Noise in STM due to atoms moving in the tunneling space

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A theory of electron tunneling through an adiabatically time-dependent potential barrier is applied to describe fluctuations of the scanning-tunneling-microscope current, induced by the motion of atoms in the tunneling gap. We show that atoms of a gas intervening between the tip and the sample introduce a noise small compared to the shot and thermal-electron noises. On the contrary, the noise induced by the movement of adsorbed atoms can be large enough to be observed. Simple formulas for the average current and temporal correlation functions of the current are offered to treat data on surface diffusion.

I. INTRODUCTION

Noise in the scanning-tunneling-microscope (STM) current is usually a feature one tends to suppress or remove as a factor obscuring the signal. Only recently, Möller, Esslinger, and Koslovski[1] carried out specially designed noise measurements that can themselves be regarded as a tool to obtain the surface atomic-scale landscapes, particularly promising in the case of low bias voltages, when the tunneling current is small. Having managed to distinguish the thermal noise, the power spectrum of which is proportional to $k_B TG$, where G is the conductance of the tunneling gap, the authors of Ref. 1 suggested working in the constant noise regime, adjusting the distance a between the tip and the sample subject to the exponential dependence of $G(a)$. The results obtained so far do not seem to give images different from those given by the conventional STM, which was regarded as a verification of this new method.[1] However, this method is, indeed, advantageous in the case of a small signal-to-noise ratio, encountered in some situations that require an application of very small tunneling currents.

The strategy used in the present paper is different. We wish to focus on the features of the STM noise, which are directly related to the atomic dynamics at interfaces. This is the noise due to fluctuations of the tunneling barrier induced by the motions of "third" particle(s) between (near) the tip and the sample. Binnig, Fuchs, and Stoll were the first, to our knowledge, to show that the diffusion of adatoms gives rise to fluctuations of the STM current that can be used to evaluate diffusive properties of adsorbates.[2] Further progress in this direction may help to resolve a problem of identification and characterization by STM of weakly adsorbed species.

Motions of a particle intervening between the tip and the sample must affect the measured average current and introduce a contribution to the current noise. It is interesting to make use of these effects to investigate the surface diffusion of adsorbed atoms[2,3] or the properties of the medium in the case of *in situ* STM (electrochemical configuration).[4] However, to suggest an instructive experimental approach one has to establish a theoretical framework for a description of these phenomena.

Below we develop a theory for the cases of adsorbates moving along the substrate surface and of gas atoms moving near the STM tip. We obtain analytical expressions for the average current, the current temporary correlation functions, and the noise spectral density via the temperature, density of atoms, and few parameters which characterize the tunneling barrier and the interaction between a tunneling electron and moving atoms. We show that over a wide range of gas temperatures and pressures the contribution of gas atoms to the average current and current noise is negligible. However, the influence of adsorbed atoms moving near the STM tip could be large enough to be resolved at the background of other contributions to the noise. That might give us a new method for the study of surface diffusion.

Our results suggest that one could study the properties of moving adsorbed atoms by analyzing the dependence of the transmitted electron current and the current noise on the variable parameters such as the tip-sample distance a, system temperature T, the particle density n, and the type of atoms and molecules under investigation. Such investigations could, furthermore, be useful for obtaining additional information about the tunnel junction and the surface of the substrate.

The outline of the paper is as follows. We first discuss the fundamentals for a calculation of the average current and the noise-characterizing functions, distinguishing the thermal, shot, and barrier-fluctuation-induced noise (Sec. II). In Sec. III we choose a model of interaction between the tunneling electrons and the intervening atoms. In Sec. IV all the basic formulas for the average current and temporary current correlation functions are derived. These formulas are applied to a particular case of free gas atoms in Sec. V. Section VI deals with atoms diffusing in a liquid in which the tip and the sample are immersed,

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and with surface diffusion of adsorbed atoms. *The main results* (qualitative effects, simple analytical formulas for the treatment of experimental data, etc.) *are formulated in Sec. VII so that one can benefit from this article without reading the detailed derivations in Secs. IV–VI.* A short discussion and an outlook (Sec. VIII) conclude the paper.

II. AVERAGE CURRENT AND THE SPECTRAL FUNCTION OF NOISE

The interaction among the current-carrying electrons and between the electrons and any quasiparticle excitations in a tunnel-junction system leads to the temporary current fluctuations. The corresponding current noise has, generally, a complicated nature. According to the experiments of Möller, Esslinger, and Koslovski,[1] carried out at room temperature, it is the *Nyquist thermal noise,* proportional to the conductance of the tunnel junction, that is observed in STM for the zero applied voltage. At a small but finite voltage of several meV and for typical tip-sample distances of several angströms, the $1/f$ *noise* becomes dominant. With a further decrease of voltages (down to ~ 1 meV) the *shot noise* appears, linear in current and compatible with the thermal and $1/f$ noise. There is a narrow voltage interval where the thermal and shot noises are dominant. The interval where the shot noise prevails, presumably, *increases* with a temperature decrease and the increase of the tunneling gap.

The goal of this paper is to describe the average current and the noise induced by the motion of "extra" particles in the tunneling gap. We must, however, first establish the conditions when this "atomically driven" contribution to the noise could be registered at the background of shot and thermal noises.

The problem of quantum noise in microscopic junctions is a topic of recent interest.[5,6] The current-noise spectral density is defined as

$$S(\omega)=\int_{-\infty}^{\infty} dt\, e^{i\omega t}\{\tfrac{1}{2}\langle\langle \hat{J}(t)\hat{J}(0)+\hat{J}(0)\hat{J}(t)\rangle\rangle - \langle\langle \hat{J}\rangle\rangle^2\}\ , \tag{2.1}$$

where $\hat{J}(t)$ is the current operator expressed via the creation and annihilation operators of electrons, and $\langle\langle\ \rangle\rangle$ means the averaging with the electron density matrix. In STM we deal with the exponentially small tunneling probability. For this case, at relatively small applied voltage V and temperature T, Larkin and Ovchinnikov obtained[7]

$$S(0)=2eJ\frac{\exp\left[\dfrac{eV}{k_BT}\right]+1}{\exp\left[\dfrac{eV}{k_BT}\right]-1}\ , \tag{2.2}$$

where the average current

$$J=\langle\langle \hat{J}\rangle\rangle=eVG\ . \tag{2.3}$$

Here, the tunneling conductance is given by the three-dimensional Landauer formula[8]

$$G=(e/\pi\hbar)\mathrm{Tr}(\hat{t}^{\dagger}\hat{t})\ , \tag{2.4}$$

where $\hat{t}$ is the transmission operator. In Ref. 9 one can find examples of analytical formulas for G, obtained in the semiclassical approximation subject to the STM geometry. The limiting cases of the thermal noise $S(0)=4k_BTG$ and of the shot noise $S(0)=2eJ$ follows from Eq. (2.2) for small and large values of eV/k_BT, respectively.

Formulas (2.1)–(2.4) were obtained for the static voltage across the junction and hence for the time-independent transmission probability. Our goal is to study the case of *time-dependent* $G=G(t)$ caused by particle motions in the tunneling space. Generally, such a time dependence could give rise to the excitation of tunneling electrons and the appearance of nonequilibrium electron gas in the leads. A solution to this problem, particularly for the mesoscopic STM confinement, is an extremely complicated task. We may, however, avoid it in the adiabatic approximation when all the relevant degrees of freedom of particles have characteristic times greater than those of the current-carrying electrons. Acting in the manner of Refs. 5 and 6, we can deduce an expression for the noise spectral density. The adiabatic approximation [valid under an assumption that the characteristic time of barrier fluctuations t_c is large compared with the tunneling time[10] and also compared with the characteristic electron correlation time, the magnitude of which is estimated by the smallest of the two values, $\hbar/(k_BT)$ and $\hbar/(eV)$] leads to a simple result:

$$S(\omega)=S_0+S_a(\omega)\ ,$$

$$S_0=2e\langle J(t)\rangle\frac{\exp\left[\dfrac{eV}{k_BT}\right]+1}{\exp\left[\dfrac{eV}{k_BT}\right]-1}\ , \tag{2.5}$$

$$S_a(\omega)=\int_{-\infty}^{\infty} dt\, e^{i\omega t}K(t)\ ,$$

where we introduce the temporary correlation function

$$K(t)=\langle J(t+\tau)J(\tau)\rangle-\langle J(\tau)\rangle^2\ , \tag{2.6}$$

with the current

$$J(t)=eVG(t) \tag{2.7}$$

averaged with electron-density matrix (not over configurations of moving particles). The brackets $\langle\ \rangle$ mean averaging over the time, or, equivalently, over the configurations of atoms in the barrier region.

The typical tunneling time for the barrier ~ 5 Å thick is 10^{-14}–10^{-15} s. At room temperature and for $eV\sim 0.1$ eV we have $\hbar/(eV)\sim\hbar/(k_BT)\sim 10^{-14}$ s. It takes much more time, $t_c\sim 10^{-12}$ s, for a free atom to pass a region of ~ 5 Å; the corresponding time for adsorbate surface diffusion is much greater. Thus, the adiabatic approximation is valid and Eqs. (2.5) and (2.6) are justified. The noise cannot be smaller than the first term in Eq. (2.5). Proportional to the tunneling conductance $G(t)$, this term is finite even in the limit of zero current at finite

temperatures. The second term is proportional to the current squared. Thus, for the sufficiently small currents the second term in Eq. (2.5) becomes negligible. In the case studies we shall derive the detailed criteria when the contribution of the second term becomes considerable and could be resolved at the background of the first one.

III. MODELS FOR ATOMS IN THE BARRIER REGION

We take into account the presence of the particles (atoms), randomly distributed in the tunneling space, via their contribution to the potential barrier between the tip and the substrate[4] (Fig. 1). The potential in a system with no particles in the tunneling space can, itself, be complicated enough. We ignore these complications, approximating the *bare potential* in the tunneling space by a barrier with a rectangular cross section:

$$V_0(\mathbf{r})=V_0=\text{const} \quad (\text{between boundaries } S_0 \text{ and } S) , \tag{3.1}$$

where S_0 and S stand for the surface of the tip and the substrate, respectively, and assume the substrate surface to be flat. In Sec. VIII we discuss how to account for the real shape of $V_0(\mathbf{r})$ in the final formulas.

Each atom gives an extra contribution, a well or a hump, on top of the bare potential barrier. We parametrize the interaction of a tunneling electron with an atom located at a point $\mathbf{r}_j$ either by a spherically symmetric potential with a "polarization tail"

$$U(\mathbf{r}-\mathbf{r}_j)=-\frac{U_0 b^4}{(|\mathbf{r}-\mathbf{r}_j|^2+b^2)^2} \tag{3.2}$$

or by a Gaussian

$$U_0(\mathbf{r}-\mathbf{r}_j)=-U_0\exp(-|\mathbf{r}-\mathbf{r}_j|^2/b^2) , \tag{3.3}$$

where the range of interaction b is of the order of atomic size.

Since the atoms move more slowly than electrons, we ignore the nonadiabatic effects.[11] Thus, we first consider electrons as moving in a static three-dimensional potential $V(\mathbf{r})$, defined by the sum of the bare potential V_0, and the potentials due to atoms positioned at points $\mathbf{r}_j$,

$$V(\mathbf{r})=V_0(\mathbf{r})+\sum_{j=1}^{N} U(\mathbf{r}-\mathbf{r}_j) . \tag{3.4}$$

Then, we solve the Schrödinger equation,

$$(\hbar^2/2m)\Delta\psi+[E-V(\mathbf{r})]\psi=0 , \tag{3.5}$$

to find the ψ function that describes the behavior of electrons in the barrier region for the momentary value of the barrier. That allows us to calculate the current $J(t)$ for the potential barrier (3.4), formed by atoms "fixed" at a time moment t at positions $\mathbf{r}_j(t)$. To find the mean current and current correlation functions, we then apply Eqs. (2.5) and (2.6) to the averaging over random realizations of atom coordinates $\mathbf{r}_j(t)$.

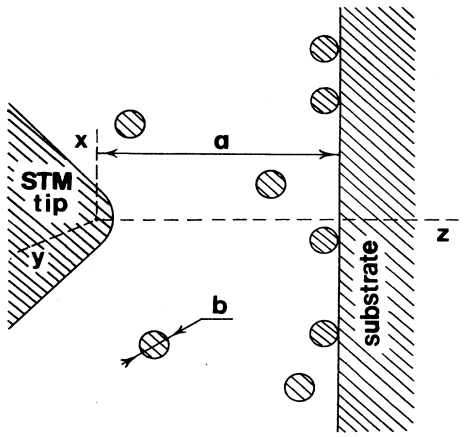

FIG. 1. Gas atoms moving and adatoms between the STM tip and the substrate.

IV. THEORY

In this section we derive expressions for the average current and current correlation functions through the distribution function of particles moving in the tunneling space. For the weak electron-atom interaction, Sec. IV A, we solve the Schrödinger equation (3.5) by the semiclassical perturbation theory. For the strong attractive electron-atom interaction, Sec. IV B, we use the approach based on the existence of most probable tunneling paths.

Assume that an electron tunnels from the s state of the tip with the energy E. Then, the asymptotics of its wave function in the barrier region adjacent to the tip,

$$\psi_0(\mathbf{r})=\frac{A}{r}\exp(-\gamma r), \quad \gamma=\frac{1}{\hbar}[2m(V_0-E)]^{1/2} , \tag{4.1}$$

could be used as the boundary condition for the solution of the Schrödinger equation (3.5) in the barrier region.

A. Weak interaction between tunneling electrons and moving atoms

In semiclassical perturbation theory, the case of a *weak interaction* is defined by inequalities

$$\left|\sum_{j=1}^{N} U(\mathbf{r}-\mathbf{r}_j)\right| \ll V_0-E , \tag{4.2}$$

$$\left|\frac{\partial}{\partial \mathbf{r}}\sum_{j=1}^{N} U(\mathbf{r}-\mathbf{r}_j)\right| \ll \gamma(V_0-E) . \tag{4.3}$$

With use of the potentials (3.2) or (3.3), these inequalities give two criteria,

$$m|U_0|/(\hbar\gamma)^2 \ll 1 , \tag{4.4}$$

$$m|U_0|/(\hbar^2\gamma^3 b) \ll 1 . \tag{4.5}$$

For atoms, usually, $\gamma b \sim 1$, and these criteria coincide.

Upon the validity of these criteria, the continuation of wave function (4.1) into the barrier region $\psi(\mathbf{r})$ can be found by the semiclassical perturbation theory,

$$\psi(\mathbf{r})=\frac{A}{r}\exp\left[-\gamma r-\frac{m}{\hbar^2\gamma}\sum_{j=1}^{N}\int_0^r dr\, U(\mathbf{r}-\mathbf{r}_j)\right]. \tag{4.6}$$

The integral in Eq. (4.6) is taken along the straight line connecting the tip and point $\mathbf{r}$. Integrating the flux of the wave function (4.6) over the substrate surface we find the current between the tip and the substrate,

$$J(\mathbf{r}_1(t),\ldots,\mathbf{r}_N(t);\mathbf{r}_0)=\frac{\hbar A^2 B}{m}e^{-2\gamma a}\int_0^{2\pi}d\varphi\int_0^{\infty}d\vartheta\,\vartheta\exp\left[-\gamma a\vartheta^2-\frac{2m}{\gamma\hbar^2}\sum_{j=1}^{N}\int_0^a dr\, U[\mathbf{r}-\mathbf{r}_j(t)+\mathbf{r}_0]\right], \tag{4.7}$$

where $\mathbf{r}=(r\sin\vartheta\cos\varphi, r\sin\vartheta\sin\varphi, r\cos\vartheta)$, and $\mathbf{r}_0$ is the coordinate of the tip. Note that we have used the free-electron approximation in the bulk of the substrate. Constant $B\sim 1$ comes from the continuation of the wave function (4.6) across the substrate surface into the interior of the metal; its exact value depends on the form of the true potential near the surface. It is also assumed that the main contribution to the integral over ϑ in Eq. (4.7) is given by the small-angle cone, i.e., the trajectories near the z axis give the dominating contribution to the tunneling current.

1. Average current

The form of Eq. (4.7) is suitable for averaging over the atom coordinates $\mathbf{r}_j$ due to their factorization. Assume, hereafter, that the distribution of atoms in the space where they are present is homogeneous. Then, the average current takes the form

$$\begin{aligned}\langle J\rangle&=\Omega^{-N}\int_\Omega d\mathbf{r}_1\int_\Omega d\mathbf{r}_j\cdots\int_\Omega d\mathbf{r}_N J(\mathbf{r}_1,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_N;\mathbf{r}_0)\\&=\frac{A^2B}{m}\exp(-2\gamma a)\int_0^{2\pi}d\varphi\int_0^{\infty}d\vartheta\,\vartheta\left[\Omega^{-1}\int_\Omega d\mathbf{r}_1\exp\left[-\gamma a\vartheta^2-\frac{2m}{\gamma\hbar^2}\int_0^a dr\, U(\mathbf{r}-\mathbf{r}_1+\mathbf{r}_0)\right]\right]^N.\end{aligned} \tag{4.8}$$

Here, Ω denotes the space available for atoms. In the case of adsorbed atoms, this is the substrate surface S. For atoms moving in the space between the STM tip and a substrate, Ω has a meaning of the corresponding volume V.

Using Eq. (4.8), it is easy to find the limiting value of $\langle J\rangle$ for $N,\Omega\to\infty$ at a constant value of atomic density $n=N/\Omega$. Note that the integrand in Eq. (4.8) tends rapidly to unity for $\mathbf{r}$ away from $\mathbf{r}_1$. Rewriting the integrand in the form $\exp(\cdots)=[\exp(\cdots)-1]+1$ we find for $N\to\infty$

$$\langle J\rangle=\frac{\hbar A^2B}{m}\exp(-2\gamma a)\times\int_0^{2\pi}d\varphi\int_0^{\infty}d\vartheta\,\vartheta\exp(-\gamma a\vartheta^2+n\alpha), \tag{4.9}$$

$$\alpha=\int_\Omega d\mathbf{r}_1\left[\exp\left[\frac{2m}{\gamma\hbar^2}\int_0^a dr\, U(\mathbf{r}-\mathbf{r}_1)\right]-1\right]. \tag{4.10}$$

Due to the unlimited integration domain, the result no longer depends on the lateral coordinate of the tip.

Equations (4.9) and (4.10) have a form similar to the one obtained in Ref. 12 for the statistical sum of an ideal gas in an external field; similar kinds of expressions can also be found in Ref. 13. We apply these formulas to atoms moving in the volume around the tip (Sec. IV A 1 *a*) and atoms moving along the substrate surface (Sec. IV A 1 *b*).

a. Atoms uniformly distributed between the tip and the substrate. Let us consider a gas of atoms moving freely in a volume near the tunneling region. Assume that the distance a between the tip and the substrate is large compared to the atomic size b, and, for simplicity, that the electron atom potential is spherically symmetrical, $U(\mathbf{r}-\mathbf{r}_j)=U_s(|\mathbf{r}-\mathbf{r}_j|)$. In this case the expression (4.10) for α can be simplified: $\alpha=a\sigma$,

$$\sigma=2\pi\int_0^{\infty}dy\,y\left\{\exp\left[-\frac{2m}{\gamma\hbar^2}\int_{-\infty}^{\infty}dx\, U_s[(x^2+y^2)^{1/2}]\right]-1\right\}, \tag{4.11}$$

i.e., α becomes proportional to the barrier width a with a factor σ independent of φ and ϑ.

Note that the value σ looks like the expression for the total electron-atom scattering cross section found in the *eikonal* approximation.[14] The difference is that σ given by Eq. (4.11) is found for the scattering in the *underbarrier* region. Thus, instead of the imaginary exponent in the conventional expression,[14] we have the real one. Unlike the usual cross section, σ can be either positive or negative, for an attractive or repulsive potential U, respectively; in a general case, the sign of σ is determined by the sign of the exponent in Eq. (4.11).

Calculating the integrals in Eq. (4.9) one finds

$$\langle J\rangle=\frac{\pi\hbar A^2B}{\gamma am}\exp[-(2\gamma-n\sigma)a]. \tag{4.12}$$

Thus, the presence of atoms gives rise to an effective barrier wave number, $\gamma_{\text{eff}}=\gamma-n\sigma/2$. Equation (4.12) holds for $n\sigma$ small compared with γ. Attractive potential $U(r)$ gives positive σ and $\gamma_{\text{eff}}<\gamma$. For the repulsive potential $U(r)$ we have $\sigma<0$ and $\gamma_{\text{eff}}>\gamma$.

Substituting the model potential (3.2) into Eq. (4.11) we obtain

$$\sigma=\frac{2\pi b^2}{3}\xi^{2/3}\int_0^{\xi}\frac{dx}{x^{5/3}}(e^x-1), \tag{4.13}$$

where we introduced, the dimensionless parameter

$$\xi=\frac{\pi mb}{\gamma\hbar^2}U_0 \ . \tag{4.14}$$

For small $|\xi|\ll 1$,

$$\sigma\cong 2\pi\xi b^2=\frac{2\pi^2 mb}{\gamma\hbar^2}U_0 \ . \tag{4.15}$$

For the repulsive potential with large negative $\xi(\ll -1)$,

$$\sigma=-\pi b^2 \ , \tag{4.16}$$

which shows the blocking effect of the cross section of such an atom, nontransparent for tunneling electrons.

For the attractive potential with $\xi\gg 1$,

$$\sigma=\frac{2\pi b^2}{3\xi}e^{\xi} \ . \tag{4.17}$$

At first glance, we meet a striking effect here. The value of σ, given by Eq. (4.17), when substituted into Eq. (4.12), predicts the double exponential-current dependence on the potential strength U_0. The nature of this effect is similar to the double exponential enhancement of the barrier permeability due to the time dependence of potential, considered in Refs. 15. Note, however, that conditions (4.4) and (4.5) do not allow us to consider the case of $\xi\gg 1$, unless $\gamma b\gg 1$. Since an upper estimate for γ is around 0.5 Å $^{-1}$, even for atoms with very strong polarizability the value γb could hardly exceed 2 (it could be greater only for molecules or atomic clusters). Considering formally the case $\gamma b\gg 1$, we still have to deal with the limitations on Eq. (4.11), valid under the condition $a\gg b$. The latter, together with condition $\gamma b\gg 1$, demands extremely large γa, i.e., very small barrier permeability. Thus, the considered effect could have been met only in the regime of extremely low tunneling currents. However, in order to obtain simple estimating formulas we consider below both the cases of large and small ξ.

Let us see what will happen if we use the potential (3.3) instead of (3.2). Then, instead of Eq. (4.13), we get

$$\sigma=\pi b^2\int_0^{2\xi/\pi^{1/2}}\frac{dx}{x}(e^x-1) \ . \tag{4.18}$$

For small ξ the value σ found from this equation is $\pi^{1/2}$ times smaller than the one given by Eq. (4.15). On the other hand, for large ξ Eq. (4.18) gives σ exponentially large compared to the one given by Eq. (4.17). However, ξ is, usually, of the order of unity and the estimates given by expressions (4.13) and (4.18) are of the same order of magnitude.

b. Atoms uniformly distributed along the substrate surface. In the case of adsorbates moving independently along the plane surface S of the conducting substrate, the Ω volume in Eq. (4.10) is two-dimensional and the role of n in Eq. (4.9) is played by the surface density of adsorbates n_s. If we again assume that the size of the atom, b, is small compared to the width of the barrier, a, then we have $\alpha=\sigma$ with σ defined in Eq. (4.11). Thus, the average current, instead of Eq. (4.12), is given by

$$\langle J\rangle=\frac{\pi\hbar A^2B}{\gamma am}\exp[-(2\gamma a-n_s\sigma)] \ . \tag{4.19}$$

There is no potential-barrier renormalization in this expression, unlike in Eq. (4.12). The case calculations of σ do not differ from those given in Sec. IV A 1 *a*.

2. *Temporary correlation function*

Dynamic properties of moving particles do not figure in Eqs. (4.9) and (4.10) for the average current. The only assumption of importance was the—on average—uniform distribution of particles in space. The same applies to the calculation of the current mean-square displacement. However, in order to find the current correlation function, one must consider a particular dynamic model of atomic motion.

Calculating the temporary current correlation function (2.6), we again assume the uniform distribution function of atoms in space. Let $f(\mathbf{r}_0,\mathbf{r}_1,t)$ be the density of a probability for the atom, which has the coordinate $\mathbf{r}_0$ at the moment $t=0$, to appear in point $\mathbf{r}_1$ at a moment t. This function is normalized,

$$\int_\Omega d\mathbf{r}_1 f(\mathbf{r}_0,\mathbf{r}_1,t)=1 \ . \tag{4.20}$$

At $t=0$,

$$f(\mathbf{r}_0,\mathbf{r}_1,0)=\delta(\mathbf{r}_0-\mathbf{r}_1) \ . \tag{4.21}$$

Analogously to the derivation of Eqs. (4.9) and (4.10) we obtain

$$K(t)=\frac{\hbar^2A^4B^2}{m^2}e^{-4\gamma a}\int_0^{2\pi}d\varphi\int_0^{2\pi}d\varphi'\int_0^{\infty}d\vartheta\int_0^{\infty}d\vartheta'\,\vartheta\vartheta'\exp\{-\gamma a[\vartheta^2+(\vartheta')^2]+n\beta(\mathbf{r},\mathbf{r}',t)\}-\langle J\rangle^2 \ , \tag{4.22}$$

$$\mathbf{r}=(r\sin\vartheta\cos\varphi, r\sin\vartheta\sin\varphi, r\cos\vartheta) \ ,$$

$$\mathbf{r}'=(r\sin\vartheta'\cos\varphi', r\sin\vartheta'\sin\varphi', r\cos\vartheta') \ ,$$

with

$$\beta(\mathbf{r},\mathbf{r}',t)=\int_\Omega d\mathbf{r}_1\int_\Omega d\mathbf{r}_2 f(\mathbf{r}_1,\mathbf{r}_2,t)\left\{\exp\left[-\frac{2m}{\gamma\hbar^2}\int_0^a dr[U(\mathbf{r}-\mathbf{r}_1+\mathbf{r}_0)+U(\mathbf{r}'-\mathbf{r}_2+\mathbf{r}_0)]\right]-1\right\}$$
$$=\int d\mathbf{r}_1\int d\mathbf{r}_2 f(\mathbf{r}_1-\mathbf{r}_2,t)\left[\exp\left[-\frac{2m}{\gamma\hbar^2}\int_0^a dr\,U(\mathbf{r}-\mathbf{r}_1+\mathbf{r}_0)\right]-1\right]$$
$$\times\left[\exp\left[-\frac{2m}{\gamma\hbar^2}\int_0^a dr\,U(\mathbf{r}'-\mathbf{r}_2+\mathbf{r}_0)\right]-1\right]+2\alpha\ . \tag{4.23}$$

Consider, for instance, the case of small density n and weak electron-atom interaction $U(r)$. Then, expanding the exponents in Eqs. (4.22) and (4.23) and Eqs. (4.9) and (4.10) one has

$$K(t)=\frac{4A^4B^2n}{\gamma^2\hbar^2}e^{-4\gamma a}\int_0^{2\pi}d\varphi\int_0^{2\pi}d\varphi'\int_0^\infty d\vartheta\int_0^\infty d\vartheta'\vartheta\vartheta'\exp\{-\gamma a[\vartheta^2+(\vartheta')^2]\}$$
$$\times\int d\mathbf{r}_1\int d\mathbf{r}_2 f(\mathbf{r}_1-\mathbf{r}_2,t)\left[\int_0^a dr\,U(\mathbf{r}-\mathbf{r}_1+\mathbf{r}_0)\right]$$
$$\times\left[\int_0^a dr\,U(\mathbf{r}'-\mathbf{r}_2+\mathbf{r}_0)\right]\ . \tag{4.24}$$

It is seen from Eq. (4.24) that in this case the correlation function is a quadratic functional of the electron-atom interaction, hence it is independent of the sign of $U(r)$.

Concluding Sec. IV A, we stress that the expressions for the average current [(4.9) and (4.10)] and the temporary current correlation function [(4.22) and (4.23)] could be applied when the interaction $U(r)$ between the tunneling electrons and the moving atoms is sufficiently weak and smooth.

B. STRONG INTERACTION BETWEEN TUNNELING ELECTRONS AND MOVING ATOMS

In the case of a strong interaction between electrons and atoms the above-developed semiclassical theory fails, and we have to choose another approach. Let us assume that the current flows mostly along the narrow tubes in the barrier region that connect the tip, the atoms, and the substrate. Suppose that electron-atom interaction $U(\mathbf{r})$ is spherically symmetric in the vicinity of atoms and is small at a distance away from them. We may then neglect interaction of an electron with other atoms when considering its interaction with a given atom. This is an important simplification. Under this assumption, the most probable tunneling trajectories between the tip, the atoms, and the substrate are the straight segments. In order to calculate the current carried through a series of k atoms (see Fig. 2) we must connect them by the most probable tunneling paths, s_{ij}, and continue the wave function (4.1) along them. Then, the wave function after passing kth atom takes the form

$$\psi_k(\mathbf{r})=\left[\frac{A}{\gamma^{1/2}}\prod_{j=1}^{k}\frac{\Lambda_j\exp(-\gamma|\mathbf{r}_j-\mathbf{r}_{j-1}|)}{|\mathbf{r}_j-\mathbf{r}_{j-1}|}\right]\times\frac{\exp(-\gamma|\mathbf{r}-\mathbf{r}_k|)}{|\mathbf{r}-\mathbf{r}_k|}\ , \tag{4.25}$$

where $\mathbf{r}_j$ and Λ_j are the coordinate and the scattering amplitude of atom j, respectively.

Let us introduce the partial current through a series of k atoms:

$$J_k(\mathbf{r}_1,\ldots,\mathbf{r}_k)=\frac{\hbar B}{m}\int_S d\mathbf{s}\left|\Psi_k^*\frac{\partial\Psi_k}{\partial z}\right|$$
$$\cong\frac{\hbar B\gamma}{m}\int_S d\mathbf{s}|\Psi_k(\mathbf{r})|^2_{\mathbf{r}=(\mathbf{s},a)}\ , \tag{4.26}$$

where the integral is taken along the substrate surface S. The approximate equality in Eq. (4.26) is valid under the semiclassical assumption $\gamma|a-z_k|\gg1$. The quantity $B(\sim1)$ is a constant, analogous to the factor B in Eq. (4.7). The region where $\gamma|a-z_k|\sim1$ has, usually, a size comparable to the characteristic size of the atom, b. Therefore, in this region expression (4.25) fails. However, the contribution of this region to the net tunneling current will be relatively small due to the large gap $a\gg\gamma^{-1}$.

Under the assumption $\gamma|a-z_k|\gg1$, using the expansion for $|\mathbf{a}-\mathbf{r}_k|$ similar to the Eq. (4.29), we find from Eqs. (4.25) and (4.26)

$$J_k(\mathbf{r}_1,\ldots,\mathbf{r}_k)=\frac{\pi A^2B}{m\gamma}\left[\prod_{j=1}^{k}\frac{|\Lambda_j|^2\exp(-2\gamma|\mathbf{r}_j-\mathbf{r}_{j-1}|)}{|\mathbf{r}_j-\mathbf{r}_{j-1}|^2}\right]\frac{\exp[-2\gamma(a-z_k)]}{(a-z_k)}\ . \tag{4.27}$$

The dominant contribution to the net current is made by atoms located near the z axis because they are "linked" by the paths that have the shortest lengths $|\mathbf{r}_j-\mathbf{r}_{j-1}|$ with $z_j>z_{j-1}$. For such a series of atoms we can replace $|\mathbf{r}_j-\mathbf{r}_{j-1}|$ by $|z_j-z_{j-1}|$ in the denominator of Eq. (4.27). Thus simplified, Eq. (4.27) could be used for the calculation of the average current and current correlation function.

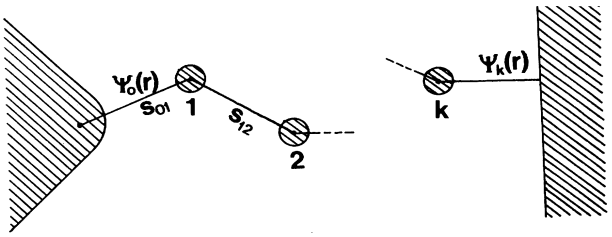

FIG. 2. Illustration of the strong interaction model. s_{ij} are the most probable tunneling paths connecting atoms in the barrier region.

As before, we assume that the distribution of atoms in space is uniform.

1. Average current

For a homogeneous distribution of atoms, the definition of the average current passing through a series of k atoms reads

$$\langle J_k \rangle = \Omega^{-k} \int_\Omega d\mathbf{r}_1 \cdots \int_\Omega d\mathbf{r}_k J_k(\mathbf{r}_1, \ldots, \mathbf{r}_k) . \quad (4.28)$$

Substituting Eq. (4.27) into Eq. (4.28) we can integrate over the transversal components $\mathbf{u}_j$ of the coordinates of atoms, $\mathbf{r}_j = (\mathbf{u}_j, z_j)$. An expansion

$$|\mathbf{r}_j - \mathbf{r}_{j-1}| \approx (z_j - z_{j-1}) + |\mathbf{u}_j - \mathbf{u}_{j-1}|^2 / [2(z_j - z_{j-1})] , \quad (4.29)$$

Inserting into the exponent of Eq. (4.27), gives

$$\langle J_k \rangle = \Omega^{-k} \int_{a > z_j > z_{j-1} > 0} dz_1 \cdots dz_k \langle J_k \rangle_{\mathbf{u}_1 \cdots \mathbf{u}_k} , \quad (4.30)$$

$$\langle J_k \rangle_{\mathbf{u}_1 \cdots \mathbf{u}_k} = \frac{\pi^{k+1} A^2 B |\Lambda|^{2k}}{m \gamma^{k+1}} \times e^{-2\gamma a} \left[\prod_{j=1}^{k} \frac{1}{z_j - z_{j-1}} \right] \frac{1}{a - z_j} ,$$

where we put $\Lambda_j = \Lambda$, assuming that all the atomic particles are identical.

The integrals over z_j in Eq. (4.30) have a logarithmic divergence for $z_j = z_{j-1}$. The simplest way to deal with this difficulty is to cut this integral off at $z_j - z_{j-1} = b$, because the distance of closest approach of atoms to each other cannot be considerably smaller than b. Of course, in three dimensions that does not exclude the possibility of the arbitrary small values of $z_j - z_{j-1}$. However, among different relative atom positions with small $z_j - z_{j-1}$, the largest contribution to the current is given by the positions with small $|\mathbf{u}_j|$ and $|\mathbf{u}_{j-1}|$, i.e., by atoms located near the z axis and hence having $|\mathbf{r}_j - \mathbf{r}_{j-1}| \cong |z_j - z_{j-1}|$.

Note that the divergence comes from the approximation (4.29). We can avoid this approximation in the calculation of the tunneling current (see below) and thereby evaluate the precise value of the cutoff. However, we see no way to avoid expansion (4.29) for obtaining analytical expressions for correlation functions. Therefore, we consider first an approximate and then the exact solution for an average current in order to understand how reliable this approximation could be.

Assume that the space Ω contains N atoms. There are $C_N^k k! = N!/(N-k)! \approx N^k$ ways to choose from them a sequence of $k \ll N$ atoms. The current through k atoms averaged over their positions in $\langle J_k \rangle$, and the net average current is

$$\langle J \rangle = \sum_{k \geq 0} N^k \langle J_k \rangle . \quad (4.31)$$

For the small particle density, the principal contribution to $\langle J \rangle$ is made by the two first terms in Eq. (4.31). Then, using Eq. (4.30) for $\langle J_1 \rangle$ and using the suggested cutoff procedure, we find, to the accuracy of a term linear in particle density n,

$$\langle J \rangle = J_0 \left[1 + \frac{2\pi |\Lambda|^2}{\gamma} n \ln \frac{a}{b} \right], \quad n = \frac{N}{\Omega} ,$$
$$J_0 = \frac{\pi \hbar A^2 B}{m \gamma a} \exp(-2\gamma a) . \quad (4.32)$$

Compare this result with the one obtained for the weak interaction case (Sec. IV A). For small n we can rewrite Eq. (4.12) in the form $\langle J \rangle = J_0(1 + n\sigma a)$. Thus, for the low-density n, the strong interaction model gives much weaker dependence on the tunneling distance than the weak interaction model. The next terms of expansion (4.31) could be similarly calculated using Eq. (4.30) and cutting integrals for $z_j - z_{j-1} < b$ and for $a - z_k < b$, $z_1 - z_0 < b$.

Now let us calculate the average current $\langle J \rangle$ up to the first order in n, avoiding expansion (4.28). Using Eqs. (4.25) and (4.26), we can find the value of $\langle J_1 \rangle$ from Eq. (4.28) and thus obtain

$$\langle J \rangle = J_0 \left[1 + \frac{2\pi |\Lambda|^2}{\gamma} n [\ln(4\gamma a) + 0.5772\ldots] \right] . \quad (4.33)$$

Since $\gamma a \gg 1$ and usually $\gamma b \sim 1$, Eqs. (4.33) and (4.32) give very similar answers for the average current. Thus, the cutoff used in the derivation of Eq. (4.32) seems reasonable.

2. Temporary correlation function for the low density of atoms

For small n we again, as in Eq. (4.32), take into account the current J_0 and the currents $J_1(\mathbf{r}_k)$ passing through single atoms with coordinates $\mathbf{r}_k$. The net current will be given by the sum

$$J(t) = J_0 + \sum_{k=1}^{N} J_1[r_k(t)] , \quad (4.34)$$

which leads to an expression for the correlation function

$$K(t) = n \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 f(\mathbf{r}_1, \mathbf{r}_2, t) J_1(\mathbf{r}_1) J_1(\mathbf{r}_2) . \quad (4.35)$$

Below, calculating the noise for the strong electron-atom interaction, we restrict the analysis by the case of small density of atoms.

V. GAS OF ATOMS MOVING IN THE TUNNELING SPACE

In this section we deal with an ideal equilibrium gas of atoms moving between the tip and the substrate surface and find the influence of the gas on the average current and noise characteristics of the tunneling gap.

The Maxwell-Boltzmann distribution for a gas of free atoms gives

$$f(\mathbf{r}_0,\mathbf{r}_1,t)=\left[\frac{M}{2\pi k_B T t^2}\right]^{3/2}\exp\left[-\frac{M|\mathbf{r}_1-\mathbf{r}_0|^2}{2k_B T t^2}\right], \quad (5.1)$$

where M is the mass of an atom and k_B is the Boltzmann constant. In the derivation of analytical expressions for the noise-characterizing functions we will use the approximations corresponding to both the weak and strong electron-atom interaction. However, there is a general result which follows from the basic expressions of Sec. VI and the distribution function (5.1). It is the universal, $T^{-1/2}$, temperature dependence of the low-frequency noise $S_a(0)$.

A. Current noise for the weak electron-atom interaction

Equations (4.22) and (4.24) will be the starting point for the calculations in this section. We distinguish between the cases of small and large ξ and of the low and high gas density.

1. Gas of low density

Assume that the particle density n in Eq. (4.22) is so low that $n\beta \ll 1$. Then one can use expression (4.24) for the temporary correlation function. Calculating the integrals in Eq. (4.24) we distinguish between the small and large ξ defined by Eq. (4.14).

a. The case of $\xi \ll 1$. Consider the situation of the small interaction potential $U(r)$ so that the correlation function is defined by Eq. (4.24). We can obtain the asymptotic expression for the zero-frequency Fourier transform of this eleven-dimensional integral with model potential (3.2) under a natural assumption $\gamma b^2/a \ll 1$. Using polarization model potential (3.2), after long and cumbersome calculations we obtain an extremely simple result:

$$S_a(0)=\frac{nb^4}{2\pi}\left[\frac{\gamma a M}{k_B T}\right]^{1/2}\xi^2\left[\ln\left[\frac{a}{\gamma b^2}\right]-1.29\right]\langle J\rangle^2 ,$$

$$\langle J\rangle \approx J_0=\frac{\pi\hbar A^2}{m\gamma a}e^{-2\gamma a} , \quad (5.2)$$

$$\xi \ll 1, \quad \gamma b^2/a \ll 1, \quad n\xi a b^2 \ll 1 .$$

We failed to find a transparent expression for the correlation function $K(t)$ using the model potential (3.2). However, using the exponential potential (3.3) we obtain

$$K(t)=\begin{cases}\dfrac{Q}{g(t)}\left\{a\,\mathrm{erf}\left[\dfrac{a}{g(t)^{1/2}}\right]+\left[\dfrac{g(t)}{\pi}\right]^{1/2}\left[\exp\left[-\dfrac{a^2}{g(t)}\right]-1\right]\right\}, & g(t)\gg a/\gamma \\ Q\left[\dfrac{\gamma a}{2g(t)}\right]^{1/2}\arctan\left[\left[\dfrac{2a}{\gamma g(t)}\right]^{1/2}\right], & g(t)<a^2 .\end{cases} \quad (5.3)$$

$$Q=4b^4\xi^2 n\langle J\rangle^2, \quad g(t)=2b^2[1+(k_B T/Mb^2)t^2] .$$

Since $a\gamma \gg 1$ and $a/b \gg 1$, Eq. (5.3) covers all values of t. In particular, for $1 \ll a^2/g(t) \ll \gamma a$ the first and the second lines in Eq. (5.3) give identical results. Usually $a \gg \gamma b^2$, so that the second line of Eq. (5.3) gives the correlation time,

$$t_c=(aM/\gamma k_B T)^{1/2}, \quad (a \gtrsim \gamma b^2) \quad (5.4)$$

independent of the size of the atom. This is the time required for an atom, moving with the thermal velocity $v_T=(2k_B T/M)^{1/2}$ to pass along the current tube cross section with the radius of the order of $(a/\gamma)^{1/2}$. In the opposite case of b large enough one finds from Eq. (5.3) the correlation time

$$t_c=(M/k_B T)^{1/2}b , \quad (5.5)$$

which is the time for an atom to pass the distance equal to its own size b. Using Eq. (5.3) we find for the low-frequency noise

$$S_a(0)=2\pi b^4\xi^2\langle J\rangle^2\left[\frac{\gamma a M}{k_B T}\right]^{1/2} \times\ln\left[\left[\frac{a}{\gamma b^2}\right]^{1/2}+\left[\frac{a}{\gamma b^2}+1\right]^{1/2}\right] . \quad (5.6)$$

For $a \gg \gamma b^2$ this expression differs from Eq. (5.2) only by a factor of $\pi/2$. This indicates at the usual proximity of results given by the polarization model of electron-atom interaction, Eq. (3.2), and by the Gaussian one, Eq. (3.3).

b. The case of $\xi \gg 1$. Here, the exponent in Eq. (4.23) is large for the values of $\mathbf{r}_1$ and $\mathbf{r}_2$, which give the main contribution to the integral. Applying the saddle-point method in the integration over $\mathbf{r}_1$ and $\mathbf{r}_2$ we find

$$\beta=\frac{\pi b^4 M e^{2\xi}}{2^{1/2}3\xi(3\xi k_B T t^2+2b^2M)}\int_0^a dz\exp\left[-\frac{3\xi M[\vartheta^2+\vartheta'^2-2\vartheta\vartheta'\cos(\varphi-\varphi')]z^2}{2(3\xi k_B T t^2+2b^2M)}\right] . \quad (5.7)$$

Calculating the integral (4.24) with the use of Eq. (5.7) we obtain

$$K(t)=\frac{2^{3/2}\pi nab^4\gamma}{9\xi^2}e^{2\xi}\langle J\rangle^2\int_0^a dz\left[z^2+\gamma a\left[\frac{kT}{M}t^2+\frac{2b^2}{3\xi}\right]\right]^{-1}$$
$$=\frac{\pi n(a\gamma)^{1/2}b^3[u(t)]^{1/2}}{2^{1/2}(3\xi)^{3/2}}e^{2\xi}\text{arctg}\left[\left[\frac{3\xi a}{\gamma b^2}u(t)\right]^{1/2}\right]\langle J\rangle^2 , \tag{5.8}$$
$$u(t)=\left[2+\frac{3\xi k_BT}{Mb^2}t^2\right]^{-1}, \quad \langle J\rangle\approx J_0 ,$$
$$\xi\gg 1, \quad nab^2e^{\xi}/\xi\ll 1, \quad u(t)\sim 1 .$$

One finds from this equation the expression for the correlation time:

$$t_c=\begin{cases}(aM/\gamma k_BT)^{1/2}, & \xi a\gtrsim\gamma b^2\\ (\xi M/k_BT)^{1/2}b, & \xi a\lesssim\gamma b^2 .\end{cases} \tag{5.9}$$

Usually the inequality $\xi a\gtrsim\gamma b^2$ holds and Eq. (5.9) gives the result coinciding with Eq. (5.4).

Using Eq. (5.9) one finds for the low-frequency noise,

$$S_a(0)=\frac{\pi nb^4e^{2\xi}}{36\xi^2}\left[\frac{\gamma aM}{2k_BT}\right]^{1/2}\ln\left[\frac{6a\xi}{\gamma b^2}\right]\langle J\rangle^2 , \tag{5.10}$$
$$\xi a/(b^2\gamma)\gg 1 .$$

2. High gas density

The condition $n\beta\gg 1$ [see Eq. (4.22)] will define the case of high gas density. Concerning free gas, we are not allowed to deal with very high densities. This condition, however, could be fulfilled for moderate densities, but for the sufficiently large electron-atom interaction. Therefore, we consider here only the strong-interaction case $\xi\gg 1$.

The integrals over angles in Eq. (4.22) are calculated as follows. For large values of n, the main contribution to this integral is given by the region near the maximum value of β considered as a function of ϑ, ϑ', φ, and φ'. This maximum corresponds to the zero value of the exponent of the integrand in Eq. (5.7). Expanding the integrand up to the linear term in the exponent we evaluate the integrals over ϑ, ϑ', φ, and φ' and obtain

$$K(t)=\frac{2^{5/2}3\gamma e^{-2\xi}}{\pi na^2[u(t)]^2}\times\exp\left[\frac{nab^2e^{\xi}}{3\xi}[2^{-1/2}e^{\xi}u(t)-2]\right]\langle J\rangle^2 , \tag{5.11}$$
$$\langle J\rangle=J_0\exp\left[\frac{2\pi ab^2n}{3\xi}e^{\xi}\right] ,$$
$$\xi\gg 1, \quad nab^2e^{\xi}/\xi\gg 1, \quad \xi a/(b^2\gamma)\gg 1, \quad u(t)\sim 1 ,$$

where $u(t)$ is defined in Eq. (5.8).

It follows from Eq. (5.11) that $K(t)\gg\langle J\rangle^2$ at least for $\xi a/(b^2\gamma)\sim 1$. Then, with use of the saddle-point method, we find for the low-frequency noise

$$S_a(0)=\frac{2^{3/4}24M^{1/2}\gamma e^{-3\xi}}{\pi^2n^{3/2}(k_BT)^{1/2}a^{5/2}}\times\exp\left[\frac{\pi nab^2e^{\xi}}{3\xi}(2^{-3/2}e^{\xi}-2)\right]\langle J\rangle^2 . \tag{5.12}$$

The prefactor of $\langle J\rangle^2$ has the exponential dependence on the distance a and the universal (for the free gas) $T^{-1/2}$ temperature dependence.

B. Current noise for the strong electron-atom interaction

The calculations presented in this section are based on Eq. (4.35), which is valid for the strong electron-atom interaction and low gas density. Substituting $J_1(\mathbf{r}_1)$ of Eq. (4.27) into Eq. (4.35) and using the approximation similar to the one employed in the derivation of Eq. (4.32), we can reduce the six-dimensional integration in Eq. (4.34) to a double integral:

$$K(t)=\frac{\pi^3n}{\gamma^3t}(A_0|\Lambda|)^4\left[\frac{M}{2\pi kT}\right]^{1/2}e^{-4\gamma a}\times\int_{-\infty}^{\infty}dx\exp\left[-\frac{Mx^2}{2k_BTt^2}\right]\times\oint dz\left[z(a-z)(z+x)(a-z-x)\times\left[2z+x+\frac{2k_BT}{M}\gamma t^2\right]\right]^{-1} . \tag{5.13}$$

The integral over z is taken for the positive values of the parentheses with an integration cutoff at a distance b from the singularities where the denominator of the integrand turns to zero [cf. the derivation of Eq. (4.32) for the average current; see the discussion after Eq. (4.30)]. Since we have assumed that $a\gg b$, the main contribution to the integral comes from the vicinity of $z=0$, and this allows us to evaluate the a dependence of this integral as $\sim a^{-2}$. In order to proceed with an analytical evaluation of the correlation-function dependence on other parameters we adopt the semiclassical condition $\gamma b\gg 1$ (bearing in mind, however, that γb is usually ~ 1). Then

$$K(t)=\frac{\pi n}{\gamma}|\Lambda|^4\langle J\rangle^2\int_b^\infty\frac{dz}{z^2(z+k_BT\gamma M^{-1}t^2)}$$
$$=\frac{\pi nM}{2k_BT\gamma^2bt^2}|\Lambda|^4\langle J\rangle^2$$
$$\times\left[1-\frac{Mb}{k_BT\gamma t^2}\ln\left[1+\frac{k_BT\gamma t^2}{Mb}\right]\right]. \quad (5.14)$$

The characteristic correlation time found from this expression is

$$t_c=(bM/\gamma k_BT)^{1/2}. \quad (5.15)$$

To find the low-frequency noise, it is easier to use the first equality of Eq. (5.14) and change the order of integration. We then have

$$S_a(0)=\frac{\pi^2}{6}\left[\frac{M}{k_BT}\right]^{1/2}\frac{n|\Lambda|^4}{(\gamma b)^{3/2}}\langle J\rangle^2, \quad (5.16)$$

with $\langle J\rangle\approx J_0$.

Compare this result with the one obtained for the case of the weak electron-atom interaction in Sec. V A, i.e., Eqs. (5.2) and (5.10). The most important difference is that the prefactor of $\langle J\rangle^2$ in Eq. (5.16) is independent of a, while in Eqs. (5.2) and (5.10) the prefactor is proportional to $a^{1/2}$. Let us take into account the expressions for the scattering cross section σ, obtained in Section IV A 1 a for $\xi\ll1$ and $\xi\gg1$, and the meaning of Λ as a scattering amplitude (i.e., $\sigma\sim|\Lambda|^2$). Then one obtains that for $\gamma b\sim1$ and $\xi\sim1$ the intensity of the low-frequency noise given by Eq. (5.16) is $\sim(\gamma a)^{1/2}$ times smaller than the noise described by Eqs. (5.2) and (5.10). Since the value of $(\gamma a)^{1/2}$ usually does not exceed 5, the order of magnitude of the low-frequency noise, predicted by all the three equations, is the same.

VI. NOISE INTRODUCED BY DIFFUSION

In this section we study the influence of atomic particles diffusively moving between the tip and the substrate on the current temporary correlation function and the current noise. The result strongly depends on the dimension d of the space Ω in which the particles are moving. The distribution function $f(\mathbf{r}_0,\mathbf{r}_1,t)$, introduced in Eqs. (4.23) and (4.35), now has the form

$$f(\mathbf{r}_0,\mathbf{r}_1,t)=(4\pi D|t|)^{-d/2}\exp\left[-\frac{|\mathbf{r}_1-\mathbf{r}_0|^2}{4D|t|}\right], \quad (6.1)$$

where D is the diffusion coefficient.

The temperature dependence enters through D. Note, that we need no detailed calculations to evaluate the dependence of spectral density $S_a(\omega)$ on D and ω for small ω. For a three-dimensional motion $d=3$, we have $S_a(0)\sim D^{-1}$; for the in-plane motion $d=2$, $S_a(\omega)\sim_{\omega\to0}D^{-1}\ln(\omega)$; for the one-dimensional motion $d=1$, $S_a(\omega)\sim_{\omega\to0}(\omega D)^{-1/2}$.

Below, we derive complete analytical expressions for the temporary correlation function and noise spectral density separately for the cases of $d=3$ and $d=2$. The latter corresponds to isotropic diffusion along the surface of the substrate.

A. Three-dimensional atom diffusion in the tunneling gap

Consider atomic particles independently moving in the space between the STM tip and the substrate with the three-dimensional ($d=3$) distribution function (6.1). In this section we apply the weak-interaction model for a calculation of temporary current correlation function and the low-frequency noise introduced by these particles. We again distinguish between the cases of low and high particle densities.

1. *Low particle density*

Assume, first, that $\xi\ll1$. The temporary current correlation function could be obtained without a new calculation, if we make use of the fact that the distribution function (6.1) can be obtained from the distribution function (5.1) by the substitution $(k_BT/M)t^2\to D|t|$. Then, for the Gaussian model of electron-atom interaction (3.3) we obtain

$$K(t)=\begin{cases}\dfrac{Q}{q(t)}\left\{a\,\mathrm{erf}\left[\dfrac{a}{q(t)^{1/2}}\right]+\left[\dfrac{q(t)}{\pi}\right]^{1/2}\left[\exp\left[-\dfrac{a^2}{q(t)}\right]-1\right]\right\}, & q(t)\gg a/\gamma,\\ Q\left[\dfrac{\gamma a}{2q(t)}\right]^{1/2}\arctan\left[\left[\dfrac{2a}{\gamma q(t)}\right]^{1/2}\right], & q(t)\ll a^2,\end{cases} \quad (6.2)$$

$$Q=4b^4\xi^2n\langle J\rangle^2,\quad q(t)=2b^2[1+(D/b^2)|t|].$$

The principal difference between this expression from Eq. (5.8) found for the free-atom gas is that in order to find the low-frequency noise, one should use not only the first but also the second line in Eq. (6.2). Indeed, Eq. (5.3) gave $g(t)\sim t^2$ for $t\to\infty$ and the integral of $[g(t)]^{-1/2}\arctan\{[2a/\gamma g(t)]^{1/2}\}$ was converging. Now $q(t)\sim|t|$ for $t\to\infty$ and the integral of $[q(t)]^{-1/2}\arctan\{[2a/\gamma q(t)]^{1/2}\}$ logarithmically diverges. Eq. (6.2) gives the correlation time

$$t_c=a/(\gamma D)\quad(a\geq\gamma b^2). \quad (6.3)$$

After integrating Eq. (6.2) over time, we obtain a simple expression for the low-frequency noise:

$$S_a(0)=4na\frac{b^4}{D}\xi^2 J_0^2\left[\ln\frac{2\gamma a}{1+\delta}+C-2\delta^{1/2}\arctan(\delta^{-1/2})\right], \quad (6.4)$$

$\delta=\gamma b^2/a$, $C=0.5772\ldots$.

Usually, $\delta\ll 1$ and it is only $\ln(\gamma a)$ that remains in square brackets in Eq. (6.43).

We have not succeeded in analytically calculating the temporary correlation function for the polarization model of the electron-atom interaction potential (3.2). However, after cumbersome calculations, we have found the corresponding expression for the low-frequency noise under the condition $\delta\ll 1$:

$$S_a(0)=2^{1/2}\pi na\frac{b^4}{D}\xi^2 J_0^2\ln(\gamma a) . \quad (6.5)$$

Results (6.4) and (6.5) differ only by the constant factor $\pi/2^{3/2}\approx 1.1$. It is, thus, natural to suggest that other results of this section would not be sensitive to a particular form of the interaction potential, either.

In the case of $\xi\gg 1$, treated with the help of polarization potential, we find

$$S_a(0)=\frac{4\pi^{1/2}nab^4e^{2\xi}}{9D\xi^2}J_0^2\ln(a\xi^{1/2}/b) . \quad (6.6)$$

Comparing Eqs. (6.4)–(6.6) with Eq. (4.17), which determines the electron-atom scattering cross section σ, we find that the low-frequency noise $S_a(0)$ is proportional to σ^2 for both the weak and relatively strong interactions.

2. High particle density

Let us consider the case of high particle density n and $\xi\gg 1$. Then the integrals in Eqs. (4.22), (4.23) can be calculated by the saddle-point method, formally regarding n as a large parameter. Using the polarization potential, we find the temporary correlation function in the form

$$K(t)=J_0^2\exp\left[\frac{\pi^{1/2}nab^2e^{2\xi}}{3\xi}-\pi^{1/2}naDe^{2\xi}|t|\right], \quad (6.7)$$

which gives the correlation time

$$t_c=(naDe^{2\xi})^{-1} . \quad (6.8)$$

Unlike the correlation time (6.3) this result depends strongly on the electron-atom interaction through the parameter ξ. The low-frequency noise obtained from Eq. (6.7) is given by

$$S_a(0)=\frac{2e^{-2\xi}}{\pi^{1/2}naD}J_0^2\exp\left[\frac{\pi^{1/2}nab^2e^{2\xi}}{3\xi}\right] . \quad (6.9)$$

Equations (6.7)–(6.9) are valid only when $nab^2e^{2\xi}/\xi\gg 1$. Note that the assumption of independent atomic particles made in this paper imposes a strong limitation on the value of density n. Evidently, for the large atomic density n the movement of particles will strongly depend on their mutual interaction.

B. Surface diffusion of adatoms

Let us consider now the surface diffusion of adsorbed atoms.[16] We will use the spherically symmetric model of electron-atom interaction that can serve only as an approximation to the real asymmetric interaction between the electron and adsorbed atom. However, it can be shown[17] that the functional form of the temporary current correlation function [Eq. (7.7)] holds for the asymmetric electron-adatom interaction as well, with a proper value of the cross section σ.

1. Temporary correlation function for the weak electron-atom interaction

Applying the saddle-point method to the calculation of the integral for β, Eq. (4.23), with distribution function (6.1), $d=2$, and polarization potential (3.2), we find for $\xi\gg 1$

$$\beta=\frac{\pi b^2}{3\xi(1+3\xi D|t|b^{-2})}\times\exp\left[2\xi-\frac{3\xi|\mathbf{u}-\mathbf{u}'|^2}{4b^2(1+3\xi D|t|b^{-2})}\right], \quad (6.10)$$

$\mathbf{u}=a\sin\vartheta(\cos\varphi,\sin\varphi)$, $\mathbf{u}'=a\sin\vartheta'(\cos\varphi',\sin\varphi')$.

The expression (4.22) for the correlation function in this case reads

$$K(t)=\frac{A^4B^2\hbar^2}{a^4m^2}\int_S d\mathbf{u}\int_S d\mathbf{u}'\exp\left[-4\gamma a-\frac{\gamma}{a}[u^2+(u')^2]+n_s\beta\right]+\langle J\rangle^2 . \quad (6.11)$$

a. Limits of low and high adsorbate density. In the case of low adsorbate density $n_sb^2e^{2\xi}/\xi\ll 1$, the exponential function in Eq. (6.11) can be expanded up to the first order of $n_s\beta$, giving

$$K(t)=\frac{2\pi n_s\gamma b^4e^{2\xi}}{9\xi^2(a+2\gamma D|t|)}\langle J\rangle^2 , \quad \langle J\rangle=J_0=\frac{\pi\hbar A^2B}{m\gamma a}e^{-2\gamma a} . \quad (6.12)$$

The correlation time

$$t_c=a/(\gamma D) , \quad (6.13)$$

found from Eq. (6.12), does not depend on the detail form of the electron-atom interaction. Using Eq. (6.12) we find the noise spectral density

$$S_a(\omega)=\frac{2n_sb^4e^{2\xi}}{9\xi^2D}\exp\left[\frac{i\omega a}{2\gamma D}\right]E_1\left[\frac{i\omega a}{2\gamma D}\right]\langle J\rangle^2 , \quad (6.14)$$

where $E_1(x)$ is the integral exponential function.

Consider the case of large adsorbate density $nb^2e^{2\xi}/\xi\gg 1$. Then

$$G(t)=\frac{2\gamma}{\pi a n_s}\left[1+\frac{3\xi D|t|}{b^2}\right]^2 \times\exp\left[-2\xi+\frac{\pi b^2 e^{\xi} n_s}{3\xi}\left[\frac{e^{\xi}}{1+3\xi D|t|b^{-2}}-4\right]\right]\langle J\rangle^2 ,$$
$$\langle J\rangle=\frac{\pi\hbar A^2 B}{m\gamma a}\exp\left[-2\gamma a+\frac{2\pi b^2 n_s}{3\xi}e^{\xi}\right] . \quad (6.15)$$

Equation (6.15) is valid for $\xi D|t|b^{-2}\gg 1$, then $K(t)\gg\langle J\rangle^2$. The correlation time in this case is

$$t_c=b^2/(\xi D) . \quad (6.16)$$

This is a characteristic time for an atom to diffuse along the distance equal to its own size. It is much less than t_c for the low adsorbate density case.

b. Low frequency noise. An analytical expression for the low-frequency noise can be obtained from the general expressions for the correlation function independently of the detailed form of the electron-atom interaction and the limiting case under study. This is possible due to the logarithmic divergence of the low-frequency noise for the two-dimensional diffusive processes.

From Eqs. (4.22) and (6.1) we find that for large $|t|$,

$$\beta=2\alpha+\frac{\alpha^2}{4\pi D|t|} , \quad (6.17)$$

where α is defined by Eq. (4.10). Thus,

$$S_a(\omega)\underset{\omega\to 0}{\approx}\frac{\langle J\rangle^2\alpha^2 n_s}{8\pi^2 D}\int_{-\infty}^{\infty}dt\frac{e^{i\omega t}}{|t|+t_c} \underset{\omega\to 0}{\approx}\frac{\langle J\rangle^2\alpha^2 n_s}{4\pi^2 D}\ln(\omega t_c) , \quad (6.18)$$
$$\langle J\rangle=\frac{\pi\hbar A^2 B}{\gamma a m}\exp(-2\gamma a+n_s\alpha) ,$$

where, according to Sec. IV B 1 *a*, the order of magnitude of t_c lies between $a/(\gamma D)$ and $b^2/(\xi D)$.

2. Strong electron-atom interaction

The correlation function for the model of strong electron-atom interaction is calculated with the help of Eq. (4.25) for the electron wave function Ψ_1. We find

$$K(t)=\frac{\pi n_s B^2\hbar^2}{D|t|m^2}\left[\frac{A_0|\Lambda|}{a}\right]^4 \times\int_S d\mathbf{r}_1\int_S d\mathbf{r}_2\exp\left[-\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{4D|t|}-2\gamma(|\mathbf{r}_1-\mathbf{r}_0|+|\mathbf{r}_2-\mathbf{r}_0|)\right] . \quad (6.19)$$

The main contribution to this integral comes from a small area of the substrate surface near the point $(0,0,a)$. Making the expansion similar to (4.29), we keep in the exponent of Eq. (6.19) only the terms quadratic in $|\mathbf{r}_1-\mathbf{a}|$, and $|\mathbf{r}_2-\mathbf{a}|$, where $\mathbf{a}=(a,0,0)$, and calculate the arising Gaussian integral to obtain

$$K(t)=\frac{2\pi n_s\gamma|\Lambda|^4\langle J\rangle^2}{(a+2\gamma D|t|)} . \quad (6.20)$$

This result coincides with Eq. (6.12) if we put $|\Lambda|^2$ equal to $b^2e^{\xi}/(3\xi)$.

VII. MAIN RESULTS

Let us summarize the principal results of the paper and estimate the role of the effects studied.

A. Average current

For the atomic particles *independently* moving and *uniformly* distributed in the tunneling gap, the average STM current is

$$\langle J\rangle=J_0 e^{na\sigma} , \quad (7.1)$$

where J_0 is the STM current for the "bare" gap (without moving atoms), a is the tip-substrate distance, n is the density of atoms, and σ is the scattering cross section of tunneling electrons on an atom. Usually $\sigma\sim 1-10$ Å^2. For a typical gas density $n\sim 10^{19}$ cm^{-3} the exponent $na\sigma\sim 10^{-5}$. Thus, *the presence of the gas atoms does not affect the average current.*

For the adsorbates independently moving and uniformly distributed along the substrate surface, the average current is

$$\langle J\rangle=J_0 e^{n_s\sigma} , \quad (7.2)$$

where n_s is the adsorbate surface density. Even for surface densities as high as $n_s=0.01$ Å^{-2}, the exponent $n_s\sigma$ cannot exceed 0.1. Therefore, in estimates for the correlation functions we can replace, as a rule, J_0 by an observable quantity $\langle J\rangle$.

B. Low-frequency current noise and correlation time for gas atoms moving in the tunneling gap

The low-frequency noise introduced by gas atoms is[18]

$$S_a(0)\sim n\left[\frac{M}{k_B T}\right]^{1/2}\sigma^2\langle J\rangle^2 . \quad (7.3)$$

The characteristic time of the current temporary correlation function (2.6) in this case,

$$t_c=\left[\frac{aM}{k_B T\gamma}\right]^{1/2} , \quad (7.4)$$

is the time during which the gas atom crosses the tube of tunneling electrons of radius $(a/\gamma)^{1/2}$. For room temperature, $t_c\sim 10^{-12}$ sec. This time is too short to study experimentally the temporary current correlation function in the gas environment.

For a gas of density $n \sim 10^{19}$ cm^{-3} at room temperature and for an average current $\langle J \rangle \sim 10^{-9}$ A, typical for STM, one finds $S_a(0)$ to be 10^8 times smaller than the shot or thermal-electron noise, $S_0(0) \sim e\langle J \rangle$. It is, therefore, hopeless to distinguish the low-frequency current noise due to gas atoms on the background of the fundamental electron noise.

The general conclusion from the estimates of Sec. VII B and VII C is that *the gas in the tunneling gap has a negligible influence on both the STM current and the current noise.*

C. Low-frequency current noise and correlation time for atoms diffusively moving in the tunneling gap

For particles diffusively moving in the tunneling gap between the STM tip and the substrate (which could be the case of solute molecules in diluted solutions) the low-frequency noise introduced by the solute molecules has the form

$$S_a(0) \sim \frac{na\sigma^2}{D}\langle J \rangle^2 , \tag{7.5}$$

where D is the diffusion coefficient of solute particles. The temporary correlation function in this case is given by Eq. (6.2) and the correlation time is

$$t_c = a/(\gamma D) . \tag{7.6}$$

We may try to use Eq. (7.5) to estimating the noise coming from the solution as a whole. Having put $D \sim 10^{-5}$ cm^2/sec, $\langle J \rangle \sim 1$ nA and $n \sim 10^{22}$ cm^{-3}, we find that the low-frequency noise $S_a(0)$ has *the same* order of magnitude as the electron noise S_0. The time t_c in this case has the order of 10^{-10} sec.

D. Correlation function and noise for surface diffusion

The movement of adsorbate atoms diffusing along the substrate surface is usually much slower than the diffusion in liquid, which makes possible to observe the process of individual atom diffusion near the STM tip.[2,3] The appearance of atoms near the tip results in a peak of the tunneling current. The shape of the peak depends on the random adsorbate trajectory along the substrate surface under the tip. Of course, each particular trajectory is unknown and it is more rewarding to extract from the experimental data the temporary current correlation function $K(t)$, found by averaging the value $J(t+\tau)J(t)$ over time t at a fixed position of the tip.

We have calculated the corresponding correlation function by averaging over the atom configurations with the distribution function of adsorbates, taken uniform and isotropic. The result for small adsorbate density, $n_s b^2 \ll 1$, is

$$K(t) = \frac{n_s \gamma \sigma^2}{2\pi(a + 2\gamma D_s |t|)}\langle J \rangle^2 , \tag{7.7}$$

where D_s is the surface diffusion coefficient. The correlation time that follows from this equation is again given by Eq. (7.6), but with D_s standing for D.

This result could be used for a treatment of experimental data, since it establishes a new relationship between parameters of the tunneling gap and surface diffusion coefficient.

The low-frequency noise, as follows from Eq. (7.7),

$$S_a(\omega) \underset{\omega t_c \to 0}{\approx} -\frac{n_s \sigma^2}{4\pi^2 D_s}\ln(\omega t_c)\langle J \rangle^2 , \tag{7.8}$$

can be much greater than the one defined by Eq. (7.5) for a diffusion in liquid due to much smaller values of D_s compared to D, and, therefore, greater than the thermal and shot electron noise. More general expressions for $S_a(\omega)$, valid also for $\omega t_c \sim 1$, are given in Sec. VI B.

VIII. CONCLUSION AND OUTLOOK

We considered the influence on the STM current noise of the gas atoms and atoms adsorbed on the surface of substrate separately. Generally speaking, there is no such situation in reality because the bulk and surface concentrations of atoms are related by an adsorption isotherm. However, we have shown that the effect of the gas on the STM current noise is negligible, so that one could safely consider the scattering of the tunneling electrons on adsorbates only.

We did not consider the noise effects due to jumps of atoms to the apex of the tip. This important effect[19] must be excluded to provide the pure investigation of diffusion on the substrate.

The main assumptions used in the theory developed are the homogeneity and the isotropy of the substrate surface and the distribution function of the moving particles. However, the homogeneity area must be large in comparison with the cross section of a tunneling current tube, ~ 3 Å in radius only. Therefore only the *local* homogeneity is required. In order to use our theory, experimental results should be averaged over the position of the tip in each homogeneous domain. The averaging is of principal importance because the noise depends, in reality, on the precise position of the tip above the crystal lattice, the structure of which was ignored. As a result we may hope to get the mean diffusion coefficients in each homogeneity domain and, thereby, draw a map of diffusion properties of the substrate.

The nonspherical models of electron-particle interaction and surface anisotropy could be incorporated into the developed theory by substitution of a nonspherical potential and an anisotropic distribution function in our basic equations.[17] Also, the suggested formalism can be extended to include the case of rotating asymmetric particles by introducing the orientational degrees of freedom and the subsequent averaging with a corresponding distribution function.

The profile of the barrier without intervening particles was assumed to have a rectangular shape. We also assumed the monoenergetic spectrum of tunneling electrons, which is true for small applied voltage. In the resulting expressions, however, the exponential dependence of the barrier parameters and the energy distribution function of the tunneling electrons was "hidden" in the value of the mean current which can be experimentally measured. We may, therefore, hope that these results

will be valid under more general assumptions with use of an effective wave number γ.

Note added in proof. We have recently become aware of the work by R. Gomer, Appl. Phys. A **39**, 1 (1986), where the noise in the STM current due to surface diffusion was theoretically studied. The case of weak electron-adatom interaction was considered there, treated by first-order perturbation theory. The form of the time dependence of the current temporary correlation function in this particular case coincides with that obtained by Gomer; the difference in the adopted models of the tunneling barrier and electron-adatom interaction change only the coefficients in this dependence. The principal difference of our paper from the work of Gomer is that we have considered the case of strong interaction between adatoms and tunneling electrons which is, presumably, closer to experimental situation (see Ref. 2).

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