Many-Body effects and resonances in universal quantum sticking of cold atoms to surfaces

Eric. R. Bittner
Department of Chemistry and Biochemistry,
The University of Texas at Austin,
Austin, Texas 78712-1167

John C. Light
The James Franck Institute and the Department of Chemistry,
The University of Chicago,
Chicago, Illinois 60637
(October 31, 1994)

The role of shape resonances and many-body effects on universal quantum sticking of ultra cold atoms onto solid surfaces is examined analytically and computationally using an exactly solvable representation of the Dyson equation. We derive the self-energy renormalization of the the transition amplitude between an ultra cold scattering atom and the bound states on the surface in order to elucidate the role of virtual phonon exchanges in the limiting behavior of the sticking probability. We demonstrate that, to first order in the interactions for finite ranged atom-surface potentials, virtual phonons can only rescale the strength of the atom-surface coupling and do not rescale the range of the coupling. Thus, universal sticking behaviour at ultra-low energies is to be expected for all finite ranged potentials. We demonstrate that the onset of the universal sticking behavior depends greatly on the position of the shape resonance of the renormalized potential and for sufficiently low energy shape resonances, deviations from the universal \( s(E) \propto \sqrt{E} \) can occur near these energies.

We believe that this accounts for many of the low energy sticking trends observed in the scattering of sub-millikelvin H atoms from superfluid \(^4\)He films.

I. UNIVERSAL QUANTUM STICKING

The exact limiting behavior of the quantum sticking probability has been repeatedly discussed over the past 25 years, with various authors arriving at various conclusions. Since the limiting behavior is expected only at extremely low scattering energies, only recently have direct experimental measurements of sticking at the required energies been obtained, most notably in the sticking of spin polarized hydrogen to liquid He films and in the desorption of cold positronium from metal surfaces. At source of the theoretical controversy is the role that the many-body aspects of the scattering might play at extremely low energies and the effect of the long ranged behavior of the attractive part of the static potential.

The first complete formal analysis of the problem was by Goodman in the early 1970’s. Using a WKB analysis of the low energy wavefunction, it was demonstrated that that \( \lim_{E \to 0} s(E) > 0 \) for potentials with ranges longer than exponential and vanishes for those with ranges less than exponential even within the distorted wave Born approximation (DWBA) and that many-body effects are not needed in order to account for non-vanishing sticking. However, it must be pointed out that these results are semi-classical and that the WKB approximation used to derive their sticking results may not permit rigorous extrapolation of \( s(E) \) for energies below the WKB validity condition. Interestingly enough for attractive inverse power law potentials with a characteristic exponent \( r \leq 2 \), the WKB approximation is valid down to \( E = 0 \) and classical and quantum predictions agree to within a constant factor.

In support of these results Knowles and Suhl have constructed a variational polaron model in which the scattering atom is dressed by its interaction with the surface phonons. Within such a basis, the adatom becomes a quasi-particle with an effective mass \( m^* \) which is position dependent and much larger than the bare mass \( m \) over the potential region. This leads to an increase in the density of low energy resonances which increases penetration of the wavefunction into the potential region and leads to non-vanishing sticking even for square well potentials. Later, Brenig and co-workers showed that within the DWBA: (1) sticking should always vanish for short ranged wells, (2) sticking can be enhanced by polarization induced resonances for longer ranged potentials, (3) for the Coulombic potential,
quantum and classical analysis yield identical results. Recently Carraro and Cole [7] applied Brenig’s equations to study H sticking to liquid He film and obtained remarkable agreement with the experimental results [11].

As far as we know, the most comprehensive examination of the quantum sticking problem is that of Cloughtery and Kohn who developed an analytic model for quantum sticking. Working up from a surface composed of N discrete lattice atoms to the continuum, N → ∞, they demonstrated that within their one dimensional model, while polarization effects due to virtual phonon exchanges may lead to an increase in the sticking coefficient, eventually these effects will be lost as pure reflection becomes more important at low energy.

Experimental evidence for quantum sticking has come from a variety of different sources. Most notably in the desorption of positronium (Ps) from Al surfaces [12] and the sticking of spin polarized hydrogen atoms on liquid 4He films [13,14]. Slow Ps atoms, composed of an electron and a positron, are almost ideal atoms for studying quantum sticking. At experimentally accessible scattering energies of 7.5 meV, the thermal de Broglie wavelength of Ps is on the order of 100 Å and is much larger than the range of the potential well. Measurements of the thermal desorption rates of Ps from clean Al(111) along with detailed balance arguments indicate that the Al surface is a “blackbody” for Ps emission and hence the system fails to exhibit perfect reflection of ultraslow Ps atoms. For the case of H on He films, the interactions are considerably weaker and there are a number of examples of experiments in which the sticking data extrapolates to s(0) = 0 [13,14,15,16,17,18,19,20,21]. Surprisingly enough, recent data for H sticking onto thin He films, reported a gradual increase in the sticking probability as the temperature decreased below 10 mK and .1 mK [11]. This prompted Hijmans, Walraven, and Shlyapnikov [22] to propose that the atom-surface potential might be affected by very long-range van der Waals forces (with relativistic retardation) from the underlying substrate. Indeed, calculations by Hijmans, Walraven, and Shlyapnikov [22] and by Carraro and Cole [7] indicate that substrate effects could account for this trend and predict that the √T behavior will be recovered at slightly lower temperatures. More recent work which measured the sticking coefficient as a function of the He film thickness gave reasonable agreement with the theoretical predictions in temperature regimes above .1 mK [11]. That is, as the film thickness was increased, the sticking probability was reduced and eventually the universal s(T) ∝ √T behavior was observed.

In this paper we wish to examine two issues which we believe have not been adequately addressed, and yet are necessary in order to properly interpret the experimental results mentioned above. The first issue is the role of many-body effects on the limiting behavior, and the second is the role of low energy shape resonances. In the next section, we examine the many-body contributions by solving formally the Lippmann-Schwinger equation for the scattering wavefunction in which we include the self-energy due to the virtual phonon transitions between the scattering wave and the inelastic channels. Since our theory incorporates the dynamical evolution of the surface directly into the final equations of motion, it is essentially exact (for single phonon exchanges) and non-perturbative. Using approximate forms of the low energy scattering wavefunction, which we show to become exact as k → 0, we derive the renormalization of the sticking probability due to the the many-body interactions for realistic atom-surface interactions. We then demonstrate that polarization due to many-body effects serves only to rescale the strength of the interactions and does not rescale the effective range. We next examine the effect of low lying shape resonances and demonstrate the effect of increased penetration of the scattering wave into the potential region near these resonances. Finally, in the last section we apply the methods which we developed to examine the low energy limiting behavior of H sticking to thin and thick 4He films.

II. THEORY

The starting point of our theory is the Lippmann-Schwinger (or Dyson) equation for the scattering wavefunction in which we include explicitly the self-energy or polarization due to virtual phonon exchanges. The self-energy reflects the many-body nature of the problem and we shall assume that only single exchange processes are important. Close coupled forms of this equation have been used extensively by Stiles, et. al [23,24] and Jackson [25,26,27,28,29,30,31] to study inelastic molecule-surface scattering and Whaley and Bennett have used the formalism to study atom scattering from disordered surfaces [32]. We write the elastically scattered component of the wavefunction as

$$\phi_{\alpha}(E) = \phi_{bare}(E) + G_{bare}(E)V_{self}(E,T)\phi_{\alpha}(E),$$  

where $\phi_{bare}(E)$ and $G_{bare}$ are the bare wavefunction and Green’s functions in the absence of surface vibrations and $V_{self}(E,T)$ is the self energy operator

$$V_{self}(E,T) = \frac{1}{N} \sum_{q} V_{q}^{ph}(G_{q}^{+}(E,T) + G_{q}^{-}(E,T))V_{q}^{ph}. $$
Our notation is such that superscripted $+$ and $-$ refer to whether or not a virtual phonon was initially created or annihilated. Also, throughout this paper we shall define $H_o$ as the static (zero-phonon) Hamiltonian and $V_{ph}^q(z)$ as the force between the scattering atom and a phonon with wavevector $q$. We have also assumed that the bath is harmonic.

Closure is accomplished in the usual way by iteratively substituting $\phi_o$ back into the Lippmann-Schwinger equation and analytically performing the summation over single phonon exchange diagrams.

$$\phi_o = \phi_{bare} + G_{bare} V_{self} \phi_{bare} + \cdots$$

$$= (1 - G_{bare} V_{self})^{-1} \phi_{bare} \quad (3)$$

Before applying our theory to a physically realistic system, it is important to explore the effects induced by the additional polarization due to virtual phonon exchanges. Let us consider the “golden rule” transition rate between a very low energy scattering state and a single bound state, $\psi_B$, and attempt to relate the transition probabilities predicted using a dressed wave to those predicted from using the bare wavefunction. In short, we need to consider the matrix elements

$$\langle \psi_B | V_{ph} | \phi_o \rangle = \langle \psi_B | \left( 1 - V_{ph} G_o(E) V_{ph} (G^+(E) + G^-(E)) \right)^{-1} V_{ph} | \phi_{bare} \rangle, \quad (4)$$

where $G_o(E)$ is a solution of

$$(H_o - E) G_o(z, z') = \delta(z - z') \quad (5)$$

subject to the boundary condition $G_o(-\infty, z) = 0$ and $G_o(z, z') \to 0$ as $z \to \infty$.

To evaluate this matrix element we need to make a series of approximations regarding the functional form of $\phi_{bare}$. The bare scattering wave, $\phi_{bare}$, is an solution of $(H_o - E) \phi_{bare} = 0$ subject to the boundary conditions: $\phi_{bare}(-\infty) = 0$ and $\phi_{bare}(z) \to \sin(kz) + \tan(\delta k) \cos(kz)$ as $z \to +\infty$. We can also define the real regular and irregular functions, $\psi_{r,i}(z)$, as solutions of

$$(H_o - E) \psi_{r,i}(z; E) = 0 \quad (6)$$

subject to the boundary conditions

$$\psi_r(z, k) \xrightarrow{z \to \infty} \sin(kz + \delta)$$

$$\psi_i(z, k) \xrightarrow{z \to \infty} \cos(kz + \delta). \quad (7)$$

Using these functions and the Wronskien relation, we can write $G_o(z, z'; k)$ as

$$G_o(z, z'; k) = -\frac{1}{k} \left\{ \begin{array}{c} \psi_r(z; k) \psi_i(z'; k) + i \psi_r(z; k) \psi_i(z'; k) \quad z \leq z', \\ \psi_r(z'; k) \psi_i(z; k) + i \psi_r(z'; k) \psi_i(z; k) \quad z > z', \end{array} \right\} \quad (8)$$

where $k = \sqrt{2mE}$ is the scattering momentum.

For very low energies and temperatures, virtual transitions are predominantly to the bound state and we can obtain the single phonon exchange propagator from the bound (asymptotically closed) wavefunctions, weighted by the appropriate phonon densities of states, which in the continuum limit can be taken as

$$G^+(z, z') = \psi_B(z) \psi_B(z') \int_{2\pi} d^2q \frac{\cos^2(qa/2)}{\omega(q)(E_B - \omega(q) + k^2)} (n_q(T) + 1)$$

$$= \psi_B(z) \psi_B(z') \int_0^{\omega_D} d\omega \rho(\omega) \frac{\cos^2(q(\omega)a/2)}{(k^2 + E_B - \omega + i\eta)\omega} (n(\omega, T) + 1). \quad (9)$$

where $\omega_D$ is the Debye frequency of the lattice, $n_q(T)$ and $n(\omega, T)$ are the Bose-Einstein occupation numbers, and $\rho(\omega)$ is the density of states. The integral can be evaluated by choosing the appropriate contour which avoids the pole at $\omega = k^2 + E_B$ and the result is (using a Debye model for the phonons)

$$G_k^+(z, z') = \psi_B(z) \psi_B(z') F(k), \quad (10)$$

where
particular, a threshold resonance or a shape resonance nearly at the threshold may produce an additional pole close to the pole of the self-energy. The notation $\int_a^b dx$ means that we take the Cauchy principal value when evaluating the integral.

In order to take the $k \to 0$ limit of these expressions, we first need to make an assumption regarding the extreme low energy behavior of the $\psi_{0,1}(z;k)$ functions used to construct $G_o$. (Justification for this assumption for the $1/z^3$ potential is included in the Appendix.)

$$\lim_{k \to 0} \psi_r(z;k) \approx k\psi_r(z,k = 0)$$  \hspace{1cm} (15)$$
$$\lim_{k \to 0} \psi_i(z;k) \approx \psi_i(z,k = 0)$$  \hspace{1cm} (16)

where $\psi_{r,i}(z,k = 0)$ are solutions of $H_o\psi_{0,1}(z) = 0$ which are regular and irregular at the surface and are independent of $k$. Using these, we can construct the $E \to 0$ Green’s function

$$\lim_{k \to 0} G_o(z,z';k) = \begin{cases} \psi_r(z;k = 0)\psi_r(z';k = 0) + ik\psi_r(z;k = 0)\psi_i(z';k = 0) & z \leq z' \\ \psi_i(z';k = 0)\psi_i(z;k = 0) + ik\psi_r(z';k = 0)\psi_i(z;k = 0) & z > z' \end{cases}$$  \hspace{1cm} (17)

Thus the integral, $I(z;k)$, which occurs in the self-energy expression can be broken into real and imaginary components, both independent of $k$. That is

$$(z|1 - V^{ph} G_o V^{ph} G_k^+|z') \overset{k \to 0}{\approx} \delta(z - z') - V^{ph}(z)\psi_B(z') (I_1(z) + ikI_2(z)) F(k),$$  \hspace{1cm} (18)

where

$$I_1(z) = \Re I(z;k \to 0)$$  \hspace{1cm} (19)
$$I_2(z) = \Im I(z;k \to 0).$$  \hspace{1cm} (20)

Finally, substituting this back into Eq. \[\text{13}\] yields for small $k$

$$\langle \psi_B | V^{ph} | \phi_o \rangle = \langle \psi_B | V^{ph} | \phi_{bare} \rangle (1 + \Sigma(k) + \Sigma^2(k) + \cdots) = \langle \psi_B | V^{ph} | \phi_{bare} \rangle / (1 - \Sigma(k)),$$  \hspace{1cm} (21)

where $\Sigma(k)$ is the polarization renormalization due to virtual phonon exchanges ( in the small $k$ limit).

$$\Sigma(k) = F(k) \int dz V^{ph}(z) (I_1(z) + ikI_2(z)).$$  \hspace{1cm} (22)

Since the integral in $\Sigma(k)$ is at most linearly dependent on $k$, any deviations from the DWBA results are likely to come from $F(k)$. We note that the denominator, $1 - \Sigma(k)$, should approach a non-zero limit as $k \to 0$. The limiting low energy behaviour will thus be determined by the perturbation integral, $\langle \psi_B | V^{ph} | \phi_{bare} \rangle$, which approaches zero as $\sqrt{E}$ in the limit of $k \to 0$ for finite ranged atom-phonon interactions.

What we have neglected in this evaluation is the possible contribution from shape and threshold resonances. In particular, a threshold resonance or a shape resonance nearly at the threshold may produce an additional pole close
enough to the real energy axis to change the limiting behavior of $F(k)$. For the moment, let us consider the case that there are no threshold resonances and that we are well below the last shape resonance of the static potential surface. In this case, $\Sigma(0)$ is a constant between 1 and -1 and Eq. (23) produces only a rescaling correction to the DWBA result, i.e. there is no change in the effective range of the potential and the $s \rightarrow \sqrt{E}$ limiting behaviour should hold.

Interestingly enough, the calculations which we presented in Ref. [9], did not show the limiting behavior predicted above and we have identified the reasons. In that paper, we computed the sticking probability as a function of surface temperature at a scattering energy $E \rightarrow 0$ for a model He atom scattering from a featureless Cu surface. We first tested the model by comparing finite $E$ results to results published previously for the same model and obtained good agreement. We then varied both the attractive range of the potential, from long ranged $V_{att} \propto -1/z^3$ to the short ranged $V_{att} \propto -e^{-az}$ and the atom-phonon interaction by varying the phonon force constants and by changing the effective mass of the surface atoms. We then reported that the model produces sticking as $E \rightarrow 0$ which decreases as the range of the potential is decreased and decreases as the phonon force constants are increased. Since this is precisely the behavior one would expect for potentials with longer ranged interactions or if the effective scattering mass of the atom is increased, we concluded that the inclusion of the virtual phonon processes causes a renormalization of the range of the static potential and/or an enhancement of the effective mass of the scattering atom and, hence, leads to non-vanishing sticking.

Later analysis indicates that these calculations may be in error due to our particular choice of a linear trial function used in our numerical calculations to generate the $E \rightarrow 0$ solutions. In our original calculations, we tested the method against results published by Jackson for He scattering from Cu(100) at 5.1 meV and normal incidence and found satisfactory agreement and convergence. The problem with the low $E$ results occurs because the finite ranged basis and the linear auxiliary trial function used imposes an artificial energy minimum in the convergence properties of the equations and the method can not converge wavefunctions with energies below that critical value. Usually, convergence errors occur at the high end of the energy spectrum where one does not have enough high energy components in the basis used to represent the Green’s function and thus to adequately represent the wavefunction. In the present calculations, however, we use $\sin(kz)$ as the auxiliary trial function and do obtain the correct limiting behaviors predicted by the above analytical model.

In the next section, we apply the equations derived above to study H reflection from He films. Since hydrogen is an extremely light atom and the He-H potential is well characterized this is an ideal physical system for this type of study. Also, it has been demonstrated recently, that the sticking behavior is strongly dependent upon the long ranged interactions with the underlying substrate [11,7,22]. We shall demonstrate that the increased polarization from the atom-phonon interaction by varying the phonon force constants and by changing the effective mass of the surface atoms. We then reported that the model produces sticking as $E \rightarrow 0$ which decreases as the range of the potential is decreased and decreases as the phonon force constants are increased. Since this is precisely the behavior one would expect for potentials with longer ranged interactions or if the effective scattering mass of the atom is increased, we concluded that the inclusion of the virtual phonon processes causes a renormalization of the range of the static potential and/or an enhancement of the effective mass of the scattering atom and, hence, leads to non-vanishing sticking.

Later analysis indicates that these calculations may be in error due to our particular choice of a linear trial function used in our numerical calculations to generate the $E \rightarrow 0$ solutions. In our original calculations, we tested the method against results published by Jackson for He scattering from Cu(100) at 5.1 meV and normal incidence and found satisfactory agreement and convergence. The problem with the low $E$ results occurs because the finite ranged basis and the linear auxiliary trial function used imposes an artificial energy minimum in the convergence properties of the equations and the method can not converge wavefunctions with energies below that critical value. Usually, convergence errors occur at the high end of the energy spectrum where one does not have enough high energy components in the basis used to represent the Green’s function and thus to adequately represent the wavefunction. In the present calculations, however, we use $\sin(kz)$ as the auxiliary trial function and do obtain the correct limiting behaviors predicted by the above analytical model.

In the next section, we apply the equations derived above to study H reflection from He films. Since hydrogen is an extremely light atom and the He-H potential is well characterized this is an ideal physical system for this type of study. Also, it has been demonstrated recently, that the sticking behavior is strongly dependent upon the long ranged interactions with the underlying substrate [11,7,22]. We shall demonstrate that the increased polarization from the atom-phonon interaction by varying the phonon force constants and by changing the effective mass of the surface atoms. We then reported that the model produces sticking as $E \rightarrow 0$ which decreases as the range of the potential is decreased and decreases as the phonon force constants are increased. Since this is precisely the behavior one would expect for potentials with longer ranged interactions or if the effective scattering mass of the atom is increased, we concluded that the inclusion of the virtual phonon processes causes a renormalization of the range of the static potential and/or an enhancement of the effective mass of the scattering atom and, hence, leads to non-vanishing sticking.

III. STICKING OF ATOMIC HYDROGEN ON LIQUID HELIUM FILMS

The interactions between H and liquid He are known rather well. In fact, variational estimates of the binding energy of H on liquid $^3$He and $^4$He date back to the late 70’s [43]. At long range, the potential can be obtained from summing over all pairwise van der Waals interactions between the H and the He atoms. At large distances (over 200Å), retardation effects need to be included in order to provide the proper cut off in the attractive forces. At shorter ranges, the potential can obtained from empirical fits to atomic beam scattering data. [43]. To lowest order, the effective H–liquid He potential can be constructed by integrating over H-He pairwise potentials and assuming that the liquid He is a semi–infinite and incompressible fluid extending from $z = -\infty$ to $z = 0$ and with a sharp density profile, $\rho(R, z) = \rho_o \Theta(z + u(R))$.

\[
V(z) = \rho_o \int d^2 R' \int_{-\infty}^{+\infty} dz' v_{pair}(r) \Theta(z' + R'),
\]

where $r = \sqrt{R^2 + (z - z')^2}$, $v_{pair}$ is the H-He pair potential, and $\rho_o$ is the number density of bulk liquid $^4$He. ($\rho = 0.0218A^{-1}$)

There have been numerous theoretical treatments of the H-He pair potential, most recently by Bhattacharyya and Anderson using a quantum Monte Carlo method and the reader is referred to their paper for a comprehensive listing
of previous treatments \[15\]. A number of forms for the effective potential have been proposed ranging from Morse potentials used by Zimmerman and Berlinski \[13\] to much more realistic forms which include the $1/z^3$ van der Waals contributions both from the He film and the underlying substrate. The effective potential used in our study is similar to that used by Carraro and Cole \[8\] and by others \[34\]. We included both He film and substrate van der Waals polarization contributions as well as a relativistic cut off factor which limits the long range behavior of the potential at distances greater than $\lambda = 200 \text{Å}$.

$$V_o = \Delta(z) - C_3 \left( \frac{z^3}{(z - z_o)^3} + \frac{1}{(z + d)^3} \right) \gamma(z) - C_s \left( \frac{1}{(z + d)^3} \right) \gamma(z + d), \quad (24)$$

where $\Delta(z) = D \exp(-\beta(z - z_o))$ and arises from atomic core repulsions. As discussed in the introduction, the final results should not be very sensitive to the exact form of this part of the potential. Retardation effects in the attractive terms are included in $\gamma(z)$ which we assume to take the form $\gamma(z) = (1 + z/\lambda)^{-1}$ where $\lambda = 200 \text{Å}$ is the characteristic range of the effect. The remaining parameters, $\beta$, $z_o$ and $D$ are tabulated in Table I and were constrained to produce a single bound state with a binding energy within the range of the latest experimental estimates of 1.0 ± 0.1 K for an infinitely thick He film. The polarization terms are $C_3 = 219.7 \text{ K Å}^3$ and $C_s = 5000 \text{ K Å}^3$. Finally, we note that any effective potential, $V$, can be generated by an effective two-body potential, $v$ by directly inverting Eq. \[24\], \[25\]

$$v(r) = \frac{1}{2\pi\rho_o \partial^2} V(z). \quad (25)$$

We treated the He film as a smooth structureless surface. In this system, the inelastic effects are mediated through the capillary motion of the film. For the temperature ranges in which we are interested, these capillary waves, called ripplons, provide the only remaining inelastic channels, the other inelastic channels, such as those mediated by the phonons and the rotons are effectively frozen out. Mathematically, the ripplons and phonons are essentially equivalent quantities, differing only in dispersion and coupling. The displacement of the He surface can be written in terms of the ripplon operators as

$$u(R) = \frac{1}{S^{1/2}} \sum_q \left( \frac{\hbar q}{M \rho \omega_q} \right)^{1/2} (a_q^\dagger + a_{-q}) e^{i\mathbf{q}\cdot\mathbf{R}}. \quad (26)$$

The ripplon dispersion for thick He films is given by the well known form for surface capillary waves

$$\omega_q^2 = g q + \frac{\alpha}{M} q^3, \quad (27)$$

where $\alpha$ is the He surface tension ($\alpha = 0.27 \text{ KÅ}^{-2}$) \[34\], and the “gravitational” acceleration is given by, $g = C_s/d^4$.

As with He scattering from metal surfaces, we make the ansatz that the complicated dependence upon $q$ in the atom-ripplon interaction can be factored into two terms, one which includes all information regarding momentum transfer and one which depends upon only the core interactions at the surface. The form which we use is

$$V_{ph}^q = \sqrt{\frac{g}{2M \omega q}} \frac{2\beta}{4\beta^2 + q^2} \Delta. \quad (28)$$

The fact that we are using an approximate form for the coupling may introduce an overall error in our final results; however, the overall limiting behavior (i.e. whether or not the sticking vanishes) is expected to be universal and should not depend strongly upon the exact form of this coupling.

Finally, the sticking probability is obtained from the transition probability between the dressed scattering state and the bound states.

$$s(T, E) = \frac{4\pi^2 m}{k_z} \sum_n \left| \langle \phi_n | V_{ph}^q | \phi_0 \rangle \right|^2 \psi''(E/\hbar - \omega_q)/(1 - e^{-\hbar\omega_q/\beta}) \quad (29)$$

where $\psi''(\omega)$ is the imaginary part of the ripplon susceptibility, which can be approximated using a Debye model,

$$\psi''(\omega) = \frac{3\pi}{2M \omega_D} \Theta(\omega_D - |\omega|), \quad (30)$$

where $\omega_D$ is the surface Debye frequency, which we take to be on the order of 1 meV, or about 12 K. This produces a cut off in the ripplon momentum dispersion of $q_D = 1 \text{ Å}^{-1}$.  

6
Figure A shows the variation of \( s(T) \) for a 30 Å He film and bulk He as the H scattering energy is reduced below 10 mK. Superimposed are the experimental data for the same temperature regime. Given the uncertainties in both the experimental data and in the sensitivity of our calculation to variations in the potential parameters, the agreement is somewhat satisfactory. For scattering from bulk He films, the substrate polarization is attenuated by the thickness of the film. Although the binding energy of H on bulk He is somewhat less than that for thin films, the shape resonances are far enough into the continuum that penetration into the potential region is not enhanced below 1 mK and quantum reflection begins to dominate. For thin films, the situation is just the opposite. The additional polarization due to the underlying substrate dominates the long ranged behavior of the potential and the density of the shape resonances near threshold is increased. This gives rise to the observed increase in the sticking as the film thickness is decreased. Below about 0.1 mK, which is at the end of the most recent available sticking data, barring the presence of a lower lying shape resonance, the resonance enhancement effect is diminished and quantum reflection should be observed.

In the next figure, (Figure 2), we show the changes in \( s(T) \) as the He film thickness is increased from thin film to bulk at a constant scattering energy of .35 mK. Again, although our results differ from the experimental values by perhaps a factor of two or three on the average, the agreement between our calculations and the experimental data is on the whole quite good, especially given the apparent sensitivity of \( s(T) \) to the long ranged part of the potential and the lack of an accurate measurement of the substrate interactions. What is striking about our calculations is the lack of an accurate measurement of the substrate interactions. In fact, the experiments were done using either sintered silver or epoxy as a substrate. For coverages above 30 Å, the pores in the sinter should be filled \[11\]; however, for coverages below that the pores may be only partially filled. In any case, the experimental data also indicates an abrupt change in the sticking behavior which occurs when the He film thickness is below 20 to 30Å.

As a final demonstration of the role of shape resonances in quantum sticking, we consider the case of H sticking to “pseudo” liquid He where we have replaced the realistic effective potential used above with a square well. By adjusting the width of this well, \( \lambda \), we can very easily examine (analytically, if we want), the enhancements to the sticking due to low lying resonances. In Fig. 3 we plot \( s(T) \) vs \( \lambda \) at constant scattering energy well into the quantum reflection regime \( (E = 0.01 \text{ meV}) \). For the narrowest well \( (\lambda = 10 \text{ Å}) \), the potential barely supports a single bound state with a binding energy of 0.031558 K. As \( \lambda \) is increased to 50Å, more bound states are added to the well. This affects the sticking in a profound way. At each peak in this figure, an additional bound state is added to the well. As \( \lambda \) increases further, the binding energy of the new state increases and sticking decreases.

Lastly, in Fig. 4 we consider a rather exceptional case in which the effective range of the atom-phonon interaction was chosen to be longer than the effective range of the attractive part of the potential. Here, we set \( 1/\beta = 20\text{Å} \) and vary both the range of the square well, \( \lambda \), and the scattering energy. Two features are immediately apparent. First is that the universal sticking behaviour is observed in all cases indicating that for finite ranged atom-phonon interactions, universal sticking is to be expected. Secondly, is the dramatic enhancement of the sticking due to the low lying resonances.

IV. DISCUSSION

We have presented a theory for the sticking of ultra-cold atoms from surfaces, and we have presented evidence for what we believe to be the proper limiting behavior of \( s(T) \) for non-Coulombic potentials. Although our model calculations are limited to low scattering energy where only transitions to bound states are allowed, we believe that the limiting behavior shown here is in fact correct, agreeing with the predicted behaviors. Our calculations indicate that \( s(T) \) can have non-vanishing limiting behavior only in the presence of extremely low lying (threshold) resonances. We demonstrate that many body effects do persist into the quantum sticking regime; however, their net effect at very low energy is to rescale the strength of the potential but not to rescale the effective range. Since sticking is most sensitive to the range of the potential, the limiting low E behavior becomes independent of the strength of the interaction and the coupling to the inelastic channels. At very low scattering energy, there is a competition between polarization effects due to the virtual phonon exchanges and quantum mechanical reflection by the long ranged part of the potential. In the absence of shape and threshold resonances, quantum reflection is expected to win out and the universal \( s(E) \propto \sqrt{E} \) limit is obtained.

There are a number of fundamental questions which remain unresolved both experimentally as well as theoretically. When the inelastic interactions are very weak, as in the case of H on He films, subtle details, such as relativistic
retardation effects and substrate contributions to the potential become very important and can dramatically change
the sticking behavior. These subtle contributions are very difficult to quantify experimentally due in part to the
technical difficulties of working in the submillikelvin regime [10]. However, given the sensitivity of the sticking to very
subtle details of the long range part of the potential, these low energy experiments offer unique insight to substrate
effects and relativistic retardation effects that would otherwise be unmeasurable.

ACKNOWLEDGMENTS

We wish to thank Professor Steven J. Sibener and Dr. Carl Williams for for many discussions and suggestions this
work. This work was supported by the Materials Research Center of the University of Chicago under the NSF grant
DMR-88-19860.

APPENDIX A: ZERO ENERGY WAVEFUNCTIONS FOR $1/Z^3$ POTENTIALS

The essence of the theory of quantum sticking at very low scattering energies boils down to the fact that near the
classical turning point, the scattering wavefunction vanishes linearly with momentum, $k$. Thus, any matrix element
coupling this low energy scattering state to a bound state will also vanish. A demonstration of this can be seen by
solving the following Schrödinger equation, written in dimensionless units.

$$\psi''_k + \left(\frac{g^2}{z^3} + k^2\right)\psi_k = 0$$

(A1)

on $z \geq 1$ and subject to the boundary condition, $\psi_k(1) = 0$. Exact analytic solutions for this exist only for $k = 0$
and the result is [8]

$$\psi_0(z) = A\sqrt{z} [N_1(x) - N_1(2g)/J_1(2g)J_1(x)],$$

(A2)

where $N_1(x)$ and $J_1(x)$ are Neumann and Bessel functions with arguments, $x = 2g/\sqrt{z}$. The asymptotic expansion
of $\psi_0$ is obtained by taking $x \rightarrow 0$ and using the known asymptotic expansions for the Bessel and Neumann functions

$$J_1(x) = \frac{x}{2} \left[\frac{x^3}{16} + \cdots\right]$$

(A3)

$$N_1(x) = \frac{1}{\pi} \left[x \ln(\gamma \sqrt{x}) - \frac{2}{x} + \frac{x}{2}\right] + \cdots,$$

(A4)

where $\gamma$ is the Euler constant ($\ln \gamma = 0.5772 \cdots$). Also, we can use the $x \rightarrow \infty$ asymptotic forms of $J_1$ and $N_1$ to obtain

$$N_1(2g)/J_1(2g) = \tan(2g - \frac{3}{4}\pi).$$

(A5)

Putting things together, one obtains

$$\psi_0(z) = -Ag \left\{\tan \phi_o + \frac{1}{\pi} \ln \left(\frac{z}{\gamma^2 g^2} + \frac{z}{g^2} + 1\right) + \cdots\right\}.$$  

(A6)

For $k \neq 0$, approximate solutions can be obtained from the $k = 0$ solution by partitioning the potential into interior
and exterior portions. The interior part,

$$v_o(z) = \begin{cases} 
\frac{g^2}{z^3} - k^2 & \text{for } z \leq z_c \\
0 & \text{otherwise},
\end{cases}$$

where the critical distance, $z_c$ is determined by $k^2 = g/z_c^3$. From this particular choice, it is obvious that for $z \leq z_c$,
the above expression for $\psi_0$ is the solution, and for $z \geq z_c$, the asymptotic form,

$$\psi_k = \sin(kz_c + \delta_k),$$

(A7)

is the solution. The phase shift, $\delta_k$, and coefficient, $A$, are determined by requiring the the logderivative, $\gamma_k(z) = \psi_k'/\psi_k$
be continuous at $z = z_c$. From the matching condition, as $k \rightarrow 0$,
Similarly the phase shift can be estimated. The important observation is that the amplitude of the wavefunction inside the interaction region, as defined by $z < z_c$, vanishes linearly with $k$. This is to say, that there is no transmission of probability flux past $z_c$, and thus the wavefunction is totally reflected by the attractive part of the potential before it even reaches the spatial region in which it can interact strongly enough with the phonons to cause sticking to occur. This is the origin of universal quantum reflection.

\[ A = -\pi g k + \mathcal{O}[k^{5/2} \ln k]. \]  
(A8)

[1] F. O. Goodman, J. Chem. Phys. 55, 5742 (1971).
[2] F. O. Goodman and N. Garcia, Phys. Rev. B 20, 813 (1979).
[3] T. R. Knowles and H. Suhl, Phys. Rev. B 39, 1417 (1977).
[4] W. Brenig, Z. Phys. B 36, 227 (1980).
[5] J. Böheim, W. Brenig, and J. Stutzki, Z. Phys. B 48, 43 (1982).
[6] W. Brenig and R. Russ, Surf. Sci. 278, 397 (1992).
[7] C. Carraro and M. W. Cole, Phys. Rev. B 45, 12930 (1992).
[8] D. P. Clougherty and W. Kohn, Phys. Rev. B 46, 4921 (1992).
[9] E. R. Bittner, J. Chem. Phys. 100, 5314 (1994).
[10] J. M. Doyle et al., Phys. Rev. Lett. 67, 603 (1991).
[11] I. A. Yu et al., Phys. Rev. Lett. 71, 1589 (1993).
[12] A. P. Mills et al., Phys. Rev. Lett. 66, 735 (1991).
[13] D. S. Zimmerman and A. J. Berlinsky, Can. J. Phys. 61, 508 (1983).
[14] Y. Kagen and G. V. Shlyapnikov, Phys. Lett. 95 A, 309 (1983).
[15] B. Castaing and M. Papoular, J. Phys. Lett. 44, L537 (1983).
[16] Y. Kagen, G. V. Shlyapnikov, and N. A. Glukhov, JETP Lett. 40, 1072 (1984).
[17] B. W. Statt, Phys. Rev. B 32, 7160 (1985).
[18] V. V. Goldman, Phys. Rev. Lett. 56, 612 (1986).
[19] I. B. Mantz and D. O. Edwards, Phys. Rev. B 20, 4518 (1979).
[20] J. J. Berkhout, O. J. Luiten, I. D. Setja, T. W. Hijmans, and T. Mizusaki, Phys. Rev. Lett. 63, 1689 (1989).
[21] V. G. Lupov, W. A. Kaufman, K. M. Hill, R. S. Raymond, and A. D. Krisch, Phys. Rev. Lett. 71, 2045 (1993).
[22] T. W. Hijmans, J. T. M. Walraven, and G. V. Shlyapkinov, Phys. Rev. B 45, 2561 (1992).
[23] M. D. Stiles, J. W. Wilkins, and M. D. Persson, Phys. Rev. B 34, 4985 (1986).
[24] M. D. Stiles, J. W. Wilkins, and M. D. Persson, Phys. Rev. B 37, 7306 (1988).
[25] B. Jackson and H. Metiu, J. Chem. Phys. 84, 3535 (1986).
[26] B. Jackson, J. Chem. Phys. 88, 1383 (1988).
[27] B. Jackson, J. Chem. Phys. 90, 140 (1989).
[28] B. Jackson, J. Chem. Phys. 92, 1458 (1990).
[29] B. Jackson, J. Chem. Phys. 94, 787 (1991).
[30] B. Jackson, Comp. Phys. Comm. 63, 154 (1991).
[31] B. Jackson, J. Chem. Phys. 97, 6792 (1992).
[32] K. B. Whaley and A. Bennett, J. Chem. Phys. 95, 6136 (1991).
[33] A. Bhattacharya and J. B. Anderson, Phys. Rev. A 49, 2441 (1994).
[34] V. V. Goldman, Phys. Rev. Lett. 56, 612 (1986).
[35] L. D. Landau and E. M. Lifshitz, Fluid Mechanics (Pergamon, Oxford, 1958).
TABLE I. Effective Potential Parameters and Computed Binding Energies for H on Bulk $^4$He and on thin $^4$He films ($d = 30 \text{ Å}$). The reported value of $E_o$ for bulk $^4$He is 1.0K (See Ref. [11].)

| $D$ [K] | $\beta$ [Å$^{-1}$] | $z_o$ [Å] | $E_o$ [K] (thin) | $E_o$ [K] (bulk) |
|--------|----------------|---------|----------------|----------------|
| 3.0    | 0.20           | 4.8     | -0.981589      | -0.855165      |
| 2.9    | 0.20           | 4.8     | -1.059139      | -0.931325      |
| 2.8    | 0.19           | 4.8     | -1.155515      | -1.025170      |
| 2.8    | 0.20           | 4.8     | -1.139079      | -1.009945      |
| 2.8    | 0.21           | 4.8     | -1.122955      | -0.994995      |
| 2.7    | 0.20           | 4.8     | -1.221373      | -1.090980      |
| 2.6    | 0.20           | 4.8     | -1.305987      | -1.174390      |

FIG. 1. Trapping probability versus atom energy for H onto a 3 nm thick and bulk He films (1 mm). The curves labeled A and B are the results obtained from our calculations for thin and thick He films. Superimposed are the experimental results for each of these limits.

FIG. 2. Sticking probability versus He film thickness. In each case, the scattering energy and surface temperature was .35 mK. The diamonds are the experimental data points from Ref.[10]. The bump in our computed data is due to a threshold resonance which appears when the film is less than about 30 Å thick.

FIG. 3. Sticking vs. well width for a square well potential at constant scattering energy. (well depth = 2.8 K) The increases in the sticking are due to the appearance of additional weakly bound states as the well width is increased. For the narrowest case considered, the well supports a single bound state almost at threshold (binding energy = 0.03 K). Threshold well widths for each additional bound state are indicated by arrows.

FIG. 4. Sticking vs. Scattering energy for a square well potential. Here we have chosen the effective range of the atom-phonon to be 20Å and vary the width parameter, $\lambda$ from 9.5Å to 21.5Å in which we pass from 1 bound state to 2 bound states in the square well potential. See text for details.