Theory of the Eigler-switch

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Abstract

We suggest a simple model to describe the reversible field-induced transfer of a single Xe-atom in a scanning tunneling microscope, — the Eigler-switch. The inelastically tunneling electrons give rise to fluctuating forces on and damping of the Xe-atom resulting in an effective current dependent temperature. The rate of transfer is controlled by the well-known Arrhenius law with this effective temperature. The directionality of atom transfer is discussed, and the importance of use of non-equilibrium-formalism for the electronic environment is emphasized. The theory constitutes a formal derivation and generalization of the so-called Desorption Induced by Multiple Electron Transitions (DIMET) point of view.

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Eigler and Schweizer [1] have been able to manipulate Xe atoms and place them with atomic precision on a Ni surface using an ultra high vacuum scanning tunneling microscope (STM) operated at 4 Kelvin. Experiments by Eigler, Lutz and Rudge show [2], that a single Xe atom physisorbed to a particular kink site on a single crystal Ni-(110) surface, can be transferred reversibly between this surface-site and the W tip in the STM. These experiments are done at 4 Kelvin. Using voltage pulses of $\pm 0.8V$ for $64msec$, they are able to toggle the Xe atom from surface to tip and back to the same position on the surface at will, and find that the direction of transfer is the same as that of the tunneling electrons. For a particular tip-surface configuration with the Xe adatom on the surface, the transfer rate, $\tau^{-1}$, goes as $I^{4.9\pm 0.2}$, $I$ being the tunneling current. The voltage range in these measurements is from $18mV$ to $180mV$ with $V/I = 906k\Omega \pm 2\%$. These phenomena has been investigated theoretically by Walkup, Newns and Avouris [3] and Gao, Persson and Lundquist [4]. These authors suggest that the main mechanism behind the transfer is that the current excite the Xe atom vibrationally in the double-well potential, sustained by the van der Waal attraction to surface and tip. On the other hand the Xe atom dissipates energy to the surface phonons, so they calculate the rate of transfer using rate-equations (Pauli master equations) including the competition between dissipation to surface-phonons and “heating” by inelastically tunneling electrons. In Ref. [3] the possible mehanisms behind the directionality of transfer is discussed, and they conclude that the adsorbtion-induced dipole is the dominant effect.

In this paper we concentrate on showing that the key-features of the experiments can be explained from a less phenomenological point of view, based on a simple model.

The main idea in our calculation is the following. We view the Xe atom as a quantum Brownian particle interacting with the environment of electrons in the tip and surface via the adsorbate-resonance, through which the electrons tunnel. Besides this environment the Xe atom also interact with an environment of surface-phonons. The influence of these environments on the atom is described in a path-integral framework using the influence-functional introduced by Feynman and Vernon [5,6], giving an effective action describing the motion of the atom. For two independent environments, the influence-functional will simply
be the product of the individual influence-funtionals \[6\]. The influence-functional for a harmonic oscillator with a linear coupling to a continuous distribution of harmonic oscillators in thermal equilibrium has been calculated by Caldeira and Legget \[7\]. This influence-functional contains the fluctuating force and dissipation caused by the environment which in the classical limit are the ingredients in the Langevin equation describing the classical motion \[8\]. Our contribution is the calculation of the influence-functional corresponding to the non-equilibrium electronic environment. In general, when a Brownian particle is in equilibrium with a heat-bath, the fluctuating force acting on the particle and the corresponding friction force are “connected” by the fluctuation-dissipation theorem (FDT). This is the situation when no chemical-potential difference between tip and surface drives a current through the adsorbate-resonance, and the Xe atom is in equilibrium, the surface-phonons and the electrons acting as heat baths. When an external field in some way is transferring energy to the Brownian particle the relation between the fluctuating force and the dissipation, found in the equilibrium case, no longer holds. There will in general occur a extra current-dependent fluctuating force not “compensated” by friction.

We show this general feature in our model, where the interaction with the inelastically tunneling electrons give rise to the uncompensated fluctuating force. At sufficiently low temperature compared with the oscillation frequency in the adsorption well, as in the actual experiment, this force will be the dominant. The temperature independent dissipation is due to exitation of surface-phonons and electron-hole-pairs in the surface and tip by the vibrating Xe atom. The time scale of desorption is much longer than than the relaxation time of the dissipative system, thus we have a quasi-stationary situation a relaxation time after the current is turned on. In this quasi-stationary situation we can consider the Xe-atom as a damped harmonic oscillator with a wavepacket width given by the usual FDT-result plus a contribution due to the non-equilibrium fluctuating force. From this width we define our effective temperature. The desorption rate is then given by the well-known results for escape of a Brownian particle from a potential well in equilibrium with a heat-bath where the new effective temperature depends on the voltage. This leads to the experimentally
found result if we assume that the adsorbtion well contains about five bound states, as was
done in Refs. [3] and [4]. The dependence of the direction of transfer on the polarity of field
follows in our model from the mean occupation of the Xe atom. We stress that it is crucial
to use a non-equilibrium formalism to calculate the occupation.

Let us now introduce the model and sketch the derivation of our results. The reason why
a rare-gas atom like Xe actually can be imaged by STM is explained by Eigler et al. [9]. Thus
we will only consider this adsorbate state. Denoting the operator and energy associated with
the Xe 6s-orbital \( d \) and \( \epsilon_a \), and the operators associated with surface, respectively tip, \( c_k \), \( c_l \),
we write the Hamiltonian for the electronic part,

\[
H_{el} = H_{surf} + H_{tip} + \epsilon_a d\dagger d + \sum_{k,l} d\dagger (T_k c_k + T_l c_l) + h.c.
\]

We define the weighted density of states for surface and tip,

\[
\rho_s(E) = \sum_k |T_k|^2 \delta(E - \epsilon_k)
\]

\[
\rho_t(E) = \sum_l |T_l|^2 \delta(E - \epsilon_l).
\]

For simplicity we use the wideband limit and take these to be constant. The current,
corresponding to the model above, can be expressed by a non-equilibrium Green’s function
which is evaluated using the Keldysh technique [10], yielding

\[
I(V) = \frac{4e}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\pi \rho_t (\pi \rho_s) (n_F(\omega - eV) - n_F(\omega))}{(\pi (\rho_t + \rho_s))^2 + (\omega - \epsilon_a)^2}.
\]

We have neglected the small influence of the vibrations of the Xe atom on the current.

The parameters of the electronic Hamiltonian (1) depends on the position of the adatom.
This of course leads to the picture of effective potential energy-surfaces, which is the basis of
most surface dynamics calculations. We shall see that this dependence also is responsible for
the fluctuations in the force experienced by the atom. Denoting by \( \hat{x} \) the operator associated
with the position of the Xe-atom, relative to the equilibrium distance from the surface, and
expanding the onsite energy to first order in $\hat{x}$ we obtain the coupling between electrons and Xe

$$V_{el-vib} = g (d^\dagger d - \langle d^\dagger d \rangle_{eq}) \hat{x},$$

(5)

where $g$ is the positive coupling-constant. (For simplicity we neglect the $\hat{x}$-dependence of $T_k$ and $T_l$). Note that we have subtracted the equilibrium ($eV = 0$) mean population of the site, because this contribution is assumed already to be incorporated in the adsorption potential-surface. The physical picture of the interaction is that the temporary increase in charge on the site, when an electron tunnel through it, will cause the atom to be attracted more strongly towards the strongest image, which will be the one in the surface when the atom is located at the surface. Thus $g$ will be positive. The interaction results in a fluctuating force acting on the Xe atom, due to the electrons, jumping on and off the site. This physical effect is what has been dubbed DIMET (desorption induced by multiple electron transitions) \[11\]. On the other hand, the vibration of the atom will, because of this interaction, excite electron-hole pairs in the metal-surface and dissipate energy to the electronic part of the system. A similar model has been used by Persson and Baratoff \[12\] to describe the influence of inelastic tunneling on the current in the STM.

We use the Feynman-Vernon theory of influence-functionals to do a systematic calculation of these features. Considering a quantum system interacting with a general environment, one is often only interested in the influence of the environment on the system. This can be accomplished by the reduced density operator, tracing out all superfluous information of the environment. This is elegantly done in a path-integral framework \[6\]. The result of this procedure is an effective action of the system. This approach has been used on the problem of a quantum oscillator in equilibrium with a heat-bath consisting of a continuum of quantum oscillators, and is treated thoroughly in Refs. \[5–8\]. In our problem we will be concerned only with the behavior of the Xe-oscillator and thus trace out the equilibrium phonon environment as well as the non-equilibrium electronic environment.

The propagator for the reduced density-operator for the oscillator can be written as a
double path integral,

\[ J(x_f, y_f, t; x_i, y_i, 0) = \]
\[ \int \mathcal{D}x \int \mathcal{D}y \ e^{i(S(x) - S(y))/\hbar} F_{el}(x, y) F_{ph}(x, y), \]

where \( S \) is the action for the non-interacting oscillator, and \( F_{el} \) and \( F_{ph} \) are the influence-functionals containing all relevant information of the electronic and phonon environments, respectively. These will, in general, couple the paths moving “forward” (\( x \)) and “backward” (\( y \)) in time. The phonon influence functional, corresponding to the oscillator coupled to a continuum of oscillators, has been evaluated in Ref. \[7\],

\[ \Delta S_{ph}^{\text{eff}}(x(\tau), y(\tau)) = -i\hbar \ \text{ln}[F_{ph}(x, y)] \]
\[ = -\frac{\eta_{ph}}{2} \int_0^t (\dot{x} + \dot{y})(x - y) d\tau \]
\[ + i\eta_{ph} \int_0^\infty \omega \coth \left( \frac{\hbar \omega}{2kT} \right) \]
\[ \int_0^t \int_0^t (x(\tau) - y(\tau)) \cos(\omega(\tau - s))(x(s) - y(s)) d\tau ds \frac{d\omega}{2\pi}. \]

The real part of \( S_{\text{eff}} \) describes the friction \[13\] and the imaginary is the correlation function of the time-non-local fluctuating force. These two terms are related through the equilibrium FDT.

The new feature here is the contribution to \( S_{\text{eff}} \) from the non-equilibrium electronic environment. This is calculated using a technique similar to the one used in Ref. \[14\], extended to cover this non-equilibrium case. The first order term is,

\[ \Delta S_{el,1}^{\text{eff}}(x, y) = \]
\[ -g \left( N(eV) - N(0) \right) \int_0^t dt' (x(t') - y(t')), \]

where \( N(eV) \) is the mean population of the Xe site after the voltage is applied, and is given by,

\[ N(eV) = \]
\[ \int_{-\infty}^{\infty} d\omega \frac{\rho_t n_F(\omega - eV) + \rho_s n_F(\omega)}{(\omega - \epsilon_a)^2 + \pi^2(\rho_t + \rho_s)^2}, \]
where the $\epsilon_{\text{surf}} = 0$ and $\epsilon_{\text{tip}} = eV$. This corresponds to a simple change of the potential energy surface due to the change of population of the site. The mean-population of the resonance increases for $eV$ positive, and thus increase the energy-barrier between the surface and tip adsorbtion-sites, whenever the electrons tunnel from tip to surface. Reversing the polarity, so the electrons tunnel from surface to tip, decreases the barrier. When the Xe-atom is located on the tip, the roles played by tip and surface are exchanged. This can explain the observed dependence of transfer on the polarity.

To second order in the coupling constant $g$ we find terms similar to (7) with a friction-coefficient, $\eta_{\text{el}}(eV)$, which can be expressed in terms of $g$, $\rho_s$, $\rho_t$ and $eV$. Besides these terms we find the additional imaginary term in $\Delta S_{\text{eff}}^{\text{el}(2)}$,

$$
\alpha(eV) \int_0^t \int_0^t \int_{-\infty}^{\infty} \left[ \coth \left( \frac{\hbar \omega - eV}{2kT} \right) - \coth \left( \frac{\hbar \omega}{2kT} \right) \right] \left( x(\tau) - y(\tau) \right) \cos(\omega(\tau - s))(x(s) - y(s)) \, d\tau \, ds \, \frac{d\omega}{2\pi},
$$

with

$$
\alpha(eV) = -\frac{g^2}{2} \int_0^{eV} \frac{\rho_s \rho_t}{\left[ (\omega - \epsilon_a)^2 + \pi^2(\rho_t + \rho_s)^2 \right]^2} \, d\omega.
$$

The effective action obtained so far is quadratic in the Xe-atom coordinate, and the remaining path-integral is Gaussian and can be worked out exactly.

The width of a wave-packet describing the spatial motion of a damped harmonic oscillator with frequency $\omega_0$ and mass $M$ in equilibrium with a heatbath is determined by the imaginary part of the response function for damped oscillator $\chi''(\nu)$ through the FDT,

$$
\sigma^2 = \frac{\hbar}{\pi} \int_0^{\infty} \coth \left( \frac{\hbar \nu}{2kT} \right) \chi''(\nu) \, d\nu
$$

$$
\chi''(\nu) = \frac{1}{M} \frac{\left( \frac{\nu}{M} \right)}{\left( \nu^2 - \omega_0^2 \right)^2 + \left( \frac{\nu}{M} \right)^2}.
$$

From the discussion by Caldeira and Legget, it follows immediatly that this also will be the case in equilibrium ($eV = 0$) for our model, with $\eta = \eta_{\text{ph}} + \eta_{\text{el}}$. For sufficiently low damping, where the energy eigenstates of the oscillator is welldefined, $\chi''(\nu)$ will be a narrow function centred around $\omega_0$, and for low temperature we get,
\[ \sigma^2 \propto 1 + 2e^{-\hbar \omega_0 / kT}. \]  

(14)

Carrying out a similar analysis in our non-equilibrium case, we find in the same limit, that

\[ \sigma^2 \propto 1 + 2e^{-\hbar \omega_0 / kT} + \frac{|\alpha(eV)|}{\eta_{tot}(eV)\omega_0}. \]  

(15)

Comparing the non-equilibrium expression (15) with the equilibrium expression (14) enable us to define an effective temperature by equating the small terms:

\[ \exp\left(-\frac{\hbar \omega_0}{kT_{\text{eff}}(eV)}\right) = e^{-\hbar \omega_0 / kT} + \frac{|\alpha(eV)|}{2\eta_{tot}(eV)\omega_0}. \]  

(16)

In figure 1 we have plotted the effective temperature as a function of the voltage \( eV \).

In the case where we can neglect the exponentially small \( e^{-\hbar \omega_0 / kT} \), the effective Boltzmann factor is proportional to \( \alpha \) and thus to \( eV \). The observed rate can now be understood from the Arrhenius-factor \( e^{-U_0 / kT} \) dominating the rate-expressions of escape problems in general \[16\], where \( U_0 \) is the barrier-height. If we, as suggested in \[3,4\], assume that \( U_0 \approx 5\hbar \omega_0 \), we conclude that \( \tau^{-1} \propto (eV)^5 \). In figure 2 the escape rate is plotted as a function of voltage for different temperatures. We predict a drastic change in this behavior as the temperature is raised which can be verified experimentally.

We have not, in this calculation, taken into account the dependence of the tunnelmatrixelements on the adsorbate position \( (T_k(x), T_l(x)) \). This will contribute to the friction as well as the fluctuating forces on the Xe-atom. Taking this dependence into account also, the general scheme described above can be used to calculate the friction coefficient from a microscopic starting point, using given expressions for \( \epsilon_a(x) \) and \( T_k(x), T_l(x) \). This will be applied in a future publication to the problem of laser-induced desorption, where the resulting temperature dependent friction coefficient is used in the Langevin equation. \[17\]

In conclusion we have outlined a formalism that provide a theoretical foundation of the DIMET point of view of desorption and applied this to the non-equilibrium Eigler experiment.
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FIGURES

FIG. 1. The effective temperature as a function of the applied voltage $eV$. The absolute ratio $\alpha/\eta$ is estimated roughly using the ratio, Xe vibrational- to electronic life-time, $\tau_{el}/\tau_{ph} \approx 100$, and $\omega_0 \approx 3meV$.

FIG. 2. The transfer rate, $\tau^{-1}$, as a function of junction voltage, for $T = 0K, 4K, 6K$ and $8K$.