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The Effect of the Atomic Dynamics in a Crystalline Catalyst on the Rate Constant for a Catalyzed Chemical Reaction[†]

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Transition-state theory is often used to calculate the rate constant of a chemical reaction. Usually, it gives quite good results for gas-phase reactions but not for reactions in solution since the interactions of the solvent molecules with the reactants are not included in the theory. Kramers formulated an extension of the transition-state theory that included these interactions. They are represented by a friction coefficient that often is related to the viscosity of the solvent by Stoke's law. For reactions on the surface of a crystalline catalyst, there will also be an effect on the rate constant from the interaction between the reactants and the oscillating substrate atoms. In contrast to reactions in solution, where the friction coefficient is related to the viscosity of the solvent, there exists no simple property of the solid that may be directly related to a friction coefficient for the motion of the adsorbed molecule on the surface. In this paper, we propose a method that may be used to calculate a friction coefficient that may be used in Kramers theory to calculate the rate constant for a chemical reaction on the surface of a crystalline solid.

I. Introduction

Many catalyzed reactions take place on the surface of a solid crystalline catalyst. Today it is possible to supplement experimental investigations of a given catalytic reaction by extensive and realistic density functional theory (DFT) calculations of the potential-energy surface (PES) of the reaction.[1] With this tool, we have a direct and powerful method for exploring the energetics and structure of a reacting molecule on the surface of a catalytic active substrate.

Once the transition state and the PES have been determined by the DFT method, transition-state theory (TST)[2] is often used to calculate the rate constant for the reaction of interest. The calculated rate constant often differs from the experimental result for many reasons. The theoretical PES may not be accurate enough to mimic the experiment, and the approximations in the TST may not be justified for the system considered. The TST theory is developed for a gas-phase reaction and does therefore not include the interactions between the solvent or solid and the molecule for a reaction in solution or on a solid surface, and even then, there are serious approximations involved in the theory, like the establishment of thermal equilibrium between reactant and transition-state molecules and the assumption of no recrossings of the transition state. That is, once the reaction coordinate has passed the transition state from reactant to product, the theory does not include the possibility of going back from products to reactants. This implies that the TST result usually is larger than the experimental result. Moreover, if TST is used for reactions in solution or on a surface, the discrepancy may even be larger because recrossings of the transition state will be more important in these systems.

Most modern investigations of the effects of a solvent on the rate constant are based on a classical paper by Kramers.[3] His theory is based on the TST approach. In the TST approach, we only consider the motion in the reaction coordinate right at the transition state and assume it to be a free translational motion in the direction from reactant to product. Kramers' idea was to give a more realistic description of the dynamics in the reaction coordinate, not only at the transition state but along the entire reaction coordinate. Instead of giving a deterministic description of the dynamics, he proposed a stochastic description of the motion similar to that of the Brownian motion of a heavy particle in a fluid.

The result of Kramers' theory for a reaction in solution is very simple. The rate constant is equal to the product of the TST rate constant and a correction factor κ that only depends on the ratio between a friction coefficient γ and the magnitude of the imaginary frequency associated with the curvature of the PES at the transition state along the reaction coordinate. For reactions in solution, the friction coefficient γ is often related to the viscosity η of the solvent by Stoke's law, and the correction factor κ is smaller than one, so the effect of the solvent molecules is always to reduce the TST rate constant.

For reactions taking place on a crystalline surface, there is no single property of the solid, such as the viscosity of the solvent, that allows us to make an estimate of the friction coefficient to be used in Kramers' expression for the rate constant. In general, both electrons and phonons of the bulk solid constitute sinks for the energy dissipation that is associated with friction. In this paper, we will only consider the purely phononic friction and later consider the electronic friction, since that may also be important in a molecule/metal system.[4]

Specifically, we address the Brownian friction of a gas molecule that is adsorbed on a crystal surface. In recent molecular dynamics simulation studies of adsorbate systems,[5−8] it was investigated what the time scale of energy dissipation in the substrate is. The substrate dynamics are known to influence the frequency and damping of the vibrations of commensurate monolayer lattice.[6] There also is expected to be an effect on the temporal persistence of correlations in monolayer fluids.[8] As a limiting case, we consider the one-dimensional motion in the reaction coordinate of a dissociating molecule on a crystal

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surface. The model is formulated for a gas molecule on a crystalline surface and then applied to the N_2/Fe(111) system. The dynamics of the Fe substrate is given by a lattice dynamics calculation on an Fe crystal slab. The Brownian friction coefficient for a gas molecule on Fe(111) is obtained as a function of position and determined at the position of a DFT calculation of the transition state of the molecule.

Brownian friction or generalized Langevin Theory has previously been applied to various gas−surface reactive scattering systems, and trajectory calculations have shown details of the dynamics in catalyzed chemical reactions.[9−11] This method differs from those in that it is not based on trajectory calculations of the reactive scattering event.

The organization of the paper is as follows. Section 2 contains the basic Langevin theory of Brownian motion on the surface of a crystal. Section 3 describes the determination of the fluctuating forces in the Langevin theory, and section 4 is a summary of the theory and its implementation. Section 5 describes the application of the theory to the N_2/Fe(111) system. Section 6 contains results and a discussion.

II. Langevin Theory

It is well known that an isolated molecule in a bulk solution exhibits random motion, usually referred to as Brownian motion, caused by interactions with the solvent molecules. A phenomenological description of this motion is given by the Langevin equation for the center of mass velocity of the molecule in the solution. Likewise, an isolated mobile molecule adsorbed on a crystal surface exhibits random two-dimensional (2D) motion caused by interactions with oscillating substrate atoms. Let us therefore also describe the motion of the adsorbed molecule by the Langevin equation. For the α component of the velocity V_α of the adsorbed molecule or atom, we have

$$m\frac{\mathrm{d}V_\alpha}{\mathrm{d}t} = -m\gamma_\alpha V_\alpha + f_\alpha \tag{1}$$

where m is the mass of the gas atom, f_α the α (x, y, or z) component of the random force, and γ_α the friction coefficient for motion in the α direction. Its dimension is s^{-1}, and note that we associate a friction coefficient with motion in each of the Cartesian directions, since anisotropy may be significant on a crystalline surface.

Let us begin with setting up an internally consistent equation for the friction coefficient. A formal integration of the Langevin equation in eq 1 (an inhomogeneous first-order linear differential equation) gives the result

$$V_\alpha(t) = V_\alpha(0)\exp(-\gamma_\alpha t) + \int_0^t \mathrm{d}t' \frac{1}{m}\exp(\gamma_\alpha(t'-t))f_\alpha(t') \tag{2}$$

We square the velocity in eq 2 and take the ensemble average with the result

$$\frac{k_BT}{m} = \frac{k_BT}{m}\exp(-2\gamma_\alpha t) + \frac{1}{m^2}\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \exp(\gamma_\alpha(t'+t''-2t))\langle f_\alpha(t')f_\alpha(t'')\rangle \tag{3}$$

In eq 3, we have used the statistical independence of initial velocity and random force at time t

$$\langle V_\alpha(0)f_\alpha(t)\rangle = 0 \tag{4}$$

and the equipartition theorem at T/K

$$\langle V_\alpha(t)^2\rangle = \langle V_\alpha(0)^2\rangle = k_BT/m \tag{5}$$

Note that the correlation function in eq 3 can only depend on the time difference τ at equilibrium, that is, on

$$\tau = t'' - t' \tag{6}$$

and not on the absolute times t' and t'', so

$$\begin{aligned}\langle f_\alpha(t')f_\alpha(t'')\rangle &= \langle f_\alpha(t')f_\alpha(t'+\tau)\rangle \\ &= \langle f_\alpha(0)f_\alpha(\tau)\rangle\end{aligned} \tag{7}$$

Hence, it will be independent of time t', for example, and the integrals in eq 3 may be written

$$\int_0^t \mathrm{d}t' \int_{-t'}^{t-t'} d\tau \exp(2\gamma_\alpha(t'-t))\exp(\gamma_\alpha\tau)\langle f_\alpha(0)f_\alpha(\tau)\rangle \tag{8}$$

where we have expressed t'' by t' and τ as given in eq 6. The double integral in eq 8 may be replaced by a single integral, when the order of integration is interchanged, and eq 8 becomes

$$\frac{1}{\gamma_\alpha}\int_0^\infty \mathrm{d}\tau \exp(-\gamma_\alpha\tau)\langle f_\alpha(0)f_\alpha(\tau)\rangle \tag{9}$$

so eq 3 finally may be written

$$\frac{k_BT}{m} = \frac{1}{m^2\gamma_\alpha}\int_0^\infty \mathrm{d}\tau \exp(-\gamma_\alpha\tau)\langle f_\alpha(0)f_\alpha(\tau)\rangle \tag{10}$$

where we also have taken the limit $t \rightarrow \infty$. This is justified, because we are interested in the behavior of the system on a much longer time scale than the correlation time for the random force. We may then solve for γ_α and find

$$\gamma_\alpha = \frac{1}{mk_BT}\int_0^\infty \mathrm{d}\tau \exp(-\gamma_\alpha\tau)\langle f_\alpha(0)f_\alpha(\tau)\rangle \tag{11}$$

This is the central self-consistent relation between the friction coefficient γ_α and the fluctuating force f_α. It is a fluctuation−dissipation relation securing that the system will relax to equilibrium at T/K, when disturbed. It differs slightly from the ordinary form of the fluctuation−dissipation theorem, where the exponential factor in the integrand is missing. It appears here because we have used an exact integration of the Langevin equation in eq 2. Ordinarily, an approximate solution is used. If the time scale for the fluctuating force is much shorter than γ_α^{-1}, then the exponential essentially will be equal to one when the correlation function is nonzero, so it may be omitted. It is obvious that γ_α has to be found iteratively from this equation.

III. Determination of the Fluctuating Forces

We assume that the adatom−crystal interaction energy may be written as a sum of atom−atom potentials $\phi_{as}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|)$, where $\mathbf{R}$ is the position vector of the gas atom and $\mathbf{R}_{d,\mathbf{l}}$ the position vector of the (d,$\mathbf{l}$)th crystal atom. The latter may generally be written as

$$\mathbf{R}_{d,\mathbf{l}} = \mathbf{R}_d + \mathbf{l} \tag{12}$$

where $\mathbf{R}_d$ is the position vector of atom d in the unit cell and $\mathbf{l}$ is a lattice vector. There may be say n_c atoms per unit cell. It is also assumed, as indicated in the argument to ϕ_{as}, that the atom−atom potential only depends on the distance. Then the total potential energy $U(\mathbf{R})$ is

$$U(\mathbf{R}) = \sum_{\mathbf{l}} \sum_{d} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|) \tag{13}$$

where the summations over d and $\mathbf{l}$ include all atoms in the crystal.

The force on the gas atom is determined by the relation

$$\mathbf{F} = -\nabla_{\mathbf{R}} U(\mathbf{R}) = -\sum_{\mathbf{l}} \sum_{d} \nabla_{\mathbf{R}} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|) \tag{14}$$

The fluctuations in the force are caused by fluctuations in the crystal atom positions $\delta\mathbf{R}_{d,\mathbf{l}}$ as a result of the vibrational motions of the crystal atoms and are determined by expanding $\mathbf{F}$ in terms of $\delta\mathbf{R}_{d,\mathbf{l}}$. We find

$$\begin{aligned}
\mathbf{F} &= \mathbf{F_0} + \sum_{\mathbf{l}} \sum_{d} (\nabla_{\mathbf{R}_{d,\mathbf{l}}} \mathbf{F})_0 \cdot \delta\mathbf{R}_{d,\mathbf{l}} \\
&= \mathbf{F_0} - \sum_{\mathbf{l}} \sum_{d} (\nabla_{\mathbf{R}_{d,\mathbf{l}}} \nabla_{\mathbf{R}} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|))_0 \cdot \delta\mathbf{R}_{d,\mathbf{l}} \\
&= \mathbf{F_0} + \sum_{\mathbf{l}} \sum_{d} (\nabla_{\mathbf{R}} \nabla_{\mathbf{R}} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|))_0 \cdot \delta\mathbf{R}_{d,\mathbf{l}} \\
&= \mathbf{F_0} + \mathbf{f}
\end{aligned} \tag{15}$$

The subscript 0 indicates that the derivatives are calculated with the crystal atoms at their equilibrium positions. $\mathbf{F}_0$ is the static force on the gas atom with all crystal atoms at their equilibrium positions, and $\boldsymbol{f}$ is the fluctuating part of the force. We have used eq 14 in the second line of the equation, and in the third line we have used the assumption that $\phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|)$ only depends on the distance $\Delta R = |\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|$ between the gas atom and the crystal atom. It is noted that $(\nabla_{\mathbf{R}} \nabla_{\mathbf{R}} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|)_0$ in eq 15 is a tensor and that the α component of the fluctuating force is given by

$$f_{\alpha} = \frac{\partial}{\partial R_{\alpha}} \sum_{\mathbf{l}} \sum_{d} \sum_{\beta} \left[\left(\frac{\partial \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|)}{\partial R_{\beta}} \right)_0 \delta R_{\beta,(d,\mathbf{l})} \right] \tag{16}$$

The time correlation function in eq 11 for the fluctuating force may now be determined from the time dependence of the $\delta\mathbf{R}_{d,\mathbf{l}}$, which are determined by the motion of the atoms in the crystal.

A. Harmonic Crystal. We begin with the exact quantum expression for the displacements of the crystal atoms $\delta\mathbf{R}_{d,\mathbf{l}}$ in terms of the normal-mode excitations[12] and use the classical limit of that expression. It is

$$\delta\mathbf{R}_{d,\mathbf{l}} = \sum_{\nu,\mathbf{k}} \left(\frac{\hbar}{2NM_{\mathrm{d}}\omega_{\nu}(\mathbf{k})} \right)^{1/2} [\mathbf{e_d}(\nu,\mathbf{k})\hat{a}(\nu,\mathbf{k}) \exp(i(\mathbf{k}\cdot\mathbf{l} - \omega_{\nu}(\mathbf{k})t)) + \mathrm{h.c.}] \tag{17}$$

N is the number of unit cells in the crystal and equal to the number of atoms in a simple Bravais lattice. If there are n_{c} atoms per unit cell, the number of atoms will be $n_{\mathrm{c}}N$. M_{d} is the mass of atom d in the unit cell. If there is more than one atom in a unit cell, these masses may differ. $\omega_{\nu}(\mathbf{k})$ is the νth normal-mode frequency with wave vector $\mathbf{k}$. $\mathbf{e_d}(\nu,\mathbf{k})$ is that part of the $3n_{\mathrm{c}}$ dimensional eigenvector associated with wave vector $\mathbf{k}$ and branch ν, which gives the displacement of atom d in that particular mode. $\hat{a}(\nu,\mathbf{k})$ and its complex conjugate are the Bose operators for the crystal atoms. h.c. is the Hermite complex conjugate of the first term in the square bracket.

We insert eq 17 in eq 15 and find the following expression for the fluctuating forces at time t

$$\mathbf{f}(t) = \sum_{\mathbf{l}} \sum_{d} (\nabla_{\mathbf{R}} \nabla_{\mathbf{R}} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|))_0 \sum_{\nu,\mathbf{k}} \left(\frac{\hbar}{2NM_{\mathrm{d}}\omega_{\nu}(\mathbf{k})} \right)^{1/2} \times [\mathbf{e_d}(\nu,\mathbf{k})\hat{a}(\nu,\mathbf{k}) \exp(i(\mathbf{k}\cdot\mathbf{l} - \omega_{\nu}(\mathbf{k})t)) + \mathrm{h.c.}] \tag{18}$$

The time correlation function for the fluctuating forces is found by first multiplying the expressions for the fluctuating forces at time t and time 0 and then taking an ensemble average. When the correlation function of the fluctuating forces is formed from eq 18, only the following four combinations of the Bose operators will appear, $\langle n|\hat{a}(\nu,\mathbf{k})\hat{a}(\nu,\mathbf{k})|n\rangle$, $\langle n|\hat{a}(\nu,\mathbf{k})\hat{a}^*(\nu,\mathbf{k})|n\rangle$, $\langle n|\hat{a}^*(\nu,\mathbf{k})\hat{a}(\nu,\mathbf{k})|n\rangle$, $\langle n|\hat{a}^*(\nu,\mathbf{k})\hat{a}^*(\nu,\mathbf{k})|n\rangle$, since the Bose operators are orthogonal in both the wave vector $\mathbf{k}$ and the normal-mode index ν.[13] We first evaluate the expectation value of these expressions for the crystal being in a vibrational eigenstate $|n\rangle$ and then determine the thermal average over all vibrational states. We use the definition of the Bose operators[13]

$$\begin{aligned}
\hat{a}^*|n\rangle &= (n+1)^{1/2}|\, n+1\rangle \\
\hat{a}|n\rangle &= n^{1/2}|n-1\rangle
\end{aligned} \tag{19}$$

and it is easy to see that only the second and third combination above are nonzero. The thermal average are determined from equilibrium statistical mechanics, and we find[12,13]

$$\begin{aligned}
\langle n|\, \hat{a}^*\hat{a}|n\rangle_{\mathrm{th}} &= \frac{\sum_n \exp(-E_n/(k_{\mathrm{B}}T))\langle n|\, \hat{a}^*\hat{a}|n\rangle}{\sum_n \exp(-E_n/(k_{\mathrm{B}}T))} \\
&= \frac{\sum_n n \exp(-\hbar n\omega_{\nu}(\mathbf{k})/(k_{\mathrm{B}}T))}{\sum_n \exp(-\hbar n\omega_{\nu}(\mathbf{k})/(k_{\mathrm{B}}T))} \\
&= \frac{1}{\exp(\hbar\omega_{\nu}(\mathbf{k})/(k_{\mathrm{B}}T)) - 1} = n(\omega_{\nu}(\mathbf{k}))
\end{aligned} \tag{20}$$

and similar for

$$\langle n|\, \hat{a}\hat{a}^*|n\rangle_{\mathrm{th}} = n(\omega_{\nu}(\mathbf{k})) + 1 \tag{21}$$

The correlation function for the fluctuating force may therefore be written

$$\langle \mathbf{f}(t)\mathbf{f}(0)\rangle = \frac{k_{\mathrm{B}}T}{2N} \sum_{\nu,\mathbf{k}} \frac{1}{\omega_{\nu}(\boldsymbol{k})^2} |\mathbf{b}(\mathbf{k},\nu,\mathbf{R})|^2\, 2\cos(\omega_{\nu}(\mathbf{k})t) \tag{22}$$

where

$$\mathbf{b}(\mathbf{k},\nu,\mathbf{R}) = \sum_{\mathbf{l}} \sum_{d} (\nabla_{\mathbf{R}} \nabla_{\mathbf{R}} \phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|))_0 \frac{1}{M_{\mathrm{d}}^{1/2}} \cdot \mathbf{e_d}(\nu,\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{l}) \tag{23}$$

is a vector with three Cartesian components.

In eq 22, we have taken the classical limit in eq 20

$$n(\omega_{\nu}(\mathbf{k})) = \frac{1}{\exp(\hbar\omega_{\nu}(\mathbf{k})/(k_{\mathrm{B}}T)) - 1} \sim \frac{k_{\mathrm{B}}T}{\hbar\omega_{\nu}(\mathbf{k})} \gg 1 \tag{24}$$

and approximated the term $1 + n(\omega_{\nu}(\mathbf{k}))$ in eq 21 by $n(\omega_{\nu}(\mathbf{k}))$.

B. Translation Symmetry. We take advantage of the translational symmetry of the crystal and use a Fourier expansion of the interaction potential[14] to simplify the summation in eq 23.

Let us begin with a specification of the geometry of our system. The surface is placed perpendicular to the z direction with the surface at $z = 0$. The atoms in the crystal are arranged in layers parallel to the surface such that layer β has the z coordinate, z_β. It is a negative number since the crystal extends to $-\infty$ along z. In the lateral x and y directions, there is an infinite translational symmetry, so the lattice vector $\mathbf{l}$ is a 2D vector. This means that, in addition to index d used to specify the atoms in the unit cell, we also need an index β to specify the layers.

The 2D lattice vector $\mathbf{l}$ in the layers of the crystal parallel to the surface are defined by

$$\mathbf{l} = l_1\mathbf{a_1} + l_2\mathbf{a}_2 \tag{25}$$

where l_1 and l_2 are integers and $\mathbf{a_1}$ and $\mathbf{a_2}$ are the 2D lattice vectors. The reciprocal lattice vectors $\mathbf{b_1}$ and $\mathbf{b_2}$ are defined according to

$$\mathbf{a}_{\boldsymbol{i}}\cdot\mathbf{b}_{\boldsymbol{j}} = \delta_{ij} \tag{26}$$

and the reciprocal lattice vectors $\mathbf{g}$ are given by

$$\mathbf{g} = g_1\mathbf{b}_1 + g_2\mathbf{b}_2 \tag{27}$$

Let us start with an evaluation of the adsorption energy of a gas atom, since we may use the result directly in the evaluation of the gradients in the sum in eq 23. The adsorption energy $U(\mathbf{R})$ of an adatom will be a periodic function of the lateral position of the gas atom. Let us therefore write the position vector $\mathbf{R}$ of the gas atom in terms of a lateral vector $\mathbf{r}$ and the z component, z

$$\mathbf{R} = \mathbf{r} + z\hat{z} \tag{28}$$

where $\hat{z}$ is the unit vector along z.

The periodicity of $U(\mathbf{R})$ may be expressed by a Fourier expansion in the reciprocal lattice vectors $\mathbf{g}$

$$U(\boldsymbol{r},z) = \sum_{\mathbf{g}} w_{\mathbf{g}}(z)\exp(i\mathbf{g}\cdot\mathbf{r}) \tag{29}$$

Clearly, if we add a lattice vector $\mathbf{l}$ to the position vector $\mathbf{r}$, we get the same energy as before, when we use the relation in eq 26. The coefficients in the Fourier expansion are given by

$$w_{\mathbf{g}}(z) = \frac{1}{a_s}\int_a \exp(-i\mathbf{g}\cdot\mathbf{r})U(\mathbf{r},\boldsymbol{z})\,\mathrm{d}\mathbf{r} \tag{30}$$

where $a_s = |\mathbf{a}_1 \times \mathbf{a}_2|$ is the area of the 2D unit cell and label a on the integral indicates an integration over a unit cell.

We may determine the adsorption energy of the gas atom at $(\boldsymbol{r} + z\hat{z})$ as a sum of interaction energies between adatom and crystal atoms in the different layers β

$$U(\mathbf{r},z) = \sum_\beta U(\mathbf{r}, z - z_\beta) \tag{31}$$

where z_β (a negative number) is the z coordinate of the βth layer in the crystal. So let us first determine an expression for the energy between the adatom and the crystal atoms in layer β. It is assumed that this energy may be determined as a sum of atom−atom potentials such as

$$U(\mathbf{r}, z - z_\beta) = \sum_{\mathbf{l}}\sum_{\mathrm{d}(\beta)}\phi_{\mathrm{as}}(\mathbf{r} - (\mathbf{r}_{\mathrm{d}(\beta)} + \mathbf{l}), z - z_\beta) \tag{32}$$

where $\mathbf{r}_{\mathbf{d}(\beta)}$ is the position vector of atom $d(\beta)$ in the unit cell in layer β. In a 3D crystal, d normally runs over all the atoms in a 3D unit cell, but here where we only have a 2D lattice, it must include the atoms in the 2D unit cells in all layers; it is therefore necessary with a specification of which layer we are considering. We now introduce eq 32 into eq 30 and get

$$\begin{aligned} w_{\mathbf{g}}(\mathbf{z} - \mathbf{z}_\beta) &= \frac{1}{a_s}\sum_{\mathbf{l}}\sum_{d(\beta)}\int_a \exp(-i\mathbf{g}\cdot\mathbf{r})\phi_{\mathrm{as}}(\mathbf{r} - (\mathbf{r}_{d(\beta)} + \mathbf{l}), \\ &\qquad z - z_\beta)\,\mathrm{d}\mathbf{r} \\ &= \frac{1}{a_s}\sum_{d(\beta)}\exp(-i\mathbf{g}\cdot\mathbf{r}_{d(\beta)}) \times \\ &\qquad \int \exp(-i\mathbf{g}\cdot\mathbf{s})\phi_{\mathrm{as}}(\boldsymbol{s}, z - z_\beta)\,\mathrm{d}\mathbf{s} \end{aligned} \tag{33}$$

where we have introduced the substitution

$$\mathbf{s} = \mathbf{r} - (\boldsymbol{r}_{d(\beta)} + \mathbf{l}) \tag{34}$$

and used $\exp(i\mathbf{g}\cdot\mathbf{l}) = 1$. The integration over $\mathbf{r}$ was limited to a unit cell a, but with the substitution in eq 34 and the summation over all $\mathbf{l}$, the integration over s will extend over the entire layer, hence no label on the integral in the second line of eq 33.

We restrict our discussion to atom−atom potentials, where the energy only depends on the distance between the atoms $(s^2 + (z - z_\beta)^2)^{1/2}$, so it will be natural to shift to polar coordinates in the integration. We have

$$\begin{aligned} s &= |\boldsymbol{s}| \\ d\mathbf{s} &= s\,\mathrm{d}\xi\,\mathrm{d}s \end{aligned} \tag{35}$$

where ξ is the polar angle of $\mathbf{s}$. If the polar angle of $\mathbf{g}$ is η, then

$$\mathbf{g}\cdot\mathbf{s} = gs\cos(\eta - \xi) \tag{36}$$

so

$$\begin{aligned} w_{\mathbf{g}}(z - z_\beta) &= \frac{1}{a_s}\sum_{d(\beta)}\exp(-i\mathbf{g}\cdot\mathbf{r}_{d(\beta)})\int_0^\infty \phi_{\mathrm{as}}((s^2 + \\ &\qquad (z - z_\beta)^2)^{1/2})s\,\mathrm{d}s\int_0^{2\pi}\exp(igs\cos(\eta - \xi))\,\mathrm{d}\xi \end{aligned} \tag{37}$$

The integral over ξ gives[15]

$$\int_0^{2\pi}\exp(igs\cos(\eta - \xi))\,\mathrm{d}\xi = 2\pi J_0(gs) \tag{38}$$

where $J_0(gs)$ is the zero order Bessel function, so finally

$$\begin{aligned} w_{\mathbf{g}}(z - z_\beta) &= \frac{2\pi}{a_s}\sum_{d(\beta)}\exp(-i\mathbf{g}\cdot\mathbf{r}_{d(\beta)})\int_0^\infty J_0(gs)\phi_{\mathrm{as}}((s^2 + \\ &\qquad (z - z_\beta)^2)^{1/2})s\,\mathrm{d}s \equiv \sum_{d(\beta)}\exp(-i\mathbf{g}\cdot\mathbf{r}_{d(\beta)})V_{\mathrm{g}}(z - z_\beta) \end{aligned} \tag{39}$$

with

$$V_{\mathbf{g}}(z - z_\beta) = \frac{2\pi}{a_s}\int_0^\infty J_0(gs)\phi_{\mathrm{as}}((s^2 + (z - z_\beta)^2)^{1/2})s\,\mathrm{d}s \tag{40}$$

This is the central result for the Fourier coefficients. To evaluate them, we need an explicit expression for the atom−atom potential.

In conclusion, the interaction energy between an adatom and atoms in the β layer of the crystal is given by the expression

$$U(\mathbf{r}, z - z_\beta) = \sum_{\mathbf{g}} \sum_{d(\beta)} \exp(-i\mathbf{g}\cdot\mathbf{r}_{d(\beta)}) V_{\mathrm{g}}(z - z_\beta) \exp(i\mathbf{g}\cdot\mathbf{r}) \tag{41}$$

and the total potential energy

$$U(\mathbf{r}, z) = \sum_{\beta} \sum_{\mathbf{g}} \sum_{d(\beta)} \exp(-i\mathbf{g}\cdot\mathbf{r}_{d(\beta)}) V_{\mathbf{g}}(z - z_\beta) \exp(i\mathbf{g}\cdot\mathbf{r}) \tag{42}$$

Then let us evaluate the sum over **l** in eq 23. We may rewrite the expression according to

$$\begin{aligned}\mathbf{b}(\mathbf{k},\nu,\boldsymbol{R}) &= \sum_{\mathbf{l}} \sum_{d} (\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}\phi_{\mathrm{as}}(|\mathbf{R} - \mathbf{R}_{d,\mathbf{l}}|))_0 \frac{1}{M_{\mathrm{d}}^{1/2}} \cdot\mathbf{e}_{\mathrm{d}}(\nu,k) \exp(i\mathbf{k}\cdot\mathbf{l}) \\ &= \nabla_{\mathbf{R}}\nabla_{\mathbf{R}} \sum_{\beta} \sum_{d(\beta)} \frac{1}{M_{\mathrm{d}(\beta)}^{1/2}} \cdot\mathbf{e}_{\mathrm{d}(\beta)}(\nu,\boldsymbol{k}) \times \\ &\qquad \sum_{\mathbf{l}} \phi_{\mathrm{as}}(\mathbf{r} - (\mathbf{r}_{d(\beta)} + \mathbf{l}), z - z_\beta) \exp(-i\mathbf{k}\cdot\mathbf{l})\end{aligned} \tag{43}$$

The sum over **l** is written as a Fourier expansion according to

$$\sum_{\mathbf{l}} \phi_{\mathrm{as}}(\mathbf{r} - (\mathbf{r}_{d(\beta)} + \mathbf{l}), z - z_\beta)\exp(-i\mathbf{k}\cdot\mathbf{l}) = \sum_{\mathbf{g}} \exp(i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r}) W_{\mathbf{k}+\mathbf{g}}(z - z_\beta) \tag{44}$$

and the Fourier coefficients are given by the expression

$$W_{\mathbf{k}+\mathbf{g}}(z - z_\beta) = \frac{1}{a_{\mathrm{s}}} \sum_{\mathbf{l}} \int_{\mathrm{a}} \exp(-i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r})\phi_{\mathrm{as}}(\mathbf{r} - (\mathbf{r}_{d(\beta)} + \mathbf{l}), \mathbf{z} - \mathbf{z}_\beta) \exp(i\mathbf{k}\cdot\mathbf{l})\, \mathrm{d}\mathbf{r} \tag{45}$$

With the same substitution as in eq 34, we find

$$\begin{aligned}W_{\mathbf{k}+\mathbf{g}}(z - z_\beta) &= \frac{1}{a_{\mathrm{s}}} \int \phi_{\mathrm{as}}(\mathbf{s}, z - z_\beta) \exp(-i(\mathbf{k} + \mathbf{g})\cdot\mathbf{s}) \times \\ &\qquad \exp(- i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r}_{d(\beta)})\, \mathrm{d}\mathbf{s} \\ &= \exp(- i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r}_{d(\beta)}) \frac{1}{a_{\mathrm{s}}} \int \phi_{\mathrm{as}}(\mathbf{s}, z - z_\beta) \times \\ &\qquad \exp(-i(\mathbf{k} + \mathbf{g})\cdot\mathbf{s})\, \mathrm{d}\mathbf{s} \\ &= \exp(-i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r}_{d(\beta)}) \times \\ &\qquad \frac{2\pi}{a_{\mathrm{s}}} \int_0^\infty J_0(|\mathbf{k} + \mathbf{g}|s)\phi_{\mathrm{as}}((s^2 + (z - z_\beta)^2)^{1/2}) s\, \mathrm{d}s \\ &= \exp(- i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r}_{d(\beta)}) V_{\mathbf{k}+\mathbf{g}}(z - z_\beta)\end{aligned} \tag{46}$$

Like in the derivation of the expression for the adsorption energy, we have switched to polar coordinates in the third line of the equation, and from eq 40, we get the last line in the equation.

When finally introduced into eq 43 we get the expression

$$\begin{aligned}\mathbf{b}(\mathbf{k},\nu,\mathbf{R}) &= \nabla_{\mathbf{R}}\nabla_{\mathbf{R}} \sum_{\beta} \sum_{d(\beta)} \frac{1}{M_{\mathrm{d}(\beta)}^{1/2}} \cdot\mathbf{e}_{\mathrm{d}(\beta)}(\nu,\mathbf{k}) \times \\ &\qquad \sum_{\mathbf{g}} \exp(- i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r}_{d(\beta)}) V_{\mathbf{k}+\mathbf{g}}(z - z_\beta) \exp(i(\mathbf{k} + \mathbf{g})\cdot\mathbf{r})\end{aligned} \tag{47}$$

IV. Summary and Implementation

When the expression for the time correlation function of the fluctuating forces, eq 22, is introduced in the expression for γ_α in eq 11, we see that the temperature cancels, so we get a temperature independent friction coefficient and also that it depends on the position of the adatom.

To facilitate the calculation, let us introduce a spectral density $\rho_\alpha(\omega)$ of the function $|b_\alpha(\mathbf{k},\nu,\mathbf{R})|^2/\omega_\nu(\mathbf{k})^2$ such that

$$\sum_{\nu,\mathbf{k}} \frac{1}{\omega_\nu(\mathbf{k})^2} |b_\alpha(\mathbf{k},\nu,\mathbf{R})|^2 \cos(\omega_\nu(\mathbf{k})t) = \int_0^{\omega_{\max}} \mathrm{d}\omega\, \rho_\alpha(\omega) \cos(\omega t) \tag{48}$$

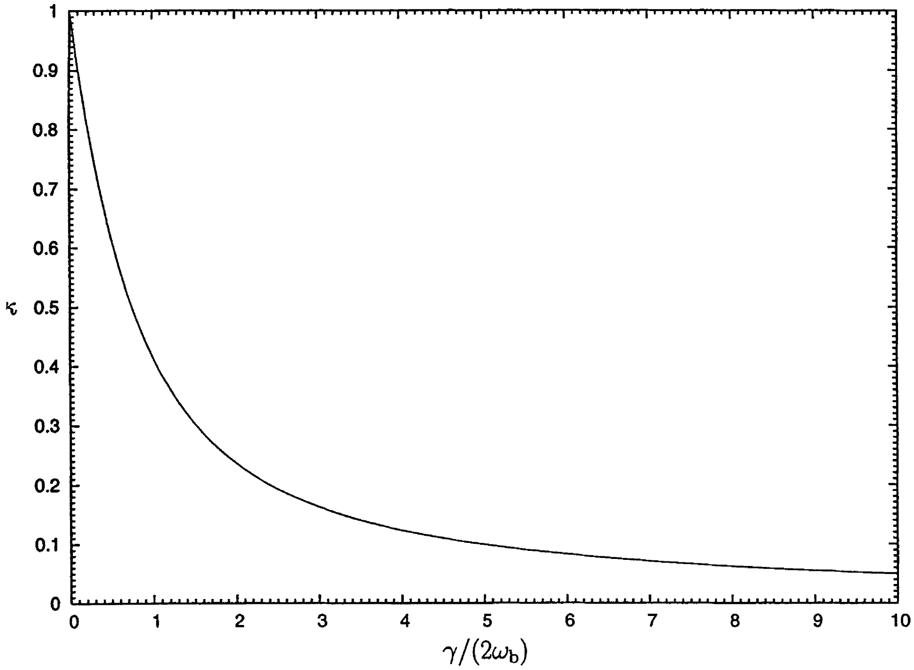

Figure 1. The correction factor κ (eq 51) in Kramers' theory to the TST rate constant as a function of $\gamma/(2\omega_{\mathrm{b}})$.

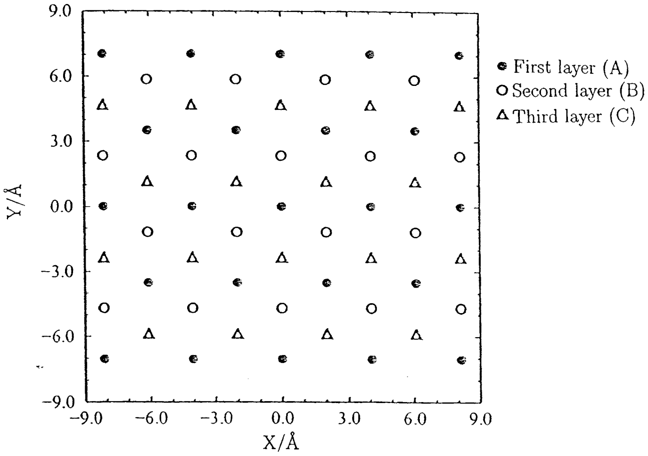

Figure 2. A top-down view of the Fe(111) surface. The Fe atoms are arranged in a hexagonal pattern in layers in an ABCABC... stacking order. The distance between layers is 0.8285 Å.

The equation for γ_α is then

$$\gamma_\alpha = \frac{1}{mN}\int_0^\infty \mathrm{d}t \exp(-\gamma_\alpha t) \int_0^{\omega_{\max}} \mathrm{d}\omega \rho_\alpha(\omega) \cos(\omega t) = \frac{1}{mN}\int_0^{\omega_{\max}} d\omega \frac{\gamma_\alpha \rho_\alpha(\omega)}{{\gamma_\alpha}^2 + \omega^2} \quad (49)$$

The phonon frequencies and polarization vectors are calculated for a uniform distribution of wave vectors in the irreducible Brillouin zone. The results for each wave vector are sorted into a histogram of ω values between zero and $\omega_{\max}$ giving the spectral density $\rho_\alpha(\omega)$.

V. Application to the N_2/Fe(111) System

The rate constant k_{sol} for a chemical reaction in solution is given by

$$k_{\mathrm{sol}} = k_{\mathrm{TST}}\kappa \quad (50)$$

following Kramers' theory.[3] k_{TST} is the rate constant determined by TST, and κ represents the influence of the solvent molecules on the rate constant and is given by

$$\kappa = (1 + (\gamma/(2\omega_b))^2)^{1/2} - \gamma/(2\omega_b) \quad (51)$$

γ is the friction coefficient and ω_b the magnitude of the imaginary frequency along the reaction coordinate at the saddle point in the PES representing the transition state. κ is shown as a function of $\gamma/(2\omega_b)$ in Figure 1. It is clear that the rate constant in solution always will be smaller than the TST rate constant. The latter may be determined from the energetics of the transition state and the reactants. The magnitude of the imaginary frequency at the transition state may be determined from the calculated potential energy surface, and the friction coefficient for a reaction on a crystalline surface may be determined by the method described above.

J.J. Mortensen et al.[16] have reported extensive DFT calculations of the energetics of N_2 adsorption and dissociation on an Fe(111) surface. In Figure 2 we have shown a top view of the Fe(111) surface. The Fe atoms are arranged in a hexagonal pattern in layers that are arranged in an ABCABC... stacking as we go down through the crystal. Mortensen et al. proposed the dissociation path as sketched in Figure 3. The N_2 molecule is first adsorbed on top of an Fe atom in the top layer with the molecular axis perpendicular to the surface, the γ state. Then it moves over to the δ site on top of an Fe atom in the B layer below the top layer, still with the molecular axis perpendicular to the surface. From there it moves to the α state with the molecular axis parallel to the surface and finally ends up in the α_2 state from where the dissociation to the β state takes place. There is a barrier to dissociation from this state, and that is the rate-limiting step. From their energy calculations, we have estimated the magnitude of the imaginary frequency at the transition state to be $\omega_b \simeq 70$ THz.

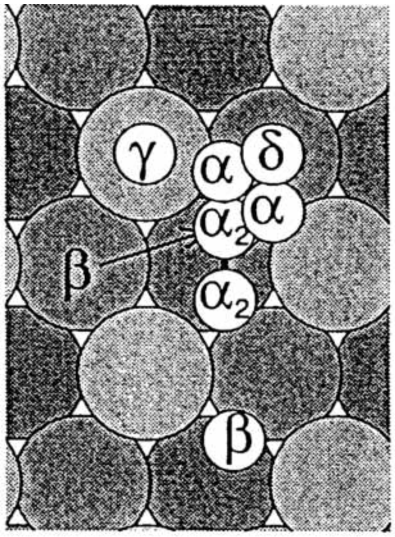

Figure 3. Top view of an Fe(111) surface with different molecular states of N_2. In the γ and δ states, the molecular axis is perpendicular to the surface and only the top atom is seen. The dissociation to the β state takes place from the α_2 state.[20]

The dynamics of the Fe crystal has been determined by a lattice dynamics calculation of a crystalline slab with translation symmetry in the x and y directions and a finite number of layers along z. We have used the potential model by ref 17, where the interaction between the Fe atoms are given by

$$\phi(r) = -0.188917(r - 1.827)^4 + 1.70192(r - 2.50849)^2 - 0.198294 \qquad 0 \le r \le 3.44$$
$$\phi(r) = 0 \qquad r \ge 3.44 \quad (52)$$

The energy is in eV and the distance r in Å. The parameters in the potential are determined from a lattice dynamics calculation of the density of states and an experimental determination by inelastic incoherent neutron scattering.[18] The number of layers in the slab is determined on the basis of the criteria that the normal-mode frequencies do not change by addition of more layers. The dependence of a low-frequency and a high-frequency normal mode on the number of layers is shown in Figure 4. The figure shows that we should consider at least about 75 layers before the frequencies become almost independent of the number of layers, so we have used 75 layers in our computations.

For the N/Fe interaction, we have used a Morse potential

$$\phi_{\mathrm{as}} = D[\exp(-2a(\Delta R - R_{\mathrm{eq}})) - 2\exp(-a(\Delta R - R_{\mathrm{eq}}))] \quad (53)$$

The parameters $D = 8.1455 \times 10^{-2}$ eV, $a = 5.78$ Å^{-1}, and $R_{\mathrm{eq}} = 3.38$ Å are the same as those used by Lajer et al.[19] We need the Fourier coefficients $V_g(z)$ for the Morse potential that are given by eq 40. The integral may be evaluated numerically, if an analytic solution cannot be found. In the case of the Morse

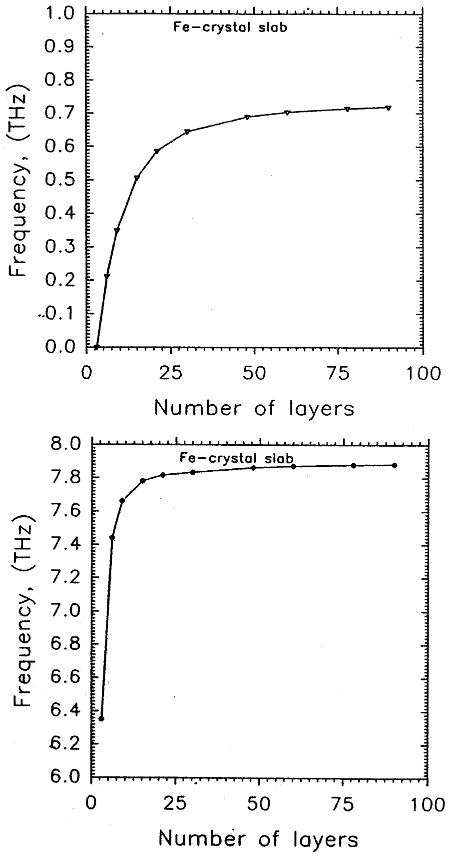

Figure 4. Lattice dynamics result for an Fe−crystal slab. The frequencies of two normal modes with respectively a small and a high frequency are shown as function of the number of layers in the slab.

potential it is possible to find an analytic expression. After lengthy arithmetic manipulations, one finds[15]

$$V_g(z - z_\beta) = \frac{2\pi}{a_s} D \exp(aR_{eq}) \Bigg[\frac{2a(z - z_\beta)}{4a^2+g^2} \left(1 + \frac{1}{(z - z_\beta)(4a^2 + g^2)^{1/2}}\right) \times \exp(aR_{eq}) \exp(-(z - z_\beta)(4a^2 + g^2)^{1/2}) - \frac{2a(z - z_\beta)}{a^2 + g^2} \left(1 + \frac{1}{(z - z_\beta)(a^2 + g^2)^{1/2}}\right) \times \exp(-(z - z_\beta)(a^2 + g^2)^{1/2}) \Bigg] \quad (54)$$

We now have the necessary ingredients for a determination of the **b** vector in eq 47. It is determined at a number of wave vectors **k** in the Brillouin zone. We used 400. The results are binned according to the frequency and added to form the spectral density ρ_α in eq 48. The friction coefficient γ_α is finally determined iteratively from eq 49.

VI. Results and Discussion

For the α_2 position of the nitrogen atoms, we have found a friction coefficient of 20−30 THz for each of the nitrogen atoms. The reaction coordinate is the relative motion of the two nitrogen atoms, so the friction coefficient for that motion is about 40−60 THz. With $\omega_b \simeq 70$ THz, we find that the ratio $\gamma/(2\omega_b)) \simeq 0.35$. From Figure 1 is seen that $\kappa \simeq 0.75$, which corresponds to a 25% reduction of the TST rate constant k_{TST}. Mortensen et al.[16] made an estimate of k_{TST} and found that it was 2 orders of magnitude larger than in experiments. Our calculations show that the phononic friction cannot account for such a large discrepancy. This may indicate that the electronic friction also may be important. However, the uncertainties are quite large in these calculations. The friction coefficient depends strongly on the position of the adatom on the surface and a systematic investigation of this dependency will be desirable. Also, the DFT potentials may be inaccurate. These questions will be investigated further.

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