Transmission-coefficient singularities in emission from condensed phases

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It is shown that, when interactions between quasiparticles are neglected, transmission of an electron (a ^{4}He atom) from the vacuum into a crystal (liquid He II) can be treated as a multichannel scattering process. Thresholds of new channels correspond to the vacuum energy, and (i) for crystals, to the appearance of a new diffracted wave either in the reflection or the transmission pattern, (ii) for ^{4}He, to the roton minimum. At these points, the transmission coefficients must exhibit either discontinuities (reflection thresholds of solids) or singularities with vertical slope (transmission thresholds of solids and roton minimum). The observability of these singularities in emission experiments is discussed in the cases of photoemission and He II evaporation.

I. INTRODUCTION

In all experimental methods for studying condensed phases which rely on emission of particles, the physical process resulting in the emission current involves an excitation, which creates the departure from equilibrium, and is specific of the type of experiment (excitation by photons, electrons, a heat pulse, an electrical bias, a difference of pressure, ...); and a flow of the excited particles—or quasiparticles—out of the solid or liquid into another medium, which may be either another solid (tunnelling, internal photoemission, ...) or the vacuum. This flow process is common to all types of emission.

We want to show here that when interactions between the quasiparticles of the condensed phase are neglected the flow process can be described within the standard formalism of multichannel scattering. General results of scattering theory can then be directly applied, which provides predictions about the shape of the energy and angular distribution of the emission current in the vicinity of "threshold points" (energies and angles at which excitations from a given branch of the spectrum start or cease to contribute to the emission). We will illustrate these results on two cases of such thresholds: roton minimum singularity in the evaporation spectrum of He II and diffraction threshold effects in photoemission from crystals. Modifications of these results due to lifetime effects will be discussed briefly. For the sake of clarity, we restrict ourselves here to the case of emission into the vacuum (the generalization to emission into a solid then being straightforward).

II. TRANSMISSION AS MULTICHANNEL SCATTERING

Let us first forget about emission mechanisms, and consider the following question only: Can one describe the propagation of an electron in a semi-infinite-crystal—plus—vacuum system as a scattering process?

Inside the solid, far from the surface (assumed to lie in the y, z plane), the potential and the interactions felt by the electron are those characteristic of the infinite crystal. Far in the vacuum, the potential has the form:

$$V(x) = E - e^2/4x, \tag{1}$$

where E is the vacuum level, and the image potential, $(-e^2/4x)$ describes the long-distance effect of Coulomb forces (note that it is absent in the case of neutral particles such as He atoms).

Close to the surface (in a region typically a few atomic layers thick), the atomic arrangement is perturbed compared with the bulk arrangement, as well as exchange and correlation effects. That is, the surface potential—which is defined with respect to the bulk crystal potential— is composed of (i) a short-range nonlocal and retarded (pseudo) potential, which depends on the material, surface state, etc., and (ii) a long-range one-body potential corresponding to (i). This potential does not go to zero at infinity; $V(x\to\infty) - V(x\to-\infty)$ is finite.[1] For example, for conduction electrons of a metal emitter,

$$\lim_{x\to\infty} V - \lim_{x\to-\infty} V = \mu + \phi\ ,$$

where μ is the Fermi energy and ϕ is the extraction work of the metal. In ^{4}He at low temperature, it is equal to the latent heat of evaporation.

Transmission of an electron from the solid to the vacuum, of course, involves scattering by the surface potential. However, since $V(\infty) \neq V(-\infty)$, this cannot be described by ordinary potential scattering theory (the effect on the outgoing waves cannot be expressed in terms of phase shifts only, since the group velocity at infinity in vacuum is different from that at infinity in the solid). Inci-

dent and transmitted waves, far from the surface, refer to different zeros of kinetic energy. This is precisely the situation which occurs in multichannel scattering; a particle is said to be scattered into a channel different from the incidence one when, in the scattering process, it has lost a finite amount of energy E (which has been transferred to the target). Here, the physical source of the energy shift is slightly different; the kinetic-energy shift

$$E = \lim_{x \to \infty} V - \lim_{x \to -\infty} V$$

is balanced by an increase of potential energy.[2] However, the mathematical formulation is completely identical, provided we assume that the lifetime of the excitations in the solid is infinite (or, equivalently, neglect interactions between quasiparticles). Indeed, within that assumption, the wave functions of the excitations of the system are solutions of a Schrödinger-like equation

$$\left(\omega + \frac{\hbar^2}{2m}\vec{\nabla}^2 - V(\vec{r})\right)\psi_\omega(\vec{r}) - \int d^3r'\,\Sigma_\omega(\vec{r},\vec{r}')\psi_\omega(\vec{r}') = 0\,, \tag{2}$$

where $V(\vec{r})$ is the one-body potential, and the self-energy (or pseudopotential) Σ_ω is real, since lifetime effects have been neglected. Therefore the corresponding complete pseudo-Hamiltonian

$$H_\omega = \vec{p}^2/2m + V + \Sigma_\omega \tag{3}$$

is Hermitian. Moreover, channel Hamiltonians are easily defined as

$$H_{v,\omega} = \lim_{x,x' \to \infty} H_\omega(\vec{r},\vec{r}') \equiv \delta(\vec{r}-\vec{r}')\ [\vec{p}^2/2m + E] \tag{4}$$

for the "vacuum channel," and

$$H_{s\omega} = \lim_{x,x' \to \infty} H_\omega(\vec{r},\vec{r}') \equiv \delta(\vec{r}-\vec{r}')[\vec{p}^2/2m + V_s(\vec{r})] + \Sigma_{s,\omega}(\vec{r},\vec{r}') \tag{5}$$

for the "solid channel." V_s and $\Sigma_{s\omega}$ are the potential and self-energy in the bulk solid. The eigenwaves corresponding to H_v and H_s are the free channel waves of scattering theory. They are, naturally, free-electron plane waves for the vacuum, and the bulk quasiparticle waves for the solid.

Let us for the sake of simplicity of the present argument, assume that the solid channel defined by $H_{s,\omega}$ is unique as well as the vacuum one, i.e., that to a wave incident from the vacuum correspond only one transmitted and one reflected wave (this assumption will be discussed and relaxed later on).

Finally, the two channel scattering Hamiltonians associated with H_v and H_s,

$$H'_{v,\omega} = H_\omega - H_{v,\omega} \quad \text{and} \quad H'_{s,\omega} = H_\omega - H_{s,\omega}, \tag{6}$$

satisfy all the requisites (Hermiticity, boundedness) necessary for multichannel scattering theory to apply, and all of the results of that theory proceed in a straightforward manner.

The eigenstates of the system can be classified into in and out states, which develop, respectively, from and into free channel waves, and satisfy Lippman-Schwinger equations. For example, in-states $\psi^{(+)}_{\vec{k}_v}, \psi^{(+)}_{\vec{k}_s}$, describe waves which develop from a free wave of energy ω incident onto the surface from the vacuum (solid) side into a reflected and a transmitted part. They are labeled by the value of the momentum of the corresponding free channel waves of energy ω; $\varphi_{\vec{k}_v}, \varphi_{\vec{k}_s}$). The reflected part corresponds to the part of $\Psi^{(+)}$ which is scattered in the incidence channel.

It is seen immediately, when comparing the usual definitions of the reflection and transmission coefficients $\mathcal{R}$ and $\mathcal{T}$ of the surface barrier (ratios of reflected and transmitted to incident flux) with the definition of the multichannel S matrix,[3] that

$$\mathcal{R} = |S_{\vec{k}_v,\vec{k}^r_v}|^2 = |S_{\vec{k}_s,\vec{k}^r_v}|^2\,, \qquad \mathcal{T} = |S_{\vec{k}_v,\vec{k}^r_s}|^2 = |S_{\vec{k}_s,\vec{k}^r_v}|^2, \tag{7}$$

where $\vec{k}^r_v$ ($\vec{k}^r_s$) are the momenta of the reflected parts of $\Psi^{(+)}_{\vec{k}_v}$ ($\Psi^{(+)}_{\vec{k}_s}$) and

$$S_{\vec{k}_i,\vec{k}_j} \equiv \langle \varphi_{\vec{k}_i} | S | \varphi_{\vec{k}_j} \rangle\,. \tag{7a}$$

The unitarity of the S matrix is simply equivalent to the flux conservation relation

$$\mathcal{R} + \mathcal{T} = 1. \tag{7b}$$

Let us recall one more definition: A channel is said to be open when waves can propagate in this channel. Here, for example, the vacuum channel is open, for a one-dimensional system, for energies $\omega > E$.[4] Below its threshold E, only the solid channel is open; scattering reduces to total reflection.

We will make use of the following general results,[3] which are concerned with the energy variation of the S-matrix elements (or, equivalently, scattering cross sections) close to the thresholds corresponding to the opening of new channels. Let ω_α be such a threshold, for channel α, and let i label the other channels which are open in the energy range $\omega \sim \omega_\alpha$ (here $\alpha \equiv v$, $i \equiv s$). Two cases occur:

(a) *Channel scattering potential is short ranged (no Coulomb part).* Then close to ω_α,

$$|S_{\vec{k}_i,\vec{k}_\alpha}|^2 \quad \text{and} \quad |S_{\vec{k}_\alpha,\vec{k}'_\alpha}|^2$$

(which are zero for $\omega < \omega_\alpha$) vary, for $\omega > \omega_\alpha$, as (const) $(\omega - \omega_\alpha)^{1/2}$. $S_{\vec{k}_\alpha,\vec{k}'_\alpha}$ characterizes scattering inside the new channel (here, vacuum-vacuum reflection). Also,

$$|S_{\vec{k}_i,\vec{k}_{i'}}|^2 \begin{cases} \sim C_>(\omega-\omega_\alpha)^{1/2} + G_{ii'}(\omega), & \omega > \omega_\alpha \\ \sim C_<(\omega_\alpha-\omega)^{1/2} + G_{ii'}(\omega), & \omega < \omega_\alpha. \end{cases} \tag{8}$$

$G_{ii'}(\omega)$ is a function of ω which is regular at ω_α.

The constants $C_>$ and $C_<$ are in general different; each of them may be either positive or negative (or, accidentally, zero). Their values and signs depend on the details of the system, and can be calculated only by completely solving the specific scattering problem at hand. The corresponding scattering cross sections (here, reflection or transmission coefficients) therefore exhibit vertical structures with infinite slope and either cusp or rounded step shapes (Fig. 1).

(b) *Potential contains an attractive Coulomb part.* This is precisely what occurs in the case of electron emission because of the image potential. In this case, all of the $|S_{\vec{k},\vec{k}'}|^2$ have finite discontinuities at $\omega = \omega_\alpha$.

The above results are completely general in the case, considered in scattering theory, where the free channel waves correspond to propagation of a free particle in the vacuum. In the case that we are studying here of scattering into a condensed medium, one must be slightly more cautious and note the following fact: Results (a) and (b) quoted above hold if and only if close above the threshold ω_α of the opening channel the flux ϕ_α transmitted into that channel has the form[3]

$$\phi_\alpha = \text{const}\ (\omega - \omega_\alpha)^{1/2}|A|^2\ , \tag{9}$$

where A is the scattering amplitude for the process considered, and is regular at the threshold. That is, the current j_α carried by the α-channel state of energy ω must be proportional to $(\omega - \omega_\alpha)^{1/2}$ close to ω_α. We will define as well behaved a threshold at which this condition is fulfilled. It is clear that all ω_α's are well behaved in the standard situation of scattering theory, where $j_\alpha \propto k_\alpha = [(2m_\alpha/\hbar^2)(\omega - \omega_\alpha)]^{1/2}$, while when free channel states correspond to excitations in a condensed medium one must check in detail on the nature of the thresholds. This will be discussed in Secs. II and IV.

In the case of the simple two-channel model depicted above, there is one single threshold, E. It corresponds to the opening of the vacuum channel, and is therefore well behaved. Then results (a) and (b) simply amount to stating that for a one dimensional system (i) the transmission coefficient for uncharged particles increases as $(\omega - E)^{1/2}$ close to the vacuum level, and (ii) the transmission coefficient for charged particles jumps, at $\omega = E$, from zero to a finite value. These results hold whatever the details of the short-range part of the surface potential. Result (ii), in particular, is of importance in the study of the thermionic effect.[5]

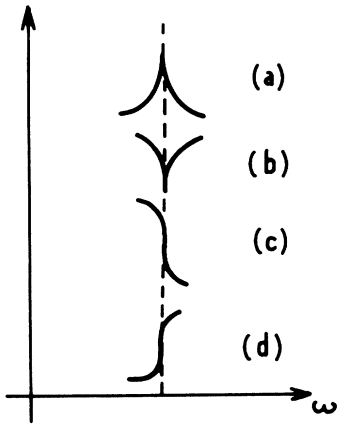

FIG. 1. (a), (b) Cusp and (c), (d) rounded step non-Coulombian singularities of transmission or reflection coefficients.

III. TRANSMISSION INTO CRYSTAL

As we will now see, the threshold effects in the case of solids derive from the band structure of the energy spectrum. Therefore, as a first-order approximation we will completely neglect interactions in the solid. That is, we assume that ω lies in a range where self-energy effects are negligible, so that the potential in the "solid Hamiltonian" reduces to the local periodic term $V_s(\vec{r})$.

Let us now come back to discuss the simplifying assumption that the Hamiltonian $H_{s,\omega}$ of Eq. (5) corresponds to only one solid channel. As we shall now see, this is actually not true in general. Indeed, owing to the periodic atomic structure, when an electron wave falls on a crystal (which we assume to be perfect with a perfect plane surface), it is partly specularly reflected, and partly back-diffracted (which gives rise to the low-energy-electron diffraction pattern). For the same reason, it gives rise, inside the solid, not only to the ordinary refracted wave, but also to a superposi-

tion of this and other, diffracted, transmitted waves. Moreover, as has been analyzed in detail by Stern, Perry, and Boudreaux,[6] there also appears, both in the vacuum and in the solid, a quasi-infinite number of evanescent waves. This is easily found in the simplest model (independent electrons and steplike surface potential) by mere inspection of the matching equations which must be satisfied by the wave function at the surface.

Equivalently, this result follows from the nature of the energy spectrum of electrons in a crystal. As developed in Ref. (6), the dispersion relation $\omega = \epsilon(\vec{k})$ for a band spectrum can be considered, in the reduced zone scheme, as a multivalued function, each sheet corresponding to a given band. When an electron is sent onto the solid, with given energy ω and direction (θ, ϕ)(given parallel momentum $\vec{k}_{\parallel}$ at infinity in vacuum), ω is conserved in the transmission process, and $\vec{k}_{\parallel}$ is conserved up to a vector $\vec{G}$ of the reciprocal surface lattice. That is, the reduced parallel wave vector $\vec{k}_{\parallel}^{(r)}$ is conserved, and the incident electron excites as many transmitted waves as there are bands or, equivalently, sheets of the $\epsilon(k_x, \vec{k}_{\parallel}^{(r)}) - \omega = 0$ surface. Of course, only a few of the corresponding values of k_x are real; most (even possibly all, in case of total reflection) transmitted waves are evanescent. Real solutions for k_x occur in pairs, corresponding to waves travelling towards and from the surface. Obviously, only those with a negative x component of the group velocity $v_{gx} = \partial/\partial k_x\, \epsilon(\vec{k})$ are of interest in our problem.

The transmission problem thus reduces, in the reduced zone scheme, to a one-dimensional scattering, where the occurrence (or disappearance) of a new diffracted travelling wave (i.e., new real value of k_x) appears as the opening (or closing) of a new channel. The points at which a new pair of real solutions of the $\omega - \epsilon(k_x, \vec{k}_{\parallel}^{(r)}) = 0$ equation appears or disappears we shall define as "diffraction thresholds." Their positions, of course, depend on the kind of experiment that is performed (e.g., scanning ω at constant $\vec{k}_{\parallel}$, scanning incidence angle at constant ω, etc.). They appear as thresholds in the variable ξ ($\xi \equiv \omega$, θ, ϕ, ...) which is scanned in the experiment.

In order for these to be well-behaved thresholds in the sense of multichannel scattering theory, one more condition must be satisfied: Close above the threshold point, the x component of the current carried by the electronic excitation in the new channel, $j_x^{(\alpha)}$, must vary as $|\xi - \xi_\alpha|^{1/2}$. Since the channel functions are Bloch functions, the current $j_x^{(\alpha)}$ is simply the group velocity $v_{gx}^{(\alpha)}$. Therefore a well-behaved threshold implies a $|\xi - \xi_\alpha|^{1/2}$ behavior of $v_{gx}^{(\alpha)}$ near $\xi = \xi_\alpha$. This is most generally the case, the only exception occurring when the threshold corresponds to a conic point of the $z = \epsilon(\vec{k})$ hypersurface.

Let us first prove this statement in the simple (although not very realistic, experimentally) case where ω is varied at constant $\vec{k}_{\parallel}$. For a given ω, the possible values of k_x in the solid correspond to the intersections of the various sheets of the surface of constant energy $\omega = \epsilon(\vec{k})$ with the straight line $\vec{k}_{\parallel} = \vec{k}_{\parallel}^{(r)} = \text{const}$. A diffraction threshold is reached for each value ω_α of ω at which the line becomes tangent to the surface, at a point $\vec{k}^{(\alpha)} \equiv (\vec{k}_{\parallel}^{(r)}, k_x^{(\alpha)})$, where $v_{gx}^{(\alpha)} = 0$. (Of course the tangent may also intersect the surface.) For $\omega \simeq \omega_\alpha$, the double intersection at $k_x^{(\alpha)}$ evolves into two distinct intersections $k_{x1}(\omega)$ and $k_{x2}(\omega)$, which are either real or imaginary, depending on the sign of $\omega - \omega_\alpha$ (see Fig. 2). Let k_{x1} be the real intersection at which $v_{gx} < 0$. $v_{gx}(k_{x1}, \vec{k}_{\parallel}^{(r)})$ is easily calculated by developing $\epsilon(\vec{k})$ in the vicinity of $\vec{k}^{(\alpha)}$. It is found that

$$v_{gx}(k_{x1}, \vec{k}_{\parallel}^{(r)}) \simeq -2\left(\frac{\partial^2 \epsilon}{\partial k_x^2}\bigg|_{\vec{k}=\vec{k}^{(\alpha)}} (\omega - \omega_\alpha)\right)^{1/2} . \quad (10)$$

Therefore on the open-channel side of the threshold which is defined by

$$\mathrm{sgn}(\omega - \omega_\alpha) = \mathrm{sgn}\left(\frac{\partial^2 \epsilon}{\partial k_x^2}\bigg|_{\vec{k}=\vec{k}^{(\alpha)}}\right),$$

v_{gx} does have the wanted square-root behavior. This holds provided that $\epsilon(\vec{k})$ can be expanded in power series around $\vec{k}^{(\alpha)}$, i.e., that $\vec{k}^{(\alpha)}$ is a regu-

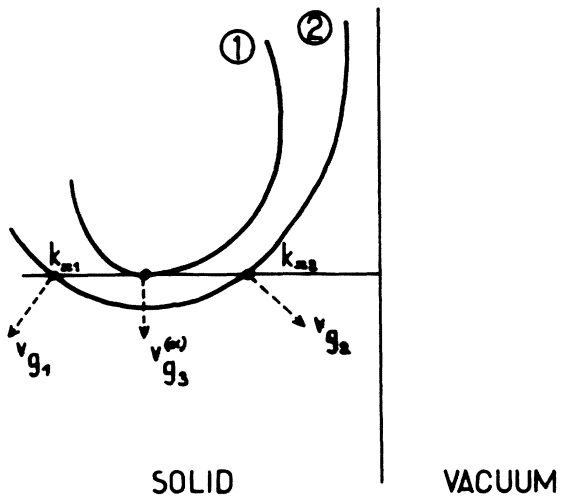

FIG. 2. Intersections between the $\vec{k}_{\parallel} = \vec{k}_{\parallel}^{(r)}$ line and surfaces of constant energy $\omega = \epsilon(\vec{k})$. Surface (1) corresponds to a transmission threshold $\omega = \omega^{(\alpha)}$ and surface (2) to an energy ω close to ω_α. Intersection k_{x1}, for which $v_{gx} < 0$, defines the wave transmitted into channel α.

lar rather than a conic point of the dispersion hypersurface.[7]

Analogous geometrical analyses can be made for the other possible experimental situations [variable ω, constant θ, ϕ; variable $\theta(\phi)$, constant ω and $\phi(\theta)$]. It is found that in all situations, close to the threshold ξ_α, on the open-channel side, provided that $\epsilon(\vec{k})$ is regular around the corresponding $\vec{k}^{(\alpha)}$ point, $v_{gx} \cong C_\xi |\xi - \xi_\alpha|^{1/2}$. The proportionality constant C_ξ depends both on the geometrical properties of the surface of constant energy at point $\vec{k}^{(\alpha)}$ and on the nature of the scanning parameter ξ.

In the foregoing discussion we have concentrated on transmitted waves. Quite obviously, the same analysis can be repeated for reflected waves. To each possible vector $\vec{G}$ of the surface reciprocal lattice corresponds a possible reflection channel and an associated threshold. This may look at first sight somewhat paradoxical, since reflected waves propagate in the vacuum, as does the incident wave. However, since in the reflection process $\vec{k}_\parallel$ is changed into $\vec{k}_\parallel + \vec{G}$, the transverse energy, which is the energy relevant to the one-dimensional reduced scattering problem, is shifted by $(\hbar^2/2m)[\vec{k}_\parallel^2 - (\vec{k}_\parallel + \vec{G})^2]$. This shift is finite,[8] and therefore the reflection channel is different from the incidence one, except for specular reflection ($\vec{G} = 0$). It can therefore be concluded that a semi-infinite crystal behaves with respect to reflection and transmission as a regular multichannel scatterer, offering an infinite number of channels for forward (transmission) as well as backward (reflection) scattering, only a few of which are open at the same time.

The generalization of Eqs. (7) is obvious. Let us call $\{i\}$ ($\{\nu\}$) the transmission (reflection) channels which are open in a given situation, (given incidence momentum $\vec{k}$). The partial transmission and reflection coefficients, which measure what fraction of the incident flux is scattered into channel i or ν are defined by

$$\mathcal{T}_i = |S_{\vec{k},\vec{k}_i}|^2, \quad \mathcal{R}_\nu = |S_{\vec{k},\vec{k}_\nu}|^2 , \tag{11}$$

where S is the standard multichannel S-matrix, and they satisfy the unitarity condition

$$\sum_i \mathcal{T}_i + \sum_\nu \mathcal{R}_\nu = 1 . \tag{11a}$$

It is now possible, with the help of the general results (a) and (b), to predict the threshold behavior of these coefficients. Obviously, two cases must be distinguished, depending on the structure of the channel scattering potential.

(i) *Reflection channels.* At their thresholds, the transverse kinetic energy in the opening channel (r) (in the reduced one-dimensional scattering problem) is zero. In the reflection region (i.e., the vacuum), the potential contains the image-force Coulomb contribution. These are precisely the conditions required for result (b) to apply. Namely, the new reflection coefficient $\mathcal{R}_r$ starts discontinuously from zero at the threshold value ξ_r of the scanning variable (i.e., when a diffraction spot appears or disappears on the reflection pattern), while the $\mathcal{T}_i$ and other $\mathcal{R}_\nu (\nu \neq r)$ must exhibit, at that point, finite discontinuities.

(ii) *Transmission channels.* At their thresholds, the transverse kinetic energy in the vacuum channels is finite. That is, the Coulomb potential in the vacuum does not induce any singularity (since the Coulomb-induced discontinuous behavior appears at the zero of the Coulomb potential, which is a point of accumulation of bound states). On the other hand, there is no Coulomb potential inside the crystal, i.e., in the transmission region. Consequently, at a transmission threshold ξ_t, the reflection and transmission coefficients behave according to result (1); $\mathcal{T}_t$ increases as $|\xi - \xi_t|^{1/2}$ on the open side of ξ_t, while the $\mathcal{R}_\nu$ and $\mathcal{T}_i$ ($i \neq t$) have cusp or rounded step singularities.

IV. CHANNEL THRESHOLD SINGULARITIES IN PHOTOEMISSION SPECTRA

Now the question naturally arises of the possible observability of the singularities predicted in Sec. III. This would of course be of interest, on one hand, for the study of the transmission process itself, but also, on the other hand, because it should yield information on the band spectra of solids. In particular, do such singularities appear in emission spectra, and how? In order to answer this question, we will now analyze it in the particular case of photoemission.

When the lifetime (or, equivalently, the mean free path) of excitations in the emitter is assumed to be infinite (therefore when, for coherence, inelastic effects are also neglected), the excitation and flow processes responsible for photoemission become separable. This has been proved by Feibelman and Eastman,[9] who have thus shown that, under the above stated ideal conditions, the semiclassical step model[10] is exact. More exactly, in the infinite mean-free-path limit, they find that the photocurrent at energy ω and in the direction $\hat{R}$ (angles θ, ϕ) is given at a distance R from the emitter by [Eq. (17) of Ref. 9]

$$R^2 j_r(\omega,\theta,\phi) = C v(\omega) \sum_{\text{occupied } n} \delta(\omega - E_n - \Omega) \times |\langle \phi_> | \tfrac{1}{2} (\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}) | \psi_n \rangle|^2, \tag{12}$$

where $v(\omega) = [(2/m)(\omega - E)]^{1/2}$ is the velocity in vacuum, C is a numerical constant, n labels the occupied electron states in the crystal at equilibrium, and Ω is the frequency of the photons.

The final-state wave function $\phi_>(\vec{r})$ which appears in the optical matrix element is exactly the ingoing function of scattering $\Psi^{(+)}_{\vec{k}_v}$ defined in Sec. II for $\vec{k}_v = -[(2m/\hbar^2)(\omega - E)]^{1/2}\hat{R}$. That is, $\phi_>$ is the wave function describing an electron incident onto the solid from the vacuum side at energy ω and in the direction (θ, ϕ). As discussed in Sec. II, $\phi_>$ therefore contains, in the vacuum region, an incident and one or several reflected parts, depending on whether some nonspecular reflection channels are open for state (ω, θ, ϕ). Far inside the solid (i.e., at distances from the surface larger than the thickness d of the layer in which the potential is different from that of the perfect bulk crystal) $\phi_>$ is a superposition of purely transmitted Bloch waves:

$$\phi_>(\vec{r}) = \sum_i t_i \varphi^i_{\vec{k}_s}(\vec{r}), \quad x < -d \ , \tag{13}$$

where i labels the transmission channels open for the incident state (ω, θ, ϕ) and the $\vec{k}^i_s$ are the corresponding channel wave vectors ($\vec{k}^i_{s\parallel} = \vec{k}^{(r)}_{\parallel}$, where $\vec{k}^{(r)}_{\parallel}$ is the value, reduced to the first Brillouin zone, of the incident parallel wave vector). The transmission amplitudes t_i are related to the partial transmission coefficients by

$$\mathcal{T}_i = (v^{(i)}_{gx}/v^{(0)}_{gx})|t_i|^2 \ , \tag{14}$$

where $v^{(0)}_{gx} = v(\omega)\cos\theta$ is the x component of the group velocity of the incident electron and the $v^{(i)}_{gx}$ are the group velocities along $\hat{x}$ of the "channel states" $\varphi^{(i)}_{\vec{k}_s}$. At that stage, one does not seem to recover from Eq. (12) the step model, since j_r does not appear as the sum of contributions of all possible optical transitions, weighted by the corresponding transmission coefficients, but as due to optical excitation into the single coherent superposition of final states described by Eq. (13). (In other words, it seems *a priori* that j_r measures not a sum of intensities but the square of a sum of amplitudes.) However, it is shown in Ref. 9 that in the long-mean-free-path limit, in spite of the presence of the perturbed surface layer, the matrix element of expression (12) imposes that, as in a bulk crystal, the electron momentum—which is of course the momentum inside the solid—must be conserved in the optical transition. This reduces considerably the number of final states which can contribute to the photocurrent. Feibelman and Eastman then rightly argue that owing to the selection rule in general only at most one of the $\varphi^{(i)}_{\vec{k}_s}$ of Eq. (13) gives a nonzero contribution. In that case, the step model is recovered, with either none or one final state that we will call $\varphi^{(j)}_{\vec{k}_s}$ contributing to $j_r(\omega, \theta, \phi)$. In the directions of emission,

$$j_r(\omega,\theta,\phi) \sim |t_j|^2 |M_{nj}|^2, \tag{15}$$

where M_{nj} is the optical matrix element between initial and final Bloch states φ_n and $\varphi^{(j)}_{\vec{k}_s}$.

In practice, the shape of the emission pattern at energy ω can be obtained with the help of the following geometrical construction: (i) Draw the surfaces of constant energy S_ω(surface $\epsilon(\vec{k}) = \omega$ in the reduced $\vec{k}$ space) and $S_{\omega-\Omega}$; (ii) build the curve C of intersection between S_ω and $S_{\omega-\Omega}$ (C is in general a skew curve); (iii) build the projection P_C of C on the plane of the surface and the projection cylinder $\mathcal{C}$ based on P_C parallel to the x-axis; (iv) build all of the cylinders $\mathcal{C}_i$ obtained from $\mathcal{C}$ by all translations $\vec{G}_i$ of the reciprocal surface lattice of the solid; (v) the angular photocurrent pattern is given by the (warped) cone(s) of apex $\vec{k} = 0$ based on the curve of intersection, C_{vac} of the various $\mathcal{C}_i$ with the half-sphere Σ defined by $\vec{k}^2_{\parallel} + k^2_x = 2m/\hbar^2(\omega - E)$, $k_x > 0$.

Note that the projected emission curve P_C may have, accidentally, double points. If such is the case, at these points two $\varphi^{(i)}_{\vec{k}_s}$ contribute to j_r, which at the corresponding (θ, ϕ)'s is given not by (15) but by more general expression [Eqs. (12) and (13)] including interference effects.

In order to know whether threshold singularities may manifest themselves in the energy and angular distribution of photocurrent, let us consider the following experimental set up: ω is kept constant, and $j_r(\omega, \theta, \phi)$ is measured *along the emission pattern* [i.e., the detection angles θ, ϕ are varied with the constraint $\phi = f_\omega(\theta)$ provided by the equation of the emission cone]. When these conditions are fulfilled, the transmission channel j is, by definition, open. But, besides this, other transmission[11] (i) or nonspecular reflection (ν) channels may also be open for some values of (θ, ϕ). When θ and ϕ are scanned along the emission pattern, these other channels may close, at threshold points $\xi_{i(\nu)} \equiv [\theta_{i(\nu)}, \phi_{i(\nu)} = f(\theta_{i(\nu)})]$. Since at these points $v^{(j)}_{gx}$ and $v^{(0)}_{gx}$ are regular, $|t_j|^2$ has singularities of the same nature as those of $\mathcal{T}_j$, and so does j_r. That is, one should be able to detect two types of singularities of j_r along the constant-ω emission cones: at transmission thresholds ξ_i, vertical singularities (cusps or

rounded steps) exist; at reflection thresholds ξ_ν, discontinuities exist.

The thresholds, if they exist for a given ω, are again best defined geometrically. Consider the intersection of the cylinder $\mathcal{C}$ with the surface of constant energy S_ω. If $\mathcal{C}$ cuts S_ω at points other than those belonging to C, there are for a given direction of emission $(\omega, \vec{k}_{\parallel}^{0})$ as many other transmission channels open $(i \neq j)$ as there are intersections of the line $\vec{k}_{\parallel} = \vec{k}_{\parallel}^{0(r)}$ with S_ω not belonging to C and having $v_{gx}^{(i)} < 0$. The threshold ξ_i of such a nonphotoemitting transmission channel is reached when and if, as θ and ϕ vary along the emission cone, the $\vec{k}_{\parallel} = \vec{k}_{\parallel}^{0(r)}$ line becomes tangent to S_ω, out of curve C, i.e., when the cylinder $\mathcal{C}$ merges out of S_ω. Nonspecular reflection thresholds ξ_ν, analogously, correspond to the points where one of the $\mathcal{C}_i$ merges out of the free-electron-half sphere Σ.

Therefore it appears that threshold effects of the two types (vertical slope and discontinuity) should appear on the angular distribution of the photocurrent at constant energy, at least in particular ranges of values of final-state energy ω. They should correspond to values (ω, θ, ϕ) of the detection parameters at which, when following the emission cone, one spot appears or disappears either on the transmission or the reflection electron diffraction pattern.

Of course, this result holds as such only if, as we have assumed, electronic excitations at the final energy ω have a mean free path much larger than atomic distances. If this condition is not fulfilled, it breaks down for two different reasons:

(i) As discussed in Ref. 9, the elastic current is no longer given by the step-model expression. Indeed, owing to interaction effects, the only region which now contributes effectively to the matrix element of Eq. (12) is the elastic extraction layer, of thickness $\delta \simeq l$ (one can say that $\phi_>$ now decays on a length l). In that region, $\phi_>$ is no longer given by its asymptotic expression (13), so that j_r is no longer expressible in terms of transmission coefficients.

(ii) Moreover, if excitations in the solid have a finite lifetime τ, the general results (a) and (b) of Sec. II about threshold behavior are modified. This is readily understandable; a finite lifetime means that the self-energy part $\Sigma_\omega(\vec{r}, \vec{r}')$ of the potential in the pseudo-Hamiltonian H_ω of Eq. (3) now has a nonzero imaginary part. H_ω is no longer Hermitian, and consequently the S matrix on the energy shell is no longer unitary. Unitarity is recovered only in its less restrictive form including contributions, off the energy shell, of final states involving more than one particle. In other words, when an electron is sent on the solid, part of it is scattered elastically, and part, because of interaction processes, inelastically, the energy balance being provided by some excitation of the electrons of the solid. In emission processes, this corresponds to the existence of the so-called inelastic current. This of course affects the threshold behavior of the elastic transmission and reflection coefficients. One shows[3] that as can be expected the singularities are smoothed out and spread on a width $\Delta\omega \sim \hbar/\tau$.

For all of these reasons, one cannot hope to observe any threshold singularity in the range of values of ω characteristic of far-uv photoemission and low-energy-electron diffraction experiments (typically $15 \lesssim \omega - E \lesssim 50$ eV) where $l(\omega)$ is at most of atomic order. The x-ray range, $\omega - E \gtrsim 1$ keV, where scattering effects due to the surface potential are very small, is not suitable either. Finally, it is at the small values of $\omega - E$ typical of visible or near-uv photoemission that the singularities of $j_r(\omega, \theta, \phi)$ should be narrow enough to become observable. Since, in that regime, $l(\omega)$ increases when ω decreases, the lowest possible ω are the more favorable. In practice, the best case should be met with those cesiated semiconductors in which, at ω close above the (lowered) photoelectric threshold, an electron cannot decay into pairs, and $l(\omega)$, being limited only by phonon scattering, is much larger than it is at the same energies in metals. Moreover, if these singularities are observed, it will be quite difficult to use them to get detailed information about the band spectrum because of the complexity of the geometrical operation defined above which is necessary to connect them with the surface of constant energy S_ω. This results from a feature characteristic of photoemission itself: owing to the optical selection rule, the population of final states at a given energy ω is highly selective. Therefore it is of interest to search for channel singularities in order to check their existence in angular photoemission spectra, which are presently measured with very good accuracy. In particular, their observation would be a check of the validity and practical applicability of the step model. But it seems that systematic exploitation should be much more fruitful if in the emission process all of the states at the detection energy are equally populated. This situation is met in thermoemission, and the behavior of the angular distribution of the thermoionic current $j_{th}(\omega, \theta, \phi)$ is currently being investigated.

V. EVAPORATION OF He II

Let us now turn to the case of transmission of an atom from the vacuum into the liquid phase of

its own species (the reverse of the evaporation process). In order for a microscopic scattering analysis to be meaningful—especially since we require quasiparticles in the liquid to be well-defined, i.e., long lived—we must restrict ourselves to a quantum liquid. Thus we will consider here only the particular case of superfluid ^{4}He.[12] Let ω and $\vec{k}_{\parallel}$ be the energy and parallel momentum of the atom at infinity in the vacuum. $\vec{k}_{\parallel}$ is now conserved in transmission,[13] which thus reduces to a one-dimensional problem in the x direction. The excitation spectrum of liquid He II is represented on Fig. 3 for the low-temperature case ($T \ll T_\lambda$), where the roton minimum ω_r lies 1.5 °K above the vacuum energy (which, for $T \to 0$ is equal to the latent heat of evaporation L_0). It is immediately seen that while at energies smaller than ω_r only one excitation (a phonon) can propagate in the liquid, for $\omega \gtrsim \omega_r$ three modes (two rotons and one phonon) exist. That is, a double new channel (containing the two roton modes $k < k_r$ and $k > k_r$) opens at $\omega = \omega_r$.

The fact that the position of the threshold does not depend on $\vec{k}_{\parallel}$ results from the particular shape of the roton spectrum, together with the numerical values of L_0 and ω_r. As is shown in Ref. 15, since at energies $\omega \simeq \omega_r$, k_r is much larger than the wave vector in vacuum, the refraction indices for atom-roton and atom-phonon transmission are larger than 1. In particular, roton waves can propagate as soon as rotons exist, whatever the direction of incidence in vacuum.

Of course, owing to the zero slope of the $\epsilon(k)$ curve at (ω_r, k_r), the group velocity close to the threshold varies as $(\omega - \omega_r)^{1/2}$. However, the analysis of the threshold behavior is slightly more subtle than in the case of crystals. Indeed, the existence of the roton minimum does not derive from a one-body potential effect, but results from the interaction between ^{4}He atoms. That is, the $\Sigma_{s,\omega}$ real self-energy term of the pseudo-Hamiltonian [Eq. (5)] is by no means negligible.[16] The excitations we are dealing with are quasiparticles, so that the current carried by an excitation of momentum $\vec{k}$ is $\vec{k}/M$, where M is the mass of the bare atom, and not its group velocity $\vec{v}_g(\vec{k})$. (The difference represents the backflow current associated with the presence of the "dressing cloud"[17]). Therefore, close above the roton threshold, the current carried by a *single* roton is not $\sim(\omega - \omega_r)^{1/2}$, but finite and of magnitude $\sim k_r$. Thus it could seem at first sight that the roton minimum is not a well-behaved scattering threshold in the sense defined in Sec. II.

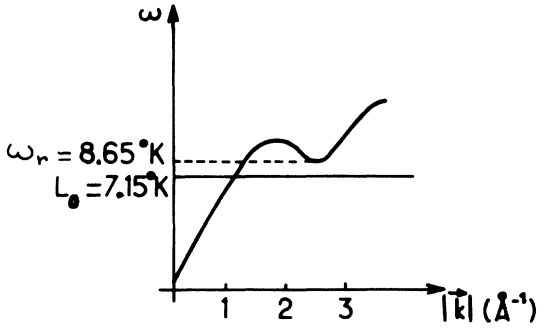

FIG. 3. Dispersion curve for quasiparticles in superfluid ^{4}He below T_λ. L_0 is the heat of evaporation of the liquid.

However, one must keep in mind the following fact: In the limit of energies close above ω_r, roton states can be excited only in pairs. Indeed, for example, in the transmission situation considered above, for a given value of $\vec{k}_{\parallel}$, there are two roton states available in the liquid, namely, those with a negative x component of the group velocity. They correspond to transverse momenta

$$k_{x1} \cong (k_r^2 - k_{\parallel}^2)^{1/2} + B(k_{\parallel})(\omega - \omega_r)^{1/2},$$
$$k_{x2} \cong -(k_r^2 - k_{\parallel}^2)^{1/2} + B(k_{\parallel})(\omega - \omega_r)^{1/2}, \tag{16}$$

where

$$B(k_{\parallel}) = [(2\mu_r/\hbar^2)k_r^2/(k_r^2 - k_{\parallel}^2)]^{1/2}$$

and μ_r is the roton mass.

The flux transmitted into the opening double-roton channel is therefore, to lowest order in $(\omega - \omega_r)$,

$$\phi_{\text{rot}} = (k_{x1} + k_{x2})|A(\omega_r, k_{\parallel})|^2, \tag{17}$$

where the scattering amplitude A is the same for the two modes since to lowest order it must be calculated at the minimum itself. Finally, using Eq. (16), it is seen that $\phi_{\text{rot}} \sim C(k_{\parallel})(\omega - \omega_r)^{1/2}$, and owing to the compensation between the two roton branches, ω_r appears as a regular well-behaved threshold.

Since there is no Coulomb potential present, transmission and reflection coefficients behave close to ω_r according to result (a). The atom-roton transmission coefficient, for $\omega \gtrsim \omega_r$, increases from zero as $(\omega - \omega_r)^{1/2}$, while the atom-phonon transmission and atom-atom reflection coefficients must have the cusp or rounded step singularities predicted by Eq. (8).

Let us consider the (ideal) experimental situation of evaporation of the liquid at temperature T ($\ll T_\lambda$) into the vacuum and study how, in that case, the roton threshold singularity may be

pictured in the evaporation spectrum. If one neglects interactions between quasiparticles, again the excitation and flow processes separate simply in the expression of the current. Indeed, a microscopic formal calculation of the current based on the same techniques as those used in the theory of tunneling shows that the kinetic model applies[18] even in the presence of nonlocal self-energy (pseudopotential) in the liquid phase, provided this is assumed real; namely, the energy distribution of the total current is given by

$$j(\omega) = C f_l(\omega) \int d^2k_{\parallel} [1 - R(\omega, k_{\parallel})] , \qquad (18)$$

where C is a numerical constant and $f_l(\omega)$ is the thermal occupation function in the liquid. $R(\omega, k_{\parallel})$ is the specular reflection coefficient for a ^{4}He atom incident onto the liquid from the vacuum side with energy ω and parallel momentum $\vec{k}_{\parallel}$.[19] Of course, R can be expressed immediately in terms of the partial transmission coefficients into the channels which are open in the $(\omega, \vec{k}_{\parallel})$ situation of incidence,

$$1 - R(\omega, k_{\parallel}) = \sum_{\text{open } i} \mathcal{T}_i(\omega, k_{\parallel}). \qquad (19)$$

As we have seen in Sec. II B, for energies ω close to the roton minimum ω_r the phonon channel is always open. The roton channels open, whatever $\vec{k}_{\parallel}$, at $\omega = \omega_r$. Consequently, close above (below) ω_r,

$$1 - R(\omega, k_{\parallel}) = G_r(\omega, k_{\parallel}) + C_{><}(k_{\parallel})(\omega - \omega_r)^{1/2}. \qquad (20)$$

That is, $j(\omega)$ must exhibit a vertical singularity at ω_r (cusp or rounded edge). This result, which contradicts previous predictions based on an approach inspired by Bardeen's tunneling Hamiltonian, was first derived[15] from a direct microscopic approach. This calculation relies on the assumptions that the self-energy in the liquid phase is local in the surface region, and that the liquid density has there a steplike shape. The present approach shows that the result is not an artifact of these approximations, but an exact consequence of the structure of the ^{4}He energy spectrum. Lifetime effects, as were discussed in Sec. IV, result in a broadening of the structure.[15] Note that since the threshold of the roton channel is independent of $k_{\parallel}$ it is not necessary, contrary to what occurs with solids, to study the angular distribution of the current to observe the associated singularity.

The ideal experiment considered above, in practice, cannot be realized as such, nor, it seems, could be the also ideal experiment analogous to tunneling in solids, this would consist of pumping on the gas so as to maintain a constant pressure p smaller than that of the saturating vapor and measuring the rate of flow in the pump! Present evaporation experiments[20] use a heat pulse as the excitation, so that the relevant population factor is no longer $f_l(\omega)$ but a quantity characterizing the pulse and the thermalization processes in the liquid, which is, to a large extent, unknown. There is much more hope of observing the predicted threshold singularity if one may perform experiments with excitations of definite and known energy. This is realized in the recent reflection experiments of Edwards *et al.*[14] These confirm the absence of the enhancement of transmission ω_r predicted by earlier theories, but in order to check on the presence (or absence) of a vertical slope singularity a more detailed study of the roton-minimum region is needed.

VI. CONCLUSION

In conclusion, studying channel threshold singularities in emission spectra of ^{4}He and of solids should be of interest as a first step for a better understanding of transmission processes and, later, as a possible tool in the study of energy spectra. Although such singularities have been observed mostly in particle physics, one case exists in solid-state physics where this phenomenon has been observed and interpreted.[21] The optical reflectivity of CdS exhibits a cusp owing to a threshold in the polariton spectrum. This gives good hope for the observability of the roton and diffraction thresholds which have been described in this paper.

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[1] When $V(-\infty)$ is not a constant but a periodic function (or when, as in ^{4}He, interaction effects do not reduce to a one-body potential), the quantity $V(\infty) - V(-\infty)$ should be replaced by $E - \epsilon$, where ϵ is the energy, in the bulk solid or liquid, of the excitation of zero momentum.

[2] Moreover, here the two different channels correspond to different regions of the geometrical space, while in usual multichannel scattering various channels correspond to different "regions" of the Hilbert space of the particle plus target system.

[3] See, for example, R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw Hill, New York, 1966), Chaps. 16 and 17; L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Nonrelativistic Theory* (Pergamon, Oxford, 1958), p. 565.

[4]For a two- or three-dimensional system, if transmission conserves the component $\vec{k}_{\parallel}$ of the momentum parallel to the surface, the vacuum channel opens, for electrons of parallel momentum $\vec{k}_{\parallel}$, at $E+\hbar^2 k_{\parallel}^2/2m$. The general case, where $\vec{k}_{\parallel}$ is not conserved, will be discussed below.

[5]A. K. Bhattacharjee, B. Caroli, and D. Saint-James, J. Phys. (to be published).

[6]R. M. Stern, J. J. Perry, and D. S. Boudreaux, Rev. Mod. Phys. 41, 275 (1969).

[7]Note that if $\vec{k}^{(\alpha)}$ coincides with a Van Hove analytic singularity [i.e., a saddle point of the $z=\epsilon(\vec{k})$ hypersurface], although the surface of constant energy $\omega_\alpha=\epsilon(\vec{k})=\epsilon(\vec{k}^{(\alpha)})$ degenerates around $\vec{k}^{(\alpha)}$ into a cone, $\epsilon(\vec{k})$ has a regular power expansion around $\vec{k}^{(\alpha)}$, and the threshold is well behaved.

[8]Accidental degeneracy may occur when one works at constant $\vec{k}_{\parallel}$. If $\vec{k}_{\parallel}^2=(\vec{k}_{\parallel}+\vec{G})^2$, the $\vec{G}$ channel is the same as the incidence one.

[9]P. J. Feibelman and D. E. Eastman, Phys. Rev. B 10, 4932 (1974).

[10]W. E. Spicer, Phys. Rev. 112, 114 (1958).

[11]These correspond to states which would contribute to emission into direction (θ,ϕ) if they were populated, but which cannot be populated by the photon excitation since they do not satisfy the optical selection rule.

[12]The case of ^{3}He is much less favorable, since the roton part of the spectrum is considerably broadened by interaction with the pair continuum.

[13]This implies that the surface is a perfect plane, i.e., that ripplon effects are negligible. That assumption is substantiated by the experimental results of Edwards *et al.*, Ref. 14.

[14]D. O. Edwards, P. Fatouros, G. G. Ihas, P. Mrozinski, S. Y. Shen, F. M. Gasparini, and C. P. Tam, Phys. Rev. Lett. 34, 1153 (1975).

[15]C. Caroli, B. Roulet, and D. Saint-James, preceding paper, Phys. Rev. B 13, 3875 (1976).

[16]The presence of a real self-energy term necessarily implies an associated imaginary lifetime term. However, as is discussed in Ref. 15, in the range of energy that we consider here ($\omega\sim\omega_r$) this can be reasonably, at least as a first approximation, neglected.

[17]See, for example, P. Nozières, *Le Problème à N Corps*, (Dunod, Paris, 1963), p. 5.

[18]B. Caroli and D. Saint-James (unpublished).

[19]Such a kinetic expression has also been used by M. W. Cole [Phys. Rev. Lett. 28, 1622 (1972)] to study He II evaporation. However, that reference does not take properly into account the energy variations of the transmission coefficients.

[20]K. Andres, R. C. Dynes, and V. Nayaramurti, Phys. Rev. A 8, 2501 (1973); S. Balibar, Phys. Lett. A 51, 455 (1975).

[21]J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).