Lifetime of surface-state electrons on liquid ⁴He. I. Free electron

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Electrons trapped on the surface of liquid ⁴He by the image potential can escape into the gas by thermal ionization. We have calculated the rate of ionization on the assumption that the electrons are strongly coupled to each other and weakly coupled to the liquid and gas. The first electrons to leave the surface extract their ionization energy from the kinetic energy of the electrons that remain behind. This adiabatic cooling effect rapidly lowers the electron temperature to a small fraction of the temperature of the surrounding gas and liquid. Above about 1.2 K gas-atom collisions determine the ionization rate and below 1 K it is determined by ripplon scattering. It is only for temperatures below 1 K that the life-time measurement can be used to determine the surface-state binding energy.

I. INTRODUCTION

Since Cole and Cohen^{1,2} and Shikin³ predicted that electrons could be localized outside liquid helium, several experiments⁴⁻⁸ have been performed to measure the properties of these unique surface states. In the model of the surface state, the electron executes free-electron-like motion parallel to the liquid surface but it is bound perpendicular to the surface. Cyclotron-resonance⁴ and mobility⁵ measurements support the free-electron nature of the parallel motion. However, the experiments⁶⁻⁸ designed to measure the electron lifetime in the surface state yield conflicting results. The binding energy of the electron remains unknown.

The surface state arises from two competing forces. Near the liquid the long-range attractive force due to the electrostatic polarization is opposed by the short-range repulsive force due to the exclusion principle. This gives a potential minimum just outside the liquid. The authors 1^{-3} described the polarization force by the one-dimensional classical image potential. The electronic states in this potential are nearly hydrogenic for their motion perpendicular to the liquid surface. Associated with each hydrogenic level is a band of free-electron states for motion parallel to the liquid surface. Williams, Crandall, and Willis⁶ placed electrons on liquid ⁴He and showed that they were indeed bound to the liquid. They measured lifetimes for escape from the surface state as long as 10^{-4} s. Ostermeier and Schwartz⁷ repeated these measurements with a different experimental arrangement and concluded that the lifetime must be shorter than 10^{-5} s.

This paper describes a theoretical estimate of the lifetime of an electron for thermal excitation from the bound to the continuum states. Both helium atoms in the vapor above the liquid and sur-

face excitations (ripplons) in the liquid contribute to the electron ionization. At high temperature, gas atoms determine the ionization rate, whereas at low temperature it is the surface waves. Since neither the surface waves nor gas atoms can transfer sufficient energy to an electron to ionize it, the ionization process is complicated. However, a gas atom or ripplon can transfer energy from the parallel to the perpendicular electron motion. If the energy in the parallel motion is equal to or greater than the binding energy, ionization can take place. Thus, two steps determine the lifetime, i.e., the ionization probability and the addition of energy to the parallel motion of the electron by the ripplon or gas-atom system. We find that, above 1 K, it is the latter process that determines the lifetime. Thus, a lifetime measurement can not yield the binding energy except at low temperature.

In Sec. II the surface state model is outlined. Section III contains the model calculation of the ionization rate. In Sec. IV the energy input and loss rates are calculated. Section V discusses these results in terms of the experiments.

II. SURFACE-STATE MODEL

Since Ref. 2 gives a detailed discussion of the surface-state model, we shall merely outline it here. At the liquid surface the short-range repulsive interaction dominates the long-range attractive interaction. Therefore, the electron experiences an energy barrier. Away from the surface the short-range repulsive potential can be neglected compared with the long-range potential due to the polarization of the liquid by the electron. This attractive potential then localizes the electron outside the liquid surface. Because the electron is assumed to be weakly bound to the surface and

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therefore far enough away from the liquid so that the surface may be treated as planar, the electron motions parallel and perpendicular to the liquid surface are uncoupled in first order. For a plane surface, the polarization potential can be described by the classical image potential.⁹ If the liquid occupies the half space $z \leq 0$ and z is the distance between the electron in the gas and the liquid surface, the potential energy of the electron is

$$V(z) = -\alpha e^{2}/z, \quad z > 0$$

= + V₀, $z \le 0.$ (1)

The potential V_0 in the liquid results from the short-range repulsive interaction. The strength of the image charge is

$$\alpha = (\epsilon_1 - \epsilon_p) / (4[\epsilon_1 + \epsilon_p]).$$
⁽²⁾

The quantities ϵ_1 and ϵ_s are the static dielectric constants of the liquid and gas, respectively. For ⁴He, α is¹⁰ about 0.006. Therefore, the binding is weak. The solid line in Fig. 1 represents the potential energy V(z). The authors in Refs. 1-3 assumed that V(z) given by Eq. (1) is the only potential in the z direction, and furthermore that the potentials in the x and y directions serve only to give the electron an effective mass. It is, of course, reasonable that if electron-electron interactions are ignored, the motion in the x-yplane is free-electron-like. Recent $experiments^{4,5}$ tend to support this idea at high temperature, e.g., cyclotron resonance measurements⁴ show that the electron motion parallel to the surface is freeelectron-like with the mass equal to the free-electron mass.

For this model, the energy spectrum is

$$E = E_{\parallel} + E_{z} , \qquad (3)$$

where the energy of the motion parallel to the

Ec



FIG. 1. Sketch of the potential energy of an electron outside of liquid helium. Potential energy is plotted vertically and the z coordinate horizontally. The solid line represents the image potential. The dashed line is the image potential plus potential due to an applied electric field. E_0 is the binding energy. E_v is the vacuum level of energy. E_c is the conduction band in the liquid.

surface is

$$E_{\parallel} = \hbar^2 K^2 / 2 m_{\parallel} . \tag{4}$$

The wave vector and effective mass in the x-yplane are \vec{K} and m_{\parallel} , respectively. In the limit $V_0 \rightarrow \infty$, the one-dimensional wave equation for the z motion has energy eigenvalues that are of the same form as for the hydrogen atom, i.e.,

$$E_{z} = -\alpha m e^{4} / 2\hbar^{2} n^{2} = -\hbar^{2} / 2 m n^{2} z_{c}^{2} . \qquad (5)$$

Here *n* is an integer, *m* the free-electron mass, and z_c the Bohr radius of this one-dimensional hydrogen atom. For ⁴He the ground-state energy is about 0.0007 eV below the continuum and $z_c \approx 70$ Å. Because of the weak binding energy and a liquid barrier of about 1 eV,¹¹ this hydrogenic approximation is reasonable for ⁴He. The wave functions are identical to those for the *s* state of the hydrogen atom multiplied by z/z_c .

III. THERMAL IONIZATION OF THE SURFACE STATE

Using the model of the surface state described above, we now calculate the electron lifetime against thermal ionization. To do this, one must calculate the rate at which an electron in the ground state makes transitions to the continuum. The gas atoms above the helium liquid and the liquid surface waves cause these transitions. Because little of the electron wave function penetrates the liquid, bulk liquid excitations are ineffectual in causing transitions.

To show that this transition rate is actually a good measure of the ionization rate, one must consider the actual experimental configuration used in a lifetime measurement. In equilibrium, for the potential given by Eq. (1), the electron will be distributed amongst the various bound and continuum levels. If the temperature is low enough⁸ (<1 K) the majority of the electrons will be in bound states rather than continuum states. In this case, the surface state is bound. If a weak electric field F is applied to the surface so as to draw electrons into the gas, the potential energy has the form

$$V(z) = -\alpha e^2/z - eFz .$$
 (6)

The dotted line in Fig. 1 represents this potential. If an electron receives enough energy from the liquid or gas to be excited to a continuum state, it can leave the surface state. Once in a continuum state the electron must diffuse to the righthand side of the potential barrier before it can make a transition back to the ground state. The electric field is kept weak enough so that it may be treated as a perturbation and the hydrogenic states are the same as those obtained in the absence of the field.

How does the electron gain the thermal energy from the liquid or gas? Because momentum conservation severely limits the amount of energy transferred in a collision, direct transfer of the binding energy to the electron is improbable. For example, in a collision with a gas atom, the maximum energy transfer to the electron is about $(m/M)^{1/2}kT$, where *M* is the mass of a gas atom. The surface excitations are similarly ineffectual in transferring energy. These surface excitations are called capillary-gravity waves. Their dispersion relation is

$$\omega^2 = Gq + (\sigma/d)q^3, \qquad (7)$$

where G is the gravitational constant, σ the surface tension, d the liquid mass density, ω the frequency, and q the magnitude of the wave vector. In their quantized form,² the surface waves are called ripplons. Both energy and momentum are conserved in a collision. Therefore, in a singleripplon collision, the ratio of the energy transfer to the average electron energy is $10^{-3}T^{-1/4}$. Since the binding energy is several kT, neither ripplons nor gas atoms can remove an electron from the surface in a single collision. Since multiple-gasatom or ripplon collisions are improbable, it would seem unlikely that the surface state could be ionized.

Nevertheless, there is a way to ionize the surface state in a single-gas-atom or ripplon collision. Since the parallel and perpendicular motions of the electron are uncoupled, it is possible for the total energy to be positive with the electron still bound to the surface, i.e., the positive kinetic energy of the parallel motion can be greater than the binding energy. The surface state could then be ionized if the energy in the parallel motion were transferred to the perpendicular motion. A perturbation that mixes the parallel and perpendicular motions can cause this transfer. Since the energy transfer from the perturbation is small, its chief role is to mix the electron states while conserving parallel momentum. Both gas atoms and ripplons can do this.

We now consider this process and calculate the ionization rate for both gas-atom and ripplon scattering. This will be the rate-limiting step in the escape from the surface as long as the electron system remains in thermal equilibrium. This means that the ripplon or gas-atom system must be able to supply energ; to the parallel motion fast enough to keep it in thermal equilibrium. If not, then it will be the energy exchange between the electron gas and its surroundings that will be the rate-limiting step.

To estimate the transition rate we calculate the perturbation of the electron states by the ripplons and gas atoms. The forms of these perturbations were proposed by $Cole^2$ in his calculation of the mobility parallel to the surface. For scattering by gas atoms he described the perturbation as a contact interaction, i.e.,

$$V_{\mathbf{G}} = v_0 \delta(\mathbf{\vec{r}} - \mathbf{\vec{r}}_{\mathbf{G}}), \quad v_0 = \hbar^2 2\pi a_s / m, \tag{8}$$

where a_s is the gas-atom s wave scattering length, $\mathbf{\bar{r}} = \mathbf{\bar{\rho}} + \mathbf{\bar{z}}$ is the electron coordinate, and $\mathbf{\bar{r}}_{g}$ is the gas-atom coordinate.

We consider the process where the electron is initially in its ground-hydrogenic state and the gas atom is in a plane-wave state described by the wave vector $\vec{P} = \vec{P}_{\parallel} + \vec{P}_{z}$. The perturbation causes a transition from the ground to a continuum state labeled by the wave vector \vec{k}_{z} . The parallel component of the electron wave vector changes to \vec{K}' with an accompanying change in the parallel component of gas-atom momentum. Because momentum is conserved $\Delta \vec{K} = \vec{K}' - \vec{K} = \Delta \vec{P}_{\parallel} = \vec{P}_{\parallel} - \vec{P}_{\parallel}'$. Thus the energy of the parallel motion is transferred to the perpendicular motion. The matrix element for this perturbation is calculated in the Appendix; it is

$$|\langle V_G \rangle|^2 = (v_0^2 \pi k_z 8 z_c^2 / V^2 L) (1 + Q^2)^{-3} F(p, G),$$
 (9)

where V is the volume of the gas space, L the length of the gas space, Q = p + G, $p = k_z z_c$, and $G = \Delta P_z z_c$, where ΔP_z is the perpendicular component of the wave-vector change for the gas. The quantity F(p, G), which is defined in the Appendix, is the order of unity for p < 1.

For ripplon scattering we consider the same change in the electron states. The ripplon produces a distortion of the liquid surface, which causes the image potential to become a function of the parallel as well as the perpendicular coordinate. This change in the image potential is expressed in terms of surface displacements, which are in turn expanded in ripplon normal modes.

Cole obtained¹²

$$V_{R} = -\sum_{\substack{\mathbf{q},\mathbf{K}}} M(c_{\mathbf{K}+\mathbf{q},1}^{\dagger}a_{\mathbf{K}-\mathbf{q}}^{\dagger} + c_{\mathbf{K}+\mathbf{q},1}^{\dagger}a_{\mathbf{q}}^{\star})c_{\mathbf{K},m}$$
(10)

$$M = \pi n_1 \alpha_1 e^2 (\tilde{h} q^3 / 8 dA \omega)^{1/2} \\ \times \langle \vec{\mathbf{K}} + \vec{\mathbf{q}}, 1 | [K_1(qz)/z] e^{i \vec{\mathbf{q}} \cdot \vec{p}} | \vec{\mathbf{K}}, m \rangle$$
(11)

for the lowest-order perturbation in secondquantized notation. Here n_1 is the density of liquid atoms, α_1 the liquid polarizability, A the area of the liquid surface, and $K_1(qz)$ is a modified Bessel function of the second kind. Momentum conservation in the parallel direction is implicit in the above expressions. The $c_{\vec{k},m}^{\ddagger}$ and $c_{\vec{k},m}$ are creation and annihilation operators for the electronic states. The $a_{\vec{k},-\vec{q}}^{\dagger}$ and $a_{\vec{q}}$ are ripplon creation and annihilation operators. In the Appendix we calculate $\langle V_R \rangle$ between the plane-wave states $|\vec{K}\rangle$ and $|\vec{K}+\vec{q}\rangle$ and the ground hydrogenic state and a continuum hydrogenic state. It is

$$|\langle V_R \rangle|^2 = \frac{2\pi^2 \hbar k_g \alpha_L^2 e^4 n_1^2}{d V q \omega z_d^4} (2N_q + 1), \qquad (12)$$

where N_q is the ripplon density. We have added ripplon absorption and emission together, since they both contribute to the transition. Momentum conservation gives $\Delta \vec{K} = \vec{q}$.

To calculate the transition probability in lowest order we use time-dependent perturbation theory where the transition probability per unit time is

$$W = \frac{2\pi}{\hbar} \sum_{f} |\langle V \rangle|^2 \delta(E_f - E_i), \qquad (13)$$

where the sum over final states f depends on the interaction. It is carried out in the Appendix. Using the perturbation given in Eq. (9), the ion-ization probability for gas-atom scattering is

$$W_{IG} = P_G(E_{\parallel}/E_0 - 1)\Theta(E_{\parallel} - E_0), \qquad (14)$$

$$P_{G} = 3 m v_{0}^{2} n_{G} / 4 \hbar^{3} z_{c} , \qquad (15)$$

where n_G is the density of gas atoms and E_0 is the absolute value of the binding energy.

Similarly, the transition rate for ripplon scattering is

$$W_{IR} = P_R(E_{\parallel}/E_0 - 1)\Theta(E_{\parallel} - E_0), \qquad (16)$$

$$P_{R} = \frac{\pi (n_{1} \alpha_{1} e^{2})^{2} kT}{4 \hbar \sigma z_{e}^{4} E_{0}} .$$
 (17)

The ionization rate is the sum of the transition probabilities (14) and (16) averaged over the distribution of electron states of parallel motion. For the low electron densities considered here, the distribution is Maxwellian. Thus the ionization rate W_I is

$$W_{I} = (P_{R} + P_{G})(kT_{e}/E_{0})e^{-E_{0}/kT_{e}}, \qquad (18)$$

where T_e is the electron temperature. The electron temperature is to be distinguished from T, the temperature of the liquid or gas, since we shall show below that $T_e \leq T$. Both P_R and P_G depend on T. At high temperature, since $P_G \gg P_R$, gas-atom scattering dominates the ionization process. Since P_G decreases rapidly with decreasing temperature owing to the decrease in n_G , ripplon scattering dominates the ionization at low temperature (<1 K).

In calculating the above transition rates, we make certain approximations to obtain the results

in closed form; these are: $k_z z_c < 1$ and $q z_c > 1$. Both these approximations have little effect on the results because of the threshold nature of the transition. We also omitted the transitions from higher bound states to the continuum, since an investigation of the contribution from these states shows that it decreases as $1/n^2$.

We now proceed to the calculations of the energy-input and -loss rates, since they determine T_e .

IV. ENERGY BALANCE

When an electron leaves the surface state, it carries away E_0 , which is much greater than the average energy per electron. If this energy is not replenished rapidly enough by the gas atoms or ripplons, the electron system must cool. Since the energy-loss rate \dot{E}_1 decreases with decreasing temperature, the electron gas cools until the energy loss is balanced by the energy input from the gas atoms and ripplons. Because the energy transfer in a collision with a gas atom or ripplon is a small fraction of kT, many collisions are required to replace the energy lost.

In the steady state, the average energy-input $\langle \dot{E}_i \rangle$ and -loss $\langle \dot{E}_i \rangle$ rates are equal, giving the energy-balance equation. It is

$$\langle \dot{\boldsymbol{E}}_{1} \rangle - \langle \dot{\boldsymbol{E}}_{i} \rangle = 0.$$
 (19)

The averages are over the electron distribution that satisfies the Boltzmann or other appropriate kinetic equation. However, to find this distribution requires a complex numerical calculation that is beyond the scope of this paper. Hence, at this stage, it is appropriate to make what is called the electron-temperature approximation¹³ and assume that the distribution is Maxwellian. There is no rigorous justification for this approximation, but it is thought to hold when the electron-electron scattering is sufficiently rapid to maintain an electron temperature. For the present situation, one can show that the energy-exchange rate due to electron-electron scattering is larger than the energy-exchange rate due to gas-atom or ripplon scattering.

The average energy-loss rate is given by the product of the ionization rate and the energy lost per ionization event, i.e.,

$$\dot{E}_{1} = E_{0}W_{I} = (P_{R} + P_{C})kT_{e}e^{-E_{0}/kT_{e}}$$
(20)

Using perturbation theory, we find that the energy-input rate for a single collision with a gas atom or ripplon is

$$\dot{E}_{i} = \frac{2\pi}{\hbar} \sum_{f} \Delta E |\langle V' \rangle|^{2} \delta(E_{f} - E_{i}), \qquad (21)$$

where ΔE is the energy transfer in a collision.

Since the electron states quantized in the z direction are widely separated in energy, this energy is transferred to the parallel motion.

The perturbations, which are derived in the Appendix, are

$$|\langle V_G \rangle|^2 = (v_0/V)^2 (1 + \frac{1}{4}G^2)^{-3}$$
(22)

for gas-atom scattering and

$$|\langle V_{R} \rangle|^{2} = \left(\frac{\pi n_{1} \alpha_{1} e^{2}}{z_{c}^{2}}\right)^{2} \frac{\hbar q}{4 dA \omega} (2N_{q} + 1 + \delta N) \qquad (23)$$

for ripplon scattering. Here δN is +1 or -1 for ripplon emission and absorption, respectively.

In a collision with a ripplon an amount of energy $\hbar \omega$ is exchanged. For a collision with a gas atom, the energy exchange is

$$\Delta E_G = -(\hbar^2/2M) [\Delta K^2 - 2\Delta K P_{\parallel} \cos \gamma], \qquad (24)$$

where γ is the angle between $\Delta \vec{\mathbf{K}}$ and $\vec{\mathbf{P}}_{\parallel}$.

After performing the sum over final states in Eq. (21) as outlined in the Appendix, one has

$$\dot{E}_{iG} = (P_G m/4M)(E_G - E_{\parallel})$$
 (25)

for the energy-exchange rate between an electron and the gas atoms. Here $E_G = \hbar^2 P_{\parallel}^2 / 2M$. When \dot{E}_{iG} is averaged over the electron and gas-atom distributions, Eq. (25) becomes

$$\langle \dot{E}_{iG} \rangle = (P_G m k/4M)(T - T_e). \qquad (26)$$

This expression shows, as expected, that for energy to be transferred to the electrons, their temperature T_e must be less than the gas temperature.



FIG. 2. Ionization rate plotted as a function of reciprocal temperature. The solid curve is for the same electron and liquid temperatures. The dashed curve is for the electron temperature determined from Eq. (19).

A similar expression results for ripplon scattering

$$\langle \dot{E}_{iR} \rangle = P_R \frac{\sigma E_0}{d\hbar T} \left(\frac{32\pi^3 m^3}{kT_e} \right)^{1/2} (T - T_e) . \qquad (27)$$

One may now combine Eqs. (20), (26), and (27) in the energy balance Eq. (19). The solution of this equation determines the electron temperature. Then Eq. (18) is used to obtain the ionization rate. The dashed curve in Fig. 2 shows this ionization rate as a function of temperature. It is instructive, however, to write the energy balance at high temperature, where only gas-atom scattering is important. It is

$$\langle \dot{E}_{iG} \rangle - \langle \dot{E}_{1G} \rangle = P_G k [(m/4M)(T - T_e) - T_e e^{-E_0/kT_e}] = 0.$$

(28)

It is then apparent that the electron temperature is independent of P_{G} and hence of the gas-atom density. In fact, T_e is virtually independent of temperature. The electron temperature is less than 1 K at all temperatures. The electron temperature does not depend on the gas-atom density or strength of the interaction because the gas atoms contribute equally to both the energy input and loss. The ionization rate, however, has a temperature dependence owing to the temperature dependence of the gas-atom density. When the gas-atom density has decreased at lower temperature, the ripplons become important. Below about 1.4 K they dominate the energy-input rate, while the gas atoms dominate the loss rate. In this region the electron temperature rises slightly with decreasing temperature because, while the energy input changes slowly with temperature, the loss rate decreases rapidly with decreasing temperature. At 1 K and below, the ripplon dominates both energy input and loss. Below about 0.8 K the energy-loss rate is so low that the electron temperature remains nearly equal to the lattice temperature. In this region the ionization process is temperature activated.

V. DISCUSSION

From the above calculation, we see that the inability of the electron system to remain in thermal equilibrium with its surroundings hinders the determination of the surface-state binding energy. In Fig. 2 the ionization rate is plotted versus reciprocal temperature. The solid curve is calculated assuming that the electron system has the same temperature as the gas and liquid, which are in equilibrium. The dashed curve is calculated using the energy-balance equation to determine the electron temperature. The electron cooling effect clearly reduces the ionization rate above 1 K because the electron temperature is about 0.8 K and is virtually independent of the liquid temperature. The temperature dependence of the ionization rate (dashed curve) is caused by the temperature dependence of the gas-atom density. Above T_A gas atoms dominate the energy exchange; above T_B they dominate the ionization process.

Even with the electron cooling effect included, the theoretical values of the ionization rate are higher than the experimental values. There are two reasons for this discrepancy. First, the electron-temperature model overestimates the density of electrons in the vicinity of E_0 . The actual electron distribution has fewer electrons in the region of energy space $E_{\parallel} > E_0$ than does a Maxwellian distribution with the same average energy. Such failures of the electron-temperature model have been observed in non-Ohmic transport.¹⁴ Second, crystallization of the electron gas occurs for low-electron concentrations. A dilute electron gas, as pointed out by Wigner, attains its minimum-energy configuration by forming a regular array. We find that for the electrons on liquid helium that electrons are well correlated about their lattice points below 1 K.¹⁵ Thus one might expect the escape rate to be affected if the electrons are in a regular array rather than free.

Note added in proof. Preliminary results of a calculation of the ionization rate based on the electron crystal model¹⁵ will appear in Physics Letters. We find that W_I is at least an order of magnitude lower than for the free-electron case discussed here.

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APPENDIX

To calculate the matrix element for gas-atom scattering using the perturbation V_G given by Eq. (8), one uses plane waves for the initial and final gas-atom wave functions, i.e.,

$$\varphi_{c} = V^{-1/2} e^{-i \vec{\mathbf{p}} \cdot \cdot \vec{\mathbf{r}}_{G}} . \tag{A1}$$

The initial and final wave functions for the parallel motion of the electron are, following Cole,² chosen as Bloch functions. The ground-state wave function for the perpendicular motion is

$$\varphi_0(z) = 2 z z_c^{-3/2} e^{-z/z} c \tag{A2}$$

and the continuum wave function, for a container

of length L, is¹⁶

$$\varphi_{c} = (2/L)^{1/2} |\Gamma(i/p)| (z/z_{c}) e^{\pi/2p - ik_{g}z}$$
$$\times F(1 + i/p, 2, 2ik_{g}z), \qquad (A3)$$

where the function F is a confluent hypergeometric function, $p = k_z z_c$, and $\Gamma(i/p)$ is the Γ function.

Integration over the parallel coordinates of the gas atom and electron gives momentum conservation. Integration over the z component of the gas atom removes $\delta(z - z_G)$. The remaining integral, apart from constants is

$$I = \int dz \, e^{-az/z} c \, z^2 F(1 + i/p, 2, 2ik_z z)$$

= $(2z_c^3/a^3)F(1 + i/p, 3, 2, 2ip/a),$ (A4)
 $a = 1 + i(p+G).$

For energy exchange, the initial and final gasatom and parallel electron states are the same as above. The electron remains in the ground state of its hydrogenic motion. The integration over the z coordinate gives

$$I_2 = z_c^3 / 4(1 + \frac{1}{2}iG) . \tag{A5}$$

To treat the scattering by ripplons we use the perturbation V_R given by Eq. (10). For the ionization process when the initial perpendicular state is the ground state of the electron and the final state is the continuum state, the integration over the z coordinate is

$$J = 2\sqrt{2} |\Gamma(i/p)| e^{\pi/2p} (Lz_c^5)^{-1/2}$$

$$\times \int_0^\infty e^{-z/z_c - ik_z \cdot z} K_1(qz) z$$

$$\times F(1 + i/p; 2; 2ik_z z) dz . \qquad (A6)$$

The integral in (A6) does not appear to be representable by simple functions that would facilitate further integrations in the matrix element. However, as we shall show, the transition probability is strongest for $k_z z_c < 1$. Since the main contribution to the integral in (A6) comes from z values less than z_c , we can use the small-argument approximation for the hypergeometric function which is to replace it by unity. Then the integral in (A6) is¹⁷

$$I_{3} = \frac{16F(3; \frac{3}{2}; \frac{5}{2}; S)}{3q^{2}(1 + r + i\kappa)^{3}}, \qquad (A7)$$

where $r = (qz_c)^{-1}$ and $S = (r - 1 + i\kappa)/(r + 1 + i\kappa)$. The quantity $\kappa = k_z/q \ll 1$. Using the integral representation of F we find that¹⁸

$$I_3 = G(\boldsymbol{\gamma}, \, \kappa) q^{-2} \,, \tag{A8}$$

$$G(r, \kappa) = \frac{2}{(1+r+i\kappa)^3} \left[\frac{1+S}{S(1-S)^2} + \ln\left(\frac{1+S-2\sqrt{S}}{1-S}\right) / 2S^{3/2} \right].$$
(A9)

For values of $r \le 1$ we find that $G(r, \kappa)$ is the order of unity. We take $\kappa \ll 1$. Thus we approximate *I* by q^{-2} . It, on the other hand. $r \ge 1$, $G(r, \kappa)$ can be well approximated by r^{-1} , so that in this regime $I = z_c/q$. Since the important contributions to the transition probability come from the region where $r \le 1$, we set $G(r, \kappa) = 1$.

For energy exchange where the z motion remains unchanged, the integration over the z coordinate is

$$I_{4} = \int_{0}^{\infty} e^{-2z/z} c \, z K_{1}(qz) dz \simeq z_{c}/2q \,, \quad qz_{c} \ll 1.$$
(A10)

Since the dominant q values in energy exchange are much less than z_{e}^{-1} , the approximate value of the integral is sufficient.

To perform the sum over final states for ionization by gas atoms, we replace the sum over the final states by an integral using the transformation

$$\sum_{f} = \frac{VL}{(2\pi)^4} \int dk_z \, d\Delta P_z \, d\theta \, \Delta P_{\parallel} \, d\Delta P_{\parallel} \, . \tag{A11}$$

Momentum conservation limits the final states of the parallel motion to two momentum-space dimensions. Since there is no momentum conservation in the perpendicular direction, there are both the final-electron and gas-atom states in this direction. The energy conserving δ function for this process is

$$\delta(E_{f} - E_{i}) = \delta(\hbar^{2}/2m)(k_{z}^{2} + z_{c}^{-2} + \Delta P_{\parallel}^{2} - 2\Delta \vec{\mathbf{P}}_{\parallel} \cdot \vec{\mathbf{K}})$$
$$+ (\hbar^{2}/2M)(\Delta P_{\parallel}^{2} + 2\Delta \vec{\mathbf{P}}_{\parallel} \cdot \vec{\mathbf{P}}_{\parallel} + \Delta P_{z}^{2}$$
$$+ 2\Delta P_{z}P_{z}, \qquad (A12)$$

where momentum conservation was used to write \vec{K}' in terms of $\Delta \vec{P}_{\mu}$. Because M/m is over 10³, the terms multiplied by $\hbar^2/2M$ can be neglected with respect to those multiplied by $\hbar^2/2m$. Integrating over the angular variable to remove the δ function gives for the integral in the transition probability

$$I_{5} = \int \frac{k_{z} dk_{z} \Delta P_{\parallel} d\Delta P_{\parallel} d\Delta P_{z}}{(1+Q^{2})^{3} \left[4\Delta P_{\parallel}^{2} K^{2} - (\Delta P_{\parallel}^{2} + k_{z}^{2} + z_{c}^{-2})^{2} \right]^{1/2}}$$
(A13)

The limits on this integral are determined by the condition that the δ function [Eq. (A12)] must vanish. This restricts ΔP_{\parallel} to lie in the interval

$$K - (K^{2} - k_{z}^{2} - z_{c}^{-2})^{1/2} \leq \Delta P_{\parallel} \leq K + (K^{2} - k_{z}^{2} - z_{c}^{-2})^{1/2}$$

The upper limit on k_z is determined by the condition that ΔP_{\parallel} be real. We take the upper limit on the ΔP_z integration as $M/mz_c \gg \Delta P_z \gg z_c^{-1}$, so that omitting the ΔP_z term in the δ function remains justified. Therefore (A13) is

$$I_{5} = (3\pi^{2}/32)z_{c}^{-3}(E_{\parallel}/E_{0}-1)\Theta(E_{\parallel}-E_{0}), \qquad (A14)$$

where Θ is the unit step function. Much the same procedure is used for ripplon ionization. The sum over final states is replaced by

$$\sum_{\boldsymbol{f}} = \frac{AL}{(2\pi)^3} \int q \, d\boldsymbol{q} \, d\theta \, d\boldsymbol{k}_{\boldsymbol{z}} \, . \tag{A15}$$

The integration over the angle θ gives, apart from constant factors

$$I_{6} = \int \frac{dq \, k_{g} \, dk_{g}}{q^{3} (k^{2} q^{2} - (q^{2} + C^{2})^{2} / 4)^{1/2}}, \qquad (A16)$$

where $C^2 = k_z^2 + z_c^{-2}$. In obtaining this expression, we used the high-temperature approximation for N_q and also neglected the term linear in q in the dispersion relation. These approximations are valid above about 0.1 K. The limits on the q integation are to insure that the argument of the δ function vanishes. This requirement restricts qto lie in the range $K - (K^2 - C^2)^{1/2} \leq q$ $\leq (K^2 - C^2)^{1/2} + K$. The upper limit on k_z is determined by the condition that q be real. Performing these integrations we obtain

$$I_{6} = \frac{1}{2}\pi z_{c}^{2} (E_{\parallel} / E_{0} - 1) \Theta (E_{\parallel} - E_{0}) .$$
 (A17)

For energy exchange the integration over final states in Eq. (21) can be simplified because the collisions are nearly elastic. In this case, it is convenient to expand the δ function in powers of the energy transfer. Thus we write

$$\delta(E_{f} - E_{i}) = \delta(E'_{||} - E_{||} + \Delta E)$$

$$= \left(1 + \Delta E \frac{\partial}{\partial E'_{||}} + \cdots\right) \delta(E'_{||} - E_{||}),$$
(A18)

where E'_{\parallel} is the final energy of the electron. This expansion is only defined in terms of an integration over the δ function. Since ΔE is small compared to E_{\parallel} , the expansion need only be carried to first order. This technique was not appropriate for the ionization rate, since $\Delta E \sim E_{\parallel}$ in that case.

For the rate of energy exchange between electrons and gas atoms the final states are the electron states characterized by \vec{K}' and the z com-

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ponent of the momentum transfer to the gas atom. The integration over the magnitude of \vec{K}' is converted into an integration over E'_{μ} . Then the summation in Eq. (21) becomes

$$I = \int d\Delta P_{g} \langle V_{G} \rangle^{2} \int d\theta \, dE'_{\parallel} \, \delta(E'_{\parallel} - E_{\parallel}) \\ \times \left(\Delta E_{G} - \frac{\partial}{\partial E'_{\parallel}} (\Delta E_{G})^{2} \right), \qquad (A19)$$

where the derivative of the δ function was removed by an integration by parts. Using Eq. (24) for ΔE_c and performing the required integrations, we arrive at

$$I = \frac{3\pi^2 v_0^2}{\hbar z_c V^2} \frac{m}{M} (E_{\parallel} - E_c)$$
(A20)

correct to first order in (m/M).

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Similarly we have for the energy-exchange rate for ripplon scattering an integral of the form

$$I = \int dE'_{\parallel} d\theta q [N_{q} \delta(E'_{\parallel} - E_{\parallel} - \hbar \omega) - (N_{q} + 1) \delta(E'_{\parallel} - E_{\parallel} + \hbar \omega)], \quad (A21)$$

which, after expanding the δ function to first order and integrating over E'_{\parallel} , becomes

$$I = -(2K)^{1/2} \int d\theta \left((1 - \cos\theta)^{1/2} - \frac{\hbar}{K} \sqrt{2} \frac{\partial (q \omega N_g)}{\partial E'_{\parallel}} \right|_{E'_{\parallel} = E_{\parallel}} \right). \quad (A22)$$

If we make the high-temperature approximation for N_q , Eq. (A22) becomes

$$I = 8K^{1/2}(kT/2E_{\parallel}-1).$$
 (A23)

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