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Multiphonon processes in a quantum-statistical theory of desorption

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A complete fourth-order quantum-statistical calculation of the isothermal desorption time t_d in a gas-solid system is presented showing localized physisorption including all one-phonon and two-phonon processes in fourth order. The multiphonon interaction terms arising from higher-order derivatives of the surface potential turn out to contribute significantly to the desorption rate. Extensive numerical work confirms that the relaxation time approach to desorption phenomena is acceptable for weakly coupled systems for which $h/|E_0| \ll t_d$ where E_0 is the energy of the bound state. Second-order calculations are sufficient as long as $|E_0| \lesssim k_BT \lesssim \hbar\omega_D$, where $\hbar\omega_D$ is the Debye energy of the solid. Fourth-order contributions become important for $|E_0| < \hbar\omega_D$ and $k_BT \gtrsim \hbar\omega_D$. Moreover, for $\hbar\omega_D \le |E_0| \le 2\hbar\omega_D$ fourth-order terms are essential because second-order contributions are zero in this region of bound-state energies.

I. INTRODUCTION

We have recently formulated, and worked out the details of a quantum-statistical theory of the adsorption[1] and desorption[2-4] of a gas at the surface of a solid in systems which show localized physisorption, i.e., in which no chemical reactions take place during the adsorption process and in which lateral diffusion in the adsorbate along the surface of the solid is negligible. 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 the helium-constantan system.[5] For this and related systems we have calculated isothermal and flash desorption[2,3] times for phonon-mediated desorption.

The term "shallow bound state" refers to a bound state whose energy E_0 is, in magnitude, less than the maximum phonon energy of the solid (the Debye energy $\hbar\omega_D$ or some maximum energy of optical phonons), i.e., for which $|E_0| \le \hbar\omega_D$. In such a situation a particle of the adsorbate (the latter being defined as the sum total of those gas particles trapped in the bound states of the surface potential) can leave the surface, i.e., make a transition from a bound state E_0 into the gas-particle continuum of energy E_k by absorbing one (thermal) phonon of energy $\hbar\omega = E_k - E_0$. We can therefore calculate desorption times in second-order time-dependent perturbation theory, thus taking account of one-phonon processes only.

Let us next look at a gas-solid system with a surface potential such that a "deep" bound state develops at an energy E_0 with $\hbar\omega_D < |E_0| < 2\hbar\omega_D$. A gas particle trapped in such a bound state can obviously not desorb unless it absorbs at least two phonons whose combined energy $(\hbar\omega_1 + \hbar\omega_2) > |E_0|$. To calculate desorption times for such a system all two-phonon processes must be included which we will do in this paper by developing a fourth-order time-dependent perturbation theory. Before we do this, let us mention that a gas-solid system with a deep bound state will most likely have other bound states; e.g., in the H-NaCl system the surface potential develops four bound states[6] at energies $E_0/k_B = -315$ K, $E_1/k_B = -247$ K, $E_2/k_B = -166$ K, and $E_3/k_B = -110$ K with the Debye temperature of NaCl at $T \sim 35$ K being $\hbar\omega_D/k_B = 275$ K. In this example H can desorb from the higher bound states E_1 to E_3 by absorbing a single phonon, whereas a particle can leave the lowest bound states E_0 by absorbing two phonons either simultaneously or in a two-step cascade-like $E_0 \rightarrow E_1 \rightarrow$ continuum in which the two phonons are absorbed in succession.

Because a full quantum-statistical calculation of the desorption times in systems like H-NaCl is rather involved, with several new features appearing that are not present in simpler systems like He-constantan, we have divided our program into two parts: In this first paper we will study a model system in which the surface potential develops only one bound state whose energy E_0 we vary between $0 > E_0 > -2\hbar\omega_D$, and calculate the isothermal desorption time in fourth-order perturbation theory, taking all one-phonon and two-phonon processes into account. In a subsequent paper we will then treat a system with several bound states and study the importance of the above-mentioned phonon cascade in desorption.

The task of calculating desorption times in a fourth-order time-dependent perturbation theory including all one-phonon and two-phonon processes is, of course, an enormous one. It is eased somewhat by a judicious choice of the surface potential which we take to be a separable nonlocal potential[7] following our earlier work.[1-4] For such a potential all static properties can be worked out analytically, a necessary prerequisite for an exact calculation of desorption times, i.e., exact in the framework of fourth-order perturbation theory. The relation between local and separable nonlocal surface potentials has been worked out by us in a recent paper[4] where detailed numerical comparisons are given, demonstrating the advantages of using separable potentials in desorption theories. A nonlocal potential consisting of just one separable term is particularly advantageous for our present purpose because it can develop, at most, one bound state.

Whereas the one-phonon theory of desorption was proposed in its rudiments some forty years ago,[8,9] there has been, to our knowledge, no calculation of desorption times including two-phonon processes reported in the literature. Bendow and Ying[10] formulate a van Hove-type integral equation for multiphonon processes; however, neither they nor anyone else have tried to use and solve this equation. Such an attempt seems quite hopeless in any case, unless one invokes drastic approximations or proceeds via standard perturbation theory. In theories of the scattering of particles from solid surfaces, a feeble attempt to include two-phonon processes has been made by Allen and Feuer.[11] We will see in this paper that their calculation is quite incomplete, because they calculate only one of the many two-phonon contributions, indeed one of the smaller ones. Their calculation also has no direct relevance to our program because, by choosing a purely repulsive surface potential, they exclude all bound-state effects. This might be a good approximation for scattering at high enough energy, but is obviously unacceptable for a calculation of desorption times, simply because there cannot be either adsorption or desorption if there are no bound states. We want to stress here that only a full and complete fourth-order calculation is acceptable to study the importance of two-phonon contributions because it turns out, as one could have anticipated from similar calculations in quantum electrodynamics, that some of the individual contributions give rise to divergent integrals; these divergences, however, cancel to yield a finite result if all contributions are calculated exactly as we will show in this paper.

As for the contents of this paper, we will, in Sec. II, set up the Hamiltonian of the gas-solid system. Because one can anticipate that a fourth-order calculation of desorption times must have certain similarities to fourth-order calculations of transition rates in quantum electrodynamics, it seems natural to perform the analogous Bloch-Nordsieck transformation on our Hamiltonian to take explicit account of some higher-order self-energy terms, thus removing some of the spurious divergences that would appear in a straightforward perturbation calculation. Similar transformations are employed in other areas of physics and are known, e.g., in field theory as dressing transformations.[12]

We start Sec. III by setting up the proper initial-value problem for isothermal desorption within the framework of our quantum-statistical theory of desorption. We then illustrate the methods for calculating desorption times by briefly outlining the calculation of the second-order contributions. This is then followed by a computation of all one- and two-phonon processes in fourth order. Calculational details are given in Appendices A to D. In Sec. IV we present a detailed numerical analysis of all one-phonon and two-phonon contributions to the isothermal desorption time for several model systems.

Our main conclusions are as follows: In a fourth fourth-order perturbation theory it is essential to calculate one-phonon 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, i.e., up to cubic in phonon creation and annihilation operators. A relaxation time description of desorption from a bound state at energy E_0 is possible as long as $h/|E_0| \ll t_d$, where t_d is the isothermal desorption time. We find that a second-order calculation of the latter 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 $\hbar\omega_D \leqslant |E_0| \leqslant 2\hbar\omega_D$ fourth-order terms are essential because second-order contributions are zero in this region of bound-state energies.

II. GAS-SOLID HAMILTONIAN

In this section we set up the Hamiltonian of the interacting gas-solid system as it is needed to formulate the appropriate quantum-statistical initial-value problem for the calculation of the isothermal desorption time. As shown elsewhere,[2] we can restrict ourselves to a one-dimensional system, because the translational degrees of freedom of the gas particles parallel to the surface of the solid are of little consequence in localized physisorption. We assume then that the total Hamiltonian of the gas-solid system can be split into three parts:

$$H = H_g + H_s + H_{gs}, \tag{1}$$

where H_g is the Hamiltonian of the gas which we assume to be noninteracting; i.e.,

$$H_g = -\frac{\hbar^2}{2m}\int \psi^\dagger(x)\frac{d^2}{dx^2}\psi(x)\,dx\,, \tag{2}$$

with $\psi(x)$ being the field operator in second quantization of the gas particles of mass m. It is advantageous to introduce free-particle creation and annihilation operators via the expansion.

$$\psi(x) = \sum_k \langle x\,|\,k\rangle a_k\,, \tag{3}$$

where a_k is the annihilation operator of a gas particle in momentum state k, and

$$\langle x\,|\,k\rangle = \sqrt{2/L}\,\sin kx \tag{4}$$

is the free-particle wave function normalized in a box of length L and assumed to vanish at the solid surface $x=0$. Inserting (4) into (2) we get

$$H_g = \sum_k \epsilon(k) a_k^\dagger a_k\,, \tag{5}$$

where $\epsilon(k) = \hbar^2k^2/2m$ is the kinetic energy of the gas particles.

The second part of the Hamiltonian (1), namely H_s, describes the dynamics of the solid in the absence of the gas. We assume that it can be adequately described in the harmonic approximation, i.e.,

$$H_s = \sum_p \hbar\omega_p b_p^\dagger b_p\,, \tag{6}$$

where $b_p^\dagger$ and b_p are creation and annihilation operators of phonons of momentum p and frequency ω_p.

Next we turn our attention to the gas-solid interaction H_{gs}. It consists of two parts, a static and a dynamic one. The static potential describes the interaction of gas particles with the solid with the thermal motion of its surface neglected. It enters the Hamiltonian H_{gs} as a term

$$H_{gs}^{(0)} = V_{\text{st}} = \int \psi^\dagger(x)\langle x\,|\,V\,|\,x'\rangle\psi(x')\,dx\,dx'\,, \tag{7}$$

where $\langle x\,|\,V\,|\,x'\rangle$ is the generally nonlocal surface potential. Its presence leads to a qualitative change in the wave functions of the gas particle. Moreover, since the static surface potential is generally attractive, it leads to a drastic change in the energy spectrum of the gas particles through the appearance of bound states. The occupation of the latter defines the adsorbate, i.e., that fraction of gas particles bound to the surface of the solid.

We have shown in previous work[2] that it is of great calculational advantage to choose the surface potential $\langle x\,|\,V\,|\,x'\rangle$ to be separable,[7] i.e.,

$$\langle x\,|\,V\,|\,x'\rangle = g\tilde{V}(x)\tilde{V}(x')\,. \tag{8}$$

Such a potential, consisting of one separable term, can develop at most one bound state, appropriate, e.g., for the helium-constantan system. If we want to deal with systems with more than one bound state in the surface potential, we can either employ a nonlocal potential consisting of a sum of separable terms, or use local potentials for which $\langle x\,|\,V\,|\,x'\rangle = \delta(x-x')V(x)$. All the following calculations in which we want to study the role of multiphonon processes in desorption will be performed for a potential, (8) with the potential form factor $\tilde{V}(x)$ chosen as

$$\tilde{V}(x) = (1/\sqrt{2})e^{-\gamma x}\,. \tag{9}$$

Its Fourier transform is

$$V(k) = L^{1/2}\int dx\,\langle k\,|\,x\rangle\tilde{V}(x) = k/(k^2+\gamma^2)\,, \tag{10}$$

so that the static part of the Hamiltonian reads

$$H_{\text{st}} = H_g + H_{gs}^{(0)} = \sum_k \epsilon(k)a_k^\dagger a_k + gL^{-1} \times \sum_{k,k'} V(k)V(k')a_k^\dagger a_{k'}\,. \tag{11}$$

To include the dynamic aspects of the gas-solid interaction, we next consider the thermal motion of the solid surface, represented by a displacement

$$u = (N_sM_s)^{-1/2}\sum_p \left(\frac{\hbar}{2\omega_p}\right)^{1/2}(b_p^\dagger + b_p)\,, \tag{12}$$

where M_s is the mass of an atom in the solid and N_s is their total number. We generalize (7) to

$$H_{gs} = \int \psi^\dagger(x)V(x-u, x'-u)\psi(x')\,dx\,dx' \tag{13}$$

and expand in a Taylor series in u,

$$H_{gs} = H_{gs}^{(0)} + H_{gs}^{(1)} + H_{gs}^{(2)} + \cdots\,, \tag{14}$$

where $H_{gs}^{(0)}$ is given in (7) and, for the potential form factor (9),

$$H_{gs}^{(1)} = -gu\int \psi^\dagger(x)\left(\tilde{V}(x)\frac{d\tilde{V}(x')}{dx'} + \frac{d\tilde{V}(x)}{dx}\tilde{V}(x')\right)\psi(x')\,dx'\,dx = 2gp\left(\frac{\hbar}{2M_sN_s}\right)^{1/2}L^{-1}\sum_{k,k'}V(k)V(k')a_k^\dagger a_{k'} \times \sum_p \omega_p^{-1/2}(b_p^\dagger + b_p)\,, \tag{15}$$

$$\begin{aligned} H_{gs}^{(2)} &= gu^2\int \psi^\dagger(x)\left(\frac{d\tilde{V}(x)}{dx}\,\frac{d\tilde{V}(x')}{dx} + \tilde{V}(x')\frac{d^2\tilde{V}(x)}{dx^2}\right)\psi(x')\,dx\,dx' \\ &= -2g\gamma^2L^{-1}\left(\frac{\hbar}{2M_sN_s}\right)\sum_{k,k'}V(k)V(k')a_k^\dagger a_{k'}\sum_{p,p'}(\omega_p\omega_{p'})^{-1/2}(b_p^\dagger + b_p)(b_{p'}^\dagger + b_{p'})\,, \end{aligned} \tag{16}$$

and

$$H_{gs}^{(3)} = -gu^3 \int \psi^\dagger(x)\left(\frac{d\tilde{V}(x)}{dx}\frac{d^2\tilde{V}(x')}{dx'^2} + \frac{d^2\tilde{V}(x)}{dx^2}\frac{d\tilde{V}(x')}{dx'} + \tfrac{1}{3}\tilde{V}(x)\frac{d^3\tilde{V}(x')}{dx'^3} + \tfrac{1}{3}\frac{d^3\tilde{V}(x)}{dx^3}\tilde{V}(x')\right)\psi(x')\,dx\,dx'$$

$$= \tfrac{4}{3}g\gamma^3 L^{-1}\left(\frac{\hbar}{2M_sN_s}\right)^{3/2}\sum_{k,k'} V(k)V(k')a_k^\dagger a_{k'} \sum_{p,p',p''}(\omega_p\omega_{p'}\omega_{pp''})^{-1/2}(b_p^\dagger + b_p)(b_{p'}^\dagger + b_{p'})(b_{p''}^\dagger + b_{p''})\,. \qquad (17)$$

As long as one need consider one-phonon processes only, one can terminate the Hamiltonian (14) with the term $H_{gs}^{(1)}$ in (15). However, if two-phonon and multiphonon processes become important it is mandatory to keep higher-order derivatives in H_{gs} such as (16) and (17), because we will see in Sec. IV that higher-order terms like (16) and (17) contribute significantly.[13]

Any adsorption or desorption process changes the number of gas atoms trapped in the bound states of the surface potential. In order to follow the time dependence of the bound-state occupation, i.e., the adsorbate concentration, it is therefore necessary to transform the Hamiltonian H into such a form in which creation and annihilation operators of particles in the bound states occur explicitly. This amounts to diagonalizing its static part (11) which can be accomplished by a linear transformation to quasiparticle operators α_q:

$$a_k = \sum_q \phi_q(k)\alpha_q\,, \qquad (18)$$

where $q=0$ refers to the bound state and $q>0$ enumerates the continuum. The respective single-particle wave functions in momentum space are denoted by $\phi_q(k)$ and are given explicitly for the potential form factor (10) in Appendix A. In the α representation the total Hamiltonian (1) reads

$$H = \sum_q E_q\alpha_q^\dagger\alpha_q + \sum_p \hbar\omega_p b_p^\dagger b_p + L^{-1}\sum_{q,q'} X^{(1)}(q,q')\alpha_q^\dagger \sum_p \omega_p^{-1/2}(b_p^\dagger + b_p)\alpha_{q'}$$

$$+ L^{-1}\sum_{q,q'} X^{(2)}(q,q')\alpha_q^\dagger \sum_{p,p'}(\omega_p\omega_{p'})^{-1/2}(b_p^\dagger + b_p)(b_{p'}^\dagger + b_{p'})\alpha_{q'}$$

$$+ L^{-1}\sum_{q,q'} X^{(3)}(q,q')\alpha_q^\dagger \sum_{p,p',p''}(\omega_p\omega_{p'}\omega_{p''})^{-1/2}(b_p^\dagger + b_p)(b_{p'}^\dagger + b_{p'})(b_{p''}^\dagger + b_{p''})\alpha_{q'}\,, \qquad (19)$$

where

$$X^{(1)}(q,q') = 2g\gamma(\hbar/2M_sN_s)^{1/2}W_q^* W_{q'}\,, \qquad (20)$$

$$X^{(2)}(q,q') = \gamma(\hbar/2M_sN_s)^{1/2}X^{(1)}(q,q')\,, \qquad (21)$$

$$X^{(3)}(q,q') = \tfrac{2}{3}\gamma^2(\hbar/2M_sN_s)X^{(1)}(q,q')\,, \qquad (22)$$

and

$$W_q = \sum_k V(k)\phi_q(k) \qquad (23)$$

is given in Appendix A. Moreover, E_q are the eigenvalues of H_{st} with E_0 the energy of the bound state.

In the calculation of the two-phonon contributions to the isothermal desorption times it will be advantageous (from a bookkeeping point of view) not to work with the Hamiltonian (19) but to rewrite it slightly by performing a "dressing" transformation[12] on its bound-state part. We introduce dressed bound-state operators

$$\tilde{\alpha}_0 = e^{iS}\alpha_0 e^{-iS} = \exp\left((\hbar L)^{-1}X^{(1)}(0,0)\sum_p \omega_p^{-3/2}(b_p^\dagger - b_p)\right)\alpha_0\,, \qquad (24)$$

and dressed phonon operators

$$\tilde{b}_p = e^{iS}b_p e^{-iS} = b_p + (\hbar L)^{-1}\omega_p^{-3/2}\alpha_0^\dagger\alpha_0\,, \qquad (25)$$

where

$$S = iX^{(1)}(0,0)(\hbar L)^{-1}\sum_p \omega_p^{3/2}\alpha_0(b_p^\dagger - b_p)\alpha_0 \qquad (26)$$

or

$$S=iX^{(1)}(0,0)(\hbar L)^{-1}\sum_p \omega_p^{-3/2}\tilde{\alpha}_0(\tilde{b}_p^\dagger-\tilde{b}_p)\tilde{\alpha}_0 \tag{27}$$

in terms of the dressed operators. Performing these transformations on the Hamiltonian, we get

$$\begin{aligned}H=&\tilde{E}_0\tilde{\alpha}_0^\dagger\tilde{\alpha}_0+\sum_{k>0}E_k\alpha_k^\dagger\alpha_k+\sum_p\hbar\omega_p\tilde{b}_p^\dagger\tilde{b}_p-\tfrac{1}{2}\Delta E_0\hbar\tilde{\alpha}_0^\dagger\tilde{\alpha}_0^\dagger\tilde{\alpha}_0\tilde{\alpha}_0+L^{-1}\sum_{\substack{k>0,\\k'>0}}X^{(1)}(k,k')\alpha_k^\dagger\sum_p\omega_p^{-1/2}(b_p^\dagger+b_p)\alpha_{k'}\\&+\hbar L^{-1}\sum_{k>0}X^{(1)}(0,k)\tilde{\alpha}_0^\dagger B^\dagger\sum_p\omega_p^{-1/2}(\tilde{b}_p^\dagger+\tilde{b}_p)\alpha_k+\hbar L^{-1}\sum_{k>0}X^{(1)}(k,0)\alpha_k^\dagger\sum_p\omega_p^{-1/2}(\tilde{b}_p^\dagger+\tilde{b}_p)B\tilde{\alpha}_0+H_{gs}^{(2)}+H_{gs}^{(3)}\,,\end{aligned}\tag{28}$$

where we introduced

$$B=\exp\left(-(\hbar L)^{-1}X^{(1)}(0,0)\sum_p\omega_p^{-3/2}(\tilde{b}_p^\dagger-\tilde{b}_p)\right) \tag{29}$$

and

$$\tilde{E}_0=E_0+\Delta E_0\,, \tag{30}$$

with

$$\Delta E_0=-2[X^{(1)}(0,0)]^2/(L^2\hbar)\sum_p\omega_p^{-2}\,. \tag{31}$$

The effect of the transformation (24)–(26), therefore, is to eliminate the bound-state–bound-state interaction of the form $\alpha_0(b_p^\dagger+b_p)\alpha_0$ from (19) in lieu of a quartic term $\tilde{\alpha}_0^\dagger\tilde{\alpha}_0^\dagger\tilde{\alpha}_0\tilde{\alpha}_0$ in (28) which will be of no consequence in the calculation of the desorption times. The remaining interaction terms in (28) are slightly more complicated through the appearance of the operator B. Moreover, the bound-state energy E_0 is shifted by ΔE_0 in (31), which is a part of the self-energy correction.

III. CALCULATION OF THE ISOTHERMAL DESORPTION TIME

A. Initial-value problem

We now want to develop a quantum-statistical theory of isothermal desorption[1-4] based on the Hamiltonian (28) and calculate the isothermal desorption time to fourth order in g, i.e., including all one-phonon and two-phonon processes. We must recall that in an isothermal desorption experiment one starts from an initial state in which gas and solid are in thermal equilibrium at a temperature T. Maintaining this temperature throughout, the gas pressure is suddenly at time $t=0$ reduced substantially (ideally to zero), and the resulting nonequilibrium time evolution in which the adsorbate gas particles are desorbed (and pumped out of the system), is measured and, assuming an exponential decay, characterized by an isothermal desorption time $t_d(T)$. To formulate the corresponding initial-value problem we can assume that the initial equilibrium state of the system for $t<0$ is adequately described by the static part of the Hamiltonian (19) or (28). The macroscopic time evolution in the system is then started at time $t=0$ by switching on the dynamic part of H by writing, recall (11),

$$H=H_{\mathrm{st}}+H_s+\theta(t)[H_{gs}^1+H_{gs}^2+H_{gs}^3]\,, \tag{32}$$

where $\theta(t)=0$ for $t<0$ and $\theta(t)=1$ for $t\geq 0$. We furthermore must insist that no gas particles are present, whatsoever, in the final state.

The physical quantity to be calculated is the time-dependent occupation of the bound state which is given by

$$n_0(t)=\mathrm{Tr}[\alpha_0^\dagger\alpha_0\hat{\rho}(t)]=\mathrm{Tr}[\tilde{\alpha}_0^\dagger\tilde{\alpha}_0\hat{\rho}(t)]\,, \tag{33}$$

where the time-dependent statistical operator is

$$\hat{\rho}(t)=e^{-iHt/\hbar}\hat{\rho}(0)e^{iHt/\hbar}=e^{-iHt/\hbar}\hat{\rho}_g\hat{\rho}_s e^{iHt/\hbar}\,, \tag{34}$$

and

$$\hat{\rho}_g=\exp[-\beta(H_{\mathrm{st}}-\mu\hat{N}_g)]/\mathrm{Tr}\exp[-(H_{\mathrm{st}}-\mu\hat{N}_g)] \tag{35}$$

is the initial equilibrium statistical operator for the gas with $\beta=1/(k_BT)$ the inverse temperature. The gas particle number operator is

$$\hat{N}_g=\sum_k a_k^\dagger a_k=\sum_q\alpha_q^\dagger\alpha_q=\tilde{\alpha}_0^\dagger\tilde{\alpha}_0+\sum_{k>0}\alpha_k^\dagger\alpha_k\,, \tag{36}$$

and

$$e^{\beta\mu}=\frac{L}{N}\left(\frac{k_BTm}{\hbar^2\pi}\right)^{1/2} \tag{37}$$

is the chemical potential of an ideal gas consisting of N particles in a one-dimensional box of length L. Similarly, we identify

$$\hat{\rho}_s=\exp(-\beta H_s)/\mathrm{Tr}\exp(-\beta H_s) \tag{38}$$

as the initial equilibrium statistical operator for the phonons. To facilitate the calculation of $n_0(t)$ we shift the time evolution from $\hat{\rho}(t)$ to the particle operators and get

$$n_0(t)=\mathrm{Tr}[\alpha_0^\dagger(t)\tilde{\alpha}_0(t)\hat{\rho}(0)]\,, \tag{39}$$

where

$$\tilde{\alpha}_0(t)=e^{iHt/\hbar}\tilde{\alpha}_0(0)e^{-iHt/\hbar} \tag{40}$$

must satisfy Heisenberg's equation of motion

$$i\hbar\dot{\tilde{\alpha}}_0=[\tilde{\alpha}_0,H]\,. \tag{41}$$

In integral form it reads

$$\tilde{\alpha}_0(t)=\frac{1}{\hbar}\,e^{-(i/\hbar)\tilde{E}_0(t-t_1)}\tilde{\alpha}_0(0)$$

$$-\frac{i}{\hbar}\int_0^t dt_1 e^{-(i/\hbar)\tilde{E}_0(t-t_1)}\Big(-\tfrac{1}{2}\Delta E_0\tilde{\alpha}_0^\dagger(t_1)\tilde{\alpha}_0(t_1)\tilde{\alpha}_0(t_1)+L^{-1}\sum_{k>0}X^{(1)}(0,k)B^\dagger(t_1)\sum_p\omega_p^{-1/2}[\tilde{b}_p^\dagger(t_1)+\tilde{b}_p(t_1)]\alpha_k(t_1)$$

$$+L^{-1}\sum_{k>0}X^{(2)}(0,k)B^\dagger(t_1)\sum_{p,p'}(\omega_p\omega_{p'})^{-1/2}[\tilde{b}_p^\dagger(t_1)+\tilde{b}_p(t_1)][\tilde{b}_{p'}^\dagger(t_1)+\tilde{b}_{p'}(t_1)]\,\alpha_k(t_1)$$

$$+L^{-1}\sum_{k>0}X^{(3)}(0,k)B^\dagger(t_1)\sum_{p,p'p''}(\omega_p\omega_{p'p''})^{-1/2}[\tilde{b}_p^\dagger(t_1)+\tilde{b}_p(t_1)][\tilde{b}_{p'}^\dagger(t_1)+\tilde{b}_{p'}(t_1)]$$

$$\times[\tilde{b}_{p''}^\dagger(t_1)+\tilde{b}_{p''}(t_1)]\alpha_k(t_1)\Big)\,, \tag{42}$$

with a similar equation holding true for $\alpha_k(t)$ with $k>0$.

To calculate all one-phonon and two-phonon contributions to the isothermal desorption time we must iterate (42) and its Hermitian conjugate four times, insert the result into (39), and take the appropriate long-time limit. This is a very lengthy and arduous calculation which cannot be reproduced here in any detail. Instead, we will outline the procedure in the following subsections indicating some of the tricks and pointing out some of the pitfalls one has to be aware of.

The notion of a relaxation time, e.g., the isothermal desorption time, implies that the system decays exponentially in time after possible nonexponential transients have died out. For isothermal desorption we therefore assume that the adsorbate particles desorb at a constant rate according to

$$n_0(t)=n_0(0)e^{-t/t_d} \tag{43}$$

with no gas particles left in the end, because whatever desorbs is pumped out of the system immediately. As noted above, our procedure to compute t_d is to calculate (39) in a time-dependent perturbation expansion and to extract its large-time behavior linear in t, yielding

$$n_0(t)\approx n_0(0)(1-Rt). \tag{44}$$

Comparing (43) and (44) we are then led to identify the isothermal desorption time as

$$t_d=R^{-1}. \tag{45}$$

This observation simplifies our computational task considerably because we obviously do not have to keep terms involving $n_0^2(0)$, i.e., the square of the bound-state occupation at time $t=0$. This in turn means that we can drop the term $\tilde{\alpha}_0^\dagger\tilde{\alpha}_0\tilde{\alpha}_0$ from (42) and that we can approximate

$$\tilde{b}_p(t)\approx e^{-i\omega_p t}\tilde{b}_p(0) \tag{46}$$

because any dynamic correction to (46), arising from Heisenberg's equation of motion for $\tilde{b}_p(t)$, will involve factors like $n_0(0)$. The approximation (46) simply states that the phonon system of the solid does not get disturbed greatly during the desorption process which, after all, takes place at the surface of the solid only. But note that (46) linearizes the equation of motion (42).

B. One-phonon processes in second order

We have previously calculated isothermal[3,4] and flash desorption[2] times taking only one-phonon processes into account in second order. This calculation is simple enough to be repeated here as a demonstration of the methods to be used in subsequent sections for the fourth-order calculations. Iterating (42) twice, we see that one-phonon processes, i.e., terms involving products of two-phonon operators $\tilde{b}_p$ or $\tilde{b}_p^\dagger$, arise in second order from the term with $X^{(1)}(0,k)$ only. Setting $B(t)=1$, we get

$$\tilde{\alpha}_0(t)=\tilde{\alpha}_0^{(0)}(t)+\tilde{\alpha}_0^{(1)}(t)+\tilde{\alpha}_0^{(2)}(t)+\cdots\,, \tag{47}$$

with

$$\tilde{\alpha}_0(t)=e^{-(i/\hbar)\tilde{E}_0 t}\tilde{\alpha}_0(0)\,,$$

$$\alpha_0^{(1)}(t)=-e^{-(i/\hbar)\tilde{E}_0 t}\frac{i}{L\hbar}\sum_{k>0}X^{(1)}(0,k)\alpha_k(0)\sum_p\omega_p^{-1/2}\Big[f_1\Big(\frac{i}{\hbar}(\tilde{E}_0-E_k+\hbar\omega_p),t\Big)\tilde{b}_p^\dagger(0)$$

$$+f_1\Big(\frac{i}{\hbar}(E_0-E_k-\hbar\omega_p),t\Big)b_P(0)\Big]+\cdots\,,$$

$$\tilde{\alpha}_0^{(2)}(t) = e^{-(i/\hbar)\tilde{E}_0 t}\left(\frac{i}{L\hbar}\right)^2 \sum_{k>0}\sum_{k'\geq 0} X^{(1)}(0,k)X^{(1)}(k,k')\alpha_{k'}(0)$$
$$\times \sum_{p,p'}(\omega_p\omega_{p'})^{-1/2}\left[f_2\left(\frac{i}{\hbar}(\tilde{E}_0 - E_k + \hbar\omega_p),\ \frac{i}{\hbar}(E_k - E_{k'} - \hbar\omega_{p'}),t\right)\tilde{b}_p^\dagger(0)\tilde{b}_{p'}(0)\right.$$
$$\left. + f_2\left(\frac{i}{\hbar}(\tilde{E}_0 - E_k - \hbar\omega_p),\ \frac{i}{\hbar}(E_k - E_{k'} + \hbar\omega_{p'}),t\right)\tilde{b}_p(0)\tilde{b}_{p'}^\dagger(0) + \cdots\right], \quad (48)$$

where the ellipsis represents terms with $\tilde{b}\tilde{b}$ and $\tilde{b}^\dagger\tilde{b}^\dagger$ and,

$$f_1(A,t) = \int_0^t dt' e^{iAt'} = \frac{e^{iAt}-1}{iA} \quad (49)$$

and

$$f_2(A,B,t) = \int_0^t dt' \int_0^{t'} dt'' e^{iAt'} e^{iBt''}$$
$$= \frac{e^{iAt}-1}{AB} - \frac{e^{i(A+B)t}-1}{B(A+B)}. \quad (50)$$

Inserting (47) into (39) we get

$$n_0(t) = \mathrm{Tr}[\tilde{\alpha}_0^{(0)\dagger}(t)\tilde{\alpha}_0^{(0)}(t)\hat{\rho}(0)] + \mathrm{Tr}[\tilde{\alpha}_0^{(1)\dagger}(t)\tilde{\alpha}_0^{(1)}(t)\hat{\rho}(0)]$$
$$+ \mathrm{Tr}\{[\tilde{\alpha}_0^{(0)\dagger}(t)\tilde{\alpha}_0^{(2)}(t) + \tilde{\alpha}_0^{(2)\dagger}(t)\tilde{\alpha}_0^{(0)}(t)]\hat{\rho}(0)\} + \cdots, \quad (51)$$

which we can evaluate further by noting that

$$\mathrm{Tr}[\tilde{\alpha}_0^\dagger(0)\tilde{\alpha}_0(0)\hat{\rho}(0)] = n_0(0) = (e^{\beta(\tilde{E}_0-\mu)} \pm 1)^{-1} \quad (52)$$

is the initial equilibrium occupation of the bound state $\tilde{E}_0$. If the gas particles are fermions, the plus sign has to be taken; if they are bosons, one must take the minus sign. As desorption experiments are always performed at very low pressures, one can, in most cases, approximate (52) by the Maxwell-Boltzmann distribution:

$$n_0(0) \approx e^{-\beta(\tilde{E}_0-\mu)}. \quad (53)$$

Also note that in our theory of isothermal desorption we fix the time $t=0$ as that instant at which, e.g., by rapid pumping, the gas phase has been essentially removed from the system, implying that for the continuum,

$$\mathrm{Tr}[\alpha_k^\dagger(0)\alpha_k(0)\beta(0)] = n_k(0) = 0. \quad (54)$$

Thus the second term in (51) does not contribute and we get

$$n_0(t) = n_0(0)\left\{1 - (L\hbar)^{-2}\sum_{k>0} X^{(1)}(0,k)X^{(1)}(k,0)\sum_p \omega_p^{-1}\left[f_2\left(\frac{i}{\hbar}(\tilde{E}_0 - E_k + \hbar\omega_p),\ \frac{i}{\hbar}(E_k - \tilde{E}_0 - \hbar\omega_p),t\right)n_p^{(\mathrm{ph})}\right.\right.$$
$$\left.\left. + f_2\left(\frac{i}{\hbar}(\tilde{E}_0 - E_k - \hbar\omega_p),\ \frac{i}{\hbar}(E_k - \tilde{E}_0 + \hbar\omega_p),t\right)(n_p^{(\mathrm{ph})}+1) + \mathrm{c.c.}\right]\right\}, \quad (55)$$

where

$$\mathrm{Tr}[\tilde{b}_p^\dagger(0)\tilde{b}_{p'}(0)\hat{\rho}(0)] = \delta_{pp'}/(e^{\beta\hbar\omega_p}-1) = n_p^{(\mathrm{ph})}\delta_{pp'}. \quad (56)$$

To extract the large-time behavior we use the relation

$$\sin^2(\Delta t)/\Delta^2 \xrightarrow[t\to\infty]{} \pi t\delta(\Delta) \quad (57)$$

and find for (55) an expression like (44) where the rate to this order is given by

$$R^{(1)} = 2\pi L^{-2}\sum_{k>0}|X^{(1)}(0,k)|^2\sum_p(\hbar\omega_p)^{-1}n_p^{(\mathrm{ph})}\delta(\tilde{E}_0 - E_k + \hbar\omega_p). \quad (58)$$

The energy-conserving δ function ensures that a particle can leave the adsorbate, i.e., the bound state $\tilde{E}_0$, by absorbing a phonon of energy $\hbar\omega_p = E_k - \tilde{E}_0$.

To evaluate (58) numerically we assume that the phonon spectrum of the solid is adequately represented by the Debye model so that we can replace phonon sums by integrals according to

$$\sum_p \cdots = \frac{3N_s}{\omega_D^3}\int_0^{\omega_D}\omega^2 d\omega \cdots. \quad (59)$$

Moreover, we replace sums over particle momenta by integrals in the large volume limit according to

$$L^{-1}\sum_{k>0} \longrightarrow \pi^{-1}\int_0^\infty dk. \quad (60)$$

Introducing dimensionless variables according to

$$r = \frac{2m\omega_D}{\hbar\gamma^2},\quad w = \frac{\omega}{\omega_D},\quad \epsilon_0 = \frac{|E_0|}{\hbar\omega_D},\quad \tilde{\epsilon}_0 = \frac{|\tilde{E}_0|}{\hbar\omega_D},\quad \delta = \frac{\hbar\omega_D}{k_B T}, \quad (61)$$

we finally obtain

$$R^{(1)}=\omega_D\frac{(3)2^4\sqrt{\epsilon_0}(1+\sqrt{\epsilon_0 r})^3}{r^2}\frac{m}{M_s}\int_{\epsilon_0}^1 S(w)wn(w)dw\,, \tag{62}$$

with

$$n(w)=(e^{\delta w}-1)^{-1} \tag{63}$$

and $S(w)$ given by (A11) in Appendix A.

Observe that as we make the bound state shallower, i.e., let $\tilde{E}_0\to 0$, we find $R^{(1)}\to 0$. We also see that $R^{(1)}=0$ if $\tilde{E}_0\leq -\hbar\omega_D$, because in this case a single phonon cannot supply enough energy to transfer a gas particle from the bound state $\tilde{E}_0$ into the continuum E_k.

C. One- and two-phonon processes: Fourth order in $H_{gs}^{(1)}$

We now want to outline the fourth-order perturbative calculation of the isothermal desorption time. For this we must consider the terms arising from $H_{gs}^{(1)}$. $H_{gs}^{(2)}$ can contribute one- and two-phonon processes in second order and also in the first order interfering with the second-order terms in $H_{gs}^{(1)}$. In addition, we get contributions from the interference term involving $H_{gs}^{(1)}$ and $H_{gs}^{(3)}$, both in first order. These contributions will be discussed in Sec. IV.

Iterating (42) four times, and keeping only terms involving $\tilde{\alpha}_0(0)$ which are the only initial states contributing to the isothermal desorption time [see the discussion around (54)], we get

$$\tilde{\alpha}_0(t)=\tilde{\alpha}_0^{(0)}(t)+\tilde{\alpha}_0^{(2)}(t)+\tilde{\alpha}_0^{(3)}(t)+\tilde{\alpha}_0^{(4)}(t)+\tilde{\alpha}_0^{(4')}(t)\,, \tag{64}$$

where in analogy to (48),

$$\tilde{\alpha}_0^{(0)}(t)=e^{-(i/\hbar)\tilde{E}_0 t}\tilde{\alpha}_0(0)\,, \tag{65}$$

$$\begin{aligned}\tilde{\alpha}_0^{(2)}(t)=e^{-(i/\hbar)\tilde{E}_0 t}\tilde{\alpha}_0(0)\left(-\frac{i}{L\hbar}\right)^2\sum_{k>0}X^{(1)}(0,k)X^{(1)}(k,0)\\ \times\int_0^t dt_1\int_0^{t_1}dt_2 e^{i(\tilde{E}_0-E_k)t_1/\hbar}e^{i(E_k-\tilde{E}_0)t_2/\hbar}B^\dagger(t_1)b(t_1)b(t_2)B(t_2)\,,\end{aligned} \tag{66}$$

$$\begin{aligned}\tilde{\alpha}_0^{(3)}(t)=e^{-(i/\hbar)\tilde{E}_0 t}\tilde{\alpha}_0(0)\left(-\frac{i}{L\hbar}\right)^3\sum_{k>0}\sum_{k'>0}X^{(1)}(0,k)X^{(1)}(k,k')X^{(1)}(k',0)\\ \times\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3 e^{i(\tilde{E}_0-E_k)t_1/\hbar}e^{i(E_k-E_{k'})t_2/\hbar}e^{i(E_{k'}-\tilde{E}_0)t_3/\hbar}\\ \times b^\dagger(t_1)b(t_1)b(t_2)b(t_3)B(t_3)\,,\end{aligned} \tag{67}$$

$$\begin{aligned}\tilde{\alpha}_0^{(4)}(t)=e^{-(i/\hbar)\tilde{E}_0 t}\tilde{\alpha}_0(0)\left(-\frac{i}{L\hbar}\right)^4\sum_{k>0}\sum_{k'>0}X^{(1)}(0,k)X^{(1)}(k,0)X^{(1)}(0,k')X^{(1)}(k',0)\\ \times\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4 e^{i(\tilde{E}_0-E_k)t_1/\hbar}e^{i(E_k-\tilde{E}_0)t_2/\hbar}\\ \times e^{i(\tilde{E}_0-E_{k'})t_3/\hbar}e^{i(E_{k'}-\tilde{E}_0)t_4/\hbar}\\ \times B^\dagger(t_1)b(t_1)b(t_2)B(t_2)B^\dagger(t_3)b(t_3)b(t_4)B(t_4)\,,\end{aligned} \tag{68}$$

$$\begin{aligned}\tilde{\alpha}_0^{(4')}(t)=e^{-(i/\hbar)\tilde{E}_0 t}\tilde{\alpha}_0(0)\left(-\frac{i}{L\hbar}\right)^4\sum_{k>0}\sum_{k'>0}\sum_{k''>0}X^{(1)}(0,k)X^{(1)}(k,k')X^{(1)}(k',k'')X^{(1)}(k'',0)\\ \times\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4 e^{i(\tilde{E}_0-E_k)t_1/\hbar}e^{i(E_k-E_{k'})t_2/\hbar}\\ \times e^{i(E_{k'}-E_{k''})t_3/\hbar}e^{i(E_{k''}-\tilde{E}_0)t_4/\hbar}\\ \times B^\dagger(t_1)b(t_1)b(t_2)b(t_3)b(t_4)B(t_4)\,,\end{aligned} \tag{69}$$

where

$$b(t)=\sum_p \omega_p^{-1/2}[\tilde{b}_p^\dagger(t)+\tilde{b}_p(t)]\,. \tag{70}$$

Note that in (66)–(69) we do not list the contributions involving $\alpha_k(0)$, but contrary to (48), we keep the operators $B(t)$ defined in (29), without approximation. To calculate the isothermal desorption time we must insert (64) into (39). To perform the phonon averages we expand the $B(t)$ operators to maximal terms quadratic in $X^{(1)}(0,0)$:

$$B(t) \approx 1 - X^{(1)}(0,0) \sum_{p} \omega_p^{-3/2}[\tilde{b}_p^\dagger(t) - \tilde{b}_p(t)] + \tfrac{1}{2}[X^{(1)}(0,0)]^2 \sum_{p,p'} (\omega_p \omega_{p'})^{-3/2}[\tilde{b}_p^\dagger(t) - \tilde{b}_p(t)][\tilde{b}_{p'}^\dagger(t) - \tilde{b}_{p'}(t)]\,. \tag{71}$$

We then keep the necessary terms to ensure that in $\langle \tilde{\alpha}_0^\dagger(t)\tilde{\alpha}_0(t)\rangle$, in addition to the one-phonon contributions (see Sec. III B), all two-phonon contributions are kept which will arise from averages of all possible products of two-phonon creation and two-phonon annihilation operators. They are given explicitly in Appendix B. Note that of the four phonon sums appearing in the fourth-order terms in $\tilde{\alpha}_0^\dagger(t)\tilde{\alpha}_0(t)$, two are eliminated upon taking phonon averages through the Kronecker δ's in (B1)–(B6). After this, all time integrations in $\langle \tilde{\alpha}_0^\dagger(t)\tilde{\alpha}_0(t)\rangle$ can be performed, as done in (C5)–(C14) where their long time limits are also given.

This rather lengthy calculation leads to the following result:

$$\frac{n_0(t)}{n_0(0)} = 1 - \sum_i R^{(i)} t\,, \tag{72}$$

where $R^{(1)}$ is the second-order contribution to the rate given in (58). The contributions $R^{(2)}$ to $R^{(5)}$ are classified according to the number of intermediate continuum states. Thus $R^{(2)}$ does not contain intermediate continuum states:

$$\begin{aligned} R^{(2)} = \frac{2\pi}{L^4\hbar^3} \sum_{k>0} \sum_{p,p'} & X^{(1)}(0,k)X^{(1)}(k,0)[X^{(1)}(0,0)]^2(\omega_p\omega_{p'})^{-1} \\ & \times \Bigg\{ \frac{1}{\omega_{p'}} \left[n_p^{(\mathrm{ph})} n_{p'}^{(\mathrm{ph})} \left(\frac{2}{\omega_p} - \frac{1}{\omega_{p'}} \right) - n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1) \left(\frac{2}{\omega_p} + \frac{1}{\omega_{p'}} \right) \right] \delta(\tilde{E}_0 - E_k + \hbar\omega_p) \\ & + \tfrac{1}{2} n_p^{(\mathrm{ph})} n_{p'}^{(\mathrm{ph})} \left(\frac{1}{\omega_p} + \frac{1}{\omega_{p'}} \right)^2 \delta(\tilde{E}_0 - E_k + \hbar\omega_p + \hbar\omega_{p'}) \\ & + n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1) \left(\frac{1}{\omega_p} - \frac{1}{\omega_{p'}} \right)^2 \delta(\tilde{E}_0 - E_k + \hbar\omega_p - \hbar\omega_{p'}) \Bigg\}. \end{aligned} \tag{73}$$

$R^{(3)}$ and $R^{(4)}$ both contain one intermediate continuum state and are given by

$$\begin{aligned} R^{(3)} = -\frac{4\pi}{L^4\hbar^2} \sum_{k>0} \sum_{k'>0} & X^{(1)}(0,k)X^{(1)}(k,k')X^{(1)}(k',0)X^{(1)}(0,0) \\ & \times \sum_{p,p'} (\omega_p\omega_{p'})^{-1} \Bigg(\Bigg\{ n_p^{(\mathrm{ph})} n_{p'}^{(\mathrm{ph})} \left[\left(\frac{1}{\omega_p} + \frac{1}{\omega_{p'}} \right) \frac{1}{E_k - \tilde{E}_0 - \hbar\omega_p - \hbar\omega_{p'}} + \frac{1}{\omega_{p'}(E_k - \tilde{E}_0)} \right] \\ & \qquad + n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1) \Bigg[\left(\frac{1}{\omega_p} - \frac{1}{\omega_{p'}} \right) \frac{1}{E_k - \tilde{E}_0 - \hbar\omega_p + \hbar\omega_{p'}} \\ & \qquad - \frac{1}{\omega_{p'}(E_k - \tilde{E}_0)} \Bigg] \Bigg\} \delta(\tilde{E}_0 - E_{k'} + \hbar\omega_p) \\ & \qquad + \tfrac{1}{2} n_p^{(\mathrm{ph})} n_{p'}^{(\mathrm{ph})} \left(\frac{1}{\omega_p} + \frac{1}{\omega_{p'}} \right) \left(\frac{1}{E_k - \tilde{E}_0 - \hbar\omega_p} + \frac{1}{E_k - \tilde{E}_0 - \hbar\omega_{p'}} \right) \delta(\tilde{E}_0 - E_{k'} + \hbar\omega_p + \hbar\omega_{p'}) \\ & \qquad + n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1) \left(\frac{1}{\omega_p} - \frac{1}{\omega_{p'}} \right) \left(\frac{1}{E_k - \tilde{E}_0 - \hbar\omega_p} + \frac{1}{E_k - \tilde{E}_0 + \hbar\omega_{p'}} \right) \\ & \qquad \times \delta(\tilde{E}_0 - E_{k'} + \hbar\omega_p - \hbar\omega_{p'}) \Bigg)\,, \end{aligned} \tag{74}$$

$$\begin{aligned} R^{(4)} = -\frac{2\pi}{L^4\hbar} \sum_{k>0} \sum_{k'>0} & X^{(1)}(0,k)X^{(1)}(k,0)X^{(1)}(0,k')X^{(1)}(k',0) \\ & \times \sum_{p,p'} (\omega_p\omega_{p'})^{-1} \Bigg(\Bigg\{ n_p^{(\mathrm{ph})} n_{p'}^{(\mathrm{ph})} \Bigg[\frac{3}{(E_{k'} - \tilde{E}_0 - \hbar\omega_{p'})^2} \\ & \qquad + \frac{2}{\hbar\omega_p + \hbar\omega_{p'}} \left(\frac{1}{E_{k'} - \tilde{E}_0 - \hbar\omega_p} + \frac{1}{E_{k'} - \tilde{E}_0 - \hbar\omega_{p'}} \right) \Bigg] \\ & \qquad + n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1) \Bigg[\frac{3}{(E_{k'} - \tilde{E}_0 + \hbar\omega_{p'})^2} \\ & \qquad + \frac{2}{\hbar\omega_p - \hbar\omega_{p'}} \left(\frac{1}{E_{k'} - \tilde{E}_0 - \hbar\omega_p} + \frac{1}{E_{k'} - \tilde{E}_0 + \hbar\omega_{p'}} \right) \Bigg] \Bigg\} \\ & \qquad \times \delta(\tilde{E}_0 - E_k + \hbar\omega_p) + \left(\frac{n_p^{(\mathrm{ph})} n_{p'}^{(\mathrm{ph})}}{E_{k'} - \tilde{E}_0 - \hbar\omega_{p'}} + \frac{n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1}{E_{k'} - \tilde{E}_0 + \hbar\omega_{p'}} \right) \delta'(\tilde{E}_0 - E_k + \hbar\omega_p) \Bigg)\,. \end{aligned} \tag{75}$$

Finally, $R^{(5)}$ contains two intermediate continuum states:

$$\begin{aligned}
R^{(5)}=\frac{2\pi}{L^4\hbar}\sum_{k>0}\sum_{k'>0}\sum_{k''>0}&X^{(1)}(0,k)X^{(1)}(k,k')X^{(1)}(k',k'')X^{(1)}(k'',0)\\
&\times\sum_{p,p'}(\omega_p\omega_{p'})^{-1}\Bigg(2\Bigg\{n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\Bigg[\frac{1}{(E_k-\tilde{E}_0-\hbar\omega_{p'})(E_{k'}-\tilde{E}_0)}\\
&\qquad+\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_p-\hbar\omega_{p'}}\left(\frac{1}{E_k-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_k-\tilde{E}_0-\hbar\omega_{p'}}\right)\Bigg]\\
&\quad+n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\Bigg[\frac{1}{(E_k-\tilde{E}_0+\hbar\omega_{p'})(E_{k'}-\tilde{E}_0)}\\
&\qquad+\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_p+\hbar\omega_{p'}}\left(\frac{1}{E_k-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_k-\tilde{E}_0+\hbar\omega_{p'}}\right)\Bigg]\Bigg\}\\
&\times\delta(\tilde{E}_0-E_{k''}+\hbar\omega_p)+\tfrac{1}{2}n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\left(\frac{1}{E_k-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_k-\tilde{E}_0-\hbar\omega_{p'}}\right)\\
&\times\left(\frac{1}{E_{k''}-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_{k''}-\tilde{E}_0-\hbar\omega_{p'}}\right)\delta(\tilde{E}_0-E_{k'}+\hbar\omega_p+\hbar\omega_{p'})\\
&+n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\left(\frac{1}{E_k-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_k-\tilde{E}_0+\hbar\omega_{p'}}\right)\\
&\times\left(\frac{1}{E_{k''}-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_{k''}-\tilde{E}_0+\hbar\omega_{p'}}\right)\delta(\tilde{E}_0-E_{k'}+\hbar\omega_p-\hbar\omega_{p'})\Bigg).
\end{aligned}\tag{76}$$

A short discussion of these formulas is in order. Note that they are valid for any potential, local or nonlocal. Observe that in fourth order, we also get one-phonon transitions as signaled by the appearance of the energy-conserving δ functions $\delta(\tilde{E}_0-E_k+\hbar\omega_p)$. All these terms, of course, involve two Bose-Einstein factors for the phonons with one real phonon of energy $\hbar\omega_p$ being absorbed, whereas the second phonon remains virtual contributing to vertex and self-energy corrections. The appearance of the derivatives of the δ functions in $R^{(4)}$ reflects the fact that in a fourth-order calculation based on the dressed Hamiltonian, only self-energy corrections in $\tilde{E}_0$ are kept to all orders. Transferring the derivative from the δ function onto the matrix elements we get the lowest-order vertex correction.

Apart from the one-phonon terms we have also two-phonon contributions in the rates (73)–(76) with the factors

$$n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\delta(\tilde{E}_0-E_k+\hbar\omega_p+\hbar\omega_{p'})\tag{77}$$

for the absorption of two phonons, and the factor

$$n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)(\tilde{E}_0-E_k+\hbar\omega_p-\hbar\omega_{p'})\tag{78}$$

for the absorption of a phonon of energy $\hbar\omega_p$ and the simultaneous emission of a phonon of energy $\hbar\omega_{p'}$. Trivially it is only terms with a factor (77) that survive for deep bound states with $-2\hbar\omega_D<\tilde{E}_0<-\hbar\omega_D$.

It still remains to rewrite the rates (73)–(77) in the dimensionless units (60). This is done for the general case in Appendix D. The formula become very simple for deep bound states with $1<\tilde{\epsilon}_0=|\tilde{E}_0|/\hbar\omega_D<2$, namely,

$$\begin{aligned}
t_d^{-1}=\omega_D\frac{2^5 3^2(1+\sqrt{r\epsilon_0})^5\sqrt{\epsilon_0}}{r^4}\left(\frac{m}{M_s}\right)^2&\\
\times\int_{\tilde{\epsilon}_0-1}^{1}dw\int_{\tilde{\epsilon}_0-w}^{1}dw'\,wn(w)w'n(w')S(w+w')&\\
\times\Bigg[\sqrt{\epsilon_0}\left(\frac{1}{w}+\frac{1}{w'}\right)&\\
-[F_>(w)+F_>(w')]\Bigg]^2&,
\end{aligned}\tag{79}$$

where we have not included terms arising from $X^{(2)}$ which will be given in Sec. III D. The functions S and $F_>$ are given in Appendix D.

D. One- and two-phonon processes from $H_{gs}^{(2)}$ and $H_{gs}^{(3)}$

To calculate the contributions to the isothermal desorption time arising from $H_{gs}^{(2)}$, we must iterate (42) four times keeping also the terms with $X^{(2)}$. After that, one continues the calculation in complete analogy to the outline given in Sec. III C leading to (72) with additional terms in the rate; the first one is second order in $H_{gs}^{(2)}$,

$$R^{(6)}=\frac{4\pi}{L^2\hbar}\sum_{k>0}X^{(2)}(0,k)X^{(2)}(k,0)$$

$$\times\sum_{p,p'}(\omega_p\omega_{p'})^{-1}[n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\delta(\tilde{E}_0-E_k+\hbar\omega_p+\hbar\omega_{p'})+2n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\delta(\tilde{E}_0-E_k+\hbar\omega_p-\hbar\omega_{p'})]. \tag{80}$$

In addition, there will be several terms in which second-order terms in $H_{gs}^{(1)}$ interfere with the first-order terms in $H_{gs}^{(2)}$. They are again classified according to the number of intermediate continuum states. With no intermediate continuum state we get

$$R^{(7)}=\frac{2\pi}{L^3\hbar}\sum_{k>0}X^{(2)}(0,0)X^{(1)}(0,k)X^{(1)}(k,0)\sum_{p,p'}(\omega_p\omega_{p'})^{-1}\left[4\left(\frac{n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}}{\hbar\omega_p+\hbar\omega_{p'}}+\frac{n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)}{\hbar\omega_p-\hbar\omega_{p'}}\right)\delta(\tilde{E}_0-E_k+\hbar\omega_p)\right.$$

$$\left.+3[n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}+n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)]\,\delta'(\tilde{E}_0-E_k+\hbar\omega_p)\right], \tag{81}$$

$$R^{(8)}=\frac{4\pi}{L^3\hbar^2}\sum_{k>0}X^{(1)}(0,k)X^{(2)}(k,0)X^{(1)}(0,0)$$

$$\times\sum_{p,p'}(\omega_p\omega_{p'})^{-1}\left\{\left[n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\left(\frac{1}{\omega_p}+\frac{2}{\omega_{p'}}\right)+n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\left(\frac{1}{\omega_p}-\frac{2}{\omega_{p'}}\right)\right]\delta(\tilde{E}_0-E_k+\hbar\omega_p)\right.$$

$$+n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\left(\frac{1}{\omega_p}+\frac{1}{\omega_{p'}}\right)\delta(\tilde{E}_0-E_k+\hbar\omega_p+\hbar\omega_{p'})$$

$$\left.+2n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\left(\frac{1}{\omega_p}-\frac{1}{\omega_{p'}}\right)\delta(\tilde{E}_0-E_k+\hbar\omega_p-\hbar\omega_{p'})\right\}. \tag{82}$$

With one intermediate continuum state, one has

$$R^{(9)}=-\frac{4\pi}{L^3\hbar}\sum_{k>0}\sum_{k'>0}X^{(2)}(0,k)X^{(1)}(k,k')X^{(1)}(k',0)$$

$$\times\sum_{p,p'}(\omega_p\omega_{p'})^{-1}\left\{\left[n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\left(\frac{2}{E_k-\tilde{E}_0-\hbar\omega_p-\hbar\omega_{p'}}+\frac{2}{E_{k'}-\tilde{E}_0-\hbar\omega_{p'}}+\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_{k'}-\tilde{E}_0}\right)\right.\right.$$

$$+n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\left(\frac{2}{E_{k'}-\tilde{E}_0-\hbar\omega_p+\hbar\omega_{p'}}+\frac{2}{E_{k'}-\tilde{E}_0+\hbar\omega_{p'}}\right.$$

$$\left.\left.+\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_{k'}-\tilde{E}_0}\right)\right]\delta(\tilde{E}_0-E_k+\hbar\omega_p)$$

$$+n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}\left(\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_{p'}}\right)\delta(\tilde{E}_0-E_k+\hbar\omega_p+\hbar\omega_{p'})$$

$$\left.+2n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)\left(\frac{1}{E_{k'}-\tilde{E}_0-\hbar\omega_p}+\frac{1}{E_{k'}-\tilde{E}_0+\hbar\omega_{p'}}\right)\delta(\tilde{E}_0-E_k+\hbar\omega_p-\hbar\omega_{p'})\right\}. \tag{83}$$

In addition, the interference terms involving $H_{gs}^{(1)}$ and $H_{gs}^{(3)}$ both in first order contribute to the one-phonon processes via a rate

$$R^{(10)}=\frac{12\pi}{L^2\hbar}\sum_{k>0}X^{(1)}(0,k)X^{(3)}(k,0)\sum_{p,p'}(\omega_p\omega_{p'})^{-1}[n_p^{(\mathrm{ph})}n_{p'}^{(\mathrm{ph})}+n_p^{(\mathrm{ph})}(n_{p'}^{(\mathrm{ph})}+1)]\delta(\tilde{E}_0-E_k+\hbar\omega_p). \tag{84}$$

These rate contributions $R^{(6)}$ to $R^{(10)}$ are given in dimensionless form in Appendix D. Here we just give the isothermal desorption time, calculated exactly in fourth order, including all two-phonon processes, for deep bound states with $1<\tilde{\epsilon}_0=-\tilde{E}_0/\hbar\omega_D<2$:

$$t_d^{-1}=\omega_D\frac{2^6 3^2(1+\sqrt{r\epsilon_0})^4\sqrt{\epsilon_0}}{r^3\sqrt{r}}\left(\frac{m}{M_s}\right)^2\int_{\tilde{\epsilon}_0-1}^{1}dw\int_{\tilde{\epsilon}_0-w}^{1}dw'\,wn(w)w'n(w')S(w+w')$$

$$\times\left\{\frac{1+\sqrt{r\epsilon_0}}{2\sqrt{r}}\left[\sqrt{\epsilon_0}\left(\frac{1}{w}+\frac{1}{w'}\right)-[F_>(w)+F_>(w')]\right]^2\right.$$

$$\left.+2\left(\frac{\sqrt{r}}{4(1+\sqrt{r\epsilon_0})}+F_>(w)-\frac{\sqrt{\epsilon_0}}{w}\right)\right\}, \tag{85}$$

where the terms in the large square brackets in the integrand are from (79) and the last terms are the new ones with the first of these, namely the one containing $\sqrt{r}/4(1+\sqrt{r\epsilon_0})$ being the contribution from the second-order term in $H_{gs}^{(2)}$.

After these calculations one convinces oneself quite easily that higher Hamiltonians in the expansion (14) will not contribute in the long-time limit to the isothermal desorption time in fourth order.

IV. NUMERICAL RESULTS AND DISCUSSION

We have in Sec. III set up the appropriate initial-value problem for an isothermal desorption experiment and calculated the isothermal desorption time in fourth-order perturbation theory for a system controlled by the Hamiltonians (32) and (28). We will now present a detailed numerical study of the various contributions to the desorption rate, i.e., $t_d^{-1}=\sum_i R^{(i)}$. Let us recall that, to simplify matters, we choose to examine a gas-solid system which develops just one bound state in its surface potential into which gas particles are trapped forming the absorbate. It is then of interest to know how the various rates $R^{(1)}$ to $R^{(10)}$, as given in Appendix D, depend on (a) the energy of the bound state, (b) the temperature of the solid, and (c) the strength of the coupling of the adsorbate particles to the phonons of the solid. The parameters of the model are, accordingly, the bound-state energy E_0, the range $\lambda=\gamma^{-1}$ of the potentials (8)–(10) (note that bound-state energy and range determine the strength g of the potential uniquely), the Debye energy $\hbar\omega_D$ of the solid, the ratio m/M_s of the masses of a gas particle m and a solid particle M_s, and the temperature T of the system. Note that for a given bound-state energy, the coupling between adsorbate and phonons increases as the range λ is decreased.

We have previously applied our second-order theory of flash desorption to a gas-solid system where helium is adsorbed on constantan (an Ni-Cu alloy with a high thermal conductivity), a system for which flash desorption times have been measured.[5] In our first numerical examples, we have therefore chosen the range λ of the potential, the mass ratio m/M_s, and the Debye energy $\hbar\omega_D$ appropriate for the He-constantan system. Observe that the mass ratio multiplies the second-order rate $R^{(1)}$ linearly and appears quadratically as an overall factor in the fourth-order rates $R^{(2)}$–$R^{(10)}$. The Debye energy, on the other hand, sets our energy scale. For this system the renormalized bound-state energy $\tilde{\epsilon}_0$, Eq. (30), is only slightly larger than ϵ_0 by at most 2% at $\tilde{\epsilon}_0=2$.

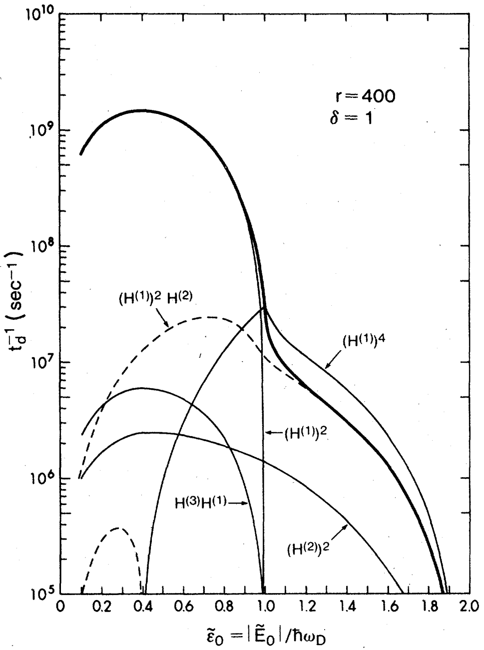

FIG. 1. Isothermal desorption rate t_d^{-1} as a function of the renormalized bound-state energy $\tilde{\epsilon}_0$. $\delta=\hbar\omega_D/k_BT$ and $r=2m\omega_D/\hbar\gamma^2$ [see (59)]. The curve labeled $(H^{(i)})^n\,(H^{(j)})^m$ gives the contribution to the total rate (heavy line) arising from the nth order in the Hamiltonian term $H_{gs}^{(i)}$ and the mth order in $H_{gs}^{(j)}$ [see (16)]. The dashed portions of these curves are *negative*.

In Fig. 1 we give, among others, the total isothermal desorption rate $t_d^{-1}=R=\sum_{i=1}^{10}R^{(i)}$ as a function of the renormalized bound-state energy $\tilde{\epsilon}_0=|\tilde{E}_0|/\hbar\omega_D$ for a temperature such that $\delta=\hbar\omega_D/k_BT=1$ for a rather weakly coupled solid-gas system with the range of the potential $\lambda=2.5$ Å. We see that for $\tilde{\epsilon}_0\lesssim 0.9$, the rate is dominated by the second-order contribution. The curves labeled $(H^{(1)})^2$, $(H^{(1)})^4$, $(H^{(2)})^2$, $(H^{(1)})^2H^{(2)}$, and $H^{(1)}H^{(3)}$ are the contributions $R^{(1)}$, $(R^{(2)}+R^{(3)}+R^{(4)}+R^{(5)})$, $R^{(6)}$, $(R^{(7)}+R^{(8)}+R^{(9)})$, and $R^{(10)}$, respectively. Note that the cross term $(H^{(1)})^2H^{(2)}$ is negative for all bound-state energies $0<\tilde{\epsilon}_0<2$. As $\tilde{\epsilon}_0=|\tilde{E}_0|/\hbar\omega_D$ approaches one, the second-order contribution $R^{(1)}$ goes to zero because a gas particle trapped in a bound state with $\tilde{\epsilon}_0>1$ cannot be freed by absorbing a single phonon. For desorption from bound states with $\tilde{\epsilon}_0>1$, two-phonon processes are necessary. Note that in the latter region the negative contribution from $(H^{(1)})^2H^{(2)}$ is about half of that from $(H^{(1)})^4$! Of course, all ten contributions $R^{(1)}$ to $R^{(10)}$ conspire at $\tilde{\epsilon}_0=1$ to make the total rate change continuously across this point at which all one-phonon processes vanish.

Because in this example the rate is dominated by the second-order contribution for $0\lesssim\tilde{\epsilon}_0\lesssim 0.9$ and for $kT\lesssim\hbar\omega_D$, we can expect that the rate drops appreciably as one-phonon processes become inoperative for $\tilde{\epsilon}_0>1$, though one can anticipate that for $1 \lesssim \tilde{\epsilon}_0 \lesssim 2$, fourth-order perturbation theory is sufficient for the calculation of desorption times as it is the lowest order giving nonvanishing contribution to the rate in this regime of bound-state energies. In Table I we list the individual rate contributions for selected values of $\tilde{\epsilon}_0$ from which one can assess their relative importance. Note that the second-order rate $R^{(1)}$ goes to zero as $\tilde{\epsilon}_0$ approaches zero, but that the rates $R^{(5)}$ and $R^{(9)}$ approach a nonzero, though very small value in this limit. Though in a gas-solid system with $\tilde{\epsilon}_0 = 0$ there is no bound state and there should therefore be no time evolution, i.e., $R = 0$, the nonzero limits of $R^{(5)}$ and $R^{(9)}$ indicate a breakdown of the relaxation time approach. For the latter to be valid one must have two distinct time scales in the system, namely, the microscopic time $t_{\mathrm{micr}} = h/|E_0|$ and the macroscopic relaxation time t_d, and one must require that

$$t_{\mathrm{micr}} = h/|E_0| \ll t_d\,. \tag{86}$$

Because t_d^{-1} approaches a nonzero limit as $|E_0| \to 0$ in fourth order, condition (86) is violated for $|E_0| \lesssim h/t_d$ and the results cannot be trusted for such small binding energies. Another way of looking at this result is to interpret the rate t_d^{-1} as the decay width $\Gamma = \hbar t_d^{-1}$ of the bound state $\tilde{E}_0$, in which case we must demand that Heisenberg's uncertainty relation $|\tilde{E}_0| t_d \gtrsim \hbar$ or $\Gamma/|\tilde{E}_0| < 1$ must hold.

One can suspect that for lower temperatures the fourth-order terms are even less important for $0 < \tilde{\epsilon}_0 < 1$ and that the drop in the desorption rate across $\tilde{\epsilon}_0 = 1$, i.e., as one-phonon processes become ineffective, becomes even more pronounced. This is well illustrated in Fig. 2 for $\delta = 5$. Note that in this case the curve labeled $(H^{(1)})^4$, i.e., the rate contributions $(R^{(2)} + R^{(3)} + R^{(4)} + R^{(5)})$, are negative over a wider region of energies $\tilde{\epsilon}_0$ as compared to the $\delta = 1$ case. Moreover, one can see nicely now that in the cross term $(H^{(1)})^2 H^{(2)}$, i.e., contributions $(R^{(7)} + R^{(8)} + R^{(9)})$, certain terms are switched off at $\tilde{\epsilon}_0 = 1$.

Figure 3 gives the rates for the same gas-solid system as that of Figs. 1 and 2 but at a (unrealistically) high temperature with $\delta = 0.1$. The interesting feature here is the small cusp in R at $\tilde{\epsilon}_0 = 1$. It can be traced back to the fact that the Debye phonon spectrum used in our calculations is cut off sharply at $\hbar\omega_D$. The above cusp is therefore a model-dependent unphysical feature. It would disappear if the phonon spectrum were terminated at the high-frequency end ω_0 by a van Hove-type singularity, e.g., like $\sqrt{\omega_0 - \omega}$.

In Fig. 4 we plot the isothermal desorption time t_d as a function of inverse temperature $\delta = \hbar\omega_D / k_B T$. At low enough temperature, i.e., for $\delta \gg \tilde{\epsilon}_0^{-1}$ or $k_B T \ll |\tilde{E}_0|$, t_d can be approximated over limited temperature regions by an Arrhenius-Frenkel parameterization $t_d = t_d^0 \exp(Q/k_B T)$. But observe that for large δ we get from the second-order rate (62),

$$t_d^{-1} \approx \omega_D \frac{24(1+\sqrt{\epsilon_0 r})^3}{r^2 \epsilon_0} \left(\frac{\pi\epsilon_0}{\delta}\right)^{1/2} e^{-\delta\epsilon_0}\,, \tag{87}$$

where we have put $\epsilon_0 = \tilde{\epsilon}_0$ for simplicity. It is also obvious from Fig. 4 that for $k_B T \gtrsim |E_0|$, an Arrhenius-Frenkel parameterization becomes meaningless. If an Arrhenius-Frenkel parameterization is invoked around $\delta \approx 15$ or so, one finds that Q is larger than $|\tilde{E}_0|$ by about 10% and that the prefactor t_d^0 is typically of the order of 10^{-7} to 10^{-9} sec depending on the bound-state energy $|\tilde{E}_0|$.

We next look at a gas-solid system which differs from the previously studied case by choosing the range λ of the potential to be $\lambda = 0.5$ Å rather than $\lambda = 2.5$ Å as used before. Figure 5 gives the various contributions to the rate for $\delta = 1$. It is obvious that fourth order becomes really important above $\tilde{\epsilon}_0 \approx 0.4$. For $\tilde{\epsilon}_0 \lesssim 0.4$ the fourth-order contribution to the rate is about 10% of the second-order one, necessitating a fourth-order

TABLE I. Various contributions to the isothermal desorption rate $r_d^{-1} = \sum_i R_i$ (sec^{-1}) for the system studied in Fig. 1: $\delta = 1$, $r = 400$.

$\tilde{\epsilon}_0$	R_1	R_2	$(R_3 + R_4)$	R_5	R_6	$(R_7 + R_8)$	R_9	R_{10}
0	0	0	0	9.397	0	0	3.594×10^3	0
0.1	5.989×10^8	-8.788×10^4	-1.447×10^4	4.974×10^3	9.944×10^5	-1.276×10^6	2.319×10^5	2.418×10^6
0.2	1.075×10^9	-2.396×10^4	-6.618×10^4	9.355×10^3	1.730×10^6	-3.893×10^6	4.702×10^5	4.340×10^6
0.5	1.365×10^9	1.541×10^6	-5.674×10^5	1.602×10^4	2.399×10^6	-1.781×10^7	8.114×10^5	5.511×10^6
0.9	2.120×10^8	2.108×10^7	-9.480×10^5	6.562×10^3	1.619×10^6	-1.876×10^7	2.712×10^5	8.561×10^5
1.0	0	3.165×10^7	-4.716×10^5	2.730×10^3	1.348×10^6	-1.069×10^7	1.198×10^5	0
1.1	0	1.585×10^7	-3.081×10^5	1.656×10^3	1.084×10^6	-8.017×10^6	8.434×10^4	0
1.5	0	3.932×10^6	-6.189×10^4	2.465×10^2	2.813×10^5	-2.097×10^6	1.664×10^4	0
1.9	0	8.544×10^4	-1.068×10^3	3.341	5.341×10^3	-4.272×10^4	2.672×10^2	0

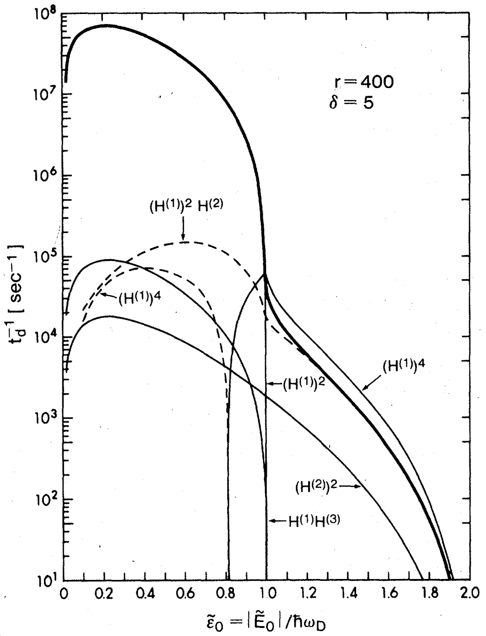

FIG. 2. See Fig. 1.

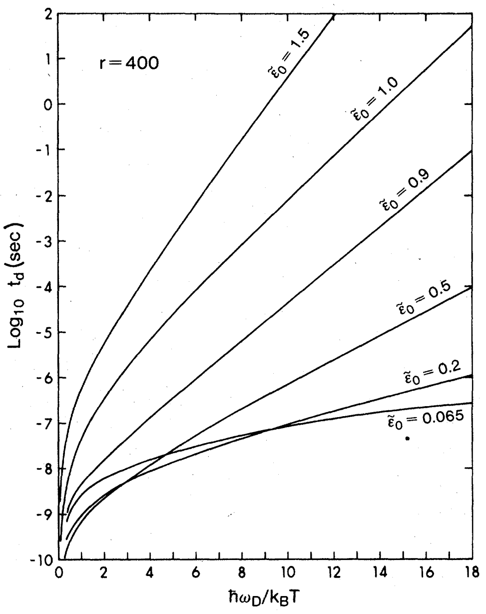

FIG. 4. Logarithm of the desorption time as a function of inverse temperature for various systems with different bound-state energies $\tilde\epsilon_0$ but the same range of the surface potential. $\tilde\epsilon_0 = 0.065$ corresponds to helium adsorbed on constantan.

calculation even for such shallow bound states. The need for the latter is also signaled by the fact that our basic inequality (86) for the validity of the relaxation time approach is not satisfied too well because, e.g., at $\tilde\epsilon_0 = 0.1$, $t_{\text{micr}} \approx 10^{-1} t_d$. The situation becomes completely unacceptable for this system ($\lambda = 0.5$ Å) at very high temperatures ($\delta = 0.1$) where one finds that $t_d \approx t_{\text{micr}}$, indicating that the relaxation time approach is no longer valid. In this case, one moreover finds that fourth-order perturbation theory is totally inadequate because t_d turns out to be negative for a limited region of bound-state energies, namely $0.4 \lesssim \epsilon_0 \lesssim 0.8$, indicating the need of higher-order contributions.

Because the rate calculated for $\delta = 1$ is rather large, we choose as a last example in Fig. 6 a low temperature, i.e., $\delta = 10$ for the same system. Second order gives an adequate relaxation

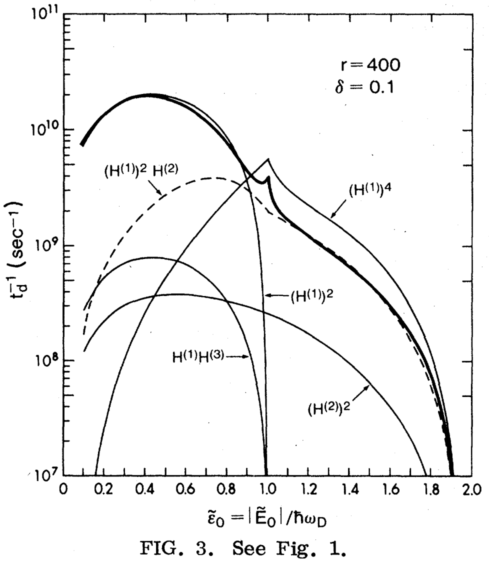

FIG. 3. See Fig. 1.

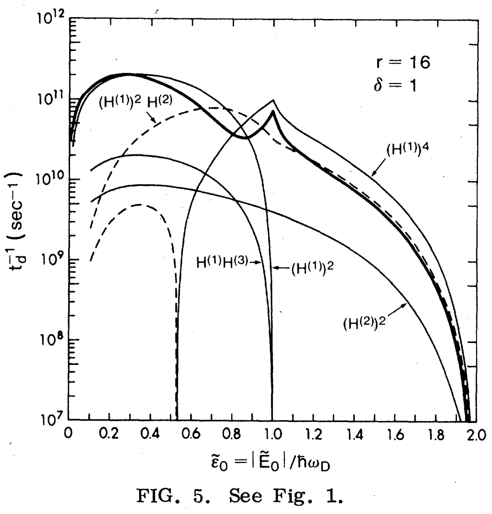

FIG. 5. See Fig. 1.

time up to $\tilde{\epsilon}_0 \lesssim 0.2$, and fourth-order calculations can likely be trusted up to about $\tilde{\epsilon}_0 \lesssim 1.8$.

Summarizing, we want to stress once more that the relaxation time approach to desorption is only valid for gas-solid systems for which the inequality (86) is satisfied. Such systems one might descriptively call weakly coupled ones. The gas-solid systems studied in Figs. 1–4 with the range of the surface potential $\lambda = 2.5$ Å turn out to be weakly coupled for all temperatures considered, whereas the second system studied in Figs. 5 and 6 (with $\lambda = 0.5$ Å) is weakly coupled for $k_B T \lesssim \hbar\omega_D$.

For a weakly coupled system we can trust a second-order calculation of the desorption times as long as $|\tilde{E}_0| \lesssim k_B T \lesssim \hbar\omega_D$, with fourth-order contributions being important for $|\tilde{E}_0| < \hbar\omega_D$ and $k_B T \gtrsim \hbar\omega_D$. If, on the other hand, $\hbar\omega_D \lesssim |\tilde{E}_0| \lesssim 2\hbar\omega_D$, then the fourth-order terms are essential because second-order contributions are zero in this region of bound-state energies.

In the fourth-order calculations, one cannot limit oneself to the term $H_{gs}^{(1)}$ in the Hamiltonian (32), as commonly done in the literature,[10] but must calculate all contributions generated by $H_{gs}^{(1)}$, $H_{gs}^{(2)}$, and $H_{gs}^{(3)}$ in (32). In particular, we have seen that interference terms between second order in $H_{gs}^{(1)}$ and first order in $H_{gs}^{(2)}$ are very important (and negative). Second-order terms in $H_{gs}^{(2)}$, which are the only fourth-order terms taken into account by Allen and Feuer,[11] are generally small, making up at most 10% of the fourth-order contributions to the total rate in our numerical examples.

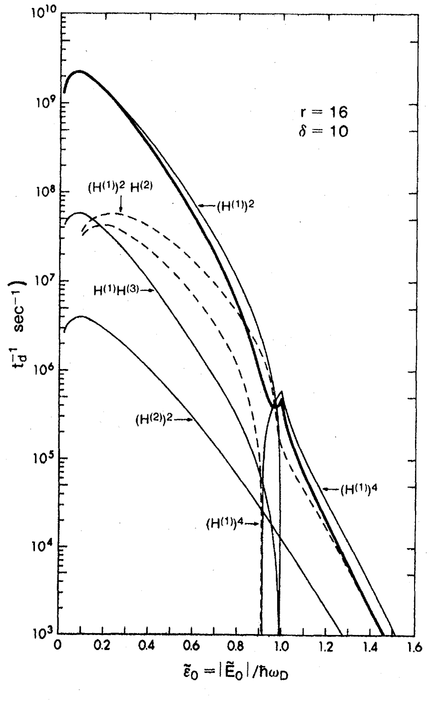

FIG. 6. See Fig. 1.

In this paper we have calculated isothermal desorption time in gas-solid systems in which the surface potential develops only one bound state. More relatistic models must account for the fact that most gas-solid systems, showing physisorption, have surface potentials that develop more than one bound state, say n bound states, at energies $E_1, \ldots, E_n$. Desorption in such systems can proceed in two ways: (a) by direct, if necessary multiphonon, transitions from bound state E_i to the continuum, or (b) through cascades $E_i \rightarrow E_{i+1} \rightarrow \cdots \rightarrow$ continuum. As a result of this paper we will be justified to develop a desorption theory for weakly coupled systems taking into account one-phonon cascades only.[14]

In this paper we have used a simple Debye phonon spectrum, for which a clear comparison of different types of one- and two-phonon processes is very easy. If one wants to calculate multiphonon contributions to the desorption rate for a particular system, more realistic phonon spectra including local nodes and surface modes can be used, though qualitatively no changes are expected from the picture emerging from this paper. A discussion of this point has been given by Bendow and Ying.[10]

In (4) we have imposed boundary conditions such that the wave functions of the adsorbed particles have modes at the wall. Knowles and Suhl[15] have argued that one should use polaron-type wave functions which do not possess nodes resulting, in their words, in a "squashy" rather than a static surface potential. The choice of boundary conditions becomes particularly crucial at very low temperatures. For our numerical examples the commonly used rigid boundary conditions seem appropriate, though modifications might be necessary at very low temperatures.

ACKNOWLEDGMENT

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APPENDIX A

In this appendix we want to summarize the necessary details about the static part of the gas Hamiltonian

$$H_{st} = H_g + V_{st} = \sum_k \epsilon(k) a_k^\dagger a_k + gL^{-1} \sum_{k,k'} V(k)V(k') a_k^\dagger a_{k'} \,. \qquad \text{(A1)}$$

The continuum wave functions of momentum q

can be calculated exactly and are given in the momentum space representation by

$$\phi_q(k) = \delta_{qk} + gL^{-1}W_q V(k)/(E_q - E_k + i\epsilon) , \tag{A2}$$

where W_q is given by

$$\begin{aligned} W_q &= \sum_k \phi_q(k) V(k) \\ &= V(q)\Big(1 - gL^{-1}\sum_k V^2(k')/(E_q - E_{k'} + i\epsilon)\Big)^{-1} . \end{aligned} \tag{A3}$$

If the Hamiltonian (A1) develops a bound state for $g<0$, its wave function is given by

$$\phi_0(k) = |g|\, L^{-1}W_0 V(k)/(E_k - E_0) , \tag{A4}$$

where the bound-state energy E_0 must be calculated as a root of

$$1 - |g|\, L^{-1}\sum_k V^2(k)/(E_k - E_0) = 0 .$$

The normalization of $\phi_0(k)$ fixes W_0 to be

$$W_0^{-2} = g^2 L^{-2}\sum_k V^2(k)/(E_k - E_0)^2 . \tag{A5}$$

For the potential (10), we get explicitly

$$W_q = \frac{q}{q^2+\gamma^2}\,\frac{(q+i\gamma)^2}{(q-ia_1)(q-ia_2)} , \tag{A6}$$

$$W_0 = \frac{\sqrt{2}\,\hbar^2}{m|g|}\sqrt{\gamma a_1}\,(\gamma + a_1)^{3/2} , \tag{A7}$$

where

$$a_{1,2} = -\gamma \pm \left(\frac{m|g|}{2\hbar^2\gamma}\right)^{1/2} . \tag{A8}$$

The equation for a_1 in (A8) determines the bound-state energy $E_0 = -\hbar^2 a_1^2/2m$ for the potential (10).

For the calculation of the desorption time we need some integrals involving $|W_q|^2$. They can be calculated explicitly and, using dimensionless units (61), can be expressed as follows:

$$\sum_q |W_q|^2\delta(E_q - \tilde{E}_0 - \hbar\omega) = \frac{Lm}{\pi\hbar^2\gamma^3\sqrt{r}}\,\theta(w - \tilde{\epsilon}_0)S(w) , \tag{A9}$$

$$\sum_q \frac{|W_q|^2}{E_q - \tilde{E}_0 - \hbar\omega} = \frac{Lm}{2\hbar^2\gamma^3\sqrt{r}\,(1+\sqrt{r\epsilon_0})} \times[\theta(w-\tilde{\epsilon}_0)F_<(w) + \theta(\tilde{\epsilon}_0 - w)F_>(w)] , \tag{A10}$$

where

$$S(w) = \frac{\sqrt{w-\tilde{\epsilon}_0}}{(w+\epsilon_0-\tilde{\epsilon}_0)[4+4\sqrt{r\epsilon_0}+rw+r(\epsilon_0-\tilde{\epsilon}_0)]} , \tag{A11}$$

$$F_<(w) = \frac{\sqrt{r}(\epsilon_0+\tilde{\epsilon}_0) + 2\sqrt{\epsilon_0} - \sqrt{r}\,w}{(w+\epsilon_0-\tilde{\epsilon}_0)[4+4\sqrt{r\epsilon_0}+rw+r(\epsilon_0-\tilde{\epsilon}_0)]} , \tag{A12}$$

$$F_>(w) = \frac{1}{(\sqrt{\epsilon_0}+\sqrt{\tilde{\epsilon}_0 - w})[2+\sqrt{r}\,(\sqrt{\epsilon_0}+\sqrt{\tilde{\epsilon}_0 - w})]} . \tag{A13}$$

APPENDIX B

The thermal averages of all possible products of two-phonon creation and two-phonon annihilation operators at time $t=0$, needed in Secs. IIIC and IIID, are as follows:

$$\langle b_{p_1}^\dagger b_{p_2}^\dagger b_{p_3} b_{p_4}\rangle = n_{p_1}^{(\mathrm{ph})} n_{p_2}^{(\mathrm{ph})}(\delta_{13}\delta_{24} + \delta_{14}\delta_{23}) , \tag{B1}$$

$$\langle b_{p_1} b_{p_2} b_{p_3}^\dagger b_{p_4}^\dagger\rangle = (n_{p_1}^{(\mathrm{ph})}+1)(n_{p_2}^{(\mathrm{ph})}+1) \times(\delta_{13}\delta_{24} + \delta_{14}\delta_{23}) , \tag{B2}$$

$$\langle b_{p_1}^\dagger b_{p_2} b_{p_3}^\dagger b_{p_4}\rangle = n_{p_1}^{(\mathrm{ph})} n_{p_3}^{(\mathrm{ph})}\delta_{12}\delta_{34} + n_{p_1}^{(\mathrm{ph})}(n_{p_3}^{(\mathrm{ph})}+1)\delta_{14}\delta_{23} , \tag{B3}$$

$$\langle b_{p_1} b_{p_2}^\dagger b_{p_3} b_{p_4}^\dagger\rangle = (n_{p_1}^{(\mathrm{ph})}+1)(n_{p_3}^{(\mathrm{ph})}+1)\delta_{12}\delta_{34} + (n_{p_1}^{(\mathrm{ph})}+1)n_{p_3}^{(\mathrm{ph})}\delta_{14}\delta_{23} , \tag{B4}$$

$$\langle b_{p_1} b_{p_2}^\dagger b_{p_3}^\dagger b_{p_4}\rangle = (n_{p_1}^{(\mathrm{ph})}+1)n_{p_4}^{(\mathrm{ph})}(\delta_{12}\delta_{34} + \delta_{13}\delta_{24}) , \tag{B5}$$

$$\langle b_{p_1}^\dagger b_{p_2} b_{p_3} b_{p_4}^\dagger\rangle = n_{p_1}^{(\mathrm{ph})}(n_{p_4}^{(\mathrm{ph})}+1)(\delta_{12}\delta_{34} + \delta_{13}\delta_{24}) , \tag{B6}$$

where

$$n_p^{(\mathrm{ph})} = \langle b_p^\dagger b_p\rangle = (e^{\beta\hbar\omega_p} - 1) . \tag{B7}$$

APPENDIX C

In fourth-order time-dependent perturbative theory integrals of the form

$$f_n(A_1,\ldots,A_N,t) = \int_0^t dt_1\int_0^{t_1} dt_2\cdots\int_0^{t_{N-1}} dt_N\, e^{iA_1t_1}\cdots e^{iA_nt_n} , \tag{C1}$$

will appear where $N=1$, 2, 3, 4. To calculate the isothermal desorption time, according to Fermi's golden rule one must take the long-time limits of the functions (C1) and their products, and extract the terms linear in time. To do the latter one uses the following relations for $-\infty < x < +\infty$:

$$4\sin^2(\tfrac{1}{2}xt)/x^2 \xrightarrow[t\to\infty]{} 2\pi t\delta(x)\,, \tag{C2}$$

$$4\sin^2(\tfrac{1}{2}xt)/x^3 \xrightarrow[t\to\infty]{} -2\pi t\delta'(x)\,, \tag{C3}$$

$$t\sin(xt)/x^2 \xrightarrow[t\to\infty]{} -\pi t\delta'(x)\,. \tag{C4}$$

With this we find

$$f_1(A,t)f_1(-A,t) = 4\sin^2(\tfrac{1}{2}At)/A^2 \xrightarrow[t\to\infty]{} 2\pi t\delta(A)\,, \tag{C5}$$

$$\begin{aligned} if_1(A,t)f_2(-(A+C),C,t)+\text{c.c.} &= \frac{-1}{CA(A+C)}\{4\sin^2[\tfrac{1}{2}(A+C)t] + 4\sin^2(\tfrac{1}{2}At) - 4\sin^2(\tfrac{1}{2}Ct)\} \\ &\quad + \frac{8\sin^2(\tfrac{1}{2}At)}{A^2C} \xrightarrow[t\to\infty]{} +4\pi\frac{\delta(A)}{C}\,, \end{aligned} \tag{C6}$$

$$if_1(0,t)f_2(B,-B,t)+\text{c.c.} = -\frac{2t^2}{B} - 2\frac{t\sin Bt}{B^2} \xrightarrow[t\to\infty]{} 2\pi t\delta'(B)\,, \tag{C7}$$

$$f_2(A,-A,t)+\text{c.c.} = \frac{4\sin^2(\tfrac{1}{2}At)}{A^2} \xrightarrow[t\to\infty]{} 2\pi t\delta(A)\,, \tag{C8}$$

$$\begin{aligned} f_2(A,B,t)f_2(C,-(A+B+C),t)+\text{c.c.} &= \left(\frac{e^{i(A+B)t}-1}{B(A+B)} - \frac{e^{iAt}-1}{AB}\right) \\ &\quad \times \left(\frac{e^{iCt}-1}{C(A+B+C)} + \frac{e^{-i(A+B)t}-1}{(A+B)(A+B+C)}\right) + \text{c.c.} \xrightarrow[t\to\infty]{} 4\pi t\frac{\delta(A+B)}{BC}\,, \end{aligned} \tag{C9}$$

$$\begin{aligned} f_2(A,-A,t)f_2(C,-C,t)+\text{c.c.} &= \left(\frac{1-e^{iAt}}{A^2} + \frac{it}{A}\right)\left(\frac{1-e^{iCt}}{C^2} + \frac{it}{C}\right) + \text{c.c.} \\ &\xrightarrow[t\to\infty]{} 2\pi t\left(\frac{\delta(A)}{C^2} + \frac{\delta(C)}{A^2} - \frac{\delta'(A)}{C} - \frac{\delta'(C)}{A}\right), \end{aligned} \tag{C10}$$

$$if_3(A,-(A+C),C,t)+\text{c.c} = \frac{1}{A+C}\left(\frac{4\sin^2(\tfrac{1}{2}At)}{A^2} - \frac{4\sin^2(\tfrac{1}{2}Ct)}{C^2}\right) \xrightarrow[t\to\infty]{} 2\pi t\left(\frac{\delta(A)}{C} - \frac{\delta(C)}{A}\right), \tag{C11}$$

$$if_3(A,-A,0,t)+\text{c.c.} = if_3(0,A,-A,t)+\text{c.c.} = \frac{4\sin^2(\tfrac{1}{2}At)}{A^3} - \frac{t^2}{A} \xrightarrow[t\to\infty]{} -2\pi t\,\delta'(A)\,, \tag{C12}$$

$$\begin{aligned} f_4(A,B,-(A+B+D),D,t)+\text{c.c.} &= -\frac{4\sin^2(\tfrac{1}{2}Dt)}{D^2(A+D)(A+B+D)} + \frac{4\sin^2(\tfrac{1}{2}At)}{A^2B(A+D)} \\ &\quad - \frac{4\sin^2[\tfrac{1}{2}(A+B)t]}{(A+B)^2B(A+B+D)} \xrightarrow[t\to\infty]{} 2\pi t\left(-\frac{\delta(D)}{A(A+B)} + \frac{\delta(A)-\delta(A+B)}{BD}\right), \end{aligned} \tag{C13}$$

$$f_4(A,-A,C,-C,t)+\text{c.c.} = \frac{4\sin^2(\tfrac{1}{2}Ct)}{C^3(C-A)} - \frac{4\sin^2(\tfrac{1}{2}At)}{A^3(A-C)} - \frac{t^2}{AC} \xrightarrow[t\to\infty]{} 2\pi t\left(\frac{\delta(A)}{C^2} + \frac{\delta(C)}{A^2} - \frac{\delta'(A)}{C} - \frac{\delta'(C)}{A}\right). \tag{C14}$$

APPENDIX D

In this appendix we give the expressions for the rates $R^{(2)}$ to $R^{(10)}$ in an integral form. With

$$C = \omega_D 3^2 2^6 [1 + (r\epsilon_0)^{1/2}]^5 \epsilon_0^{3/2} (m/M_s)^2 / r^4\,, \tag{D1}$$

we have

$$\begin{aligned} C^{-1}R^{(2)} = {} & \int_{\tilde{\epsilon}_0-1}^{1} dw\, n(w) \int_{\tilde{\epsilon}_0-w}^{1} dw' n(w')S(w+w') - 2\int_{\tilde{\epsilon}_0}^{1} dw\, n(w)S(w) \\ & + \int_{\tilde{\epsilon}_0-1}^{1} dw\, wn(w) \int_{\tilde{\epsilon}_0-w}^{1} \frac{dw'}{w'} n(w')S(w+w') - \int_{\tilde{\epsilon}_0}^{1} dw\; wn(w)S(w) \int_{-1}^{1} \frac{dw'}{w'} n(w')\ , \end{aligned} \tag{D2}$$

$$\begin{aligned} C^{-1}[R^{(3)}+R^{(4)}] = {} & \int_{\tilde{\epsilon}_0}^{1} dw \frac{\partial(wn(w))}{\partial w} S(w) \left(\int_{-1}^{\tilde{\epsilon}_0} dw' w' n(w') F_>(w') + \int_{\tilde{\epsilon}_0}^{1} dw' w' n(w) F_<(w') \right) \\ & - 2F_>(0) \int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w)S(w) - \int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w)S(w) \left[\int_{-1}^{\tilde{\epsilon}_0} dw' w' n(w') \left(3\frac{\partial F_>(w')}{\partial w'} + 2\frac{F_>(w')}{w+w'} \right) \right. \\ & \left. + \int_{\tilde{\epsilon}_0}^{1} dw' w' n(w') \left(3\frac{\partial F_<(w')}{\partial w'} + 2\frac{F_<(w')}{w+w'} \right) \right] \\ & - 2\int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w)S(w)F_<(w) \int_{-1}^{1} \frac{dw'}{w+w'}\, w' n(w') - 2\int_{\tilde{\epsilon}_0}^{1} dw\, n(w)S(w) \left(\int_{-1}^{\tilde{\epsilon}_0-w} dw' (w+w') n(w') F_>(w+w') \right. \\ & \left. + \int_{\tilde{\epsilon}_0-w}^{1} dw' (w+w') n(w') F_<(w+w') \right) \\ & - 2\left[\int_{\tilde{\epsilon}_0-1}^{\tilde{\epsilon}_0} dw\, n(w)F_>(w) + \int_{\tilde{\epsilon}_0}^{1} dw\, n(w)F_<(w) \right] \int_{\tilde{\epsilon}_0-w}^{1} dw' (w+u') n(w') S(w+w')\ , \end{aligned} \tag{D3}$$

$$\begin{aligned} C^{-1}R^{(5)} = {} & 2F_>(0) \int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w) S(w) \left(\int_{-1}^{\tilde{\epsilon}_0} dw' w' n(w') F_>(w') + \int_{\tilde{\epsilon}_0}^{1} dw' w' n(w') F_<(w') \right) \\ & + 2\int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w)S(w) \left(\int_{-1}^{\tilde{\epsilon}_0-w} dw' w' n(w') F_>(w+w')[F_<(w)+F_>(w')] \right. \\ & \left. + \int_{\tilde{\epsilon}_0-w}^{\tilde{\epsilon}_0} dw' w' n(w') F_<(w+w')[F_<(w)+F_>(w')] + \int_{\tilde{\epsilon}_0}^{1} dw' w' n(w') F_<(w+w')[F_<(w)+F_<(w')] \right) \\ & + \tfrac{1}{2} \int_{\tilde{\epsilon}_0}^{1} dw\; wn(w) \left(\int_{\tilde{\epsilon}_0-w}^{\tilde{\epsilon}_0} dw' w' n(w') S(w+w')[F_<(w)+F_>(w')]^2 \right. \\ & \left. + \int_{\tilde{\epsilon}_0}^{1} dw' w' n(w') S(w+w')[F_<(w)+F_<(w')]^2 \right) \\ & + \tfrac{1}{2} \int_{0}^{\tilde{\epsilon}_0} dw\, w\, n(w) \int_{\tilde{\epsilon}_0-w}^{\tilde{\epsilon}_0} dw' w' n(w') S(w+w')[F_>(w)+F_>(w')]^2 \\ & + \tfrac{1}{2} \int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w) \int_{\tilde{\epsilon}_0-w}^{\tilde{\epsilon}_0} dw' w' n(w') S(w+w')[F_<(w)+F_>(w')]^2\ , \end{aligned} \tag{D4}$$

$$C^{-1}2[1+(r\epsilon_0)^{1/2}]^2\epsilon_0 r^{-1}R^{(6)} = \int_{\tilde{\epsilon}_0-1}^{1} dw\; w\, n(w) \int_{\tilde{\epsilon}_0-w}^{1} dw' w' n(w') S(w+w')\ , \tag{D5}$$

$$\begin{aligned} C^{-1}[1+(r\epsilon_0)^{1/2}]\epsilon_0^{1/2} r^{-1/2}[R^{(7)}+R^{(8)}] = {} & 2\int_{\tilde{\epsilon}_0}^{1} dw\, w\, n(w)S(w) \left(1 - \int_{-1}^{1} \frac{dw'}{w+w'}\, w' n(w') \right) \\ & + \tfrac{1}{2} \int_{\tilde{\epsilon}_0}^{1} dw\, n(w)S(w) \left(1 + 3w\frac{\partial n(w)}{\partial w} \right) \int_{-1}^{1} dw' w' n(w') \\ & - 2\int_{\tilde{\epsilon}_0-1}^{1} dw\, n(w) \int_{\tilde{\epsilon}_0-w}^{1} dw' w' n(w') S(w+w')\ , \end{aligned} \tag{D6}$$

$$
\begin{aligned}
C^{-1}[1+(r\epsilon_0)^{1/2}]\epsilon_0 r^{-1/2}R^{(9)} = {} & \left(F_>(0)\int_{\tilde{\epsilon}_0}^{1} dw\, wn(w)S(w) + \int_{\tilde{\epsilon}_0}^{1} dw\, wn(w)S(w)F_<(w)\right)\int_{-1}^{1} dw'\, w'n(w') \\
& + 2\int_{\tilde{\epsilon}_0}^{1} dw\, wn(w)S(w)\left(\int_{-1}^{\tilde{\epsilon}_0} dw' w'n(w')F_>(w') + \int_{\tilde{\epsilon}_0}^{1} dw' w'n(w')F_<(w')\right) \\
& + 2\int_{\tilde{\epsilon}_0}^{1} dw\, wn(w)S(w)\left(\int_{-1}^{\tilde{\epsilon}_0-w} dw'\, w'n(w')F_>(w+w') \right.\\
& \qquad\qquad \left. + \int_{\tilde{\epsilon}_0-w}^{1} dw' w'n(w')F_<(w+w')\right) \\
& + 2\left(\int_{\tilde{\epsilon}_0-1}^{\tilde{\epsilon}_0} dw\, wn(w)F_>(w) + \int_{\tilde{\epsilon}_0}^{1} dw\, wn(w)F_<(w)\right)\int_{\tilde{\epsilon}_0-w}^{1} dw' w'\, n(w')S(w+w')\ ,
\end{aligned}
\tag{D7}
$$

$$
C^{-1}[1+(r\epsilon_0)^{1/2}]^2\epsilon_0 r^{-1}R^{(10)} = \int_{\tilde{\epsilon}_0}^{1} dw\, wn(w)S(w)\int_{-1}^{1} dw' w'n(w')\ . \tag{D8}
$$

Observe that the integrals containing functions $S(w)$ describe one-phonon processes while those with $S(w+w')$ account for two-phonon processes. All integrals with singular integrands are principal-value integrals. Note that in (D2) the last two integrals are divergent by themselves; however, their difference is finite. This demonstrates that great care must be taken to include all one-phonon and two-phonon processes in fourth order. The rates $R^{(5)}$ and $R^{(9)}$ are nonzero in the limit $\epsilon_0 \to 0$ arising from the terms proportional to $F_>(0)$. This is discussed in Sec. IV around (86). Note that the rate $R^{(10)}$, i.e., the contribution from the cross term $H_{gs}^{(1)}H_{gs}^{(3)}$, is proportional to the second-order rate $R^{(1)}$ with a temperature-dependent factor of proportionality that happens to be one, e.g., for $\delta = 1$ and $r = 16$.

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