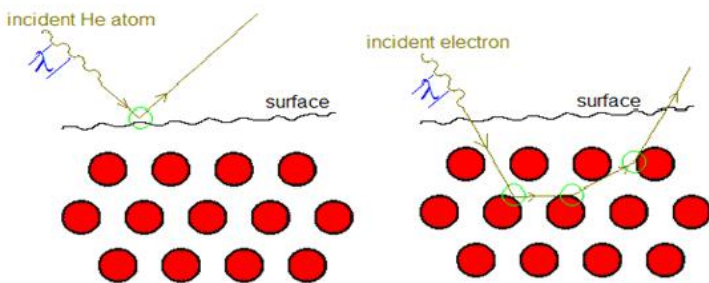
<sup>1</sup>T. Sahoo and E. Pollak, J. Chem. Phys. **143**, 064706 (2015)

# Introduction

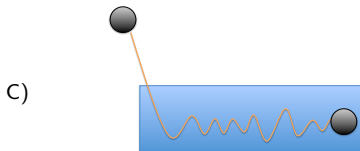
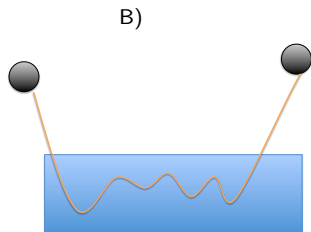
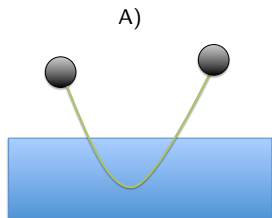
## Importance

- ▶ 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.

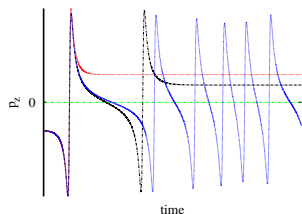
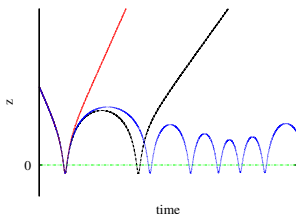
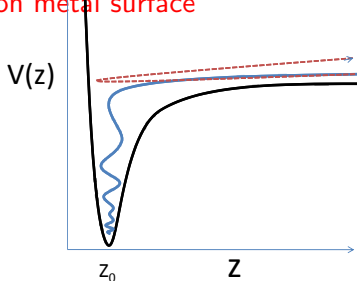
## Difference between Atom and electron scattering



## Trapping of atom on metal surface



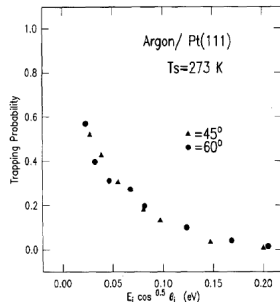
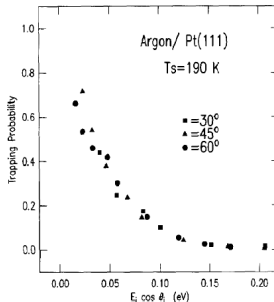
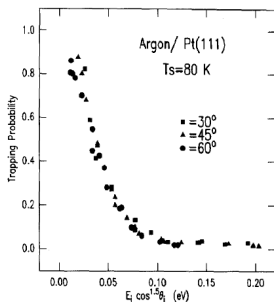
## Trapping of atom on metal surface



- ▶ 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  $\theta_i$ , 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<sup>2</sup>.

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<sup>2</sup>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

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

- ▶ The initial conditions for the bath phase space variables 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  $c_j$ :

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

## 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:

$$\begin{aligned} E_B(t_0) &\equiv E_B(-t_0) + \sum_{j=1}^N [p_{jt_0,0}(p_{jt_0,1} + p_{jt_0,2})] + \omega_j^2 x_{jt_0,0}(x_{jt_0,1} + x_{jt_0,2}) \\ &+ \frac{1}{2} \sum_{j=1}^N (p_{jt_0,1}^2 + \omega_j^2 x_{jt_0,1}^2), \\ E_B(t_0) - E_B(-t_0) &\equiv \delta E_{B,1} + \delta E_{B,2} + \langle \Delta E_B \rangle. \end{aligned}$$

- ▶  $\langle \Delta E_B \rangle$  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:

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

- ▶ For Ohmic friction

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

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

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

### The final momentum distribution

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

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

## The Final Energy Distribution

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

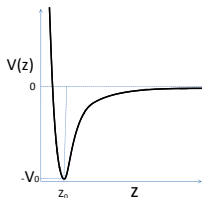
$$P_1(E_f|E_i) = \left( \frac{\beta}{4\pi\langle\Delta E_B\rangle} \right)^{\frac{1}{2}} \exp\left( -\frac{\beta(E_f - E_i + \langle\Delta E_B\rangle + \langle\delta E_{B,2}\rangle)^2}{4\langle\Delta E_B\rangle} \right).$$

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

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

and has the correct average energy loss:

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



## The Trapping Probability

- ▶ To obtain the sticking probability, we follow the multiple collision theory of Fan and Manson<sup>3</sup>.
- ▶ The probability  $T_1$  that the particle escapes after this first traversal is:

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

- ▶ 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:

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

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<sup>3</sup>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

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

where

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

- Parameters for numerical calculation:

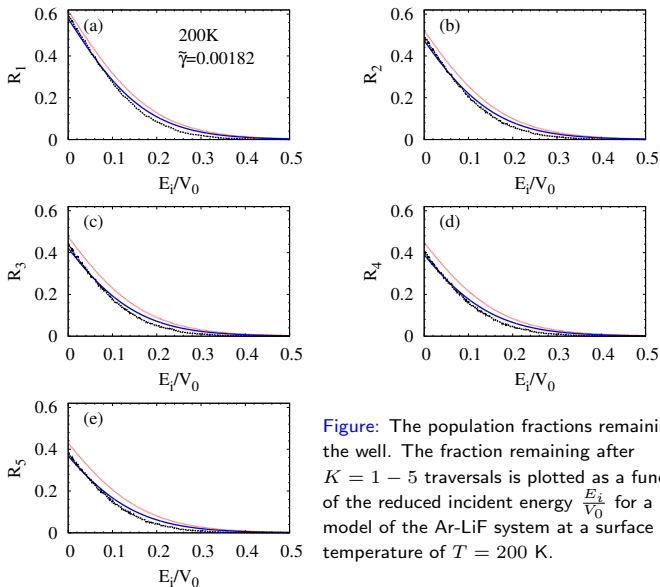
Well depth,  $V_0 = 88$  meV;

Stiffness parameter,  $\alpha = 0.5 \text{ \AA}^{-1}$ ;

Mass of Ar,  $M = 39.948$  amu;

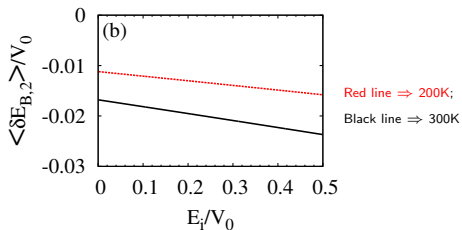
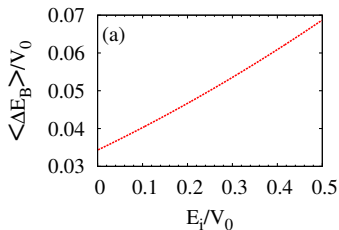
Reduced friction coefficient,  $\tilde{\gamma} = 0.00182$ .

## 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.

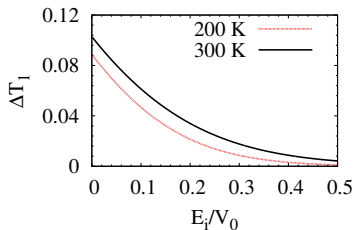
## The Energy Loss and Relative Contribution of The Second Order Term



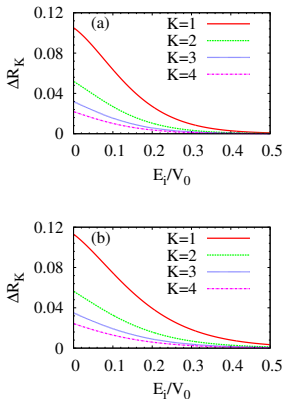
$$P_1(E_f|E_i) = \left( \frac{\beta}{4\pi \langle \Delta E_B \rangle} \right)^{\frac{1}{2}} \exp \left( - \frac{\beta (E_f - (E_i - \langle \Delta E_B \rangle - \langle \delta E_{B,2} \rangle))^2}{4 \langle \Delta E_B \rangle} \right).$$

The relative contribution  $\Delta T_1$  of the second order term  $\delta E_{B,2}$  to the fraction of particles escaping the interaction region after one traversal of the well.

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

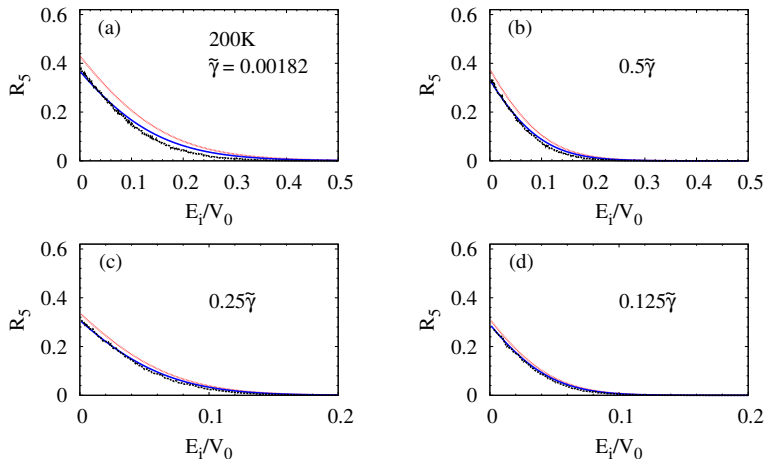


$$\Delta R_K = R_K - R_{K+1}, \quad K \geq 0$$



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

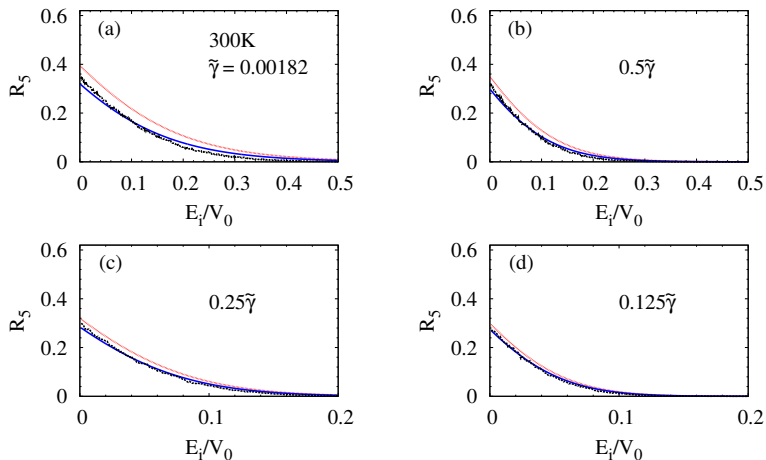
## Sticking probability at 200K



**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

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

In the limit of vanishing incident energy

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

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
- ▶ Questions?

## Numerical Results of Energy Loss

$$\langle \Delta E_B \rangle = \frac{1}{2M} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' \frac{dV'(z_{t'},0)}{dt'} \frac{dV'(z_{t''},0)}{dt''} \gamma(t'' - t'),$$

$$\text{where } \gamma(t) = \sum_{j=1}^N \frac{c_j^2}{\omega_j} \cos(\omega_j t).$$

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

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