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Atom-phonon interactions studied using a consistent quantum treatment

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A consistent approach to atom—surface-energy transfer in one dimension is presented. A semigroup technique is employed to establish equations of motion for a quantal phonon reservoir, which is coupled to the propagation of a wave packet. The time-dependent Schrödinger equation is solved using a pseudospectral technique. The average energy transfer to the bath is then determined. This study supersedes conventional perturbative treatments and reveals the utility of one-dimensional models in the study of particle-surface collisions at low energies.

I. INTRODUCTION

The mechanism by which a gas particle transfers its energy to a crystalline surface is imperfectly understood, despite several attempts to model this phenomenon.[1] The particular case of a small-mass atom scattering from, or adsorbing onto, a surface composed of large-mass atoms at low surface temperatures must be treated quantum mechanically. That is, not only must the propagation of the scattering particle be given by the Schrödinger equation, the bulk atom motion must also be described by quantum mechanics.

One practical instance in which these concerns dominate is the flow of a gas along a surface which need not be at the same temperature as the gas. The microscopic transfer of energy to or from the surface has macroscopic consequences for the flow of the gas. In the usual continuum description of the gas flow, the temperature jump at the surface alters the boundary conditions of the hydrodynamic equations which then modify the macroscopic properties of the moving particles. A convenient dimensionless parameter which links the microscopic and macroscopic descriptions is the thermal accommodation coefficient $\alpha(T_s,T_g)$, which is usually a function of both the gas temperature T_g and the surface temperature T_s. The conventional definition of this quantity is[2]

$$\alpha(T_s,T_g)=\frac{\overline{E}_i-\overline{E}_f}{2k_B(T_g-T_s)}\ , \tag{1}$$

where $\overline{E}_i$ and $\overline{E}_f$ are the initial and final energies of the scattering particle and k_B is Boltzmann's constant. If the temperature of the gas and the surface are equal, this quantity is known as the equilibrium accommodation coefficient[2] (EAC)

$$\alpha(T)=\lim_{T_g\to T_s=T}\alpha(T_s,T_g)\ . \tag{2}$$

The equilibrium accommodation coefficient is the relevant quantity for several experimental situations, especially flash desorption,[3] in which the gas and surface are equilibrated and then suddenly pumped to reduce the gas pressure. The desorbing particles are collected and the surface coverage is then monitored as a function of time. Although the first theoretical calculations date from Lennard-Jones and Strachan,[4] there remains qualitative disagreement between theory and experiment as the temperature of the gas is lowered.[5] For He on W, the predicted EAC $\alpha(0)=0$, whereas the experimental data indicates $\alpha(0)\neq 0$. This behavior persists even with the inclusion of a binding potential well in one dimension;[5] hence, it has been speculated that one-dimensional theories must be inherently deficient.

On the other hand, these calculations were perturbative results which did not incorporate higher phonon-gas couplings.[6] When more extensive, but still perturbative, computations were performed, it was observed that one-dimensional models could be used successfully, at least for very weakly bound gas-surface systems.[7] The extension of this reasoning requires numerical rather than analytical techniques for the solution of Schrödinger's equation. In order to bypass the limitations of simple time-dependent or time-independent perturbation theory, the Schrödinger equation must be solved for a gas particle interacting with a quantum-mechanical reservoir of phonons. To accomplish the solution of the time-dependent Schrödinger equation, a fast-Fourier-transform (FFT) technique is used to solve the partial-differential equation.[8] The phonon bath is treated by a semigroup expansion technique[9] similar to that used in studies of vibrational relaxation of liquids.[10] Although we only consider couplings to second order between the gas particle and phonons, this is not an essential limitation of the technique; furthermore, the model potential chosen supports 11 bound states, indicating that the previous restriction to a few shallow bound states can be removed.[7] The main qualitative result of this work is that one-dimensional quantum-mechanical models can be usefully employed in the examination of the EAC without many of the limitations, or complicated expressions, arising from the use of perturbation theory.

The following section examines the details of the phonon-bath construction and the equations of motion that follow. Section III provides examples of the computations performed for the fully coupled system, which demonstrate nonvanishing behavior of the average energy transfer as the gas temperature is lowered. Section IV concludes this work with a brief discussion of the results and limitations of the model.

II. PHONON-BATH DESCRIPTION

The equations of motion describing the time evolution of the quantum reservoir may be realized by the use of a completely dissipative Liouville operator.[9] The semigroup description of the dynamics on the Heisenberg representation is given by

$$\dot{X}=L(X)=L_H(X)+L_D(X)\ , \tag{3}$$

where X is an operator in the Hilbert space of the system. L is the Liouville superoperator, which naturally decomposes into Hermitian, L_H, and dissipative, L_D, terms. The Hermitian superoperator is given by the usual Heisenberg bracket

$$L_H(X)=i[H,X]\ . \tag{4}$$

The dissipative part has a structure and interpretation similar to that of a quantal master equation:

$$L_D(X)=\sum_i \gamma_j(V_jXV_j^+-\tfrac{1}{2}[V_jV_j^+,X]_+)\ , \tag{5}$$

in which the γ_j are real numbers controlling the rate of relaxation and the equilibrium properties of the system, the V_j are operators within the Hilbert space, and the bracket $[A,B]_+$ is the anticommutator $[A,B]_+=AB+AB$. Once the parameters γ_j and operators V_j are specified, the dynamical motion is completely determined.

As an example, consider an operator evolving by first-order processes in contact with an harmonic oscillator at equilibrium. This implies that

$$H=\omega a^\dagger a \tag{6}$$

and the operators $V_1=a$ and $V_2=a^\dagger$. For a phonon reservoir, boson statistics demand that

$$\gamma_1/\gamma_2=\exp(-h\omega/k_BT)\ , \tag{7}$$

with either γ_1 or γ_2 unconstrained in the absence of further information about the system. Any operator then evolves in time according to the equation of motion:

$$\begin{aligned}\dot{X}=i\omega[a^\dagger a,X]&+\gamma_1[aXa^\dagger-\tfrac{1}{2}(aa^\dagger X+Xaa^\dagger)]\\&+\gamma_2[a^\dagger Xa-\tfrac{1}{2}(a^\dagger aX+Xa^\dagger a)]\ .\end{aligned} \tag{8}$$

Specifically, a, a^2, and $aa^\dagger=N$ are

$$\dot{a}(t)=-i\omega a(t)+\tfrac{1}{2}(\gamma_1-\gamma_2)a(t)\ , \tag{9a}$$

$$\dot{a}^2(t)=-2i\omega a^2(t)+(\gamma_1-\gamma_2)a^2(t)\ , \tag{9b}$$

$$\dot{N}(t)=(\gamma_1-\gamma_2)N(t)+\gamma_1\ . \tag{9c}$$

Note that at equilibrium $[\dot{X}(t)=0]$, $a_{\mathrm{eq}}=0$, $a_{\mathrm{eq}}^2=0$, and

$$N_{\mathrm{eq}}=1/[\exp(h\omega/k_BT)-1]\ ,$$

as expected. It is thus consistent to use known equilibrium values of the operators as initial conditions for the differential equations.

In the more general case, an expansion of the interaction Hamiltonian proves to be useful. During the course of a particle collision with phonon bath, energy may either be transferred to the bath oscillators, which is then dissipated as heat, or as internal energy transfer in which the energy of the different oscillator modes is rearranged. For low-energy scattering from a surface, the excitation of the reservoir phonons is not extremely violent; hence it is a good approximation to retain only second-order expansion terms in the amplitude X_i of the interaction potential:

$$V_{\mathrm{int}}(z,X)\simeq V_0(z)+\sum_i V_1(z)X_i+\sum_{i,j}V_2(z)X_iX_j\ . \tag{10}$$

This procedure produces a separable interaction, of course, which has been used previously.[7] Since this expansion is a Taylor's series in X_i, the individual terms are

$$V_1(z)=\left.\frac{\partial V}{\partial X_i}(z,X_i)\right|_{X_i=0} \tag{11a}$$

and

$$V_2(z)=\left.\frac{\partial^2 V}{\partial X_i\partial X_j}(z,X_i,X_j)\right|_{X_i=0,\ X_j=0}\ . \tag{11b}$$

Transforming the quadratic expression into normal modes

$$\gamma_j=\xi_j(a_j+a_j^\dagger)=\sum_{i,k}c_{ik}X_k\ ,$$

where $\xi_i=\sqrt{1/2}M_j\omega_j$ gives the total Hamiltonian operator as

$$\begin{aligned}H=\sum_j \omega_j a_j^\dagger a_j+V_0(z)+V_1(z)\sum_{i,j}\xi_j c_{ij}^{-1}(a_j+a_j^\dagger)\\+V_2(z)\sum_{i,j,k}\xi_j\xi_k c_{ij}^{-1}c_{ik}^{-1}(a_j+a_j^\dagger)(a_k+a_k^\dagger)\ ,\end{aligned} \tag{12}$$

or, separating out the diagonal terms,

$$\begin{aligned}H=\sum_j \omega_j a_j a_j^\dagger+V_0(z)+2V_2(z)\sum_{i,j}\xi_i^2(c_{ij}^{-1})^2a_j^\dagger a_j+V_1(z)\sum_{i,j}\xi_i c_{ij}^{-1}(a_j+a_j^\dagger)+V_2(z)\sum_{i,j}\xi_j^2(c_{ij}^{-1})^2[a_j^2+(a^\dagger)_j^2]\\+V_2(z)\sum_{i,j\,(\neq k)}\xi_j\xi_k c_{ij}^{-1}c_{ik}^{-1}(a_ja_k+a_j^\dagger a_k^\dagger+a_ja_k^\dagger+a_j^\dagger a_k)\ ,\end{aligned} \tag{13}$$

from which the dissipative equations of motion follow:

$$\dot{a}_j=-iV_1(z)\xi_j c_{ij}^{-1}-\{i[\omega_j+2V_2(z)\xi_j^2(c_{ij}^{-1})^2]+\tau_j/2\}a_j-2iV_2(z)\xi_j^2(c_{ij}^{-1})^2a_j^\dagger-iV_2(z)\xi_j(c_{ij}^{-1})\sum_k \xi_k c_{ik}^{-1}(a_k+a_k^\dagger)\ , \tag{14a}$$

where $\tau_j=\gamma_{j2}-\gamma_{j1}$,

$$(a_j^{\dagger\cdot}a_j)=iV_1(z)\xi_j(c_{ij}^{-1})(a_j-a_j^{\dagger})-i2V_2(z)\xi_j^2(c_{ij}^{-1})^2[(a^{\dagger})_j^2-a_j^2]-\tau_j a_j^{\dagger}a_j+\gamma_{1j}$$
$$+iV_2(z)\xi_j(c_{ij}^{-1})\sum_k \xi_k c_{ik}^{-1}(a_j a_k-a_j^{\dagger}a_k^{\dagger}+a_j a_k^{\dagger}-a_j^{\dagger}a_k)\ , \tag{14b}$$

$$\dot{a}_j^{\,2}=-\{i[2\omega_j+4V_2(z)\xi_j^2(c_{ij}^{-1})^2]+\tau_j\}a_j^2-i2V_1(z)\xi_j c_{ij}^{-1}a_j-iV_2(z)\xi_j^2(c_{ij}^{-1})^2(2a_j^{\dagger}a_j+1)$$
$$-i2V_2(z)\xi_j(c_{ij}^{-1})\sum_k \xi_k(c_{ik}^{-1})(a_k^{\dagger}a_j+a_k a_j)\ , \tag{14c}$$

$$(a_j^{\dagger\cdot}a_k)=(-i\{\omega_k-\omega_j+2V_2(z)[\xi_k^2(c_{ik}^{-1})^2-\xi_j^2(c_{ij}^{-1})^2]\}-(\tau_j+\tau_k)/2)a_j^{\dagger}a_k+i2V_2(z)[\xi_j^2(c_{ij}^{-1})^2a_j a_k-\xi_k^2(c_{ik}^{-1})^2a_j^{\dagger}a_k^{\dagger}]$$
$$+iV_1(z)[\xi_j(c_{ij}^{-1})a_k-\xi_k(c_{ik}^{-1})a_j^{\dagger}]+iV_2(z)\xi_j(c_{ij}^{-1})\sum_k \xi_k(c_{ik}^{-1})(a_k^2+a_k^{\dagger}a_k)$$
$$-iV_2(z)\xi_k(c_{ik}^{-1})\sum_j \xi_j(c_{ij}^{-1})[(a_j^{\dagger})^2+a_j^{\dagger}a_j+1]\ , \tag{14d}$$

$$(a_j{}^{\cdot}a_k)=(-i\{\omega_j+\omega_k+2V_2(z)[\xi_k^2(c_{ij}^{-1})^2+\xi_k^2(c_{ij}^{-1})^2]\}-(\tau_j+\tau_k)/2)a_j a_k-i2V_2(z)[\xi_j^2(c_{ij}^{-1})^2a_j^{\dagger}a_k+\xi_k^2(c_{ik}^{-1})^2a_j a_k^{\dagger}]$$
$$-iV_1(z)[\xi_j(c_{ij}^{-1})a_k+\xi_k(c_{ik}^{-1})a_j]-iV_2(z)\xi_j(c_{ij}^{-1})\sum_k \xi_k(c_{ik}^{-1})(a_k^2+a_k^{\dagger}a_k)-iV_2(z)\xi_k(c_{ik}^{-1})\sum_j \xi_j(c_{ij}^{-1})(a_j^2+a_j^{\dagger}a_j)\ . \tag{14e}$$

The interest here is in simple one-dimensional models with appropriate modeling parameters so that it is only necessary to examine the relaxation of one oscillator coupled to a dissipative bath. The coupling of the translational motion into the bath-oscillator description is achieved in a self-consistent-field fashion, by quantum mechanically averaging the bath variables. In Eq. (10), $V_1(z)$ and $V_2(z)$ are replaced by $\langle V_1(t)\rangle$ and $\langle V_2(t)\rangle$, where

$$\langle A(t)\rangle=\int \psi^{\dagger}(z,t)A(z,t)\psi(z,t)dz\ . \tag{15}$$

These equations of motion become

$$\dot{a}(t)=-i\langle V_1(t)\rangle\xi-\{i[\omega+2\langle V_2(t)\rangle\xi^2]+\tau/2\}a$$
$$-2i\langle V_2(t)\rangle\xi^2a^{\dagger}\ , \tag{16a}$$

$$\dot{a}^{\,2}(t)=-\{i[2\omega+4\langle V_2(t)\rangle\xi^2]+\tau\}a^2$$
$$-2i\langle V_2(t)\rangle\xi a-i\langle V_2(t)\rangle\xi^2(2a^{\dagger}a+1)\ , \tag{16b}$$

$$[a^{\dagger\cdot}a(t)]=i\langle V_1(t)\rangle\xi(a-a^{\dagger})-2i\langle V_2(t)\rangle\xi^2[(a^{\dagger})^2-a^2]$$
$$-\tau a^{\dagger}a+\gamma_1\ , \tag{16c}$$

where $\tau=\gamma_2-\gamma_1$. Introducing the real combinations,

$$X_1=a^{\dagger}+a\ , \tag{17a}$$

$$X_2=i(a^{\dagger}-a)\ , \tag{17b}$$

$$X_3=a^{\dagger}a\ , \tag{17c}$$

$$X_4=(a^{\dagger})^2+a^2\ , \tag{17d}$$

$$X_5=i(a^{\dagger})^2-ia^2\ , \tag{17e}$$

the equations of motion are

$$\dot{X}_1=-1/2\tau X_1+\omega X_2\ , \tag{18a}$$

$$\dot{X}_2=-\tfrac{1}{2}\tau X_1-[\omega+4\langle V_2(t)\rangle\xi^2]X_1-2\langle V_1(t)\rangle\xi\ , \tag{18b}$$

$$\dot{X}_3=-\tau X_3-\langle V_1(t)\rangle\xi X_2-2\langle V_2(t)\rangle\xi^2X_5+\gamma_1\ , \tag{18c}$$

$$\dot{X}_4=-\tau X_4+[2\omega+4\langle V_2(t)\rangle\xi^2]X_5+2\langle V_1(t)\rangle\xi X_2\ , \tag{18d}$$

$$\dot{X}_5=-\tau X_5-[2\omega+4\langle V_2(t)\rangle\xi^2]X_4-2\langle V_1(t)\rangle\xi X_1$$
$$-2\langle V_2(t)\rangle\xi^2(2X_3+1)\ . \tag{18e}$$

It is more convenient numerically to integrate the real equations (18) than the equivalent complex set (16).

Some qualitative features of these equations may be readily ascertained. The variables X_1 and X_2 are uncoupled from the remaining variables, and they basically serve as driving terms for the other variables X_3, X_4, and X_5, which eventually induce two-phonon processes. Elementary manipulations in the limit $\langle V_2(t)\rangle \ll \langle V_1(t)\rangle$ (which always holds for reasonably choices of particle-surface interaction at the beginning of the collision) produce

$$X_1(t)=C_1(e^{(i\omega+\Delta\gamma)t}-e^{-(i\omega-\Delta\gamma)t})\ , \tag{19a}$$

$$X_2(t)=C_2(e^{(i\omega+\Delta\gamma)t}-e^{-(i\omega-\Delta\gamma)t})$$
$$+C_3\int_0^t\langle V_1(s)\rangle ds\ , \tag{19b}$$

where $\Delta\gamma=\gamma_1-\gamma_2<0$ and where C_i are constants.

TABLE I. Numerical values used in the computations for He-W.

Grid values
$N_{\mathrm{FFT}}=256$
$N_{\mathrm{time}}=880\,000$
$\Delta t=1.0$ a.u.
Potential parameters
$D_0=5.0976\times10^{-4}$ hartree
$\alpha=0.688$ bohr^{-1}
$z_0=3.0$ bohr
Model parameters
$\gamma_2=6.3\times10^{-3}$ rad/a.u.
$\omega=2.42\times10^{-6}$ rad/a.u.

Clearly, the phonon-bath variables are initially disturbed from equilibrium by the first-derivative form. Significant excursions from equilibrium can only arise when $\langle V_2(t)\rangle$ becomes large. In the case of particle-surface scattering, this situation only arises when the particle is within the vicinity of the potential minimum. Once this situation obtains, the system then exhibits pronounced nonlinearity and deviations from equilibrium. Within the model, then higher-order processes necessarily lag behind the first-order processes, which, in turn, are influenced initially only by the lowest-order coupling and then driven by the second-order term.

Similarly, after the collision if there is a short residence time of the particle near the surface, $\langle V_1(t)\rangle$ and $\langle V_2(t)\rangle$ will both vanish as $t\rightarrow\infty$ and the number operator becomes constant. On the other hand, if trapping does

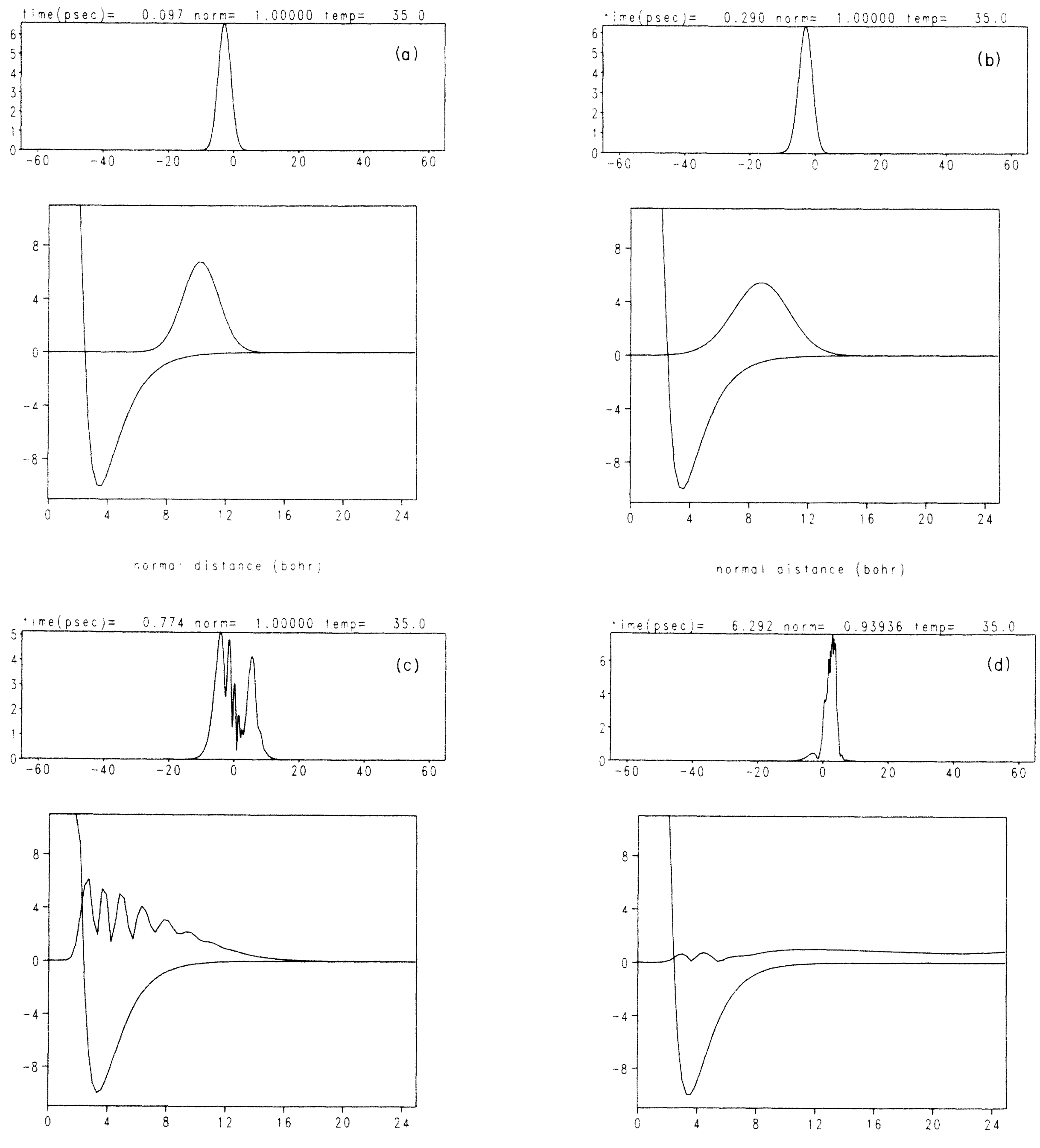

FIG. 1. (a)–(d) These figures display a temporal sequence of helium-atom scattering from a static surface at 35 K. The upper part of each figure is a plot of the Fourier-transformed wave-function amplitude. The lower part is a plot of the wave-function amplitude as a function of normal distance to the surface. The Morse potential used to model the interaction is superimposed. There is no trapping or energy transfer within the accuracy of the calculation.

occur, the equations will be continuously driven and the phonon number X_3 will remain time dependent. That is, it will not achieve a new equilibrium value after the collision.

III. COMPUTATIONAL RESULTS

The one-dimensional model above was employed to study the scattering of helium atoms from W as a function of temperature. The initial wave packet was chosen to have a Maxwell-Boltzmann distribution in momentum space. That is, the width and normalization of the wave packet were determined by the temperature as

$$\psi(t=0,z=+\infty)=\left[\frac{mk_BT}{\pi}\right]^{1/4} e^{-z^2/(2mk_BT)}e^{ip_0z} . \quad (20)$$

This choice mimics the conditions of most desorption and accommodation experiments. As the temperature approaches 0 K, a Bose-Einstein distribution must be used for the incident He atoms. For the temperature range

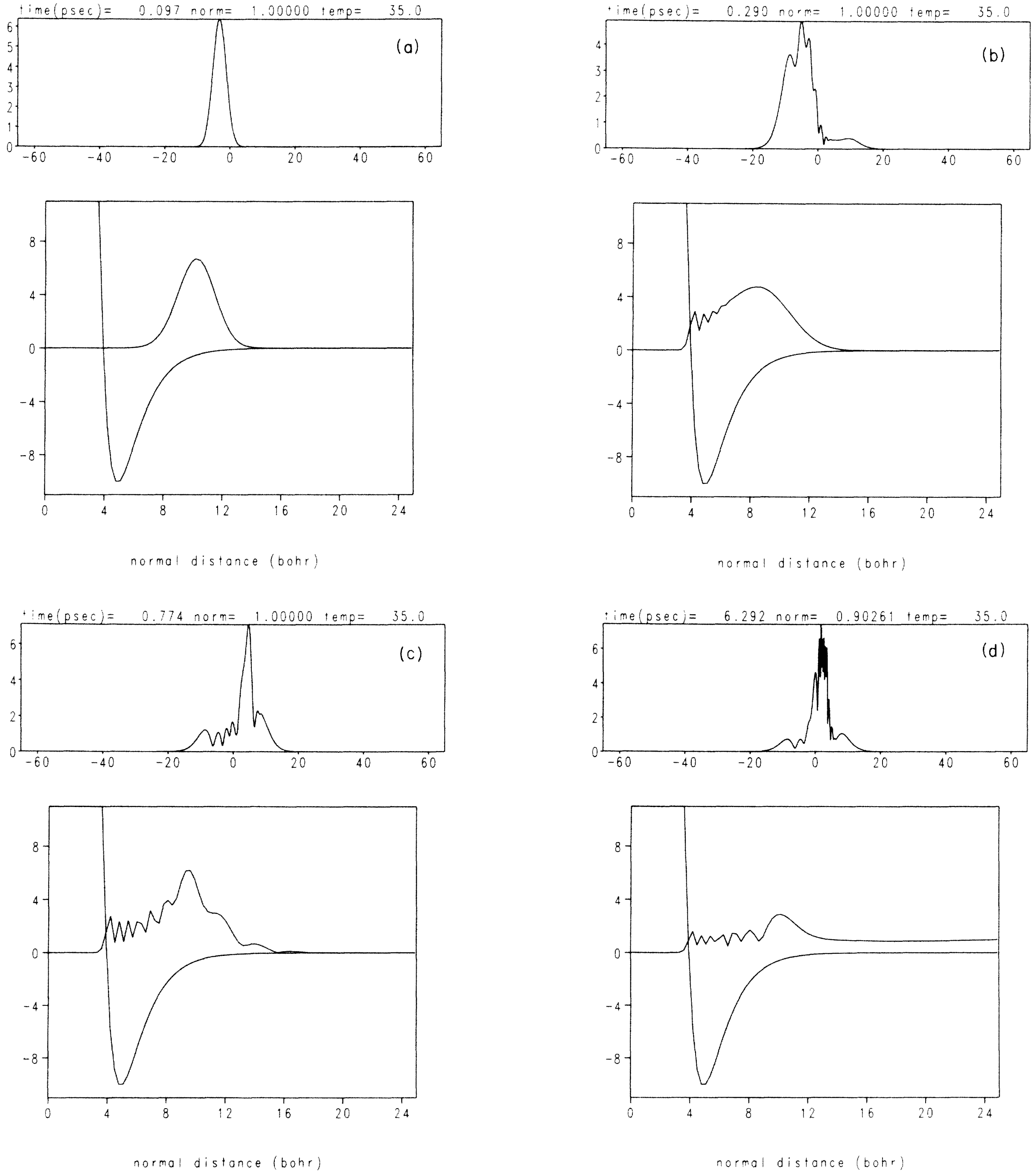

FIG. 2. (a)—(d) Same plots as Fig. 1 with a time-dependent interaction between the scattering particle and surface.

considered here, these statistics were not distinguishable from the Maxwell-Boltzmann distribution. The wave packet was then propagated by the time-dependent Schrödinger equation

$$i\frac{\partial\psi}{\partial t} = -\frac{1}{2m}\frac{\partial^2\psi}{\partial z^2} + [V_0(z)+V_s(z,X(t))]\psi_1 \qquad (21)$$

using the FFT algorithm to evaluate the kinetic-energy operator and second-order differencing for the time dependence.[8] The time dependence in Eq. (2) is implicit, arising from the reservoir values. Their time evolution is given in Eqs. (18a)—(18e), with initial conditions dictated by the known equilibrium values: $X_i=0$ $(i\neq 3)$, $X_3=N_{\mathrm{eq}}$. A standard predictor-corrector algorithm was used to solve these equations.[11] Also, since relatively long propagation times were considered, it was necessary to absorb the wave function at the edge of the numerical grid by an attenuator.[12]

The method essentially incorporates the following algorithm. A temperature is chosen which determines the energy and shape of the wave packet. The propagating wave function is averaged over the coupling terms to produce

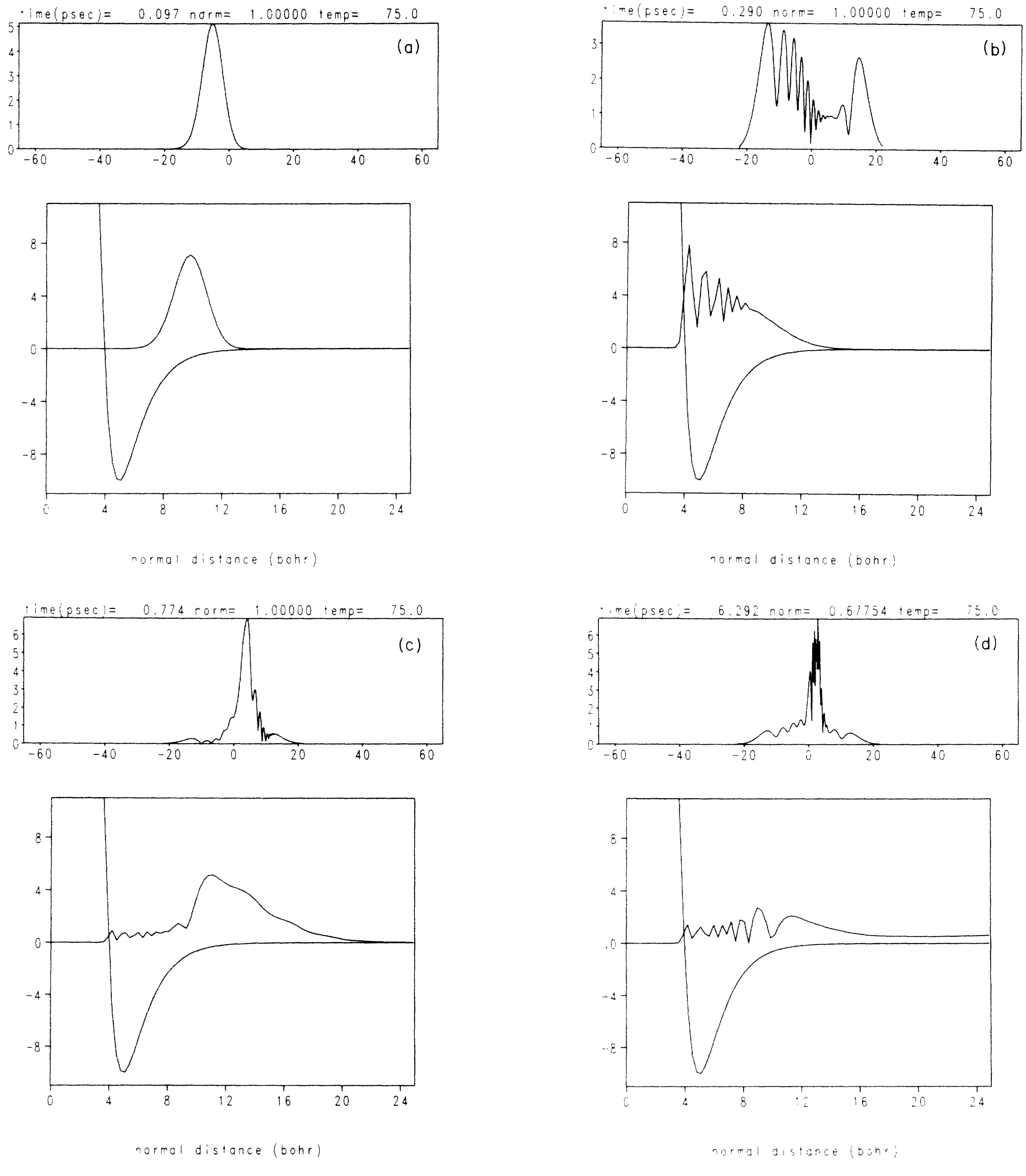

FIG. 3. (a)—(d) Same plots as Fig. 2 at 75 K.

$\langle V_1(t) \rangle$ and $\langle V_2(t) \rangle$, which are then used to evaluate the $X_i(t)$. These terms supply the implicit time dependence in Eq. (21) and the next propagation step is determined. This technique is a type of self-consistent-field approach which has been previously used.[13] The particle-surface potential was a Morse form with parameters given by Goodman[14] for a similar one-dimensional study of the He-W system. For the parameters chosen the potential supports 11 bound states.

The parameters γ_1, γ_2, and ω, the bath oscillator frequency, are considered as adjustable variables. γ_1 and γ_2 are only constrained by the requisite boson distribution, Eq. (7). It is possible to relate γ_2 to the phonon spectral density following Tully,[15] or by choosing a simplified model for the bulk solid. Likewise, it may be estimated from experimental parametrizations or slab calculations.[16] Given the uncertainty in these procedures, it seemed appropriate to vary these parameters over the ranges suggested by these techniques for this specific problem. It has already been observed that the final results of a scattering calculation are not exceedingly sensitive to their precise values.[15] A cursory scan of the possible values for

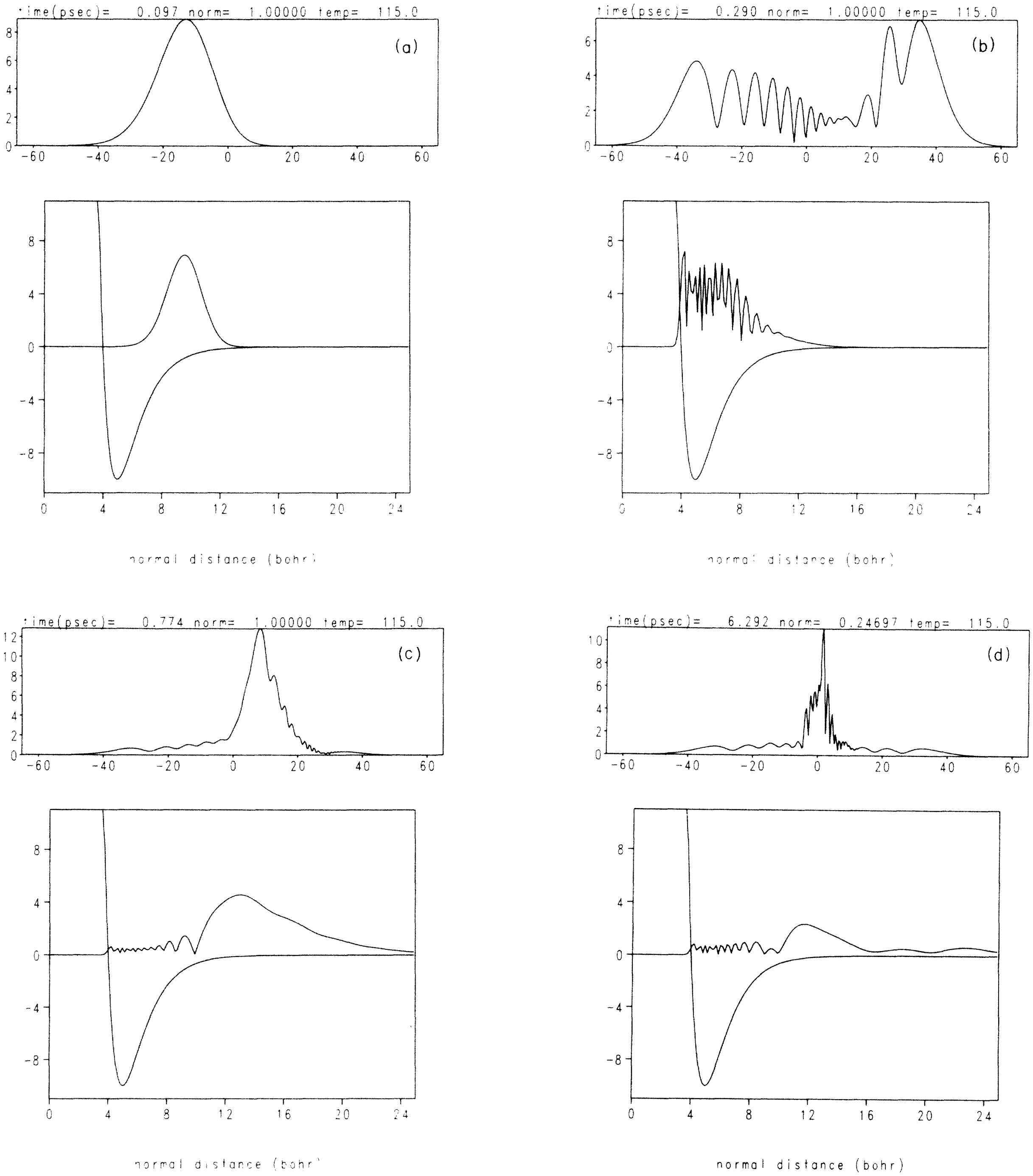

FIG. 4. (a)—(d) Same plots as Fig. 2 at 115 K.

TABLE II. Average energy change, fractional energy change, and normalization as a function of temperature after 16 psec.

T (K)	$\overline{\Delta E}_{\text{final}}$ (10^{-5} bohr)	$\overline{\Delta E}/E_{\text{init}}$	Normalization
35	1.50	0.112	0.39
75	1.95	0.066	0.29
115	2.55	0.056	0.26

γ_2 and ω was made until a significant interaction of the particle and surface was observed. This procedure roughly corresponds to finding a resonance region which dominates the interaction. It should be noted that for small values of $\omega < 10^{-6}$ rad/a.u., the surface atoms are too weakly bound and the surface disintegrates. The Morse-potential parameters, the modeling parameters, and the propagation-grid information are displayed in Table I.

Calculations were performed at 35, 75, and 115 K. Initial runs at these temperatures were made with the time dependence removed—that is, for a completely static surface. To the accuracy of the calculation no bound-state trapping occurred. A representative time sequence at 35 K is given in Figs. 1(a)–1(f).

The initial wave packet is placed outside the interaction region and given negative momentum. The wave packet spreads as it moves toward the wall; the leading edge (greatest momentum component) collides with the repulsive wall. The remainder of the wave packets arrives later, interfering with the reflected wave. As the collision progresses, the wave packet resides briefly in the interaction region and then decays away over a long time span. As expected, there are two timescales in the collision: the bulk of the wave packet interacts and leaves quickly with the decay of the residual trapping occurring slowly. The time-dependent amplitude is measured by the normalization of the wave packet and it is clearly zero within the accuracy of the computation at the end of about 15 psec. These runs demonstrate that static interactions are inadequate in treating accommodation in one dimension.

Figures 2(a)–2(d), 3(a)–3(d), and 4(a)–4(d) display time sequences using the modeling parameters in Table I for the three different temperatures, 35, 75, and 115 K. These differ from the static case in that long-time adherence to the surface does take place. In all cases, substantial energy accommodation occurs as given in Table II. The amount of energy transferred to the surface remains essentially constant as the temperature is lowered. These results are in accord with similar time-dependent perturbation approaches,[7] which indicates that it is not the one-dimensional aspect of the previous models that is deficient but rather the limitations of the perturbative treatments.

IV. DISCUSSION

The general conclusions to be drawn from this work are twofold. First, it is possible to couple a translating particle to a quantal phonon bath in a physical fashion and to treat it consistently. The use of semigroup techniques to evaluate the dynamics of dissipative systems leads to a tractable formalism for the phonon reservoir. The application of a self-consistent-field method to the particle-bath coupling presents an examination of nonlinear effects which would be quite difficult to evaluate with perturbation theory. Indeed, in this study a moderately deep interaction well was handled easily in the presence of damping effects.

The semigroup technique includes certain higher-order effects, such as phonon dispersion, and may be readily generalized to incorporate others such as multiphonon effects. The scan over the modeling parameters would then select the physically relevant resonance conditions for more general interactions. That is, the model should generalize and display increasingly realistic behavior. The conditions for maximal energy transfer between particles and surface could be determined. Also, it should be emphasized that adsorption to the surface presents no difficulty for the propagation technique since it is stable and accurate over long periods of time. These features make the model attractive for more general particle-surface interactions.

Second, the value of one-dimensional models for particle-surface interactions should not be underestimated. It is certainly true that higher-dimensional effects are absent, such as lateral motion on the surface. These effects can play an important role in some circumstances. As a first step, though, the utility of simple models should be explored to determine their true limitations, not those imposed by lower-order perturbation theory. A serious obstacle to any type of surface study remains the uncertainty in the choice of bath-particle interaction parameters. At present, it appears to be reasonable to take these values as fitting variables, but this is not a completely satisfactory procedure. Possibly the simple one-dimensional models could be used in conjunction with other computations of surface behavior and experiment to establish a better understanding of the dynamic coupling.

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