

Multiphonon theory of scattering of atoms from solid surfaces: Tetradic scattering approach

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The tetradic scattering formalism is used to develop a theory for inelastic scattering of atoms from solid surfaces. The theory accounts for the correlated dynamics of the colliding atom and the solid surface, and an analytical expression is derived for the multiphonon energy transfer probability in a collinear collision. The present formulation does not rely on a separation of time scales and is thus valid for any value of the lattice correlation time τ_c relative to the gas-surface interaction strength d . In the high temperature and strong coupling limits, $d\tau_c \gg 1$ and the inelastic cross section contains a Gaussian broadening term. In the extreme Markov limit, $d\tau_c \ll 1$ and the cross section contains a Lorentzian broadening term. In both extremes, the lattice dynamics is weakly correlated with the collision. We discuss and analyze the behavior of the inelastic cross section under various physical limits.

I. INTRODUCTION

Energy transfer processes between gas atoms and solid surfaces are of great fundamental interest for the understanding of the chemistry and physics of solid surfaces. In addition, they have very important practical applications for heterogeneous catalysis, condensation, etc.¹ Recent experimental developments in molecular beam scattering from solid surfaces provide accurate measurements of angular distributions and inelastic scattering cross sections under a variety of experimental conditions (surface Debye temperature, surface temperature, masses, beam velocity, etc.).¹

The theoretical problem of calculating the cross section for inelastic atom-surface scattering has been the subject of numerous studies of various degrees of sophistication.¹⁻⁶ Examples are the quantum distorted wave Born theory of Lennard-Jones, Devonshire, and Strachan (LDS),^{2,3} the hard cube model of Logan and Stickney,⁴ and numerical calculations of the dynamics of atomic clusters.⁵ The fundamental problem in constructing a theory for the scattering of atoms from solid surfaces is the necessity to solve for the correlated time evolution of the combined atom and solid which involves, in principle, all the degrees of freedom of the solid. Since there is not an obvious separation of time scales in the problem, this is a true many-body problem and very little can be done for the problem in its most general form.

Adelman and Doll⁷ have recently proposed a new approach towards the calculation of the dynamics of gas-solid scattering processes within the framework of classical mechanics. The method consists of dividing the surface atoms into few relevant ones (the "system") which interact directly with the gas atom and whose dynamics are being followed, and the rest (the "bath") which are weakly correlated with the scattering process. It is then possible to write generalized Langevin equations^{8,9} for the motion of the system atoms and to couple them to the dynamics of the collision. The many-body surface effects enter into the Langevin equations via a random force and a friction kernel which can be evaluated in principle for harmonic lattices.^{10,11} In practice, application of this method requires the calculation of a large number of stochastic classical trajec-

tories. Shugard, Tully, and Nitzan¹² have developed approximate computational schemes for evaluating the quantities appearing in the Langevin equations and have carried out extensive numerical studies of the Langevin equations. The Langevin approach is very useful for solving for the correlated gas-surface dynamics. Its main limitations, however, are the necessity of running large scale computations and the usage of classical mechanics. In practice, it is of interest to study the surface temperature effects on the energy transfer for a wide range of temperatures and classical description obviously fails when the temperature is sufficiently low.

The quantum theory of LDS¹⁻³ is based on the low order perturbation theory and does not include the correlated time evolution of the system and the bath. The many-body effects of the surface enter into the final expression via the density of surface modes $g(|\epsilon|)$ which multiplies the cross section for the transfer of energy ϵ . This is a common feature to all other quantum perturbative approaches.¹³⁻¹⁵ Metiu¹⁵ has recently presented a quantum theory for gas surface scattering. However, he evaluates the multiphonon contributions using a short time expansion which again amounts to a classical description of the lattice.

In this paper, we present a quantum mechanical theory of scattering of atoms from solid surfaces based on the tetradic scattering formalism of Fano and Zwanzig.¹⁶⁻¹⁸ This formulation enables us to perform the necessary thermal averages over the lattice modes in a straightforward way. We further invoke the distorted wave Born approximation (DWBA) but use a general solid-gas interaction which allows for multiphonon processes and has been previously proven very useful in the theoretical treatments of other related problems such as impurity spectra in solids,¹⁹ vibrational relaxation of impurity molecules in solid matrices,^{20,21} and radiationless processes in large molecules.^{22,23} Our general expression for the inelastic scattering cross section [Eqs. (31) and (47)] takes into account the correlated dynamics of the lattice and the translational motion of the scattering process. It has the form of a product of a translational factor and a generalized line shape function $I(\epsilon)$, where ϵ is the energy transferred to the lattice.

$I(\epsilon)$ goes smoothly between the static limit (strong coupling, high temperatures), in which the motions in the solid are much slower than the inverse gas-solid interaction, and the reverse, the Markovian limit. In the static limit, the broadening of $I(\epsilon)$ arises from the ensemble average over the bath static configurations. $I(\epsilon)$ may thus be regarded as being inhomogeneously broadened and has a Gaussian form. In the Markovian limit, the bath motions are so fast relative to the gas-solid interaction that the projectile merely feels an "averaged" surface atom. In this case, $I(\epsilon)$ may be regarded as homogeneously broadened and assumes a Lorentzian form.

In both limits, the bath and projectile motions are uncorrelated (due to different reasons). Our general expression (47), however, interpolates smoothly between the two limits and thus is valid for any time scale of motions for the bath relative to the interaction. A perturbative expansion of our final result in the gas-solid interaction strength reduces to the LDS result.

In Sec. II, we present the basic relations of the tetradic scattering formulation of Fano and Zwanzig which are used in the present work. In Sec. III, we apply this formulation to the scattering of an atom from a solid surface and derive Eq. (28), which is our most general expression for the inelastic cross section. Section IV contains a derivation of a closed expression for the multiphonon energy transfer probabilities in a collinear collision. The final result [Eqs. (47)-(49)] is then analyzed and discussed in Sec. V, where we also consider its limiting behavior and compare with other works.

II. THE TETRADIC SCATTERING FORMALISM

The tetradic scattering formalism^{16-18,24} is a formulation of scattering theory in terms of density matrices in Liouville space rather than with wavefunctions in Hilbert space. The main feature which makes this formulation useful is the fact that density matrix elements (and not their squares) are related directly to the experimental observables. If we are interested in information which is contained in a part of the density matrix, we can (by using projection operators, or other methods) obtain a closed equation of motion (a master equation) for the reduced density matrix of interest. This enables us to solve directly for the relevant quantities. If we were to use the ordinary (Hilbert space) formulation of scattering theory, we would have to find the total wavefunction for the scattering problem, which contains the complete information regarding the scattering process, square it, and only then can we average over the irrelevant states or degrees of freedom. The tetradic scattering formulation has been extensively applied to problems of pressure broadening of spectral lines¹⁸ and resonance and Raman fluorescence of molecules.^{25,26} It has been also recently applied to the dynamics of chemical reactions involving complex formation.²⁷ Tetradic scattering has been recently reviewed by Ben-Reuven.¹⁸ We shall now present the basic notation and results of this approach.

The tetradic operator \mathfrak{u} corresponding to an ordinary operator U is defined by its action on an ordinary operator A :

$$\mathfrak{u}A \equiv [U, A], \quad (1)$$

which can be written as

$$(\mathfrak{u}A)_{ab} = \sum_{c,d} \mathfrak{u}_{ab,cd} A_{cd}. \quad (2)$$

Comparison of Eqs. (1) and (2) results in

$$\mathfrak{u}_{ab,cd} = U_{ac} \delta_{b,d} - U_{b,d}^* \delta_{a,c}. \quad (3)$$

We further introduce the double-bracket notation where by an ordinary operator $|a\rangle\langle b|$ is written as a vector $|ab\rangle$, whereas a tetradic operator is written as

$$\mathfrak{u} = \sum_{ab,cd} |ab\rangle\langle\langle cd|. \quad (4)$$

The scalar product in Liouville space is defined as

$$\langle\langle ab|cd\rangle\rangle = \text{tr} |b\rangle\langle a|c\rangle\langle d| = \delta_{a,c} \delta_{b,d}. \quad (5)$$

The tetradic S matrix s is defined as the transformation of the density matrix before $\rho(-\infty)$ and after $\rho(+\infty)$ the collision:

$$\rho_{ab}(+\infty) = \sum_{c,d} s_{ab,cd} \rho_{cd}(-\infty). \quad (6)$$

The S matrix is related to the tetradic T matrix \mathcal{T} by¹⁸

$$s_{ab,cd} = \delta_{ca} \delta_{db} - 2\pi i \delta(\omega_{cd} - \omega_{ab}) \mathcal{T}_{ab,cd}(\omega_{ab}) \quad (7)$$

and $\mathcal{T}(\omega)$ is defined as

$$\mathcal{T}(\omega) = \mathfrak{V} + \mathfrak{V} \mathfrak{G}(\omega) \mathfrak{V}. \quad (8)$$

Here, \mathfrak{V} is the appropriate interaction for the particular scattering problem defined as

$$\mathfrak{V} = L - L_0. \quad (9)$$

L is the total Liouville operator (tetradic Hamiltonian), whereas L_0 is the Liouvillian corresponding to the projectile and target at infinite separation. The tetradic Green's function \mathfrak{G} is given by

$$\mathfrak{G}(\omega) = (\omega - L + i\eta)^{-1}, \quad \eta \rightarrow 0^+. \quad (10)$$

Equations (6)-(10), which constitute the basic results of the formal tetradic scattering theory, have analogous equations in ordinary Hilbert space, obtained by replacing each tetradic operator by the corresponding dyadic and ρ by the wavefunction ψ .

The cross section for the scattering process from an initial state $|a\rangle$ to a final state $|b\rangle$ is given by

$$\sigma(a \rightarrow b) = \frac{-i}{F_a} \mathcal{T}_{bb,aa}(0), \quad (11)$$

where F_a is the incident flux in the $|a\rangle$ channel. a and b are complete quantum numbers (for the projectile and target).

III. APPLICATION TO THE INELASTIC SCATTERING OF ATOMS FROM SOLID SURFACES

We consider an inelastic scattering of an atom from a solid surface. The total Hamiltonian is

$$H = H_S + H_B + H_{SB} = H_0 + H_{SB}, \quad (12)$$

where

$$H_S = -\frac{\hbar^2}{2m_S} \nabla_R^2, \quad (12a)$$

$$H_B = \sum_{\nu} \omega_{\nu} (p_{\nu}^2 + q_{\nu}^2) = \sum_{\nu} \omega_{\nu} b_{\nu}^{\dagger} b_{\nu}, \quad (12b)$$

$$H_{SB} = \sum_j V(|R - Q_j|), \quad (12c)$$

and

$$Q_j - Q_j^0 = \sum_{\nu} \beta_{\nu j} q_{\nu}. \quad (12d)$$

Here, H_S , H_B , and H_{SB} denote the Hamiltonians for the free gas atom, the lattice (the bath), and their interaction, respectively. m_s is the mass of the gas atom and R is its distance from the surface. The bath Hamiltonian H_B is assumed to be purely harmonic, where p_{ν} and q_{ν} are the (dimensionless) momentum and coordinate of the ν th normal mode, respectively, whereas b_{ν}^{\dagger} and b_{ν} are the corresponding creation and annihilation operators, respectively. The atom-surface interaction H_{SB} is assumed to be a sum of pairwise contributions. Q_j is the position of the j th lattice atom and Q_j^0 is its equilibrium point.

We are interested in the cross section $\sigma(\mathbf{k} \rightarrow \mathbf{k}')$ for the scattering process where the incident particle with initial momentum \mathbf{k} is scattered with a final momentum \mathbf{k}' . Using Eq. (11), we can write

$$\sigma(\mathbf{k} \rightarrow \mathbf{k}') = \frac{-i}{F_i} \langle \mathcal{T}_{\mathbf{k}'\mathbf{k}, \mathbf{k}\mathbf{k}}(0) \rangle, \quad (13)$$

where F_i is the incident flux and

$$\langle \mathcal{T}_{\mathbf{k}'\mathbf{k}, \mathbf{k}\mathbf{k}}(\omega) \rangle = \sum_{\alpha, \beta} P_B(\alpha) \langle \langle \mathbf{k}'\mathbf{k}^{\beta} | \mathcal{T}(\omega) | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle \quad (14)$$

is the bath-averaged \mathcal{T} matrix. Here, $|\alpha\rangle$, $|\beta\rangle$ are eigenstates of H_B , whereas $|\mathbf{k}\rangle$, $|\mathbf{k}'\rangle$ are eigenstates of H_S :

$$H_B |a\rangle = \omega_a |a\rangle, \quad a = \alpha, \beta, \quad (15a)$$

$$H_S |l\rangle = \epsilon_l |l\rangle, \quad l = k, k', \quad (15b)$$

and

$$\epsilon_l = \hbar^2 l^2 / 2m_s. \quad (15c)$$

The combined (direct product) states of the system and bath are $|\mathbf{k}\alpha\rangle$, etc., and $|\mathbf{k}\mathbf{k}^{\beta}\rangle\rangle$ is the tetradic state corresponding to $|\mathbf{k}\alpha\rangle\langle\mathbf{k}'\beta|$. The bath averaged \mathcal{T} matrix [Eq. (14)] is obtained by averaging the full (system + bath) \mathcal{T} matrix over the thermal distribution of bath states $P_B(\alpha)$ and summing over all possible final bath states β .

We shall now evaluate the tetradic \mathcal{T} matrix elements using the distorted wave basis set. For that purpose, we define an elastic scattering problem by freezing all the lattice atoms at their equilibrium positions. We thus write

$$H_{SB} = H' + H'', \quad (16)$$

where

$$H' = \sum_j V(R - Q_j^0) \quad (16a)$$

and

$$H'' = H_{SB} - H'. \quad (16b)$$

The corresponding Liouville operators will be denoted by L_{SB} , L' , and L'' , respectively.

The states $|\mathbf{k}^+\rangle$ and $|\mathbf{k}^-\rangle$ will now be defined as the full elastic scattering states corresponding to the Hamiltonian $H_S + H'$, i. e.,

$$|\mathbf{k}^{\pm}\rangle = |\mathbf{k}\rangle + \frac{1}{\epsilon_k - H_S + i\eta} H' |\mathbf{k}^{\pm}\rangle, \quad (17)$$

where the $+$ ($-$) superscripts denote the usual outgoing (incoming) boundary conditions.^{28,29}

The complete formal analogy between the tetradic and the ordinary scattering formulations enables us to use directly all the well developed machinery of the latter. In particular, we shall make use of the formalism of scattering by two potentials^{28,29} to write (for $\mathbf{k}' \neq \mathbf{k}$)

$$\begin{aligned} \mathcal{T}_{\mathbf{k}'\mathbf{k}, \mathbf{k}\mathbf{k}}^{\beta\beta, \alpha\alpha}(\omega) &\equiv \langle \langle \mathbf{k}'\mathbf{k}^{\beta} | L_{SB} \mathcal{G}(\omega) L_{SB} | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle \\ &= \langle \langle \mathbf{k}'\mathbf{k}^{\beta} | L' \mathcal{G}(\omega) L'' | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle \\ &= \langle \langle \mathbf{k}'\mathbf{k}^{\beta} | L'' \frac{1}{\omega - L_0 - L' - L'' + i\eta} L'' | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle \\ &= -i \int_0^{\infty} d\tau \langle \langle \mathbf{k}'\mathbf{k}^{\beta} | L'' \\ &\quad \times \exp[i(\omega - L_0 - L' - L'' + i\eta)\tau] L'' | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle. \end{aligned} \quad (18)$$

We now invoke the distorted wave Born approximation (DWBA) by expanding \mathcal{T} [Eq. (18)] to second order in L'' . This amounts to the substitution

$$\begin{aligned} \exp[i(\omega - L_0 - L' - L'' + i\eta)\tau] \\ = \exp[i(\omega - L_0 - L' + i\eta)\tau] \end{aligned} \quad (19)$$

in Eq. (18). We can now recast Eq. (18) in the form

$$\begin{aligned} \mathcal{T}_{\mathbf{k}'\mathbf{k}, \mathbf{k}\mathbf{k}}^{\beta\beta, \alpha\alpha}(\omega) &= -i \int_0^{\infty} \langle \langle \mathbf{k}'\mathbf{k}^{\beta} | L''(\tau) \\ &\quad \times \exp[i(\omega - L_S - L' + i\eta)\tau] L''(0) | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle d\tau, \end{aligned} \quad (20)$$

where we have switched to the interaction representation in L_B , i. e.,

$$L''(\tau) = \exp(iL_B\tau) L''(0) \exp(-iL_B\tau), \quad (21)$$

and we have made use of the relation

$$\langle \langle \mathbf{k}'\mathbf{k}^{\beta} | \exp(iL_B\tau) = \langle \langle \mathbf{k}'\mathbf{k}^{\beta} |, \quad (22)$$

which is a direct consequence of Eq. (15). From Eq. (3), we have

$$L''(\tau) | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle = V''(\tau)_{\mathbf{k}'\beta, \mathbf{k}\alpha} | \mathbf{k}'\mathbf{k}^{\alpha} \rangle \rangle - V''(\tau)_{\mathbf{k}'\beta, \mathbf{k}\alpha} | \mathbf{k}\mathbf{k}^{\alpha} \rangle \rangle, \quad (23)$$

where

$$\begin{aligned} V''_{\mathbf{k}'\beta, \mathbf{k}\alpha}(\tau) &\equiv \langle \mathbf{k}'\beta | \exp(iH_B\tau) V'' \exp(-iH_B\tau) | \mathbf{k}\alpha \rangle \\ &= \exp(i\omega_{\beta\alpha}\tau) \langle \mathbf{k}'\beta | V'' | \mathbf{k}\alpha \rangle \end{aligned} \quad (24)$$

and

$$\omega_{\beta\alpha} = \omega_{\beta} - \omega_{\alpha}. \quad (24a)$$

Substitution of Eq. (23) in (20) gives us

$$\mathcal{T}_{\mathbf{k}'\mathbf{k}, \mathbf{k}\mathbf{k}}^{\beta\beta, \alpha\alpha}(0) = i \int_0^{\infty} d\tau [\exp(i\epsilon_{\mathbf{k}\mathbf{k}}\tau) V''_{\mathbf{k}'\beta, \mathbf{k}\alpha}(\tau) V_{\mathbf{k}'\beta, \mathbf{k}\alpha}(0) + \text{c. c.}], \quad (25)$$

where

$$\epsilon_{\mathbf{k}\mathbf{k}'} = \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}. \quad (25a)$$

Equation (25) together with (14) yield

$$\langle T_{\mathbf{k}'\mathbf{k}, \mathbf{k}\mathbf{k}'}(0) \rangle = i \int_0^\infty d\tau [\exp(i\epsilon_{\mathbf{k}\mathbf{k}'}\tau) \langle V''_{\mathbf{k}\mathbf{k}'}(\tau) V''_{\mathbf{k}'\mathbf{k}}(0) \rangle + \text{c. c.}], \tag{26}$$

where the two-time correlation function of the bath operators C and D is defined as

$$\begin{aligned} \langle C(\tau)D(0) \rangle &\equiv \sum_{\alpha, \beta} P_B(\alpha) C_{\alpha\beta}(\tau) D_{\beta\alpha}(0) \\ &= \sum_{\alpha, \beta} P_B(\alpha) C_{\alpha\beta}(0) D_{\beta\alpha}(0) \exp(i\omega_{\alpha\beta}\tau). \end{aligned} \tag{27}$$

$V''_{\mathbf{k}\mathbf{k}'}$ is the $\mathbf{k}\mathbf{k}'$ system matrix element of V'' and is thus a bath operator.

Our final expression for the inelastic scattering cross section is thus

$$\begin{aligned} \sigma(\mathbf{k} \rightarrow \mathbf{k}') &= \frac{1}{F_i} 2 \operatorname{Re} \int_0^\infty d\tau \exp(i\epsilon_{\mathbf{k}\mathbf{k}'}\tau) \langle V''_{\mathbf{k}\mathbf{k}'}(\tau) V''_{\mathbf{k}'\mathbf{k}}(0) \rangle \\ &= \frac{1}{F_i} \int_{-\infty}^\infty d\tau \exp(i\epsilon_{\mathbf{k}\mathbf{k}'}\tau) \langle V''_{\mathbf{k}\mathbf{k}'}(\tau) V''_{\mathbf{k}'\mathbf{k}}(0) \rangle, \end{aligned} \tag{28}$$

where we have made use of the relation

$$\langle C(\tau)D(0) \rangle^* = \langle C(-\tau)D(0) \rangle. \tag{29}$$

We note in passing that Eq. (28) could be derived by using a Fermi golden rule expression. The present derivation, however, gives us insight into the approximations involved in the derivation and Eq. (18) may be used to generate systematic corrections to Eq. (28), if necessary.

If the interaction between the system and the bath is separable, i. e.,

$$V''(q_\nu, R) = A(q_\nu)B(R), \tag{30}$$

we can rewrite Eq. (28) in the form

$$\sigma(\mathbf{k} \rightarrow \mathbf{k}') = \frac{|B_{\mathbf{k}'\mathbf{k}}|^2}{F_i} \int_{-\infty}^\infty d\tau \exp(i\epsilon_{\mathbf{k}\mathbf{k}'}\tau) \langle A(\tau)A(0) \rangle. \tag{31}$$

IV. MULTIPHONON ENERGY TRANSFER IN A COLLINEAR COLLISION

We shall now apply the results of Sec. III [Eqs. (28)–(31)] to the collinear scattering of an atom from a solid surface. We thus assume that the projectile is moving perpendicular to the solid surface and is interacting directly only with one surface atom, which in turn is confined to move along the line of incidence. The interaction H_{SB} [Eq. (16)] is taken to be

$$H_{SB}(R, Q_0) = C \exp[-\alpha(R - Q_0)]. \tag{32}$$

Here, R and Q_0 are the coordinates of the interacting projectile and the surface atom, respectively. The origin is taken to be the equilibrium position of the surface atom.

Using the expansion of Q_0 in terms of the dimensionless lattice normal modes (12d), we have

$$Q_0 = \sum_\nu \beta_{\nu 0} q_\nu. \tag{33}$$

The interaction (32) thus assumes the form (30), i. e.,

$$H_{SB}(R, Q_0) = A(q_\nu)B(R) + B(R), \tag{34}$$

where

$$A(q_\nu) = \exp\left(\sum_\nu \Delta_\nu q_\nu\right) - 1, \tag{35}$$

$$B(R) = C \exp(-\alpha R), \tag{36}$$

and

$$\Delta_\nu = \alpha \beta_{\nu 0}. \tag{37}$$

The operators H' and H'' [Eqs. (16a) and (16b)] for our model are given, respectively, by

$$H' = B(R), \tag{38a}$$

$$H'' = B(R)A(q_\nu), \tag{38b}$$

and the inelastic cross section is given by Eq. (31).

The distorted wavefunctions as well as the matrix elements of $B(R)$ for the Hamiltonian (38a) were solved by Jackson and Mott.³⁰ They are

$$\begin{aligned} B_{\mathbf{k}\mathbf{k}'} &= \langle k'^- | C \exp(-\alpha R) | k^+ \rangle \\ &= \frac{(\sinh 2\pi q \sinh 2\pi q')^{1/2}}{\cosh 2\pi q - \cosh 2\pi q'} (q^2 - q'^2), \end{aligned} \tag{39}$$

where

$$q = k/\alpha, \quad q' = k'/\alpha \tag{39a}$$

is the dimensionless momentum.

In Eq. (39), $|k^\pm\rangle$ are energy normalized, i. e.,

$$\langle k'^- | k^+ \rangle = \delta(\epsilon_k - \epsilon_{k'}), \tag{40}$$

where

$$\epsilon_k = k^2 \hbar^2 / 2m_S \tag{41}$$

Using this normalization, the incident flux F_i [Eq. (13)] is

$$F_i = 1, \tag{42}$$

and $B_{\mathbf{k}\mathbf{k}'}$ is dimensionless.

We shall turn now to the evaluation of the correlation function $\langle A(\tau)A(0) \rangle$ [Eq. (31)]:

$$\langle A(\tau)A(0) \rangle = \left\langle \left(\exp \sum_\nu \Delta_\nu q_\nu(t) - 1 \right) \left(\exp \sum_\nu \Delta_\nu q_\nu - 1 \right) \right\rangle. \tag{43}$$

This can be done using standard commutator algebra,³¹ making use of the relation

$$\begin{aligned} q_\nu(t) &= \frac{1}{\sqrt{2}} [b_\nu(t) + b_\nu^*(t)] \\ &= \frac{1}{\sqrt{2}} [b_\nu \exp(-i\omega_\nu t) + b_\nu^* \exp(i\omega_\nu t)]. \end{aligned} \tag{44}$$

The result is^{20,22}

$$\langle A(\tau)A(0) \rangle = \exp(G) \exp[G_+(\tau) + G_-(\tau)] - 2 \exp(\frac{1}{2}G) + 1, \tag{45}$$

where

$$G_+(\tau) = \int_0^\infty d\omega g(\omega) \frac{\Delta(\omega)^2}{2} \bar{n}(\omega) \exp(i\omega\tau), \tag{45a}$$

$$G_-(\tau) = \int_0^\infty d\omega g(\omega) \frac{\Delta^2(\omega)}{2} [\bar{n}(\omega) + 1] \exp(-i\omega\tau), \tag{45b}$$

$$G = G_+(0) + G_-(0) = \int_0^\infty d\omega g(\omega) \frac{\Delta(\omega)^2}{2} [2\bar{n}(\omega) + 1], \tag{45c}$$

and

$$\bar{n}(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}. \tag{46}$$

Here, we have substituted $\sum_{\nu} \rightarrow \int_0^{\infty} d\omega g(\omega)$, where $g(\omega)$ is the density of lattice modes. $\bar{n}(\omega)$ is the mean thermal population of the ω mode. For our collinear collision model, $\sigma(\mathbf{k}-\mathbf{k}')$ is not a cross section but rather a transition probability per collision. We shall thus write $\sigma(\mathbf{k}-\mathbf{k}') \equiv P(\epsilon_k \rightarrow \epsilon_{k'})$, where $P(\epsilon_k \rightarrow \epsilon_{k'}) d\epsilon_{k'}$ is the probability that the scattered particle (with initial energy ϵ_k) will have after the collision energy between $\epsilon_{k'}$ and $\epsilon_{k'} + d\epsilon_{k'}$.

For inelastic collisions where $\epsilon_k \neq \epsilon_{k'}$, only the first term in Eq. (45) will contribute to the transition probability [the second and third terms are τ independent and will contribute only to elastic scattering upon substitution in Eq. (31)]. We thus get, utilizing Eqs. (31), (42), and (45),

$$P(\epsilon_k \rightarrow \epsilon_{k'}) = |B_{kk'}|^2 I(\epsilon) \tag{47a}$$

and

$$P(\epsilon_k \rightarrow \epsilon_k) = 1 - \int_0^{\infty} d\epsilon_{k'} P(\epsilon_k \rightarrow \epsilon_{k'}), \tag{47b}$$

where

$$\epsilon \equiv \epsilon_k - \epsilon_{k'} \tag{48}$$

is the energy transferred to the lattice and where the generalized line shape function $I(\epsilon)$ is given by

$$\begin{aligned} I(\epsilon) &= \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle A(\tau)A(0) \rangle \\ &= \exp(G) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \exp[G_+(\tau) + G_-(\tau)]. \end{aligned} \tag{49}$$

$B_{kk'}$ is given by Eq. (39).

V. GENERAL DISCUSSION AND ANALYSIS

Equations (47)–(49) together with Eqs. (39) and (45) constitute our general results for the multiphonon energy transfer in a collinear collision. In this section, we shall analyze these results and discuss their limiting behavior in several physical conditions.

A. Linearized coupling–single phonon transitions

If we expand A [Eq. (35)] to first order in Δ_{ν} , we have

$$A = \sum_{\nu} \Delta_{\nu} Q_{\nu}. \tag{50}$$

Making use of Eq. (44), we have

$$\langle A(\tau)A(0) \rangle = G_+(\tau) + G_-(\tau), \tag{51}$$

where G_{\pm} were defined in Eqs. (45). Substitution of Eq. (51) in (31) and performing the τ integration results in Eq. (47), where

$$\begin{aligned} I(\epsilon) &= \int_0^{\infty} d\omega g(\omega) \frac{\Delta^2(\omega)}{2} \\ &\times \{ \bar{n}(\omega) \delta(\epsilon + \omega) + [\bar{n}(\omega) + 1] \delta(\epsilon - \omega) \}, \end{aligned} \tag{52}$$

i. e.,

$$I(\epsilon) = \begin{cases} \frac{g(-\epsilon)}{2} \Delta^2(-\epsilon) \bar{n}(-\epsilon), & \epsilon < 0, \\ \frac{g(\epsilon)}{2} \Delta^2(\epsilon) [\bar{n}(\epsilon) + 1], & \epsilon > 0. \end{cases} \tag{53}$$

This is the result of LDS,^{2,3} provided we put $\Delta = 1$. In this case, there are no multiphonon effects and the phonon bath enters in a trivial way as a multiplicative factor involving the density of modes $g(\epsilon)$. This model thus does not allow for a correlated dynamics of the scattering process and the lattice.

B. Einstein spectrum of the lattice

We assume that the lattice is characterized by a single frequency, i. e.,

$$g(\omega) = \delta(\omega - \omega_0). \tag{54}$$

We can now expand $\exp(G_+ + G_-)$ in Eq. (49) in a power series and obtain^{19,32,33}

$$\begin{aligned} I(\epsilon) &= \exp(G) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \\ &\times \sum_{p,q=0}^{\infty} \frac{[S\bar{n}]^p [S(\bar{n}+1)]^q}{p!q!} \exp[i(p-q)\omega_0\tau], \end{aligned} \tag{55}$$

where

$$S = \int_0^{\infty} d\omega g(\omega) \frac{\Delta(\omega)^2}{2} = \frac{\Delta^2(\omega_0)}{2} \tag{55a}$$

and

$$\bar{n} = \bar{n}(\omega_0). \tag{55b}$$

The integration over τ now yields $2\pi\delta[\epsilon + (p-q)\omega_0]$.

Denoting $p-q=N$, we get

$$I(\epsilon) = 2\pi \exp(G) \sum_{N=-\infty}^{\infty} \Omega_N \cdot \delta(\epsilon + N\omega_0), \tag{56}$$

where

$$\Omega_N = \sum_{q=0}^{\infty} \frac{(S\bar{n})^{q+N} [S(\bar{n}+1)]^q}{q!(q+N)!} = I_N[\sqrt{2S\bar{n}(\bar{n}+1)}], \tag{56a}$$

and where I_N is a modified Bessel function of order N .³⁴

In this case, the problem reduces to the scattering of an atom from a single harmonic oscillator and the N th term in Eq. (56) corresponds to the transfer of N quanta to the gas atom. We further see that $I(\epsilon)$ is just a sum of δ functions with no spectral broadening. The broadening of $I(\epsilon)$ is caused by the *dephasing* of the Q_0 oscillator as it is not a normal mode and does not commute with H_B . This dephasing is analogous to the broadening of spectral lines,^{35,36} and is reflected in the correlation function $\langle Q_0(t)Q_0(0) \rangle$. When assuming an Einstein spectrum, Q_0 is indeed a normal mode, and it does not dephase.

C. Symmetry of $I(\epsilon)$

For any bath which is in thermal equilibrium at temperature T , we have³⁵

$$\begin{aligned} \exp(-\beta\epsilon) \int_{-\infty}^{\infty} d\tau \langle C(\tau)D(0) \rangle \exp(i\epsilon\tau) \\ = \int_{-\infty}^{\infty} d\tau \langle C(\tau)D(0) \rangle \exp(-i\epsilon\tau), \end{aligned} \tag{57}$$

where C and D are two bath operators and $\beta = 1/kT$. Using Eqs. (49) and (57), we get

$$I(-\epsilon) = \exp(-\beta\epsilon) I(\epsilon). \tag{58}$$

From Eq. (31), we see that $I(\epsilon)$ thus becomes sym-

metric [i. e., $I(-\epsilon) = I(\epsilon)$] whenever $\langle A(-\tau)A(0) \rangle = \langle A(\tau)A(0) \rangle$, which means that $\langle A(\tau)A(0) \rangle$ is real. This will be always the case in the high temperature limit [as is clear also from Eq. (58)]. In this case, we have

$$\bar{n}(\omega) = kT/h\omega \gg 1 \quad (59)$$

for all ω , and we get

$$I(\epsilon) = \exp(G) \int_0^\infty d\tau \cos(\epsilon\tau) \exp\left[\int_0^\infty \frac{kT}{\omega} \Delta^2 g(\omega) \cos\omega\tau d\omega\right]. \quad (60)$$

D. The Markovian and static limits

Equations (47)–(49) are valid for any time scale of the system relative to the bath. Let us use the identity

$$f(t) - f(0) \equiv \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 f''(\tau_2) = \int_0^t d\tau (t - \tau) f''(\tau), \quad (61)$$

which holds for any function $f(t)$, to write

$$G_+(t) + G_-(t) = G - \int_0^t d\tau (t - \tau) \Phi(\tau), \quad (62)$$

where

$$\Phi(\tau) = -G_+''(\tau) - G_-''(\tau), \quad (63a)$$

i. e.,

$$\Phi(\tau) = \int_0^\infty d\omega g(\omega) \frac{\Delta(\omega)^2}{2} \times \omega^2 \{ \bar{n}(\omega) \exp(i\omega\tau) + [\bar{n}(\omega) + 1] \exp(-i\omega\tau) \}. \quad (63b)$$

We shall further define

$$\Phi(\tau) = d^2 \phi(\tau), \quad (64)$$

where

$$d^2 \equiv \Phi(0) = \frac{1}{2} \int_0^\infty d\omega g(\omega) \Delta^2(\omega) \omega^2 [2\bar{n}(\omega) + 1] \quad (65)$$

and

$$\begin{aligned} \phi(\tau) &\equiv \Phi(\tau)/d^2 \\ &= \frac{1}{2d^2} \int_0^\infty d\omega g(\omega) \Delta^2(\omega) \end{aligned} \quad (66)$$

$$\times \omega^2 \{ \bar{n}(\omega) \exp(i\omega\tau) + [\bar{n}(\omega) + 1] \exp(-i\omega\tau) \},$$

so that

$$\phi(0) = 1. \quad (66a)$$

Substitution of Eq. (63a) in (49) and utilizing the definition (64)–(66), we get

$$\begin{aligned} I(\epsilon) &= 2 \exp(2G) \operatorname{Re} \int_0^\infty d\tau \exp(i\epsilon\tau) \\ &\times \exp\left[-d^2 \int_0^t d\tau (t - \tau) \phi(\tau)\right]. \end{aligned} \quad (67)$$

d is a characteristic energy of the system and is a measure of the solid–gas coupling strength. $\phi(\tau)$ contains the detailed dynamics of the bath atom Q_0 , $\phi(0) = 1$ and $\phi(\infty) = 0$. Let us characterize $\phi(\tau)$ by a typical time scale τ_c which is actually a bath correlation time. Equation (67), which contains all the multiphonon contributions, is a highly nonlinear function of $d\tau_c$. $d\tau_c$ is an

important parameter which determines whether the motions of the bath (τ_c) are slow or fast relative to the mean bath–system interaction (d). Let us consider now the limiting behavior of Eq. (67).

1. The Markovian limit ($d\tau_c \ll 1$)

In this limit, τ_c is extremely short relative to the interaction strength. On a coarse-grained time scale $d^{-1} \gg t \gg \tau_c$, we can thus write

$$\exp\left[-d^2 \int_0^t d\tau (t - \tau) \phi(\tau)\right] \cong \exp\left[-d^2 t \int_0^\infty d\tau \phi(\tau)\right]. \quad (68)$$

Substitution of Eq. (68) in (67) results in

$$I(\epsilon) = \exp(2G) [\Gamma/(\epsilon^2 + \frac{1}{4}\Gamma^2)], \quad (69)$$

where

$$\Gamma = 2d^2 \int_0^\infty d\tau \phi(\tau) \cong 2d^2 \tau_c. \quad (70)$$

In this limit, the motion of the bath (τ_c) is so fast relative to the duration of a collision (τ_d) that each projectile actually sees an averaged surface atom. The spectral broadening function $I(\epsilon)$ thus assumes a Lorentzian form which is characteristic of *homogeneous broadening* of line shapes.³⁶ We can verify *a posteriori* that the condition $d\tau_c \ll 1$ actually means that $\tau_c/\tau_d \ll 1$. From Eq. (69), we know that the time delay³⁷ τ_d which represents the average delay time of the projectile due to the interaction with the target and which is a measure of the collision time is $\tau_d \sim 1/\Gamma$; thus, when $d\tau_c \ll 1$, we have, utilizing Eq. (70),

$$\tau_c/\tau_d \cong \Gamma\tau_c \cong 2(d\tau_c)^2 \ll 1. \quad (71)$$

Thus, the condition $d\tau_c \ll 1$ is equivalent to $\tau_c/\tau_d \ll 1$.

2. The static limit ($d\tau_c \gg 1$)

In this case, the correlation time τ_c is very long compared to the interaction strengths. We can thus use a short time expansion to write

$$\exp\left[-d^2 \int_0^t d\tau (t - \tau) \phi(\tau)\right] \cong \exp(-\frac{1}{2}d^2 t^2), \quad (72)$$

and $I(\epsilon)$ [Eq. (67)] assumes a Gaussian form

$$I(\epsilon) = \frac{1}{2} \left(\frac{2\pi}{d^2}\right)^{1/2} \exp(2G) \exp\left(-\frac{\epsilon^2}{2d^2}\right). \quad (73)$$

The spectral broadening function $I(\epsilon)$ thus corresponds to *inhomogeneous broadening*³⁶ where the lattice dynamics during the scattering event does not play any role. The broadening simply arises from the fact that the lattice is an *ensemble of static configurations*, and τ_c does not appear in Eq. (73).

To summarize, we have shown that Eq. (67) is valid for any time scale of the bath motions relative to the collision time and goes smoothly from a Lorentzian to a Gaussian form. In the intermediate range where $d\tau_c \sim 1$, the exact form of $I(\epsilon)$ will depend on the details of the dynamics of the solid.

We shall now consider more closely the expressions for d and $\phi(\tau)$ in order to relate $d\tau_c$ to the physical parameters of the problem. First we note that d^2 [Eq. (65)] is proportional to Δ^2 , whereas $\phi(\tau)$ [Eq. (66)], and hence also τ_c , are independent on the magnitude of Δ

[as both numerator and denominator in Eq. (66) are proportional to Δ^2]. We recall that Δ^2 is a measure of the gas-solid surface interaction strength. Thus, in the strong coupling limit ($\Delta \gg 1$), we have $d\tau_c \gg 1$ and $I(\epsilon)$ assumes its static, Gaussian form (73). In the weak coupling limit, $\Delta \ll 1$, then $d\tau_c \ll 1$, and $I(\epsilon)$ becomes the Lorentzian (69).

Let us consider now the temperature dependence of $I(\epsilon)$. Substitution of $\bar{n}(\omega)$ [Eq. (46)] into our expression for d^2 [Eq. (65)] and $\phi(\tau)$ [Eq. (66)] results in

$$d^2 = \frac{1}{2} \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2 \left\{ 2 \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right]^{-1} + 1 \right\} \quad (74a)$$

and

$$\phi(\tau) = \frac{1}{2d^2} \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2 \left\{ \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right]^{-1} \exp(i\omega\tau) + \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right]^{-1} + 1 \right\} \exp(-i\omega\tau). \quad (74b)$$

We further assume that the solid has a Debye spectrum¹⁰

$$g(\omega) = \begin{cases} 3\omega^2/\omega_D^3, & 0 < \omega < \omega_D, \\ 0, & \omega > \omega_D. \end{cases} \quad (75)$$

In the high temperature limit ($kT \gg \hbar\omega_D$), we get, from Eq. (75),

$$d^2 = kT \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \cdot \omega \quad (76a)$$

and

$$\phi(\tau) = \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega \cos\omega\tau / \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega. \quad (76b)$$

In the low temperature limit ($kT \ll \hbar\omega_D$), we get

$$d^2 = \frac{1}{2} \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2 \left[1 + 2 \exp\left(-\frac{\hbar\omega}{kT}\right) \right] \quad (77a)$$

and

$$\phi(\tau) = \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2 \times \left[\exp(-i\omega\tau) + 2 \exp\left(-\frac{\hbar\omega}{kT}\right) \cos\omega\tau \right] / \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2 \left[1 + 2 \exp\left(-\frac{\hbar\omega}{kT}\right) \right]. \quad (77b)$$

At $T=0$, we have

$$d^2 = \frac{1}{2} \int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2 \quad (78a)$$

and

$$\phi(\tau) = \frac{\int_0^{\omega_D} d\omega g(\omega) \Delta(\omega)^2 \omega^2 \exp(-i\omega\tau)}{\int_0^{\omega_D} d\omega g(\omega) \Delta^2(\omega) \omega^2}. \quad (78b)$$

Using Eq. (76), we see that, at high temperatures ($kT \gg \hbar\omega_D$), d^2 is increasing linearly with T , whereas $\phi(\tau)$ (and hence τ_c) become temperature independent. Thus, $d\tau_c$ is linearly increasing with T at high temperatures and we expect the static limit to hold at sufficiently high temperatures, resulting in a Gaussian line shape

(73). This behavior is just the opposite than the motional narrowing phenomena in magnetic resonance line shapes^{36,38} where, at high temperatures, spectra assume the Markovian (Lorentz) form. The reason for the difference is that, for magnetic interaction in liquids, the interaction strength d is temperature independent whereas τ_c , which is related to the inverse velocity, goes to 0 as $T \rightarrow \infty$.

In the present model, the coupling d^2 is associated with the mean square displacement of the oscillator which grows linearly with T . τ_c becomes temperature independent as the harmonic oscillator frequency does not depend on its energy.

Calculations of inelastic cross sections for atom-surface scattering which use classical lattice correlation functions thus correspond to the static limit of the present theory. Shugard, Tully, and Nitzan¹² have recently assumed in their Langevin calculations that τ_c is temperature independent and $d^2 \propto kT$. This is exactly the high temperature behavior of the present model when $d\tau_c \gg 1$. If we assume that Q_0 projects equally well to all lattice modes (which is true for a cubic lattice), we may write

$$\Delta^2(\omega) = \Delta_0^2(\omega_D/\omega), \quad (79)$$

where Δ_0 is ω independent. (The ω_D/ω factor comes from the scaling of the dimensionless displacement.)

Substitution of $\bar{n}(\omega) = kT/\hbar\omega$, $g(\omega)$ [Eq. (75)], and Δ^2 [Eq. (79)] in Eq. (49) results in the following high temperature expression for $I(\epsilon)$:

$$I(\epsilon) = \exp\left(\frac{3\Delta_0^2 kT}{\omega_D}\right) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \exp\left(\frac{3\Delta_0^2 kT}{\omega_D} \frac{\sin\omega_D\tau}{\omega_D\tau}\right). \quad (80)$$

When $\Delta_0^2 kT/\omega_D \gg 1$, we can perform a short time expansion

$$I(\epsilon) = \exp\left(\frac{6\Delta_0^2 kT}{\omega_D}\right) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \exp\left(-\frac{1}{2} \Delta_0^2 kT \omega_D \tau^2\right) \quad (81)$$

and $I(\epsilon)$ assumes the Gaussian form (73), where

$$G = \frac{3\Delta_0^2 kT}{\omega_D} \quad (81a)$$

and

$$d^2 = \Delta_0^2 kT \omega_D. \quad (81b)$$

E. Effects of anharmonicities

In the present model, we have considered the lattice to be purely harmonic. This assumption together with the distorted wave Born approximation enabled us to evaluate the appropriate lattice correlation function rigorously with no further approximations.

In practice, however, atoms on solid surfaces are not harmonically bound and, if we want to include the effects of anharmonicities as well as to go beyond the DWBA, we need to invoke some approximations.

Suppose the incoming projectile is interacting directly only with few lattice atoms (the "primary zone").⁷ The interaction v in Eq. (8) is thus a function only of the primary zone and projectile coordinates, and thus commutes with the operation of averaging over all other lattice modes. The averaged τ matrix (13) will now be

$$\langle \mathcal{T}(\omega) \rangle = v \langle \mathcal{G}(\omega) \rangle v, \quad (82)$$

where $\langle \dots \rangle$ denotes averaging over all degrees of freedom other than the primary zone and the projectile.

$\langle \mathcal{G}(\omega) \rangle$ is the Fourier transform of the *reduced propagator* for the time evolution of the primary zone.

Using the cumulant expansion,³⁹ we can have different forms for the reduced propagator, depending on our choice of time ordering.³⁹⁻⁴¹ In particular, we may consider two reduction schemes which yield formally³⁹⁻⁴²

$$\langle \mathcal{G}(\omega) \rangle^{\text{COP}} = \frac{1}{\omega - L_0 - \langle \tilde{R}(\omega) \rangle} \quad (83a)$$

or

$$\langle \mathcal{G}(\omega) \rangle^{\text{POP}} = -i \int_0^\infty d\tau \exp(i\omega\tau) \exp[-\langle \tilde{R}(\tau) \rangle], \quad (83b)$$

where both $\langle \tilde{R}(\omega) \rangle$ and $\langle \tilde{R}(\tau) \rangle$ are reduced primary zone operators averaged over the remaining degrees of freedom. $\langle \mathcal{G} \rangle^{\text{COP}}$ is derived by using a chronological time ordering prescription whereas $\langle \mathcal{G} \rangle^{\text{POP}}$ is a renormalized version of $\langle \mathcal{G} \rangle^{\text{COP}}$ obtained by using a partial time ordering prescription.

We have shown^{41,42} that the two expressions (83a) and (83b) are equivalent in the Markovian limit but are very different otherwise, once $\langle \tilde{R}(\omega) \rangle$ or $\langle \tilde{R}(\tau) \rangle$ are evaluated in some approximate way. From our analysis,^{41,42} it is suggestive that the POP form might be far more adequate when dealing with problems with many degrees of freedom, and thus this reduction scheme should be used for generalization of the present model to anharmonic lattices.

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