The following is the conservation equation:

$$I_0 = I + C + P_0 + P_1 + P_2 + P_3 + P_4 + P_5 + P_6 \,.$$

APPENDIX B

The following are values used for the α_i in the solution for the concentrations of each complex:

$$\alpha_1 = \frac{K_5}{K_6 + K_9}\,, \quad \alpha_2 = \frac{K_{10}}{K_6 + K_9}\,,$$

$$\alpha_3 = \frac{\alpha_2 K_6 + K_8}{K_5 + K_7 + K_{11} + K_{13} - \alpha_1 K_6}\,,$$

$$\alpha_4 = \frac{K_{12}}{K_5 + K_7 + K_{11} + K_{13} - \alpha_1 K_6}\,,$$

$$\alpha_5 = \frac{K_{14}}{K_5 + K_7 + K_{11} + K_{13} - \alpha_1 K_6}\,,$$

$$\alpha_6 = \frac{K_3}{\alpha_3 K_{11} V}\,, \quad \alpha_7 = \frac{-K_4 V}{K_3 K_{11}}\,,$$

$$\alpha_8 = \frac{-\alpha_4}{\alpha_3 V}\,, \quad \alpha_9 = \frac{-\alpha_5 V}{\alpha_3}\,, \quad \alpha_{10} = \frac{K_{12}}{\alpha_3 K_{11} V}\,,$$

$$\alpha_{11} = [\,(K_7 + K_9\alpha_1)\alpha_3 + K_9\alpha_2 - K_{10} - K_8\,]\,V - K_1\,,$$

$$\alpha_{12} = \frac{-K_2 V}{\alpha_{11}}\,, \quad \alpha_{13} = \frac{-(K_7 + K_9\alpha_1)\alpha_4}{\alpha_{11}}\,,$$

$$\alpha_{14} = \frac{-(K_7 + K_9\alpha_1)\alpha_5 V^2}{\alpha_{11}}\,, \quad \alpha_{15} = \alpha_{12} + \alpha_{14} - \alpha_9\,,$$

$$\alpha_{16} = \alpha_8 + \alpha_{10} - \alpha_{13}\,, \quad \alpha_{17} = \alpha_{15}(\alpha_8 + \alpha_{10}) + \alpha_9\alpha_{16}\,,$$

$$\alpha_{18} = \alpha_6(\alpha_{15} + \alpha_9) + \alpha_7(\alpha_{16} - \alpha_8 - \alpha_{10})\,,$$

$$\alpha_{19} = \alpha_3\alpha_{17} V + \alpha_4\alpha_{15} + \alpha_5\alpha_{16} V^2\,,$$

$$\alpha_{20} = \alpha_3\alpha_{18} V - \alpha_7\alpha_4 + \alpha_6\alpha_5 V^2\,,$$

$$\alpha_{21} = \alpha_1\alpha_{19} + \alpha_2 V\alpha_{17}\,, \quad \alpha_{22} = \alpha_1\alpha_{20} + \alpha_2 V\alpha_{18}\,,$$

$$\alpha_{23} = \alpha_{16} + \alpha_{17} + \alpha_{19} + \alpha_{21}\,,$$

$$\alpha_{24} = \alpha_6 - \alpha_{16} I_0 + \alpha_{18} + \alpha_{20} + \alpha_{22}\,.$$

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Phonon-Induced Desorption of Adatoms from Crystal Surfaces. I. Formal Theory*

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A three-dimensional multiphonon first-principles theory of the desorption of adatoms from crystal surfaces via interaction with phonons is presented. A central quantity in the theory is the time- and position-dependent displacement-displacement correlation function of the lattice. Explicit expressions are derived for the desorption rate from localized states at low temperatures. Calculations are performed for a Debye substrate and Morse-like interaction between the adatom and substrate atoms. Angular and energy distributions, and temperature dependence, of the single-phonon rate are investigated. Under typical conditions, it is found that the angular distribution deviates strongly from the $\cos\theta$ distribution, and that the energy distribution peaks strongly for final adatom energies near zero. At low temperatures the rate is proportional to $e^{-\beta E_0}$, a dependence similar to classical theory.

I. INTRODUCTION

Extensive studies have been made of the adsorption and desorption of atoms on solid surfaces,[1] both experimentally and theoretically. However, in most of the past works, the processes of adsorption and desorption were considered only from a thermodynamic and phenomenological point of view. While these statistical methods may often yield a satisfactory explanation of global quantities such as adsorption isotherm and entropy change, they are unable to provide a detailed understanding of the microscopic mechanisms involved. The existing quantum theory of these processes is based on a series of papers[2] by Lennard-Jones, Devonshire and Strachan (LJDS), in which they described the interaction of atoms and molecules with vibrational modes of the solid. Although the general approach is correct, the LJDS theory nevertheless has some serious shortcomings. Its major defect is that it is essentially a one-dimensional theory: The interaction of a gas atom with only a single solid-surface atom is considered, and the motion of the adatom and the substrate atoms parallel to the surface is either neglected or assumed to be unchanged. These assumptions lead to some serious difficulties. It is known,[3] e.g., that the LJDS model overestimates the transition probabilities and yields abnormally small values of adsorption probability. It is also clear that the model cannot supply a correct prediction of the angular distribution of desorbed or scattered atoms.

To resolve these difficulties, we introduce in this paper a fully three-dimensional formulation of the problem of the desorption process, pictured as a transition from a bound state to a continuum state. A principal purpose of this work is to investigate how the results of LJDS are qualitatively changed when more realistic interactions and three-dimensional motion are incorporated into the model. Also, in the work of LJDS, the vibrational modes of the substrate are described in a relatively unfamiliar classical picture. We have recast the description into a much more concise form in terms of phonons and the displacement-displacement correlation function, similar to that employed in neutron-diffraction[4] theory.

Although considerable attention has been given to the effects of surfaces and adatoms on the electronic and vibrational energy levels of the substrate and adatoms as well, it is apparent that very few first-principles quantum treatments of dynamical processes at surfaces have been advanced. Recently, however, there have been some efforts in this direction, notably in connection with the chemisorption of hydrogen on metals by Suhl *et al.*,[5] and in the molecular-beam scattering problem by Bagchi,[6] and by Beeby.[7] In addition to the specific goal of formulating a three-dimensional multiphonon-quantum theory of desorption, it is the purpose of the present work to illustrate in general fashion, via the desorption problem, how the dynamics of interaction processes at solid surfaces may be formulated. Also, we wish to consider in some detail the practical problems that one encounters, such as those arising from the loss of translational invariance at the surface, from the necessity of considering boundary conditions, and from the necessity of differentiating between free-particle states and those bound to the crystal. Preliminary reports of certain aspects of the present work have been made previously.[8]

A general formulation of the theory will be presented in Sec. II. In the remainder of the paper, we specialize to the case of localized desorption at low temperatures. The corresponding transition rate is calculated in Secs. III–V, and a discussion given in Sec. VI. In the following paper, henceforth referred to as II, numerical results for model systems are presented that demonstrate that the theory provides a practical way of calculating the total desorption rate, angular distributions, and energy distributions.

II. HAMILTONIAN AND DESORPTION RATE

A. Hamiltonian and Energy Levels

The Hamiltonian for the adatom interacting with the crystal is taken as

$$H=\frac{p^2}{2m_a}+\sum_l \frac{P_l^2}{2m_s}+\sum_{lm}\Phi(\vec{R}_{lm})+\sum_l v(\vec{r}-R_l)\ , \tag{2.1}$$

where $\vec{p}$, $\vec{r}$, and m_a are the momentum, position, and mass of the adatom, respectively, and where $\vec{P}_l$, $\vec{R}_l$, and m_s are the analogous quantities for the lth lattice atom; $\vec{R}_{lm}=\vec{R}_l-\vec{R}_m$; $v(\vec{r}-\vec{R}_l)$ and $\Phi(\vec{R}_{lm})$ are the interaction potentials between the adatom and lattice atom $\vec{R}_l$, and between lattice atoms at $\vec{R}_l$ and $\vec{R}_m$, respectively. For simplicity, we have written H for just a single substrate mass species m_s; the extension to a multiatomic substrate will be self-evident. In what follows, we adopt the convention that the z axis points in the direction normal to the crystal surface (see Fig. 1).

We break up H into an unperturbed part $H_0\equiv H_1+H_2$, and a perturbation term H_3:

$$\begin{aligned} H&=H_1+H_2+H_3=H_0+H_3\ ,\\ H_1&\equiv p^2/2m_a+V^0(\vec{r})\ ,\\ H_2&\equiv\sum_l \frac{P_l^2}{2m_s}+\sum_{lm}\Phi(\vec{R}_{lm})\ ,\\ H_3&\equiv\sum_l\,[v(\vec{r}-\vec{R}_l)-v(\vec{r}-\vec{R}_l^0)]\ , \end{aligned} \tag{2.2}$$

where

$$V^0(\vec{r})\equiv\sum_l v(\vec{r}-\vec{R}_l^0)\ .$$

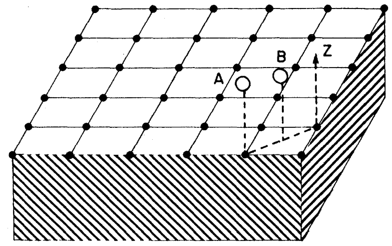

FIG. 1. Adsorption sites above a crystal surface: site *A* directly above a substrate atom and site *B* directly above a surface-cell center.

$\{R_l^0\}$ is the equilibrium substrate lattice configuration in the absence of the adatom. H_1 describes motion of the adatom in the field V^0 of the static substrate, H_2 is the unperturbed substrate Hamiltonian, and H_3 is the effective adatom-substrate interaction. The above choice for the unperturbed part of H is most appropriate when the lattice distortion induced by the adatom in its vicinity is minimal. Physisorbtion of rare-gas atoms on a solid surface is the sort of physical system that the theory is expected to describe best.

The potential V^0 has been computed numerically in various places,[9] for a variety of substrate configurations and interactions v. In general, the potential in the vicinity of the surface is characterized by three-dimensional minima ("wells") at various symmetry sites above the substrate, where adatoms have large probabilities of being found, and which thus constitute "adsorption sites." In the simplest case, there exists just a single stable adsorption site above any unit cell of the substrate. In general, however, a multiplicity of such sites may exist, either stable or metastable. In either instance, the spectrum of H_1 consists of a set of "bound states," in which the adatom is constrained to motion along the surface, and a continuum of free states corresponding asymptotically (i.e., at large distances from the surface) to desorbed adatoms. The two-dimensional periodicity of the crystal surface implies that the adsorbed spectrum may be characterized by the combination of two-dimensional quasi-momentum $\vec{\eta}$ and a band index α. We note that the energies of desorbed and adsorbed adatoms may be equal, which leads to degeneracy in the energy spectrum of H_1. Desorbed atoms are conveniently characterized by their asymptotic momentum $\vec{k}$, which, in principle, is directly measurable by the experimentalist.

Figure 2(a) illustrates a narrow band of states of H_1 of energy $E(\vec{\eta})$, and a free state $E(\vec{k})$ in the continuum. The oscillatory potential of height $2U_0$ represents the periodic potential along the surface plane. Generally, $2U_0$ is much smaller than the "binding energy" E_0 (energy difference between the lowest state and bottom of the continuum). In Fig. 2(b) the effective potential $V^0(z)$ [defined as the average of $V^0(\vec{r})$ over the surface plane] is illustrated; as indicated, the adatom is adsorbed at a distance z_0 above the substrate.

The lowest order eigenstates of H_2 are the phonons,[10] or undamped normal modes of vibration of the lattice. In general, H_2 also includes higher-order (anharmonic) terms,[11] which shift and damp the phonons, and which may be important for certain materials, and/or at sufficiently high temperatures. In the present treatment, we are concerned principally with the harmonic (undamped phonon) portion of H_2.

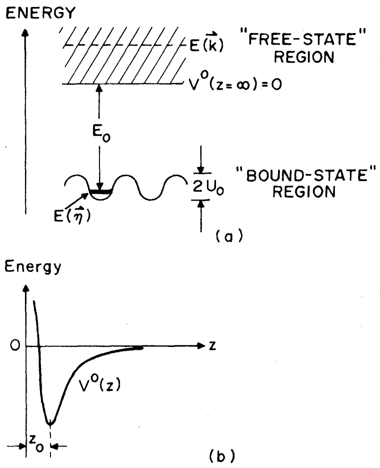

FIG. 2. (a) Schematic diagram indicating energy levels of an adatom while bound and free. The periodic variation of the potential (at $z=z_0$) in an arbitrary direction along the xy plane is indicated along the horizontal in the figure. (b) Schematic of $V^0(z)$, the xy averaged potential, vs z.

B. Transition Rates

The probability per unit time for transition of an adatom from a state $(\alpha, \vec{\eta})$ to a free state $\vec{k}$ may be expressed as[4,12]

$$R(\alpha, \vec{\eta}; \vec{k}) = \frac{2\pi}{\hbar} \frac{\sum_{if} e^{-\beta\epsilon_i} |\langle i; \alpha; \vec{\eta} | \mathcal{T}(\epsilon_i + E(\alpha, \vec{\eta})) | f; \vec{k}\rangle|^2}{\sum_i e^{-\beta\epsilon_i}} \times \delta(\epsilon_i - \epsilon_f - \omega(\alpha, \vec{\eta}; \vec{k})) , \quad (2.3)$$

where $\beta^{-1} \equiv k_B T$, T is the temperature,

$$\omega(\alpha, \vec{\eta}; \vec{k}) = |E(\alpha, \vec{\eta})| + k^2/2m_a , \quad (2.4)$$

(i, ϵ_i) and (f, ϵ_f) represent the initial and final lattice states and energies, and $\mathcal{T}$ is the scattering operator[12]

$$\mathcal{T}(E) \equiv H_3 + H_3 \, \mathcal{G}(E) H_3 , \qquad \mathcal{G}(E) \equiv (E - H + i\epsilon)^{-1} . \quad (2.5)$$

To lowest order in H_3, only the first term in $\mathcal{T}$ contributes, and one obtains the Fermi's "Golden-rule" expression (dropping the α for notational simplicity)

$$R(\vec{\eta}, \vec{k}) = \frac{2\pi}{\hbar} \frac{\sum_{if} e^{-\beta\epsilon_i} |\langle i, \vec{\eta} | H_3 | f, \vec{k}\rangle|^2 \delta(\epsilon_i - \epsilon_f - \omega(\vec{\eta}, \vec{k}))}{\sum_i e^{-\beta\epsilon_i}} . \quad (2.6)$$

One similarly defines the rate $R(\vec{\eta})$ from $\vec{\eta}$ to all possible free states $\vec{k}$, and the rate $R(\vec{k})$ to $\vec{k}$ from all possible $\vec{\eta}$'s, as

$$R(\vec{\eta})=\sum_{\vec{k}} R(\vec{\eta},\vec{k})\ ,\quad R(\vec{k})=\frac{\sum_{\vec{\eta}} e^{-\beta E(\vec{\eta})}\,R(\vec{\eta},\vec{k})}{\sum_{\vec{\eta}} e^{-\beta E(\vec{\eta})}}\ . \tag{2.7}$$

Note that a thermal average over the adsorbed states is required in computing $R(\vec{k})$. Finally, one has the rate R of desorption from all states $\vec{\eta}$ to all $\vec{k}$,

$$R=\sum_{\vec{k}} R(\vec{k})\ . \tag{2.8}$$

One may obtain a compact representation for the transition rate $R_{\text{tot}}(\vec{\eta})$ from a state $\vec{\eta}$ to all possible final states by employing the "optical theorem,"[12] which yields in the present case

$$R_{\text{tot}}(\vec{\eta})=-\frac{2}{\hbar}\,\text{Im}\left(\frac{\text{Tr}\,e^{-\beta H_2}\langle\vec{\eta}\,|\,\mathcal{T}(E'(\vec{\eta}))\,|\,\vec{\eta}\rangle}{\text{Tr}\,e^{-\beta H_2}}\right)\ , \tag{2.9}$$

where the prime indicates that in taking the trace over the ith configuration of H_2, we employ the total system energy $E'\equiv E(\vec{\eta})+\epsilon(\{i\})$. In computing the desorption rate $R(\vec{\eta})$ one must incorporate a restriction to just free final states $\vec{k}$ of H_1. As discussed in Appendix A, this leads to the appearance of additional terms in the expansion for R as compared to R_{tot}, as well as to restrictions on the sums over states which appear.

We now specialize to the case of harmonic H_2. Employing the Van Hove formalism,[4] it is shown in Appendix A that the following expression for the "Golden-rule" rate is obtained:

$$\begin{aligned}R(\vec{\eta},\vec{k})=\hbar^{-1}\sum_{lj\vec{q}\vec{q}'}&\exp[i(\vec{q}'\cdot\vec{R}^0_l-\vec{q}\cdot\vec{R}^0_j)]\\&\times v_{\vec{q}}v^*_{\vec{q}'}f_{\vec{q}}(\vec{k},\vec{\eta})f^*_{\vec{q}'}(\vec{k},\vec{\eta})\int_{-\infty}^{\infty}dt\\&\times\exp[-i\omega(\vec{\eta},\vec{k})t-\mathcal{W}_{jl}(\vec{q},\vec{q}';\beta)+\vec{q}\cdot\overleftrightarrow{C}_{jl}(t;\beta)\cdot\vec{q}']\ ,\end{aligned} \tag{2.10}$$

where

$$\begin{aligned}&v_{\vec{q}}\equiv\int d\vec{r}\,e^{-i\vec{q}\cdot\vec{r}}\,v(\vec{r})\ ,\\&f_{\vec{q}}(\vec{k},\vec{\eta})\equiv\int d\vec{r}\,e^{i\vec{q}\cdot\vec{r}}\,\phi^*_{\vec{\eta}}(\vec{r})\,\phi_{\vec{k}}(\vec{r})\ ,\\&\mathcal{W}_{jl}(\vec{q},\vec{q}';\beta)\equiv\tfrac{1}{2}\langle\langle(\vec{q}\cdot\vec{u}_j)^2+(\vec{q}'\cdot\vec{u}_l)^2\rangle\rangle\ ,\\&\overleftrightarrow{C}_{jl}(t;\beta)\equiv\langle\langle\vec{u}_j(t)\,\vec{u}_l(0)\rangle\rangle\ .\end{aligned} \tag{2.11}$$

Here the ϕ's are eigenfunctions of H_1; $\vec{u}_j(t)\equiv\vec{R}_j(t)-\vec{R}^0_j$ is the displacement of lattice atom j from equilibrium, where $\vec{R}_j(t)$ is $\vec{R}_j$ in the Heisenberg representation, i.e.,

$$\vec{R}(t)\equiv e^{iH_2t}\,\vec{R}\,e^{-iH_2t}\ . \tag{2.12}$$

We have employed the notation

$$\langle\langle A\rangle\rangle\equiv\text{Tr}\,e^{-\beta H_2}A/\text{Tr}\,e^{-\beta H_2}\ . \tag{2.13}$$

Physically, $\mathcal{W}$ is a Debye-Waller-like[13] exponent characterizing the mean-square lattice displacement, and $\overleftrightarrow{C}_{jl}$ is the time- and position-dependent displacement-displacement correlation tensor of the lattice.[10] We note that both $\mathcal{W}$ and C differ from their bulk counterparts because of the lack of translational invariance in the z direction.

One may obtain similar results for the full rate $R(\vec{\eta})$, in the form of an expansion in powers of v, as detailed in Appendix A:

$$R(\vec{\eta})=\sum_{n=2}^{\infty}\varphi^{(n)}\ ,$$

where

$$\begin{aligned}\varphi^{(n)}=\sum_{1,2,3,\ldots,n}{}'\;&\exp[i(\vec{q}_1\cdot\vec{R}^0_1+\cdots+\vec{q}_n\cdot\vec{R}^0_n)]\\&\times f_{\vec{q}_1}(\vec{\eta}\gamma_1)f_{\vec{q}_2}(\gamma_1\gamma_2)\cdots f_{\vec{q}_n}(\gamma_{n-1}\vec{\eta})\,v_{\vec{q}_1}\cdots v_{\vec{q}_n}\\&\times\int_{-\infty}^{\infty}dt_1\cdots dt_{n-1}\exp[it_1\,\omega(\vec{\eta}\gamma_1)+it_2\,\omega(\vec{\eta}\gamma_2)+\cdots\\&+it_{n-1}\,\omega(\vec{\eta}\gamma_{n-1})]\;\mathcal{A}(\vec{q}_1,\vec{q}_2,\ldots,\vec{q}_n;t_1,t_2,\ldots,t_{n-1})\ ,\end{aligned} \tag{2.14}$$

where

$$\omega(\gamma\gamma')\equiv E(\gamma)-E(\gamma')$$

and $\mathcal{A}$ is the functional of $\overleftrightarrow{C}$ given explicitly by Eq. (A21). An abbreviated notation 1, 2, 3, ..., has been employed above in place of $i_1, i_2, i_3, \ldots$. The prime indicates that in the sum over γ_i we must restrict each γ_i in turn to just free final states, while summing unrestricted over the remaining γ_i's, as detailed in Appendix A. We note that the $\varphi^{(2)}$ term is just the "Golden-rule" rate of Eq. (2.10).

An important advantage of the above formulation is the clear separation of the input to the computation into three distinct categories: (a) the adatom properties, appearing in just $f_{\vec{q}}$, through the wave functions $\phi_{\vec{\eta}}$ and $\phi_{\vec{k}}$; (b) the lattice properties, specified entirely through C and $\mathcal{W}$; and (c) the lattice-adatom interaction, specified entirely by $v_{\vec{q}}$. In principle, of course, these three properties are strongly interdependent. For example, the sum of $v_{\vec{q}}$'s determines the V^0, which yields the ϕ's and thus $f_{\vec{q}}$; V^0 itself depends on the substrate configuration, information which is employed in calculating C and $\mathcal{W}$. Although such self-consistency is a highly desirable goal in a complete theory, in practice, obtaining V, C, $\mathcal{W}$, and f from a single first-principles model represents a formidable task. Also, one often has more complete or reliable information regarding certain properties than others. For these reasons, treating the lattice, adatom, and their interaction separately becomes advisable, and sometimes indispensible, in carrying out actual computations.

We may incorporate the two-dimensional periodicity on the surface by breaking up $\vec{q}=(\vec{Q},q_z)$, where $\vec{Q}$ is a two-dimensional vector, and noting that[13]

$$\sum_{lj\vec{q}\vec{q}'} \exp i(\vec{q}\cdot\vec{R}_j^0 - \vec{q}'\cdot\vec{R}_l^0) \to N \sum_{\substack{q_z q_z' \; z_j z_l; \\ \vec{Q},\vec{Q}';\vec{X}_j-\vec{X}_l,\vec{G}}} e^{i(q_z z_j^0 - q_z z_l^0)} \times e^{i\vec{Q}\cdot(\vec{X}_j-\vec{X}_l)}\Delta(\vec{Q}-\vec{Q}'-\vec{G}) , \qquad (2.15)$$

where $\vec{R}_l^0 \equiv (\vec{X}_l^0, z_l^0)$, Δ is the Kronecker symbol, and $\vec{G}$ is a reciprocal-lattice vector. The terms with $\vec{G}\neq 0$ are referred to as Umklapp terms. In the present paper we concern ourselves principally with just the $\vec{G}=0$ term, although a brief discussion of the relative importance of the Umklapp terms is given in Sec. VI.

III. LOCALIZED DESORPTION AND WKB METHOD FOR DESORPTION STATES

A. Desorption from Localized Initial States

We consider an adatom to be in a localized state when (a) the adatom wave function is strongly localized about adsorption sites (e.g., the effective adatom vibrational distance is much less than the lattice constant), (b) $2U_0 \ll E_0$, and (c) $T < 2U_0$. The better these conditions are realized, the more "localized" the adsorption; the adatom is then restricted to a few narrow bands near the well bottom, such as pictured in Fig. 2(b). One indication of the existence of such localized states is the temperature dependence of experimentally measured specific heats in various adsorption systems. Such observations indicate that one may distinguish between "localized" and "mobile" adsorption.[14] The treatment of localized desorption is of special interest in the present context, for it allows a number of significant simplifications toward the explicit computation of the desorption rate. In what follows, it is convenient to restrict ourselves to temperatures so low that just the lowest adatom band in the well has a non-negligible occupancy. More generally, one may also pursue a qualitative treatment of a multiband system by employing an appropriate "average" energy band.

It is useful to expand $\phi_{\vec{\eta}}$, in the present case, in a set of highly localized Wannier functions[15] W, which we take to be peaked above each lattice site l, at a distance z_0 above the surface, and at a position $\vec{X}_c$ within the surface cell. Then (N_s is the number of surface atoms)

$$\phi_{\vec{\eta}}(\vec{r}) = (1/\sqrt{N_s}) \sum_l e^{i\vec{\eta}\cdot\vec{X}_l} W(\vec{X}-\vec{X}_l-\vec{X}_c, z) ,$$

$$\begin{aligned} f_{\vec{q}}(\vec{\eta}\vec{k}) &= (1/\sqrt{N_S}) \sum_l e^{i\vec{\eta}\cdot\vec{X}_l} \times \int d\vec{r}\, W(\vec{X}-\vec{X}_l-\vec{X}_c, z) e^{i\vec{q}\cdot\vec{r}} \phi_{\vec{k}}(\vec{r}) \\ &= (1/\sqrt{N_S}) e^{i\vec{Q}\cdot\vec{X}_c} \sum_l \exp[i(\vec{\eta}+\vec{Q}+\vec{K}_\parallel)\cdot\vec{X}_l] \times \int d\vec{r}\, W(\vec{X}-\vec{X}_l-\vec{X}_c, z) \\ &\quad \times \exp[i(\vec{Q}+\vec{K}_\parallel)\cdot(\vec{X}-\vec{X}_l-\vec{X}_c)+q_z z]\, \phi_{\vec{k}}(z) , \end{aligned} \qquad (3.1)$$

where we have assumed the form

$$\phi_{\vec{k}}(\vec{r}) = e^{i\vec{K}_\parallel\cdot\vec{X}} \phi_{\vec{k}}(z) ,$$

and where we have, as is done henceforth, dropped zero superscripts on the lattice-site vectors. Employing

$$\sum_l e^{i\vec{S}\cdot\vec{X}_l} = \sum_{\vec{G}} \Delta(\vec{S}-\vec{G}) N_s , \qquad (3.2)$$

one obtains

$$f_{\vec{q}}(\vec{\eta}\vec{k}) = \sqrt{N_s} \sum_{\vec{G}} \Delta(\vec{\eta}+\vec{Q}-\vec{G}) \bar{f}_{\vec{q}}(\vec{k}) e^{i(\vec{Q}+\vec{K}_\parallel)\cdot\vec{X}_c} , \qquad (3.3)$$

where

$$\bar{f} \equiv \int d\vec{r}\, W(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \phi_{\vec{k}}(\vec{r}) .$$

The average over a narrow band involves

$$\frac{N_s \sum_{\vec{q}\vec{q}'\vec{G}\vec{G}'\vec{\eta}} e^{-\beta E(\vec{\eta})} \Delta(\vec{\eta}+\vec{Q}+\vec{K}_\parallel-\vec{G}) \Delta(\vec{\eta}+\vec{Q}'+\vec{K}_\parallel-\vec{G}') R_{\vec{q}\vec{q}'}}{\sum_{\vec{\eta}} e^{-\beta E(\vec{\eta})}} \approx \frac{\sum_{\vec{q}\vec{q}'} e^{-\beta E(\vec{\eta}_0)} R_{\vec{q}\vec{q}'}}{e^{-\beta E_0}} \approx \sum_{\vec{q}\vec{q}'} R_{\vec{q}\vec{q}'} \equiv R_1 , \qquad (3.4)$$

where $\vec{\eta}_0 = -(\vec{Q}+\vec{K}_\parallel)$ [with G and G' having been chosen such that $(\vec{Q}+\vec{K}_\parallel)$ lies in the first Brillouin zone] and R_1 is the rate $R(\vec{\eta}\vec{k})$, but now corresponding to a single level, with wave function $W(\vec{r})$ instead of $\phi_{\vec{\eta}}(\mathrm{r})$.

B. WKB Final-State Wave Function

In principle, $\phi_{\vec{k}}(\vec{r})$ is a continuum eigenfunction of the adatom Hamiltonian H_1 with asymptotic momentum $\vec{k}$. However, the full three-dimensional potential V^0, for any realistic system, is not expressible in closed analytic form. Even if it were, the calculation of the wave functions in the presence of such a nonspherically symmetric three-dimensional potential would constitute a formidable task. Thus, an approximate procedure for dealing with $\phi_{\vec{k}}$ is a practical necessity.

The crudest approximation would be to replace $\phi_{\vec{k}}$ with just a free wave. However, it is clear that the adatom wave function is strongly distorted from its asymptotic free wave form as it emerges from the potential well in the vicinity of the surface. Since this is the region of overlap with the potential v, it is essential to account for this distortion in computing the relevant transition matrix elements.

For this purpose we adopt an approach intermediate to the free wave and full eigenstate extremes, by (a) neglecting diffraction (periodic) effects in the plane in computing $\phi_{\vec{K}}$ and (b) treating the motion in z within the WKB method.[16]

Procedure (b) is most accurate when the well bottom occurs many wavelengths past the turning point, and when the potential varies sufficiently slowly compared to a wavelength in the regions of interest. For almost all cases, however, the WKB picture should supply at least a qualitatively appropriate description of the final-state wave function. Incorporating (a) and (b), one has[16] for $\phi_{\vec{K}}$ $(\hbar = 1)$

$$\phi_{\vec{K}}(\vec{r}) \cong \frac{1}{\sqrt{A_s}}\, e^{i\vec{K}_{\parallel}\cdot\vec{X}}\, \phi_{\vec{K}}(z)\,,$$
$$\phi_{\vec{K}}(z) = [c/(k(z))^{1/2}] \sin\left[\int_a^z dz'\, k(z') + \tfrac{1}{4}\pi\right]\,, \tag{3.5}$$

where A_s is the surface area, a is the WKB turning point (see Fig. 3), c is a normalization factor, and

$$k(z) \equiv [2m_a(-V^0(z) + E_z)]^{1/2}\,, \quad E_z = k_z^2/2m_a\,. \tag{3.6}$$

k is thus the effective wave vector of the desorbed particle. In the above we have assumed that the atom is restricted from diffusing into the solid, so that the potential barrier becomes infinite near the surface. The explicit form for $\phi_{\vec{K}}(z)$ as a function of z depends in detail on the shape of the potential $V^0(z)$.

If the potential V^0 is sufficiently deep and/or narrow, then one has

$$\phi_{\vec{K}} \cong (c/\sqrt{\tilde{k}_z}) \sin\left[\int_a^{z_0} dz'\, k(z') + \tilde{k}_z(z - z_0) + \tfrac{1}{4}\pi\right]\,, \tag{3.7}$$

with

$$c = (2/L)^{1/2}(2m_a E_z)^{1/4}\,, \quad \tilde{k}_z \equiv [2m_a(\bar{E}_0 + E_z)]^{1/2}\,,$$

where L is the dimension of the normalization volume in the z direction and $\bar{E}_0 \equiv E_0 - U_0 + \epsilon_0$ is the xy-averaged well-depth energy of a particle moving in the potential $V^0(z)$.

To obtain $f_{\vec{q}}$ for the above model, one may apply the arguments of Sec. III A, with the result that $\bar{f}$ takes the form (unit normalization volume)

$$\bar{f} = (c/2i\sqrt{\tilde{k}_z})(e^{iF_a}M_+ - e^{-iF_a}M_-)\,, \tag{3.8}$$

where

$$F_a \equiv i\int_a^{z_0} k_z\, dz + \tfrac{1}{4}\pi\,,$$
$$M_+ = \int d\vec{r}\, W(\vec{r}) \exp\{i[\vec{q}\cdot\vec{r} + \vec{K}_{\parallel}\cdot\vec{X}_{\parallel} + \tilde{k}_z(z - z_0)]\}\,,$$
$$M_- = M_+(\tilde{k}_z \to -\tilde{k}_z)\,. \tag{3.9}$$

Dropping the bar over f, we note that the rate involves

$$f_{\vec{q}} f^*_{\vec{q}'} = (c^2/4\tilde{k}_z)(M_+M_+^{*\prime} + M_-M_-^{*\prime} - e^{2iF_a}M_+M_-^{*\prime} - e^{-i2F_a}M_-M_+^{*\prime})\,, \tag{3.10}$$

employing an abbreviated notation. Since the rate is invariant under $(\vec{q}, \vec{q}\,' \to -\vec{q}, \vec{q}\,')$, we may employ for ff^* the form

$$f_{\vec{q}} f^*_{\vec{q}'} \to \sqrt{E_z}(\bar{E}_0 + E_z)^{-1/2}(M_+M_+^{*\prime} - \tfrac{1}{2}e^{2iF_a}M_+M_-^{*\prime} - \tfrac{1}{2}e^{-2iF_a}M_-M_+^{*\prime})\,. \tag{3.11}$$

This result constitutes a convenient starting point for calculations of the desorption rate R.

IV. DESORPTION RATE FOR MODEL SYSTEM

A. Substrate-Lattice Properties

The lattice properties are built into the rate R through W_{lj} and $\overleftrightarrow{C}_{lj}(t)$. Since

$$2W_{lj} = \vec{q}\cdot\overleftrightarrow{C}_{jj}(0)\cdot\vec{q} + \vec{q}\,'\cdot\overleftrightarrow{C}_{ll}(0)\cdot\vec{q}\,'\,, \tag{4.1}$$

just the single function $\overleftrightarrow{C}_{lj}(t)$ specifies the lattice properties uniquely. Of course, the nature of the lattice configuration also enters the rate through the sums over sites.

For a single mass species, we may express $\vec{u}_l(t)$ as[10,13]

$$\vec{u}_l(t) = \sum_m (\hbar/2\omega_m m_S)^{1/2} \times [\vec{B}(m,l)\, e^{-i\omega_m t} a_m^- + \vec{B}^*(m,l)\, e^{i\omega_m t} a_m^+]\,, \tag{4.2}$$

where $a_m^{\pm}$ are creation-annihilation operators for the mth phonon mode, ω_m its frequency, and $\vec{B}(m,l)$ a complex vector. The composite index m stands for $(\vec{k}, \alpha)$, where α is a branch index. For bulk phonons, for example,

$$B(m,l) = e^{i\vec{k}\cdot\vec{R}_l}\, \hat{\epsilon}(\vec{k}, \alpha) N^{-1/2}\,, \tag{4.3}$$

where $\hat{\epsilon}$ is a unit polarization vector. $\overleftrightarrow{C}$ takes the form

$$\overleftrightarrow{C}_{jl}(t) = \sum_m (\hbar/2m_S\omega_m)[(n_m + 1)\, e^{-i\omega_m t}\, \vec{B}(m,j)\vec{B}^*(m,l)$$

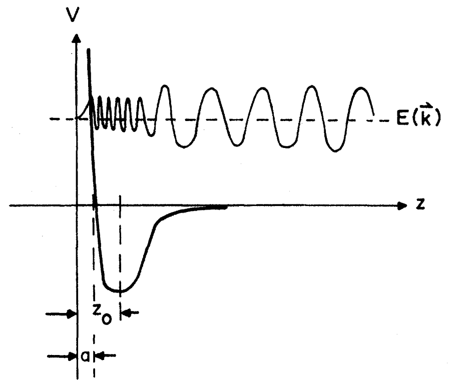

FIG. 3. Schematic of the WKB wave function describing a desorbed adatom.

$$+n_m e^{i\omega_m t}\vec{\mathrm{B}}^*(m,j)\vec{\mathrm{B}}(m,l)] \;. \qquad (4.4)$$

In cubic crystals the tensor $\overleftrightarrow{\mathrm{C}}$ may be chosen diagonal. With $C_1 \equiv C_{xx} = C_{yy}$ and $C_3 \equiv C_{zz}$, one has

$$\vec{\mathrm{q}}\cdot\overleftrightarrow{\mathrm{C}}\cdot\vec{\mathrm{q}}' = q_z q_z' C_3 + \vec{\mathrm{Q}}\cdot\vec{\mathrm{Q}}' C_1 \;. \qquad (4.5)$$

Periodicity in the surface plane implies

$$\overleftrightarrow{\mathrm{C}}_{jl} = \overleftrightarrow{\mathrm{C}}(\vec{\mathrm{X}}_{jl}, z_l, z_j) \;, \quad \overleftrightarrow{\mathrm{C}}_{jj} = \overleftrightarrow{\mathrm{C}}(z_j) \;. \qquad (4.6)$$

For the purposes of the present treatment, we consider appropriately simplified models for $\overleftrightarrow{\mathrm{C}}$. The simplest possible phonon model, the Einstein model,[10] sets all $\omega_m = \omega_0$, a constant. However, this model is unrealistic in that phonon dispersion is entirely suppressed, so that energy transfer over a continuous range is impossible. The simplest model incorporating dispersion is the Debye model,[10] in which $\omega(\vec{\mathrm{k}}, \alpha) = v_s^\alpha k$, where v_s^α is a constant. We consider a single-branch isotropic Debye model, with $C_{xx} = C_{yy} = C_{zz} = C$, so that

$$\vec{\mathrm{q}}\cdot\overleftrightarrow{\mathrm{C}}\circ\vec{\mathrm{q}}' = \vec{\mathrm{q}}\cdot\vec{\mathrm{q}}' C \;. \qquad (4.7)$$

In actually computing C, we are at liberty to consider either bulk, surface, or mixed phonons, or any combination thereof. With respect to bulk and mixed phonons, one must give special attention to the boundary conditions at the surface. These are expressed as requirements on linear combinations of the u's and their derivatives at the surface, corresponding to conditions such as free or stressed surfaces, which enable the determination of the $\vec{\mathrm{B}}$'s. Following the analogy of a string with a free end, where the derivative of the displacement vanishes, we here take cosine waves for the B's, $B = \cos(\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}_l)$. Considering that for the pure bulk case $B = e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}_l}$, we find

$$C_B = \tfrac{1}{2}[C_B^0(\vec{\mathrm{X}}_{lj}, z_l - z_j) + C_B^0(\vec{\mathrm{X}}_{lj}, z_l + z_j)] \;, \qquad (4.8)$$

where C_B^0 is the pure-bulk correlation function. Following Appendix B, one has for the isotropic Debye model

$$C_B^0(\vec{\mathrm{r}}, t) = (1/4\pi)\,\overline{r}_4^2 \int_0^1 d\vec{\mathrm{k}}\,\omega^{-1}(\vec{\mathrm{k}})\, e^{i[k_0\vec{\mathrm{k}}\cdot\vec{\mathrm{r}} - \omega(\vec{\mathrm{k}})t]}$$
$$+ 2\cos[k_0\vec{\mathrm{k}}\circ\vec{\mathrm{r}} - \omega(\vec{\mathrm{k}})t]\,(e^{\beta\omega(\vec{\mathrm{k}})} - 1)^{-1} \;, \qquad (4.9)$$

in which $k_0 \equiv k_D a_0 = (6\pi^2)^{1/3}$, where k_D is the Debye wave vector, a_0 the lattice parameter, and $\overline{r}_4^2 = 3/(2m_s)$. In (4.9), we have adopted a convenient set of dimensionless variables which are employed henceforth in this paper. We define dimensionless variables m, $\vec{\mathrm{r}}$, E, T, C, and t as

$$m \leftrightarrow mE_D a_0^2 \hbar^{-2} \;, \qquad T \leftrightarrow T/T_D \;,$$
$$E \leftrightarrow E/E_D \;, \qquad t \leftrightarrow t\omega_D \;, \qquad (4.10)$$
$$\vec{\mathrm{r}} \leftrightarrow \vec{\mathrm{r}}/a_0 \;, \qquad C \leftrightarrow C/a_0^2 \;,$$

where E_D, ω_D, and T_D are the Debye energy, frequency, and temperature, respectively.

In the development to follow, we require the Fourier transform of C_B^0, namely ($\omega > 0$),

$$\rho^B(\vec{\mathrm{r}}, \omega) = (2\pi)^{-1}\int dt\, e^{-i\omega t} C_B^0(\vec{\mathrm{r}}, t)$$
$$= \overline{r}_4^2 n(\omega)(k_0 r)^{-1}\sin(k_0 r\omega)\Theta(1-\omega) \;,$$
$$\rho(-\omega) = e^{\beta\omega}\rho(\omega) \;. \qquad (4.11)$$

For a surface-state Debye model, with $\omega_{\vec{\mathrm{k}}} = \omega_0 + v_{ss}k$, one obtains ($\omega > 0$)

$$\rho^s(\vec{\mathrm{X}}, \omega) = \tfrac{2}{3}\overline{r}_4^2 \sigma n(\omega)(1 - \omega_0/\omega) J_0[k_{os}\sigma(\omega - \omega_0)X]$$
$$\times\Theta(\omega_0 + \sigma - \omega)\Theta(\omega - \omega_0) \;, \qquad (4.12)$$

as detailed in Appendix B, where J_0 is the Bessel function, $\sigma = v_{ss}k_{os}/v_s k_o$, and $k_{os} = 2\sqrt{\pi}$.

B. Adatom Wave Functions and Interaction Potential

Initial-state wave function. As demonstrated in Sec. III A, for localized desorption we require just the Wannier function for the adatom to compute f. The potential near the bottom of the well may be assumed to be nearly harmonic. This being the case, the Wannier function is well represented by

$$W(\vec{\mathrm{r}}) \cong A\exp\{-[\tfrac{1}{4}(x^2+y^2)/r_2^2] - [\tfrac{1}{4}(z-z_0)^2/r_3^2]\} \;, \qquad (4.13)$$

the lowest harmonic-oscillator wave function, where A is a normalization factor,

$$A = (2\pi)^{-3/4} r_3^{-1/2} r_2^{-1} \;, \qquad (4.14)$$

and we have assumed an azimuthally symmetric potential in the plane about the adsorption site. In this approach r_2 and r_3 characterize the curvature of the potential near its minimum. In a more general treatment, higher-order variations in the potential, and mixing due to the periodic properties of the surface, would be accounted for.

Final-state wave function. We adopt the localization approximation to the WKB function, as specified in Eq. (3.7). In this approach the maximum well depth E_0 and adsorption height z_0 are the principal quantities describing the distorted wave in the desorption process.

Interaction potential v. In a variety of physisorption systems, the Lennard-Jones 6-12 interaction potential v_{LJ} is appropriate.[17] Unfortunately, this potential is difficult to handle analytically in explicit computations. For example, it cannot be straightforwardly Fourier transformed. For this reason, we adopt the following Morse-like potential for v:

$$v(\vec{\mathrm{r}}) = \tilde{V}_0\{\exp[-\tfrac{1}{4}(r^2 - r_0^2)/r_1^2]$$
$$-\exp[-\tfrac{1}{8}(r^2 - r_0^2)/r_1^2]\} \;, \qquad (4.15)$$

which is especially convenient for actual computations. As may be seen from Fig. 4, $v(\vec{\mathrm{r}})$ may be

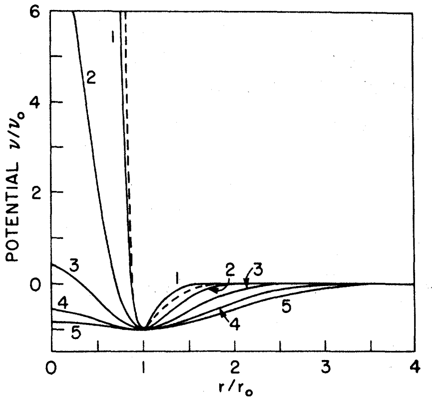

FIG. 4. Potential v/v_0 vs r/r_0. Curves 1–5 illustrate the Morse-like potential v corresponding to values of $r_1/r_0 = 0.2$, 0.3, 0.4, 0.5, and 0.6, respectively. The dotted line indicates the Lennard-Jones potential v_{LJ}.

chosen so as to simulate the hard-core or long-range properties of $v_{\mathrm{LJ}}(\vec{r})$. Note that v_{LJ} contains just a single independent range parameter, corresponding to our r_0, while v contains the additional parameter r_1.

Although we employ the $v(\vec{r})$ of Eq. (4.15) in calculating the desorption matrix elements, we nevertheless employ parameters for V^0, the sum of $v(\vec{r}-\vec{R}_i)$'s, appropriate to a sum of v_{LJ}'s. In so doing, we are treating the adatom binding on a different footing than the adatom-lattice interaction. Such a procedure, which is here motivated by expediency, is best justified where the rate turns out to be a relatively insensitive function of the shape of v. We shall find that for the present model, the rate is relatively insensitive to variations in the shape parameter r_1, as compared to variations in other parameters in the model. This point is discussed further in Paper II.

C. Desorption Rate for Model System

In this section we derive an explicit expression for the desorption rate, employing the lattice, adatom, and interaction models specified above.

Employing the results of Sec. III B, one finds, after some algebra,

$$U \equiv v_{\vec{q}}\, v^*_{\vec{q}'}\, f_{\vec{q}}\, f^*_{\vec{q}'} = U_{\mathrm{no}} + U_{\mathrm{os}}\ , \tag{4.16}$$

where

$$\begin{aligned} U_{\mathrm{no}} = h\{&\exp[-r_3^2(q_z^2+q_z'^2) + iz_0(q_z - q_z') \\ &- 2r_3^2(q_z+q_z')\tilde{k}_z - r_2^2(Q^2+Q'^2) - 2r_2^2\vec{\mathrm{K}}_{\parallel}\cdot(\vec{\mathrm{Q}}+\vec{\mathrm{Q}}')]\} \\ &\times\{\exp(-r_1^2(q^2+q'^2)) + V_0^2\exp(-2r_1^2(q^2+q'^2)) \\ &- V_0[\exp(-r_1^2(q^2+2q'^2)) + (q \rightleftarrows q')]\}\ , \end{aligned} \tag{4.17}$$

$$U_{\mathrm{os}} = \exp[2i(F_a - \tilde{k}_z z_0)]\, U_{\mathrm{no}}(\tilde{k}_z \to -\tilde{k}_z) + \mathrm{c.\,c.}\ ,$$

where

$$\begin{aligned} h &= h_0^2 E_z^{1/2}(\overline{E}_0 + E_z)^{-1/2}\exp(-2\tilde{k}_z^2 r_3^2 - 2K_{\parallel}^2 r_2^2)\ , \\ h_0^2 &= 2^{11}(\tfrac{1}{2}\pi)^{1/2}\pi^4\,\tilde{V}_0^2 r_1^6 r_2^2 r_3\, e^{r_0^2/2r_1^2}\ . \end{aligned} \tag{4.18}$$

In obtaining the above we employed the following transforms:

$$\begin{aligned} W(\vec{\mathrm{q}}) &= 8(\tfrac{1}{2}\pi)^{3/4} r_2\sqrt{r_3}\,\exp(-iq_z z_0 - q_z^2 r_3^2 - Q^2 r_2^2)\ , \\ V(\vec{\mathrm{q}}) &= 8\pi^{3/2} r_1^3 e^{r_0^2/4r_1^2}\,\tilde{V}_0[e^{-r_1^2 q^2} - V_0 e^{-2r_1^2 q^2}]\ , \\ V_0 &\equiv 2^{5/2} e^{-r_0^2/8r_1^2}\ . \end{aligned} \tag{4.19}$$

The abbreviations os and no refer to terms which are, respectively, oscillatory and nonoscillatory with respect to the energy variable.

To compute the $\vec{\mathrm{G}} = 0$ (nonumklapp) rate $R_{\vec{k}}$, we need

$$\begin{aligned} \mathfrak{F}_{lj} = \int dq_z\, dq_z'\, d\vec{\mathrm{Q}}\, \exp\{&(q_z q_z' + Q^2)C_{lj}(t) - iq_z z_j + iq_z' z_l \\ &- i\vec{\mathrm{Q}}\cdot(\vec{\mathrm{X}}_j - \vec{\mathrm{X}}_l) - \tfrac{1}{2}[(q_z^2+Q^2)C_{jj}(0) \\ &+ (q_z'^2 + Q^2)C_{ll}(0)]\}\, U(\vec{\mathrm{Q}} = \vec{\mathrm{Q}}')\ . \end{aligned} \tag{4.20}$$

By direct integration one obtains

$$(\mathfrak{F}_{lj})_{\mathrm{no}} = h\sum_{i=1}^{4} I(\{s_j^i\})\ , \tag{4.21}$$

where I is the following functional of C:

$$\begin{aligned} I(\{s_j^i\}) \equiv \frac{\pi^2 s_0^i}{(s_3^i)^3 - C_{lj}^2(t)}&[s_1^i s_2^i - \tfrac{1}{4}C_{lj}^2(t)]^{1/2} \\ \times\exp\{&\tfrac{1}{4}[(s_6^i)^2 + (s_7^i)^2][s_3^i - C_{lj}(t)]^{-1} \\ &+ \tfrac{1}{4}[s_1^i(s_5^i)^2 + s_2^i(s_4^i)^2 + s_4^i s_5^i C_{lj}(t)][s_1^i s_2^i - \tfrac{1}{4}C_{lj}^2(t)]^{-1}\} \end{aligned} \tag{4.22}$$

where the s^i's are listed in Table I. The quantity $2r_4^2 \equiv C_{ll}(0)$ is the mean-square displacement of lattice atom l from equilibrium. Thus the rate involves the five characteristic lengths r_i $(i = 0, 1, \ldots, 4)$. r_0 characterizes the equilibrium distance between an isolated surface atom and an adatom, r_1 the shape and range of the potential v, r_2 and r_3 the range of vibration of the localized adatom about its adsorption site, along the surface plane and normal to the surface, respectively, and r_4 the lattice vibrational range. To obtain $\mathfrak{F}_{\mathrm{os}}$ one simply employs $\tilde{k}_z \to -\tilde{k}_z$ in (4.22).

We have displayed forms appropriate to $\vec{\mathrm{G}} = 0$, the non-umklapp term in the rate. For $\vec{\mathrm{G}} \neq 0$, additional terms proportional to $\vec{\mathrm{G}}$ appear in the s_j^i's. Although these may be obtained directly in a fashion analogous to the above, for simplicity we omit treating these terms explicitly. Rather, we discuss the principal features of these terms in Sec. VI.

The rate $R(\vec{k})$ follows as

$$R(\vec{k})=\frac{\omega_D}{(2\pi)^3}\,\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega(\vec{k})t}\sum_{z_l z_j \vec{X}_{lj}}\mathfrak{F}_{lj}[C_{lj}(t)]\;. \tag{4.23}$$

Thus, to compute $R(\vec{k})$ explicitly in the present model, there remains just a sum over sites and a single Fourier transform over t. Computation of R and $dR/d\Omega$ involve additional integrations over $\vec{k}$.

It is convenient to define various rates to be employed in the following discussion, through the relations

$$\begin{aligned} R&=\int d\vec{k}\,R(\vec{k})=\int d\varphi\,d(\cos\theta)\,dk\,k^2R(\vec{k})\\ &=\int d\varphi\,d(\cos\theta)\,R(\theta,\varphi)=\int d(\cos\theta)\,dk\,k^2R(k,\theta)\\ &=\int d(\cos\theta)\,R(\theta)\;. \end{aligned} \tag{4.24}$$

Note that we have above absorbed a factor of $(2\pi)^{-3}$ into $R(\vec{k})$, as compared to our previous definition. It should also be noted, that despite the abbreviated notation, the various rates under the integral signs actually represent differential rates, with respect to angles and $\vec{k}$. For example, $R(\theta,\varphi)$ is a shorthand for $dR/d\Omega$, the transition rate per unit solid angle.

V. MULTIPHONON EXPANSION

A. Convolution Expansion

The final form for $R(k)$ involves the Fourier transform of $\mathfrak{F}(t)$, which, in even the simplest cases, turns out to be a rather complicated functional of $C(t)$. This suggests the expansion of $\mathfrak{F}(t)$ in a small parameter. Since C is itself proportional to the small parameter $C_0\equiv m_s^{-1}\sim 10^{-3}$–$10^{-4}$, an expansion in powers of C is appropriate. The result is a convolution-type expansion[18] taking the form $(\omega\neq 0)$

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,\mathfrak{F}[C(t)]=\sum_{n=1}^{\infty}\frac{1}{n!}\,\rho_n(\omega)\,\frac{\partial^n\mathfrak{F}(C)}{\partial C^n}\bigg|_{C=0}\,, \tag{5.1}$$

where

$$\rho_n(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,C^n(t)\;. \tag{5.2}$$

TABLE I. Coefficients s_j^i.

$i \backslash j$	0	1	2	3
1	1	$r_1^2+r_3^2+r_4^2$	$r_1^2+r_3^2+r_4^2$	$2(r_1^2+r_2^2+r_4^2)$
2	V_0^2	$2r_1^2+r_3^2+r_4^2$	$2r_1^2+r_3^2+r_4^2$	$2(2r_1^2+r_2^2+r_4^2)$
3	$-V_0$	$r_1^2+r_3^2+r_4^2$	$2r_1^2+r_3^2+r_4^2$	$3r_1^2+2r_2^2+2r_4^2$
4	$-V_0$	$2r_1^2+r_3^2+r_4^2$	$r_1^2+r_3^2+r_4^2$	$3r_1^2+2r_2^2+2r_4^2$

$$\begin{matrix}\text{all}\\ i\end{matrix}\left\{\begin{aligned} s_4&=2r_3^2\tilde{k}_z+i(z_j-z_0)\\ s_5&=2r_3^2\tilde{k}_z-i(z_l-z_0)\\ s_6&=4r_2^2k_x^2-2ix_{lj}\\ s_7&=4r_2^2k_y^2-2iy_{lj}\end{aligned}\right.$$

An important property of the ρ's is $(\rho\equiv\rho_1)$

$$\rho_{n+1}(\omega)=\int_{-\infty}^{\infty}\rho_n(\omega')\,\rho(\omega-\omega')\,d\omega'\;. \tag{5.3}$$

Thus the ρ's may be computed recursively, which is especially advantageous for computer calculations. Also, for the Debye model, each ρ_n is restricted to just the range $\pm n\omega_D$ in ω, which greatly facilitates numerical computation. $\rho(\omega)$ for bulk and surface isotropic Debye models were specified in Eqs. (4.11) and (4.12).

Physically, ρ_n is the n-phonon contribution to the rate, involving n real or virtual phonons. This may be seen, in that a factor $\sqrt{C_0}$ accompanies each creation or annihilation operator in the Hamiltonian. Since R involves the square of H_3, a term in R proportional to C_0^n involves exactly n phonon interactions. Actually, $e^{-W_{lj}}$ does include a set of phonon interactions to infinite order. These, however, are independent of t, and hence do not correspond to dynamical interactions.

Since $C_0\ll 1$, the single-phonon contribution, when energetically allowed $(\omega_D>E_0)$, dominates the rate. For this reason, we give special attention to the single-phonon rate in Sec. V B.

B. Single-Phonon Rate

To obtain the single-phonon contribution to $R(\vec{k})$, we note that

$$\begin{aligned}\frac{\partial I}{\partial C}\bigg|_{C=0}&=\sum_{i=1}^{4}\frac{\pi^2 s_0^i}{s_3^i(s_1^i s_2^i)^{1/2}}\\ &\quad\times\left[\frac{1}{s_3^i}+\frac{1}{4}\left(\frac{s_4^i s_5^i}{s_1^i s_2^i}+\frac{(s_6^i)^2+(s_7^i)^2}{(s_3^i)^2}\right)\right]\\ &\quad\times\exp\left[\frac{1}{4}\left(\frac{(s_6^i)^2+(s_7^i)^2}{s_3^i}+\frac{(s_4^i)^2}{s_1^i}+\frac{(s_5^i)^2}{s_2^i}\right)\right]\;.\end{aligned} \tag{5.4}$$

The nonoscillatory portion of the single-phonon rate $R(k)$ takes the form

$$\begin{aligned}R^{(1)}(\vec{k})&=R_0^{(1)}\sum_{i,\vec{X}_{lj},z_l,z_j,r^\pm}f_1^i(\pm,lj,\beta,E)\\ &\quad\times(a_0^i+a_1^i\tilde{k}_z-\bar{a}_2^i\vec{X}_{lj}\cdot\vec{K}_\parallel+a_3^iK_\parallel^2+a_4^i\tilde{k}_z^2)\\ &\quad\times\exp(-d_0^i+d_1^i\tilde{k}_z-\bar{d}_2^i\vec{X}_{lj}\cdot\vec{K}_\parallel+d_3^iK_\parallel^2+d_4^i\tilde{k}_z^2)\,,\end{aligned} \tag{5.5}$$

where

$$f_1^i(\pm,lj,\beta,E)\equiv\frac{\sin[k_0r_{lj}^\pm E(\vec{k})]}{r_{lj}^\pm}\,\frac{1}{e^{\beta E(\vec{k})}-1}\times\left(\frac{E_z(\vec{k})}{\bar{E}_0+E_z(\vec{k})}\right)^{1/2}\frac{s_0^i}{s_3^i(s_1^is_2^i)^{1/2}}\,,$$

$$r_{lj}^\pm\equiv[X_{lj}^2+(z_l\pm z_j)^2]^{1/2}\,,\quad R_0^{(1)}\equiv\tfrac{1}{16}\pi\,\omega_D\,r_4^2h_0^2k_0^{-1}\,,$$

$$a_0^i = \frac{1}{s_3^i} - \frac{X_{lj}^2}{(s_3^i)^2} + \frac{\bar{z}_j \bar{z}_l}{4 s_1^i s_2^i} ,$$

$$a_1^i = \tfrac{1}{2} i r_3^2 (z_j - z_l)/s_1^i s_2^i , \qquad \bar{a}_2^i = 4 i r_2^2/(s_3^i)^2 ,$$

$$a_3^i = 4 r_2^4/(s_3^i)^2 , \qquad a_4^i = r_3^4/s_1^i s_2^i , \tag{5.6}$$

$$d_0^i = -\left[(X_{lj}^2/s_3^i) + (\tfrac{1}{4}\bar{z}_j^2/s_1^i) + (\tfrac{1}{4}\bar{z}_l^2/s_2^i)\right] ,$$

$$d_1^i = i\left[(\bar{z}_j/s_1^i) - (\bar{z}_l/s_2^i)\right] r_3^2 ,$$

$$\bar{d}_2^i = 4 i r_2^2/s_3^i , \quad d_3^i = (4 r_2^4/s_3^i) - 2 r_2^2 ,$$

$$d_4^i = \left[(1/s_1^i) + (1/s_2^i)\right] r_3^4 - 2 r_3^2 , \quad \bar{z}_l = z_l - z_0 .$$

We have displayed only the nonoscillatory portion of the rate above; it being clear how the oscillatory terms may be included in a perfectly analogous fashion.

We note that $R^{(1)}(\vec{k})$ is not azimuthally symmetric, since $\vec{K}_\parallel \cdot \vec{X}_{lj}$ involves the angle in the plane. For most purposes, one is interested in the rate integrated over all angles in the plane, which becomes

$$\bar{R}^{(1)}(k,\theta) = \int_{-\pi}^{\pi} d\varphi\, R^{(1)}(k,\theta,\varphi)$$

$$= 2\pi R_0^{(1)} \sum_{i, \vec{X}_{lj}, z_l, z_j, \pm} f_1^i(\pm, lj, \beta, E)$$

$$\times \left[J_0(d_2^i X_{lj} k \sin\theta)(a_0^i + a_1^i \tilde{k}_z + a_3^i k^2 \sin^2\theta + a_4^i \tilde{k}_z^2) \right.$$

$$\left. - a_2^i X_{lj} k \sin\theta\, J_1(d_2^i X_{lj} k \sin\theta) \right]$$

$$\times \exp(d_0^i + d_1^i \tilde{k}_z + d_3^i k^2 \sin^2\theta + d_4^i \tilde{k}_z^2) , \tag{5.7}$$

where we may express $\tilde{k}_z^2 = 2 m_a \bar{E}_0 + k^2 \cos^2\theta$, and

$$d_2^i \equiv -4 r_2^2/s_3^i , \quad a_2^i \equiv -4 r_2^2/(s_3^i)^2 . \tag{5.8}$$

We note that $R(\theta)$, the rate per unit solid angle integrated over φ and k, is proportional to the product of $\cos\theta$ with a general function of $\cos\theta$. Thus the angular distribution is not a $\cos\theta$ distribution,[19] and the computation of the total rate $R^{(1)}$ involves a nontrivial integration over $\cos\theta$.

In the limits $E_0/E_D \sim 1$ and/or $k_m^2 r_3^2 \gtrsim 1$, where k_m satisfies $k_m^2/2m_a = E_D$, an expansion in the expression for $R^{(1)}$ of $\tilde{k}_z$ in powers of $k_z^2/2m_a E_0$, is justified. Keeping terms to $O(k_z^2)$, one finds, after some algebra,

$$R^{(1)}(\theta) \cong R_0^{(1)} \sum_{\pm lji} \sum_{n=1}^{\infty} \left(\frac{2\pi s_0^i}{s_3^i (s_1^i s_2^i)^{1/2}\, 2 m_a \bar{E}_0} \right.$$

$$\times \exp[-d_0^i + i k_0 r_{lj}^\pm E_0 - \beta n E_0$$

$$+ d_1^i (2 m_a \bar{E}_0)^{1/2} + d_4^i\, 2 m_a \bar{E}_0]$$

$$\times \int_0^\infty dy\, y\, e^{g_4^i y^2} \left[(g_1^i + g_2^i y^2) J_0(d_2^i X_{lj} y) \right.$$

$$\left.\left. - g_3^i y J_1(d_2^i X_{lj} y) \right] \right) + (k_0 \to -k_0) \Big] , \tag{5.9}$$

where

$$g_1^i \equiv -\frac{t_2^i}{2 t_1^i} \left(1 - \frac{t_2^i}{t_1^i (4 m_a \bar{E}_0)} + \frac{a_1^i}{2(2 m_a \bar{E}_0) t_1^i} + \frac{a_4^i}{t_1^i} \right),$$

$$g_2^i \equiv -\frac{a_3^i - t_2^i (4 m_a \bar{E}_0)^{-1}}{2 t_1^i} , \quad g_3^i \equiv -\frac{a_2^i X_{lj}}{2 t_1^i} ,$$

$$t_1^i \equiv d_4^i + \tfrac{1}{2} d_1^i (2 m_a \bar{E}_0)^{-1/2} + i k_0 r_{lj}^\pm (2 m_a)^{-1}$$

$$- \beta n (2 m_a)^{-1} , \tag{5.10}$$

$$t_2^i \equiv a_0^i + a_1^i (2 m_a \bar{E}_0)^{1/2} + a_4^i\, 2 m_a \bar{E}_0 ,$$

$$g_4^i \equiv d_3^i + i k_0 r_{lj}^\pm (2 m_a)^{-1} - \beta n (2 m_a)^{-1} .$$

The integral in Eq. (5.9) is easily evaluated, and yields the result

$$(2 g_4^i)^{-1} \exp[-\tfrac{1}{4}(d_2^i)^2 X_{lj}^2/g_4^i]$$

$$\times \left[g_1^i + \left(\frac{1}{g_4^i} - \frac{(d_2^i)^2 X_{lj}^2}{(g_4^i)^2} \right) g_2^i + \frac{g_3^i}{2 g_4^i} \right] . \tag{5.11}$$

Thus, for the present case, the total rate is reduced to a sum over sites, sets i, and the index n (the summation index in the expansion of the Bose–Einstein function). For $\beta E_0 \gg 1$, only $n = 1$ is important. Likewise, since the factor $e^{-d_0^i}$ indicates an exponential decay with increasing sites, after some finite number of sites, the series over sites converges very rapidly. The above results are especially convenient for numerical computations for the limits discussed above, as well as for examining the dependences of R on various system parameters.

VI. DISCUSSION

A. General Properties of Desorption Rate

An inspection of the multiphonon rate of Eqs. (4.16)–(4.23) and the single-phonon rate of Eq. (5.5) reveals various general features of the angular and energy distributions in desorption, and the dependence of desorption on temperature and on material parameters. In this section we point out the principal conclusions, while in Paper II we carry out detailed numerical computations illustrating these properties, and provide further discussion.

The exponential decrease of the rate with increasing k^2 is evident from, for example, Eq. (5.7). Thus the energy distribution of desorbed adatoms peaks strongly near $E_k \sim 0$. Physically, this is a reflection of the fact that the effective well is deeper for desorption to states of higher energy.

The multiphonon rate of Eqs. (5.1) and (5.2) reveals that as the energy increases to where n phonons are required to conserve energy, the rate decreases by c_0^{n-1}. Thus multiphonon contributions to the rate decrease very rapidly at low temperatures so that the lowest-order process allowed by energy conservation dominates the rate.

The angular distribution is observed, in general, to deviate from the $\cos\theta$ distribution. The deviation is strongest when r_2/r_3 differs substantially from unity. When $r_2 > r_3$, as is generally the case, the distribution peaks strongly in the forward direction, while the distribution flattens out for $r_2 < r_3$. A weak azimuthal dependence, reflecting the particular structure of the substrate in the vicinity of the adatom, is also evident.

At very low temperatures only the lowest-order term in the Bose–Einstein expansion in Eq. (5.9) need be kept, and the dependence of the rate on temperature is of the form $e^{-\beta E}$, which is the classical form.[12] At higher temperatures (but $T < E_0$), contributions from the higher terms of the expansion lead to deviations from the exponential law. We note that the total rate follows a thermal behavior analogous to the energy distribution, since the latter is a strongly peaked function of energy.

As to sensitivity on material parameters, we note that the rate depends exponentially on the r_i and E_0. It turns out that for typical values of the r_i, the dependence on r_2^2 and r_3^2 is dominant; typically, $r_0 \sim 1$ for physisorbtion and the dependence on r_1 is relatively weak. These sensitivities may be understood physically in terms of the transfer of energy to a particle with a rapidly decaying wave function, such that the particle is "kicked out" of its well. The depth of the effective well, and the character of the initial state are indeed expected to play a crucial role in determining the desorption rate. Naturally, the rate is also proportional to the square of the interaction strength $\tilde{V}_0^2$.

Inspection of the sum over sites in Eq. (5.5) shows that for typical parameters, many layers of substrate atoms need to be included to obtain convergence. This is partly a consequence of the oscillating magnitude and sign of the contributions by site. The oscillating character implies that the detailed geometrical structure of the substrate has a weak influence on desorption (if the other material parameters remained fixed). Actual examples illustrating these properties are considered in Paper II.

B. Umklapp Contributions

We have not considered umklapp terms explicitly in the present work. These terms are given by Eq. (4.17) with $\vec{Q}' - \vec{Q} = \vec{G} \neq 0$. We now briefly discuss the relative contribution made by these terms to the rate.

From Eq. (4.17) one observes that each of the terms making up $U_{\vec{G}}$ (i.e., U for $\vec{Q}' = \vec{Q} + \vec{G}$) is smaller than the corresponding one in U_0 by approximately a factor of $\exp(-nr_1^2G^2)$, where $n=1$ or 2 (we have assumed that $K_\parallel r_2^2 \ll 1$ and $r_2^2 \ll r_1^2$, which is generally the case). When $V_0 \gg 1$, as is also usually the case, the $n=2$ terms (which are proportional to V_0^2) are the important ones, and an over-all decrease with G as $\exp(-2r_1^2G^2)$ obtains. In addition, s_6 and s_7 are changed to $s_6 + 2CG_x$ and $s_7 + 2CG_y$, and the oscillatory factors $\exp(i\vec{G}\cdot\vec{X}_l)$ and $\exp(i4r_2^2\vec{K}_\parallel\cdot\vec{G})$ appear. This combination of exponentially decreasing and oscillatory factors is expected to lead to rapid convergence of the sum over $\vec{G}$'s in the rate. One may obtain an *upper* estimate of the effect of $\vec{G} \neq 0$ terms by ignoring the oscillatory factors; whence one finds

$$R/R(\vec{G}=0) \cong \xi \equiv \sum_{\vec{G}} e^{-2r_1^2G^2}\,. \qquad (6.1)$$

For a simple-cubic substrate, for example, $\xi(r_1 = 1) \cong 1.00$, while $\xi(r_1 = \frac{1}{2}\pi^{-1}) \cong 1.6$. The general characteristics of the thermal and energy dependence of the $\vec{G} \neq 0$ terms can be observed to be similar to the $\vec{G} = 0$ term, although the $\vec{K}\cdot\vec{G}$ factors in the $\vec{G} \neq 0$ terms will influence the non-normal desorption.

In summary, the umklapp contributions to R may be computed in close analogy to the $\vec{G}=0$ rate computed here. The full rate may be as much as several times larger than the $\vec{G}=0$ rate, for typical parameters. Energy and temperature dependences remain qualitatively similar, although differing in detail, depending on the values of parameters involved.

C. Multistep Processes

The contribution of multistep processes is given by the terms higher than second order in H_3 in the Born series. The rigorous evaluation of the relative contribution of these terms is a difficult task, as indicated by the complications involved in computing just the "Golden-rule" term in the previous sections. We here content ourselves with presenting speculative arguments regarding the relative size of the multistep contributions.

Because the function $C(t)$ is appreciable only for values of $t \sim 1/\omega_D$, the natural variable for scaling all times, temperatures, and energies is ω_D, as has been specified in Eq. (4.10). Each succeeding term in the series for R then involves an additional power of v_0/ω_D. Thus, for $v_0/\omega_D \ll 1$, the leading terms to all orders of multiphonon processes are contained in just the lowest-order term in the Born series. This argument is, of course, not rigorous, because the contribution of the multiple time integrals differ for different terms in the series, although it is expected that with the present scaling scheme the latter are, in fact, all of the same order of magnitude.

It should be noted that for a dense series of levels, where phonon-induced transitions between adjoining levels are equally or more probable than desorption, a thermodynamic treatment, as opposed to dynamical, may be the only one appropriate. However, as mentioned previously, when considering transitions from an isolated band of closely spaced levels, it still may be useful to think of desorption from a characteristic "average" level describing the thermalized band.

D. Limitations of Model

We briefly discuss limitations associated with the general formalism when dealing with real surfaces, and associated with the use of simplified phonon spectra even for the case of idealized surfaces.

For surfaces that are rough on an atomic scale, desorption is no longer limited to symmetry sites associated with a perfect substrate lattice. In general, sites at "singular points," such as edges, are characterized by lower binding energies (and thus larger probabilities of desorption) than sites on flat portions of the surface. The contribution to desorption from such sites must therefore be accounted for when roughness is present. Another effect, present even when roughness is absent, is the relaxation of surface atoms,[20] which leads, for example, to different lattice spacings and force constants than in the bulk, with relaxation effects falling off slowly into the bulk. Relaxation may be accounted for within the present formalism by employing the relaxed lattice configuration, and its associated parameters in computing the potential V^0 and the phonon spectrum of the substrate and in carrying out the sum over sites in the rate.

In this paper we have considered the use of simplified bulk and surface Debye models in calculating desorption. Real crystals, of course, are characterized by complex phonon spectra and frequency distributions which account for bulk, surface, and mixed modes, and which may, in general, depart substantially from those given by simplified models.[10] It is clear that the structure present in realistic distributions will be reflected in the details of the energy and angular distributions in desorption. Thus accurate computations for realistic systems requires incorporation of such structure in the calculation of C. However, regarding total rates and prefactors (where integrations over energy and angles have been carried out), one expects only weak dependence on details of the phonon spectrum, and results obtained employing appropriate simplified models should be accurate to an order of magnitude. Use of such models in computing bulk thermodynamic functions has, of course, long been a familiar procedure.[10] The use of realistic phonon spectra, and relative contributions of surface and bulk modes in desorption, will be discussed further in Paper II.

VII. CONCLUDING REMARKS

We have presented a three-dimensional multiphonon-quantum theory of phonon-induced desorption. We have here applied the theory to the particular case of desorption from localized states at low temperatures. We believe that the theory should also be useful in treating a wide variety of related problems, such as desorption from mobile states, the thermodynamics of physisorbtion systems, and the transition from localized to mobile adsorption.

A major obstacle in carrying out calculations of the desorption rate remains the lack of information regarding the fundamental material parameters entering the computation. It is our hope that future experimental investigation of adsorption systems will become more strongly directed toward the determination of these fundamental parameters. It is only then that a truly comprehensive and meaningful comparison between basic theory and experiment can be effected.

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APPENDIX A: DERIVATION OF TRANSITION RATES

We here derive the expressions for the transition rate presented in Sec. II B.

"Golden-rule" rate. The system described in Sec. II is characterized by the lowest-order transition rate

$$R(\vec{\eta},\vec{k}) = \frac{(2\pi/\hbar)\sum_{if} e^{-\beta\epsilon_i} |\langle i,\vec{\eta}| H_3 |f,\vec{k}\rangle|^2 \delta(\epsilon_i-\epsilon_f-\omega(\vec{\eta}\vec{k}))}{\sum_i e^{-\beta\epsilon_i}}, \tag{A1}$$

where $\vec{\eta}$ and $\vec{k}$ are eigenstates of H_1, and i and f of H_2. Let us take

$$\langle i,\vec{\eta}|H_3|f,\vec{k}\rangle = \sum_l \left\langle i \right| \left\{ \int d\vec{r}\, \phi_{\vec{\eta}}(\vec{r})\, \phi_{\vec{k}}(\vec{r}) \times [v(\vec{r}-\vec{R}_l)-v(\vec{r}-\vec{R}_l^0)] \right\} \left| f \right\rangle$$

$$= \sum_{\vec{q}\,l} \langle i|\ e^{-\vec{q}\cdot\vec{R}_l} - e^{-i\vec{q}\cdot\vec{R}_l^0}\ |f\rangle\, v_{\vec{q}} f_{\vec{q}}\,, \tag{A2}$$

where

$$v_{\vec{q}} = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\, v(\vec{r})\,,$$

$$f_{\vec{q}} = \int d\vec{r}\, \phi^*_{\vec{\eta}}(\vec{r})\, e^{i\vec{q}\cdot\vec{r}}\, \phi_{\vec{k}}(\vec{r})\,. \tag{A3}$$

Employing (A2) and the representation

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ixy}\, dy\,, \tag{A4}$$

one obtains

$$R(\vec{\eta}, \vec{k}) = \Big(\hbar \sum_i e^{-\beta\epsilon_i}\Big)^{-1} \sum_{if\vec{q}\vec{q}'lj} e^{-\beta\epsilon_i} v_{\vec{q}} v^*_{\vec{q}'} f_{\vec{q}} f^*_{\vec{q}'}$$

$$\times \int_{-\infty}^{\infty} dt\, e^{-i\omega(\vec{\eta}\vec{k})t} \langle i | e^{i\epsilon_i t} (e^{-i\vec{q}\cdot\vec{R}_j} - e^{-i\vec{q}\cdot\vec{R}^0_j}) e^{i\epsilon_f t} | f\rangle$$

$$\times \langle f | e^{iq'\cdot\vec{R}_l} - e^{i\vec{q}'\cdot\vec{R}^0_l} | i\rangle$$

$$= \hbar^{-1} \sum_{\vec{q}\vec{q}'lj} e^{i(\vec{q}'\cdot\vec{R}^0_l - \vec{q}\cdot\vec{R}^0_j)} v_{\vec{q}} v^*_{\vec{q}'} f_{\vec{q}} f^*_{\vec{q}'}$$

$$\times \int_{-\infty}^{\infty} dt\, e^{-i\omega(\vec{\eta}\vec{k})t} \langle\langle (e^{-i\vec{q}\cdot\vec{u}_j(t)} - 1)(e^{i\vec{q}\cdot\vec{u}_l(0)} - 1)\rangle\rangle , \qquad \text{(A5)}$$

where

$$\vec{R}_l = \vec{R}^0_l + \vec{u}_l ,$$

$$A(t) = e^{iH_2 t} A e^{-iH_2 t} , \qquad \text{(A6)}$$

$$\langle\langle A\rangle\rangle = \mathrm{Tr}\, e^{-\beta H_2} A / \mathrm{Tr}\, e^{-\beta H_2} ,$$

and where we have employed the relations

$$e^{i\epsilon_i t} | i\rangle = e^{iH_2 t} | i\rangle , \text{ etc.}, \qquad \text{(A7)}$$

and the closure property $\sum_f |f\rangle\langle f| = 1$ in obtaining the last line. Glauber's theorem[21] states that for harmonic H_2

$$\langle\langle e^{-i\vec{q}\cdot\vec{u}_j(t)} e^{i\vec{q}\cdot\vec{u}_l(0)}\rangle\rangle$$

$$= \exp[-\mathcal{W}_{jl}(\vec{q}, \vec{q}') + \vec{q}\cdot\overleftrightarrow{C}_{jl}(t)\cdot\vec{q}'] , \qquad \text{(A8)}$$

where

$$\mathcal{W}_{jl} \equiv \tfrac{1}{2}\langle\langle (\vec{q}\cdot\vec{u}_j)^2 + (\vec{q}'\cdot\vec{u}_l)^2\rangle\rangle ,$$

$$\overleftrightarrow{C}_{jl} \equiv \langle\langle \vec{u}_j(t)\vec{u}_l(0)\rangle\rangle . \qquad \text{(A9)}$$

One then has the final form for $\omega \neq 0$:

$$R(\vec{\eta}\vec{k}) = \hbar^{-1} \sum_{\vec{q}\vec{q}'lj} \exp[i(\vec{q}\cdot\vec{R}^0_l - \vec{q}'\cdot\vec{R}^0_j)] v_{\vec{q}} v^*_{\vec{q}'} f_{\vec{q}} f^*_{\vec{q}'}$$

$$\times \int_{-\infty}^{\infty} dt \exp[i\omega(\vec{\eta}\vec{k})t - \mathcal{W}_{jl}(\vec{q}, \vec{q}') + \vec{q}\cdot\overleftrightarrow{C}_{jl}(t)\cdot\vec{q}'] . \qquad \text{(A10)}$$

Note that the only terms that survive in the "Golden-rule" rate are those arising from the "dynamic term" $v(\vec{r} - \vec{R}_l)$.

The above technique may be extended directly to obtain similar, although more complicated, expressions for higher-order contributions to the rate.

Rates $R_{\text{tot}}(\vec{\eta})$ and $R(\vec{\eta})$: expansion in powers of H_3. We now outline the derivation of an expansion in H_3, to all orders, of the exact expression for the transition rate from a state $\vec{\eta}$ to all possible final states $R_{\text{tot}}(\vec{\eta})$. For this purpose, one can directly take advantage of the optical theorem.[12] It turns out that the desorption rate R in which transitions are restricted to free final states, does not take the simplified form arising from the optical theorem, which depends on the accessibility of all final states for its derivation.[12] However, it can be demonstrated by direct expansion of the Born series that R is, in fact, easily obtained through straightforward modifications of the R_{tot} expansion. Because the demonstration is direct but lengthy, it will not be included here. We here present the derivation for R_{tot}, which involves all the necessary manipulations in deriving the form of the terms in R as well, and follow these directly by stating the results for R.

The optical theorem yields for the present case

$$R_{\text{tot}}(\vec{\eta}) = -2\hbar^{-1}\, \mathrm{Im}\langle\langle\langle \vec{\eta} | H_3\, \mathcal{G}(E'(\vec{\eta}))\, H_3 | \vec{\eta}\rangle\rangle\rangle ,$$

$$\mathcal{G}(E) \equiv (E - H + i\epsilon)^{-1} . \qquad \text{(A11)}$$

The prime indicates that in taking the trace over the ith configuration of H_2, we employ the total system energy $E' = E(\vec{\eta}) + \epsilon(\{i\})$ in $\mathcal{G}$. To obtain an expansion of R in powers of H_3, we employ

$$\mathcal{G}(E) = \mathcal{G}_0(E) + H_3\, \mathcal{G}_0(E)\, H_3$$

$$+ H_3\, \mathcal{G}_0(E)\, H_3\, \mathcal{G}_0(E)\, H_3 + \cdots , \qquad \text{(A12)}$$

$$\mathcal{G}_0(E) \equiv (E - H_1 + i\epsilon)^{-1} .$$

Then ($\hbar = 1$)

$$R_{\text{tot}}(\vec{\eta}) = \sum_{n=2}^{\infty} \varphi^{(n)} , \qquad \text{(A13)}$$

where

$$\varphi^{(2)} \equiv -2\, \mathrm{Im}\langle\langle\langle \vec{\eta} | H_3\, \mathcal{G}_0\, H_3 | \vec{\eta}\rangle\rangle\rangle ,$$

$$\varphi^{(3)} \equiv -2\, \mathrm{Im}\langle\langle\langle \vec{\eta} | H_3\, \mathcal{G}_0\, H_3\, \mathcal{G}_0\, H_3 | \vec{\eta}\rangle\rangle\rangle , \text{ etc.} \qquad \text{(A14)}$$

Employing Eq. (A7) and the representation

$$(x + i\epsilon)^{-1} = \frac{1}{i}\int_0^{\infty} e^{i(x+i\epsilon)t}\, dt , \qquad \text{(A15)}$$

$\varphi^{(n)}$ may be manipulated into the form

$$\varphi^{(n)} = -2\, \mathrm{Im} \sum_{1,2,3,\ldots,n} \exp[i(\vec{q}_1\cdot\vec{R}^0_1 + \vec{q}_2\cdot\vec{R}^0_2 + \cdots + \vec{q}_n\cdot\vec{R}^0_n)] v_{\vec{q}_1} v_{\vec{q}_2} \cdots v_{\vec{q}_n} (i)^{1-n} \int_0^{\infty} dt_1\, dt_2 \cdots dt_{n-1}$$

$$\times \{\langle\langle\langle \vec{\eta} | (e^{i\vec{q}_1\cdot\vec{u}_1} - 1) e^{i\vec{q}_1\cdot\vec{r}} e^{it_1[E'(\vec{\eta}) - H_1 - H_2]} (e^{i\vec{q}_2\cdot\vec{u}_2} - 1) e^{i\vec{q}_2\cdot\vec{r}} e^{it_2[E'(\eta) - H_1 - H_2]} \cdots e^{it_{n-1}[E'(\eta) - H_1 - H_2]}$$

$$\times (e^{i\vec{q}_n\cdot\vec{u}_n} - 1) e^{i\vec{q}_n\cdot\vec{r}} | \vec{\eta}\rangle\rangle\rangle\} . \qquad \text{(A16)}$$

The quantity in braces may be manipulated into the form

$$\sum_{\gamma_1\gamma_2\cdots\gamma_{n-1}} \langle\vec{\eta}|e^{i\vec{q}_1\cdot\vec{r}}|\gamma_1\rangle\langle\gamma_1|e^{i\vec{q}_2\cdot\vec{r}}|\gamma_2\rangle\cdots\langle\gamma_{n-1}|e^{i\vec{q}_n\cdot\vec{r}}|\vec{\eta}\rangle$$

$$\times\exp\{it_1[E(\vec{\eta})-E(\gamma_1)]+it_2[E(\vec{\eta})-E(\gamma_2)]+\cdots+it_{n-1}[E(\vec{\eta})-E(\gamma_{n-1})]\}$$

$$\times\langle\langle\{\exp[i\vec{q}_1\cdot\vec{u}_1(t_1+t_2+\cdots+t_{n-1})]-1\}\{\exp[i\vec{q}_2\cdot\vec{u}_2(t_2+t_3+\cdots+t_{n-1})]-1\}\cdots(e^{i\vec{q}_n\cdot\vec{u}_n}-1)\rangle\rangle\,, \quad \text{(A17)}$$

where we have inserted unit operators appropriate to H_1, $1=\sum_\gamma|\gamma\rangle\langle\gamma|$, in obtaining the above form. A generalized Glauber theorem, given in Ref. 22, shows that

$$\langle\langle e^{iq_1\cdot u_1}e^{i\vec{q}_2\cdot\vec{u}_2}\cdots e^{i\vec{q}_n\cdot\vec{u}_n}\rangle\rangle$$

$$=\exp[-\tfrac{1}{2}\vec{q}_1\cdot\overleftrightarrow{C}(11)\cdot\vec{q}_1-\cdots-\tfrac{1}{2}\vec{q}_n\cdot\overleftrightarrow{C}(nn)\cdot\vec{q}_n$$

$$-\vec{q}_1\cdot\overleftrightarrow{C}(12)\cdot\vec{q}_2-\vec{q}_1\cdot\overleftrightarrow{C}(13)\cdot\vec{q}_3-\cdots$$

$$-\vec{q}_{n-1}\cdot\overleftrightarrow{C}(n-1,n)\cdot\vec{q}_n]\,,$$

$$\overleftrightarrow{C}(ij)=\langle\langle\vec{u}(i)\vec{u}(j)\rangle\rangle\,, \quad \text{(A18)}$$

where we have abbreviated the notation in an obvious fashion. In order to extend the time integrations to ±∞, we employ the fact that R is invariant under $\vec{k}\to-\vec{k}$ and that

$$v_{\vec{q}}=v^*_{-\vec{q}}\,,\quad C_{ij}(t)=C^*_{ij}(-t)\,,\quad f(\vec{q},\vec{k})=f^*(-\vec{q},-\vec{k}). \quad \text{(A19)}$$

Combining the various relations given above with the various definitions introduced here, one finally has

$$\varphi^{(n)}=\sum_{1,2,\ldots,n}\exp[i(\vec{q}_1\cdot\vec{R}^0_1+\cdots+\vec{q}_n\cdot\vec{R}^0_n)]\,v_{\vec{q}}\cdots v_{\vec{q}_n}f_{\vec{q}_1}(\vec{\eta}\gamma_1)\cdots f_{\vec{q}_n}(\gamma_{n-1}\vec{\eta})$$

$$\times\int_{-\infty}^{\infty}dt_1\cdots dt_{n-1}\exp[-it_1\,\omega(\gamma_1\vec{\eta})-it_2\,\omega(\gamma_2\vec{\eta})-\cdots-it_{n-1}\,\omega(\gamma_{n-1}\vec{\eta})]\,\mathfrak{a}(\vec{q}_1\cdots\vec{q}_n;\,t_1\cdots t_{n-1})\,, \quad \text{(A20)}$$

where

$$\mathfrak{a}(\vec{q}_1\cdots\vec{q}_n;t_1\cdots t_{n-1})\equiv\{\exp[-\mathcal{W}_1(\vec{q}_1)-\mathcal{W}_2(\vec{q}_2)-\cdots-\mathcal{W}_n(\vec{q}_n)-\vec{q}_1\cdot\overleftrightarrow{C}_{12}(t_1)\cdot\vec{q}_2-\vec{q}_1\cdot\overleftrightarrow{C}_{13}(t_1+t_2)\cdot\vec{q}_3-\cdots$$

$$-\vec{q}_{n-1}\cdot\overleftrightarrow{C}_{n-1,n}(t_{n-1})\cdot\vec{q}_n]\}+(-1)^n\{\exp[-\mathcal{W}_2(\vec{q}_2)-\mathcal{W}_3(\vec{q}_3)-\cdots-\mathcal{W}_n(\vec{q}_n)-\vec{q}_2\cdot\overleftrightarrow{C}_{23}(t_2)\cdot\vec{q}_3-\cdots$$

$$-\vec{q}_{n-1}\cdot\overleftrightarrow{C}_{n-1,n}(t_{n-1})\cdot\vec{q}_n]+[\text{all other permutations involving }(n-1)\,\vec{q}\text{'s}]\}+\cdots$$

$$+(-1)^{n-1}\{e^{-\mathcal{W}_1(\vec{q}_1)}+e^{-\mathcal{W}_2(\vec{q}_2)}+\cdots+e^{-\mathcal{W}_n(\vec{q}_n)}\}+(-1)^n\{1\}\,, \quad \text{(A21)}$$

where

$$\mathcal{W}_l(\vec{q}_l)\equiv\tfrac{1}{2}\vec{q}_l\cdot\overleftrightarrow{C}_{ll}(0)\cdot\vec{q}_l\,,$$

$$\omega(12)=E(1)-E(2)\,.$$

The last two braces in $\mathfrak{a}$ never contribute to the rate, as these are independent of the t_n. All other braces except the first lead to δ functions in the sums over states which simplify their contributions to the rate. One observes that the higher-order $\varphi^{(n)}$'s rapidly increase in complexity. The proliferation of terms for large n is a result of the subtraction of the $v(\vec{r}-\vec{R}^0_l)$ term in H_3. In the absence of this term just the first bracket in $\mathfrak{a}$ would remain. It appears that no simplified theorem of the form of Eq. (A18) exists for factors of the sort $e^{i\vec{q}\cdot\vec{u}}-1$. It should be noted, however, that all of the terms arising from the 1's involve at least a single transition between adatom states in which no phonons are exchanged. It is expected that the probability for such processes is small, if the eigenstates of H_1 are indeed stationary. For the special case where degeneracy between adsorbed states and free states may be neglected, it is easy to see that these terms which carry δ functions between energy states of H_1 are indeed negligible.

To obtain the desorption rate R, one must sum each $\varphi^{(n)}$ $(n-1)$ times, with the following prescription: Each γ_i in turn must be restricted to free final states, while the remaining γ_i are summed over unrestricted. For $\varphi^{(2)}$, for example, one has just the single term with γ_1 restricted to free final states. For $\varphi^{(3)}$ there are two terms: one with γ_1 restricted to free final states and one with γ_2 so restricted. It can be seen that the restriction to free final states adds considerable complexity to the higher-order contributions.

APPENDIX B: ISOTROPIC DEBYE MODEL

In this appendix we derive expressions for the correlation function $C(\vec{r},t)$ for an isotropic Debye model. Consider bulk modes with dispersion $\omega(\vec{k})$

$= v_s k$. The corresponding correlation function C_B^0 is given by[21]

$$C_B^0(\vec{r}, t) = \sum_{\vec{k}} \frac{\hbar^2}{2Nm_s\,\omega(\vec{k})} \left[(n(\vec{k})+1)\,e^{i(\vec{k}\cdot\vec{r}-\omega(\vec{k})t)} + n(\vec{k})\,e^{-i(\vec{k}\cdot\vec{r}-\omega(\vec{k})t)}\right]$$

$$= (2\pi)^{-3}\frac{3}{2}\frac{\hbar^2}{m_s\,\omega_D}(k_D a_0)^3 \int \frac{d\vec{x}}{x} \times\left[\exp\left(ik_D a_0 \vec{x}\cdot\frac{\vec{r}}{a_0} - i\omega_D xt\right) + \frac{2\cos[k_D a_0 \vec{x}\cdot(\vec{r}/a_0) - \omega_D xt]}{e^{\hbar\beta\omega_D x}-1}\right], \quad \text{(B1)}$$

where $k_D = \omega_D / v_s$ and the integration is carried out over a unit sphere. We now switch to dimensionless variables:

$$C_B/a_0^2 \to C_B\,, \quad m_s E_D a_0^2/\hbar^2 \to m_s\,,$$
$$\omega/\omega_D \to \omega\,, \quad \beta E_D \to \beta\,, \quad \text{(B2)}$$
$$t\omega_D \to t\,, \quad r/a_0 \to r\,, \quad ka_0 \to k\,.$$

Noting that $k_0 \equiv k_D a_0 = (6\pi^2)^{1/3}$ for the bulk case, one has

$$C_B^0(\vec{r}, t) = \tfrac{3}{2}(4\pi m_s)^{-1}\int \frac{d\vec{x}}{x} \times\left(e^{i(k_0\vec{x}\cdot\vec{r}-xt)} + \frac{2\cos(k_0\vec{x}\cdot\vec{r}-xt)}{e^{\beta x}-1}\right). \quad \text{(B3)}$$

The Fourier transform of C_B follows as

$$\rho_B^0(\vec{r}, \omega) \equiv \frac{1}{2\pi}\int dt\, e^{-i\omega t}\, C_B^0(\vec{r}, t)$$

$$= \frac{1}{4\pi}\,\frac{3}{2m_s}\int_{-\infty}^{\infty} dt \int_{-1}^{1} dy \int_0^1 dx\, x\, \{e^{ik_0 x(ry-t)} \times[1+n(x)] + e^{-ik_0 x(ry-t)}\,n(x)\}\, e^{-i\omega t}$$

$$= (3/2m_s)(k_0 r)^{-1}\int_0^1 dx\{\delta(\omega+x)[1+n(x)] + \delta(\omega-x)n(x)\}\sin(k_0 xr)\,. \quad \text{(B4)}$$

Then for $\omega > 0$,

$$\rho_B^0(\omega) = \tfrac{3}{2}\, m_s^{-1}\, n(\omega)\,(k_0 r)^{-1}\sin(k_0\,\omega r)\,\Theta(1-\omega)\,,$$
$$\rho(-\omega) = e^{\beta\omega}\rho(\omega)\,, \quad \text{(B5)}$$

where Θ is the Heaviside function.

A surface mode isotropic Debye model may be similarly constructed. Here the dispersion is taken as $\omega(\vec{K}) = \omega_0 + v_{ss}\vec{K}$. Then the correlation function $C_s(\vec{X}, t)$ may be written, employing relations analogous to the bulk case, as

$$C_s(\vec{X}, t) = \frac{1}{2\pi m_s}\int \frac{d\vec{K}}{\omega(\vec{K})}\left(\exp\{i[\vec{K}\cdot\vec{X} - \omega(\vec{K})t]\} + \frac{2\cos\{i[\vec{K}\cdot\vec{X} - \omega(\vec{K})t]\}}{e^{\beta\omega(\vec{K})}-1}\right) \quad \text{(B6)}$$

in dimensional units. After some algebra, one obtains for ρ_s the following expression, in the previously defined dimensionless units ($\omega > 0$):

$$\rho_s(\vec{X}, \omega) = m_s^{-1}\,\sigma n(\omega)\,J_0[k_{os}\,\sigma(\omega-\omega_0)X](1-\omega_0/\omega) \times\Theta(\omega_0+\sigma-\omega)\,\Theta(\omega-\omega_0)\,, \quad \text{(B7)}$$

where $k_{0s} \equiv k_{Ds} a_0 = 2\sqrt{\pi}$, $\sigma \equiv v_{ss} k_{0s}/v_s k_0$, and J_0 is a Bessel function.

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