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# Desorption times from rate equations, the master equation, and the Fokker-Planck equation

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A set of rate equations for the bound-state occupation functions with transition probabilities calculated microscopically serves as a basis for a detailed study of various approximations available for the calculation of desorption times in gas-solid systems exhibiting physisorption. The exact time evolution of the adsorbate during the desorption process shows that quasiequilibrium is only maintained at low temperatures, where perturbation theory of the master equation yields a simple analytic expression for the desorption time in weakly coupled gas-solid systems. At intermediate temperatures we derive another simple expression from the Fokker-Planck equation. Classical and phenomenological equilibrium theories of desorption are critically assessed. Lower limits for the preexponential factor in the desorption time of the order of $10^{-16}$ sec proportional to the inverse of the heat of adsorption are derived.

## I. INTRODUCTION

In the preceding paper[1] we have derived kinetic equations that govern the kinetics of adsorption and desorption in gas-solid systems that show physisorption, i.e., in which the adsorbed gas particles do not undergo any substantial modification, electronic or chemical, apart from a weak polarization. We have concentrated on systems in which the surface potential, i.e., the net interaction between the particles of the gas and solid phases, respectively, develops many bound states, as it happens, e.g., in the Xe-W system which has a few hundred bound states. Gas particles trapped into these bound states constitute the adsorbate. In the specific model that we examined the surface potential is taken to be a Morse potential and the adsorption and desorption process is mediated by phonons. Moreover, we restricted ourselves to physisorption processes at low coverage so that the interaction between gas particles in the adsorbate can be neglected. Also, our model is one dimensional. In Ref. 2 we have studied desorption kinetics on the basis of the set of rate equations[3]

$$\frac{dn_i(t)}{dt} = -\left[R_{ci} + \sum_{\substack{j=0\\ j\neq i}}^{N} R_{ji}\right] n_i + \sum_{\substack{j=0\\ j\neq i}}^{N} R_{ij} n_j, \quad i = 0, \ldots, N . \tag{1}$$

Here $n_i(t)$ is the time-dependent occupation of the $i$th bound state, $R_{ji}$ is the probability for a transition of a gas particle from the $i$th into the $j$th bound state, and $R_{ci}$ is the probability for a transition from the $i$th bound state into the continuum. Continuum—bound-state transitions were not included as we concentrated on the calculation of the isothermal desorption time. Recall that in an isothermal desorption experiment the gas is pumped out of the system so that no transitions from the continuum back into any of the bound states can occur. Including them now in order to be able to consider adsorption as well, we get instead of (1)

$$\frac{dn_\iota(t)}{dt} = \sum_{\iota'\neq\iota} R_{\iota\iota'} n_{\iota'} - \sum_{\iota'\neq\iota} R_{\iota'\iota} n_\iota , \tag{2}$$

where the indices $\iota$ and $\iota'$ run over all bound states and continuum states of a gas particle in the surface potential.

Though the ingredients of the theory as developed in Ref. 2 are plausible and seem necessary for a realistic description of physisorption kinetics for systems such as Xe-W, He-graphite, He-LiF, etc., it appears desirable that a "simpler" theory be developed. At this stage we would like to stress that the theory, as developed in Ref. 2, is conceptionally very straightforward. One starts with a quantum-mechanical Hamiltonian of the interacting gas-solid systems

$$H = H_g + H_s + H_{\text{int}} \ . \tag{3}$$

Here $H_g$ is the Hamiltonian describing the gas phase, $H_s$ is the relevant part of the Hamiltonian of the solid, typically chosen to describe phonons in the harmonic approximation, e.g., by a Debye model with a cutoff frequency $\omega_D$, and $H_{\text{int}}$ accounts for the interaction between the gas and the solid. The latter is conveniently split into two parts. The first is a static part, namely the effective surface potential which we have chosen in Refs. 1 and 2 to be a Morse potential:

$$V(x) = U_0(e^{-2\gamma(x-x_0)} - 2e^{-\gamma(x-x_0)}) \ . \tag{4}$$

A dynamical part in $H_{\text{int}}$ accounts for the phonon-mediated interaction between the gas particles and the solid. To evaluate the transition probabilities $R_{\iota\iota'}$ in (1) and (2) one typically employs Fermi's golden rule or higher-order perturbation theory. Lastly, the set of rate equations (1) or (2) must be solved by matrix diagonalization to find the time evolution of the gas-solid system. Its kinetics is thus known.

What one still might want to do, and this is what we started in Ref. 1 and want to continue in this paper, is to develop approximations to the above theory that will allow one to derive simple analytic expressions for desorption times. Because we start with a well-defined model, namely (2) with the transition probabilities $R_{\iota\iota'}$ calculated quantum mechanically from first principles, and because we have obtained the exact relaxation times—exact within this model—by matrix diagonalization, we will be able to state precisely for what gas-solid systems and for what temperature regimes such approximate analytic expressions for relaxation times are valid. This last point is very crucial and has been overlooked by too many workers in the field who have argued that, because quantum-mechanical calculations of desorption times are too involved (they are conceptually simple, though) one is justified to set up simple classical models to calculate desorption times. Inevitably the range of applicability of such models cannot be delineated. We therefore feel that it is crucial to start from a realistic, i.e., microscopic quantum-mechanical model, and then, after having solved such a model satisfactorily try to develop approximations to find analytic expressions for relaxation times whose range of validity can then also be given.

We have started this program, based on the model developed in Ref. 2 , by deriving, in Ref. 1 , from (2) a continuous master equation

$$\frac{\partial n(\epsilon,t)}{\partial t} = \int_{-u_0}^{\infty} d\epsilon' \rho(\epsilon') W(\epsilon,\epsilon') n(\epsilon',t) - \int_{-u_0}^{\infty} d\epsilon' \rho(\epsilon') W(\epsilon',\epsilon) n(\epsilon,t) \ , \tag{5}$$

where $\epsilon = E/\hbar\omega_D$ and $u_0 = U_0/\hbar\omega_D$ with $\omega_D$ the Debye frequency of the solid, $n(\epsilon,t) = n_i(t)$, and $\rho(\epsilon) = (\,|\,\epsilon\,|\,)^{-1/2}$ with the kernel $W(\epsilon,\epsilon')$ given in Eqs. (22)—(24) of Ref. 1. We rewrote (5) as a Smoluchowski-Chapman-Kolmogorov equation and derived from it via a Kramers-Moyal expansion the Fokker-Planck equation

$$\frac{\partial}{\partial t}[\rho(\epsilon) n(\epsilon,t)] = -\frac{\partial}{\partial \epsilon}[\alpha_1(\epsilon)\rho(\epsilon) n(\epsilon,t)] + \frac{1}{2}\frac{\partial^2}{\partial \epsilon^2}[\alpha_2(\epsilon)\rho(\epsilon) n(\epsilon,t)] \ , \tag{6}$$

where

$$\alpha_n(\epsilon) = \int_{-u_0}^{\infty} d\epsilon' \rho(\epsilon')(\epsilon' - \epsilon)^n W(\epsilon',\epsilon) \ . \tag{7}$$

By studying the moments $\alpha_n$ in detail we showed that (6) should yield an acceptable description for the kinetics of weakly coupled gas-solid systems characterized by large values of the parameters $r$ and $u_0$ but restricted to a temperature range

$$\frac{5}{3u_0} << \delta << \left[\frac{2}{5}\frac{r}{u_0}\right]^{1/2} \tag{8}$$

where

$$\delta = \frac{\hbar\omega_D}{k_B T}, \quad r = \frac{2m\omega_D}{\hbar\gamma^2} \ . \tag{9}$$

Under such conditions we showed in Ref. 1 that the equilibrium solution of (4) is a Maxwell-Boltzmann distribution

$$n(\epsilon) = e^{\beta\mu} e^{-\delta\epsilon} \ , \tag{10}$$

where $\mu$ is the chemical potential of the gas phase.

In this paper we continue the discussion of Eqs. (2), (5), and (6) by calculating various analytic expressions for the desorption times. In Sec. II we look once more at the exact time evolution of the adsorbate as it emerges by solving (2). We will see that only at low temperatures is a quasiequilibrium maintained in the adsorbate occupation function, restricting the validity of "equilibrium theories" of desorption and perturbation theories to low temperatures where systems like Xe-W have, incidentally, immeasurably long desorption times. Looking next at the high-temperature regime we will show that the time evolution of the adsorbate during the desorption process is controlled by several time constants so that an attempt at its characterization by a single time, e.g., the mean first passage time, seems futile. We comment further on equilibrium theories of desorption and extract sticking coefficients from our desorption times, not without misgivings though. Section III presents the perturbation theory for the master equation (5) from which we derive a simple analytic expression for the desorption time in the low-temperature regime, where it approximates the exact result rather well. In Sec. IV we calculate desorption times from the Fokker-Planck equation (6) which we show to be acceptable for intermediate temperatures. The results of this paper are finally put into perspective by some remarks on classical and equilibrium theories.

## II. PERTURBATION THEORY OF THE RATE EQUATION

In this section we want to develop an appropriate perturbation theory for the calculation of the desorption time from (1) or (2). Rather than solving (1) directly as done in Ref. 1 we recall that, after inclusion of the continuum–bound-state transitions in (2), its equilibrium solution satisfies detailed balance (the Greek indices $\iota,\iota'$ run over bound states and continuum states whereas Latin indices $i,j$ run over bound states only):

$$R_{\iota\iota'}e^{-\delta\epsilon_{\iota'}}=e^{-\delta\epsilon_{\iota}}R_{\iota\iota'} \; . \tag{11}$$

The matrix $R_{\iota\iota'}$, thus far asymmetric, can therefore be symmetrized by a transformation[4]

$$S_{\iota\iota'}=e^{\delta\epsilon_{\iota}/2}R_{\iota\iota'}e^{-\delta\epsilon_{\iota'}/2}=S_{\iota'\iota} \; , \tag{12}$$

$$\chi_{\iota}(t)=n_{\iota}(t)e^{\delta\epsilon_{\iota}/2} \; .$$

Equation (1) then reads

$$\frac{d}{dt}\chi_i(t)=\sum_{\substack{j=0\\ j\neq i}}^{N}S_{ij}\chi_j(t) -\left[R_{ii}+\sum_{\substack{j=0\\ j\neq i}}^{N}e^{-\delta\epsilon_j/2}S_{ji}e^{\delta\epsilon_i/2}\right]\chi_i(t) \; . \tag{13}$$

Whereas in Ref. 2 we diagonalized the asymmetric matrix $\overleftrightarrow{\mathrm{R}}=\overleftrightarrow{\mathrm{R}}_0+\overleftrightarrow{\mathrm{R}}_c$ with elements

$$(\overleftrightarrow{\mathrm{R}}_0)_{ij}=-R_{ij}+\delta_{ij}\sum_{\nu=0}^{N}R_{\nu i} \; ,$$

$$(\overleftrightarrow{\mathrm{R}}_c)_{ij}=-\delta_{ij}R_{ci} \; , \tag{14}$$

we work now with the symmetric matrix

$$\overleftrightarrow{\mathrm{S}}=\overleftrightarrow{\mathrm{S}}_0+\overleftrightarrow{\mathrm{R}}_c \tag{15}$$

with elements

$$(\overleftrightarrow{\mathrm{S}}_0)_{ij}=-S_{ij}+\delta_{ij}\sum_{\nu=0}^{N}e^{\delta(\epsilon_\nu-\epsilon_i)/2}S_{\nu i}$$

$$=e^{-\delta(\epsilon_i-\epsilon_j)/2}R_{ij}+\delta_{ij}\sum_{\nu=0}^{N}R_{\nu i} \; . \tag{16}$$

Let us rewrite (13) as

$$\frac{\partial\vec{\chi}}{\partial t}=-\overleftrightarrow{\mathrm{S}}\cdot\vec{\chi} \; , \tag{17}$$

where $\vec{\chi}$ is a column vector with components $\chi_i$, $i=0,\ldots,N$. Diagonalizing $\overleftrightarrow{\mathrm{S}}$ we get

$$\overleftrightarrow{\mathrm{S}}\cdot\vec{\mu}^{(i)}=\lambda_i\vec{\mu}^{(i)} \tag{18}$$

with real eigenvalues $\lambda_i$, assumed to be ordered $\lambda_0<\lambda_1<\ldots<\lambda_N$, and an orthonormal set of eigenvectors $\vec{\mu}^{(i)}$. The solution of (17) then reads

$$\vec{\chi}(t)=\sum_{j=0}^{N}[\vec{\mu}^{(j)}\cdot\vec{\chi}(0)]e^{-\lambda_j t}\vec{\mu}^{(j)} \; , \tag{19}$$

which yields

$$n_i(t)=\sum_{j=0}^{N}A_{ij}e^{-\lambda_j t} \; , \tag{20}$$

where

$$A_{ij}=e^{-\delta\epsilon_i/2}\mu_i^{(j)}\sum_{k}\mu_k^{(j)}n_k(0)e^{+\delta\epsilon_k/2} \; . \tag{21}$$

Here $n_k(0)$ is the initial occupation of the $k$th bound state and $\mu_i^{(j)}$ is the $i$th component of the

$j$th eigenvector. We have shown in detail in Ref. 2 that as the temperature in the gas-solid system is lowered, the lowest eigenvalue $\lambda_0$ splits off dramatically from the others becoming much smaller. This implies that after initial fast transients with time scales $\lambda_j^{-1}$, $j>0$ have died out, the time evolution of (2) is controlled by a single time scale $\lambda_0^{-1}$ which one can identify as the desorption time

$$t_d=\lambda_0^{-1} \, . \tag{22}$$

Let us look at an explicit numerical example. We want to choose a gas-solid system whose surface potential develops many bound states. Recall from Refs. 1 and 2 that for phonon-mediated gas-solid interactions all transition probabilities $R_{ii'}$ calculated in second-order time-dependent perturbation theory, are proportional to the Debye frequency $\omega_D$ of the solid and to the ratio $m/M_s$ of the masses of a gas particle $m$ and of a particle of the solid $M_s$. To be specific, in our examples we choose $\hbar\omega_D/k_B=405$ K for tungsten and $m/M_s=0.714$ for the Xe-W system. To fix the parameters $U_0$ and $\gamma$ of the surface potential (4), we recall that the bound states in a Morse potential are at energies

$$\epsilon_i=E_i/\hbar\omega_D=-(\sigma_0-i-\tfrac{1}{2})^2/r \, , \tag{23}$$

where

$$\sigma_0^2=ru_0 \, . \tag{24}$$

We choose the depth $U_0/\hbar\omega_D=11.56$ so that for a range $\gamma^{-1}=1.5$ Å (chosen arbitrarily) the lowest bound-state energy is $\epsilon_0=E_0/k_B=-4662$ K $=-Q/k_B$ equals the heat of adsorption for the Xe-W system.[5] We thus have $r=4969.0$ and $\sigma_0=239.66$ so that this particular Morse potential develops 240 bound states.[6] Diagonalizing (18) we find that at $\delta=1.0$ $\lambda_0=3.7895\times10^6$ sec$^{-1}$, $\lambda_1=1.7352\times10^{10}$ sec$^{-1}$, $\lambda_2=2.5647\times10^{10}$ sec$^{-1}$, . . . , $\lambda_{240}=1.8680\times10^{13}$ sec$^{-1}$. More generally we find that for $\delta\gtrsim0.5$ all $\lambda_j>>\lambda_0$, $j>0$. This confirms our earlier assertion that for times $t>>(\lambda_j-\lambda_0)^{-1}$, $j>0$ all fast transients in (20) with frequencies $\lambda_j$, $j>0$ have died out and the time evolution settles down to a steady state

$$n_i(t)\approx A_{i0}e^{-\lambda_0 t} \, , \tag{25}$$

which is characterized by a single relaxation time $t_d=\lambda_o^{-1}$.

In Fig. 1 we plot the deviation of the nonequilibrium distribution function $n_i(t)$ from the initial equilibrium one for $t>>(\lambda_j-\lambda_0)^{-1}$, i.e., we plot

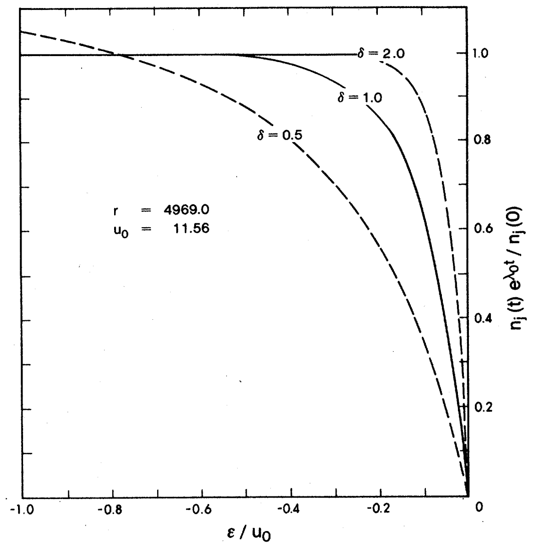

FIG. 1. Steady-state occupation of the bound states for various temperatures $\delta=\hbar\omega_D/k_BT$. Parameters: $\hbar\omega_D/k=405$ K, $m/M_s=0.714$ appropriate for the Xe-W system.

$$n_i(t)e^{\lambda_0 t}/n_i(0) \, . \tag{26}$$

Deviating markedly from the value 1 at higher bound-state energies indicates that the desorption process removes particles from these bound states faster than bound-state—bound-state transitions can manage to rearrange the bound-state occupation into an equilibrium one. Decreasing the temperature such that $\delta=2.0$ yields $\lambda_0=74.691$ sec$^{-1}$. The desorption process slows down considerably, allowing the bound-state—bound-state transitions to become more effective, so that (26) is closer to 1 up to higher bound-state energies. Also note that at higher temperatures, e.g., at $\delta=0.5$, the lower bound states are relatively more occupied in the steady state than in equilibrium simply because desorption depletes the higher levels too fast. The parameter dependence of these results can be seen by comparing Figs. 1 and 2; for the latter we choose $r=550$ and $\sigma_0=79.734$, so that this Morse potential, of the same depth $U_0$ as the previous one but of a range $\gamma^{-1}=0.5$ Å, develops only 80 bound states. Because a smaller range implies a stronger coupling of the adparticle to the phonons of the solid, bound-state—bound-state transitions become more effective maintaining the adsorbate closer to equilibrium during the desorption process.

These results confirm fully similar conclusions reached by Pagni[7] (see his Fig. 2 for comparison), who based his calculations of the transition proba-

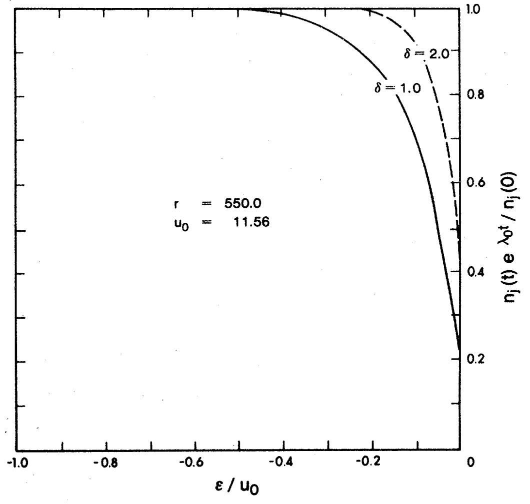

FIG. 2. See Fig. 1.

bilities $R_{ij}$ on a simple classical model. They certainly encourage one to try a perturbation calculation of $\lambda_0$ at low temperatures based on the decomposition (15). We write

$$\overleftrightarrow{S}_0 \cdot \vec{v}^{(i)} = \lambda_i^{(0)} \vec{v}^{(i)}, \quad i = 0, \ldots, N \tag{27}$$

and observe immediately that the lowest eigenvalue is $\lambda_0^{(0)} = 0$. The corresponding eigenvector $\vec{v}^{(0)}$ has components

$$v_j^{(0)} = e^{\beta E_j/2} \Big/ \left[ \sum_i e^{\beta E_i} \right]^{1/2} . \tag{28}$$

Because $\overleftrightarrow{S}$ is symmetric we can, starting from $\overleftrightarrow{S}^{(0)}$, do straightforward perturbation theory on (18) and get

$$\lambda_i = \lambda_i^{(0)} + \vec{v}^{(i)T} \cdot \overleftrightarrow{R}_c \cdot \vec{v}^{(i)} + \sum_{\substack{j=0 \\ j \neq i}}^{N} \frac{| \vec{v}^{(i)T} \cdot \overleftrightarrow{R}_c \cdot \vec{v}^{(j)} |^2}{\lambda_i^{(0)} - \lambda_j^{(0)}} + \cdots , \tag{29}$$

where $\vec{v}^{(i)T}$ is the transpose of $\vec{v}^{(i)}$. Note that

$$\lambda_0^{(0)} = 0 , \tag{30}$$

$$\lambda_0^{(1)} = \sum_i R_{ci} n_i(0) \Big/ \sum_k n_k(0) . \tag{31}$$

The calculation of $\lambda_0^{(1)}$ thus presumes that the initial equilibrium distribution $n_i(0)$ is maintained during the desorption process. We have calculated $\lambda_0$ by exact diagonalization of (18) and also by evaluating the perturbation series (31) up to third order. The results are given in Figs. 3 and 4. It is fair to say that lowest-order perturbation theory, i.e., $\lambda_0^{(1)}$, is a poor approximation to $t_d^{-1}$ throughout the range of $\delta$ depicted in particular for $1 \leq \delta \leq 4$, where $t_d$ can be measured in the Xe-W system.

For larger $\delta$, $\lambda_0^{-1}$ becomes immeasurably large, implying also that the ratios $\lambda_0/\lambda_i$ for $i > 0$ of the exact eigenvalues $\lambda_i$ of $\overleftrightarrow{S}$ become very small, indeed, smaller than $10^{-9}$. Once $\lambda_0/\lambda_i$ becomes smaller than the accuracy of the computer used to diagonalize $\overleftrightarrow{S}$, the latter cannot be done anymore.

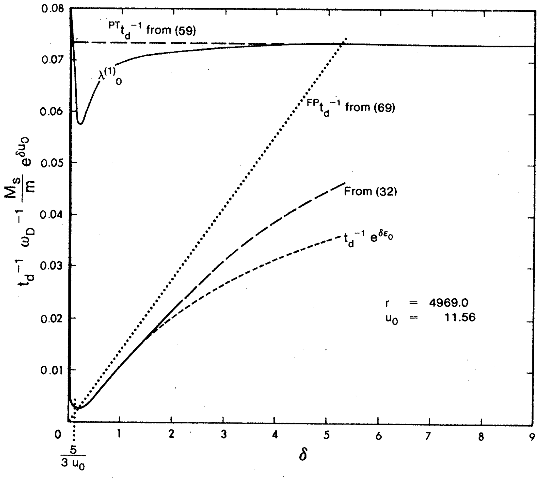

FIG. 3. Inverse desorption time in various approximations as indicated. Heavy line: mean first passage time.

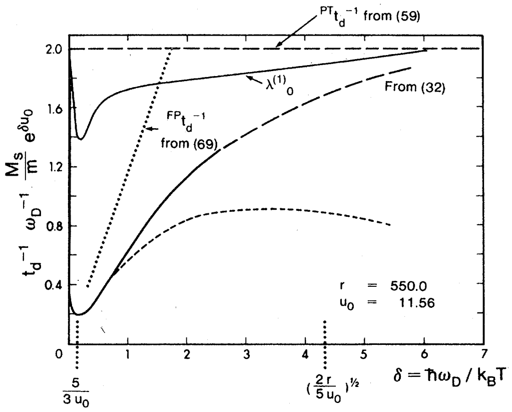

FIG. 4. See Fig. 3.

We were, therefore, not able to calculate $\lambda_0$ exactly beyond $\delta \sim 2.5$. This, however, is not too disconcerting, because the low-temperature region with $\delta \gtrsim 2.5$ is physically not too interesting because $t_d$ becomes too large and because in this region third-order perturbation theory works very well, in particular, after one resums (31) in a Padé-type fashion as

$$\lambda_0 = \lambda_0^{(1)} - \lambda_0^{(2)} + \lambda_0^{(3)} + \dots = \lambda_0^{(1)} \Big/ \left[ 1 + \frac{\lambda_0^{(2)}/\lambda_0^{(1)}}{1 + \lambda_0^{(3)}/\lambda_0^{(2)} - \lambda_0^{(2)}/\lambda_0^{(1)} + \dots} \right] . \tag{32}$$

This last expression leads to the dashed curves in Figs. 3 and 4. Let us stress once more that in the temperature region of most interest, namely for $1 \lesssim \delta \lesssim 4$, the exact diagonalization as that used in Ref. 2 yields the only trustworthy desorption times. Lowest-order perturbation theory $\lambda_0^{(1)}$ is unacceptable. However, the latter is used without question in the so-called "equilibrium theory"[8] of desorption by physicists who believe that the bound-state occupation function does not deviate from an equilibrium distribution during the desorption process. Figures 1–4 demonstrate clearly that this assumption is not warranted, except at such low temperatures where the desorption process becomes unrealistically slow. Pagni[7] has made the same point very strongly. Armand[8] has tried to justify the equilibrium approximation by quoting that the error thus introduced is less than 15% if $U_0/k_BT > 5$ and less than 10% if $U_0/k_BT > 10$. Figures 3 and 4 do not confirm these numbers. To get a 15% agreement between $\lambda_0$ and $\lambda_0^{(1)}$ one needs $\hbar\omega_D/k_BT > 9$ in Fig. 3 and $\hbar\omega_D/k_BT > 4.5$ in Fig. 4, implying with $U_0/\hbar\omega_D = 11.56$ that $U_0/k_BT > 100$ and 50, respectively. Indeed, the ratio $U_0/k_BT$ is not the crucial parameter to assess the validity of the equilibrium assumption at all. Rather, it is a question of time scales: If the bound-state–bound-state transitions are much faster than the bound-state–continuum transitions, then equilibrium will be approximately maintained during the desorption process. But these transitions are caused by the energy-dissipating coupling of the gas to the solid and not by the static surface potential alone, so that $U_0/k_BT$ cannot be the critical parameter that determines the validity of the equilibrium assumption. We will return to a discussion of equilibrium theories at the end of this section.

We have seen above that in the examples studied so far the time evolution of the adsorbate density

$$\frac{N(t)}{N(0)} = \sum_{i=0}^{N} \frac{n_i(t)}{N(0)} = \sum_{i=0}^{N} S_i e^{-\lambda_i/t} \tag{33}$$

is for $\delta \gtrsim 0.5$ dominated by a single time scale $\lambda_0^{-1}$, which we identified with the desorption time. We want to show quickly that in this situation the mean first passage time[9]

$$\bar{t} = \int_0^\infty \frac{N(t)}{N(0)} dt = \sum_{i=0}^{N} S_i \lambda_i^{-1} \tag{34}$$

yields the same time scale. Indeed, if $\lambda_0 << \lambda_j$, $j > 0$ we know from Table II in Ref. 2 that $S_j << S_0 \approx 1.0$, so that $\bar{t} \approx \lambda_0^{-1}$. This can also be substantiated straightforwardly by perturbation theory for $\delta >> 1$ and confirms similar conclusions by Kim.[4]

Things are different in the high-temperature region $\delta \leq 0.1$, which we want to explore now. We should note first that for $\delta \lesssim 0.1$ we are really stretching the limits of applicability of our model because we know from Ref. 10 that for such high temperatures, multiphonon processes become important and second-order perturbation theory which is used to calculate the transition probabilities $R_{ii'}$ is no longer sufficient. Keeping these warnings in mind, we give in Table I a few examples of eigenvalues $\lambda_i$ and coefficients $S_i$ in (33) and the mean passage time $\bar{t}$ from (34), for some unrealistically high temperatures. We see that for very small $\delta$ the $S_i$ approach some fixed values such that the mean passage time $\bar{t}$ is about a factor of 2 larger than the inverse of the lowest eigenvalue $\lambda_0$. This implies for the time evolution of the adsorbate density (33), plotted in Fig. 5, that only the long time tail is dominated by a single time scale, namely $\lambda_0^{-1}$, whereas over the time interval in which $N(t)$ drops to a value $N(t)/e$ many terms in (33) have tc be kept, indeed, as many as thirty terms for the example in Fig. 5 to get $N(t)/N(0)$

TABLE I. Eigenvalues $\lambda_i$ from Eq. (18), coefficients $S_i$ in Eq. (33), and first mean passage time $\bar{t}$ from Eq. (34) as functions of inverse temperature $\delta = \hbar\omega_D / k_B T$. Other parameters: $m/M_s = 0.174$, $\omega_D = 5.302 \times 10^{13}$ sec$^{-1}$, $r = 4969.0$, $\sigma_0 = 239.66$.

| $\delta$ | $\lambda_0$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_{100}$ | $\lambda_{240}$ |
|---|---|---|---|---|---|---|
| 0.25 | $4.5877\times 10^{9}$ | $4.4713\ \times 10^{11}$ | $1.0245\times 10^{11}$ | $1.1394\times 10^{11}$ | $3.2067\times 10^{13}$ | $7.4678\times 10^{13}$ |
| 0.1 | $2.2946\times 10^{10}$ | $1.2106\times 10^{11}$ | $2.5610\times 10^{11}$ | $2.9361\times 10^{11}$ | $8.0175\times 10^{14}$ | $1.8671\times 10^{14}$ |
| $10^{-3}$ | $3.3466\times 10^{12}$ | $1.3165\times 10^{13}$ | $2.5612\times 10^{13}$ | $3.0393\times 10^{13}$ | $7.2243\times 10^{15}$ | $1.8672\times 10^{14}$ |
| $10^{-10}$ | $3.3584\times 10^{19}$ | $1.3177\times 10^{20}$ | $2.56124\times 10^{20}$ | $3.0406\times 10^{20}$ | $7.2243\times 10^{22}$ | $1.8672\times 10^{23}$ |

within 1% of its correct value one at $t = 0$. The mean passage time $\bar{t}$ from (34), on the other hand, seems to have little relevance for this time evolution.

We therefore would like to make the following point: If during the desorption process the time evolution of the adsorbate is controlled by a single time scale $t_d$, then $t_d = \lambda_0^{-1} \approx \bar{t}$, i.e., the mean passage time coincides with the inverse of the lowest eigenvalue $\lambda_0$. At high temperatures, the time evolution is transient in nature with many exponential terms contributing, and it is futile to try to characterize such a situation by a single time scale such as the mean passage time. In any case, the latter can then only be calculated if all eigenvalues $\lambda_i$ and coefficients $S_i$ are known, in which case one might as well calculate (33) properly.[11] It would be interesting whether a time evolution in the adsorbate controlled by several time scales as depicted in Fig. 4 can actually be observed experimentally. For the Xe-W system we expect significant transients for $T \gtrsim 1500$ K; however, the time scales involved are very short, i.e., of the order of $10^{-12}$ sec, presumably too short to be measured. Also recall that at such high temperatures multiphonon processes are expected to contribute significantly also modifying a simple exponential time evolution.

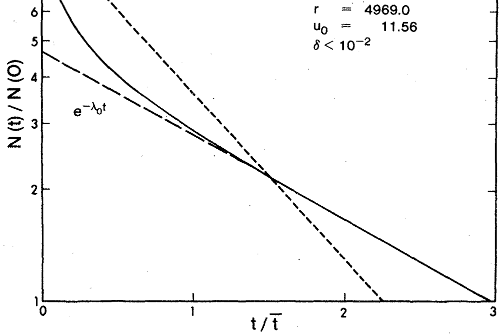

FIG. 5. Time evolution of the adsorbate for a very high temperature. $\bar{t}$ = mean first passage time. Parameters as in Fig. 1.

Let us briefly return to the high-temperature region and observe that for very small $\delta$ all transition probabilities $R_{l l'}$ in (1) and (2) are proportional to $\delta^{-1}$, so that we find for $\delta << 1$

$$\lambda_0 \approx A\delta^{-1} e^{-\delta u_0} \tag{35}$$

and

$$\bar{t} = B\delta e^{\delta u_0} = S^{-1} \frac{h}{k_B T} e^{\delta u_0} , \tag{36}$$

where for the example in Table I we find that $A = 3.3584 \times 10^{9}$, $B = 1.48 \times 10^{-10}$, and $S = 8 \times 10^{-4}$. Equation (36) is a very suggestive result. Recall that a one-dimensional theory is expected to be most adequate for gas-solid systems in which the gas particles in the adsorbate are totally mobile along the surface of the solid. In such a situation "equilibrium theory" predicts that the desorption time should be given by a formula such as (36) with $S$ being the sticking coefficient. Pleasing as this result may be, it must be regarded with caution, because we know from Figs. 1 and 2 that an "equilibrium theory" should only work at low temperatures, i.e., for large $\delta$, whereas (36) is valid for $\delta << 1$, so that it is not clear whether the coefficient $S$ in (36) still has the significance of a sticking coefficient. Without an independent and operational statistical mechanical evaluation of the sticking coefficient such speculations are futile, the more so, because we do not know whether multiphonon processes expected to be important for $\delta << 1$ modify (36) significantly.

Before we pick up our discussion of equilibrium theories let us briefly comment on our choice of plotting $t_d^{-1} e^{\delta u_0}$ as a function of $\delta$ in Figs. 3 and 4. Phenomenology assumes that the desorption time can be parametrized by a Frenkel-Arrhenius formula

TABLE I. *(Continued.)*

| $S_0$ | $S_1$ | $S_2$ | $S_3$ | $S_{100}$ | $S_{240}$ | $(\bar{t})^{-1}$ |
|---|---|---|---|---|---|---|
| 0.845 04 | 0.053 67 | 0.01 344 | 0.23 658 | $5.387\times 10^{-9}$ | $9.49\times 10^{-34}$ | $5.3832\times 10^{9}$ |
| 0.619 59 | 0.125 13 | 0.03 25 | 0.058 64 | $1.344\times 10^{-8}$ | $1.11\times 10^{-32}$ | $3.522\times 10^{10}$ |
| 0.437 86 | 0.168 93 | 0.004 90 | 0.087 27 | $5.077\times 10^{-8}$ | $1.57\times 10^{-31}$ | $6.7145\times 10^{12}$ |
| 0.436 06 | 0.169 28 | 0.04 92 | 0.087 55 | $5.0975\times 10^{-33}$ | $2.8\times 10^{-33}$ | $6.758\times 10^{19}$ |

$$t_d=t_d^0 e^{Q/k_BT} , \tag{37}$$

where $Q$ is the heat of adsorption. Figures 3 and 4 demonstrate that for the exact desorption time as calculated from (2) $Q$ cannot be identified with $U_0$ without assuming some less than linear $T$ dependence in $t_d^0$. Identifying $Q$ with the lowest bound-state energy $Q=-E_0$ produces the dotted curves in Figs. 3 and 4, which make $t_d^0$ somewhat less $T$ dependent. There is thus no natural way to parametrize our theoretical desorption time according to (37) without identifying $Q$ by some other means, calculational or experimental, as the heat of adsorption.

Let us finally add a few clarifying comments on phenomenological equilibrium theories of adsorption and desorption kinetics.[12] One typically argues that the rate of adsorption, i.e., the number of gas particles getting adsorbed per unit time and unit surface area, is

$$r_a=p/(2\pi m k_B T)^{1/2} S(T,\theta) , \tag{38}$$

where $p/(2\pi m k_B T)^{1/2}$ is the equilibrium flux of gas particles passing in one direction through a unit area in the gas with $p$ the gas pressure and $T$ the gas temperature. Within the gas phase an equal flux, of course, flows in the opposite direction. The latter is assumed absent at the wall. If during the adsorption process the gas in the surface region is not kept in equilibrium by rapidly replenishing those gas particles that got adsorbed with particles from the gas phase, then $p/(2\pi m k_B T)^{1/2}$ is not the flux arriving at the surface, and its appearance in (38) is of no significance. The factor $S(T,\theta)$ in (38) is the sticking coefficient, i.e., the probability that a gas particle hitting the surface with coverage $\theta$ gets stuck. Because any adsorbed gas particle desorbs after a while, it is virtually impossible to give a satisfactory microscopic definition of $S(T,\theta)$ outside equilibrium theory from which $S(T,\theta)$ can be calculated. Note, however, that the left-hand side of (38) can be calculated microscopically so that

$$S(T,\theta)=p^{-1}(2\pi m k_B T)^{1/2} r_a \tag{39}$$

can serve as a definition of $S(T,\theta)$.

Because one assumes overall equilibrium the adsorption (38) is cancelled by an equal amount of desorption such that in terms of rates we have,

$$r_d=r_a . \tag{40}$$

In equilibrium the pressure in (38) can be calculated according to Fowler[13] using equilibrium statistical mechanics by equating the chemical potentials of the gas phase and the adsorbate. One finds, e.g., for localized adsorption the generalized Langmuir isotherm

$$p=\frac{\theta}{1-\theta}\frac{k_BT}{h^3}(2\pi m k_B T)^{3/2} e^{-Q/k_BT} , \tag{41}$$

where $Q$ is the heat of adsorption. Using (41) and writing

$$r_d=N_a t_d^{-1} , \tag{42}$$

where $N_a$ is the number of adsorbed particles per unit area and $t_d$ is the desorption time, one finds (37) where the prefactor is

$$(t_d^0)^{-1}=\frac{1}{1-\theta}\frac{k_BT}{h}\frac{2\pi m k_B T}{h^2} S(\theta,T) \tag{43}$$

for localized adsorption or

$$(t_d^0)^{-1}=\frac{k_BT}{h} S(\theta,T) \tag{44}$$

for mobile adsorption of particles without excited internal degrees of freedom. The macroscopic time evolution of the gas-solid system is then controlled by a phenomenological rate equation

$$\frac{dN_a}{dt}=r_a-r_d . \tag{45}$$

If $\theta$ assumes its equilibrium value for given $p$ and $T$, then $r_a = r_d$ and $dN_a/dt = 0$. Reducing $p$ to zero then causes the adsorbate to deplete exponentially with a desorption time $t_d$.

In deriving the generalized Langmuir isotherm one uses the fact that the total partition function of noninteracting subsystems, i.e., adsorbate and free gas, in equilibrium factorizes into a product of two partition functions. This implies that the dynamic part of the interaction $H_{\text{int}}$ between gas particles and the solid in (3) is neglected, an approximation that seems reasonable for the calculation of equilibrium properties. Note, however, that $H_{\text{int}}$ contains the dynamics of phonon-mediated desorption that determines the desorption time in our model. We thus see that in (43) and (44) the sticking coefficient contains all the important dynamic information about the desorption mechanism and should never be guesses or approximated. One can extract the sticking coefficient from the calculated desorption time using (43) and (44) in a temperature region where the adsorbate is maintained in quasiequilibrium throughout the desorption process, i.e., where first-order perturbation theory works. For the example in Fig. 3 this is the case for $\delta \gtrsim 10$, the low-temperature region where desorption times are ridiculously long. In the physically interesting region $100 \lesssim T \lesssim 400$ K, one gets typical values like $S(100\text{ K}) = 0.73$, $S(200\text{ K}) = 0.19$, $S(300\text{ K}) = 0.1$, $S(500\text{ K}) = 0.03$, etc. But even these values cannot be trusted, because we know from Fig. 1 that for these temperatures the adsorbate is not maintained in quasiequilibrium during the desorption process, so that (40) is not valid. Moreover, the derivation of (44) assumes that $t_d$ is factorized uniquely by a Frenkel-Arrhenius formula. To get the above-mentioned values for $S$ we assumed as indicated in Fig. 3 that $Q = U_0$. We might with equal *a priori* right choose $Q = -E_0$, in which case the sticking coefficients would turn out somewhat lower. We would therefore like to make the following points: (a) It seems that a sticking coefficient can only be introduced without difficulty in "equilibrium theories" of desorption, which themselves are of limited validity. (b) To relate the sticking coefficient to the preexponential factor $t_d^0$ in the desorption time, one must assume that the Frenkel-Arrhenius parametrization is given uniquely, a feature that does not have a rigorous basis in a microscopic theory. It seems therefore advisable to base a discussion of desorption phenomena on desorption times directly which appear naturally in kinetic theories based on nonequilibrium quantum statistical mechanics.

## III. PERTURBATION THEORY FOR THE MASTER EQUATION

For gas-solid systems in which the surface potential develops many bound states we have seen[1] that the discrete set of rate equations (2) can be approximated by the continuous master equation (5). Desorption times calculated in various approximations from either (2) or (5) will obviously be very similar so that there is no need to redo the calculations of the previous section for the master equation. Instead we want to develop here, based on first-order perturbation theory of the master equation, a simple analytic expression for the isothermal desorption time at low temperature and for systems with large $r$. As derived from the master equation (31) reads

$$\lambda_0^{(1)} = \frac{\int_{-u_0}^{0} d\epsilon' \rho(\epsilon') \int_0^{\infty} d\epsilon \rho(\epsilon) W(\epsilon,\epsilon') e^{-\delta\epsilon'}}{\int_{-u_0}^{0} d\epsilon'' \rho(\epsilon'') e^{-\delta\epsilon''}} , \tag{46}$$

where the density of states is

$$\rho(\epsilon) = (\,|\epsilon|\,)^{-1/2} \tag{47}$$

and the bound-state—continuum transition probability is given by Eq. (23) in the preceding paper, namely,

$$\begin{aligned} W(\epsilon,\epsilon') = {} & \frac{3\pi}{2} r^{1/2} \omega_D \frac{m}{M_s} (-\epsilon\epsilon')^{1/2} \theta(1+\epsilon') \theta(1+\epsilon'-\epsilon) \{\exp[\delta(\epsilon-\epsilon')]-1\}^{-1} \\ & \times (\epsilon-\epsilon')^3 \frac{\sinh[2\pi(r\epsilon)^{1/2}]}{\sinh^2[\pi(r\epsilon)^{1/2}]+\cos^2[\pi(ru_0)^{1/2}]} \frac{|\Gamma((ru_0)^{1/2}+i(r\epsilon)^{1/2}+\frac{1}{2})|^2}{\Gamma((ru_0)^{1/2}+(-r\epsilon')^{1/2}+\frac{1}{2})\Gamma((ru_0)^{1/2}(-r\epsilon)^{1/2}+\frac{1}{2})} , \end{aligned} \tag{48}$$

where $\theta$ is the step function. To find an approximation for large $r$, we use the following asymptotic expansion for gamma functions for large $x$, derivable from Stirling's formula

$$\frac{\Gamma(x+1+a)}{\Gamma(x+1)} = x^a \exp\left[\sum_{n=2}^{\infty} \frac{B_n(-a)-B_n(0)}{n(n-1)x^{n-2}}\right] , \tag{49}$$

where $B_n(y)$ is a Bernoulli polynomial.[14] We use the expansion

$$\frac{\sinh[2\pi(r\epsilon)^{1/2}]}{\sinh^2[\pi(r\epsilon)^{1/2}]+\cos^2[\pi(ru_0)^{1/2}]} =2+4\sum_{n=1}^{\infty}(-1)^n e^{-2\pi n(r\epsilon)^{1/2}}\cos[2\pi n(ru_0)^{1/2}] \tag{50}$$

in (48) and, writing

$$\lambda_0^{(1)}=N/D\ , \tag{51}$$

$$N=N_0(1+N_1+\cdots)\ , \tag{52}$$

we find

$$N_0=\frac{18\pi u_0^2}{r^{3/2}}\omega_D\frac{m}{M_s} \tag{53}$$

$$N_1=(a^2-a+\tfrac{1}{6})\left[\frac{1}{3(ru_0)^{1/2}}-\frac{\delta}{2r}-\frac{2}{3ru_0}\right] -\frac{10\delta}{3r}+\frac{2}{9ru_0}\ , \tag{54}$$

where $a$ is the fractional part of $(ru_0)^{1/2}-\frac{1}{2}$. Furthermore, for large $\delta u_0$ we have

$$D=\int_{-u_0}^{0}\frac{d\epsilon}{|\epsilon|^{1/2}}e^{-\delta\epsilon}\approx D_0=\frac{1}{\delta u_0^{1/2}}e^{\delta u_0}\ , \tag{55}$$

so that for large $r$ and $\delta u_0$ such that

$$2\delta u_0/\sigma_0>>1\ , \tag{56}$$

we finally get

$$\lambda_0^{(1)}\approx N_0/D_0=\frac{18\pi u_0^{5/2}}{r^{3/2}}\omega_D\frac{m}{M_s}e^{-\delta u_0}\ . \tag{57}$$

Comparing this result with (37) and identifying $t_d^{-1}=\lambda_0^{(1)}$, we find that

$$Q=U_0\ , \tag{58}$$

and the preexponential factor is for $2\delta u_0/\sigma_0>>1$ or $\delta>>\frac{1}{2}(r/u_0)^{1/2}$

$$ {}^{\mathrm{PT}}t_d^0=\omega_D^{-1}\frac{M_s}{m}\frac{r^{3/2}}{18\pi u_0^{5/2}} =\omega_D^{-1}\frac{M_s}{m}\left[\frac{\hbar\omega_D}{U_0}\right]^4\left[\frac{2mU_0}{\hbar^2\gamma^2}\right]^{3/2}\ , \tag{59}$$

the superscript PT indicating that this expression has been derived in perturbation theory. This explicit expression has been obtained from a well-defined microscopic model by means of mathematically acceptable approximations. It is important to note its nontrivial dependence on the parameters $U_0$ and $\gamma$ of the surface potential and on the Debye frequency $\omega_D$ of the solid as a consequence of the phonon-mediated dynamic coupling between solid and gas. This is in contrast to certain equilibrium theories[12] where the preexponential factor $t_d^0$ is identified as proportional to the inverse of the frequency $\omega_{\mathrm{class}}$ with which an adparticle of mass $m$ oscillates classically at the bottom of the surface potential, i.e.,

$$\omega_{\mathrm{class}}=\left[\frac{2U_0\gamma^2}{m}\right]^{1/2}\ . \tag{60}$$

To get this one argues that the rate of desorption is given by the frequency, with which the adparticle at the bottom of the surface potential well hits the wall of height $Q$, times the probability that it at that time acquired the activation energy $Q$, presumably supplied by the thermal motion of the solid, to escape. Such a line of thought can at best serve for an interpretation of the result of a microscopic theory but cannot serve as a basis for one, as it does not allow for any dynamics.

Rewriting (59) with (60) we have

$$t_d^0=\frac{2\pi}{\omega_{\mathrm{class}}}\left[\frac{1}{18\pi^2}\frac{M_s}{m}\frac{r}{u_0^2}\right] \tag{61}$$

and find that for the Xe-W system with $r=4969$ and $u_0=11.56$ the factor in large parentheses amounts to about 0.3. The fact that numerically $2\pi/\omega_{\mathrm{class}}$ is quite reasonable, however, is no justification for accepting it as a basic ingredient of a theory of desorption. Let us also note that in (59) $t_d^0$ is proportional to the ratio $M_s/m$ of the masses of an atom of the solid $M_s$ and of an adparticle $m$. Classical theories will typically produce a dependence of $t_d^0$ on $(M_s/m)^{1/2}$, which is simply a reflection of a similar dependence of the classical frequency (60) of the harmonic oscillators used in such theories. We have plotted (59) in Figs. 3 and 4 and see that indeed for $2\delta u_0/\sigma_0>>1$ it is an acceptable approximation.

Classical theories[8] that produce prefactors $t_d^0$ that only depend on static parameters such as $\omega_{\mathrm{class}}$ and $k_BT$ typically do not calculate desorption times *per se*, but rather delay times experienced by a gas particle scattering off the surface of a solid. Such delay times are obviously not identical to desorption times and can indeed be quite different as one can see by considering a situation where the gas-solid interaction is such that gas particles cannot gain or loose energy to the solid. Desorption is then not possible and $t_d$ is infinite. However, a particle scattering from the solid will still be delayed in an elastic collision.

## IV. RELAXATION TIMES FROM THE FOKKER-PLANCK EQUATION

In this section we want to calculate the desorption time from the Fokker-Planck equation (6) which we showed in the preceding paper to be an acceptable approximation to the master equation (5) for large $r$ and for intermediate temperatures such that

$$\frac{5}{3u_0} << \delta << \left[\frac{2}{5}\frac{r}{u_0}\right]^{1/2} . \tag{62}$$

Let us look again at isothermal desorption. We must solve (6) with the boundary conditions that

$$n(\epsilon,t)=0 \quad \text{for } \epsilon \geq 0,\ t>0 \tag{63}$$

reflecting the fact that all desorbing particles are pumped out of the system instantaneously. As a second boundary condition we demand that

$$\frac{\partial n(\epsilon,t)}{\partial\epsilon}=0 \quad \text{for } \epsilon \geq 0,\ t>0 . \tag{64}$$

We have argued above that at temperatures $k_B T \leq \hbar\omega_D$ the strong bound-state—bound-state transitions guarantee that an equilibrium occupation is maintained within the surface potential with the total number of adparticles decreasing exponentially. We therefore solve (6) approximately by an ansatz;

$$\begin{aligned} n_0(\epsilon,t)&=n_0(\epsilon)e^{-\lambda_d t} , \\ n_0(\epsilon)&=A(e^{-\delta\epsilon}-1) . \end{aligned} \tag{65}$$

Integrating (6) over $\epsilon$ we get

$$\begin{aligned} &-\lambda_d \int_{-u_0}^{0} d\epsilon\, \rho(\epsilon) n_0(\epsilon) \\ &= \left[ -\alpha_1(\epsilon)\rho(\epsilon)\, n_0(\epsilon)+\frac{1}{2}\frac{\partial\alpha_2(\epsilon)\rho(\epsilon)n_0(\epsilon)}{\partial\epsilon} \right]\Bigg|_{-u_0}^{0} . \end{aligned} \tag{66}$$

But note that in the large-$r$ limit we see from Eqs. (69) and (70) of the preceding paper[1] that

$$\alpha_1(-u_0)=\alpha_2(-u_0)=\left.\frac{\partial\alpha_2(\epsilon)}{\partial\epsilon}\right|_{\epsilon=-u_0}=0 , \tag{67}$$

so that (66) reduces to

$$\lambda_d=\tfrac{1}{2}\delta\alpha_2(0)\Big/\int_{-u_0}^{0} d\epsilon\, \rho(\epsilon) n_0(\epsilon) , \tag{68}$$

which for large enough $\delta u_0$ simplifies with equation (70) of the preceding paper to

$${}^{\mathrm{FP}}t_d=\lambda_d^{-1}=\frac{1}{72\pi}\omega_D^{-1}\frac{M_s}{m}\frac{r^2}{\delta u_0^3}e^{\delta u_0} , \tag{69}$$

valid for large $r$ and intermediate temperatures such that the inequalities (62) are satisfied. We have plotted (69) in Figs. 3 and 4, where it is denoted as the Fokker-Planck approximation ${}^{\mathrm{FP}}t_d$ to the desorption time. It is amazing to see how good an approximation (69) is for larger $r$, see Fig. 3, particularly in the temperature region $0.5<\delta<3$ of interest for the Xe-W system.

It has been the aim of this paper to derive from the microscopic model (2) simple analytic expressions for the isothermal desorption time. In the limit of large $r$ and $u_0$ we found two, namely ${}^{\mathrm{PT}}t_d$, given in (59) and derived from perturbation theory in the low-temperature region $2\delta u_0/\sigma_0>>1$ and ${}^{\mathrm{FP}}t_d$ given in (69) and derived from the Fokker-Planck equation in the temperature region (62). These two approximations are plotted again together with the exact desorption times in Fig. 6 for three different systems. We see clearly that ${}^{\mathrm{PT}}t_d$ is a lower bound on $t_d$ in the low-temperature region, whereas ${}^{\mathrm{FP}}t_d$ gives a bound in the temperature region (62). Indeed, these bounds are better for larger $\sigma_0$ or $r$ and can therefore be used with confidence to estimate desorption times for such gas-solid systems. Note that the preexponentials in (59) and (69) depend quite strongly on the heat of adsorption, i.e., *cum grano salis* on $u_0$. The $r$ dependence of the preexponentials can be used to

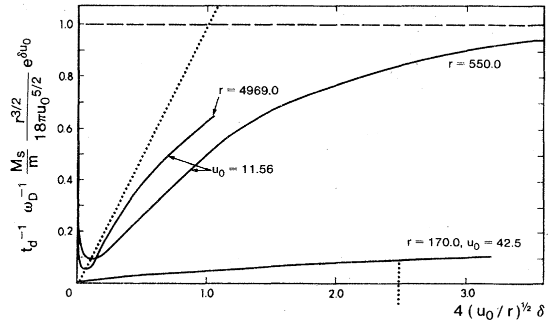

FIG. 6. Test for the approximate desorption times ${}^{\mathrm{PT}}t_d$ (dashed line) and ${}^{\mathrm{FP}}t_d$ (dotted line) for three different systems. The curves with $u_0=11.56$ have $\hbar\omega_D/k_B=405$ K and $m/M_s=0.714$ appropriate for the Xe-W system. The lowest curve with $u_0=42.5$ has $\hbar\omega_D/k_B=450$ K and $m/M_s=0.277$ for the CO-Ru system.

estimate the range of the surface potential.

In summarizing the main results of this paper, let us repeat once more the motivation behind it. Theoretical attempts at physisorption kinetics fall basically into three classes. Starting with the most sophisticated there are first the microscopic models based on quantum statistical mechanics, in which the dynamic phonon-mediated coupling between gas and solid supplies the necessary energy for a particle in the adsorbate to desorb.[15] Up until very recently such models were restricted to deal with one-phonon processes, calculated in second-order time-dependent perturbation theory (Fermi's golden rule), i.e., to gas-solid systems where the adparticle was trapped in a shallow bound state of the surface potential from which it would desorb by adsorbing a single phonon. Recently this restriction has been removed in two separate extensions of the model. In Ref. 10 we have performed a complete fourth-order calculation of one- and two-phonon processes, which among other results yields explicit criteria for the validity of one-phonon theories. In addition, various approximate multiphonon theories have been proposed.[16] The second direction of extending the microscopic theory is the study of gas-solid systems in which the surface potential develops many bound states from which desorption takes place via multiphonon cascades and controlled by rate equations such as (1) and (2).[1-3] Based on the latter with the individual transition probabilities $R_{\iota\iota'}$ accounting for one-phonon processes only, we have studied physisorption kinetics in Ref. 1 without any further approximation, calculating desorption times for a varieity of gas-solid systems such as He-Lif, He-graphite, Xe-W, etc. Because these studies are fairly involved both analytically and numerically we have addressed ourselves in this and the preceding paper to the problem of simplifying the theory invoking well-defined and numerically justifiable mathematical approximations. The desorption times in (59) and (69) are the main results of this endeavor. They can serve as estimates in their respective temperature range of validity for weakly coupled gas-solid systems as Figs. 3, 4, and 6 demonstrate.

The second class of models for physisorption kinetics are those based on classical dynamics. The most sophisticated of these is the cascade model by Pagni and Keck[17] and Pagni,[7] which starts from a master equation similar to (5), however, with the kernels $W(\epsilon',\epsilon)$ calculated using classical rather than quantum mechanics. Many of their conclusions remain valid under the scrutiny of the quantum-mechanical models. The bulk of the classical models,[8] however, is far less sophisticated. Most of them assume from the onset that the adsorbate remains in quasiequilibrium during the desorption process. This is generally not warranted as Figs. 1 and 2 demonstrate. Prefactors $t_d^0$ in (37) calculated in many such theories typically depend on $T$, the depth of the surface potential $U_0$ and perhaps the classical frequency (60). We would like to repeat our argument that such theories are principally incomplete, because adsorption and physisorption processes are energy dissipating and cannot be described by the above static parameters alone. Indeed, what is assumed implicitly in such theories apart from the (unjustified) equilibrium hypothesis is that the sticking coefficient $S$ is unity. But as we argued below Eq. (45), $S$ reflects the dynamic information about the energy-dissipating processes. The simplicity of these models can thus be physically quite misleading. As the mathematics involved in some of these classical models is at the same level of complication as the more fundamental quantum statistical models, and as their logical foundation is sometimes quite shaky, we feel that classical theories have outlived their usefulness, in particular since we are now able to derive simple analytic expressions for desorption times similiar to (59) and (60) from sophisticated quantum statistical models.

The third class of attempts to understand physisorption kinetics is phenomenological in nature, with an example outlined in Eqs. (38)–(45). Though such models can be useful in evaluating experiments, one must always bear in mind that their *a priori* equilibrium assumption is quite frequently not warranted.

As for the quantum statistical model based on Eqs. (1) and (2), we should be aware of its limitations as well. Sharing this feature with most classical models, it is one-dimensional and thus most adequate for gas-solid systems with mobile adsorbates. Attempts at three-dimensional theories[18] imply that the dimensionality of the problem does not affect the order of magnitude of the desorption time. Yet a full-fledged three-dimensional version of the present theory would be desirable and is in preparation. Similarly, the use of a Debye spectrum for the phonons can be relaxed, and more realistic spectra including surface modes can be incorporated but are not expected to change numbers by more than a factor of 2 or 3.[19]

The transition probabilities $R_{\iota\iota'}$ in (1) and (2) are so far calculated in second-order time-dependent perturbation theory (Fermi's golden rule) and thus take account of one-phonon processes only. This obviously puts restrictions on the kind of gas-solid systems that can be described. In particular, we must demand that any two neighboring bound states in the surface potential can be linked by a one-phonon process. As the deepest two bound states are separated the farthest, this implies for a Morse potential that

$$\hbar\omega_D \geq |E_0 - E_1| \tag{70}$$

or in terms of our dimensionless parameters

$$2(\sigma_0 - 1) \leq r \quad \text{or} \quad r \geq 4u_0 \,, \tag{71}$$

where we used the fact that for most gas-solid systems $\sigma_0 >> 1$. This inequality implies a lower limit on the preexponential factor in (39) which we can get from either (59) or (69).[20] From the former we find for $\delta << \frac{1}{2}(r/u_0)^{1/2}$

$$^{\mathrm{PT}}t_d^0 \geq \omega_D^{-1} \frac{M_s}{m} \frac{4}{9\pi} \frac{1}{u_0} = \frac{M_s}{m} \frac{4\hbar}{9\pi} \frac{1}{U_0} \tag{72}$$

and the latter yields for $5/3u_0 >> \sigma >> (2r/5u_0)^{1/2}$

$$^{\mathrm{FP}}t_d^0 \geq \omega_D^{-1} \frac{M_s}{m} \frac{2}{9\pi} \frac{1}{u_0\delta} = \omega_D^{-1} \frac{M_s}{m} \frac{2}{9\pi} \frac{k_B T}{U_0} \,. \tag{73}$$

Note that these two estimates, resulting from two quite different approximation schemes and valid in two different temperature regimes, are identical apart from the temperature factor $\frac{1}{2}k_B T/\hbar\omega_D$ in $^{\mathrm{FP}}t_d^0$. Also recall that both are valid for large $r$ and $u_0$. Let us apply (72) to the Xe-W system for which $u_0 = 11.56$. We get $t_d^0 \geq 3.2 \times 10^{-16}$ sec, whereas experiment says that $t_d^0 \approx 10^{-15\pm1}$ sec. We would, however, caution the reader that our estimate above is not too stringent and out at $\delta = 1$ by about a factor 15 because $r = 4u_0 = 46.24$ is not a large number for (59) or (69) to be good approximations. Such an $r$ value implies that the Xe-W surface potential would have a range $\gamma^{-1} = 0.15$ Å which, it seems to us, is too small to be acceptable without reservation.[21] It might actually reflect the fact that Xe gets weakly chemisorbed on W. Let us then look at gas-solid systems with large heats of adsorption. They typically show chemisorption, i.e., the gas particle undergoes some structural rearrangement as it gets adsorbed. We feel that such a process cannot adequately be described by a model, appropriate for physisorption, in which the gas particle otherwise unchanged gets trapped into the bound states of the surface potential. With these misgivings in mind, that seem to be of amazingly little or no concern in some of the literature, let us look at the CO-Ni system. Ibach *et al.*[22] measure in the low coverage regime $Q \approx 150$ kJ/mol and $t_d^0 \approx 10^{-17}$ sec. With $\hbar\omega_D/k_B = 400$ K for Ni, we get from (72) that $t_d^0 \gtrsim 10^{-15}$ sec, i.e., not quite as fast as the experiment requires. For the CO-Ru (001) system measured by Pfnür *et al.*[23] we get with $u_0 = 42.5$ $t_d^0 \gtrsim 10^{-16}$ sec overlapping with their experimental value $t_d^0 = 10^{-16}$ sec. Similar conclusions can be reached for the systems Cu-W, Ag-W, and Au-W measured by Bauer *et al.*[24] Our microscopic model is thus quite capable of producing very small preexponential factors $t_d^0$. Let us, however, stress once more that the ability of our theory to yield very small preexponential factors $t_d^0$ does not explain fast desorption in chemisorption systems but should only be taken as an encouragement to extend our line of attack, so far restricted to physisorption, to phenomena in chemisorption. An analysis of desorption data with Eqs. (59) and (69) or (72) and (73) should at this stage be viewed as complementing the phenomenology based on equilibrium or transition state theories to get a more complete understanding of desorption kinetics.

## ACKNOWLEDGMENT

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[1] Z. W. Gortel, H. J. Kreuzer, R. Teshima, and L. A. Turski, preceding paper, Phys. Rev. B 24, 4456 (1981).

[2] Z. W. Gortel, H. J. Kreuzer, and R. Teshima, Phys. Rev. B 22, 5655 (1980).

[3] A similar set of rate equations has recently been studied by Gopa Sorkar De, U. Landman, and M. Rasolt, Phys. Rev. B 21, 3256 (1980); S. Efrima, K. F. Freed, D. Jedrzejek, and H. Metiu, Chem. Phys. Lett. 74, 43 (1980).

[4] S. K. Kim, J. Chem. Phys. 28, 1057 (1958).

[5] H. J. Dresser, T. E. Madey, and J. T. Yates Jr., J. Chem. Phys. 55, 3236 (1971); Surf. Sci. 42, 533 (1974). These authors measure the desorption time for the Xe-W system to be $t_d^{-1}=(10^{15\pm1}\text{ sec})\exp[(4662\text{ K})/T]$

[6] This choice of parameters yields a desorption time for the Xe-W system that is $2-3$ orders of magnitude too large. To get better agreement one must choose $\gamma^{-1}\approx 0.5$ Å as done below. See Ref. 2.

[7] P. J. Pagni, J. Chem. Phys. 58, 2940 (1973).

[8] See, e.g., P. Jewsbury and J. L. Beeby, J. Phys. C 8, 3541 (1975), S. Holloway and P. Jewsbury, *ibid.* 9, 1907 (1975), or G. Armand, Surf. Sci. 66, 321 (1977) for a recent selection of such classical equilibrium theories of desorption and for references to earlier work.

[9] E. W. Montroll and K. E. Shuler, Adv. Chem. Phys. 1, 361 (1958).

[10] Z. W. Gortel, H. J. Kreuzer, and R. Teshima, Phys. Rev. B 22, 512 (1980); Chem. Phys. Lett. 73, 365 (1980).

[11] An approximate calculation of $\bar{t}$ for a simplified version of the model contained in Eqs. (1) and (2) has been given by De *et al.* in Ref. 3.

[12] These theories are presented in any book on surface kinetics, see, e.g., A. Clark, *The Theory of Adsorption and Catalysis* (Academic, New York, 1970), F. C. Tompkins, *Chemisorption of Gases on Metals* (Academic, New York, 1978), and G. Wedler, *Chemisorption: An Experimental Approach* (Butterworths, London, 1976), where some of the history can be traced.

[13] R. H. Fowler, Proc. Camb. Philos. Soc. 32, 144 (1936).

[14] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products,* 4th ed. (Academic, New York, 1965), p. 1077.

[15] These models were introduced in a series of papers: J. E. Lennard-Jones and C. Strachan, Proc. R. Soc. London Ser. A 150, 442 (1935); J. E. Lennard-Jones and A. Devonshire, *ibid.* 156, 6 (1936); 156, 29 (1936).

[16] See, e.g., the paper by Efrima *et al.* in Ref. 3.

[17] P. J. Pagni and J. C. Keck, J. Chem. Phys. 58, 1162 (1972).

[18] Z. W. Gortel, H. J. Kreuzer, and D. Spaner, J. Chem. Phys. 72, 234 (1980); B. Bendow and S. C. Ying, Phys. Rev. B 7, 622 (1973); 7, 637 (1973).

[19] A promising line of approach is that used in a slightly different context by A. C. Diebold, S. A. Adelman, and C. Y. Mou, J. Chem. Phys. 71, 3236 (1979). Desorption kinetics mediated by surface phonons have now been calculated by E. Goldys, Z. W. Gortel, and H. J. Kreuzer, Surf. Sci. (in press).

[20] In Ref. 8 G. Armand also finds lower limits on $t_d^0$ based on estimates of classical adparticle frequencies (60) and other factors appearing in his classical equilibrium theory.

[21] The object of desorption theories is to understand and reproduce desorption times that are given experimentally as a two-parameter Frenkel-Arrhenius fit (38). Physisorption theories all have as one of their ingredients a surface potential that is also characterized by two parameters, namely, depth $U_0$ and range $\gamma^{-1}$. Fixing $U_0=Q$ then forces one to fit $\gamma^{-1}$ to reproduce the preexponential factor $t_d^0$. This is not a problem . One must, therefore, be very aware that the resulting numbers, in particular $\gamma^{-1}$, are reasonable. If, e.g., Holloway and Jewsbury in their theory (see Ref. 8) must choose $\gamma^{-1}=0.09$ Å for the Ga-GaAs system, more caution should be exercised.

[22] H. Ibach, W. Erley, and H. Wagner, Surf. Sci. 92, 29 (1980). This article gives a detailed discussion of desorption data in terms of the phenomenological equilibrium theory.

[23] H. Pfnür, P. Feulner, H. A. Engelhoodt, and D. Menzel, Chem. Phys. Lett. 59, 481 (1978).

[24] E. Bauer, F. Bonczek, H. Poppa, and G. Todd, Surf. Sci. 53, 87 (1975).