PHYSICAL REVIEW B VOLUME 22, NUMBER 12 15 DECEMBER 1980

Desorption by phonon cascades for gas-solid systems with many physisorbed surface bound states

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(Received 16 June 1980)

We give the extension of our quantum-statistical theory of desorption for systems with many physisorbed bound states in the surface potential. Rate equations are set up and the desorption time t_d is properly identified as the smallest eigenvalue of the matrix of transition probabilities. The latter are calculated exactly in second-order perturbation theory for a surface Morse potential. We show that desorption in weakly coupled systems with many bound states proceeds predominantly through one-phonon cascades. Two-phonon contributions are shown to be small. Desorption times are calculated for the He-LiF, He-NaF, He-graphite, H-NaCl, He-Ar, and Xe-W systems. The temperature regime over which a Frenkel-Arrhenius parametrization $t_d = t_d^0 \exp(Q/k_B T)$ can be invoked is given. Our theory which is essentially parameter-free produces prefactors t_d^0 in the whole experimental range of physisorption from 10^{-7} to 10^{-14} sec.

I. INTRODUCTION

In a series of papers[1-7] we have developed a quantum-statistical theory of desorption of a gas from the surface of a solid in systems which show physisorption at low coverage, i.e., in which no chemical reactions take place during the adsorption process and in which interactions between particles in the adsorbate can be neglected. So far we have restricted ourselves to systems in which the surface potential, i.e., the net static interaction between the particles of the gas and solid phases develops just one shallow bound state as is the case, e.g., for helium adsorbed on Constantan, a Cu-Ni alloy.[8] For this and related systems we have calculated isothermal and flash desorption times for phonon-mediated desorption, taking account of one-phonon processes in second-order time-dependent perturbation theory.[1-5]

Even for gas-solid systems where the surface potential develops just one shallow bound state the question arises as to the suitability of second-order perturbation theory. We have therefore performed a complete fourth-order calculation including all one- and two-phonon processes as they arise from the phonon-mediated gas-solid interaction including terms up to third order in the derivative of the surface potential.[5-7] Our main conclusions, substantiated by extensive numerical work, were that a relaxation-time description of desorption from a bound state E_0 is possible as long as $h/|E_0| \ll t_d$, where t_d is the isothermal desorption time. Such systems we called descriptively weakly coupled. We found in addition that a second-order calculation of t_d can be trusted as long as $|E_0| \lesssim k_B T \lesssim \hbar\omega_D$, where $\hbar\omega_D$ is the Debye energy of the solid. Fourth-order contributions become important for $|E_0| < \hbar\omega_D$ and $k_B T \gtrsim \hbar\omega_D$. Moreover, for the range $\hbar\omega_D \leq |E_0| \leq 2\hbar\omega_D$ fourth-order terms are essential because second-order contributions are zero in this region of bound-state energies.

Most gas-solid systems showing physisorption have surface potentials that develop more than one bound state. For example, the He-LiF (Ref. 9), He-NaF (Ref. 9), H-LiF (Ref. 9), and H-NaCl (Ref. 10) systems have all four bound states, whereas the He-graphite[11,12] system develops five bound states. Before we develop in this paper a quantum-statistical theory of desorption for such systems, we must first look at the problem phenomenologically to see what is measured and which quantities must be calculated in the microscopic theory. We consider isothermal desorption. Experimentally one prepares a gas-solid system in equilibrium at a gas pressure P and a temperature T. If at time $t=0$ the gas pressure is suddenly reduced substantially, theoretically to $P=0$ keeping the solid at a temperature T, the adsorbate, i.e., the gas particles trapped in the bound states of the surface potential, desorb in a characteristic time t_d which is typically measured as a function of temperature.

Let us assume that the static surface potential develops bound states at energies $E_0, \ldots, E_N$ into which gas particles can be trapped. Under conditions of low coverage $\theta \ll \theta_{\max}$, the ith bound state has a relative occupancy in thermal equilibrium at pressure P and temperature T given by

$$n_i = e^{\beta(E_i - \mu)} \ll 1 , \qquad (1)$$

where $\mu = \mu_g$ is the chemical potential in the gas phase. In an isothermal desorption experiment, i.e., after a sudden substantial pressure reduction in the gas phase, the occupation numbers n_i will deplete as a function of time due to transitions between bound states and into the continuum for which we assume the following set of rate equations to be valid:

$$\frac{dn_i(t)}{dt} = -\left(R_{ci} + \sum_{j=0,\, j\neq i}^{N} R_{ji}\right) n_i + \sum_{j=0,\, j\neq i}^{N} R_{ij} n_j, \qquad i = 0, \ldots, N \tag{2}$$

where R_{ji} is the probability for a transition of a gas particle from the ith into the jth bound state of the surface potential, and R_{ci} is the probability for a transition from the ith bound state into the continuum. In an isothermal experiment no transitions from the continuum into any of the bound states can take place because the gas is pumped out. The set of rate equations (2) is not necessarily valid at high coverage, because then nonlinear terms in n_j may have to be included to account for the blocking of occupied states.

To find the connection between the isothermal desorption time t_d and the transition probabilities R_{ij} and R_{ci} we write (2) in matrix notation

$$\dot{\vec{n}} = -\vec{R}\vec{n}, \tag{3}$$

where $\vec{n}$ is the $(N+1)$ dimensional column matrix with elements $n_0, \ldots, n_N$, and $\vec{R}$ is the $(N+1) \times (N+1)$ matrix of transition probabilities. To evaluate the formal solution of (3),

$$\vec{n}(t) = e^{-\vec{R}t}\vec{n}(0), \tag{4}$$

we diagonalize the transition matrix

$$\vec{R}\vec{e}^{\,(i)} = \lambda_i \vec{e}^{\,(i)}, \tag{5}$$

where all eigenvalues λ_i are real and positive and assumed to be ordered $\lambda_0 < \lambda_1 < \cdots < \lambda_N$. Equation (4) can now be written

$$\vec{n}(t) = \sum_{i=0}^{N} f_i e^{-\lambda_i t} \vec{e}^{\,(i)}, \tag{6}$$

where the f_i's are determined by inverting

$$n_i(0) = n_i = \sum_{j=0}^{N} f_j e_i^{(j)}, \tag{7}$$

where $e_i^{(j)}$ is the ith component of the jth eigenvector, and n_i is given by (1). Note that the $\vec{e}^{\,(j)}$'s are not orthogonal because $\vec{R}$ is not symmetric.

The total (relative) adsorbate occupancy is given by

$$\frac{N(t)}{N(0)} = \sum_{i=0}^{N} \frac{n_i(t)}{N(0)} = \sum_{i=0}^{N} S_i e^{-\lambda_i t} \tag{8}$$

where

$$N(0) = \sum_{l=0}^{N} n_l$$

and

$$S_i = \sum_{l=0}^{N} \frac{n_l}{N(0)} \tilde{e}_l^{(i)} \sum_{k=0}^{N} e_k^{(i)}, \tag{9}$$

where $\tilde{e}_l^{(i)}$ is determined such that

$$\sum_{l=0}^{N} \tilde{e}_l^{(i)} e_l^{(j)} = \delta_{ij}. \tag{10}$$

Writing (8) as

$$\frac{N(t)}{N(0)} = S_0 e^{-\lambda_0 t}\left(1 + \sum_{j=1}^{N} \frac{S_j}{S_0} e^{-(\lambda_j - \lambda_0)t}\right), \tag{11}$$

we see that for times $t \gg (\lambda_j - \lambda_0)^{-1}$ for $j = 1, \ldots, N$ all transients have died out and the time evolution can be characterized by a single time scale

$$t_d = \lambda_0^{-1}, \tag{12}$$

provided that S_0 is not substantially smaller than any of the S_j for $j > 0$. This will be borne out by our numerical examples. Also note that $\sum_{j=0}^{N} S_j = 1$.

So far we have looked at the problem of isothermal desorption from many bound states phenomenologically. A quantum-statistical theory must provide us with the transition probabilities R_{ci} and R_{ji} in (2) and (3). To calculate the latter we set up in the next section the Hamiltonian of gas-solid systems in which the gas particles in the adsorbate are mobile in the lateral direction along the surface of the solid. Such systems can be treated adequately in a one-dimensional theory if band effects due to the lateral motion along the surface are negligible as we will show in some detail in Appendix A where some misconceptions and errors in the literature are cleared up. Though we have used in most of our previous work[1-7] a separable nonlocal surface potential, we prefer here for gas-solid systems with many bound states to use a Morse potential to account for the net interaction between particles in the gas and solid phases, respectively. Properly normalized bound state and continuum wave functions of the Morse potential are listed in Appendix B.

We assume that the dynamic part of the gas-solid Hamiltonian causing gas particles to undergo bound state-bound state and bound state-continuum transitions is due to the coupling of gas particles to the phonon system of the solid. These phonon-mediated transition probabilities are calculated in Sec. III in second-order time-dependent perturbation theory accounting for one-phonon processes.

Section IV is devoted to numerical results. We start with an analytical discussion of a model gas-solid system with two bound states in its surface potential. We show that in the low-temperature region the isothermal desorption time is, indeed, given by (12) and can be parametrized by a Frenkel-Arrhenius formula $t_d = t_d^0 \exp(Q/k_B T)$ where the activation energy is approximately equal to the energy of the lowest bound state and the prefactor t_d^0 is determined by the shallower bound state. In this subsection we also discuss numerically the dependence of t_d on the shift x_0 of the Morse potential (20) away from the wall.

Section IV B deals with systems with a few shallow bound states. We give in Table I isothermal desorption times for systems like ^{4}He-LiF, ^{4}He-NaF, and ^{4}He on graphite in the relevant temperature regime where they might be measured. We discuss the importance of bound state-bound state transitions in such systems.

In Sec. IV C we look at gas-solid systems with deep bound states like H on NaCl, He on solid Ar, and some model systems with many bound states. Even in systems where the lowest bound-state energy is in magnitude as large as 10 to 25 times $\hbar\omega_D$ (i.e., $Q \sim$ kcal/mole) desorption can occur for $T \lesssim \hbar\omega_D/k_B$ in milliseconds to seconds via cascades of one-phonon transitions from the lowest bound state through the sequence of all the higher ones. Indeed, our theory produces prefactors t_d^0 as small as 10^{-14} sec for systems with $Q \sim$ kcal/mole. In this subsection we also show, relying on our previous work,[6,7] that for weakly coupled gas-solid systems two-phonon processes are negligible.

Our quantum-statistical theory of desorption is now capable of dealing with gas-solid systems with activation energies Q ranging from fractions of $\hbar\omega_D$ (such as He-Constantan, He-LiF, etc.) to values of the order of kcal/mole (i.e., more than $10\hbar\omega_D$). The calculated prefactors t_d^0 range from 10^{-7} sec in He-Constantan to as short as 10^{-14} sec in one and the same theory.

II. THE HAMILTONIAN OF THE GAS-SOLID SYSTEM

To calculate the transition probabilities R_{ji} and R_{ci} we must specify the Hamiltonian dynamics of the gas-solid system. In cases of low coverage the interaction between the particles of the adsorbate can be neglected, and a single particle picture is appropriate for the gas-solid interaction. If the adsorption occurs at localized adsorption sites then the static surface potential is localized as well. For such a system with just one shallow bound state we have calculated flash desorption times in a fully three-dimensional theory[1] and shown numerically that these results agree quite well with predictions given by a one-dimensional theory. For systems such as He-LiF and He-graphite it is known that more or less free lateral motion within the adsorbate along the surface of the solid occurs.[9-12] For such mobile adsorption the static surface potential can be modeled by[13]

$$V(\vec{r}) = V_0(x) + V_1(x) f(\vec{R}) , \qquad (13)$$

where $\vec{r} = (x, \vec{R})$ and $f(\vec{R})$ is a periodic function in the surface plane and $V_0(x)$ and $V_1(x)$ vanish away from the wall, i.e., for $x \to \infty$. If band-structure effects for lateral motion are not important, as it seems to be in the He-LiF and He-graphite systems, one can neglect the second term in (13). This in turn implies that the calculation of desorption can be carried out in a one-dimensional model due to the fact that phonon-induced transitions between different states of lateral motion of a gas

TABLE I. Bound-state energies $|E_n|/k_B$ in Kelvin, experimental and calculated for Morse potential (20) with different potential parameters. The fourth bound state (?) in ^{4}He-NaF has been observed but not resolved.

System	^{4}He-LiF			^{4}He-NaF		^{4}He-graphite			H-NaCl		He-Ar		
γ^{-1}(Å)	1.09	1.09		0.97		0.95	0.95		1.78		1.09	1.49	1.98
n \ U_0(K)	81.75	89.0	Expt.[a]	77.78	Expt.[a]	160.54	171.34	Expt.[b]	399.3	Expt.[c]	171.93	164.63	160.07
0	62.69	68.47	68.47	57.10	57.10	129.33	139.03	139.03	346.08	351.63	143.6	144.2	144.3
1	32.16	36.45	28.55	25.30	21.70	77.04	84.54	73.46	251.03	247.18	94.5	107.4	116.1
2	11.72	11.43	9.05	6.27	6.27	38.21	43.53	34.07	171.21	165.95	55.7	76.0	90.9
3	1.38	2.44	2.44		?	12.86	16.01	11.49	106.61	110.25	27.0	50.0	68.8
4						0.98	1.97	1.97	57.24		8.64	29.5	49.9
5									23.10		0.46	14.3	33.9
6									4.19			4.57	21.0
7												0.24	11.2
8													4.43
9													0.80

[a] Reference 9.

[b] References 11 and 12.

[c] Reference 10.

particle are negligible as shown in detail in Appendix A. We can therefore write the total Hamiltonian of the gas-solid system as

$$H = H_{\mathrm{st}} + H_{\mathrm{s}} + H_{\mathrm{dyn}} , \tag{14}$$

where

$$H_{\mathrm{st}} = \sum_q E_q \alpha_q^\dagger \alpha_q , \tag{15}$$

where q labels both the bound states of energy E_0, $\ldots, E_N$ and the continuum $E_k = \hbar^2 k^2/2m$. The $\alpha_q^\dagger$'s and α_q's are creation and annihilation operators of a gas particle in state q. Likewise

$$H_{\mathrm{s}} = \sum_p \hbar \omega_p b_p^\dagger b_p \tag{16}$$

is the Hamiltonian of the solid in the harmonic approximation with $b_p^\dagger$ and b_p the creation and annihilation operators of longitudinal acoustic phonons of frequency ω_p.

In this paper we use a simple Debye spectrum for the phonon system of the solid with the Debye temperature appropriate for an infinite solid.[14] More realistic phonon spectra, e.g., the modification of the bulk spectrum due to the presence of the surface, are not expected to change the results in a qualitative way. As uncertainties in the static surface potential already imply variations in the calculated desorption times by a factor of 2, we see no point of complicating the theory at this stage. Optical phonons, on the other hand, are unimportant for desorption from shallow bound states. They contribute to a few bound state-continuum transition probabilities for which, as we will see in Sec. IV, cascades of one-acoustic-phonon processes are more effective.

The phonon-mediated gas-solid interaction is accounted for in the dynamic part of the Hamiltonian which in lowest order in the harmonic approximation is given by

$$H_{\mathrm{dyn}} = L^{-1} \sum_{q,q'} X(q,q') \alpha_q^\dagger \sum_p \omega_p^{-1/2} (b_p^\dagger + b_p) \alpha_{q'} , \tag{17}$$

where for a local surface potential we have

$$X(q,q') = L \left(\frac{\hbar}{2M_{\mathrm{s}} N_{\mathrm{s}}} \right)^{1/2} \int \phi_q^*(x) \frac{dV_0(x)}{dx} \phi_{q'}(x) dx , \tag{18}$$

where the $\phi_q(x)$'s are eigenfunctions of H_{st}, i.e.,

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_0(x) \right) \phi_q(x) = E_q \phi_q(x) . \tag{19}$$

M_{s} is the mass of a particle of the solid of which there are N_{s} in total, and L is the size of the normalization box for the gas. Note that (17) is appropriate for a second-order perturbation calculation of desorption times; higher-order derivatives in the surface potential and thus higher powers of $(b_p + b_p^\dagger)$ must be included for higher orders.[7] To arrive at (18) one uses the fact that the wave function of a gas particle vanishes sufficiently quickly inside the solid so that only the displacement of the surface atom due to the thermal motion must be included. If this is not the case then (18) must be modified due to the deformation of the bulk solid caused by the phonons [typically factors like $\cos(px)$ for $x < 0$].

It remains to specify $V_0(x)$. In our earlier work we have calculated isothermal and flash desorption times for gas-solid systems that develop only one bound state.[1,2] In such situations it is of great analytical and numerical advantage to replace the local surface potential by a separable nonlocal one.[3] For the latter choice we were also able to perform a complete (numerical) fourth-order calculation of isothermal desorption times including all two-phonon processes enabling us to delineate the validity of a second-order perturbation calculation and, indeed, the validity of the relaxation-time approach.[6,7]

To deal with a gas-solid system that develops $(N+1)$ bound states, one could choose a superposition of $(N+1)$ separable terms in the surface potential. However, the complexity increases very fast with N. Also, one would introduce too many potential parameters. We have therefore chosen $V_0(x)$ for our present work to be the Morse potential

$$V_0(x) = U_0 \left(e^{-2\gamma(x-x_0)} - 2e^{-\gamma(x-x_0)} \right) , \tag{20}$$

because it reproduces the experimentally determined bound-state energies for systems like He-LiF and He-graphite rather well, though it decreases too fast as $x \to \infty$. Moreover, scattering and bound-state wave functions are known analytically and are given in Appendix B.

There always arises the question of suitable boundary conditions for the gas-particle wave function at the surface of the solid. If the gas particle cannot diffuse into the solid we must assume that there is a strong repulsion at the surface which one can model by an infinitely high potential wall at $x = 0$ with the surface potential attached to it for $x > 0$. Thus the gas-particle wave functions must vanish at $x = 0$. More realistically one would choose a potential that grows like x^{-n} as $x \to 0$. The Morse potential with $x_0 = 0$ is deficient in this respect. However, if we choose $x_0 \gtrsim \gamma^{-1}$ then $V_0(0) \gtrsim 2U_0$ and the wave function, decaying as a double exponential, is negligibly small for $x \leqslant 0$. In (18) we can therefore restrict the integration over $0 \leqslant x < \infty$. In addition we will see in Sec. IV A that the desorption changes little if we vary x_0 from γ^{-1} to ∞.

III. CALCULATION OF TRANSITION PROBABILITIES

The input into the phenomenological rate equations (2) are the transition probabilities R_{ji} and R_{ci} which must be calculated in a quantum-statistical theory based on the Hamiltonian (14) for the initial-value problem appropriate for isothermal desorption. We assume that the initial equilibrium occupation for $t<0$ is adequately described by the static part H_{st} of (14). The macroscopic time evolution of the system is started at $t=0$ by switching on the dynamic part H_{dyn} of (14), and setting all occupation number $n_k(t)$ of the gas-continuum states equal to zero for $t \geqslant 0$ to simulate the sudden removal of the gas phase ($P=0$). The physical quantity to be calculated is the time-dependent occupation numbers of the bound states which are given by

$$n_i(t) = \mathrm{Tr}[\alpha_i^\dagger(t)\,\alpha_i(t)\hat{\rho}_g\hat{\rho}_s] , \tag{21}$$

where

$$\hat{\rho}_g = \exp[-\beta(H_{\mathrm{st}} - \mu N_g)]/\mathrm{Tr}\exp[-\beta(H_{\mathrm{st}} - \mu N_g)] \tag{22}$$

is the initial-equilibrium statistical operator for the gas with $N_g = \sum_q \alpha_q^\dagger \alpha_q$, μ the chemical potential of the gas phase, and

$$\hat{\rho}_s = \exp(-\beta H_s)/\mathrm{Tr}\exp(-\beta H_s) \tag{23}$$

is the initial-equilibrium statistical operator for the phonons with $\beta = 1/(k_B T)$. The operators $\alpha_q(t)$ are subject to Heisenberg's equation of motion

$$i\hbar\dot{\alpha}_q = [\alpha_q, H_{\mathrm{st}} + H_s + \theta(t)H_{\mathrm{dyn}}] . \tag{24}$$

One can certainly argue that during the desorption process the phonon system of the solid does not get disturbed greatly, implying that

$$b_p(t) \approx e^{-i\omega_p t} b_p(0) . \tag{25}$$

This approximation linearizes the set of equations (24) which can now be solved in second-order time-dependent perturbation theory. Details can be found in Ref. 1.

Extracting the long-time limit linear in t one finds that

$$\frac{n_i(t)}{N(0)} \approx \sum_j (\delta_{ij} - R_{ij}t)\frac{n_j(0)}{N(0)} \tag{26}$$

which is identical in form to the solution of (2) linear in t. The transition probabilities are thus determined microscopically. For bound state–bound state transitions into a lower state via emission of a phonon one finds

$$R_{ij} = \frac{2\pi}{\hbar} L^{-2} \sum_p \omega_p^{-1} |X(j,i)|^2 (n_p^{(\mathrm{ph})} + 1)\delta(E_j - E_i - \hbar\omega_p) ,$$
$$j>i \tag{27}$$

where

$$n_p^{(\mathrm{ph})} = [\exp(\beta\hbar\omega_p) - 1]^{-1} . \tag{28}$$

For bound state–bound state transitions into a higher state via absorption of a phonon one gets

$$R_{ji} = \frac{2\pi}{\hbar} L^{-2} \sum_p \omega_p^{-1} |X(i,j)|^2 n_p^{(\mathrm{ph})} \delta(E_j - E_i - \hbar\omega_p) ,$$
$$j>i . \tag{29}$$

Bound state-continuum transitions are given by

$$R_{ci} = \frac{2\pi}{\hbar} L^{-2} \sum_p \omega_p^{-1} \sum_k |X(i,k)|^2 n_p^{(\mathrm{ph})} \delta(E_i - E_k + \hbar\omega_p) , \tag{30}$$

where k is the momentum label for the continuum states. The diagonal elements of $\overleftrightarrow{\mathrm{R}}$ are given by

$$R_{ii} = R_{ci} + \sum_{j=0,\, j\neq i}^{N} R_{ji} . \tag{31}$$

The explicit expressions for these rates for the Morse potential are given in Appendix C.

IV. NUMERICAL RESULTS

A. Systems with two bound states

In this section we will present the results of explicit calculations of isothermal desorption times for systems with several bound states, in particular for the He-LiF, He-NaF, H-NaCl, He-graphite, He-Ar, and some model systems. Before we do this we want to examine analytically the structure of the time evolution (8) for a simple model system with two bound states. In this case we have from (8)

$$N(t)/N(0) = S_0 e^{-\lambda_0 t} + S_1 e^{-\lambda_1 t} \tag{32}$$

with

$$\lambda_{0,1} = \tfrac{1}{2}(R_{c0} + R_{c1} + R_{10} + R_{01})$$
$$\mp \tfrac{1}{2}[(R_{c0} + R_{10} - R_{c1} - R_{01})^2 + 4R_{01}R_{10}]^{1/2} , \tag{33}$$

$$S_{0,1} = \pm\frac{1}{\lambda_1 - \lambda_0}\left(\lambda_{1,0} - \frac{n_0}{N(0)} R_{c0} - \frac{n_1}{N(0)} R_{c1}\right) . \tag{34}$$

It is instructive to look at the low-temperature behavior of these expressions. One finds for (32)–(34) that for temperatures such that

$$\exp[-\delta(\epsilon_0 - \epsilon_1)] \ll 1 , \tag{35}$$

$$\lambda_0 \approx R_{c0} + \frac{\Gamma_{10}(R_{c1} - R_{c0})}{R_{c1} - R_{c0} + \Gamma_{10}} \exp[-\delta(\epsilon_0 - \epsilon_1)] , \tag{36}$$

$$\lambda_1 \approx R_{c1} + \Gamma_{10} + \Gamma_{10} \frac{R_{c1} - R_{10} + 2\Gamma_{10}}{R_{c1} - R_{c0} + \Gamma_{10}} \exp[-\delta(\epsilon_0 - \epsilon_1)] , \tag{37}$$

$$S_0 = 1 - S_1 ,$$
$$S_1 \approx \left(\frac{R_{c1} - R_{c0}}{R_{c1} - R_{c0} + \Gamma_{10}}\right)^2 \exp[-\delta(\epsilon_0 - \epsilon_1)] , \tag{38}$$

where

$$\delta = \hbar\omega_D / k_B T , \quad \epsilon_i = |E_i| / \hbar\omega_D .$$

R_{c0}, R_{c1}, and Γ_{10} are given in Appendix C. Note first that the coefficient S_1 becomes negligibly small in the low-temperature region implying that for $t > \lambda_1^{-1}$ the time evolution of the system is characterized by one time scale

$$t_d = \lambda_0^{-1} . \tag{39}$$

Indeed the difference $(\lambda_1 - \lambda_0)$ becomes larger for lower temperatures implying that the small transients controlled by λ_1 die out very quickly. For not too shallow states ϵ_1 one finds numerically that $\Gamma_{10} \gg R_{c1} > R_{c0}$ at low temperatures. If gas particles can desorb from both bound states by absorption of a single phonon, i.e., if $\epsilon_0 < 1$, then we have at low temperatures $\lambda_0 \sim R_{c0}$ and $\lambda_1 \sim \Gamma_{10}$. This can be understood by noting that (35) implies a negligible occupation of the upper bound state ϵ_1. Because $R_{01} \gg R_{10}$, a particle in ϵ_1 will first make a transition to ϵ_0 emitting a nonequilibrium phonon before it desorbs from ϵ_0 into the continuum. For $\epsilon_0 < 1$ and at low temperatures the desorption in such a system with two bound states thus appears to be solely controlled by the lower bound state ϵ_0. One finds numerically that over a limited temperature regime t_d can be parametrized by a Frenkel-Arrhenius formula

$$t_d = t_d^0 e^{Q/k_B T} , \tag{40}$$

where Q is slightly larger than $\epsilon_0 \hbar\omega_D$.

Turning now to a system, still at low temperature, with $2 > \epsilon_0 > 1 > \epsilon_1 > 0$ and $\epsilon_0 - \epsilon_1 < 1$ we obviously have $R_{c0} = 0$ and

$$t_d \approx \frac{R_{c1} + \Gamma_{10}}{R_{c1}\Gamma_{10}} \exp[\delta(\epsilon_0 - \epsilon_1)] . \tag{41}$$

Desorption in this situation can only proceed via a phonon cascade $0 \rightarrow 1 \rightarrow$ continuum. If $\Gamma_{10} \gg R_{c1}$ as one can check numerically, one then gets

$$t_d \approx R_{c1}^{-1} \exp[\delta(\epsilon_0 - \epsilon_1)] . \tag{42}$$

Again R_{c1} can be parametrized as

$$R_{c1} = \nu_1 e^{-Q_1/k_B T} , \tag{43}$$

where over a limited low-temperature region ν_1 is independent of T and $Q_1 \gtrsim \epsilon_1 \hbar\omega_D$, so that the Frenkel-Arrhenius parametrization of t_d again holds true with $Q = \hbar\omega_D(\epsilon_0 - \epsilon_1) + Q_1 \gtrsim \epsilon_0 \hbar\omega_D$. But this time $t_d^0 = \nu_1^{-1}$ is controlled by the matrix elements between the higher state ϵ_1 and the continuum. Thus the prefactor t_d^0 is, in this case, controlled by the upper state whereas the activation energy Q is close to the energy $\epsilon_0 \hbar\omega_D$ of the lower state.

A situation with $0 < \epsilon_1 < 1 < \epsilon_0 < 2$ is not very likely met in real systems which will always have many bound states if $\epsilon_0 > 1$. Before we turn our attention to such systems, we want to discuss briefly the dependence of t_d on the parameter x_0 in the Morse potential (20). We have seen earlier that one has to choose $x_0 \gtrsim \gamma^{-1}$ in order to prevent gas particles from penetrating into the solid. In Fig. 1(a) we show λ_0^{-1} as a function of $\xi_0 = \gamma x_0$ for systems developing two bound states for $\sigma_0 = 2mU_0/(\hbar^2\gamma^2) = 1.55$ and $\sigma_0 = 2.49$, respectively, and for $r = 2m\omega_D/(\hbar\gamma^2) = 100$. In Fig. 1(b) we give t_d for the system with $\sigma_0 = 2.49$ and $\xi_0 = \infty$ as a function of $\delta = \hbar\omega_D/k_B T$. We see from Fig. 1(a) that in the system with $\sigma_0 = 1.55$ for $\xi_0 = 1$ and at $\delta = 100$, λ_0^{-1} is smaller by some 36% from its value at $\xi_0 = \infty$ which it indeed reaches within 0.6% at $\xi_0 = 1.5$. For the larger $\sigma_0 = 2.49$ the change in λ_0^{-1} from $\xi_0 = \infty$ to $\xi_0 = 1$ amounts to only 7% for $\delta > 70$ and to 11% at $\delta = 30$ and to 20% at $\delta = 5$. For a system with $(N+1)$ bound states we know from Eq. (B5) that $N + \frac{1}{2} < \sigma_0 < N + \frac{3}{2}$, so that we can expect much less dependence of t_d on ξ_0 for systems with many bound states and can safely set $\xi_0 = \infty$ implying that the limit $\alpha = 2\sigma_0 \exp(\xi_0) \rightarrow \infty$ in (C4)–(C7) leading to (C11) and (C12) is indeed acceptable, simplifying the numerical work for systems with many bound states considerably.

B. Systems with a few shallow bound states

In this section we will present calculations of isothermal desorption times for gas-solid systems that have several shallow bound states. We call a bound state shallow if a gas particle can desorb from it by absorbing a single phonon. Systems in this category are He-LiF, He-NaF, H-LiF, H-NaF, He-graphite, etc. These systems are also known to show mobile adsorption implying that the motion of particles in the adsorbate is more or less unhindered in the direction parallel to the surface so that our one-dimensional model is adequate.

We first deal with the ^{4}He-LiF system. Its surface potential has four bound states given in Table I. In our theory these bound states must be reproduced by a Morse potential. We followed two options leading to somewhat different potential parameters. One set we get by a least-squares fit

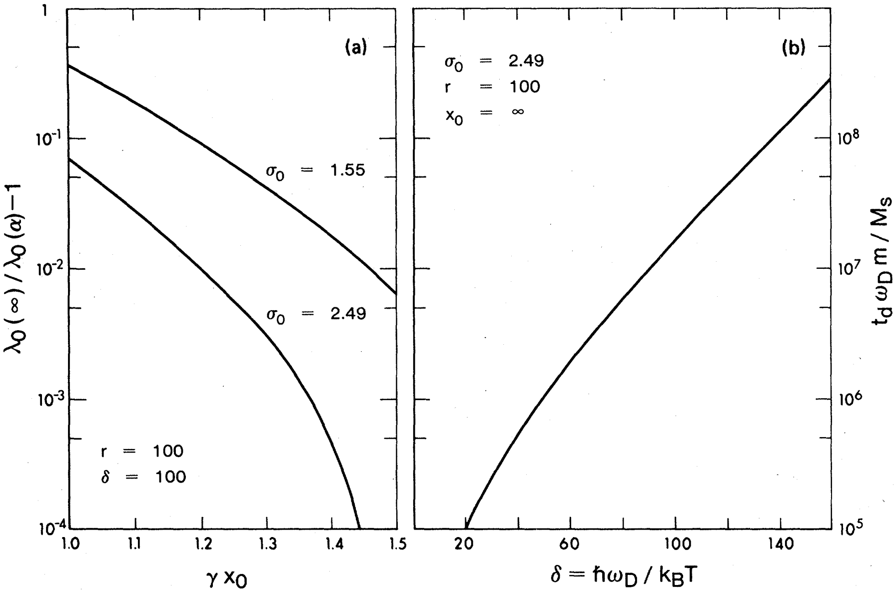

FIG. 1. (a) Relative change in λ_0 as a function of the shift x_0 in the Morse potential (20) for a gas-solid system with two bound states. $\alpha = 2\sigma_0 \exp(\gamma x_0)$; $\sigma_0 = 2mV_0/(\hbar\gamma)^2$; $r = 2m\omega_D/\hbar\gamma^2$. (b) Temperature dependence of the isothermal desorption time t_d.

to the bound-state energies (see Table I). Because we know from the previous section that the lowest bound-state energy basically defines the activation energy, we get a second set of potential parameters by fitting the deepest and shallowest bound states for this sytem. In the temperature region $T \lesssim 40$ K the Debye temperature of LiF is $\hbar\omega_D/k_B \approx 730$ K dropping sharply to a minimum of 610 K at $T \sim 60$ K.[15] In Table II we present the λ_i's and S_i's of (11) for some typical temperatures for the first potential. At high temperatures, i.e., for $\delta \lesssim 20$ all λ_i's are of the same order though the coefficient S_0 is larger than S_1 to S_3. For $\delta \gtrsim 20$ the lowest eigenvalue λ_0 splits off dramatically from λ_1 to λ_3 and S_0 approaches unity very closely indicating that apart from very small and very fast transients the system is indeed controlled by one exponential in analogy with the analytical results obtained for systems with two shallow states at low temperatures. For $\delta \gtrsim 20$ we can then identify $t_d = \lambda_0^{-1}$. This isothermal desorption time is plotted in Fig. 2 as a function of δ. Though t_d is not completely linear in δ we can parametrize it by a Frenkel-Arrhenius formula (40),

$$t_d = 1.9 \times 10^{-9} \exp(71/T)\,, \quad 4\text{ K} < T < 40\text{ K}\,, \tag{44}$$

with t expressed in sec and T in K. Again Q in (44) is larger than the lowest bound state by some 5%. In Fig. 2 we also show the desorption times calculated from the second Morse potential in Table I. We see that the two potential fits give comparable desorption times.

The He-LiF system, as mentioned above, has four shallow bound states from which gas particles can desorb by absorption of a single phonon. In

TABLE II. Eigenvalues λ_i in $\sec^{-1}$ and coefficients S_i in (8) for ^{4}He-LiF for $\gamma^{-1} = 1.09$ Å and $U/k_B = 81.75$ K as a function of $\delta = h\omega_D/k_BT$.

δ	λ_0	λ_1	λ_2	λ_3	S_0	S_1	S_2	S_3
10	4.06×10^8	6.03×10^8	1.37×10^9	1.70×10^9	0.842	0.112	0.031	0.015
20	1.08×10^8	2.47×10^8	5.96×10^8	7.23×10^8	0.979 19	0.001 10	0.015 01	0.004 70
30	3.45×10^7,	1.63×10^8	3.81×10^8	4.53×10^8	0.992 47	0.003 3	0.006 40	0.000 80
50	4.19×10^6	1.17×10^8	2.43×10^8	2.92×10^8	0.999 25	0.000 12	0.000 62	0.000 01
100	2.87×10^4	9.97×10^7	1.81×10^8	2.27×10^8	1.0	8.8×10^{-8}	4.2×10^{-7}	7.3×10^{-8}
150	2.46×10^2	9.78×10^7	1.75×10^8	2.18×10^8	1.0	6.8×10^{-11}	2.6×10^{-10}	1.9×10^{-10}

this case one might argue that only bound state → continuum transitions are important with cascades like $0 \to 1 \to \cdots \to$ continuum being negligible at least as long as k_BT is not too much smaller than ϵ_0.[16] We have checked this idea numerically by setting all bound state–bound state transition probabilities R_{ij} in (3) equal to zero. For He-LiF one finds that for $4\ \mathrm{K} < T < 40\ \mathrm{K}$ λ_0 is reduced by about a factor of 2. With uncertainties in t_d arising from different choices of potential parameters being of the same size, the approximation of setting bound state–bound state transitions equal to zero seems acceptable for the He-LiF system with its rather shallow bound states.[16] However, if the lowest bound state ϵ_0 gets much lower, for example, $\epsilon_0 \lesssim 1$, this approximation fails dismally, and, of course, is even qualitatively wrong for $\epsilon_0 > 1$, because one-phonon processes cannot empty such a deep state. As a numerical example we consider a hypothetical gas-solid system with $r = 2m\omega_D/(\hbar\gamma^2) = 60$, $\sigma_0 = 8.05$, i.e., having eight bound states, the lowest of which is $\epsilon_0 = |E_0|/\hbar\omega_D = 0.95$. In this case $t_d = 10^{-10}(M_s/m)\hbar\omega_D$ at $\delta = 20$ from (39); without bound state–bound state transitions this time is reduced by a factor 0.0013. At high temperatures, say such that $\delta \sim 1$, the approximation is still unacceptable because then the coefficient S_0 becomes substantially smaller than 1 with the other S_i increasing proportionately.

We have also done a calculation of isothermal desorption times identified as $t_d = \lambda_0^{-1}$ for ^{4}He-NaF and ^{4}He-graphite. The relevant parameters and our predicted desorption times are given in Tables II and III. The "theoretical error bars" due to

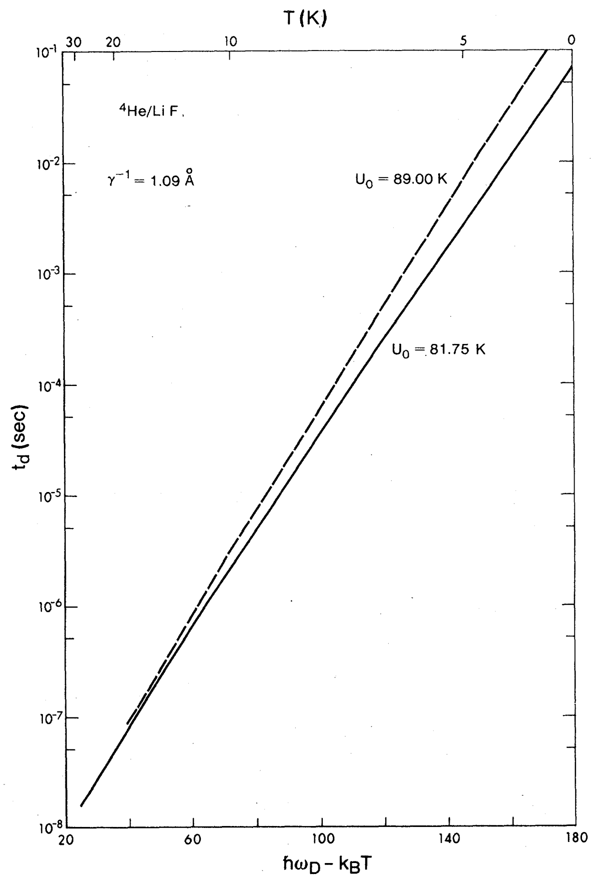

FIG. 2. Temperature dependence of the isothermal desorption time for ^{4}He-LiF for two sets of Morse potential parameters (see Tables I and III).

TABLE III. Frenkel-Arrhenius parametrization of the isothermal desorption times for various systems and Morse potential parameters.

System	Number of states	Temperature range (K)	t_d^0 (sec)	Q/k_B (K)	γ^{-1} (Å)	U_0 (K)	$\hbar\omega_D/k_B$ (K)	σ_0	r	m/M_s
^{4}He-LiF	4	4–40	1.9×10^{-9}	71	1.09	81.75	730[a]	4.023	144.55	0.1520
	4	4–40	1.4×10^{-9}	77	1.09	89.0	730	4.1979	145.79	0.1520
^{4}He-NaF	3	4–15	8.5×10^{-10}	63.2	0.97	77.78	450[b]	3.491	70.496	0.0952
^{4}He-	5	4–15	2.1×10^{-12}	139.5	0.95	160.54	185[c]	4.8818	27,464	0.3333
graphite	5	4–15	1.8×10^{-12}	149.3	0.95	171.34	185	5.041	24.436	0.3333
H-NaCl	7	15–35	7.2×10^{-12}	370	1.78	399.3	280[d]	7.242	36.773	0.0172
^{4}He-Ar	6	4–10	2.3×10^{-12}	151	1.09	171.93	92[e]	5.8	18.0	0.111
	8	4–10	2.6×10^{-12}	151	1.49	164.63	92	7.8	34.0	0.111
	10	4–10	4.14×10^{-12}	151	1.98	160.07	92	10.2	60.0	0.111

[a] Reference 15.

[b] A. M. Karo and J. R. Hardy, Phys. Rev. 129, 2024 (1963).

[c] W. N. Reynolds, *Physical Properties of Graphite* (Elsevier, Amsterdam, 1968).

[d] Reference 17.

[e] L. Finegold and N. E. Phillip, Phys. Rev. 177, 1383 (1969).

some arbitrariness in choosing γ^{-1} and U_0 are similar to those discussed for the He-LiF system.

Finally we would like to add some comments on helium adsorbed on Constantan, a Cu-Ni alloy. Cohen and King[8] have measured a flash desorption time $t_d = (2\times 10^{-7}\ \text{sec})\exp(-31\ \text{K}/T)$ in the temperature region $4\ \text{K} < T < 18\ \text{K}$. We have been able to reproduce these rather long times quite well in a three-dimensional theory of localized adsorption with a separable surface potential of range $\lambda = 2.5$ Å perpendicular and parallel to the surface developing just one bound state at an energy $E_0/k_B = -25$ K. As pointed out earlier a one-dimensional theory as developed in this paper is appropriate for mobile adsorption without any localization in the lateral direction, i.e., with a surface potential that is constant along the surface. It is instructive to try to fit the He-Constantan desorption times with the one-dimensional model presented here and based on the Morse potential. Note first that in a Morse potential the deepest bound state is given by

$$\epsilon_0 = (\sigma_0 - \tfrac{1}{2})^2/r. \tag{45}$$

If this is supposed to be the only one and located at $\epsilon_0 = 0.065$ in the He-Constantan system, one must have $0.5 < \sigma_0 < 1.5$ so that $r < 15.385$ implying that $\gamma^{-1} < 0.48$ Å, a range that seems too short. In any case desorption times calculated for such parameters are too short by at least 1 order of magnitude as compared with experimental data. To weaken the coupling between adsorbate and phonons one is then tempted to increase r and thus γ^{-1}. This, however, results in a surface potential that has more than one bound state, e.g., for $r = 400$ the Morse potential has six bound states, the deepest one being at $\epsilon_0 = 0.065$. Desorption times calculated for such parameters are again at least an order of magnitude too small, due to the fact that the reduction in coupling is compensated by opening all the cascades via the additional bound states. This, it seems to us, is evidence that He adsorbs on Constantan at localized adsorption sites having only one physisorbed bound state because reducing the lateral potential range from infinity for mobile adsorption to a finite value of the order of a few angstroms, one obviously eliminates all higher bound states and arrives at a situation modeled by a separable potential of a rather large range $\lambda \sim 2.5$ Å with only one bound state. Indeed, suppressing in a quite *ad hoc* way the cascades via the bound states $n = 1, \ldots, N$ in the one-dimensional theory based on a Morse potential with $r = 400$, one finds that R_{c0}^{-1} reproduces the experimental desorption time rather well and also agrees with the full three-dimensional theory for localized physisorption based on a separable potential. But this procedure does not seem appropriate to us.

C. Gas-solid systems with deep bound states

Thus far we have considered gas-solid systems with shallow bound states in the surface potential from which gas particles can desorb via absorption of a single phonon. In the H-NaCl system this is no longer the case because the lowest bound state is at $E_0/k_B = -351.63$ K (Ref. 10) whereas $\hbar\omega_D/k_B = 280$ K for $15\ \text{K} < T < 35$ K,[17] so that a single phonon cannot supply the necessary desorption energy. Desorption can then proceed either via multiphonon processes on which we comment later and/or via one-phonon cascades through the shallower bound states. We choose the Morse parameters to reproduce in a least-squares fit the four observed bound states. This potential produces three additional shallow states as given in Table I. Note that the range of the H-NaCl potential $\gamma^{-1} = 1.78$ Å is somewhat larger than in the He-LiF, He-NaF, and He-graphite systems. The calculated desorption times are given in Table III in the form of the Frenkel-Arrhenius parametrization. The activation energy Q is again larger than $|E_0|$ by some 7%.

We next consider a system where helium adsorbs on solid argon for which desorption times have been measured,[18] though nothing is known about the surface bound states. We choose the parameters of the Morse potential such that its lowest bound state is in magnitude about Q. For a range $\gamma^{-1} = 1.09$ Å such a potential produces 6 bound states, for $\gamma^{-1} = 1.59$ Å we get eight-bound states, and for $\gamma^{-1} = 1.98$ Å we get ten bound states. The resulting desorption times are such that the experimental $Q/k_B = 151$ K is reproduced, whereas the prefactor t_d^0 varies between 2.3×10^{-12} and 4.14×10^{-12} sec, which brackets the experimental estimate of about 3.6×10^{-12} sec that one extracts by dividing the last two columns of Table 1 in Ref. 18 where the difficulties with this procedure are discussed.

Finally we want to analyze our theory for gas-solid systems with many bound states. As detailed experimental information on such systems is scarce, we prefer here to study first some model systems for which we choose a Debye frequency $\omega_D = 5\times 10^{13}\ \text{sec}^{-1}$, and a mass ratio $m/M_s = 0.1$. (Note that ω_D and m/M_s only enter our theory as multiplicative factors in the transition probabilities if the potential parameters are given in terms of σ_0 and r.)

In Table IV we start with a gas-solid system that develops 50 bound states for gas particles in its surface potential. The value $r = 400$ would, for helium gas, correspond to a range of the surface

TABLE IV. Frenkel-Arrhenius parametrization of the isothermal desorption times for some model systems with many bound states. $\omega_D = 5\times10^{13}$ sec^{-1}, $m/M_s = 0.1$.

Number of bound states	σ_0	r	Range of δ	t_d^0 (sec)	$Q/\hbar\omega_D$	$\epsilon_0 - \epsilon_1$
50	50.0	400	1–5	5.0×10^{-13}	6.15	0.245
50	50.0	200	1–5	5.5×10^{-14}	12.3	0.49
50	50.0	100	1–5	1.8×10^{-14}	24.5	0.98
36	35.502	100	1–5	2.0×10^{-13}	12.3	0.69
71	70.504	400	1–5	5.0×10^{-13}	12.3	0.3475

potential of about 2.5 Å, implying a fairly weak phonon coupling. It turns out that in the temperature range $0.2\hbar\omega_D < k_B T < 1\hbar\omega_D$ the desorption time can be adequately parametrized by the Frenkel-Arrhenius formula (1) with an activation energy $Q = 6.15\hbar\omega_D$, about 1% larger than the deepest bound state, and a prefactor $t_d^0 \approx 5\times10^{-13}$ sec. Decreasing the range of the surface potential by a factor $\sqrt{2}$ so that $r = 200$ and keeping the number of bound states fixed, increases Q by a factor of 2 and decreases t_d^0 by an order of magnitude. Decreasing r to $r = 100$ increases Q to $24.5\hbar\omega_D$ and reduces t_d^0 to 1.8×10^{-14} sec. This very small prefactor is quite astonishing because in the latter system the two lowest bound states are separated by almost $\hbar\omega_D$; more precisely, we have $\epsilon_0 - \epsilon_1 = 0.98$. This, of course, implies a fairly sluggish desorption, e.g., at $T = \hbar\omega_D/k_B$ we have $t_d = 7.86\times10^{-4}$ sec, as compared to $t_d = 2.34\times10^{-10}$ sec in the first system with $r = 400$. The rather small prefactor t_d^0 is therefore compensated by a large activation energy Q. There have been arguments in the literature about such a compensation effect to the extent that a relation like $t_d^0 \sim \ln Q$ is supposed to hold as discussed, e.g., by Menzel.[19] We feel that this is an artifact because experimentally only systems with relaxation times of the order of seconds to microseconds can be observed implying an apparent law like the above. It can also be manufactured in our table.

The fourth entry in Table IV is a system in which we kept $r = 100$ from the previous example and reduced the number of bound states from 50 to 36 by reducing the strength of the potential via σ_0, thus also raising the lowest bound state to half its previous energy. This results in reducing the activation energy to $Q = 12.3\hbar\omega_D$ and increasing t_d^0 to 2×10^{-13} sec, giving a desorption time $t_d \approx 4.4\times10^{-8}$ sec at $T = 1\hbar\omega_D/k_B$. With the lowest bound state essentially fixing Q, we see that reducing the number of bound states implies reducing the number of cascade channels through which a particle can detrap from ϵ_0, increasing t_d^0.

Next, in the fifth entry, we keep Q fixed, increase r to 400, thus doubling the number of bound states but also decreasing the phonon coupling. As a result of increasing the number of bound states, we would expect a smaller prefactor t_d^0 because there are more cascade channels available, i.e., the matrix $\tilde{R}$ in (3) is larger. As a consequence of weakening the phonon coupling, we must anticipate a larger prefactor t_d^0 because the transition probabilities, i.e., the matrix elements R_{ij} get smaller. Going from entry 4 to 5 in Table IV, we just about compensate the two trends; but compare with entry 2.

As a last example we will try to fit the desorption time for the Xe-W system, measured to be[20]

$$t_d = 10^{-15\pm1} \exp[(4662 \pm 20)/T] \tag{46}$$

again in sec and K. Xenon is adsorbed on a tungsten surface at localized sites, so that our one-dimensional theory should be expected to produce a desorption time that is somewhat too long. We have fitted the Morse potential in such a way that the lowest bound state is at $E_0/k_B = -4662$ K. The Debye energy for tungsten is chosen to be $\hbar\omega_D/k_B = 405$ K. For our first run we choose the range $\gamma^{-1} = 1$ Å, so that $r = 2208$ and $\sigma_0 = 159.9$. Thus there are 160 bound states in this potential. In the temperature regime $100\text{ K} < T < 400$ K we get a prefactor in the Frenkel-Arrhenius formula (40) of $t_d^0 = 3\times10^{-13}$ sec and reproduce $Q = 4662$ K. Taking $\gamma^{-1} = 1.5$ Å, $r = 4969$, and $\sigma_0 = 239.66$ with 240 bound states we get $t_d^0 = 1.5\times10^{-12}$ sec. These prefactors are too large by 1 to 2 orders of magnitude. To localize the adsorbed xenon more, we choose $\gamma^{-1} = 0.5$ Å, $r = 550$, $\sigma_0 = 80.07$ with 80 bound states and get $t_d^0 = 3\times10^{-14}$ sec. In view of the above reservations to apply our theory to localized adsorption, this is in satisfactory agreement with (46).

It remains to justify the use of second-order time-dependent perturbation theory for the calculation of the bound state–bound state and bound state–continuum transition probabilities, in which only one-phonon processes are so far accounted for. We have recently made a detailed study of the importance of two-phonon processes in bound state–continuum transitions performing a complete fourth-order calculation.[6,7] Our main conclusions were that a relaxation-time description of desorption from a bound state E_0 based on perturbation theory is possible as long as $h/|E_0| \ll t_d$, where t_d is the isothermal desorption time for such systems, which we called descriptively weakly coupled; a second-order calculation of t_d can be used as long as $|E_0| \lesssim k_B T \lesssim \hbar\omega_D$. Fourth-order contributions become important for $|E_0| < \hbar\omega_D$ and $k_B T \lesssim \hbar\omega_D$. Moreover, for the range $\hbar\omega_D \leq |E_0| \leq 2\hbar\omega_D$ fourth-order terms are essential in the absence of intermediate bound states because second-order contributions are zero then.

Our fourth-order calculations were performed for a model gas-solid system in which the surface potential, chosen to be of separable form, devellops only one bound state, whereas the systems studied in this paper all develop more than one bound state. Moreover, the present theory of desorption from many bound states is based on a Morse surface potential. Rather than attempting a fourth-order calculation for the latter we will develop now a method of estimating the importance of two-phonon processes in our present theory using the model calculations based on the separable surface potential. Let us first look at the transition probability from a bound state E_i into the gas-particle continuum. The equivalent separable surface potential must obviously produce a bound state at E_i. This requirement fixes one of the two potential parameters, either the range or the depth. As the range also controls the strength of the coupling to the phonons, we keep it the same for the separable potential.

Let us first look again at the He-LiF system. At $\delta = 60$, i.e., $T = 12$ K, the desorption rate calculated from (12) is $t_d^{-1} = 1.5 \times 10^6$ sec^{-1}. Suppressing the bound state-bound state transitions we find that gas particles desorb from the lowest bound state with a rate $R_{c0} = 6.95 \times 10^5$ sec^{-1}. Calculating the desorption rate from this state in the separable potential model we get in second order $R_{c0}^{(\mathrm{sep})} = 2.9 \times 10^5$ sec^{-1} for the same value $r = 44.55$. A complete fourth-order calculation including two-phonon processes[6,7] reduces this rate to 2.76×10^5 sec^{-1}. Whereas the fourth-order correction amounts to less than 5% we see that inclusion of the bound state-bound state one-phonon cascades enhances the rate by more than a factor of 2. At a temperature of 6 K, the fourth-order corrections amount to about 10% and become more significant for lower temperatures where the overall relaxation time, however, becomes immeasurably large. There is no need for a similar analysis for the higher bound states in the He-LiF system because of their negligibly small thermal occupation at these low temperatures.

We next turn to the H-NaCl system where the lowest bound-state energy E_0 is in magnitude larger than the maximum phonon frequency. In this case one-phonon processes cannot supply enough energy for a one-step desorption from E_0 into the continuum, i.e., $R_{c0} = 0$. The system however desorbs via one-phonon bound state–bound state cascades with a rate 1.8×10^4 sec^{-1} at $T = 23$ K. For $r = 36.77$ we find that the fourth-order two-phonon rate in the separable potential model is only 7.4 sec^{-1}, i.e., smaller by nearly 4 orders of magnitude from the cascade. So also in the H-NaCl system two-phonon processes are negligible in the accessible temperature range. A similar picture emerges for the He-Ar system. We can thus say that in weakly coupled gas-solid systems with many bound states, as defined above, second-order time-dependent perturbation theory is sufficient at not too low temperatures for the calculation of the bound state–bound state and bound state–continuum transition probabilities. However, it is crucial that the isothermal desorption time is identified according to (12) as the inverse of the smallest eigenvalue of the transition matrix (3).

Summarizing we want to stress that our theory of desorption by one-phonon cascades for gas-solid systems with many physisorbed surface bound states is based on the Hamiltonian (14) from which the bound state–bound state and bound state–continuum transition probabilities are calculated in second-order perturbation theory for a Morse potential (20) without any further approximations. For weakly coupled gas-solid systems, as defined above, we have shown that higher-order contributions can be neglected. The system of rate equations (2) is solved exactly by diagonalization and it is shown that at low temperatures the smallest eigenvalue of the transition matrix $\tilde{\mathrm{R}}$ in (3)–(5) is the inverse of the isothermal desorption time t_d with transients being negligible. Our theory is essentially parameter-free, because the Morse potential must be chosen to reproduce independently measured bound-state energies. An increase in the range of the surface potential results in a weakening of the gas atom-phonon coupling and, at the same time, in an increase in the number of bound states. These two effects, indeed, compensate each other in the calculation of the desorption time in most systems so that details of the surface potential are much less important than one would have anticipated.

Finally we comment on related work. In Ref. 21 a similar theory to ours has been developed. These authors present a detailed discussion of the gas atom–metal electron coupling. In evaluating the desorption time they invoke a number of unnecessary approximations, namely: (1) starting from a Morse potential, they construct a harmonic approximation[22] and add some anharmonicity neglecting, however, the continuum altogether. Because the theory can be worked out exactly for a Morse potential, we do not see the necessity for such drastic approximations which might reproduce the lower bound states and the transition probabilities between them reasonably well but must fail close to and in the continuum. Indeed, the relative insensitivity of our exact calculations to the choice of Morse potential parameters and in particular, to the spacing between the lowest states, suggests that this procedure is unjustified. (2) In Ref. 21 all bound state–bound state transitions other than those between nearest and next-nearest states are neglected. This implies that, e.g., for the Xe-W system a large number of cascade channels is absent in their theory which must result in too small desorption rates. (3) In Ref. (21) only the first passage time is calculated whereas our exact solution of the rate equations yields all time scale including transients. Our last comment on Ref. 21 is concerned with their fit of Ehrlich's desorption data[23] on Xe-W which differ drastically from more recent experiments by Dresser *et al.*[20] which we fitted earlier. To see the significant difference between the present theory and Ref. 21 due to the approximations invoked in the latter, we have calculated the desorption time for the Xe-W system to reproduce Ehrlich's data, namely, $t_d = 10^{-12}$ sec $\exp(2520\,\mathrm{K}/T)$ as used in Ref. 21. Taking their $\hbar\omega_D/k_B = 220$ K and assuming the range of the Morse potential to be $\gamma^{-1} = 1.5$ Å, we have $r = 2698.67$, $\sigma_0 = 176.28$, i.e., 176 bound states. Around $T = 200$ K we get $t_d = 9.68\times10^{-13}$ sec $\exp(2520\,\mathrm{K}/T)$ in unbelievable agreement with the above data. This success must be contrasted with Fig. 6 of Ref. 21 where the authors get theoretical desorption rates at best 2 orders of magnitude too small. This, we think, shows conclusively that the approximations in Refs. 21 and 22 are unacceptable, and, indeed as we have demonstrated in this paper, unnecessary. We also want to point out that the coupling mechanism proposed in Ref. 21 between the adsorbed particle and the electrons of the solid assumes that the adsorbed particle carries a net charge. Though this is plausible for chemisorbed system like K-W there is no experimental evidence for the physisorbed Xe-W system that the adsorbed Xe atom carries any charge. In Ref. 20 it is estimated that the interaction of the induced dipole in the Xe with surface electric fields of W amounts to less than 5% of the total interaction energy. The authors of Ref. 21 equate this dipole interaction to the interaction of a net charge of $0.04e$ (see caption of Fig. 4 in Ref. 21) on Xe, a procedure which lacks any justification.

ACKNOWLEDGMENT

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada.

APPENDIX A

In this appendix we want to justify the applicability of a one-dimensional model for mobile desorption. We start by considering a gas particle at position $\vec{r} = (x, \vec{R})$ interacting with a solid surface. The coordinate system is chosen so that the static surface is in the (y, z) plane at $x = 0$. The surface is represented by a lattice of atoms at positions $\vec{r}_i + \vec{u}_i$, where $\vec{r}_i \equiv (0, \vec{R}_i)$ is the equilibrium position of the ith surface atom and $\vec{u}_i = (u_{ix}, \vec{U}_i)$ is its deviation from the equilibrium due to thermal vibrations of the solid. The potential energy of a gas-particle interaction with the surface is

$$U(x, \vec{R}) = \frac{1}{\mathfrak{N}} \sum_i V(x - u_{ix}, \vec{R} - \vec{R}_i - \vec{U}_i)\,, \tag{A1}$$

where $\mathfrak{N}$ is a number of surface atoms occupying an area S (periodic Born-Karman boundary conditions in two dimensions will be assumed) and V represents the two-body surface atom–gas particle interaction potential energy. We assume for simplicity that each elementary cell in the surface contains only one atom and that all surface atoms are identical. Our derivation can be easily generalized for more complex situations. In (A1) we only include the interaction with surface atoms. The effect of the bulk of the solid is indirectly contained in $\vec{u}_i$. For small deviations from equilibrium (A1) can be expanded,

$$U(x, \vec{R}) = U_0(x, \vec{R}) + \delta U(x, \vec{R})\,, \tag{A2}$$

where

$$U_0(x, \vec{R}) = \frac{1}{\mathfrak{N}} \sum_i V(x, \vec{R} - \vec{R}_i) \tag{A3}$$

is periodic:

$$U_0(x, \vec{R} - \vec{R}_i) = U_0(x, \vec{R})\,. \tag{A4}$$

$\delta U(x, \vec{R})$ is given by

$$\delta U(x, \vec{R}) = -\frac{1}{\mathfrak{N}} \sum_i \vec{u}_i \cdot \vec{\nabla} V(x, \vec{R} - \vec{R}_i)\,. \tag{A5}$$

We can now represent the deviations of surface atoms $\vec{u}_i$ from their equilibrium positions in the form of a linear combination of normal vibrational modes $(\vec{p}, \lambda)$ of the solid:

$$\vec{u}_i = \left(\frac{\hbar}{2M_s N_s}\right)^{1/2} \sum_{\vec{p},\lambda} \frac{\hat{e}_\lambda(\vec{p})}{[\omega_\lambda(\vec{p})]^{1/2}} \left(e^{i\vec{p}\cdot\vec{R}_i} b_{\vec{p},\lambda} + \mathrm{H.c.}\right). \tag{A6}$$

$b_{\vec p,\lambda}$ is the annihilation operator of a phonon (i.e., a normal mode of lattice vibrations), $\vec p\equiv(p_x,\vec P)$ and $\omega_\lambda(\vec p)$ are the wave vector and the angular frequency of the phonon of branch λ, respectively (only acoustic modes are considered here: $\lambda=1,2,3$), $\hat e_\lambda(\vec p)$ is a set of phonon polarization vectors, assumed to be normalized: $|\hat e_\lambda(\vec p)|^2=1$, M_s is a mass of each atom of the solid, and N_s is their number in the crystal. Inserting (A6) into (A5) we get

$$\delta U(x,\vec R)=-\left(\frac{\hbar}{2M_sN_s}\right)^{1/2}\times\sum_{\vec p,\lambda}\frac{\hat e_\lambda(\vec p)}{[\omega_\lambda(\vec p)]^{1/2}}\cdot\vec f(\vec P;x,\vec R)b_\lambda(\vec p)+\text{H.c.}\,, \tag{A7}$$

where

$$\vec f(\vec P;x,\vec R)=\frac{1}{\mathfrak{N}}\sum_i e^{i\vec P\cdot\vec R_i}\vec\nabla V(x,\vec R-\vec R_i)\,. \tag{A8}$$

Let us note that

$$\vec f(\vec P;x,\vec R-\vec R_j)=e^{-i\vec P\cdot\vec R_j}\vec f(\vec P;x,\vec R) \tag{A9}$$

so that it can be written in the form

$$\vec f(\vec P;x,\vec R)=e^{i\vec P\cdot\vec R}\vec\phi(\vec P;x,\vec R)\,, \tag{A10}$$

where $\vec\phi(\vec P;x,\vec R)$ is a periodic function

$$\vec\phi(\vec P;x,\vec R-\vec R_j)=\phi(\vec P;x,\vec R) \tag{A11}$$

and can therefore be expanded,

$$\vec\phi(\vec P;x,\vec R)=\sum_{\vec K_m}e^{i\vec K_m\cdot\vec R}\vec a_m(\vec P;x)\,, \tag{A12}$$

where $\vec K_m$ are the translation vectors of the reciprocal lattice having the property

$$e^{i\vec K_m\cdot\vec R_j}=1\,. \tag{A13}$$

With the help of (A10) and (A12) $\delta U(x,\vec R)$ reads

$$\delta U(x,\vec R)=-\left(\frac{\hbar}{2M_sN_s}\right)^{1/2}\sum_{\vec p,\lambda}\frac{\vec e_\lambda(\vec p)}{[\omega_\lambda(\vec p)]^{1/2}}\cdot\sum_{\vec K_m}\vec a_m(\vec P;x)e^{i(\vec P+\vec K_m)\cdot\vec R}b_\lambda(\vec p)+\text{H.c.} \tag{A14}$$

Let us note that the two equivalent forms of $\delta U(x,\vec R)$, namely, (A7) and (A14) should be used as the starting points for approximations in two different physical situations, (A7) for localized and (A14) for mobile physisorption. From (A8), (A10), and (A3) we obtain for $\vec P=0$

$$\vec\phi(0;x,\vec R)=\nabla U_0(x,\vec R)\,. \tag{A15}$$

Expanding the periodic potential $U_0(x,\vec R)$ in a Fourier series

$$U_0(x,\vec R)=\sum_{\vec K_m}e^{i\vec K_m\cdot\vec R}V_m(x) \tag{A16}$$

we obtain

$$\vec a_m(0;x)=(V_m'(x),i\vec K_mV_m(x))\,. \tag{A17}$$

For $\vec P\neq0$, we get from (A12), (A10), and (A8)

$$\sum_{\vec K_m}a_m(\vec P,x)e^{i\vec K_m\cdot\vec R}=\frac{1}{\mathfrak{N}}\sum_i e^{-i\vec P\cdot(\vec R-\vec R_i)}\vec\nabla V(x,\vec R-\vec R_i)\,. \tag{A18}$$

Multiplying both sides of (A18) by $e^{i\vec K_{m'}\cdot\vec R}$, integrating over the whole surface S, using

$$\int_S e^{i(\vec K_m-\vec K_{m'})\cdot\vec R}d_2R=S\delta_{mm'} \tag{A19}$$

and (A13) we get

$$\vec a_m(\vec P;x)=\frac{1}{S}\int_S d_2R\,e^{-i(\vec P+\vec K_m)\cdot\vec R}\vec\nabla V(x,\vec R)\,. \tag{A20}$$

So far we have not invoked any approximations and all is exact within the harmonic model of a solid.

Let us now assume that the force exerted by the solid surface on the gas particles is smooth enough so that it can be treated as independent of $\vec R$, i.e.,

$$U_0(x,\vec R)=V_0(x)\,. \tag{A21}$$

Then the gas-particle wave functions in the presence of the static surface can be approximated by

$$\psi_{q\vec K}(x,\vec R)=S^{-1/2}e^{i\vec K\cdot\vec R}u_{q\vec K}(x)\,, \tag{A22}$$

where $u_{q\vec K}(x)$ fulfills the one-dimensional Schrödinger equation with the potential energy $V_0(x)$. The total energy is $E_{q\vec K}=\hbar^2\vec K^2/2m+E_q$ with m the gas-particle mass and $\vec K$ the gas-particle wave vector parallel to the surface. The index q denotes a quantum number associated with the gas-particle motion along x and can assume both discrete n (for bound states) and continuum k_x (for continuum states) values. Let us also note that $u_{q\vec K}(x)$ depends on $\vec K$ only through the energy shift $\hbar^2\vec K^2/2m$. For the wave functions (A22) the dynamic part of the gas-solid interaction reads in second quantization

$$H_{\text{dyn}}=-\left(\frac{\hbar}{2M_sN_s}\right)^{1/2}\sum_{q\vec K}\sum_{q'\vec K'}\sum_{\vec p,\lambda}\alpha^\dagger_{q\vec K}\left(\frac{[e_\lambda(\vec p)]_x}{[\omega_\lambda(\vec p)]^{1/2}}\int u^*_{q\vec K}(x)a_{0x}(\vec P;x)u_{q'\vec K'}(x)dx\,b_\lambda(\vec p)+\text{H.c.}\right)\delta(\vec P+\vec K',\vec K)\alpha_{q'\vec K'}\,, \tag{A23}$$

where $[e(\vec p)]_x$ and $a_{0x}(\vec P;x)$ are the x components of $\hat e_\lambda(p)$ and $\vec a_0(\vec P;x)$, respectively, and $\delta(\vec K,\vec K')$ is a Kronecker δ obtained from

$$\int_S d_2R\, e^{i(\vec{K}-\vec{K}')\cdot\vec{R}} = S\delta(\vec{K},\vec{K}') . \tag{A24}$$

$\alpha^\dagger_{q\vec{K}}$ and $\alpha_{q\vec{K}}$ are the creation and annihilation operators of a gas particle in state $|\psi_{q\vec{K}}\rangle$. To determine $a_{0x}(\vec{P},x)$ for a smooth surface we observe that from (A3) and (A21) we get

$$V(x,\vec{R}-\vec{R}_i) = V_0(x) , \tag{A25}$$

which with (A19) gives

$$a_{0x}(\vec{P}',x) = V_0'(x)\frac{1}{S}\int_S d_2R\, e^{-i\vec{P}'\cdot\vec{R}} = V_0'(x)\delta(\vec{P},0) . \tag{A26}$$

Thus for a smooth surface for which the interaction with gas particles can be assumed constant along the surface only phonons with $\vec{P}=0$ can interact with the gas particles, and (A23) reads

$$H_{\text{dyn}} = -\left(\frac{\hbar}{2M_sN_s}\right)^{1/2} \sum_{qq'}\sum_{\vec{K}}\sum_{p_x} \frac{1}{[\omega_l(p_x)]^{1/2}}\, \alpha^\dagger_{q\vec{K}} \left(\int u^*_{q\vec{K}}(x)V_0'(x)u_{q'\vec{K}}(x)dx\, b_l(p_x) + \text{H.c.}\right)\alpha^\dagger_{q'\vec{K}} , \tag{A27}$$

where the index l in $\omega_l(p_x)$ and $b_l(p_x)$ denotes longitudinal phonons. If in a gas-solid system with mobile physisorption band effects for the motion along the surface are negligible, the gas-particle momentum component parallel to the surface is conserved. Only phonons with a zero lateral component of the wave vectors interact with the gas particles. Thus the energy necessary to desorb a particle out of a bound state of the surface potential must be supplied by longitudinal phonons with wave vectors perpendicular to the surface. This justifies the use of a one-dimensional model for mobile physisorption with negligible band effects. Note that (A27) and (17) are equivalent in the sense that transition probabilities calculated from (A27) and averaged over the lateral motion are identical to those calculated from (17). Goodman and Romero[24] do not have the factor $\delta(\vec{P},0)$ in (A26). As a consequence they include the possibility of drawing energy out of the lateral motion of the adsorbed atom in the desorption process. It is mysterious how in the one-dimensional version of their model, Goodman and Romero can desorb a gas particle in a one-step one-phonon process from bound states whose energies are in magnitude larger than that of the most energetic phonons.

APPENDIX B

For the Morse potential

$$V(x) = U_0\left(e^{-2\gamma(x-x_0)} - 2e^{-\gamma(x-x_0)}\right) \tag{B1}$$

we define dimensionless quantities

$$\sigma_0^2 = \frac{2mU_0}{\hbar^2\gamma^2}, \quad s_n^2 = \frac{2m|E_n|}{\hbar^2\gamma^2}, \qquad \xi=\gamma x, \quad \xi_0=\gamma x_0 , \tag{B2}$$

and get for the normalized bound-state wave functions

$$\phi_n(x) = \sqrt{\gamma}\, f_n(\xi) \tag{B3}$$

with

$$f_n(\xi) = (2\sigma_0)^{s_n}\Gamma^{-1/2}(2s_n)\binom{2s_n+n}{n}^{-1/2} \times \exp(-\sigma_0 e^{-(\xi-\xi_0)})e^{-s_n(\xi-\xi_0)}L_n^{2s_n}(2\sigma_0 e^{-(\xi-\xi_0)}) , \tag{B4}$$

where

$$s_n = \sigma_0 - n - \tfrac{1}{2}, \quad n=0,\ldots,N<\sigma_0-\tfrac{1}{2} \tag{B5}$$

and $L_n^{2s_n}(u)$ is a Laguerre polynomial. The continuum states of momentum q, normalized in a box $-L<x<L$, are given by

$$\phi_q(x) = (2L)^{-1/2}f(\eta;\xi) , \tag{B6}$$

where

$$\eta = q/\gamma \tag{B7}$$

and

$$f(\eta,\xi) = \left|\frac{\Gamma(\frac{1}{2}-\sigma_0-i\eta)}{\Gamma(2i\eta)}\right| \exp(-\sigma_0 e^{-(\xi-\xi_0)})e^{-i\eta(\xi-\xi_0)} \times \Psi(\tfrac{1}{2}-\sigma_0+i\eta, 1+2i\eta, 2\sigma_0 e^{-(\xi-\xi_0)}) , \tag{B8}$$

where $\Psi(a,b,z)$ is a confluent hypergeometric function that vanishes as $z\to-\infty$, i.e.,

$$\Psi(1-\sigma_0+i\eta,1+2i\eta,z) = \frac{i\pi}{\sinh(2\pi\eta)}\left(\frac{F(1-\sigma_0+i\eta,1+2i\eta,z)}{\Gamma(1+2i\eta)\Gamma(\frac{1}{2}-\sigma_0-i\eta)} - z^{-2i\eta}\frac{F(\frac{1}{2}-\sigma_0-i\eta,1-2i\eta,z)}{\Gamma(1-2i\eta)\Gamma(\frac{1}{2}-\sigma_0+i\eta)}\right), \tag{B9}$$

where the F functions are defined in Ref. 25.

APPENDIX C

To evaluate the transitions probabilities (29) and (30) we have to invoke the thermodynamic limit, i.e., replace

$$\sum_k \to \frac{L}{\pi} \int_0^\infty dk \tag{C1}$$

and perform the sums over phonon states. For a Debye model this implies the replacement

$$\sum_p \to \frac{3N_s}{\omega_D^3} \int_0^{\omega_D} \omega^2 d\omega . \tag{C2}$$

We also introduce the dimensionless quantities

$$\begin{aligned} r &= 2m\omega_D/(\hbar\gamma^2) , \\ \delta &= \hbar\omega_D/k_B T , \\ \epsilon_n &= |E_n|/\hbar\omega_D = s_n^2/r . \end{aligned} \tag{C3}$$

We then get for (30)

$$\begin{aligned} R_{cn} = {} & \Theta\left(\frac{1-s_n^2}{r}\right) \frac{3\sigma_0^2}{\pi r^4 \Gamma(2s_n)} \binom{2s_n+n}{n}^{-1} \\ & \times \frac{m}{M_s} \int_0^{r-s_n^2} dx (x+s_n^2) n\left(\frac{x+s_n^2}{r}\right) \sinh(2\pi\sqrt{x}) \, |\Gamma(\tfrac{1}{2}-\sigma_0+i\sqrt{x})|^2 \\ & \times \left| \int_0^\alpha du\, e^{-u} u^{\sigma_0-n-1/2+i\sqrt{x}} \left(\frac{u}{2\sigma_0}-1\right) L_n^{2s_n}(u) \Psi(\tfrac{1}{2}-\sigma_0+i\sqrt{x}, 1+2i\sqrt{x}, u) \right|^2 \end{aligned} \tag{C4}$$

where $\alpha = 2\sigma_0 e^{\xi_0}$. For (27) and (29) for $j>i$

$$R_{ij} = \Theta(r-(s_i^2-s_j^2))[n((s_i^2-s_j^2)/r)+1]\Gamma_{ji} \tag{C5}$$

for bound state–bound state transitions into a lower state via emission of a phonon and

$$R_{ji} = \Theta(r-(s_i^2-s_j^2)) n((s_i^2-s_j^2)/r)\Gamma_{ji} \tag{C6}$$

for transitions into a higher state via absorption of a phonon. Here we defined

$$\Gamma_{ji} = \omega_D \frac{6\pi\sigma_0^2}{r^4} \frac{m}{M_s} (s_i^2-s_j^2) \left[\binom{2s_j+j}{j} \binom{2s_i+i}{i} \Gamma(2s_j)(2s_i) \right]^{-1} \left[\int_0^\alpha du\, e^{-u} u^{s_j+s_i} \left(\frac{u}{2\sigma_0}-1\right) L_j^{2s_j}(u) L_i^{2s_i}(u) du \right]^2 . \tag{C7}$$

In (C4), (C5), and (C6) we denote

$$n(z) = (e^{\delta z}-1)^{-1} . \tag{C8}$$

In the limit $\alpha = 2\sigma_0 e^{\xi_0} \to \infty$ inserting $s_j = \sigma_0 - j - \frac{1}{2}$ we can calculate the integrals in (C7) and (C4) to be

$$\int_0^\infty e^{-u} u^{s_j+s_i} \left(\frac{u}{2\sigma_0}-1\right) L_j^{2s_j}(u) L_i^{2s_i}(u) du = (-1)^{j-i} \frac{j-i}{i!} \Gamma(2\sigma_0-j) \left(1-\frac{i+j+1}{2\sigma_0}\right) \text{ for } j>i \tag{C9}$$

and

$$\int_0^\infty e^{-u} u^{\sigma_0-n-1/2+i\sqrt{x}} \left(\frac{u}{2\sigma_0}-1\right) L_n^{2\sigma_0-2n-1}(u) \Psi(\tfrac{1}{2}-\sigma_0+i\sqrt{x}, 1+2i\sqrt{x}, u) du = \frac{(-1)^n}{n!} |\Gamma(\sigma_0+\tfrac{1}{2}+i\sqrt{x})|^2 \frac{x+(\sigma_0-n-\frac{1}{2})^2}{2\sigma_0} . \tag{C10}$$

For $\alpha \to \infty$ we therefore have

$$\begin{aligned} R_{cn} = {} & \Theta(r-(\sigma_0-n-\tfrac{1}{2})^2) \omega_D \frac{3\pi(2\sigma_0-2n-1)}{4r^4 n! \Gamma(2\sigma_0-n)} \frac{m}{M_s} \int_0^{r-(\sigma_0-n-1/2)^2} dx [x+(\sigma_0-n-\tfrac{1}{2})^2]^3 n\left(\frac{x+(\sigma_0-n-\frac{1}{2})^2}{r}\right) \\ & \times \frac{\sinh(2\pi\sqrt{x})}{\cos^2(\pi\sigma_0)+\sinh^2(\pi\sqrt{x})} |\Gamma(\sigma_0+\tfrac{1}{2}+i\sqrt{x})|^2 \end{aligned} \tag{C11}$$

and $(j>i)$

$$\Gamma_{ji}=\omega_D\frac{3\pi}{2r^4}\frac{m}{M_s}(j-i)^3\frac{j!}{i!}\frac{\Gamma(2\sigma_0-j)}{\Gamma(2\sigma_0-i)}(2\sigma_0-i-j-1)^3(2\sigma_0-2j-1)(2\sigma_0-2i-1)\,. \tag{C12}$$

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