PHYSICAL REVIEW B VOLUME 18, NUMBER 2 15 JULY 1978

Effect of adatom-phonon coupling on desorption kinetics in the heavy-adatom limit

C. Caroli, B. Roulet, and D. Saint-James

Groupe de Physique des Solides de l'Ecole Normale Supérieure, associé au Centre National de la Recherche Scientifique, Université Paris VII, 2 Place Jussieu, 75221 Paris-Cedex 05, France

(Received 17 December 1976)

The Kramers-Langevin stochastic equation governing desorption is derived microscopically in the case where the adatom is coupled to the lattice vibrations of the solid substrate, and in the limit where the adatom mass is much larger than the atomic mass of the substrate. The systematic potential V_{eff} and the friction coefficient η are calculated, with the help of a local harmonic approximation, in terms of the microscopic binding potential V and of the local static surface compressibility χ of the isolated substrate. η is found to be position dependent. It is shown that, for a given chemisorption potential V, two regimes may occur, depending on the value of χ. For "hard" substrates, the Kramers equation holds, but η may have significant space variations. For "soft" substrates, a dynamic instability of the local deformation of the substrate around the adatom appears at a particular value of the adatom position. This effect exhibits an intrinsic hysteresis and induces a large energy loss. It leads, in spite of the large value of the mass ratio, to the breakdown of the Kramers approximation.

I. INTRODUCTION

Recently, there has been a renewal of interest in the study of the kinetics of desorption of neutral atoms from solid surfaces. The calculation of a desorption rate can be broken down into three different steps. (a) One first expresses the equation of motion of the adsorbate particle as a "stochastic" equation, in which the interaction between the atom and the substrate manifests itself via a systematic friction force and a random force, both being, as usual, connected by a "fluctuation-dissipation" relation.

It is always possible to formally write such an equation[1] for any particle plus bath system (the bath being, here, the substrate). However, this only gives another equivalent formulation of the complete $(N+1)$-particle problem, and does not provide as such any explicit solution. Considerable simplification occurs when the fluctuations of the bath are fast compared with the motion of the particle[2,3] (this is, for example, the case in the classical Brownian-motion problem). The stochastic equation then reduces to a Langevin one, i.e., with a white-noise spectrum for the random force and a nonretarded friction coefficient (or, equivalently, to a Fokker-Planck equation for the distribution function of the particle variables).

Such an equation was first written phenomenologically, for the desorption problem, by Kramers.[4] In its Langevin version, Kramers's equation reads

$$M\frac{dv}{dt}=F(x)-M\eta v+\mathfrak{F}(t)\,, \tag{1}$$

where M, v, and x are the mass, velocity, and position of the adatom, $F(x)$ is some systematic binding force, and the friction coefficient (or viscosity) η is related to the random force $\mathfrak{F}(t)$ by

$$\eta=\frac{\beta}{M}\int_0^\infty\langle\mathfrak{F}(0)\mathfrak{F}(t)\rangle\,dt\quad\left(\beta=\frac{1}{k_BT}\right)\,, \tag{2}$$

and

$$\langle\mathfrak{F}(0)\mathfrak{F}(t)\rangle=C\delta(t)\,. \tag{3}$$

(b) If such a type of simplification is possible, one must then calculate explicitly, for a given system, the systematic force and the friction coefficient, which are in general functions of temperature and position. (c) Once the Langevin equation is completely specified, it must be solved to calculate experimentally measured quantities—that is, in our case, the desorption rate or the sticking coefficient (which are connected by a simple detailed balance relation[5]).

Part (c) of this program has been completed for Kramers's equation (1), i.e., with a constant η, by several authors.[4-7] They find that one may define three regimes: (i) low friction: $\eta\ll\omega_0k_BT/V$, where V is the depth of the systematic binding potential, and ω_0 is the vibration frequency of the adatom at the bottom of the potential well. In this case the desorption time varies as η^{-1}; (ii) high friction: $\eta\gg\omega_0$, where $\tau\propto\eta$; (iii) intermediate range: $\omega_0k_BT/V\ll\eta\ll\omega_0$ (which is very broad in the chemisorption situation where $k_BT\ll V$). In this range, the result of Eyring's absolute-rate theory[7] (ART) is valid, and $\tau=2\pi\omega_0^{-1}\exp(\beta V)$.

Parts (a) and (b) have been thoroughly investigated, especially by Suhl and co-workers,[6,8] with the restriction that they have taken into account only the interaction of the adatom with the *electronic* degrees of freedom of the substrate. With this restriction, and since the electron mass is much smaller than the mass of any adatom, the fluctuations of the bath are obviously fast with respect to the particle motion, and an equation of Kramers's type is valid. The friction coefficient associated with these interactions has been calculated for several different forms of the electronic coupling.[9,10]

However, it is clear that the adatom couples, not only to the electronic excitations of the substrate, but also to its lattice vibrations. The mass mismatch is much weaker between the adatom and the substrate atoms than between the adatom and the electrons. Therefore, one expects that the coupling to phonons gives much larger effects and controls the kinetics of desorption—except possibly when electronic effects are enhanced by the existence of a soft mode in the electronic excitation spectrum.

The effect of the coupling between adatom and substrate lattice vibrations has been studied by Beeby and coworkers,[11] whose approach is somewhat different from the one described above: they do not try to write an explicit stochastic equation for the adatom, but calculate directly the desorption time with the help of two simplifying assumptions: (i) They identify the desorption flux with the part of the atomic current which would flow away from the solid surface if the whole system was at thermal equilibrium. (ii) This current is calculated at a given value of the *relative* distance between the adatom (of mass M) and the nearest substrate atom (of mass m).

This model leads to a desorption time

$$\tau \propto \mu^{1/2},$$

where μ is the reduced mass: $\mu = Mm/(M+m)$.

It must be noted that this result predicts a finite value for the desorption time in the limit $M \to \infty$, while one must find, in that case, that $\tau \to \infty$. Indeed, when the adatom is infinitely heavy it remains at rest with respect to the center of mass C of the solid (or, equivalently, to the *average* position of the substrate surface). It is the distance of the adatom to that *fixed* point (and not to the *instantaneous* position of the vibrating surface atoms) which is the proper variable in terms of which desorption must be defined. Therefore, although the atoms of the substrate surface do vibrate, the adatom does not move and τ is infinite.

This shows that assumption (ii) is not correct, and that the current must be calculated at a given value of the absolute (i.e., measured with respect to C) position of the adatom. However, when this is done, it appears that, due to assumption (i), one simply recovers Eyring's ART result which, as shown in Ref. 4, is not valid in the low- and high-friction regimes.

One is, therefore, led to come back to the three-step stochastic approach, which avoids making an assumption of thermal equilibrium and allows for a direct out-of-equilibrium calculation. This is the point of view which we take in this paper, with the aim of completing—in the same spirit as what was done for the electronic coupling—steps (a) and (b) and obtaining, if possible, the appropriate Kramers-Langevin equation. As already mentioned, this method only applies, in practice—at least in the present state of the art—when the motion of the bath (made here of the vibrational degrees of freedom of the substrate) is much faster than that of the particle. This means that we will only treat the case of a heavy adatom adsorbed on a light substrate ($M \gg m$).

In Sec. II, we rederive the formal general stochastic equation for the adatom, and the simplified Langevin equation which follows from it in the adiabatic limit. In Sec. III, we apply the formalism to the model of a harmonic substrate with a nonharmonic adatom—solid binding potential, which we solve in the local harmonic approximation (that is, for small amplitudes of atomic vibration). We thus obtain approximate expressions for the systematic effective potential and the friction coefficient which appear in the Langevin-Kramers equation. In Sec. IV, we discuss the validity of the local harmonic approximation. We find that, for a given microscopic atom-solid binding potential, if the compressibility of the substrate is large enough, the approximation breaks down at some particular value of the adatom position, where the energy loss becomes very large. In the close vicinity of that "critical" position, the validity of the Kramers-Langevin equation itself breaks down, in spite of the large value of the mass ratio (M/m).

II. DERIVATION OF THE FORMAL STOCHASTIC EQUATION

In what follows, we restrict ourselves to a classical treatment: this is sufficient to describe the atom-phonon coupling at the high temperatures ($\sim 300\,^\circ$K) of practical interest.

Let us define our system as composed of a semi-infinite solid, made of $N (N \to \infty)$ interacting atoms of mass m, positions $\vec{r}_i$ and momenta $\vec{p}_i$ ($i = 1, \ldots, N$), and an adatom of mass M, position $\vec{R}_0$ and momentum $\vec{P}_0$, interacting with the solid via the potential $V(\vec{R}_0, \{\vec{r}_i\})$.

As discussed in Sec. I, in order to analyze desorption, one must study the motion of the adatom with respect to a solid of fixed macroscopic position and orientation. This constraint can be most conveniently imposed by fixing the positions of three atoms belonging to the surface of the solid opposite to the adsorbing surface[12] (and lying at infinity from it). This we simulate by including in the Hamiltonian H_s of the solid an external *ad hoc* potential V_e. This eliminates from H_s the spurious global translational and rotational invariances.

The Hamiltonian of the total system then reads

$$H = H_0 + \vec{P}_0^2/2M\,, \tag{4a}$$

$$H_0 = H_s + V(\vec{R}_0, \{\vec{r}_i\})\,. \tag{4b}$$

To this Hamiltonian is associated the Liouville operator

$$iL = iL_0 + iL_1\,, \tag{5a}$$

where

$$iL_0 = \sum_{i=1}^{N}\left(\frac{\partial H_0}{\partial \vec{p}_i}\cdot\frac{\partial}{\partial \vec{r}_i} - \frac{\partial H_0}{\partial \vec{r}_i}\cdot\frac{\partial}{\partial \vec{p}_i}\right), \tag{5b}$$

and

$$iL_1 = \frac{\vec{P}_0}{M}\cdot\frac{\partial}{\partial \vec{R}_0} - \frac{\partial V}{\partial \vec{R}_0}\cdot\frac{\partial}{\partial \vec{P}_0}\,. \tag{5c}$$

It is seen that iL_0 is the Liouville operator corresponding to the adiabatic Hamiltonian H_0, i.e., to the system composed of the solid interacting with the adatom *fixed* at position $\vec{R}_0$.

We then follow the method which has been developed in the microscopic theory of Brownian motion,[13] as formulated by Mazur and Oppenheim.[2] Let us introduce the projector $\mathcal{P}$ defined by

$$\mathcal{P}(\cdots) \equiv \langle\cdots\rangle = \frac{1}{Z_0}\int\prod_{i=1}^{N} d\vec{p}_i\, d\vec{r}_i\, e^{-\beta H_0}(\cdots)\,, \tag{6a}$$

$$Z_0 = \int\prod_{i=1}^{N} d\vec{p}_i\, d\vec{r}_i\, e^{-\beta H_0}\,, \tag{6b}$$

Z_0 being a function of $\vec{R}_0$.

Note that $\mathcal{P}$ describes the statistical equilibrium of the adiabatic system, which is the $M/m \to \infty$ limit of the real one. Therefore, it is intuitively clear that this choice is well suited to develop, from the general exact formalism, an approximation for the $M \gg m$ case.

We define the quantity at time $t=0$,

$$\vec{\mathfrak{F}}(0) = \dot{\vec{P}}_0(0) - \mathcal{P}\dot{\vec{P}}_0(0) \quad \left(\dot{\vec{P}}_0 \equiv \frac{d\vec{P}_0}{dt} = -\frac{\partial V}{\partial \vec{R}_0}\right), \tag{7}$$

and its time evolution in the complete system

$$\vec{\mathfrak{F}}(t) = e^{iLt}\vec{\mathfrak{F}}(0)\,. \tag{8}$$

Inserting the identity

$$e^{iLt} \equiv e^{(1-\mathcal{P})iLt} + \int_0^t d\tau\, e^{iL(t-\tau)} i\mathcal{P}L e^{(1-\mathcal{P})iL\tau} \tag{9}$$

into Eq. (8), we obtain

$$\vec{\mathfrak{F}}(t) = \vec{\mathfrak{F}}^{+}(t) + \int_0^t d\tau\, e^{iL(t-\tau)}\mathcal{P}iL_1\vec{\mathfrak{F}}^{+}(\tau)\,, \tag{10}$$

where we have taken advantage of the relation $\mathcal{P}iL_0 = 0$, and defined

$$\vec{\mathfrak{F}}^{+}(t) = e^{(1-\mathcal{P})iLt}\vec{\mathfrak{F}}(0)\,. \tag{11}$$

It follows from Eqs. (11) and (7) that

$$\langle\vec{\mathfrak{F}}^{+}(t)\rangle = \mathcal{P}e^{(1-\mathcal{P})iLt}\vec{\mathfrak{F}}(0) = \mathcal{P}\,\vec{\mathfrak{F}}(0) = 0\,, \tag{12}$$

since $\mathcal{P}(1-\mathcal{P}) = 0$.

On the other hand it may be checked easily from Eqs. (6) and (7) that $\mathcal{P}\dot{\vec{P}}_0(0) = \langle -(\partial V/\partial \vec{R}_0)\rangle_0$ is a function of $\vec{R}_0(0)$ only, so that the quantity $\exp(iLt)\mathcal{P}\dot{\vec{P}}_0(0)$ appearing in $\vec{\mathfrak{F}}(t)$ only depends implicitly on time through the time dependence of $\vec{R}_0$. That is, we may write it, in the equation of motion [Eq. (10)], as $-\partial[V_{\text{eff}}(\vec{R}_0)]/\partial\vec{R}_0$, where the effective systematic potential V_{eff} is

$$V_{\text{eff}}(\vec{R}_0) = -(1/\beta)\ln Z_0(\vec{R}_0) + \text{const.} \tag{13}$$

The constant must be chosen so that $V_{\text{eff}} \to 0$ in the limit of zero interaction (for example, in our adsorption problem, V_{eff} must go to zero when the adatom is at infinity from the solid) and $\vec{R}_0$ is to be understood, as usual in mechanical problems, as the solution $\vec{R}_0(t)$ of the equation of motion itself.

Finally,

$$\begin{aligned}\mathcal{P}iL_1\vec{\mathfrak{F}}^{+}(\tau) &= \left\langle\left(\frac{\vec{P}_0}{M}\cdot\frac{\partial}{\partial \vec{R}_0} - \frac{\partial V}{\partial \vec{R}_0}\cdot\frac{\partial}{\partial \vec{P}_0}\right)\vec{\mathfrak{F}}^{+}(\tau)\right\rangle \\ &= \frac{\vec{P}_0}{M}\cdot\left\langle\frac{\partial}{\partial \vec{R}_0}\vec{\mathfrak{F}}^{+}(\tau)\right\rangle - \frac{\partial}{\partial \vec{P}_0}\cdot\left\langle\frac{\partial V}{\partial \vec{R}_0}\vec{\mathfrak{F}}^{+}(\tau)\right\rangle.\end{aligned} \tag{14}$$

By derivating (12) with respect to $\vec{R}_0$ and using (6), we get

$$\left\langle\frac{\partial}{\partial \vec{R}_0}\vec{\mathfrak{F}}^{+}(\tau)\right\rangle = \beta\left\langle\frac{\partial V}{\partial \vec{R}_0}\vec{\mathfrak{F}}^{+}(\tau)\right\rangle. \tag{15}$$

If, moreover, one notes that

$$\frac{\partial V}{\partial \vec{R}_0} = -\vec{\mathfrak{F}}(0) + \left\langle\frac{\partial V}{\partial \vec{R}_0}\right\rangle_0 \equiv -\vec{\mathfrak{F}}^{+}(0) + \left\langle\frac{\partial V}{\partial \vec{R}_0}\right\rangle_0, \tag{16}$$

and takes once more advantage of Eq. (12), the equation of motion (10) becomes

$$\begin{aligned}\dot{\vec{P}}_0(t) = &-\frac{\partial}{\partial \vec{R}_0}V_{\text{eff}}(\vec{R}_0) + \vec{\mathfrak{F}}^{+}(t) \\ &+ \int_0^t d\tau\, e^{iL(t-\tau)}\left(\frac{\partial}{\partial \vec{P}_0} - \beta\frac{\vec{P}_0}{M}\right)\cdot\left\langle\vec{\mathfrak{F}}^{+}(0)\,\vec{\mathfrak{F}}^{+}(\tau)\right\rangle.\end{aligned} \tag{17}$$

This is the general formal stochastic equation associated with our problem, which enables one to define formally (i) an effective systematic (and temperature-dependent) potential V_{eff}, (ii) a random force $\vec{\mathfrak{F}}^{+}(t)$, of zero average value. Note that, at this stage, and due to its definition (11), which explicitly involves the projection operator $\mathcal{P}$, the time evolution of $\vec{\mathfrak{F}}^+$ does not coincide with that in any real mechanical system, but mixes mechanical and statistical effects, (iii) a retarded generalized "friction" term. Its kernel is the correlation tensor of the random force, which expresses the generalized fluctuation-dissipation relation.

Let us insist that Eq. (17) is completely exact but, of course, since one does not know, in general, how to calculate the random force $\vec{\mathfrak{F}}^+$, it is also, at this stage, devoid of practical usability, and approximations must be made.

As we have noted, the choice of the "adiabatic" projector suggests that one should look at the $M \gg m$ limit. The evolution operator defining $\vec{\mathfrak{F}}^+$ can be written (since $\mathcal{P}L_0 = 0$)

$$\exp[(1-\mathcal{P})iLt] = \exp[iL_0 t + (1-\mathcal{P})iL_1 t]. \tag{18}$$

As discussed in detail in Ref. 2, to lowest order in $(m/M)^{1/2}$, $(1-\mathcal{P})iL_1$ can be neglected with respect to iL_0; indeed, since the momenta p_i of the bath particles are of order $(m/\beta)^{1/2}$, while P_0 is of order $(M/\beta)^{1/2}$,[14] for any reasonably regular dynamical quantity B,

$$iL_1 B \sim (m/M)^{1/2} iL_0 B. \tag{19}$$

Keeping to lowest order, we, therefore, have

$$\vec{\mathfrak{F}}^+(t) \cong e^{iL_0 t}\vec{\mathfrak{F}}^+(0) \equiv \vec{\mathfrak{F}}^{(0)}(\vec{R}_0, t), \tag{20}$$

that is, the random force can be approximated by the *mechanical* force $\vec{\mathfrak{F}}^{(0)}$ acting on the adatom in the system (S_0), defined as solid plus particle *fixed* at $\vec{R}_0$. Therefore, the autocorrelation tensor of $\vec{\mathfrak{F}}^{(0)}$ is independent of $\vec{P}_0$ and [since the average is taken at equilibrium for (S_0)] stationary in time. Equation (17) then becomes

$$\dot{\vec{P}}_0 = -\frac{\partial}{\partial \vec{R}_0} V_{\text{eff}}(\vec{R}_0) + \vec{\mathfrak{F}}^{(0)}(\vec{R}_0, t) - \frac{\beta}{M}\int_0^t d\tau\, \vec{P}_0(t-\tau)\cdot\langle \vec{\mathfrak{F}}^{(0)}(\vec{R}_0, 0)\,\vec{\mathfrak{F}}^{(0)}(\vec{R}_0, \tau)\rangle. \tag{21}$$

Here again, $\vec{R}_0$ is the solution $\vec{R}_0(t)$ of the equation of motion (21), together with $M\dot{\vec{R}}_0 = \vec{P}_0$.

As shown by Mazur and Oppenheim (and as will appear below for our particular model), the assumption $M \gg m$ entails that the time range of $\langle \vec{\mathfrak{F}}^{(0)}(0)\vec{\mathfrak{F}}^{(0)}(\tau)\rangle$ is much smaller than the characteristic scale of the time variations of $\vec{P}_0$. So, to order $(m/M)^{1/2}$, one may rewrite Eq. (21) as

$$\dot{\vec{P}}_0 = -\frac{\partial}{\partial \vec{R}_0} V_{\text{eff}}(\vec{R}_0) + \vec{\mathfrak{F}}^{(0)}(\vec{R}_0, t) - \vec{P}_0(t)\cdot\overleftrightarrow{\eta}(\vec{R}_0), \tag{22a}$$

$$\overleftrightarrow{\eta}(\vec{R}_0) = \frac{\beta}{M}\int_0^\infty d\tau\,\langle \vec{\mathfrak{F}}^{(0)}(\vec{R}_0, 0)\,\vec{\mathfrak{F}}^{(0)}(\vec{R}_0, \tau)\rangle, \tag{22b}$$

which has the standard form of the Kramers-Langevin equation, but for the presence of a space dependence of the friction tensor $\overleftrightarrow{\eta}$.

III. KRAMERS'S EQUATION FOR A HEAVY ATOM ON THE SURFACE OF A LIGHT VIBRATING SOLID

We now want to apply this formalism to the case of a heavy adatom on a light solid, and we only take into account the coupling of the adsorbate to the lattice vibrations of the solid, neglecting all electronic dynamical effects (the microscopic binding potential V of course results from static electronic effects). To simplify the problem as much as possible we assume, following Beeby,[11] that (a) the solid is completely harmonic and has a perfectly plane surface (this second restriction can easily be removed if necessary); (b) the adatom solid potential V couples the adatom to one single atom—which we call atom 1—belonging to the surface of the solid; (c) the adatom is free to move in only one direction, $\hat{x}$, perpendicular to the surface, and the interaction potential V only depends on the distance between atoms 0 and 1 along the normal to the surface.

Namely, we take

$$H_0 = \sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m} + \sum_{i,j=1}^{N}\sum_{\mu,\nu=x,y,z}\tfrac{1}{2}q_{i\mu}A_{ij}^{(\mu\nu)}q_{j\nu} + V(X_0 - x_1) + V_e, \tag{23}$$

where $\vec{q}_i = \vec{r}_i - \vec{r}_i^{\,0}$, the $\vec{r}_i^{\,0}$ are the equilibrium positions of the substrate atoms in the absence of the adatom, and the $A_{ij}^{(\mu\nu)}$ are the elements of the force constant matrix $\overleftrightarrow{A}$ of the solid. In order to get a reasonable description of desorption, we must assume that V (i) has a short-range strongly repulsive part (which prevents diffusion of the adatom inside the solid); (ii) goes to zero (with a finite range a) at infinity in the vacuum $(x \to +\infty)$; (iii) has a minimum for $X_0 - x_1$ of the order of an atomic distance, and may or may not present an activation barrier.

We want to calculate the two characteristic quantities $V_{\text{eff}}(X_0)$ and $\overleftrightarrow{\eta}(X_0)$ which appear in the reduced stochastic equation (22).

A. Effective potential

Following definition (13), we have

$$V_{\text{eff}}(X_0) = -(1/\beta)\ln[Z_0(X_0)/Z_0(\infty)],$$

$$Z_0(X_0) = \int d\vec{p}_1\cdots d\vec{p}_N\, d\vec{r}_1\cdots d\vec{r}_N \times \exp[-\beta H_0(X_0, \{\vec{p}_i\}, \{\vec{r}_i\})]. \tag{24}$$

The integration on momenta factors out, yielding a trivial constant C. H_0 is a quadratic form in all the variables $\{\vec{r}_i\}$, except for the single variable x_1.[15] It is, therefore, convenient to rewrite Z_0 as

$$Z_0(X_0)=C\int dx_1 \exp\{-\beta[V(X_0-x_1)+w(x_1)]\}\,, \tag{25}$$

where

$$\exp[-\beta w(x_1)] = \int dy_1\, dz_1\, d\vec{r}_2 \cdots d\vec{r}_N \times \exp\left[-\beta\left(\sum_{i,j=1}^{N}\sum_{\mu\nu} \tfrac{1}{2} q_{i\mu} A_{ij}^{(\mu\nu)} q_{j\nu}+V_e\right)\right], \tag{26}$$

so that $w(x_1)$ is also quadratic in x_1. Clearly, up to a constant, $w(x_1)$ is the contribution of the free energy of the isolated solid due to the displacement $(x_1-x_1^0)$ of atom 1 from its equilibrium position. Therefore, it has the form

$$w(x_1)=(1/2\chi)(x_1-x_1^0)^2+C' \tag{27}$$

where χ is the (xx) component of the *local* static compressibility tensor on site 1. Expression (27) is demonstrated directly in Appendix A, where it is also shown that

$$\chi=-g_{11}^{(xx)}(\omega=0)\,, \tag{28}$$

where $g_{ij}^{(\mu\nu)}$ is the displacement Green's function of the isolated substrate, which obeys the equation

$$m\omega^2 g_{ij}^{(\mu\nu)}(\omega)-\sum_{k=1}^{N}\sum_{\xi=x,y,z} A_{ik}^{(\mu\xi)} g_{kj}^{(\xi\nu)}(\omega)=\delta_{ij}\,\delta_{\mu\nu}\,. \tag{29}$$

As is well known from the theory of Brownian motion of a system of harmonic oscillators,[16] or from the study of phonon resonances, the behavior of χ depends critically on the dimensionality of the solid.

(i) For a 1-dimensional solid (harmonic semi-infinite linear chain) $\chi^{-1}=0$. It is seen on Eq. (25) that this entails

$$V_{\text{eff}}(x_0)=0\,,$$

which simply expresses that, if the last atom of a linear chain is given a finite static displacement q_1, the chain takes a new equilibrium position with each atom displaced by q_1/N and, in the limit $N\to\infty$, this does not cost any energy.

(ii) For a two-dimensional solid, χ diverges at low frequency as $\ln\omega$, and one cannot separate out an effective static potential. As was discussed in Refs. 16, it is not possible in that case to justify a Langevin equation.

(iii) If χ is calculated for an infinite three-dimensional solid, it is found to be finite (for example, with a Debye isotropic model, one gets $\chi=3/m\omega_D^2$ where ω_D is the Debye frequency). However, in the situation we are dealing with, the solid is semi-infinite and has, in general, not only volume but also surface phonons. One may wonder whether their contribution to χ is regular or not. In Appendix B, we calculate the explicit expression of χ for a particular phonon model, and check that it does remain finite when surface phonons are taken into account.

Strictly speaking, expression (25) for Z_0 can only be calculated numerically. However, in adsorption experiments one is in general in the situation $k_BT \ll V_0$, where V_0 is the depth of the microscopic binding potential. It is thus reasonable to calculate V_{eff} with the help of a steepest descent approximation, which provides a low-temperature expansion of Z_0 (valid at temperatures such that the average thermal vibration amplitude of atom 1 be much smaller than the atomic distance).

Defining

$$U(X_0,x_1)=V(X_0-x_1)+(1/2\chi)(x_1-x_1^0)^2\,, \tag{30}$$

and calling $x_{1m}(X_0)$ the solution of

$$\frac{\partial U}{\partial x_1}=-V'(X_0-x_1)+\frac{1}{\chi}(x_1-x_1^0)=0 \tag{31}$$

[with $V'(z)\equiv dV/dz$], we obtain

$$V_{\text{eff}}(X_0)\cong U(X_0,x_{1m})+\tfrac{1}{2}k_BT\ln[1+\chi V''(X_0-x_{1m})]\,. \tag{32}$$

Note that x_{1m} is the adiabatic equilibrium position (along $\hat{x}$) of atom 1 elastically bound to the rest of the solid, and in the presence of the adatom fixed at X_0. As can be expected, V_{eff} is temperature dependent since it is an average of the microscopic V on the thermal vibrations of the substrate. This results in a decrease of the depth of V_{eff} when T increases.

In the low-temperature regime where Eq. (32) is valid, and which is usually realized in chemisorption, this shift is linear in temperature. Such a shift results, in terms of the parameters which are standardly used to analyze desorption rate data, in a linear shift of the activation energy E_{act}. Since most experimental results are interpreted within the assumption of a constant E_{act}, the shift will finally appear as a temperature-independent renormalization of the prefactor [of order of magnitude $(1+V_0\chi/a^2)^{1/2}$].

Let us now turn to the low-temperature limit of the effective potential $U(X_0,x_{1m})$. Clearly, the difference between U and V increases with χ. An example (corresponding to a Morse potential for V) is drawn in Fig. 1. It is seen that the minima of $U(X_0,x_{1m})$ and V coincide in value and in position: more precisely if the minimum of V is located at $(X_0 - x_1) = d$, the minimum of $U(X_0, x_{1m})$ corresponds to $X_0 - x_1^0 = d$. This results immediately by derivating Eq. (30) [with $x_1 = x_{1m}(X_0)$] with respect to X_0, and taking advantage of relation (31). It implies that the minimum of $U(X_0, x_{1m})$ is attained when $x_{1m}(X_0) = x_1^0$.

The minimum of U is always flatter than that of V, due to the fact that the static deformation of the substrate in S_0 is such as to minimize the total free energy. The curvature of V_{eff} is given by

$$\frac{d^2 V_{\text{eff}}}{dX_0^2} = V''(1 + \chi V'')^{-1},$$

where $V'' \equiv V''(X_0 - x_{1m})$.

B. Friction coefficient and Kramers's equation in the local harmonic approximation

We should now calculate the friction coefficient $\eta(X_0)$ in the heavy mass limit, i.e., the autocorrelation function $\langle \mathfrak{F}_x^{(0)}(X_0, 0)\mathfrak{F}_x^{(0)}(X_0, t)\rangle$ of the force on the fixed adatom due to the substrate atoms. The statistical average is to be taken on the equilibrium distribution in this "adiabatic" system (S_0).

Following definitions (16) and (20), in our model

$$\mathfrak{F}_x^{(0)}(X_0, t) = -\left(\frac{\partial}{\partial X_0} V(X_0 - x_1(t)) - \left\langle \frac{\partial V}{\partial X_0}\right\rangle\right), \qquad (33)$$

so that we need to know explicitly the time evolution of x_1 in (S_0). This means solving the following set of equations of motion:

$$\begin{aligned} m\ddot{q}_{1\mu} &= -\sum_{i=2}^{N}\sum_{\nu} A_{1i}^{(\mu\nu)} q_{i\nu} \\ &\quad - \sum_{\nu} A_{11}^{(\mu\nu)} q_{1\nu} - \delta_{\mu x}\frac{\partial}{\partial q_{1x}} V(X_0 - x_1^0 - q_{1x}), \\ m\ddot{q}_{i\mu} &= -\sum_{j=2}^{N}\sum_{\nu} A_{ij}^{(\mu\nu)} q_{j\nu} \\ &\quad - \sum_{\nu} A_{i1}^{(\mu\nu)} q_{1\nu} \quad (i = 2, \ldots, N), \end{aligned} \qquad (34)$$

where $\vec{q}_i = \vec{r}_i - \vec{r}_i^{\,0}$, $\mu, \nu = x, y, z$. Variables $\vec{q}_i$ $(i \geqslant 2)$, q_{1y}, q_{1z} can be eliminated formally, since they obey linear equations of motion, by introducing the (retarded) Green's function $\mathcal{G}_{ij}^{r(\mu\nu)}$ of the isolated substrate in which one imposes $q_{1x} = 0$. We shall not explicitly write $\mathcal{G}$ here. Clearly it obeys an equation similar to (29), with the convention that the coefficient $A_{1k}^{(x\mu)} = 0$ (but not the coefficients $A_{k1}^{(\mu x)}$). We call $q_{i\mu}^{(0)}(t)$ the displacements in that "frozen-q_{1x}" situation. Then,

$$\begin{aligned} m\ddot{q}_{1x} = &-\sum_{i=1}^{N}\sum_{\mu}(1 - \delta_{i1}\delta_{\mu x}) A_{1i}^{(x\mu)} q_{i\mu}^{(0)}(t) \\ &- A_{11}^{(xx)} q_{1x} - \frac{\partial}{\partial q_{1x}} V(X_0 - x_1^0 - q_{1x}) \\ &- \sum_{i,j=1}^{N}\sum_{\mu,\nu}(1 - \delta_{i1}\delta_{\mu x})(1 - \delta_{j1}\delta_{\mu x}) A_{1i}^{(x\mu)} \\ &\times \int_0^t dt'\, \mathcal{G}_{ij}^{r(\mu\nu)}(t - t') A_{j1}^{(\nu x)} q_{1x}(t'). \end{aligned} \qquad (35)$$

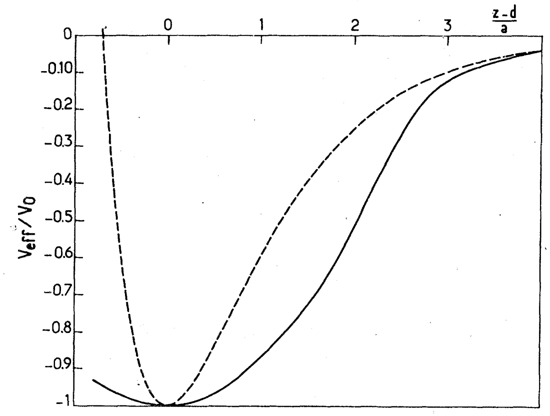

FIG. 1. Example of microscopic adatom-solid binding potential, and of the low-temperature limit of the corresponding effective potential. Dashed line: microscopic Morse potential

$$V\left(\frac{z-d}{a}\right) \equiv V_M\left(\frac{X_0 - x_1 - d}{a}\right) = V_0\left[\exp\left(-2\frac{z-d}{a}\right) - 2\exp\left(-\frac{z-d}{a}\right)\right] .$$

Full line:

$$V_{\text{eff}}\left(\frac{z-d}{a}\right) \equiv V_{\text{eff}}\left(\frac{X_0 - x_1^0 - d}{a}\right) \equiv U(X_0, x_{1m})$$

for $\frac{a^2}{2\chi V_0} = 0.15$.

The force which drives the motion of q_{1x} contains a retarded linear part (due to the rest of the solid) and a nonlinear one, due to the binding of the adatom. In such a situation, it is in general impossible to obtain an analytic solution for $q_{1x}(t)$. We must therefore look for some sort of harmonic approximation. Note that choosing for V a truncated harmonic potential is not suitable, indeed, the matching conditions at the truncation point amount to reintroducing nonlinearity into the equations of motion.

We will, therefore, use, for the bindingforce $\partial V/\partial q_{1x}$, a "local harmonic approximation." That is, for each value of X_0, we write

$$\frac{\partial V}{\partial x_1} = -V'(X_0 - b) + (x_1 - b)V''(X_0 - b), \qquad (36)$$

which amounts to developing, for each X_0, V up to second order in x_1 around some point $b(X_0)$, to be chosen so as to minimize the error. Clearly, this is realized if we choose for $b(X_0)$ the point of static equilibrium $x_{1m}(X_0)$ of atom 1 in (S_0), defined by Eq. (31). Indeed, this intuitively reasonable choice does give $\langle (x_1 - b)^3 \rangle = 0$, i.e., ensures that (to the order at which we are working) the average value of the first neglected term in zero.

Of course, our approximation will be valid if, and only if, the average vibration amplitude of atom 1 is small compared with the space range a of the potential V. It is therefore a low-temperature approximation, but which remains reasonably good for volume atoms in most materials up to room temperature—at which desorption experiments are usually performed. Its validity for a surface atom in our particular situation will be discussed at length in Sec. IV.

Before proceeding to calculate $\eta(X_0)$, it is important to realize that, in order to be coherent, we must calculate V_{eff} [Eqs. (24)–(25)] within the same approximation as that used to obtain η. Otherwise, we would get $\langle \partial V/\partial X_0 \rangle \neq -\langle \partial V/\partial x_1 \rangle$, and the conservation of total momentum would not be satisfied. We thus have, using expression (36):

$$\frac{dV_{\text{eff}}(X_0)}{dX_0} = -\left\langle \frac{\partial V}{\partial x_1} \right\rangle = V'(X_0 - x_{1m}) . \tag{37}$$

Note that, since x_{1m} itself depends on X_0, Eq. (37) does *not* imply that $V_{\text{eff}} = V$. On the contrary, it corresponds to

$$V_{\text{eff}}(X_0) = U(X_0, x_{1m}) , \tag{38}$$

i.e., to the zero temperature limit of expression (32). To the same order of approximation, the random force $\mathfrak{F}^{(0)}(t)$ defined in Eq. (33) is given by

$$\mathfrak{F}^{(0)}(t) = \frac{\partial V}{\partial x_1} - \left\langle \frac{\partial V}{\partial x_1} \right\rangle = (x_1 - x_{1m}) V''(X_0 - x_{1m}) . \tag{39}$$

Setting $x_1 - x_{1m} = u_{1x}$, and writing for simplicity $V''(X_0 - x_{1m}) \equiv V''$ we therefore have to calculate the quantity $\langle u_{1x}(0) u_{1x}(t) \rangle$.

Let us insert expression (36), with $b = x_{1m}$, into Eqs. (34). It is convenient at this point to define new displacement variables for all the substrate atoms, by

$$\vec{u}_i = \vec{r}_i - \vec{r}_i^{\,(b)} , \tag{40}$$

where the $\vec{r}_i^{\,(b)} \equiv \vec{r}_i^{\,0} + \vec{q}_i^{\,(b)}$ are the adiabatic equilibrium positions in (S_0), shifted from the $\vec{r}_i^{\,0}$ by the effect of the static binding force $-V'(X_0 - x_{1m})$. They are the solutions of

$$\sum_{j=1}^{N} \sum_{\nu} A_{ij}^{(\mu\nu)} q_{j\nu}^{(b)} = -V'(X_0 - x_{1m}) \delta_{i1} \delta_{\mu x} . \tag{41}$$

In terms of these new variables, the equations of motion now read, in matrix form

$$m \ddot{\vec{U}} = -\overleftrightarrow{B} \vec{U} . \tag{42}$$

where $\vec{U}$ is the $3N$-dimensional column vector of the $u_{i\mu}$'s ($i \geq 1$), and the new force constant matrix is defined by

$$B_{ij}^{(\mu\nu)} = A_{ij}^{(\mu\nu)} + V'' \delta_{i1} \delta_{j1} \delta_{\mu x} \delta_{\nu x} . \tag{43}$$

We solve Eq. (42) by means of a Laplace transform. This immediately gives

$$\vec{U}(t) = \overleftrightarrow{D}(t) \vec{U}(0) + \overleftrightarrow{F}(t) \vec{p}(0) . \tag{44}$$

$\vec{p}(0)$ is the column vector of the $p_{i\mu}(0)$'s ($i \geq 1$), and the matrix functions $\overleftrightarrow{D}(t)$, $\overleftrightarrow{F}(t)$ are the inverse Laplace transforms of

$$\begin{aligned} \overleftrightarrow{D}(s) &= ms(ms^2 \overleftrightarrow{I} + \overleftrightarrow{B})^{-1} , \\ \overleftrightarrow{F}(s) &= s^{-1} \overleftrightarrow{D}(s) . \end{aligned} \tag{45}$$

$\overleftrightarrow{I}$ is the $3N \times 3N$ unit matrix.

In order to obtain

$$\langle u_{1x}(0) u_{1x}(t) \rangle = \frac{1}{Z_0} \int e^{-\beta H_0} u_{1x}(0) u_{1x}(t) \times \prod_{i=1}^{N} d\vec{u}_i \, d\vec{p}_i , \tag{46}$$

we express H_0 in terms of the $\vec{u}_i$'s. Taking into account the equilibrium condition (41), we get

$$H_0(X_0) = \left(\frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu\nu} A_{ij}^{(\mu\nu)} q_{i\mu}^{(b)} q_{j\nu}^{(b)} + V(X_0 - x_{1m}) \right) + \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu\nu} B_{ij}^{(\mu\nu)} u_{i\mu} u_{j\nu} . \tag{47}$$

The first term on the right-hand side is a constant, thus gives no contribution to the average (46).

On the other hand, the term linear in $\vec{p}(0)$ in Eq. (44) does not contribute either, since $\langle u_{i\mu} p_{j\nu} \rangle = 0$. Finally,

$$\begin{aligned} C(t) &= \langle \mathfrak{F}^{(0)}(0) \mathfrak{F}^{(0)}(t) \rangle \\ &= \frac{(V'')^2}{Z_0} \int \prod_{i=1}^{N} d\vec{u}_i \exp\left(-\frac{\beta}{2} \sum_{\substack{i,j \\ \mu,\nu}} B_{ij}^{(\mu\nu)} u_{i\mu} u_{j\nu} \right) \times \sum_{l\xi} D_{1l}^{(x\xi)} u_{l\xi} u_{1x} \\ &= \frac{(V'')^2}{\beta} \sum_{l\xi} D_{1l}^{(x\xi)}(t) (\overleftrightarrow{B}^{-1})_{l1}^{(\xi x)} \\ &= \frac{(V'')^2}{\beta} (\overleftrightarrow{D} \overleftrightarrow{B}^{-1})_{11}^{(xx)} . \end{aligned} \tag{48}$$

The Laplace transform $C(s)$ of the correlation function $C(t)$ is therefore given by

$$\begin{aligned} C(s) &= \frac{V''^2}{\beta} [ms(ms^2 \overleftrightarrow{I} + \overleftrightarrow{B})^{-1} \overleftrightarrow{B}^{-1}]_{11}^{(xx)} \\ &= \frac{V''^2}{\beta s} [G_{11}^{(xx)}(s) - G_{11}^{(xx)}(0)] , \end{aligned} \tag{49}$$

where $\overleftrightarrow{G}(s) = -(ms^2\overleftrightarrow{I} + \overleftrightarrow{B})^{-1}$ is the Laplace transform of the retarded Green's function $G^r(t)$ of the linearized (S_0) system, associated with Eqs. (42). G can be expressed easily in terms of the Green's function g of the isolated substrate [defined by Eq. (29)] with the help of Eq. (43),

$$\overleftrightarrow{G} = \overleftrightarrow{g} + \overleftrightarrow{g}(\overleftrightarrow{B} - \overleftrightarrow{A})\overleftrightarrow{G},$$

which gives

$$G_{11}^{(xx)}(s) = g_{11}^{(xx)}(s) / [1 - g_{11}^{(xx)}(s) V''] . \tag{50}$$

We now make the assumption, standard in the heavy mass limit, that P_0 varies slowly on the characteristic time range of $C(t)$. We then can use Eq. (22b), which, here, gives

$$\eta(x_0) = \frac{\beta}{M} C(s=0)$$
$$= \frac{[V''(X_0 - x_{1m})]^2}{M} \frac{-i\chi'(0)}{[1 + \chi V''(X_0 - x_{1m})]^2}, \tag{51}$$

where

$$-i\chi'(0) = -i \left.\frac{d\chi(\omega)}{d\omega}\right|_{\omega=0}, \quad \chi(\omega) = -g_{11}^{(xx)}(\omega)$$

being the local dynamic compressibility of the isolated substrate at site 1. Note that $-i\chi'(0) = [dg_{11}^{(xx)}(s)/ds]_{s=0}$ is a real positive quantity. It is finite for a semi-infinite 3-dimensional solid with surface phonons (see Appendix B). An order of magnitude is given by its value for an infinite solid in the isotropic Debye model: $-i\chi'(0) = 3\pi / 2m\omega_D^3$. As was expected, η depends on X_0, which only appears, due to the local harmonic approximation, via the effective spring constant $V''(X_0 - x_{1m})$. It exhibits a local maximum in the vicinity of the value of X_0, where V'' is minimum. This is illustrated on Fig. 2, for the case where $\Lambda = (1 + \chi \min V'') = 6$. The strength of this local enhancement increases when Λ decreases.

Let us finally check that P_0 is effectively slowly varying compared with $C(t)$. The characteristic frequency giving the time range of $C(t)$ is the average phonon frequency, of order ω_D. On the other hand, the time scale of the adatom motion is controlled by the two frequency parameters η and ω_0 appearing in the Kramers-Langevin equation (22a), ω_0 being a typical vibration frequency in the effective potential $U(X_0, x_{1m})$.

Using Eqs. (51) and (30), it is easy to see that

$$\omega_0 \sim \left(\frac{m}{M}\right)^{1/2} \left(\frac{V_0}{m\omega_D^2 a^2}\right)^{1/2} \omega_D,$$
$$\eta \sim \frac{m}{M} \left(\frac{V_0}{m\omega_D^2 a^2}\right)^2 \omega_D. \tag{52}$$

In practice, for the V_0's (of the order of a few eV) appropriate for chemisorption) $V_0/m\omega_D^2 a^2$ is roughly of order 1, so that, for $M \gg m$,

$$\eta \ll \omega_0 \ll \omega_D$$

and the Kramers-Langevin equation (22) holds with $\eta(X_0)$ and V_{eff} as given by Eqs. (38) and (51).

Before discussing the validity of the quasiharmonic approximation, let us point out that, in the $M \to \infty$ limit, Eq. (22) trivially yields $\langle X_0 \rangle = \text{const.}$, i.e., gives the correct infinite limit for the desorption time τ. This is also in agreement with the fact that the $M \to \infty$ limit clearly belongs to the low friction regime $(\eta \ll \omega_0 k_B T / V_0)$ for the solution of Kramer's equation (22), which therefore also implies $\tau \xrightarrow[M\to\infty]{} \infty$.

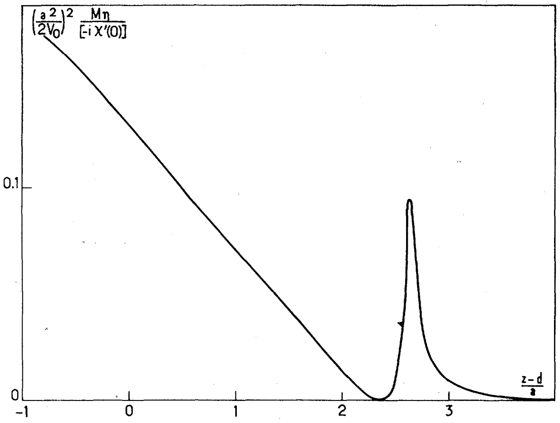

FIG. 2. Space variation of the reduced friction coefficient $\eta[(z - d/a)] \equiv \eta[(X_0 - x_1^0 - d/a)]$, for the Morse microscopic potential V_M of Fig. 1, with $a^2/2\chi V_0 = 0.15$.

IV. HARD- AND SOFT-SUBSTRATE REGIMES: BREAKDOWN OF KRAMERS'S APPROXIMATION

The local harmonic approximation (from now on referred to as LHA) implies, qualitatively, that for each value of X_0 atom 1 has, along direction x, a well-defined equilibrium position $x_{1m}(X_0)$, and a small oscillation amplitude around x_{1m}.

At a given temperature, the oscillation amplitude is proportional to

$$\left(\left.\frac{\partial^2 U(X_0, x_1)}{\partial x_1^2}\right|_{x_1 = x_{1m}}\right)^{-1/2} = [\chi^{-1}(1 + \chi V'')]^{-1/2}.$$

Therefore our approximation breaks down if $(1 + \chi V'')$ becomes very small. When this happens, the divergence of the LHA vibration amplitude for atom 1 results in the divergence of the LHA friction coefficient [Eq. (51)].

x_{1m} is well defined if the equilibrium condition (31) for atom 1 in the potential $U(X_0, x_1)$ has a single solution. Let us study graphically the solutions of Eq. (31). Any reasonable microscopic potential

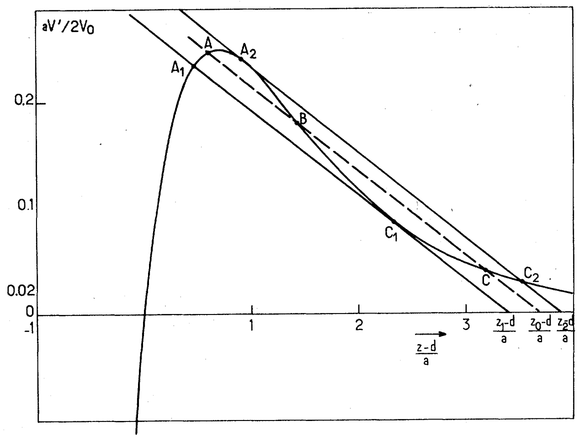

FIG. 3. Graphical determination of the adiabatic equilibrium displacement of atom 1: $z_{1m}=x_{1m}-x_1^0$, for the Morse potential V_M and $a^2/2\chi V_0=0.08$ (soft-substrate regime). For a given $z_0=X_0-x_1^0$, $(z_{1m}-d)/a$ is the abscissa of the point(s) of intersection of the curve $aV'/2V_0$ with the straight line $\chi^{-1}(z_0-z)$. For $z_1<z_0<z_2$, there are three intersections.

V has a positive curvature for small X_0-x_1, a negative one for large X_0-x_1, so that V' has the shape shown on Fig. 3 (with or without a negative minimum, depending on whether V is of the activated barrier type or not). The solution(s) of Eq. (31) for $z_m=X_0-x_{1m}$ correspond to the point of intersection of the curve $V'(z)$ with the straight line $(1/\chi)(X_0-x_1^0-z)$, of negative slope $(-\chi^{-1})$, which cuts the z axis at $z_0=X_0-x_1^0$. It is clear from Fig. 3 that two situations are possible, depending on the value of $\Lambda=1+\chi\min V''$ with respect to zero, or, equivalently, on the value of χ with respect to $\chi_c=-(\min V'')^{-1}$.

(i) $\Lambda>0$, i.e., $\chi<\chi_c$. Whatever value we have for X_0, there is only one intersection and, provided that Λ is not too small (more precisely $\Lambda>m/M$), the LHA is valid. It is precisely this situation that we have implicitly assumed to hold in Sec. III.

If Λ is positive but small ($\Lambda\lesssim m/M$), the characteristic oscillation frequency of atom 1, $\omega_1=[(1/m\chi)(1+\chi V'')]^{1/2}$ is of order ω_0 [Eq. (52)] or smaller. The adiabatic system (S_0) is no longer fluctuating rapidly with respect to the adatom motion, and it is no longer possible to justify a Kramers's equation for those X_0 such that $V''\simeq(\min V'')$.

(ii) $\Lambda<0$, i.e., $\chi>\chi_c$. Note that this may perfectly occur in the chemisorption case. Indeed, then, typically $V''\sim10^4$ erg cm^{-2}, while $\chi^{-1}\sim(10^2-10^3)A$ erg cm^{-2}, where A is the atomic number of the substrate. If this condition is realized, there exists a range of values of $X_0(z_1\leq z_0\leq z_2)$ in which there are three intersections A, B, C (see Fig. 3) and x_{1m} is no longer defined uniquely. For $z_0=z_1$ or z_2, the quantity $1+\chi V''$ is zero for the values of x_{1m} corresponding to points C_1 and A_2 defined on Fig. 3. So, at these points, $U(X_0,x_{1m})$ is no longer well defined, and the vibration amplitude of atom 1 diverges, as well as the friction coefficient η. Therefore, our approximation is clearly not valid in the immediate vicinity of $z_0=z_1,z_2$, and must be reconsidered in the rest of the three-intersection range.

Let us consider in more detail what happens in that case. Obviously, the LHA expression (38) for $V_{\text{eff}}(X_0)$ no longer has any meaning. One could be tempted to come back to the more general definition (24) and (25) of V_{eff}. The physical situation to which such a definition would correspond appears in Fig. 4, where the structure of $U(X_0,x_1)$ is depicted for various values of z_0. Equation (25), if valid, implies that x_1 has the equilibrium distribution in potential U, so that, at low enough temperature, for $z_1<z_0<z_2$ [Figs. 4(c) and 4(d)] atom 1 sits in the deeper well. This would be physically meaningful if U remained unchanged on a time $t_0\gg t_{\text{eq}}$, t_{eq} being the time of complete equilibration of the initial distribution in U.

But the situation we are dealing with is intrinsically dynamic: due to the adatom motion, U changes continuously from shape (a) to (e) (respectively, (e) to (a)] of Fig. 4 when the adatom leaves (respectively, goes towards) the surface. The characteristic time for this deformation t_0 is of order $\omega_0^{-1}\sim\omega_D^{-1}(M/m)^{1/2}$. On the other hand, the time necessary to relax from one of the wells of U into the other is $t_{\text{eq}}\sim\omega_D^{-1}\exp(\beta\Delta U)$, where ΔU is the corresponding barrier height. Note, moreover, that there is another characteristic time in the problem: the time of partial equilibration in-

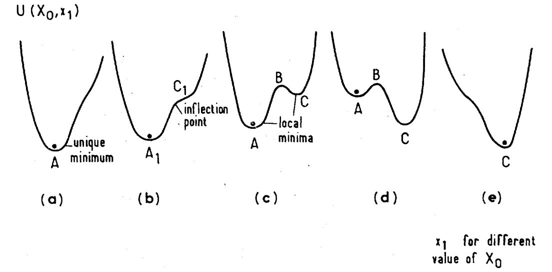

FIG. 4. Soft-substrate regime: shape of $U(X_0,x_1)$ as a function of x_1 for various values of X_0: (a) $X_0<z_1+x_1^0$: there is only one x_{1m} (see Fig. 3), U has a single minimum; (b) $X_0=z_1+x_1^0$: an inflection point with horizontal tangent appears on U, corresponding to point C_1 of Fig. 3; (c) $z_1+x_1^0<X_0<z_2+x_1^0$, there are three possible x_{1m}, i.e., three extrema to U. By dynamic continuity atom 1 stays in a position corresponding to the vicinity of minimum A: (d) X_0 approaches $z_2+x_1^0$ from the left, minimum A is shallow, the distribution of x_1 begins to leak into well C; (e) $X_0>z_2+x_1^0$: U has again only one minimum, C.

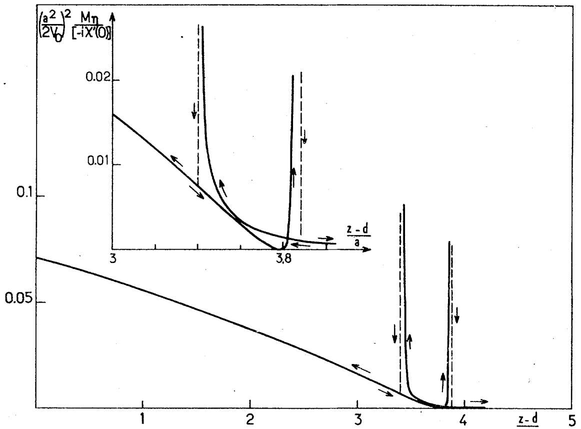

FIG. 5. Hysteretic behavior of the space variation of the reduced friction coefficient in the soft-substrate regime, and in the local-harmonic approximation, for $V=V_M$, $a^2/2\chi V_0=0.08$. (note that the LHA is not valid in the immediate vicinity of the points of discontinuity.)

side a given well, of order $\omega_D^{-1} \ll t_0$.

This enables us to make the following analysis: consider, for example, the case where the adatom is moving away from the surface, starting from X_{00} such that $z_{00}<z_1$.

(a) $z_0<z_1$ [Fig. 4(a)]. U has only one well, the LHA is valid. Atom 1 has the adiabatic equilibrium distribution in the bottom of the well.

(b) $z_0=z_1$ [Fig. 4(b)]. U develops an inflexion point C, where $1+\chi V''=0$. Atom 1 is still in the A minimum.

(c) $z_1<z_0<z_2$ [Fig. 4(c) and (d)]. Although the second minimum has developed, atom 1 stays in well A as long a $t_{\text{eq}} \gg t_0$. Since $t_0 \gg \omega_D^{-1}$, there is a Kramers-Langevin equation and the LHA is valid, with the value of V_{eff} and η corresponding to the x_{1m} of minimum A [i.e., followed by continuity from Fig. 4(a)] and not to the equilibrium definition (25).

(d) When z_0 approaches z_2 from the left, $\Delta U(z_0)$ decreases; when $\Delta U(z_0) \sim k_B T \ln(M/m)$, t_{eq} becomes of order t_0. Atom 1 then starts flowing from well A to well C. Once the atom has crept over the barrier into the top of well C, it relaxes down to its bottom in a time of order ω_D^{-1} (necessary to evacuate the excess energy of atom 1 into the solid by radiation of a bunch of phonons). However, the time τ_t needed for the whole distribution to tumble from A into C may be longer, since the time of escape from A is itself, in the important region, decreasing between t_0 and ω_D^{-1}.

In this region, all our treatment collapses; obviously, the LHA becomes meaningless, but, what is more important, the Kramers's equation (21) itself is no longer valid, since one of the characteristic times, t_{eq}, of the adiabatic system becomes comparable with the characteristic time t_0 of the adatom. For this reason, we are not able to give for τ_t an estimate better than $\omega_D^{-1}<\tau_t<t_0$.

(e) For $z_0=z_{2+}$, atom 1 has jumped into the new equilibrium position corresponding to point C_2, then when z_0 increases beyond z_2, there is only one x_{1m} [Fig. 4(e)], the LHA is valid and unambiguous, as for $z_0<z_1$.

The friction coefficient η therefore has the behavior depicted on Fig. 5: when z_0 approaches z_2 from the left, η increases as $\eta_0[2\chi V'''(z_2-z_0)]^{-1}$ (where $\eta_0=-i\chi'(0)/M\chi^2$, and V''' is the third derivative of V at point A_2), and jumps down to a finite value corresponding to point C_2 for $z_0=z_{2+}$. As already mentioned, this expression is not valid for very small ΔU's i.e., for

$$z_2-z_0 \lesssim \chi(V''')^{1/3}[k_B T \ln(M/m)]^{2/3},$$

in which region our definition of η loses its meaning. All we can do, in the absence of a more sophisticated theory, is to estimate the energy loss ΔE_0 of the adatom induced by the sudden relaxation of atom 1. The jump of atom 1 from A_2 to C_2 gives rise to a quasidiscontinuous drop, $\Delta V^{(2)}$, of V_{eff} (Fig. 6) at $X_0^{(2)}=z_2+x_1^0$

$$\Delta V^{(2)}=U(X_0^{(2)}-x_{1m}(A_2))-U(X_0^{(2)}-x_{1m}(C_2)). \tag{53}$$

Provided that χ is not too close to its critical value $\chi_c=-(\min V'')^{-1}$, $\Delta V^{(2)}$ is a finite fraction of V_0, i.e., $\Delta V^{(2)} \gg kT$ for chemisorption. Assuming—which is reasonable at least as far as orders of magnitude are concerned—that the change of the adatom velocity during the jumping time τ_t is negligible, we see that $\Delta E_0 \gg k_B T$.

Conversely, when the adatom is moving towards

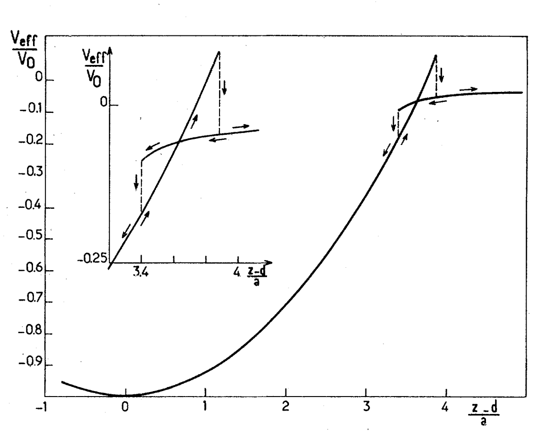

FIG. 6. Hysteretic behavior of the effective potential V_{eff} in the soft-substrate regime and in the local harmonic approximation for $V=V_M$, $a^2/2\chi V_0=0.08$.

the surface, atom 1 remains in minimum C until z_0 approaches close to z_1 (from the right), where it jumps into minimum A_1. In the three-intersection range (z_2, z_1), η (Fig. 5), and V_{eff} (Fig. 6) are to be calculated from the LHA, with the x_{1m} of point C. They are therefore different from those for the outgoing path. Again, the discontinuous drop of V_{eff} at $X_0^{(1)}$, $\Delta V^{(1)}$, is in general of order $V_0 \gg k_B T$. So, the instability exhibits a systematic hysteresis, imposed by the intrinsically dynamic character of our problem.

V. CONCLUSIONS

It therefore appears that, even in the supposedly simple large mass limit, Kramers's equation may be nonvalid. The very simple model we have used shows that, for a given microscopic binding potential V, there are two completely different regimes for desorption, depending on the value of the local static compressibility at the substrate surface.

(i) *Hard substrates* $(\chi < \chi_c)$: *a* Kramers-Langevin equation holds (as long as $1 - \chi/\chi_c > m/M$), with a well-behaved position-dependent friction coefficient, and a well-defined continuous effective potential. Both quantities can be calculated within the local harmonic approximation. In order of magnitude, $\eta/\omega_0 \sim (m/M)^{1/2}$. This ratio cannot be, in practice, smaller than at best 0.3 to 0.2. On the other hand, for chemisorption, $k_B T/V_0 \sim 10^{-2}$. Therefore in this case $\omega_0 k_B T/V < \eta < \omega_0$, which corresponds to the intermediate range where the solution of the Kramers's equation with constant η is given by Eyring's ART value. So, in order of magnitude, the desorption time

$$\tau \sim \omega_0^{-1} \exp(\beta V_0) = \omega_D^{-1} (M/m)^{1/2} \exp(\beta V_0) . \qquad (54)$$

Of course, this only gives a rough estimate of the prefactor, which may certainly be affected seriously by the X_0 dependence of η, especially in the case where the later has an important local maximum at a relatively large distance of the surface. This will have to be investigated numerically.

For $0 < 1 - \chi/\chi_c < m/M$, the Kramers-Langevin picture breaks down. This defines the size of the critical region on the hard substrate side of χ_c.

(ii) *Soft substrates* $(\chi > \chi_c)$. A dynamic instability of the local deformation of the substrate appears at a particular value of the adatom position. At this critical value of X_0 (which depends on the direction of the adatom) the deformation changes suddenly by a finite amount. In the critical region, the Kramers's approximation breaks down, due to the appearance of a slow component in the motion of the adiabatic (substrate plus fixed adatom) system. Each time the adatom passes one of the points of instability, it looses an energy $\Delta E \gg k_B T$, of the order of a finite fraction of V_0. Iche and Nozières[5] have shown that this corresponds, again, to the intermediate range (or ART) regime for desorption, from which we can again expect the order of magnitude of τ to be given by expression (54).

That is, the appearance of the instability should not affect the fact that the prefactor in the expression of τ is proportional to $M^{1/2}$. However, this estimate is certainly even poorer than in the hard substrate case, since it does not take into account the local and sudden character of the energy loss. In order to be able to improve on it, we must improve our description of the critical region (i.e., of the dynamics of the instability), by going beyond the Kramers's approximation. This is presently under study.

Finally, the question arises of whether this instability may be present in an actual chemisorption system. Indeed, our simplified model leaves out several complications: (a) the adatom couples to more than one atom of the substrate, (b) it may move in the directions parallel to the surface, (c) the microscopic potential is not translationally invariant along the surface.

Due to effect (a), the condition for instability will become slightly more complicated, but not essentially different (the elastic term in the potential $U(X_0, x_1)$ will be replaced by

$$\sum_{i \leq j} \frac{1}{2\chi_{ij}} (x_i - x_i^0)(x_j - x_j^0) ,$$

the sum running on the group of atoms which participate to the microscopic interaction].

Effect (b) results in an increase of the desorption time with the desorption angle (measured from the normal to the surface), which is essentially the same in both regimes, since it affects mostly the exponential term and not the prefactor.

Due to effect (c) there will be, instead of two critical planes $X_0^{1,2}$, two rippled critical surfaces, and the discontinuity of V_{eff} along the trajectory will depend on the position of the point of impact of the adatom on these surfaces. The modulations of ΔV will of course have the periodicity of the substrate surface. But the points of instability are found in the region of negative curvature of V, i.e., not very close to the surface. So we can expect the modulation effect to be rather weak as far as our instability is concerned.

It will certainly be interesting to include these effects into the above treatment. However, they should have no crucial influence on the existence of the instability phenomenon itself.

ACKNOWLEDGMENTS

It is a pleasure to thank P. Nozières, W. L. Schaich, and H. Suhl for stimulating discussions. We are indebted to R. F. Wallis for communication of his results on the continuous model for surface phonons prior to publication. Special thanks are due to P. Mazur for thorough discussion and cooperation on the statistical aspects of the problem.

APPENDIX A

We want to calculate the potential $w(x_1)$ defined by $(\vec{q}_i = \vec{r}_i - \vec{r}_i^{\,0})$

$$\exp[-\beta w(x_1)] = \int dq_{1y}\, dq_{1z}\, d\vec{q}_2 \ldots d\vec{q}_N \times \exp\left[-\beta\left(\sum_{i,j=1}^{N} \sum_{\mu\nu} \frac{1}{2} q_{i\mu} A_{ij}^{(\mu\nu)} q_{j\nu} + V_e\right)\right]. \tag{A1}$$

The external potential V_e, which fixes the positions of 3 far-off atoms, can be eliminated by making the corresponding elements of the force-constant matrix $\overleftrightarrow{A}$ zero.

In order to integrate over all degrees of freedom except q_{1x}, which is fixed, let us define the equilibrium positions $q_{1y}^s, q_{1z}^s, q_i^s\ (i \geq 2)$ for a given q_{1x}: they are the solutions of

$$(1 - \delta_{i1}\delta_{\mu x}) \sum_{j=1}^{N} \sum_{\nu} A_{ij}^{(\mu\nu)} q_{j\nu}^{(s)} = 0 \quad (\text{with } q_{1x}^s \equiv q_{1x}). \tag{A2}$$

We then define new displacements: $\vec{y}_j = \vec{q}_j - \vec{q}_j^{\,s}$ $(y_{1x} = 0)$. The potential energy now reads

$$\begin{aligned} \mathcal{E} &= \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu\nu} A_{ij}^{(\mu\nu)} q_{i\mu} q_{j\nu}, \\ &= \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu,\nu} [A_{ij}^{(\mu\nu)} q_{i\mu}^s q_{j\nu}^s \\ &\quad + A_{ij}^{(\mu\nu)} (q_{i\mu}^s y_{j\nu} + q_{j\nu}^s y_{i\mu}) + A_{ij}^{(\mu\nu)} y_{i\mu} y_{j\nu}]. \end{aligned} \tag{A3}$$

The term linear in the y's is zero, due to the equilibrium condition (A2), the term quadratic in the y's simply contributes to $e^{-\beta w(x_1)}$ a multiplicative constant, $\exp(-\beta C')$, independent of q_{1x}. Finally, with the help of Eq. (A2) we have

$$\begin{aligned} \mathcal{E}_s &= \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu\nu} A_{ij}^{(\mu\nu)} q_{i\mu}^s q_{j\nu}^s \\ &= \frac{1}{2} \sum_{j=1}^{N} \sum_{\nu} A_{1j}^{(x\nu)} q_{1x} q_{j\nu}. \end{aligned} \tag{A4}$$

Using (A2) once more, we can write

$$\sum_{j,k=1}^{N} \sum_{\mu\nu} (1 - \delta_{k1}\delta_{\mu x}) (\overleftrightarrow{A}^{-1})_{1k}^{(x\mu)} A_{kj}^{(\mu\nu)} q_{j\nu}^s = 0 \tag{A5}$$

or

$$q_{1x}^s \equiv q_{1x} = (\overleftrightarrow{A}^{-1})_{11}^{(xx)} \sum_{j=1}^{N} \sum_{\nu} A_{1j}^{(x\nu)} q_{j\nu}^s, \tag{A6}$$

so that

$$\mathcal{E}_s = \tfrac{1}{2} q_{1x}^2 [(\overleftrightarrow{A}^{-1})_{11}^{(xx)}]^{-1}. \tag{A7}$$

On the other hand, defining the Green's function $g_{ij}^{(\mu\nu)}$ of atomic displacements by

$$m\omega^2 g_{ij}^{(\mu\nu)}(\omega) - \sum_{k=1}^{N} \sum_{\xi} A_{ik}^{(\mu\xi)} g_{kj}^{(\xi\nu)}(\omega) = \delta_{ij}\delta_{\mu\nu}, \tag{A8}$$

we get

$$(\overleftrightarrow{A}^{-1})_{11}^{(xx)} = -g_{11}^{(xx)}(\omega = 0). \tag{A9}$$

APPENDIX B

Let us consider a semi-infinite harmonic cubic lattice of lattice spacing a, with a perfect-plane free surface in the [100] direction. We describe the harmonic couplings in the simplest possible model consistent with the symmetry and invariance relations for this system. Namely,[17]

(i) In the bulk $(i_1 \leq i_s - 1)$

$$A_{\vec{i}\vec{i}}^{(\mu\nu)} = (2\alpha + 4\beta) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{\mu\nu},$$

$$A_{\vec{i},\vec{i}\pm 100}^{(\mu\nu)} = -\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}_{\mu\nu}, \tag{B1}$$

and cyclic for $(0, \pm 1, 0)$; $(0, 0, \pm 1)$, where $\vec{i} = (i_1, i_2, i_3)$ labels the position of atom i.

(ii) At the surface $(i_1 = i_s)$

$$A_{i_s i_2 i_3; i_s i_2\pm 1 i_3}^{(\mu\nu)} = -\begin{pmatrix} \beta & \pm\frac{1}{2}\beta & 0 \\ \mp\frac{1}{2}\beta & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}_{\mu\nu},$$

$$A_{i_s i_2 i_3; i_s i_2 i_3\pm 1}^{(\mu\nu)} = -\begin{pmatrix} \beta & 0 & \pm\beta/2 \\ 0 & \beta & 0 \\ \mp\beta/2 & 0 & \alpha \end{pmatrix}_{\mu\nu},$$

$$A_{i_s i_2 i_3; i_s - 1 i_2 i_3}^{(\mu\nu)} = -\begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}_{\mu\nu}, \tag{B2}$$

$$A_{i_s i_2 i_3; i_s i_2 i_3}^{(\mu\nu)} = -\begin{pmatrix} \alpha + 4\beta & 0 & 0 \\ 0 & 2\alpha + 3\beta & 0 \\ 0 & 0 & 2\alpha + 3\beta \end{pmatrix}_{\mu\nu}.$$

Using Eq. (29) to define the displacement Green's function, and calling $\tilde{g}^{(\mu\nu)}_{i_1 j_1}(\omega, \vec{q})$ the two-dimensional space Fourier transform of $\tilde{g}$ in the plane parallel to the surface, one gets[17] for χ, defined by Eq. (28):

$$\chi = -a^2 \int \frac{d^2q}{(2\pi)^2}\, \tilde{g}^{(xx)}_{i_s, i_s}(\omega = 0, \vec{q}),$$

$$\tilde{g}^{(xx)}_{i_s, i_s}(\omega, \vec{q}) = \Delta^{-1}\, \frac{-i}{2\alpha \sin k_x a} \times \frac{\exp[-i(a/2)(k_y + k_z)]}{4\cos(k_y a)\cos(k_z a)}, \tag{B3}$$

where k_x, k_y, k_z are defined by

$$\begin{aligned} 4\alpha \sin^2(\tfrac{1}{2} k_x a) &= m\omega^2 - 4\beta[\sin^2(\tfrac{1}{2} q_y a) + \sin^2(\tfrac{1}{2} q_z a)], \\ 4\beta \sin^2(\tfrac{1}{2} k_y a) &= m\omega^2 - 4\alpha \sin^2(\tfrac{1}{2} q_y a) - 4\beta \sin^2(\tfrac{1}{2} q_z a), \\ 4\beta \sin^2(\tfrac{1}{2} k_z a) &= m\omega^2 - 4\beta \sin^2(\tfrac{1}{2} q_y a) - 4\alpha \sin^2(\tfrac{1}{2} q_z a), \end{aligned} \tag{B4}$$

and

$$\begin{aligned} \Delta = {}& \frac{\exp[-\tfrac{1}{2} ia(k_x + k_y + k_z)]}{8\cos(k_x a/2)\cos(k_y a/2)\cos(k_z a/2)} \\ & + \frac{\beta}{\alpha}\, \frac{\sin^2(q_y a)\exp(-\tfrac{1}{2} iak_z)}{8\sin k_x a \sin k_y a \cos(k_z a/2)} \\ & + \frac{\beta}{\alpha}\, \frac{\sin^2(q_z a)\exp(-\tfrac{1}{2} iak_y)}{8\sin k_x a \sin k_z a \cos(k_y a/2)}. \end{aligned} \tag{B5}$$

This system has surface phonons[17] (of the acoustical type only), only if $\alpha > \beta$, which we assume to hold from now on.

We want to check whether the $\omega = 0$ limit of χ is finite or not. Therefore, we may safely (up to a small finite correction) take the $qa \ll 1$ limit in Eq. (B3). We then obtain

$$\chi = \frac{ia}{(2\pi)^2} \int_{(q<q_m)} \frac{d^2q}{\alpha k_x + \beta[(q_y^2/k_y) + (q_z^2/k_z)]}, \tag{B5}$$

where the cutoff, as in the Debye model, is chosen so as to get the right number of modes. Using Eq. (B4), we find

$$\chi = \frac{aq_m}{(2\pi)^2\beta} \int_0^{2\pi} d\theta\, \mathfrak{D}^{-1}(\theta, \alpha, \beta),$$

$$\mathfrak{D}(\theta, \alpha, \beta) = \left(\frac{\alpha}{\beta}\right)^{1/2} - \frac{\cos^2\theta}{[(\alpha/\beta)\cos^2\theta + \sin^2\theta]^{1/2}} - \frac{\sin^2\theta}{[\cos^2\theta + (\alpha/\beta)\sin^2\theta]^{1/2}}. \tag{B6}$$

It is easily seen that, since $\alpha > \beta$, strictly

$$\mathfrak{D} > (\alpha/\beta)^{1/2} - 1 > 0,$$

so that χ is finite, even when surface phonons are taken into account.

One can also prove, by the same type of argument, that the quantity $-i\chi'(0)$ {where $\chi'(0) = [d\chi(\omega)/d\omega]_{\omega=0}$} which appears in expression (51) for the friction coefficient, is finite and positive.

The same calculation can be done with a continuous isotropic model for the semi-infinite solid.[18] Again, it is found that χ and $-i\chi'(0)$ are well-behaved finite quantities. This result, in our opinion, must be model-independent (while the values of χ and $-i\chi'(0)$ depend on the details of the coupling). Indeed, although the semi-infinite solid has a two-dimensional set of surface excitations, these coexist with the volume phonons which effectively control the resistance to deformation.

---

[1] H. Mori, Prog. Theor. Phys. 33, 423 (1965); 34, 399 (1965).

[2] P. Mazur and I. Oppenheim, Physica (Utr.) 50, 241 (1970).

[3] N. G. Van Kampen, Phys. Rep. 24C, 172 (1976).

[4] H. A. Kramers, Physica (Utr.) 7, 284 (1940).

[5] G. Iche and P. Nozières, J. Phys. Paris (to be published).

[6] E. G. d'Agliano, W. L. Schaich, P. Kumar, and H. Suhl, in *Proceedings of the XXIV Nobel Symposium at Aspenasgarden, Lerum, Sweden, 1973*, edited by B. Lundqvist and S. Lundqvist (Academic, New York, 1973); W. Brenig, H. Müller, and R. Sedlmeier, Phys. Lett. A 54, 109 (1975); W. Brenig and K. Schönhammer, Z. Phys. B 24, 91 (1976); P. B. Visscher, Phys. Rev. B 13, 3272 (1976).

[7] S. Glasstone, K. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1965).

[8] E. G. d'Agliano, P. Kumar, W. L. Schaich, and H. Suhl, Phys. Rev. B 11, 2122 (1975); H. Suhl, *ibid.* 11, 2011 (1975).

[9] K. P. Bohnen, M. Kiwi, and H. Suhl, Phys. Rev. Lett. 36, 173 (1976).

[10] A. Nourtier, Ph.D. thesis (Orsay, 1976) (unpublished).

[11] P. Jewsbury and J. L. Beeby, J. Phys. C8, 3541 (1975), and references therein.

[12] This is equivalent, in the limit $N \to \infty$, and for an interaction potential V of finite range, to fixing the position of the center of mass and the orientation of a frame bound to the solid.

[13] J. L. Lebowitz and P. Résibois, Phys. Rev. 139, A1101 (1965); W. L. Schaich, J. Chem. Phys. 60, 1087 (1974).

[14] This estimate, which is standard in microscopic statistical treatments of Brownian motion, implies that one is considering distribution functions which do not deviate too much from the equilibrium one—which is sufficient for our present purpose. However, this approximation would not be safe if we were to study the relaxation of an initial distribution such as, for example,

$$\rho(\vec{P}_0) \propto \delta[P_0 - M/(m\beta)^{1/2}].$$

[15] As discussed in Sec. II, the effect of V_e is simply to fix the boundary conditions, i.e., to impose $\vec{q}_i = 0$ for three atoms of the "far-off" surface.

[16] K. Wada and J. Hori, Prog. Theor. Phys. 49, 129 (1973); P. Mazur and E. Braun, Physica (Utr.) 30, 1973 (1964); R. R. Rubin, J. Math. Phys. 1, 309 (1960); 2, 373 (1961).

[17] W. Ludwig, *Springer Tracts in Modern Physics* (Springer-Verlag, Berlin, 1967), Vol. 43.

[18] R. F. Wallis (private communication).