Quantum diffusion on surfaces with two-phonon interactions: Keldysh formalism

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We study the quantum diffusion of hydrogen adsorbate atoms on a metal surface with the Keldysh nonequilibrium formalism. We propose a many-body model of interacting hydrogen atoms coupled to surface phonons and cast it to an effective theory, which is used to derive a quantum kinetic equation for the adsorbate motion and an effective diffusion constant. The results suggest a novel reason for importance of two-phonon interactions, can explain certain limiting behaviors of the diffusion constant, and provide a systematic way to account for surfaces with large adsorbate coverage.

I. INTRODUCTION

Quantum diffusion of light atoms, such as hydrogen, on metallic surfaces has attracted theoretical attention since the experiments by Gomer and collaborators, who observed a sudden change in the diffusion constant of hydrogen on nickel and tungsten surfaces at a characteristic temperature of around $T^* = 125$ K [1, 2]. Since then, many other experiments, mostly with hydrogen adatoms on a metallic surface, have supported Gomer’s observation, though in fact not all experiments show such a cross-over [3–5]. The commonly accepted explanation is that quantum diffusion dominates thermally-activated diffusion at low temperatures, and that the cross-over at $T^*$ can be explained with a quantum many-band model of the hydrogen adatom in localized surface sites [6]. At high temperatures $T > T^*$, the hydrogen atom tends to diffuse through thermal activation to the higher-energy bands, and at low temperatures $T < T^*$ the adatom is trapped in low-energy bands and can only migrate via quantum tunneling. It is relatively easier for the adatom to diffuse at high temperature due to the larger effective hopping parameter of higher-energy bands.

The typical approach to studying this phenomenon has been to propose a Hamiltonian with adatom-phonon interactions, write down a quantum kinetic equation using the Zwanzig projector formalism, and extract a diffusion constant in the nonequilibrium regime [6, 7]. However, the Zwanzig formalism obscures the physics of the different contributions to diffusion and does not easily account for many-body interactions. A more natural setting for writing down a quantum kinetic equation is the Keldysh formalism, also known as the non-equilibrium Green function formalism, which we will use in this paper. For example, it provides an elegant way to account for a hydrogen-hydrogen interaction which is repulsive at short range and attractive at long range. It also gives a nonperturbative way to deal exactly with the adatom-phonon interactions which interest us.

It has been suggested that the contribution of two-phonon scattering processes dominates that of one-phonon scattering processes in essentially all the processes which contribute to diffusion [7]. According to [7], this is due to the relative size of the one-phonon and two-phonon couplings to the adsorbed hydrogen; if this is true, any reasonable theory must include both one- and two-phonon scattering processes.

In this paper, we will use the Keldysh formalism to analyze a many-body model of hydrogen adatoms on a metallic surface. We include one-phonon and two-phonon interactions, as well as hydrogen-hydrogen interactions, which are assumed attractive for adatoms in adjacent lattice sites and zero in all other cases. Our analysis suggests important conclusions about which phonon scattering processes lead to thermally-activated processes, such as dephasing, and how to estimate the relative magnitudes of one- and two-phonon effects. We conclude by writing down a quantum kinetic equation, extract the effective diffusion constant, and show that our theory can reproduce many of the existing experimental results.

II. HAMILTONIAN

Consider a collection of adsorbate atoms hopping on a lattice, with the sites described by $\mathbf{x}$. Denote the energy band of the adsorbate by $\sigma$ and the momentum (i.e. in the Brillouin zone) by $\mathbf{k}$; denote the state of a phonon with $\lambda$. $\lambda$ is associated with a momentum $\mathbf{q}_\lambda$, but the $\lambda$ notation makes the phonon density of states more transparent. The creation and annihilation operators for adatoms are $a_{\mathbf{k}\sigma}^\dagger$, $a_{\mathbf{k}\sigma}$; for phonons they are $b_{\lambda}^\dagger$, $b_{\lambda}$.

The Hamiltonian, in second-quantized notation, is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{H-ph}} + \mathcal{H}_{\text{H-H}}$$

(1)

Here, $\mathcal{H}_0$ describes free adatoms and phonons,

$$\mathcal{H}_0 = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} + \sum_{\lambda} \omega_{\lambda} b_{\lambda}^\dagger b_{\lambda}.$$  

(2)

The hydrogen-phonon interaction contains one- and two-phonon contributions. We use the harmonic approximation in which phonon-particle interactions are derived from the coupling of the particle position to the lattice
displacement \[3].

\[\mathcal{H}_{\text{H-ph}} = \sum_{\sigma\sigma'} \sum_{k\lambda} U^{\sigma\sigma'}_{\lambda} a_{k\sigma}^\dagger a_{k-\mathbf{q}_{\lambda,\sigma'}} (b_\lambda + b_{-\lambda}^\dagger) + \sum_{\sigma\sigma'} \sum_{k\lambda\nu} M^{\sigma\sigma'}_{\lambda\nu} a_{k\sigma}^\dagger a_{k-\mathbf{q}_{\lambda-\nu,\sigma'}} (b_\lambda + b_{-\lambda}^\dagger)(b_\nu + b_{-\nu}^\dagger).\]

The hydrogen-hydrogen interaction is taken to be strongly repulsive when two atoms occupy the same site, weakly attractive when two atoms occupy adjacent sites, and zero everywhere else. This is a good approximation of most pairwise potentials, such as the popular Morse potential. We model this with a combination of the Gaussian solid-on-solid nearest-neighbor interaction \[9\] and the Hubbard on-site repulsion term \[10\],

\[\mathcal{H}_{\text{H-H}} = \frac{J}{2} \sum_x (n_x - n_{x'})^2 + U \sum_x n_x^2.\]

Here, \(n_x = \sum_\sigma a_{x\sigma}^\dagger a_{x\sigma}\) is the total particle number on a given site. Actually, the usual Hubbard repulsion term is

\[U \sum_x n_x (n_x - 1),\]

but the difference is irrelevant if particle number is conserved. This is true if no additional adsorbate atoms come onto the surface and if the temperature is low enough to ignore re-evaporation. We will find it most convenient to work with the hydrogen-hydrogen interaction in reciprocal space,

\[\mathcal{H}_{\text{H-H}} = \Omega \sum_{q\sigma\sigma'} V_q n_{q\sigma} n_{-q\sigma'}.\]

Here, \(\Omega\) is the total number of sites and \(V_q\) is the Fourier transform of both terms of the interaction,

\[V_q = J \sum_\delta (1 - \cos(q \cdot \delta)) + U.\]

### III. EFFECTIVE HAMILTONIAN FOR ADSORBATES

Since we are interested in the dynamics of the hydrogen adatoms, we will integrate out the bath, or phonon, modes. Unlike in the Zwanzig projector formalism, this can be done exactly in the path-integral formalism because the Hamiltonian is quadratic in the bath modes, even if two-phonon interactions are included. Though the dynamics can be extracted from the original Hamiltonian, an effective theory will make the contributions to the adsorbate motion more transparent.

#### A. Construction of effective energy

Regular Gaussian integration over complex variables

\[\int d[\tilde{z}, z] e^{-\tilde{z}z}\]

is not applicable here because of terms like \(b_\lambda b_\nu\) in the Hamiltonian. We will instead recast the complex variables into real ones, as follows.

The partition function is

\[Z = \int D[\phi, \phi] D[\eta, \bar{\eta}] e^{iS}\]

where

\[S = \int C \left( \sum_{k\sigma} \bar{\phi}_{k\sigma} i \partial_t \phi_{k\sigma} + \sum_\lambda \bar{\eta}_\lambda i \partial_t \eta_\lambda - \mathcal{H}[\tilde{\phi}, \phi, \eta, \bar{\eta}] \right)\]

and we replaced the operators with scalars, \(\phi_{k\sigma}\) for the adsorbates and \(\eta_\lambda\) for the phonons. \(C\) is the Schwinger-Keldysh contour.

If we write

\[\eta_\lambda = x_\lambda + i y_\lambda, \bar{\eta}_\lambda = x_\lambda - i y_\lambda\]

and first consider only the quadratic modes in \(\eta\) (in other words, only the kinetic term and the two-phonon interactions \(\mathcal{H}_{\text{H-ph}}^{(2)}\)), then the integral

\[\int D[\lambda, \lambda] e^{iS^{(2)}_\lambda}\]

where

\[S^{(2)}_\lambda = \int_C \left( \sum_\lambda \bar{\eta}_\lambda (i \partial_t - \omega_\lambda) \eta_\lambda - \mathcal{H}_{\text{H-ph}}^{(2)} \right)\]

can be computed (up to constants):

\[\int D_x D_y e^{iJ_{x/y}} dt \left( \sum_{x_\lambda} x_\lambda J_{x_\lambda}^{(1)} \nu + \sum_{y_\lambda} y_\lambda J_{y_\lambda}^{(y)} \nu \right)\]

\[= \exp \left( - \frac{1}{2} \text{tr} \left( \ln \mathbf{j}^{(x)} + \ln \mathbf{j}^{(y)} \right) \right)\]

The trace includes the time integral. Here,

\[\mathbf{j}^{(x/y)} = (i \partial_t - \omega_\lambda) \delta_{\lambda\nu} + W_{\lambda\nu}^{(1)} - W_{\lambda\nu}^{(2)}\]

where

\[W_{\lambda\nu}^{(1)} = W_{\lambda\nu} + W_{-\lambda-\nu}, W_{\lambda\nu}^{(2)} = W_{-\lambda+\nu} + W_{\lambda-\nu}\]

and

\[W_{\lambda\nu} = \sum_{k\sigma\sigma'} M^{\sigma\sigma'}_{\lambda\nu} \phi_{k\sigma} \phi_{k-\mathbf{q}_{\lambda-\nu,\sigma'}}.\]

Now we find the effective action for the one-phonon processes. If the couplings \(U^{\sigma\sigma'}_{\lambda}\) and \(M^{\sigma\sigma'}_{\lambda\nu}\) are assumed small, then the integral formula

\[\int d[\tilde{z}, z] e^{A_{\tilde{z}z} + \tilde{z}J + Jz} = (\det A)^{-1} e^{TA^{-1}J}\]

suggests we can ignore the two-phonon processes when integrating out the one-phonon processes. In fact, the \((\det A)^{-1}\) factor contains the two-phonon processes and
the exponential $e^{J A^{-1} J}$ contains the one-phonon contributions. Denoting $(G_0^{-1})_{\lambda\nu} = (i\hbar - \omega_\lambda)\delta_{\lambda\nu}$, the total effective action is

$$S_{\text{eff}} = S_{\phi}^{(0)} + S_{\phi}^{\text{int}} + S_{\phi}^{(1)} + S_{\phi}^{(2)}$$

where $S_{\phi}^{(0)}$, $S_{\phi}^{(1)}$, and $S_{\phi}^{(2)}$ are the kinetic term, one-phonon effective interaction and two-phonon effective interactions, respectively. They are

$$S_{\phi}^{(0)} + S_{\phi}^{\text{int}} = \int dt \left( \sum_{\kappa\sigma} \bar{\phi}_{\kappa\sigma} (i\hbar \partial_t - \epsilon_{\kappa\sigma}) \phi_{\kappa\sigma} - \sum_{q\sigma\sigma'} V_q n_q n_{-q\sigma'} \right)$$

$$S_{\phi}^{(1)} = -\int dt \left( \sum_{\lambda\kappa_1\kappa_2} \sum_{1234} \hat{V}_{\lambda\sigma_1\sigma_2\sigma_3\sigma_4} \right. \times \bar{\phi}_{\kappa_1\sigma_1} \bar{\phi}_{\kappa_2\sigma_2} \phi_{\kappa_3\sigma_3} \phi_{\kappa_4\sigma_4} \left. \phi_{\kappa_1\sigma_1} \phi_{\kappa_2\sigma_2} \phi_{-\kappa_3\sigma_3} \phi_{-\kappa_4\sigma_4} \right)$$

where $\hat{V}_{\lambda\sigma_1\sigma_2\sigma_3\sigma_4} = (G_0)_{\lambda\lambda} U_{\lambda\sigma_1\sigma_2} U_{\lambda\sigma_3\sigma_4}$, and finally

$$S_{\phi}^{(2)} = \frac{i}{2} \text{tr} \ln \left( G_0^{-1} - \hat{W}^{(1)} - \hat{W}^{(2)} \right) + \frac{i}{2} \text{tr} \ln \left( G_0^{-1} + \hat{W}^{(1)} - \hat{W}^{(2)} \right).$$

We keep only the lowest-order term,

$$S_{\phi}^{(2)} = -i \int dt \sum_{\lambda} (G_0)_{\lambda\lambda} \hat{W}_{\lambda\lambda}^{(2)}.$$

### B. Interpretation of effective energy

This form of the effective action gives us an interesting reason to argue that two-phonon processes may be more important than one-phonon processes, regardless of the sizes of the couplings $U_{\lambda\sigma\sigma'}$ and $M_{\lambda\sigma\sigma'}$. This will be true if we have reason to believe the phonon processes are fast compared to the dynamics of the adatoms.

Suppose there is only one hydrogen atom adsorbed on the substrate. It is trapped in a definite band $\sigma$, at wavevector $\mathbf{k}$. Since there is only one adatom, the effective interactions $S_{\phi}^{(1)}$ and the second sum in $S_{\phi}^{(2)}$, as well as the adsorbate-adsorbate interaction $S_{\phi}^{\text{int}}$, cannot contribute. (They are $2 \rightarrow 2$ scattering processes.) Besides the kinetic term, the only contributing term is the leading part of the two-phonon process,

$$S_{\phi}^{(2)} = -i \int dt \sum_{\lambda} (G_0)_{\lambda\lambda} \hat{W}_{\lambda\lambda}^{(2)}.$$

This lends itself to physical interpretation if we recall

$$\hat{W}_{\lambda\lambda}^{(2)} = \sum_{k\sigma\sigma'} (M_{\lambda\sigma\sigma'} + M_{\lambda\sigma'-\lambda} \delta_{k\sigma} \phi_{k\sigma'}).$$

The process with $W_{\lambda\lambda}^{(2)}$ involves the phonons of labels $\lambda$ and $-\lambda$, which have opposite momenta. However, because phonon number is not conserved, their energy may not add to zero (for example, annihilate two phonons; one with label $\lambda$ and the other with label $-\lambda$). The $W_{\lambda\lambda}^{(2)}$ process therefore can raise or lower the band index from $\sigma$ to $\sigma'$ without changing the momentum $\mathbf{k}$, or equivalently the position $x$ of the adatom. Thus, it provides a mechanism for dephasing even if the atom was trapped in a single quantum well rather than on a tight-binding lattice; we will call this process “single-site dephasing.”

Note that no comparable mechanism for single-site dephasing is provided by the one-phonon interactions, which must lead to a change in momentum of the adatom: if the adatom is localized on a single site, a change of momentum is not allowed. Of course, such momentum-conserving band transitions can also arise from three- and higher-order phonon interactions, which are subleading.

However, it is not true that single-phonon processes do not lead to dephasing. They do, but at the cost of transferring nonzero momentum to the lattice, which tends to be picked up by adatoms on other sites. If a single adatom on a single site emitted the energy for the creation of one phonon, the phonon would tend to be annihilated right away and the energy transferred back to the adatom, at least on the timescale of the adatom. (This can be compared to the interpretation of the Coulomb electrostatic interaction as an effective theory of electron-phonon coupling. The creation and subsequent annihilation in a one-phonon process corresponds to the one-loop virtual-particle correction to the electron propagator.) In reality, the one-phonon processes are not instantaneous but slightly retarded, which means their true contribution to single-site dephasing is finite but small.

This is an important conclusion because it is thought that interband-interstate hopping is quite rare compared to band transitions on a single site and quantum tunneling through a single band, so the main cause of dephasing, and therefore the main reason for the quantum-to-classical transition at $T^*$, is single-site dephasing.

### C. Antiadiabatic limit

We simplify the effective action in the antiadiabatic limit, which is the limit where the energy of the phonons, $\omega_{\lambda}$, is much greater than the hopping dispersion of the adatoms. For a square lattice, this is

$$\epsilon_{\sigma}(\mathbf{k}) - \epsilon_{\sigma}(\mathbf{k} = 0) = -2t \cos(k_x) \cos(k_y)$$

and is therefore on the order of the hopping parameter. The no-hopping energies of the bands themselves, $\epsilon_{\sigma}(\mathbf{k} = 0)$, are unimportant for taking this limit. This regime can easily be shown to hold for at least the first few energy bands of hydrogen on metal surfaces [1].

The limit follows by setting $\omega = 0$ wherever it appears next to a phonon energy [11]. This is analogous to deriving the static Coulomb coupling $V(q) = \frac{4\pi}{q^2}$ from the more elementary electron-phonon coupling. We first
consider the static limit of the one-phonon effective interaction,
\[
S^{(1)}_\phi \approx - \int_C dt \left( \sum_{k_1 k_2 q} \sum_{\sigma \sigma' \sigma'' \sigma'''} \hat{V}_{\text{eff}}^{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(q) \times \tilde{\phi}_{k_1, \sigma_1} \tilde{\phi}_{k_2 - q, \sigma_2} \phi_{k_3 \sigma_3} \phi_{k_4 - q, \sigma_4} \right)
\tag{27}
\]
where \( \hat{V}_{\text{eff}}^{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(q) = - \sum_\lambda \omega_\lambda^{-1} U_\lambda^{\sigma_1 \sigma_2} U_{-\lambda}^{\sigma_3 \sigma_4} \delta(q - q_\lambda) \).

Since the hopping dispersion is small in the adiabatic limit, we may assume
\[
\epsilon_\sigma(k) \approx \epsilon_\sigma(k = 0) = \epsilon_\sigma.
\tag{28}
\]

This is finite because \( M^{\sigma_1 \sigma_2} \) tends to be peaked around \( \epsilon = \frac{1}{2} [\epsilon_{\sigma_1} - \epsilon_{\sigma_2}] \), since the energy difference \([\epsilon_{\sigma_1} - \epsilon_{\sigma_2}]\) tends to be carried by two phonons of equal energy and opposite momentum. Again, for \( \sigma_1 = \sigma_2 \), a more careful derivation of \( \phi^{\sigma_1 \sigma_2} \) is necessary.

IV. KINETIC EQUATION FROM KELDYSH FORMALISM

We use the Keldysh formalism to write down a quantum kinetic equation for \( f_\sigma(x, k, t) \), the semiclassical distribution function for the adatoms. The Keldysh formalism involves trading the contour integral \( \int_C dt \) for a single integral \( \int_{-\infty}^\infty dt \) at the cost of doubling the number of fields; reviews can be found in \([12, 13]\). We will keep all terms to order \( \mathcal{O}(U^2) \) and \( \mathcal{O}(M) \) (there are no terms to order \( \mathcal{O}(U^4) \)) and use the notation \( D^{R/A/K}(k) \) for the adatom Green functions and \( n_\sigma(x, k, t) \) for the nonequilibrium occupation numbers. The relation between the distribution function and occupation numbers is
\[
f_\sigma(x, k, t) = 2n_\sigma(x, k, t) + 1.
\tag{34}
\]

It is well-known that the leading-order Hartree-Fock contributions to the self energy do not contribute to the collision integral since they are static effective interactions: the collision integral is a retarded physical quantity and thus we must go to higher order in the adsorbate-adsorbate self-energy. Equivalently, this is because
\[
D^{R}(t, t) + D^{A}(t, t) = 0
\tag{35}
\]
for any Keldysh Green functions \( D^{R/A} \), and because the Green functions for both the adsorbate-adsorbate and effective one-phonon interactions are approximately static.

We use the semiclassical forms of the Keldysh Green functions
\[
D^K_\sigma(\omega, p) = -2\pi i \delta(\omega - \epsilon_{p\sigma}) f_\sigma(p)
\tag{36}
\]
\[
D^R_\sigma(\omega, p) - D^A_\sigma(\omega, p) = -2\pi i \delta(\omega - \epsilon_{p\sigma})
\tag{37}
\]
which are valid approximations because the adatom hopping rate is slow.

A. Quantum kinetic equation

The result is
\[
\begin{align*}
Z^{-1} \partial_t + \hat{v}_{k\sigma} \nabla_x - \nabla_x Re \Sigma^{R}_{\sigma}(x, k) \nabla_k \right] f_\sigma(x, k) = f^{\text{coll}}[f_\sigma]
\end{align*}
\tag{38}
\]
Here, \( x = (x, t) \) and
\[
Z^{-1} = 1 - \partial_x Re \Sigma^{R}_{\sigma},
\tag{39}
\]
\[
\hat{v}_{k\sigma} = \nabla_k (\epsilon_{k\sigma} + Re \Sigma^{R}_{\sigma}).
\tag{40}
\]
and the collision integral \( I_{\text{coll}}[f_\sigma] \) has the following parts, corresponding to \( \sigma^{\text{int}}, \sigma^{(1)}, \sigma^{(2)} \):

\[
I_{\text{coll}}[f_\sigma] = I^{\text{(int)}} + I^{(1)} + I^{(2)}. \tag{41}
\]

Similarly,

\[
\Sigma^R_{\sigma} = (\Sigma^{R(1)}_{\sigma})^{\text{(int)}} + (\Sigma^{R(2)}_{\sigma})^{(1)} + (\Sigma^{R(2)}_{\sigma})^{(2)}. \tag{42}
\]

\[
I_{\text{coll}}[n_\sigma] = \sum_{\sigma'} \left| \psi^{\sigma \sigma'} \right|^2 \left[ n_{\sigma'}(k) - n_{\sigma}(k) \right] \\
+ 8 \pi \sum_{\sigma'} \int_{p_1, p_2} \delta(\epsilon_{k\sigma} + \epsilon_{p_2 \sigma'} - \epsilon_{p_1 \sigma}) \left[ \left| V_{k-k'} + \delta_{\sigma\sigma'} V_{k-p_1} \right|^2 + \left| \tilde{V}_{\text{eff}, k-p_1} + \delta_{\sigma\sigma'} \tilde{V}_{\text{eff}, k-k'} \right|^2 \right] \times \left[ n_{\sigma}(k)n_{\sigma'}(p_1)(1 + n_{\sigma}(k))(1 + n_{\sigma'}(p_2)) - n_{\sigma}(k)n_{\sigma'}(p_2)(1 + n_{\sigma'}(k))(1 + n_{\sigma}(p_1)) \right]. \tag{44}
\]

**B. Diffusion constant**

Because the adatom hopping parameters are quite small, it is inappropriate to expand around the thermodynamic equilibrium if the adatoms start relatively far away from each other. Instead, we will first find the dynamic equilibrium if the adatoms start relatively far away from each other. Instead, we will first find the dynamic equilibrium if the adatoms start relatively far away from each other. Instead, we will first find the "self-diffusion constant" which merely characterizes the adatom relaxation to local equilibrium in a static environment. Later in this subsection, we outline how to describe the relaxation of the complete many-body system to global equilibrium.

If \( \text{Re} \Sigma^R_{\sigma} \) varies strongly with position, we must ignore it if we are to extract a diffusion constant. This is not a good assumption for large coverage, in which case \( \Sigma^R_{\sigma} \) could be comparable to the band energies. However, if the particles are spread out fairly evenly on the surface, then \( \text{Re} \Sigma^R_{\sigma} \) may vary only weakly with position. Then, we can ignore \( \nabla_{x} \text{Re} \Sigma^R_{\sigma}(x, k) \) and solve for the diffusion constant with the renormalized particle velocity, \( \tilde{v}_{k\sigma} \). However, we will set \( Z = 1 \), since we expect the (dimensionless) adsorbate-adsorbate interaction to be small compared to unity.

The collision integral \( I_{\text{coll}}[n_\sigma(k)] \) is linearized by assuming all occupations except \( n_\sigma(k) \) are static, and that the occupation \( n^{\text{eq}}_\sigma(k) \) nullifies the collision integral,

\[
I_{\text{coll}}[n^{\text{eq}}_\sigma(k)] = 0. \tag{45}
\]

Then, we expand in \( n_\sigma(k) - n^{\text{eq}}_\sigma(k) \). The result is

\[
\left[ \partial_t + \tilde{v}_{k\sigma} \nabla_x \right] n_\sigma(x, k) = -\frac{1}{\tau_{k\sigma}} (n_\sigma(x, k) - n^{\text{eq}}_\sigma(x, k)) \tag{46}
\]

where the relaxation time is

\[
\frac{1}{\tau_{k\sigma}} = \frac{1}{\tau_{k\sigma}^{(1)}} + \frac{1}{\tau_{k\sigma}^{(2)}} + \frac{1}{\tau_{k\sigma}^{\text{(int)}}} \tag{47}
\]

and the contributions are

\[
\frac{1}{\tau_{k\sigma}^{(2)}} = \sum_{\sigma'} \left| \psi^{\sigma \sigma'} \right|^2 \\
\frac{1}{\tau_{k\sigma}^{\text{(int)}}} = 8 \pi \sum_{\sigma'} \int_{p_1, p_2} \delta(\epsilon_{k\sigma} + \epsilon_{p_2 \sigma'} - \epsilon_{p_1 \sigma}) \left[ \left| V_{k-k'} + \delta_{\sigma\sigma'} V_{k-p_1} \right|^2 [n_{\sigma'}(p_2)(1 + n_{\sigma'}(p_1) + n_{\sigma}(k)) - n_{\sigma}(k)n_{\sigma'}(p_2)] \right] \\
\frac{1}{\tau_{k\sigma}^{(1)}} = 8 \pi \sum_{\sigma'} \int_{p_1, p_2} \delta(\epsilon_{k\sigma} + \epsilon_{p_2 \sigma'} - \epsilon_{p_1 \sigma}) \left[ \tilde{V}_{\text{eff}, k-p_1} + \delta_{\sigma\sigma'} \tilde{V}_{\text{eff}, k-k'} \right|^2 [n_{\sigma'}(p_2)(1 + n_{\sigma'}(p_1) + n_{\sigma}(k)) - n_{\sigma}(k)n_{\sigma'}(p_1)] \tag{48}
\]

Though some of the above contributions to the scattering time could be negative, the overall scattering time is always positive. To leading order, the corresponding
diffusion constant is \[ \bar{D}_{k\sigma} = \frac{1}{2} |v_{k\sigma}|^2 \tau_{k\sigma} \] (49)

where the \( \frac{1}{2} \) corresponds to a \( d = 2 \) dimensional system. To a good approximation, \( |v_{k\sigma}| \) is direction-independent, but \( \tau_{k\sigma} \) is only direction-independent if the adsorbate atoms are evenly spread out on the surface. Therefore, \( \bar{D}_{k\sigma} \) generally depends on both the magnitude and direction of \( \mathbf{k} \).

Alternatively, when deviations from equilibrium of the entire system are small, we may extract a diffusion constant describing the relaxation to global equilibrium. The collision term is linearized around the equilibrium by substituting (for all occupations, not just \( n_{\sigma}(k) \))

\[
n_{\sigma}(x, k) = w_{\sigma}(x, k) + n_{\sigma}^{eq}(x)
\] (50)

and keeping only the terms linear in \( w_{\sigma} \). This is unconventional because usually the equilibrium distribution \( n_{\sigma}^{eq} \) is taken to be spatially uniform. However, spatial uniformity does not apply for adatoms diffusing on a surface – due to mechanisms such as Ostwald ripening, the adatoms prefer to form large islands to minimize the average loss of coordination number, and hence the thermodynamically preferred distribution function is nonuniform. In the case of sufficiently large nearest-neighbor attraction, \( J \), this equilibrium distribution function could be approximated as a circular island,

\[
n_{\sigma}^{eq}(x) = \frac{n_B(\epsilon_{\sigma})}{\sum_{\sigma'} n_B(\epsilon_{\sigma'})} \Theta(|r - \mathbf{x}_{cm}|)
\] (51)

where the adatom particle number \( N_{\text{tot}} \) is assumed large and \( N_{\text{tot}} a^2 = \pi r^2 \), where \( a \) is the lattice spacing. \( \mathbf{x}_{cm} \) is the average position of the adatoms and \( n_B \) is the Bose-Einstein distribution. (We have assumed that on-site repulsion is very high, so there is at most one particle on a single site.) However, it is not guaranteed that the adatoms can achieve the most stable configuration. If the starting positions of the adatoms are relatively far from each other, the final configuration tends to be a kinetically trapped state with multiple large islands. For reviews, see [4, 14].

C. Estimation of the temperature dependence of the diffusion constant

For this and the following subsections, we will describe the behavior of the diffusion constant. In experiments, it is not possible to distinguish between an adatom occupying band \( \sigma \) and one in a different band \( \sigma' \), so we will define the average diffusion constant, \( D \), to be the particle-average over all diffusion constants:

\[
D = \frac{\sum_{k\sigma} n_{k\sigma} D_{k\sigma}}{\sum_{k\sigma} n_{k\sigma}}
\] (52)

Though we are averaging over the occupations \( n_{k\sigma} \), the diffusion constants \( D_{k\sigma} \) themselves also depend on \( n_{k\sigma} \). Therefore, behavior of \( D \) with temperature \( T \) is more complicated than a simple Boltzmann averaging.

At high temperatures, the diffusion constant is known to obey an Arrhenius-type law with some activation energy \( E_{\text{act}} \) [4, 14].

\[
D(T) = D_0 e^{-E_{\text{act}}/kT}
\] (53)

but tends to level off at temperatures below the transition temperature \( T^* \) [1, 2]. Let us describe why this is true. Assuming the coverage \( \theta > 0 \) is sufficiently large, the two-phonon contribution to the scattering rate is small and we can focus on the adsorbate-adsorbate contribution (the case \( \theta \approx 0 \) is covered in the next subsection). At temperatures \( T < T^* \), the adatoms tend to reside in the lowest-energy band, where the hopping parameter is small. If the adatoms tend to reside in the lowest-energy band, then the adsorbate-adsorbate scattering is roughly independent of temperature for \( T < T^* \). However, for \( T > T^* \), higher-energy bands with much higher hopping parameters can be populated, and this suggests an exponentially-increasing transport velocity. Pouthier and Light [7] separated their diffusion constant into two parts, "coherent" and "incoherent," and noted that both parts of the diffusion constant exhibited the same critical temperature \( T^* \). From our point of view, this is not a coincidence, but merely a result of the fact that the temperature-dependence of \( D \) is sensitive to the temperature-dependent occupation of the bands \( \sigma \) and insensitive to both the type of collision term and the effect of temperature on the collision terms.

Therefore, the activation energy can be approximated by the following equation for \( T > T^* \):

\[
e^{-E_{\text{act}}/kT} = \frac{1}{|t_0|^2} \sum_{\sigma} \sum_{\sigma'} n_B(\epsilon_{\sigma}) |t_{\sigma'}|^2 \sum_{\sigma'} n_B(\epsilon_{\sigma'})
\] (54)

This suggests the activation energy is not perfectly constant with temperature. The critical temperature \( T^* \) can be estimated to be roughly when the largest two terms in the above sum are equal,

\[
n_B(\epsilon_0)|t_0|^2 = n_B(\epsilon_1)|t_1|^2.
\] (55)

Using this on the data given in [7] suggests the critical temperature \( T^* \approx 105 \) K. This is an attractive result, but the method is very crude. A more detailed analysis must include all of the bands as well as the effects of the collision term and renormalization of the velocity.

D. Divergence of the diffusion constant as \( T \to 0 \)

The depletion of phonon modes as \( T \to 0 \), due to the Bose-Einstein distribution, suggests that the relaxation time and diffusion constant diverge as \( T \to 0 \).
We can easily estimate the exponent $\alpha$ in the divergence of the diffusion constant at low coverage $\theta \approx 0$,

$$D(T) \sim T^{-\alpha}$$

as $T \to 0$. At low temperatures, the only contribution to the relaxation time is the two-phonon effective interaction from acoustic phonons, since the density of states of acoustic phonons tends to extend to lower energies than that of optical phonons.

The exponent $\alpha$ can be estimated from the behavior of $\gamma^{\sigma \sigma'}$ as $T \to 0$. If $\sigma \neq \sigma'$, the matrix elements $M_{\sigma \sigma', \epsilon}$ and $M_{\sigma' \sigma, \epsilon'}$ are highly peaked around the transition energy

$$\epsilon \approx \frac{1}{2} |\epsilon_\sigma - \epsilon_{\sigma'}|,$$

and this contribution to the scattering rate will be exponentially suppressed. However, if $\sigma = \sigma'$, the matrix elements may be closer to constants; this contribution to the scattering rate will be suppressed in a power-law dependence. Therefore, we count only $\sigma = \sigma'$ contributions, up to the Debye frequency $\omega_D$.

$$\gamma^{\sigma \sigma} = -\int_0^{\omega_D} d\epsilon g_{ph}(\epsilon) n_D(\epsilon) \epsilon^{-1} \times \text{const.}$$

For acoustic phonons in two dimensions, $g_{ph}(\epsilon) \sim \epsilon$. This suggests $\gamma^{\sigma \sigma} \propto \epsilon$ and thus $\alpha = 2$. However, there may be some remaining three-dimensional behavior, in which case $g_{ph}(\epsilon) \sim \epsilon^2$ and thus $\alpha = 4$. The true answer is thus expected to lie between 2 and 4, and perhaps closer to 2. A more careful calculation would account for the energy-dependence of the matrix elements $M_{\sigma \sigma', \epsilon}$ and $M_{\sigma' \sigma, \epsilon'}$ and also calculate the polynomial behavior of the phonon density of states at low energies.

### E. Estimation of the coverage dependence of the diffusion constant

In this subsection, we estimate the dependence of the diffusion constant on the adsorbate coverage, $\theta$. Let us keep the temperature constant, such that there will be no change in the relaxation time due to two-phonon interactions. Any change in the relaxation time will be due to hydrogen-hydrogen interactions.

A major weakness of our analysis is that in reality, the hopping parameter $t_\sigma$ for the band $\sigma$ increases, perhaps by orders of magnitude, with the coverage $\theta$, because hydrogen-hydrogen interactions tend to lower the potential barrier to hopping. The easiest way to account for this is to postulate a dependence

$$t_\sigma = t_\sigma(\theta),$$

which yields a corresponding coverage dependence in the band velocity,

$$\tilde{v}_{k\sigma} = \tilde{v}_{k\sigma}(\theta).$$

Experiments suggest the following qualitative dependence of $D(\theta)$ on $\theta$ [1-3] [16]. (1) At low coverage $\theta < 0.1$, $D(\theta)$ decreases slowly due to the increasing effects of adsorbate-adsorbate interactions. (2) At intermediate coverage $0.1 < \theta < 0.3$, $D(\theta)$ increases due to the increase of hopping parameter with coverage, which dominates the opposing effect of adsorbate-adsorbate interactions; the hopping parameter gets saturated and stops increasing at $\theta = 0.3$. (3) At high coverage $\theta > 0.3$, $D(\theta)$ decreases due to the adsorbate-adsorbate interactions. (In regime (3), the diffusion constant for deuterium atoms has been observed to increase, which is discussed later in the subsection.)

We can explain this with our model. To a first approximation, we assume that the coverage is uniform on the surface ($n_\sigma(p) \propto \theta$) and use the coverage-dependent velocity, accounting for the renormalization of energy level from the collisions, as well as the change of unrenormalized energy from the coverage-dependence of the hopping parameter.

With these assumptions $(\tau^{-1}_{k\sigma})^{-1}$ is independent of $\theta$, but

$$(\tau^{-1}_{k\sigma})^{-1} + (\tau^{-1}_{k\sigma})^{-1} = \kappa_{k\sigma}(1 + \theta),$$

where $\kappa_{k\sigma}$ is a constant. In this approximation, the average diffusion constant is

$$D(\theta) = \frac{1}{2} \left\langle \tilde{v}_{k\sigma}(\theta)^2 \right\rangle \frac{1}{(\tau^{-1}_{k\sigma})^{-1} + \kappa_{k\sigma}(1 + \theta)}.$$
and increases for $\theta > 0.5$. However, this is modified by the $\theta$-dependence of $\text{Re}\Sigma^R_\sigma$, which contributes to $\mathbf{v}_{\kappa\sigma}$. Its dependence on $\theta$ cannot be obtained without knowing the exact energy levels $\epsilon_\kappa$, which may lead to either an increase or decrease in $\mathbf{v}_{\kappa\sigma}(\theta)$ as $\theta$ increases. Both the renormalization of energy level and the collision term are of size $O(V^2)$, so it is plausible that the renormalization of energy level could change the minimum of $D$ to the experimentally observed $\theta = 0.6$.

Of course, these are not the only difference between the fermionic and bosonic cases. (For example, even though the occupation of a single site by two adatoms is energetically disfavored in both fermionic and bosonic cases, a virtual process in which two adatoms of the same band occupy the same site for a short time is allowed in the bosonic case and not allowed in the fermionic case.) To summarize, although our results are promising, it is not obvious whether fermionic statistics can account for the increase in the diffusion coverage at high coverage, and further analysis is required.

V. CONCLUSION

In this paper, we wrote down a model of hydrogen atoms hopping on a metal substrate, keeping one- and two-phonon interactions as well as hydrogen-hydrogen interactions, but ignoring other effects such as impurities. We integrated out the phonon modes and obtained the dynamics of the hydrogen atoms in the form of a kinetic equation, which incorporates the many-body effects. The kinetic equation yields a diffusion constant which obeys, at least qualitatively, the correct dependences on temperature and coverage as observed in experiments.

A good question is why we used the Keldysh method to write down a kinetic equation when there are simpler alternative methods, such as the projector formalism and the regular semiclassical Boltzmann transport equation. The answer is that the Keldysh formalism is superior when the coverage $\theta$ of adatoms on the surface is large. The renormalization of energy level

$$\epsilon_{\kappa\sigma} \to \epsilon_{\kappa\sigma} + \text{Re}\Sigma^R_\sigma \quad (66)$$

accounts for the influence of neighboring adatoms on the collisionless propagation of a hydrogen adatom, which is important for large $\theta$ and does not arise from the projector or semiclassical Boltzmann formalisms; most previous studies have assumed low coverage $\theta$. This correction is of the same size as the collision term, and for atoms in low bands, it may well be comparable to the hopping energies.

Another class of reasons to use the Keldysh formalism is that it can be phrased in the language of path integrals. The form of our adsorbate-adsorbate interaction, essentially a $\phi^4$-type interaction, is highly amenable to path-integral methods and avoids the use of complicated $V(\tau)$ two-body potentials between hydrogen atoms on the surface. Compared to other nonequilibrium methods, path-integral methods allow for the convenience of integrating out the phonon modes and approximating their effects as static, which is easier and more accurate than first expanding and then tracing over the phonon modes. Finally, though we have not studied it in this paper, Keldysh techniques can give us information about critical phenomena through the nonequilibrium renormalization-group methods developed in recent years [17].

A weakness of this paper is the absence of numerical values for the couplings $U_{\lambda\mu}^{\sigma\sigma'}$ and $M_{\lambda\mu}^{\sigma\sigma'}$. These coupling constants are highly dependent on the species of metal substrate and can be estimated from photoemission experiments [18] [19] or, especially in recent years, from density-functional theory simulations [20] [22]. Unfortunately, in most experiments only $U_{\lambda}^{\sigma\sigma'}$ is determined and not $M_{\lambda\mu}^{\sigma\sigma'}$, so simulations may be the preferred route. Density-functional theory simulations can also give estimates of the band energies $\epsilon_\sigma$, and perhaps estimate how the hopping parameter $t_\sigma$ increases with the coverage $\theta$, as suggested in section IV. A future direction of research, then, would be to incorporate numerical values from density-functional theory into the kinetic equation and compare the quantitative results to the results of experiments.

APPENDIX

In this appendix, we list the self-energies and collision integrals used in the paper. The collision integrals follow from the self-energies via the formula

$$I^{\text{coll}} = i\Sigma^K - if_\sigma(\Sigma^R - \Sigma^A) \quad (A1)$$

and also $\Sigma^A = (\Sigma^R)^\dagger$. In all cases, we will take

$$I^{\text{coll}}[n_\sigma] = \frac{1}{2}I^{\text{coll}}[f_\sigma] \quad (A2)$$

because $f_\sigma = 1 + 2n_\sigma$.

A. Hydrogen-hydrogen interaction

The first contribution to $\Sigma^K_\sigma$ and $\Sigma^K_\bar{\sigma}$ is the second-order Hartree self-energy. Similar to the theory of interacting electrons, we count contributions from different bands $\sigma'$, which is analogous to counting for different spinors. The second contribution to $\Sigma^K_\sigma$ and $\Sigma^K_\bar{\sigma}$ is the second-order Fock self-energy, which involves only the original band $\sigma$. In the theory of interacting electrons, this originates from the Pauli exclusion principle, which affects only same-spin electrons. In our case, it reflects how the Green function $D_\sigma(p)$ does not allow for a change of band index.

Since the interaction is static, certain vertices must appear at equal times. This greatly simplifies the calculations with the identities $D^K(t,t')D^K(t',t) = D^K(t,t')D^A(t,t') = 0$ and $D^K(t,t) + D^A(t,t) = 0$. A
The collision integral is (with further simplification: only the advanced and retarded interaction propagators $V^A_q = V^R_q$ contribute; the Keldysh interaction propagator vanishes since the interaction is static. These simplifications reduce the number of Feynman diagrams from around 15 to six or seven. The self-energies are

\[ (\Sigma^{R,\text{int}})_{\sigma}(k) = -\sum_{\sigma'} \int_{p_1p_2} |V_{p_1-p_2} + \delta_{\sigma\sigma'}V_{k-p_1}|^2 \]

\[ \begin{align*}
&\left[ D^R_{\sigma}(k - p_1 + p_2)D^K_{\sigma'}(p_1)D^K_{\sigma'}(p_2) + D^K_{\sigma}(k - p_1 + p_2)D^K_{\sigma'}(p_1)D^A_{\sigma'}(p_2) \\
&+ D^K_{\sigma}(k - p_1 + p_2)D^R_{\sigma'}(p_1)D^K_{\sigma'}(p_2) - D^R_{\sigma}(k - p_1 + p_2)(D^R_{\sigma'} - D^A_{\sigma'})(p_1)(D^R_{\sigma'} - D^A_{\sigma'})(p_2) \right] \\
\end{align*} \]

\[ (\Sigma^{K,\text{int}})_{\sigma}(k) = -\sum_{\sigma'} \int_{p_1p_2} |V_{p_1-p_2} + \delta_{\sigma\sigma'}V_{k-p_1}|^2 \]

\[ \begin{align*}
&\left[ (D^R_{\sigma} - D^A_{\sigma})(k - p_1 + p_2)(D^R_{\sigma'} - D^A_{\sigma'})(p_1)D^K_{\sigma'}(p_2) \\
&- D^K_{\sigma}(k - p_1 + p_2)(D^R_{\sigma'} - D^A_{\sigma'})(p_1)(D^R_{\sigma'} - D^A_{\sigma'})(p_2) \\
&- (D^R_{\sigma} - D^A_{\sigma})(k - p_1 + p_2)D^K_{\sigma'}(p_1)(D^R_{\sigma'} - D^A_{\sigma'})(p_2) + D^K_{\sigma}(k - p_1 + p_2)D^K_{\sigma'}(p_1)D^K_{\sigma'}(p_2) \right] \\
\end{align*} \]

The collision integral is (with $k' = k - p_1 + p_2$)

\[ I^{\text{int}}[n_\sigma] = 8\pi \sum_{\sigma'} \int_{p_1p_2} \delta(\epsilon_{k\sigma} + \epsilon_{p_2\sigma'} - \epsilon_{k'\sigma} - \epsilon_{p_1\sigma'})|V_{k-k'} + \delta_{\sigma\sigma'}V_{k-p_1}|^2 \]

\[ \left[ n_\sigma(k)n_{\sigma'}(p_1)(1 + n_{\sigma'}(k))(1 + n_{\sigma'}(p_2)) - n_\sigma(k)n_{\sigma'}(p_2)(1 + n_{\sigma'}(k'))(1 + n_{\sigma'}(p_1)) \right] \]

As described in section IV, we will also need the real part of the retarded self-energy, $\text{Re}\Sigma^R_{\sigma} = \frac{1}{2}(\Sigma^R_{\sigma} + \Sigma^A_{\sigma})$. It is

\[ \text{Re}\Sigma^R_{\sigma}(\omega, k) = 4\sum_{\sigma'} \int_{p_1p_2} |V_{p_1-p_2} + \delta_{\sigma\sigma'}V_{k-p_1}|^2 \frac{n_{\sigma'}(p_2)(1 + n_{\sigma'}(p_1)) - n_\sigma(k)n_{\sigma'}(p_2)(1 + n_{\sigma'}(k'))(1 + n_{\sigma'}(p_1))}{\omega - \epsilon_{p_1\sigma'} + \epsilon_{p_2\sigma'} - \epsilon_{k'\sigma}} \]

\[ (\Sigma^R_{\sigma})^{(2)}(k) = i \sum_{\sigma'} \int \frac{d\omega}{2\pi} \Im\epsilon^\sigma\sigma'|D^R_{\sigma}(\omega, k) |^2 \]

\[ (\Sigma^K_{\sigma})^{(2)}(k) = i \sum_{\sigma'} \int \frac{d\omega}{2\pi} \Im\epsilon^\sigma\sigma'|D^K_{\sigma}(\omega, k) |^2 \]

B. One-phonon effective interaction

The self energies in this case are similar to those for the hydrogen-hydrogen interaction. The collision integral is (with $k' = k - p_1 + p_2$)

\[ I^{(1)}[n_\sigma] = 8\pi \sum_{\sigma'} \int_{p_1p_2} \delta(\epsilon_{k\sigma} + \epsilon_{p_2\sigma'} - \epsilon_{k'\sigma} - \epsilon_{p_1\sigma'})|\tilde{V}_{\text{eff},k-p_1} + \delta_{\sigma\sigma'}\tilde{V}_{\text{eff},k-k'}|^2 \]

\[ \left[ n_\sigma(k)n_{\sigma'}(p_1)(1 + n_{\sigma'}(k))(1 + n_{\sigma'}(p_2)) - n_\sigma(k)n_{\sigma'}(p_2)(1 + n_{\sigma'}(k'))(1 + n_{\sigma'}(p_1)) \right] \]

C. Two-phonon effective interaction
The collision integral is

\[ I^{(2)}[n_\sigma] = \sum_{\sigma'} |\psi^{\sigma'}|^2 [n_{\sigma'}(k)(1 + n_\sigma(k)) - n_{\sigma}(k)(1 + n_{\sigma'}(k))]. \]  

(A9)