Quantum stochastic approach for molecule/surface scattering.
I. Atom–phonon interactions

Eric R. Bittner and John C. Light
The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

(Received 25 June 1993; accepted 10 August 1993)

We present a general, fully quantum mechanical theory for molecule surface scattering at finite temperature within the time dependent Hartree (TDH) factorization. We show the formal manipulations which reduce the total molecule–surface–bath Schrödinger equation into a form which is computationally convenient to use. Under the TDH factorization, the molecular portion of the wavefunction evolves according to a mean-field Hamiltonian which is dependent upon both time and temperature. The temporal and thermal dependence is due to stochastic and dissipative terms that appear in the Heisenberg equations of motion for the phonon operators upon averaging over the bath states. The resulting equations of motion are solved in one dimension self consistently using quantum wavepackets and the discrete variable representation. We compute energy transfer to the phonons as a function of surface temperature and initial energy and compare our results to results obtained using other mean-field models, namely an averaged mean-field model and a fully quantum model based upon a dissipative form of the quantum Liouville equation. It appears that the model presented here provides a better estimation of energy transfer between the molecule and the surface.

INTRODUCTION

The dynamical coupling of an inherently quantum mechanical system to a dense medium presents an interesting challenge both to experimental and theoretical examination. Even in the most simplified model of a quantum oscillator coupled linearly to a bath of harmonic oscillators one finds a remarkable wealth of complexity as one begins to explore the non-classical limits. The continuation of a fully quantum theory from a few-body problem to a many-body problem is a difficult road to follow if we attempt to give a complete description of the dynamics. Despite considerable effort toward this end not only by our group but many by others, rigorous, numerically exact quantum calculations are possible only for very simple systems with a few degrees of freedom. Since the amount of computer effort and time required increases exponentially as we increase the spatial size and dimensionality of the problem, exact methods become prohibitively expensive, especially when more than a few degrees of freedom become strongly correlated. However, if we are interested in only a few of the degrees of freedom and can be satisfied by a statistical description of the others, a self consistent field theory may be adequate as long as the statistical correlations between the two subsystems remain weak.1–4

One rigorous, yet tractable, strategy for examining such systems is the time dependent Hartree approximation (TDH). In the TDH approximation, the total many-body wavefunction is factored among the various degrees of freedom, typically into “system” and “bath” components, where the “system” refers to the interesting degrees of freedom and the “bath” refers to everything else. This approach is physically appealing and leads to relatively simple mean-field equations of motion that are integrated self constantly. Because the approximation neglects direct correlations between the subsystems, the amount of computational effort required is reduced substantially and scales roughly with the spatial dimensionality of the separated subsystems. The TDH approximation is a very powerful technique, especially in studying gas–surface interactions; however, it fails dramatically when correlations between the separated subsystems become important.

Fully quantal and semiclassical techniques have been developed which use TDH type approximations for the gas phase dynamics and classical mechanics for the surface and bulk degrees of freedom. Cerjan and Kosloff6–7 were among the first to advance this approach to the fully quantum level using Lindblad’s dynamic semigroup formalism for the completely dissipative Liouville operator.8,9 This formalism is attractive but limited to Markovian dissipation. We shall examine this approach in more detail later in this paper.

More recently, and perhaps more relevant to this work, are the fully quantum mechanical and semi-classical theories proposed by Jackson and co-workers. Rather than using a single molecular wavepacket, Jackson uses a multi-configuration molecule–phonon wavepacket that evolves under a time and temperature dependent Hamiltonian. By neglecting processes beyond direct phonon creation and annihilation by the scattering atom, Jackson’s scheme is not only computationally efficient but also produces physically realistic measures of energy transfer and trapping.10–15

Several approximate, but fully quantal, time independent approaches have been proposed as well. The problem with these approaches is that they are generally limited to at most few phonon processes and rely upon approximate forms of the scattering wavefunction to compute transition probabilities. Among these theories are the distorted wave Born approximation,16 the perturbative calculations by...
Buch, 17-19 and the projected continuum theory of Whaley and Bennett. 20 A multiphonon treatment of inelastic scattering at low scattering energies has recently been developed by Manson which effectively bridges the gap between few and multiquanta transitions and has been shown to produce good agreement with multiphonon backgrounds in the scattering of He from alkali halide and metal surfaces. 21 Because these techniques introduce the phonons at the end of the calculation, they will always break down near selective adsorption resonances where the cross-section for inelastic processes is greatly increased. Other time independent approaches to inelastic scattering have been developed by Choi and co-workers; however, these remain as formal results without application to realistic systems. 22,23

In this work we propose a quantum stochastic approach within the TDH approximation to study gas-surface interactions which includes phonon-phonon coupling. Our approach is to use the TDH approximation to factor the total wavefunction into a molecular term and a phonon-bath term which evolve under a set of self consistent field equations. In the Heisenberg representation, the phonon creation/annihilation operators evolve according to a stochastic generalized Langevin-like equation (gLe) which is driven by a molecule-phonon mean-field interaction. Upon taking the high temperature limit, the bath becomes classical and the equations of motion for the phonon operators become identical to the classical gLe. However, in the low temperature limit where the time scale of energy dissipation due to the mechanical coupling of the phonons becomes much shorter than the thermal time scale of the bath, quantum statistics become increasingly important and cannot be neglected. 24-27

The format of this paper is as follows: In Sec. I, we present the formal manipulations that allow one to derive a set of coupled quantum stochastic differential equations for the time development of a molecular wavepacket scattering from a solid surface. In Sec. II, we detail a generalized computational approach which we developed to solve these equations self consistently. In Sec. III, we solve these equations numerically in one spatial dimension to study energy transfer and sticking for low energy He scattering from Xe monolayers on a Ag substrate. We also compare the present model to both quantum/classical approaches and to fully quantum mechanical approaches using the fully dissipative quantum Liouville equation. 7-9 We demonstrate that both the mixed quantum/classical approach and the dissipative quantum Liouville approach grossly underestimate energy transfer when compared to our model. Finally, we summarize the important features of our approach.

I. FORMAL DEVELOPMENT

In general, the interactions between a scattering molecule and a solid are quite complicated. In this model, we shall assume that the molecule is a structureless, closed shell neutral particle which interacts most strongly with the surface atoms and phonons. We shall also assume that the surface phonons are at most linearly coupled to a bosonic bath and that the average surface/bath coupling is weak but not negligible. The total Hamiltonian for our model system is

\[
H = \frac{-\hbar^2}{2m} \left( \frac{\partial^2}{\partial z^2} + \nabla^2 \right) + V(z, R, \{u_n\}) + \sum_j \hbar \omega_j a_j^\dagger a_j + \sum_q \hbar \omega_q b_q^\dagger b_q + \sum_{j,q} \gamma_{jq} (a_j^\dagger + a_j) (b_q^\dagger + b_q) + H_s + H_B + V_{SB}.
\] (1.1)

Our notation is such that \((z, R)\) are the center of mass coordinates of the scattering molecule with mass \(m\). The \(\{a_j\}\) and \(\{b_q\}\) are the surface and bulk phonon operators. \(H_s\) is the molecular kinetic energy operator and \(V(z, R, \{u_n\})\) is the potential energy surface between the molecule and the solid lattice. \(H_s\) and \(H_B\) are the uncoupled (harmonic oscillator) Hamiltonians for the surface and bulk phonon modes which are in turn coupled via \(V_{SB}\) with coupling constants \(\{\gamma_{jq}\}\).

The interaction potential, \(V(z, R, \{u_n\})\), can be expanded in a Taylor series about the equilibrium position of the surface atoms.

\[
\hat{V} = \hat{V}_0 + \sum_j \hat{V}_j^p \cdot (a_j^\dagger + a_j) + \hat{\Sigma}(u_n^2).
\] (1.3)

Here we have defined the molecule phonon interaction operator

\[
\hat{V}_j^p = \frac{1}{\sqrt{N}} \sum_{\{Q_j\}; R_z} \varepsilon_j(q) \sum_n \left. \frac{\partial^2}{\partial u_n^2} \right|_{u_n=0} \left| n_j, \eta_q \right> \left< n_j, \eta_q \right|, \] (1.4)

where \(M\) is the mass of the surface atom, \(N\) is the total number of surface modes, \(\varepsilon_j(q)\) is the \(z\) component of the phonon polarization projected upon the surface Brillouin zone, and \(R_z\) is the position vector of the \(n\)th surface atom. Under ordinary scattering conditions, the surface atoms are displaced only slightly from their equilibrium position during the course of the interaction. With this in mind, we shall retain only up to linear terms in the displacement coordinate.

The quantum state of the system (scattering atom) and bath (bulk + surface phonons) is a solution of the time dependent Schrödinger equation

\[
i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle.
\] (1.5)

At time \(t=0\), we assume the atomic scattering states and the phonon-bath states are uncoupled so that the total quantum state, \(|\psi(t=0)\rangle\), may be factored within the TDH approximation as a direct product state of the molecular scattering state, \(|\varphi(t)\rangle\), and the surface and bulk phonon states, \(|\eta_j, \eta_q\rangle\), which are labeled by their respective occupation numbers:

\[
|\psi\rangle = \exp\left[-i\lambda \cdot |\varphi\rangle \otimes |\eta_j, \eta_q\rangle\right].
\] (1.6)
The phase factor, \( \lambda(t) \), includes any phase coherence between the molecular and surface/bath portions of the wavefunction. In the TDH approximation, one assumes that the phase coherence term, \( \lambda(t) \), is vanishingly small and can be neglected for all later times. In short, the TDH factorization is equivalent to a random phase approximation.

Projecting out the surface and bath variables from the total Schrödinger equation yields a reduced Schrödinger equation for the wavepacket of the scattering molecule which depends explicitly upon the instantaneous expectation values of surface phonon variables

\[
i \frac{\partial}{\partial t} |\varphi\rangle - iH[|a_i(t)\rangle + |a_j(t)\rangle] |\varphi\rangle ,
\]

where \( H[\tau] \) is the TDH molecule/surface Hamiltonian, and

\[
|a_i(t)\rangle + |a_j(t)\rangle = \langle n_j(t) | \{ a_i + a_j \} | n_j(t) \rangle \langle n_j(q) \rangle.
\]

Likewise, projecting out the molecular degrees of freedom produces a set of reduced equations for the bath and surface phonon states which depend explicitly upon the dynamics of the molecular wavefunction

\[
i \hbar \frac{\partial}{\partial t} |n_j(q)\rangle
\]

\[=
[i \omega_q a_i^\dagger a_j + \langle \varphi(t) | V^{ph} | \varphi(t) \rangle (a_i^\dagger + a_j)
\]

\[+ \sum_q [i \omega_q b_q^\dagger b_q + \gamma_q (a_i^\dagger + a_j)(b_q^\dagger + b_q)] |n_j(q)\rangle .\]

If the bath were limited to only a few degrees of freedom, we could in principle integrate these equations and follow the evolution of both the molecular and surface/bath states explicitly. However, since we are neglecting direct correlations between the molecular and surface/bath states, we do not necessarily need to follow the evolution of the surface and bath wavefunction in order to obtain the mean-field interaction that couples the phonons to the scattering molecule. The ideal dynamic representation for the phonons is the Heisenberg representation where we consider the time evolution of an operator under the Liouville-von Neumann equation and take the expectation value with respect to some initial fixed state. The Heisenberg equations of motion for the phonon operators are

\[
\frac{\partial}{\partial t} a(t) = -i \omega - i \hbar \Delta (a^\dagger + a) - \frac{i}{\hbar} \langle V^{ph}(t) \rangle - i \xi(t)
\]

\[= -i \hbar \int_0^t dt' (\dot{a}^\dagger(t') + \dot{a}(t')) K(t-t').\]

where

\[
\Delta = \frac{2}{\hbar^2} \sum_q \frac{\gamma_q^2}{\hbar \omega_q},
\]

produces a slight frequency shift due to the coupling to the bath.

\[\langle V^{ph}(t) \rangle = \langle \varphi(t) | V^{ph} | \varphi(t) \rangle \]

is the mean-field interaction force between the molecule and the phonons. Finally,

\[\xi(t) = \frac{1}{\hbar} \sum_q \gamma_q (\tilde{b}_q(t) + \tilde{b}_q(t)).\]

is the noise operator which acts upon the bath subspace and provides a temperature dependent driving force to the surface phonon equations of motion.

The friction kernel, \( K(t) \), is defined in terms of the phonon/bath coupling constants,

\[
K(t) = \frac{2}{\hbar^2} \sum_q \frac{\gamma_q^2}{\hbar \omega_q} \cos(\omega_q t),
\]

and introduces dissipation of energy from the surface modes to the bath modes. If the bulk density of states is sufficiently dense and the coupling constants are a smooth
function of the bath frequencies, the summation can be taken to be an integral over the bath phonon frequencies

\[ K(t) = \frac{2}{h} \int_0^\infty d\omega \gamma(\omega) e^{\omega t} \cos(\omega t). \]  

In the limit that the surface and bulk states are only weakly interacting, the density operator for the surface/bath degrees of freedom is approximately a direct product operator,

\[ \rho_{SB} = \rho_S \otimes \rho_B \]  

where \( \rho_B(t) = e^{-H_B t} / Z_B \) and \( Z_B \) is the canonical partition function for the bath. Furthermore, for all times \( t > t_0 \) it remains a direct product operator. Under this assumption, we can define the thermal average of any operator, \( \hat{A} \), operating upon the bath states at \( t = t_0 \) as

\[ \langle \hat{A}(t_0) \rangle_{th} = \text{Tr}_B [\hat{A} \rho_B] \]  

where the trace is taken over the bath variables. Inserting the bath operators, \( \{ \hat{b}_q(t) \} \), from Eq. (1.14) into Eq. (1.22) it is simple to show

\[ \langle \hat{b}_q(t) \rangle_{th} = 0, \]  

\[ \langle \hat{b}_q(t) \hat{b}_q(t') \rangle_{th} = \langle \hat{b}_q(t) \hat{b}_q(t') \rangle_{th} = 0, \]  

\[ \langle \hat{b}_q(t) \hat{b}_q(t') \rangle_{th} = (n_q + 1) e^{i \omega(q t' - t)}, \]  

and

\[ \langle \hat{b}_q(t) \hat{b}_q(t') \rangle_{th} = n_q e^{i \omega(q t' - t)}, \]

where

\[ n_q = \frac{1}{\exp(\beta \hbar \omega_q) - 1}. \]

Since the bath is assumed to be an ensemble of harmonic oscillators, any higher order expectation value can be decomposed into the above expectation values. Taking the thermal limit of Eq. (1.15), the bath operator \( \hat{\xi}(t) \) is replaced by the Gaussian random variable \( \xi(t) \) (no hat) which has zero mean and deviance given by the thermal average of the anti-commutator correlation function of \( \hat{\xi}(t) \).

\[ \langle [\hat{\xi}(t), \hat{\xi}(t')] \rangle_{th} = \frac{2}{\hbar} \sum_q \gamma(2n(\omega_q) + 1) \cos(\omega_q(t - t')) \]  

\[ = \int_0^\infty d\omega \hbar \omega K(\omega) \coth \left( \frac{\hbar \omega}{2} \right) \cos(\omega(t - t')). \]  

This last expression is the quantum mechanical version of the classical fluctuation–dissipation theorem which insures a balance between the influx and efflux of energy between the bath and the surface phonons. The fundamental difference between the classical and quantum mechanical versions of this relation is due to the fact that in the quantum regime, bath excitations carry different statistical weights than bath de-excitations due to Bose–Einstein statistics, whereas in the purely classical regime, phonon transitions receive the same statistical weighting. This has quite profound implications when one considers the long time behavior of this relation.

In the classical limit (\( \hbar \to 0 \)), Eq. (1.15) is formally equivalent to the generalized Langevin equation in classical mechanics. This limit is clearly valid as long as the longest thermal time scale, given by \( \tau_T = h / \gamma_B \), is much less than the characteristic time scale of the friction kernel, \( \tau_B = 1 / \gamma_B \). While in the classical limit, fluctuations and dissipations occur on the same time scale, in the quantum limit, where \( 2\pi kT / \hbar < \gamma_B \), these time scales are no longer necessarily the same. In fact, even in the simplest cases at low temperatures (or large \( \gamma_B \)), a thermal time scale begins to dominate which is on the order of a picosecond at \( T = 1 \, \text{K} \). Furthermore, it can be shown that in the Markov limit at \( T = 0 \, \text{K} \), the long time behavior of the anti-commutator correlation function no longer decays exponentially, but rather decays algebraically as \( t^{-2} \).

This completes the formal definition of the time evolution equations for our model system. In the subsequent section we shall first present a generalizable computational scheme for their numerical solution and use this to study low energy He scattering and sticking upon rare gas overlayers.

### II. EVOLUTION OF SURFACE PHONON VARIABLES

In the present application of this formalism, we shall assume that dissipation into the bath degrees of freedom is instantaneous, i.e., Markovian. However, in future applications we will need the computational tools to consider non-Markovian dissipation and the corresponding colored noise. If we choose to maintain a fully quantal picture, even in the Markov case we shall require a colored noise source which reflects the Bose–Einstein statistics for creating and annihilating bath phonons. For the classical case, the correlation function for the noise operator and the friction kernel are related linearly in temperature and phonons are created and annihilated with the same probability.

In general, the anti-commutator correlation function is divergent and can only be thought of as a generalized function or distribution. While this prevents us from formally analyzing the temporal behavior of the correlation function for all but the most drastic of choices of \( K(t) \), we can use the convolution theorem to produce a numerical realization of the fluctuation operator from its power spectrum:

\[ \xi(t) = \int_0^\infty d\omega e^{-i\omega t} g(\omega) \sqrt{S_\xi(\omega)}, \]  

where

\[ S_\xi(\omega) = \hbar \omega \coth \left( \frac{\hbar \omega}{2} \right) K(\omega). \]  

The \( g(\omega) \) are Gaussian random numbers with zero mean and normal deviate:

\[ g(\omega) - 0, \]  

\[ g(\omega) g(\omega') = \delta(\omega - \omega'). \]
In particular, we used the power spectrum method of Billah and Shinozuka in which the random variable, $\Phi$, is generated from a uniform deviate, using the transformation which converges as $N \to \infty$.

$$\xi(t) = \sqrt{2} \sum_{n=1}^{N} [2S_{\omega}(\omega_n)\Delta\omega]^{1/2} \cos(\omega_n t + \Phi_n), \tag{2.5}$$

where $\omega_n = n\Delta\omega$, $n=1,2,...,N$, $\Delta\omega = \omega_{\text{max}}/N$, and $\omega_{\text{max}}$ is the cutoff frequency of the power spectrum $S_{\omega}(\omega)$. The random phase $\Phi_n$ is of uniform deviate on the range $[0, 2\pi]$. As pointed out by Billah and Shinozuka, each sample run is ergodic in the mean as well as in the correlation. The advantage of this algorithm is that it directly converts a uniform deviate to a stationary Gaussian colored noise without the use of an intermediate transformation, such as the Box–Müller transformation. One can think of the difference between Eq. (2.1) and Eq. (2.5) as being simply amplitude modulation vs phase modulation. In practice, Eq. (2.5) was evaluated using the fast Fourier transform method. One point which is important to note regarding this power spectrum method is that there exists a finite recursion time, $r_R = 2\pi/\Delta\omega$. This should not cause noticeable problems as long as $r_R$ is greater than any other physically realistic correlation within the calculation.

### III. NUMERICAL APPLICATION AND COMPARISON

We employed the above formalism in a one dimensional calculation simulating a He atom impinging upon a Xe monolayer on a Ag substrate at normal incidence (see Table I). The initial wave packet was chosen to be a Gaussian centered some distance above the surface with some initial momentum toward the surface

$$\psi(0) = (\pi^2\sigma_z^2)^{-1/4} \exp[-(z-z_0)^2/2\sigma_z^2 - i k_0 \cdot z]. \tag{3.1}$$

The final projection of the outgoing wavepacket onto the asymptotic scattering states was accomplished using the wavepacket splitting algorithm of Heather and Metiu. We solved the time dependent Schrödinger equation for the atomic translational degrees of freedom self consistently with the quantum stochastic equations derived above for the surface and bath phonons. At each time step we recomputed the atom–surface interaction potential term to account for the motion of the surface atoms due to the phonons. This was done at a slight increase in computational time over that of a static surface. We used the split operator method of Feit and Fleck to estimate the Schrödinger evolution operator (here, $\hbar = 1$)

$$U_{\delta t}(t,\delta t) = e^{-iH_0\delta t/2}e^{-iV(t)\delta t}e^{-iH_0\delta t/2} + O(\delta t)^3. \tag{3.2}$$

There has been much discussion recently about the use of discrete variable representations (DVRs) in time dependent quantum mechanics, and one is referred elsewhere for a more complete discussion of DVR methods. It suffices to say that a DVR is a finite representation in which the position operator is diagonal and the DVR points, $\{x_i\}$, are its eigenvalues. If the finite basis used to compute the kinetic energy matrix corresponds to a set of classical orthogonal polynomials, then the DVR points are the Gaussian quadrature points associated with the finite basis. This has the desired advantage that all spatial integrals are reduced to matrix and vector multiplications, which are numerically efficient to compute on vector processing machines, and more important, all functions of coordinates are approximated by diagonal matrices evaluated at the DVR points. There also exists an isomorphism between the DVR and the finite basis which allows one to construct a unitary transformation, $T$, between the two representations thus allowing one to compute in whichever representation is most advantageous at any given time. The method is particularly efficient if the finite basis, $\{\phi_k\}$, may be chosen to be a complete set of eigenstates of the $H_n$ term in the propagator.

Using the DVR-finite basis transformations, Eq. (3.2) can be rewritten in a form more suitable for computation where summation is performed over repeated indices

$$U_k^{k'}(t,\delta t) \approx e^{-i\epsilon_k\delta t/2}T_{k,k'} e^{-iV(x_i,t)\delta t}T_{k,k'} e^{-i\epsilon_k\delta t/2}, \tag{3.3}$$

where

$$H_o|\phi_k\rangle = -\epsilon_k |\phi_k\rangle, \tag{3.4}$$

$$T_{k,k'}(x_i) = \sqrt{|w_{k'}|}, \tag{3.5}$$

and the $\{w_{k'}\}$ are the Gaussian quadrature weights associated with the $\{x_i\}$ points.

The He–Xe surface potential used throughout this study was constructed from a sum of He–Xe pair potentials, $U(r)$, plus a bulk polarization term which depended only upon the distance between the metal substrate and the He atom (see Table II). Three body terms, such as the Axelrod–Teller–Muto triple–dipole interaction potential, were excluded to reduce the computational effort re-
required to reconstruct the surface at each time step. The pair potential used throughout the study was an exponentially repulsive potential with damped dispersion potential of the form

$$U(R_j) = A \exp[-\alpha R_j] - F(R_j) \sum_{i=0}^{2} g_{2i+6} R_j^{2i+6}, \quad (3.6)$$

where the \( g_{2i+6} \) are the multipole interaction constants,

$$F(r) = \begin{cases} \exp\left[-\left(\frac{1.28r_m}{r} - 1\right)^2\right], & \text{for } r > 1.28 \, r_m \\ 1, & \text{otherwise,} \end{cases} \quad (3.7)$$

and \( r_m \) is the position of the potential well minimum.\(^{39}\)

The other term in the potential was the He-Ag interaction potential. Since the He atom is at all times greater than 3 Å from the Ag substrate due to the adlayer, only long range van der Waals interactions needed to be included:

$$V_{bulk}(z) = \frac{g_3}{(z-\xi)^5}. \quad (3.8)$$

The parameter \( \zeta \) is defined as

$$\zeta = n d_l - \frac{c}{2} - z_a \quad (3.9)$$

where \( d_l \) is the interlayer spacing between the adlayers and \( n \) is the number of adlayers. The other parameters, \( c \) and \( z_a \), are related to the position of the image potential above the Ag surface.

The Einstein frequency of the surface phonons was taken from the experimental data of Gibson and Sibener,\(^{40}\) and the phonons were modeled as Brownian oscillators driven by the quantum noise source in Eq. (2.5) with a Markovian memory kernel

$$K(t-t') = \gamma \delta(t-t'). \quad (3.10)$$

Since the dissipative term in the stochastic equations for the phonon operators physically represents the averaged coupling between the surface phonon and the bulk substrate, a Markov approximation in this particular case is quite easily justified, especially since relatively little is known about the coupling between the Xe adlayer and the substrate phonons. We allowed the friction constant, \( \gamma \), to be an adjustable parameter so that we could explore what effect the coupling of the surface phonons to the substrate bath phonons has upon the scattering and dynamics of the He adatom.

In Figs. 1, 2, and 3, we plot the asymptotic energy distribution, \( P(E) \), for various surface temperatures. In each case, energy transfer due to inelastic scattering can be determined by comparing the peaks which occur on either side of the central peak at exactly \( E = \pm \omega_E \). In Fig. 1, the initial scattering energy is slightly less than the Einstein frequency of the lattice, so only elastic and energy gain probabilities are collected in the asymptotic region. Thus, any energy loss to the phonons resulted in the trapping of the atom on the surface for some finite amount of time past the end of our calculations.

Figures 2 and 3 best demonstrate the attenuation of elastic scattering probabilities and the enhancement of the inelastic probabilities as the surface temperature is increased. Figure 2 clearly shows the appearance of features...
corresponding to both single and double phonon annihilation processes which increase with increasing surface temperature.

It is important to point out that the reason the energy loss features, corresponding to phonon creation, are weaker than the energy gain features is not due to the physics of this system, rather it is due to the way the asymptotic information is collected. As the wavepacket leaves the surface, the faster, higher momentum components are collected first. Since these correspond to the phonon annihilation features, all of these components will be collected first. The slower moving components, corresponding to energy loss to the phonons, are collected at the end of the calculation. In order for the calculations to finish in a reasonable amount of time, we chose to end the calculations when 95% of the initial wavepacket appeared in the asymptotic region. Thus, the lower energy components should receive an increased weighting due to the systematics of the calculation. While this makes an accurate comparison of phonon transition probabilities difficult, it will not affect quantities such as Debye-Waller attenuation rates, which are obtained from the elastic intensities. Also, this systematic error appears mostly at lower scattering energies and the effect is not as pronounced in Fig. 5 as it is in Fig. 3.

Finally, we considered the effect that the coupling to the bath has upon the energy transfer probability. Figure 4 shows $P(E)$ for three choices of $r_B$ at $T=45$ K and $E_{\text{scattering}}=15$ meV.

FIG. 4. Comparison of various choices of $r_B$ at $T=45$ K and $E_{\text{scattering}}=15$ meV.

A. Comparison to “mean-field” results

Since the surface phonons are assumed to be initially thermal, we must average over an ensemble of initial phonon states in order to produce a proper statistical distribution. We compare two different approaches for this averaging. The first and least difficult computationally is to define a “mean-field” potential which couples the quantum degrees of freedom to the phonon variables,

$$V^{\text{mf}}(z,R,t) = \frac{1}{N_i} \sum_{a=1}^{N_i} V(z,R_i\{\langle a \rangle(t)\}) + a_j(t) \langle (a) \rangle, \quad (3.11)$$

where $a$ labels the various $N_i$ initial phonon states for each mode. Such mean-field approaches are very fast computationally and in Ref. 2 are reported to produce small errors in the energy flow between the quantum and classical degrees of freedom. A more rigorous method for averaging over the initial phonon states is to average over an ensemble of asymptotic scattering amplitudes, each having a different initial state for the phonon degrees of freedom. In other words,

$$|\langle k | \psi_{\text{final}} \rangle|^2 = \frac{1}{N_r} \sum_{n=1}^{N_i} |\langle k | \psi_{(n)} \rangle|^2. \quad (3.12)$$

While the latter approach is much more intensive computationally than the “mean-field” approach, since we must perform $N_i$ scattering calculations in order to produce the final scattering state, our results indicate that energy transfer between the phonons and the molecular degrees of freedom is substantially greater than in the “mean-field case.” In Fig. 5 we compare Eqs. (3.11) and (3.12) by scattering a 10 meV He atom from a $T=45$ K Xe monolayer at normal incidence angle. While computationally much more expedient than averaging over 10 or 15 separate calculations, the “mean-field” averaging grossly underestimates the energy transfer to the lattice.

B. Comparison to completely dissipative results

In the model derived by Cerjan and Kosloff, the equations of motion describing the time development of the

FIG. 5. Comparison of “mean-field” averaging [as in Eq. (3.11)] vs averaging over final states [as in Eq. (3.12)]. The dashed curve is the “mean-field” result while the solid curve is the latter. The important difference here is the gross underestimation of the energy transfer between the phonons and the scattering atom which is obtained by using a “mean-field” treatment of the surface phonons.
surface phonons were generated using a completely dissipative form of the Liouville superoperator as given by Lindblad

$$\partial_t A = \mathcal{L}(A) = \mathcal{L}_H(A) + \mathcal{L}_{CD}(A).$$

(3.13)

The first term, $\mathcal{L}_H(A) = i[H,A]$, is Hermitian and gives the unitary (time reversible) dynamics of the isolated system. The second term, given explicitly by

$$\mathcal{L}_{CD}(A) = \sum_j \gamma_j \left( V_j A V_j^\dagger - \frac{1}{2} [V_j, V_j^\dagger, A]^+ \right),$$

(3.14)

is the completely dissipative (non-Hermitian) contribution to the Liouville superoperator which is similar in structure and form to the quantum master equation. The explicit equations of motion to which we compare are found in Ref. 5, Eq. (18a)–(18c). And for comparison, we chose

$$\gamma_3 = \gamma_B.$$  

(3.15)

In Fig. 6 we compare the results obtained from scattering a 10 meV wavepacket from a Xe overlayer surface in which the surface phonons were propagated using our stochastic model and the completely dissipative model just described (LCD). We also compare both of these to a purely elastic scattering calculation at the same initial energy. The phonon side bands, which are very prominent in our model are nowhere to be seen in the completely dissipative model. Apart from a very slight shift in $\langle E \rangle$, the LCD result is nearly indistinguishable from elastic scattering.

In both our model and the above LCD model, it is assumed that the surface atoms are displaced slightly from their equilibrium position by the impinging atom. The difference is that in our model, the surface atoms are allowed to undergo Brownian harmonic motion about their equilibrium positions at all times during the course of the calculation and thus the scattering atom evolves under an oscillating potential at all times. In the LCD model, the surface atoms are modeled only by their averaged equilibrium position, which is zero except when the scattering atom is close by. Thus, the impinging atom propagates more or less under a static potential until it is close enough to significantly deflect the surface atom from its equilibrium position, after which time it experiences a damped oscillating interaction potential.

**SUMMARY**

In this work we have presented a fully quantum mechanical formulation for molecule/phonon/bath interactions under the time dependent Hartee approximation. In doing so we have derived a self-consistent set of stochastic equations of motion for the molecular wavefunction and the phonon creation and annihilation operators. The generalized Langevin-like equations for the phonon operators are very similar in form to their classical analogs with the exception that the fluctuation–dissipation relationship is no longer a simple linear function of bulk temperature. The non-linear temperature dependence reflects the fact that at low temperatures the statistical weights for phonon creation and annihilation are not equal. Furthermore, at low enough temperatures, correlations involving the phonon operators begin to exhibit power-law like decay as opposed to exponential decay.

We have compared the results of our formalism to results obtained using other similar quantum/classical and fully quantum mechanical treatments of the surface phonons. In both cases, averaging over the initial phonon state was performed at the beginning of the calculation. This, we demonstrate, can lead to a significant decrease in energy transfer to the surface modes, even to the point that finite temperature results are nearly indistinguishable from elastic scattering. By averaging over the final asymptotic probability distribution of a number of scattering calculations we obtain a much more realistic measure of energy transfer. Although computationally much more intensive, since $N_f$ separate scattering calculations must be run to produce proper statistical convergence, each separate calculation amounts to only slightly more effort than a single wavepacket calculation. Additional computational advantage may be gained by spreading the effort among a number of separate computers and collecting and averaging the results in the end, effectively running the calculation in parallel.

These one dimensional results serve as a demonstration that mean-field methods for inelastic surface scattering can be constructed to give realistic measures of energy transfer. In a following paper, we shall present the results of our detailed study of He scattering from Xe overlayers where we use the present method to examine the enhancement of inelastic processes near selective adsorption resonances.

**ACKNOWLEDGMENTS**

We wish to thank the National Science Foundation for partial support of this work under Grants CHE-8806514 and by the Material Research Laboratory under NFS Grant DMR-88-19860.