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Bulk and surface diffusion of heavy particles in metals: A path-integral approach

F. Sols
Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
*and Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801**

F. Guinea
Departamento e Instituto de Fisica del Estado Solido, Universidad Autónoma de Madrid, 28049 Madrid, Spain

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The dynamics of a particle interacting with the electrons of a metal and moving through a lattice has been investigated. A scaling scheme based on a path-integral formulation of the problem is given which is valid for a wide range of couplings. We obtain numerical estimates for the importance of the coupling for charged particles moving within the bulk of metals or at their surfaces. Particles of charge one have couplings which lie below the threshold for self-trapping, although their values are large enough to ensure a significant influence on their dynamics at low temperatures. Finally, it is shown that a transition to a self-localized situation is in principle possible, and may be of relevance to situations where the screening cloud is slow enough as compared with the dynamics of the external particle.

INTRODUCTION

The motion of a heavy particle interacting with the electrons in a solid has always attracted a great deal of attention, both from the experimental and the theoretical point of view. For a sufficiently massive particle at high temperatures a classical approach is sufficient, and an effective friction coefficient can be defined to account for the dissipative processes associated with the interaction. At low enough temperatures we expect quantum effects to be important for such light particles as positrons, muons, or protons. Indeed, such a crossover towards behavior can be seen in a variety of experiments.[1-7] However, we also expect the polarization interaction to induce significant deviations from the well-known properties of a single quantum particle in an external potential. From a theoretical point of view, the inclusion of the interaction with the surrounding electronic medium presents severe complications. It is well known that models of a localized dynamical impurity interacting with an electron gas are plagued by infrared divergences when analyzed by conventional perturbation theory.[8] These difficulties can be overcome by appropriate scaling procedures. An independent approach to dealing with the quantum-mechanical properties of a single degree of freedom interacting with a dissipative environment has been introduced to study rather different systems, namely, the quantum properties of such macroscopic devices as superconducting quantum interference devices (SQUID's) and Josephson junctions.[9,10] Similarly to the dynamical impurity problem mentioned before, infrared singularities appear, which lead to nontrivial results such as self-localization beyond a given value of the friction coefficient and related phenomena..[11-16] In the present paper we will treat the problem of a particle interacting with an electronic (metallic) system by first integrating out the coordinates of the electrons. That leads to an effective problem to be analyzed within the path-integral formalism (second approach discussed earlier), which we will then treat by scaling methods (first approach) to obtain information about the dynamical properties of the particle under consideration.[17] As in other models analyzed in the literature, we find a transition to a self-localized state when the coupling to the electrons exceeds a given threshold. This result, however, also depends crucially on the relative time scales of the screening process and the diffusion of the particle. Only for "slow" screening, that is, when the cloud which inhibits the motion of the particle is built up of very-low-energy electron-hole pairs, can this transition take place (see Ref. 18 for a careful treatment of this point). Following the presentation of the method, we will discuss different choices of couplings and make numerical estimates of the values in various cases of practical interest, like charged particles within simple metals or at surfaces. It will be shown that coupling of particles of charge one lies close to the critical value for a localization transition. Details of the approximations involved and comparisons with other theoretical[19,20] approaches will be given along with the method and the results. We mention, in particular, Ref. 21, which follows a scheme close to the one presented here.

THE METHOD

The Hamiltonian of a particle interacting with an electron gas can, in general, be written as

$$H=\frac{P^2}{2M}+V(\mathbf{R})+\int v(|\mathbf{R}-\mathbf{r}|)\rho(\mathbf{r})d\mathbf{r}+H_0 , \tag{1}$$

where $\mathbf{P}$ and $\mathbf{R}$ are the coordinates of the particle, M is its mass, and we assume that the particle couples to local fluctuations in the electronic density via the potential v. Thus $\rho(\mathbf{r})$ is an operator which describes the charge density of the electron gas, and which can be written in terms of electronic creation and annihilation operators, in the language of second quantization. The choice of coupling in (1) ensures translational symmetry, and H_0 describes the electronic system, and can also include interactions between the electrons. The form of $v(r)$ depends on the type of coupling to be considered. For the case of charged particles it is the Coulomb potential, but other choices, such as dipolar or multipolar couplings for neutral particles, or even short-range contact potentials, can also be considered.

In order to define an effective action for the external particle we will closely follow the procedure outlined in Ref. 17. We can formally write an expansion of the path integral for the whole system in powers of the coupling potential v, as shown in Fig. 1. All those diagrams which only have self-energy insertions decoupled among themselves, such as Figs. 1(a), 1(b), and 1(c), can be resumed and expressed as an exponential of the simple graph 1(a). This is the lowest term in a cluster expansion. Higher-order terms, such as 1(d), are left out at this order. We are interested in the low-energy behavior of the external particle, which should be determined by the leading long-time dependence of the graphs shown in Fig. 1. From purely phase-space arguments, it can be shown that the diagrams which are associated with the creation of a single electron-hole pair should have a linear dependence on ω as $\omega\rightarrow 0$. Those which involve the coherent excitation of two or more pairs depend on the corresponding convolution of the density of pairs at small frequencies, leading to higher powers of ω and retarded interactions which decay faster in time.

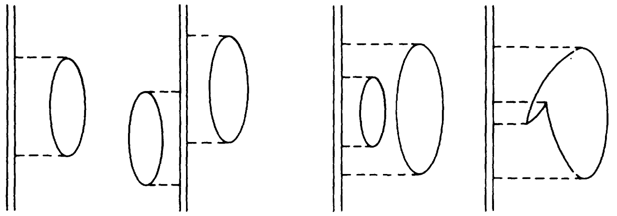

FIG. 1. Some diagrams appearing in an expansion of the path integral of the particle in powers of the coupling to the electrons. Double solid lines are the propagators of the particle, while single solid ones denote electron and hole propagators. Diagrams (a), (b), and (c) contribute to the leading terms at long times of the effective action, and are included in the scheme discussed in the text. Diagram (d) is not included in our calculation.

It is worth comparing this procedure with previous work on impurities hopping between two sites and interacting with the electron gas. The diagrammatic expansion presented in this work resembles most closely the scheme outlined in Ref. 18 (note that there the diffusion problem is treated as a succession of hops between nearest neighbors). If we neglect the momentum dependence of the coupling potential, and replace it with an effective contact potential, we obtain the same results as when using a bosonization approach.[22] On the other hand, by treating the path integral with the Nozieres–de Dominici scheme, the square of the potential obtained here is replaced by a phase shift at the Fermi level.[23,24] The appearance of this phase shift seems to imply that this procedure goes beyond linear-response theory, but it can be ascribed to the indefiniteness of a δ potential acting on the electrons at the Fermi level. This potential can only be defined within a given regularization procedure. The most commonly used ones give rise to the above-mentioned phase shift, but others reproduce the results obtained within linear-response theory. This point is discussed in detail in Ref. 22.

An alternative way of reproducing these results for contact potentials is given in Ref. 18, where a method based on the decoupling of creation and annihilation operators is used. To go beyond linear-response theory, the use of Anderson's orthogonality theorem[25] has also been suggested, assuming that the particle and its screening cloud are fixed at different lattice sites.[26–28] This procedure is very appealing, although, as it is not formulated in terms of path integrals, a scaling analysis to leading order is difficult to perform. It is worth noting that a full treatment of the motion in a periodic potential within the Nozieres–de Dominici scheme is not feasible.[21] As a heuristic intermediate approach, we suggest definition of the coupling potential needed to obtain the retarded interactions in terms of phase shifts and functions dependent on the distance traveled by the particle, in such a way as to satisfy Anderson's theorem if the particle is restricted to movement only between two sites.[26–28] Comparisons between this scheme and the linear-response approach discussed before will be given in the next sections.

Finally, it is worth noting that self-interacting effects among the electrons can be included by replacing the pair propagator in Fig. 1 by the corresponding dressed one. Provided that the low-energy behavior of the electronic system can be described in terms of weakly interacting quasiparticles, the analysis presented above of the long-time decay of the propagators should hold, and the leading dependence will come from the dressed counterparts of the diagrams shown in Figs. 1(a), 1(b), and 1(c).

Thus, in order to analyze the dynamics of the particle, we will replace the effects of the coupling to the electrons by the retarded interaction arising from the lowest self-energy diagram, Fig. 1(a). In a formulation in terms of path integrals, this means that we have to weigh each path of the particle by the effective action (in imaginary times)

$$S[\mathbf{R}(\tau)]=\frac{M}{2}\int\left[\frac{\partial\mathbf{R}}{\partial\tau}\right]^2 d\tau+\int V(\mathbf{R}(\tau))d\tau$$
$$+\int d\tau\int d\tau' W(\mathbf{R}(\tau)-\mathbf{R}(\tau'),\tau-\tau') \;, \qquad (2)$$

where the function $W(\mathbf{R},\tau)$ is the Fourier transform of

$$W(k,\omega)=v_k^2\langle\rho_k\rho_{-k}\rangle_\omega \qquad (3)$$

and $\langle\rho_k\rho_{-k}\rangle_\omega$ is the density-density correlation function of the electron gas. As discussed before, this function depends linearly on ω for small values of ω, so that we can approximate $W(\mathbf{R}-\mathbf{R}',\tau-\tau')$ at long times by

$$W(\mathbf{R}-\mathbf{R}',\tau-\tau')\simeq\hbar\frac{f(\mathbf{R}-\mathbf{R}')}{(\tau-\tau')^2} \;, \qquad (4)$$

$$f(\mathbf{R}-\mathbf{R}')=\frac{e^2/\hbar}{(2\pi)^{d+1}}$$
$$\times\int e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')}v_k\frac{\partial}{\partial\omega}\,\mathrm{Im}\,\epsilon^{-1}(k,\omega)\bigg|_{\omega\to 0} d^dk \;, \qquad (5)$$

where we have written the density-density correlation function of the electron gas in terms of the dielectric function (d is the dimension of the space). As discussed in Ref. 17, this effective action shows the same time dependence as that proposed on general grounds to describe the effects of a dissipative environment on a quantum variable. The spatial dependence is different, since $f(R)$ as defined in (5) is always bounded and decays towards zero at long distances; in other treatments $f(R)$ is chosen to be quadratic on R to keep the model as simple as possible. On the other hand, if we expand $f(R)$ for small values of R, we obtain, apart from a numerical constant,

$$\tilde{f}(R)\equiv f(R)-f(0)=\frac{\eta R^2}{4\pi\hbar} \;, \qquad (6)$$

where

$$\eta=\frac{e^2}{(2\pi)^d d}\int k^2 v_k\frac{\partial}{\partial\omega}\,\mathrm{Im}\,\epsilon^{-1}(k,\omega)\bigg|_{\omega\to 0} d^dk \qquad (7)$$

is the value for the friction coefficient of a classical particle coupled in the same way to the electrons. This is the same result as the quadratic action discussed before, and can be traced back to the fact that the classical friction coefficient is defined for massive particles which move at very low constant velocity. Such linear trajectories deviate very slowly from the origin, so that the dissipative processes associated with them depend only on the small-distance, long-time behavior of the effective action.[17]

The formalism we have presented so far is appropriate for systems with full translational invariance. Extension to other situations is straightforward, provided that correlation functions for the electron gas can be calculated. We will discuss the case of surfaces when we present our numerical estimates.

In order to proceed further, we will make the extra assumption that the potential $V(\mathbf{R})$ (which should be periodic and have the symmetry of the underlying lattice) is strong enough so that, in the absence of interactions, the particle is well described by a tight-binding approximation, and the tunneling between sites lies in the Wentzel-Kramers-Brillouin (WKB) regime. That implies that the particle is localized most of the time in the vicinity of the minima of $V(\mathbf{R})$, and the hopping matrix elements of the Hamiltonian between neighboring wells are small compared with other typical energies, like the variational level spacings associated with these minima. This approximation should be valid for massive enough particles, like protons and muons, while it is more doubtful that it can be applied to positrons inside metals. Calculations of the quantum energy bands of noninteracting protons on metal surfaces support this view.[29] It is also worth noting that in our treatment we are only including the effects of low-energy electron-hole pairs, as they are the only excitations which may lead to nontrivial changes in the behavior of the particle. Other excitations like phonons, plasmons, or high-energy electron-hole pairs only renormalize the effective mass of the particle, but this effect also decreases the tunneling rates across energy barriers, making it more likely that a tight-binding description is appropriate. The presence of low-energy polarization modes is not sufficient for nontrivial effects to appear. A proper spectral distribution is also needed. In particular, spectra of the type $\delta(\omega-ck)$ (corresponding, for example, to acoustical phonons) only give finite-mass renormalization. This is consistent with the fact that the classical friction coefficient induced by such systems is exactly zero.

Within this approximation, the paths of the particle will stay typically close to one of the wells of the potential for long times, with eventual excursions to neighboring wells, as depicted schematically in Fig. 2. Each single hopping process between sites is called an instanton. The inverse of the widths of these instantons will be of the order of the vibrational frequency around one of the wells ($\tau_c^{-1}\sim\omega_c$), if the tunneling is well described by the WKB approximation.[30] In this regime the instanton width is essentially independent (with logarithmic accuracy) of the height and width of the barrier because of the particle spends most of its tunneling time in the outermost regions of the barrier, which at low energies are well characterized by the curvature near the minimum (and thus by the intrawell level spacing). In the semiclassical regime, corrections to the above instanton width are of order $\hbar$ over the instanton action [see Eq. (10b)]. When calculating path integrals, each path has to be weighted by a factor whose exponent is simply the action (2) divided by $-\hbar$. To avoid complications with the retarded interactions within each jump, we will assume that we have first integrated out all those electron-hole pairs with energies above the inverse of the

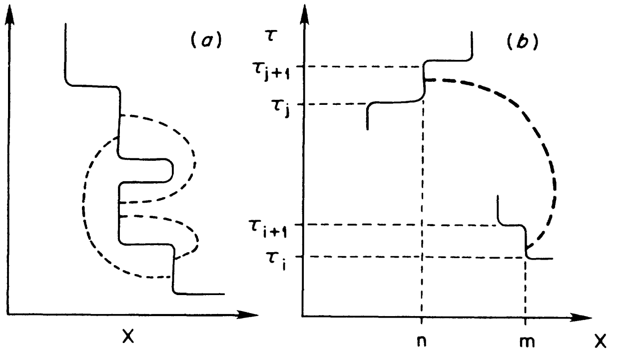

FIG. 2. Typical paths for the particle within the tight-binding approximation. Solid lines describe the path $x(\tau)$. Dashed lines denote retarded interactions. See text for details.

instanton width, leaving us with an effective action in which the retarded potential left has a short-time cutoff of the order of the width of the instantons.

It can be argued on general grounds[18] that those screening processes which take place at time scales shorter than the instanton width (or, equivalently, whose frequency is higher than the intrasite level spacing ω_c) follow adiabatically the motion of the particle and only contribute to the renormalization of the coupling between the particle and the environment. This statement applies equally to high-energy electron-hole pairs and to bound states or resonances which lie farther than ω_c from the Fermi energy. This effect is more pronounced for heavier particles, and can lead to a significant weakening of the pseudopotential. Thus the phase shift for the electrons at the Fermi surface will not exceed $\pi/2$ unless bound states or resonances whose energies lie within ω_c from the Fermi level take part in the "slow" screening process.

We are left with a sum over paths which can be expressed in terms of a set of discrete variables (the position of the minima of the potential) which includes a self-interaction decaying at long (imaginary) times like $1/(\tau-\tau')^2$. From the knowledge of the average fluctuations of these paths we obtain information which, when analytically extended to real times, leads to quantities directly related to the long-time dynamics of the particle, such as the mobility and the diffusion coefficient. For the case of the quadratic action, this analysis has been carried out within different schemes, which can always be related to effective scaling equations for the parameters entering in the theory (the hopping rate and the friction coefficient). The main result of these studies is that a transition to a self-localized regime, characterized by zero mobility at zero temperature, takes place when the value of $\eta a^2/\hbar$ (η being the friction coefficient and a the distance between neighboring wells) exceeds a critical value.[15,16,31-33]

In the following, we will take a similar scaling approach, although, due to the change in the dissipative term of the effective action, the scaling equations will be different. A general outline of scaling schemes when long-range $1/\tau^2$ interactions are present has been given by Cardy.[34] We first subtract a path-independent contribution to the effective action and work with $\tilde{f}(R)=f(R)-f(0)$. The term $f(0)$ does not affect the dynamics of the particle; by neglecting it, we only need to calculate interactions between parts of the path at which the particle is in different wells. Let us now assume that between times τ_i and τ_{i+1} the particle is in the mth well, and between j and τ_{j+1} in the nth [see Fig. 2(b)]. Then, we can integrate in (2) the contribution coming from interactions between these two parts to obtain

$$\Delta S=2\tilde{f}(R_{mn})\ln\left[\frac{(\tau_j-\tau_i)(\tau_{j+1}-\tau_{i+1})}{(\tau_j-\tau_{i+1})(\tau_{j+1}-\tau_i)}\right], \tag{8}$$

where R_{mn} is the difference between the positions of the two wells.

In our approximation, a trajectory of the particle is defined by a discrete set of times τ_i at which the particle hops from the well m_i to the well n_i ($m_{i+1}=n_i$). By rearranging terms, we can write the contribution from the retarded interaction to the effective action as

$$S_{\text{int}}=\sum_{i,j}2[\tilde{f}(R_{m_im_j})+\tilde{f}(R_{n_in_j})-\tilde{f}(R_{m_in_j})-\tilde{f}(R_{n_im_j})]\ln\left[\frac{(\tau_i-\tau_j)}{\tau_c}\right], \tag{9}$$

where the short-time cutoff corresponding to the instanton width τ_c has been introduced for convenience. When $\tau_i=\tau_j$, we substitute τ_c for $\tau_i-\tau_j=0$ (or, equivalently, we introduce in the instanton gas a hard-core repulsion of width τ_c which accounts for the renormalization of the retarded interaction mediated by e-h pairs with energy $\omega>\omega_c=\tau_c^{-1}$). Note that in this way we are also including contributions from the interactions between neighboring parts of the path.

We have to add to (9) the contribution to the action coming from the noninteracting part of the Hamiltonian. Within our tight-binding scheme, the corresponding part of the Hamiltonian is expressed in terms of hopping matrix elements Δ_{mn}. They can be related to the effective action, as we can write

$$\Delta_{mn}\simeq\omega_c\exp(-S_{mn}/\hbar), \tag{10a}$$

$$S_{mn}=\int_{R_m}^{R_n}[2MV(x)]^{1/2}dx, \tag{10b}$$

where S_{mn} is the action of a given instanton. Hence, in the language of Ref. 34, these matrix elements (in dimensionless form, $\tilde{\Delta}_{mn}=\Delta_{mn}/\omega_c$) play the role of fugacities associated with each of the kinks in the path, while from (9) we obtain an effective logarithmic interaction between them. For a general function $\tilde{f}(R)$, this interaction cannot be factorized and expressed in terms of "charges" associated with each kink, as can be done for a quadratic retarded potential. The scaling analysis proposed in Ref. 34 is rather general and does not need this requisite.

We now analyze the effects of a change in the cutoff from τ_c to $\tau_c e^l$, l small, on the action. Such a change of scale has to be compensated by a redefinition of the parameters $\tilde{\Delta}_{mn}$ and $f(R_{mn})$ entering in the action. No new parameters need to be introduced except for a trivial constant term in the free energy. The scaling equations thus obtained are

$$\frac{d\tilde{\Delta}_{mn}}{dl}=[1-2\tilde{f}(R_{mn})]\tilde{\Delta}_{mn}+\sum_{p}\tilde{\Delta}_{mp}\tilde{\Delta}_{pn}\ , \tag{11a}$$

$$\frac{d\tilde{f}(R_{mn})}{dl}=-\sum_{p}\tilde{\Delta}^2_{mp}[\tilde{f}(R_{mn})+\tilde{f}(R_{mp})-\tilde{f}(R_{np})] -\sum_{p}\tilde{\Delta}^2_{np}[\tilde{f}(R_{mn})+\tilde{f}(R_{np})-\tilde{f}(R_{mp})]\ . \tag{11b}$$

These equations arise from a rescaling of the interaction plus the replacement of instantons closer than $\tau_c e^l$ by effective interactions.[35]

It is instructive to compare Eq. (11) with the corresponding equations obtained in the case of a quadratic action[16] or a cosine retarded potential;[36] in both cases the scaling equations were obtained by exploiting the translational invariance of the model and working in momentum space. In the first case, the effective interaction between two kinks shown in Eq. (9) can be factorized and expressed in terms of charges associated with each kink. When higher-order charges are neglected (they are irrelevant in the renormalization-group sense), and Eqs. (11) are expressed in terms of these charges, we obtain the scaling equations derived previously. In the case of the cosine dissipative action, we need to keep the possibility of having long-range jumps, which are generated according to (11). Because of the periodicity of the cosine, jumps between wells which are second neighbors do not interact (they are "neutral" and carry no charge). A transition to a truly localized state cannot take place, although a transition to an intermediate state in which the "particle" only occupies even or odd sites does occur. Thus both cases are contained as particular situations in the generalized scaling equations (11).

These scaling equations have been studied by several authors.[16,21,34] We comment briefly below on some of their properties. It is clear from Eqs. (11) that $\tilde{\Delta}_{mn}=0$ is an attractive fixed point. If we assume that initially (at $l=0$) $\tilde{\Delta}_{mn}\ll 1$ (or $S_{mn}\gg\hbar$) for all sites m and n, which is consistent with the WKB approximation, then we can neglect quadratic terms in Eq. (11) and the scaling equation can be easily integrated for each $\tilde{\Delta}_{mn}$. If $\tilde{f}(R_{mn})>\frac{1}{2}$, then $\tilde{\Delta}_{mn}$ will scale down to zero at $T=0$. At finite temperature the scaling process must stop at $\hbar\omega_c\sim k_BT$, since $\hbar/k_BT$ acts as a long-time cutoff. The final renormalized hopping parameter Δ_{ren} is $\Delta_{\text{ren}}\sim\Delta(k_BT/\hbar\omega_C)^{2\tilde{f}}$, where we have removed the subscript mn. If $\tilde{f}<\frac{1}{2}$, then the scaling process must be stopped at $\tilde{\Delta}\sim 1$, when the initial assumption $\tilde{\Delta}\ll 1$ is no longer valid. The self-consistent renormalized width is $\Delta_{\text{ren}}\sim\Delta(\Delta/\omega_c)^{2\tilde{f}/(1-2\tilde{f})}$.

NUMERICAL ESTIMATES

In order to make further progress, we need to have a model for $\tilde{f}(R)$. This function describes the nature of the screening cloud around an impurity in our metallic system. We conjecture, on the basis of the Anderson's analysis of the orthogonality between the screening clouds originated by different external potential,[25–28] that an essentially exact treatment of the low-energy dynamics of the particle can be obtained if $\tilde{f}(R_{mn})$ in (11) is replaced by $K/2$, where $|\langle\psi_m|\psi_n\rangle|=N^{-K}$ is the overlap between the electronic ground states $|\psi_m\rangle$ and $|\psi_n\rangle$ corresponding to the particle located at sites m and n, respectively, and N is the total number of conduction electrons. Several authors[26–28,37] have studied the diffusion of a charged particle in an electron gas in terms of the dimensionless parameter K defined above and have reached similar conclusions about the renormalization of the hopping matrix element. We recall here that the use of the bandwidth D as a high-frequency cutoff instead of the intrawell level spacing $\hbar\omega_c$ is only legitimate when $\hbar\omega_c>D$, which is almost never satisfied for heavy impurities in metals, since ω_c is of the order of the Debye frequency.[18,38]

In principle, the knowledge of the phase shifts δ_l associated with the partial waves of angular momentum l should allow one to calculate $K(R)$ (R is the distance between sites). However, in practice this turns out to be a very difficult task and no closed expression has so far been obtained for $K(R)$ in terms of δ_l. The obvious source of difficulty is that in the calculation of $|\langle\psi_m|\psi_n\rangle|$ each partial wave centered around the site m mixes with all the partial waves centered around the site n. So far only a few limiting cases have yielded analytical expressions

Oguchi and Yosida[39] have derived expressions for $K(R)$ (arbitrary R) under the assumption that, on each site, only two partial waves, l and l', with arbitrary phase shifts δ_l and $\delta_{l'}$, contribute to the screening. They have rederived the results obtained previously by Yamada *et al.*,[26,28] who only considered one channel on each site[26] and two channels with $\delta_{l'}\ll\delta_l$.[28]

The limit $R\to\infty$ admits a closed expression that takes into account the scattering of all the channels:

$$K(\infty)=\sum_{l=0}^{\infty}2(2l+1)\left[\frac{\delta_l}{\pi}\right]^2\ . \tag{12}$$

The hopping between very distant wells is essentially equivalent to the creation or annihilation of the impurity. In such a limit, the problem recovers an effective spherical symmetry that inhibits the mixing of channels, each of which contributes an amount $(\delta_l/\pi)^2$ to the parameter $K(\infty)$.[25,26]

The limit $R\to 0$ with the inclusion of all partial waves has not been considered yet. Although there is not yet a direct proof, we find it most plausible that, from Eq. (6) and the identification $\tilde{f}\equiv K/2$, $K(R\to 0)$ will be

$$K(R\to 0)\simeq\frac{\eta R^2}{2\pi\hbar}\ , \tag{13a}$$

$$\eta=\frac{3\hbar}{k_F r_s^3}\sum_{l=0}^{\infty}(l+1)\sin^2(\delta_l-\delta_{l+1})\ , \tag{13b}$$

where η is the friction coefficient obtained from a phase-shift analysis[40–43] and $r_s=(3/4\pi\rho)^{1/3}$, ρ being the electron density. In Eq. (7) we have given the friction coefficient obtained in linear-response approximation.

The constraint on the phase shifts imposed by the Friedel sum rule

$$Z=\frac{2}{\pi}\sum_{l}(2l+1)\delta_l \tag{14}$$

implies the identify $K(\infty)=Z^2/2(2l+1)$ when only the l partial wave is present, and, in general, the inequalities $\delta_l \leq \pi Z/2(2l+1)$ and $K(\infty)\leq Z^2/2$ (Z is the charge of the diffusing impurity). These considerations rule out the possibility of localization for particles of charge $Z=1$ (for finite R the oscillations should be unusually high to reach twice the saturation value), but leave the problem open for $Z\geq 2$ and, for any value of the charge, do not provide by themselves an estimate of $K=2\tilde{f}$ at arbitrary distances (unless the above-mentioned approximations are introduced), which is of interest in learning about the renormalized dynamics. Realistics phase shifts for a number of impurity charges and electron densities are given in Ref. 40.

The main advantage of a linear-response calculation is that it allows us to obtain, with great simplicity, reliable numerical estimates of $\tilde{f}(R)$ for realistic metallic densities and arbitrary hopping distances. In addition, as we will see, a linear-response calculation can be readily applied to geometries without spherical symmetry, such as that encountered in the surface of a metal, where a phase-shift analysis is not useful. A linear-response calculation overestimates the coupling for high Z, but then Z can be replaced by an effective charge or by a suitable electronic density distribution which accounts for the binding of electrons (analogously, in a phase-shift approach, one would subtract a phase shift π for each effectively bound electron).

In general, the function $\tilde{f}(R)$ calculated from Eq. (5) will rise quadratically for small values of R, as discussed in connection with the classical friction coefficient. It will possibly have Friedel oscillations when $R\sim k_F^{-1}$, and settle to a constant value. Note that, because of the sharpness of the Fermi surface of a metal, $\tilde{f}(R)$ has Fourier components only up to $k=2k_F$. As the Friedel oscillations have a decaying envelope, it is most likely that $\tilde{f}(R)$ is always positive.

In order to analyze the possibility of a localization transition, we have to estimate $\tilde{f}(R)$ for all values of R which connect wells in the periodic potential acting on the external particle. If all these values are larger than $\frac{1}{2}$, then all hopping elements will scale down to zero, and the particle will be localized in a single potential well at zero temperature. If we further assume that the Friedel oscillations are very strongly damped, then $\tilde{f}(R)$ will have a monotonous dependence on R, and the threshold for localization will be given by $\tilde{f}(R_1)$, where R_1 is the nearest-neighbor distance.

If we describe the coupling in terms of phase shifts, values of $\tilde{f}(\infty)\geq\frac{1}{2}$ correspond to phase shifts greater than $\pi/\sqrt{2}$. Such phase shifts cannot be derived from weak pseudopotentials. That means that they can only be achieved when the electron-hole pairs responsible for the localization phenomenon feel the full unscreened potential. These e-h pairs have energies of the order of, or less than, typical ionic kinetic energies (see Ref. 18), so that, for charged impurities to induce strong phase shifts, the full screening cloud should be built up of these low-energy excitations. Otherwise, the high-energy electronic modes would dress the external particle, thus weakening its interaction with the low-energy e-h pairs responsible for friction. We suggest the qualitative criterion that renormalization will be strong when the electronic plasma frequency is much smaller than the intrawell level spacing. As discussed in detail below, this is not the case for typical metals, either in the bulk or in the surface. On the other hand, there are a variety of metallic systems, like doped semiconductors, organic conductors, graphite intercalation compounds, etc., where the screening takes place within a narrow band; a well-studied case is a doped semiconductor, where, for reasonable doping levels, the plasma frequency and the Fermi energy of the extra carriers are comparable to the phonon frequencies of the host material. We think that these systems are possibly good candidates for observation of the localization transition mentioned earlier.

We now look to numerical estimates of $\tilde{f}(R)$ for a particle moving through a three-dimensional (3D) electron gas. The dielectric function is calculated within the RPA, and the coupling potential is assumed to be the Coulomb potential. Note that, because of the self-consistency inherent to the RPA, the effective potential acting on the electrons at the Fermi level is a screened potential. This means that the replacement of the bare potential by a pseudopotential, mentioned before, is taken approximately into account. We will use atomic units in the following, $\hbar=m=e^2=1$, and express the density of the electron gas in terms of the parameter r_s defined above. We expect the RPA to be most accurate at high electronic densities, i.e., for r_s small.

The quantity entering in (5) is

$$\left.\frac{\partial\,\mathrm{Im}\epsilon^{-1}(k,\omega)}{\partial\omega}\right|_{\omega=0}=\frac{2k}{\left[k^2+k_{\mathrm{TF}}^2 g\left[\frac{k}{2k_F}\right]\right]^2},$$

$$k_{\mathrm{TF}}=\left[\frac{4k_F}{\pi}\right]^{1/2}, \tag{15}$$

$$g(x)=\frac{1}{2}\left[1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right].$$

Simple estimates of the behavior of $\tilde{f}(R)$ in the small-density limit ($k_{\mathrm{TF}}\ll k_F$) are also discussed in Ref. 21. The full dependence of $\tilde{f}(R)$ on R is given in Fig. 3 for typical metallic densities. Here, as in the rest of the paper, we give our numerical results for $Z=1$. Within the linear-response approximation our results for $\tilde{f}(R)$ should be multiplied by Z^2, where Z is the charge (or a suitable effective charge) of the impurity. Note that the parabolic dependence assumed in the Ohmic dissipation model is only valid for distances small when compared with k_F^{-1}. We plot, in Fig. 4, the friction coefficient as a function of the metallic density, which is directly proportional to the second derivative of $\tilde{f}(R)$ at $R=0$, as

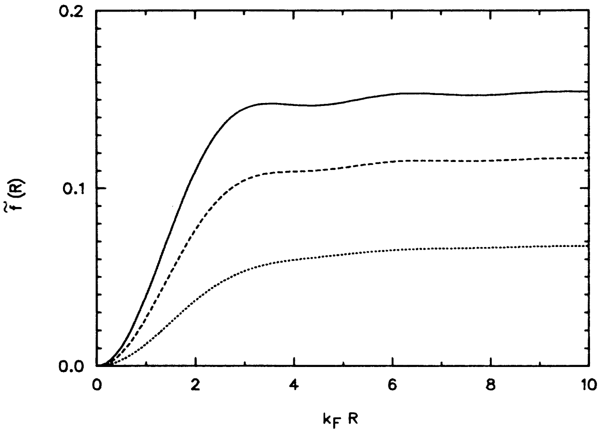

FIG. 3. Values of the function $\tilde{f}(R)$ for a particle of charge 1 interacting with the bulk excitations of an electron gas. Solid line, $r_s=6$; dashed line, $r_s=4$; dotted line, $r_s=2$.

discussed earlier. These values agree with previous estimates of the linear-response friction coefficient for an ion moving in an electron gas.[41] Echenique *et al.*[42,43] have estimated nonlinear effects in the friction coefficient from a phase-shift analysis based on a local-density approximation to the electronic charge surrounding the ion. They find nonlinear corrections to be important when the screening is weak enough to allow bound states. In the metallic range, the linear response tends to underestimate friction by a factor of 2 or less in the case of protons, and overestimates it ($\sim 20\%$ for $r_s \simeq 2$ and around 1 order of magnitude for $r_s \simeq 6$) in the case of helium ions.[42] This overestimation is still larger for heavier ions.[43] Although we lack at present a nonlinear calculation of $\tilde{f}(R)$ for $R \gtrsim k_F^{-1}$, an educated guess can be made by extrapolating the results obtained for the friction coefficient (which correspond to $R \to 0$).

If we assume that the particle hops between interestitial sites in the metallic lattice, then the typical hopping distance will be given by the lattice spacing d. If each atoms contributions with Z_0 electrons to the conduction bands, this distance is such that

$$k_F d = \pi\sqrt{2}\left[\frac{3Z_0}{2\pi}\right]^{1/3} \quad \text{(fcc lattice)} ,$$

$$k_F d = \frac{\pi\sqrt{3}}{2}\left[\frac{6Z_0}{\pi}\right]^{1/3} \quad \text{(bcc lattice)} .$$

For instance, Al has the fcc structure and $Z_0=3$, while for the alkali metals, $Z_0=1$ and the lattice is bcc. Hence

$$k_F d = 5.01 \quad \text{(Al)} ,$$

$$k_F d = 5.38 \quad \text{(alkali metals)} .$$

For the metallic densities it means that $\tilde{f}(d)$ lies close to its asymptotic value (see Fig. 3). We plot in Fig. 5 the function $\tilde{f}(R=\infty)$ as a function of the metallic densities. This dimensionless number describes the intensity of the coupling to the electron gas in the absence of strong Friedel oscillations, provided that the hops are such that the minimum hopping distance is much larger than k_F^{-1}. As expected, it is very small at high electronic densities. In this case, the screening is very effective, and only a weak residual potential acts on the quasiparticles near the Fermi level. As the electronic densities decrease, this effective potential grows, and the low-energy excitations of the electron gas become more perturbed by the presence of the external particle. Because of Friedel's sum rule for the phase shifts, the value of $\tilde{f}(\infty)$ should always be below $\frac{1}{4}$ in the absence of bound states or resonances. Our approximation violates this bound for small electronic densities (namely for $r_s \gtrsim 16$), when the RPA is expected to fail; note that even the assumption of linear response will become invalid in this limit. However, for typical metallic densities, our approximation gives presumably reliable estimates of the coupling between a charged particle and the low-energy electron-hole pairs of an electron gas.

It is worth noting that the density dependence of

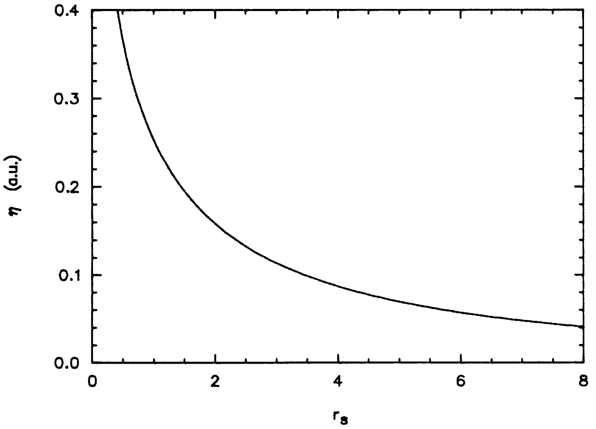

FIG. 4. Values of the friction coefficient (in atomic units) for a particle of charge 1 moving within an electron gas plotted as a function of the electronic density parameter r_s.

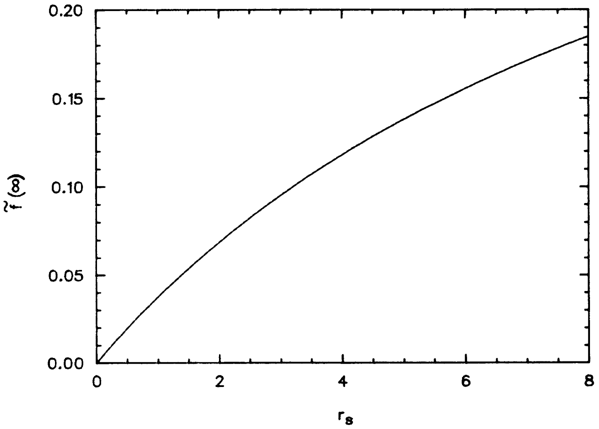

FIG. 5. Values of $\tilde{f}(R=\infty)$ for a particle of charge 1 moving in an electron gas, plotted as a function of the electronic density parameter r_s.

$\tilde{f}(\infty)$ is the opposite to that of the friction coefficient (see figures), so a sensible approximation to the coupling strength can only be obtained from the complete shape of $\tilde{f}(R)$.

We will now consider the case of surfaces. We assume that the particle is localized in the perpendicular direction to the surface, trapped in a potential well near the surface. For charged particles interacting with a metallic surface, an attractive image potential for large distances from the surface always exists. On the other hand, hard-core repulsive potentials possibly dominate at short distances. The particle is, in the absence of the coupling to the *e*-*h* pairs, free to diffuse in the direction parallel to the surface. We further assume, as before, that this diffusion process takes place by successive tunneling transitions between neighboring potential wells, an assumption which is well supported by detailed calculations for the case of protons.[29]

In order to calculate the retarded potential experienced by a particle at a fixed distance from the surface we will use the semiclassical infinite-barrier approximation (SCIB) (Ref. 44), which mimic the response of the surface by assuming that the quasiparticles are reflected specularly in the inner wall of the surface. This approximation correctly reproduces the bulk screening properties of the material and leads to the image potential outside the metal. It has been used to obtain reliable estimates for quantities such as the energy loss of a particle,[45] and the sticking of a neutral atom to a surface.[46,47] Despite its limitations, the SCIB approximation is highly valuable, since it offers a simple way of estimating the surface response.

Within this approximation, the surface counterpart of $\tilde{f}(R)$ can be shown to be

$$\begin{aligned}\tilde{f}(z,\mathbf{R}) &= \frac{1}{8\pi^3}\int d^2k\,(e^{i\mathbf{k}\cdot\mathbf{R}}-1)\frac{2\pi}{k}\\ &\quad\times e^{-2|k|z}\frac{\partial\,\mathrm{Im}\,g(k,\omega)}{\partial\omega}\bigg|_{\omega=0},\\ g(k,\omega) &= \frac{1-\tilde{\epsilon}(k,\omega)}{1+\tilde{\epsilon}(k,\omega)},\\ \tilde{\epsilon}(k,\omega) &= \frac{k}{\pi}\int_{-\infty}^{\infty}\frac{dq}{(k^2+q^2)\epsilon(k,q,\omega)},\end{aligned}\tag{16}$$

where $\mathbf{R}$ is now a vector parallel to the surface, z is the distance perpendicular to the surface, and $\epsilon(k,q,\omega)$ is the three-dimensional dielectric function of the bulk (which we have modeled again by the RPA). Note that, because of the integral which defines $\tilde{\epsilon}(k,\omega)$, all bulk *e*-*h* pairs with the same parallel wave vector k contribute to the screening. On the other hand, a weighting factor $e^{-2|k|z}$ appears, which comes from the bidimensional Fourier transform of the Coulomb potential. By analyzing the behavior of $\tilde{f}$ at a given value of z and small R's we can calculate the friction coefficient as a function of the distance to the surface, $\eta(z)$, which is done in Fig. 6 for typical metallic densities (note that we are now scaling distances in terms of k_{TF}, the inverse screening length, which is a more natural parameter). Our results are in good agreement with previous estimates of $\eta(z)$ obtained in the linear-response approximation.[48]

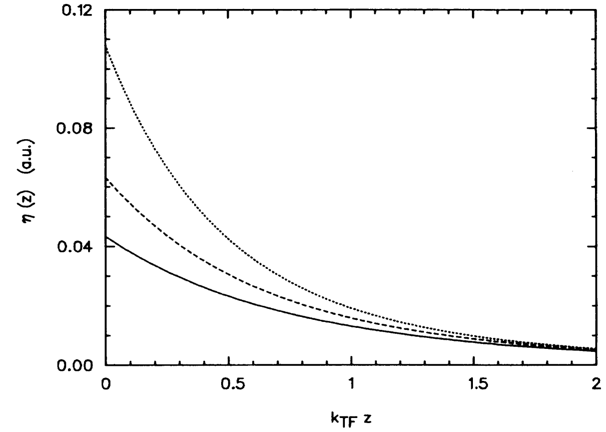

FIG. 6. Values of the friction coefficient for a particle of charge 1 moving outside the surface of an electron gas, plotted as a function of the distance from the surface. Solid line, $r_s=6$, dashed line, $r_s=4$; dotted line, $r_s=2$.

Results for $\tilde{f}(z,R)$ are plotted in Fig. 7 for two different electronic densities of experimental interest: $r_s=1.62$ (W) and $r_s=3.02$ (Ag). As before, this function deviates strongly from a quadratic behavior at typical ionic separations, and approaches a limiting value at long distances. We take this latter value as representative of the coupling of the electron gas to a charged particle. These values are plotted in Fig. 8. They decay sharply as a function of the distance between the particle and the surface, and decrease with decreasing metallic density like their bulk counterparts. It is finally worth noting that, because of the $e^{-2|k|z}$ weighting factor in (16), the effective cutoff for surface screening processes lies below the bulk value (which is of the order of the Fermi energy). Thus we can expect couplings at the surface to be smaller than those in the bulk. This is consistent with recent experiments showing evidence that H diffuses in a bandlike motion on some metal surfaces.[7]

While we have already studied the most common cases for particles interacting with metals, it is also worth mentioning some more unusual situations which may arise. As discussed earlier, a localization regime is only possible in narrow-band metallic systems. The function $\tilde{f}(R)$ for these materials can exceed $\frac{1}{2}$ for some values of R and particles of charge greater than 1. It can also be possible for this function to show strong Friedel oscillations, as the screening cloud is built up from electron states within a narrow range of wave vectors. Thus, in these systems it is feasible that, while nearest-neighbor jumps are suppressed, the particle can hop between sites which lie further apart, as this process involves no significant change of the screening cloud. Then a new phase might appear, in which the particle would be delocalized within a given sublattice, but restricted not to leave that particular sublattice. This phase is closely related to the situation which can arise in a Josephson junction with dissipation[36] and exemplifies rather well the difference between the quadratic ("Ohmic") dissipation model and others more ap-

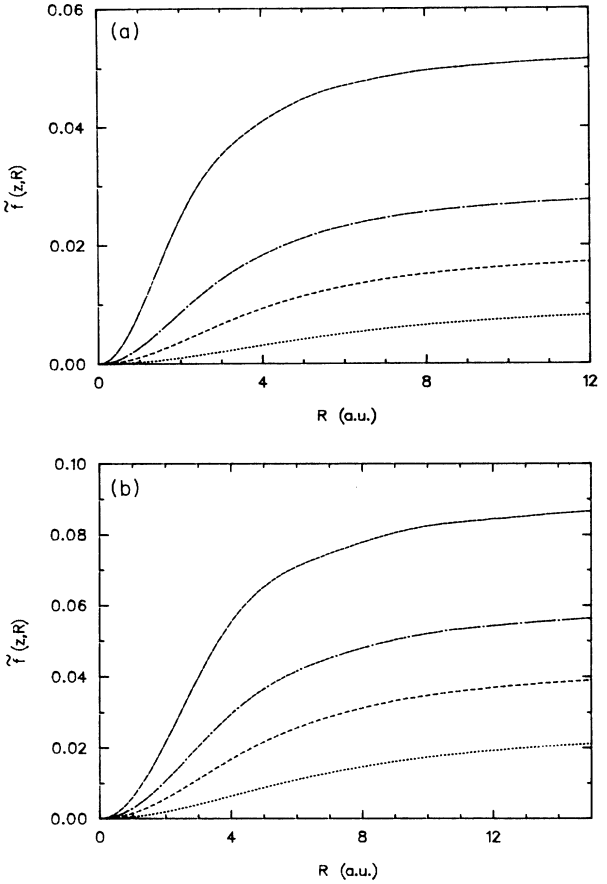

FIG. 7. Values of the function $\tilde{f}(z,R)$ for various values of the charge surface distance z for a particle of charge 1 moving outside a metallic surface. (a) corresponds to $r_s = 1.62$ (W) and (b) to $r_s = 3.02$ (Ag). Solid line, $z = 0$; dash-dotted line, $z = 0.5$ a.u.; dashed line, $z = 1$; dotted line, $z = 2$.

propriate for fermions. Finally, it is also likely that in the presence of a defect, the screening will be altered in the neighborhood. Then a new situation might happen in which hops near the defect were suppressed, but other ones further apart were not. In such a case, the particle would be free to hop between sites far from the defect but would not be able to get close to the defect. The inverse situation is also conceivable, where the particle would be restricted to movement within a narrow but finite set of sites near the defect.[49] None of these phases can be thought of when a quadratic coupling is assumed for the effective interaction with the electronic bath.

CONCLUSIONS

We have presented an analysis of the dynamics of charged particles interacting with an electronic bath. We have given a general framework in which to consistently incorporate the effects due to low-energy electron-hole pairs, based on a path-integral formulation. We use it to give numerical estimates of the magnitudes of the coupling of a charged particles to the conduction electrons of a metal, within its bulk or at its surface. We show that, although a transition to a self-trapped regime is, in principle, feasible, values for realistic electronic densities lie well below the threshold for such a transition. On the other hand, as a scaling approach is needed to treat the influence of electron-hole pairs, physical quantities such as the effective mass or the diffusion coefficient will have an exponential dependence on the coupling, which will thus change significantly the low-energy dynamics of charged particles. This situation is reminiscent of other models used to analyze quantum systems interacting with a dissipative environment via a linear coupling to a set of oscillators, and we have studied the similarities and differences between the two models. The conventional model with a quadratic coupling tends to overestimate the magnitude of the coupling, especially in connection with motion over long distances, which is the relevant situation in the delocalized regime of physical interest. It is also worth noting that no realistic (and translationally invariant) coupling to other excitations can have the same influence on the low-energy dynamics of charged particles as the one to electron-hole pairs considered here.[50,51] This is due to the continuous distribution that the excitation spectrum of the electron gas shows in the (k,ω) space.

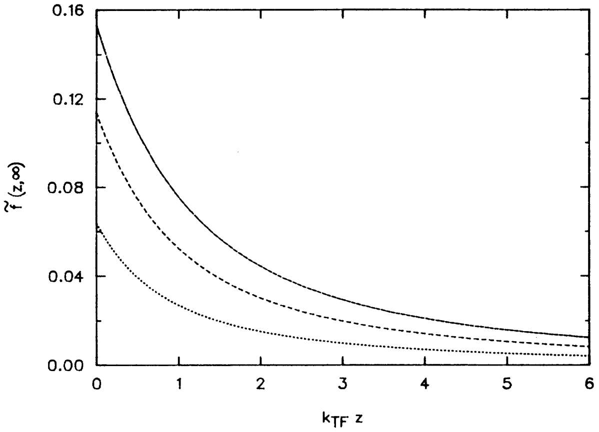

FIG. 8. Values of the function $\tilde{f}(z,\infty)$ for a particle of charge 1 moving outside the surface of an electron gas. Solid line, $r_s = 6$; dashed line, $r_s = 4$; dotted line, $r_s = 2$.

The scaling analysis presented here is only valid when the resulting hopping energy is of the order of, or smaller than, the temperature. Ideally, both quantities should be much smaller than the intrawell level spacing. In order to make further connection with possible experimental situations, studies of transport coefficients and time-dependent correlation functions are needed. We have not attempted to do it here. Furthermore, a straightforward translation of the results obtained within the model with linear coupling to a bath of oscillators[31–33,53] to the present case is probably not feasible, since the quadratic effective coupling resulting from such a model differs essentially from the long-distance coupling derived from our calculations. The particular case of a cosine dissipative potential has already been considered and shows very different correlation functions.[36]

Finally, a self-localization transition induced by the electron-hole pairs cannot be ruled out in principle and will take place if the coupling is strong enough (like particles with charge 2) and the induced screening cloud is slow as compared with the dynamics of the particle; such a situation may present itself in doped semiconductors, with a narrow band and a small plasma frequency. A third possible phase in which the particle can be localized in separate sublattices, but is free to move over the whole space, is also possible, if the Friedel oscillations in the screening cloud are large enough. When defects are present, situations are also conceivable where, due to the local modification of the screening cloud, the particle would only be allowed to tunnel in a region near the defect or far from it.

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