Chaos, Interactions, and Nonequilibrium Effects in the Tunneling Resonance Spectra of Ultrasmall Metallic Particles

Oded Agam,[1] Ned S. Wingreen,[1] and Boris L. Altshuler[1,2]
[1]*NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540*
[2]*Department of Physics, Princeton University, Princeton, New Jersey 08544*

D. C. Ralph[3] and M. Tinkham[4]
[3]*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853*
[4]*Department of Physics and Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts 02138*
(Received 18 November 1996)

We explain the observation of clusters in the tunneling resonance spectra of ultrasmall metallic particles of a few nanometer size. Each cluster of resonances is identified with one excited single-electron state of the metal particle, shifted as a result of the different nonequilibrium occupancy configurations of the other single-electron states. Assuming the underlying classical dynamics of the electrons to be chaotic, we determine the typical shift to be Δ/g where Δ is the single particle mean level spacing and g is the dimensionless conductance of the grain. [S0031-9007(97)02682-3]

PACS numbers: 73.23.Hk, 05.70.Ln, 71.70.–d

An interacting many-body system exhibits, in general, a very complicated behavior. Usually, one can analytically characterize only statistical properties of the spectrum. The fact that, for high enough energies, these properties are very well described by random matrix theory (RMT) [1] was first attributed to the complexity of the many-body system. More recently, it has become clear that RMT also describes single-particle quantum dynamics which is chaotic in the classical limit [2,3]. Examples are noninteracting electrons in small disordered metallic grains [4], and in ballistic quantum dots [5]. Real systems, however, contain a large number of interacting particles, and a question which naturally arises is how does chaos in a single-particle description manifest itself in the properties of the true many-body problem?

Experimental [6], as well as theoretical [7,8] studies of this problem, have been mainly focused on two issues: the statistical properties of the ground state energy of quantum dots as the number of electrons changes, and the lifetime of a quasiparticle in such structures. Here we consider the nonequilibrium tunneling resonance spectra of ultrasmall metallic particles [9]. These spectra can be measured experimentally with high precision [see Figs. 1(a) and 1(b)] and interpreted within the Hartree-Fock approximation. They constitute a clear demonstration of the interplay between many-body interactions and quantum chaos.

The experimental system consists of a single aluminum particle connected to external leads via high resistance ($1-5\ \mathrm{M}\Omega$) tunnel junctions formed by oxidizing the surface of the particle. In Figs. 1(a) and 1(b) we plot the differential conductance, dI/dV, of two different particles (of sizes roughly 2.5 and 4.5 nm) as a function of the source-drain bias energy eV. The spectra display three clear features: (1) The low energy resonances are grouped in clusters. The distance between nearby clusters is of order the mean level spacing Δ of the noninteracting electrons in the dot. (2) The first cluster contains only a single resonance. (3) Higher clusters consist of several resonances spaced much more closely than Δ.

In this Letter, we explain these features as consequences of the underlying chaotic dynamics of the confined electrons. Each cluster of resonances is identified with one excited single-electron state, and each resonance in turn is associated with a different occupancy configuration of the metal particle's other single-electron states. The appearance of multiple resonances reflects the strongly nonequilibrium state of the particle.

Our model for the system is given by the Hamiltonian: $H = H_0 + H_T + H_{\mathrm{int}}$. Here H_0 describes the noninteracting electrons in the left (L) and right (R) leads and in the metallic grain,

$$H_0 = \sum_{\alpha=L,R} \sum_q \epsilon_{\alpha q} d^\dagger_{\alpha q} d_{\alpha q} + \sum_l \epsilon_l c^\dagger_l c_l \,. \qquad (1)$$

Tunneling across the barriers is described by

$$H_T = \sum_{\alpha=L,R} \sum_{q,l} T^{(\alpha)}_{ql} d^\dagger_{\alpha q} c_l + \mathrm{H.c.}\,, \qquad (2)$$

where $T^{(\alpha)}_{ql}$ are the tunneling matrix elements. Interaction effects are taken into account only for the electrons in the grain, but including screening by image charges in the leads. Thus

$$H_{\mathrm{int}} = \frac{1}{2} \sum_{ijkl} U_{ijkl} c^\dagger_i c^\dagger_j c_k c_l \,, \qquad (3)$$

where U_{ijkl} is the matrix element of the Coulomb interaction for the electrons inside the grain. We remark that for the ultrasmall aluminum grains considered here one can

 0031-9007/97/78(10)/1956(4)$10.00

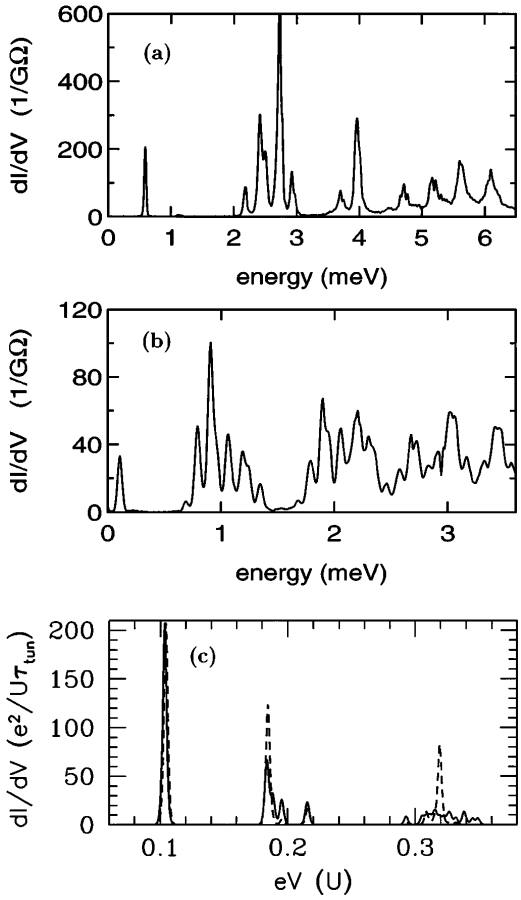

FIG. 1. (a),(b) The low temperature (30 mK) differential conductance dI/dV versus bias energy of ultrasmall Al particles with volumes (a) $\approx$40 nm^3 (b) $\approx$100 nm^3 (Ref. [9]). The first resonance is isolated while subsequent resonances are clustered in groups. The distance between nearby groups of resonances is approximately the single-particle mean level spacing Δ. (c) Model differential conductance obtained from nonequilibrium detailed-balance equations: solid line—in the absence of inelastic processes, $1/\tau_{\rm in} = 0$; dashed line—with inelastic relaxation rate larger than the tunneling rate, $1/\tau_{\rm in} = 5/\tau_{\rm tun}$.

neglect superconducting pairing since the single-particle mean level spacing, $\approx$1 meV, is larger than the BCS superconducting gap which is 0.18 meV [10].

The interaction term of the electrons is generally approximated by $\sum_{ijkl} U_{ijkl} c_i^\dagger c_j^\dagger c_k c_l \approx (e \sum_l c_l^\dagger c_l)^2/C$, where C is the effective capacitance of the grain. Within this approximation, known as the orthodox model [11], the charging energy depends only on the total number of electrons in the dot, but not on their particular occupancy configuration. The orthodox model is able to account for the Coulomb blockade [11], and the Coulomb staircase behavior of the current as the number of extra tunneling electrons in the dot increases. It can also be generalized to describe features on the scale of the single-particle level spacing [12]. However, the orthodox model cannot account for the clusters of resonances in Figs. 1(a) and 1(b), since these result from fluctuations, δU, in the interaction energy between pairs of electrons. Before discussing the origin of these fluctuations we examine their effect on the differential conductance of the dot.

We focus our attention on the (experimental) voltage regime where there is no more than one extra tunneling electron in the dot. At small voltage bias, V, within the Coulomb-blockade regime [Fig. 2(a)], current does not flow through the system. Current first starts to flow when one state i inside the grain becomes available for tunneling through the left barrier, say, as illustrated in Fig. 2(b). As the system becomes charged with an additional electron, the potential energy of the other electrons in the dot increases by $U \simeq e^2/C$, and some of the lower energy occupied electronic states are raised above the right lead chemical potential [in Fig. 2(b) these "ghost" states are shown as dashed lines]. Electrons can tunnel out from these states into the right lead leaving the particle in an excited state. There is, however, only one configuration of the electrons which allows an electron to tunnel into level i from the left lead, namely, all lower energy levels occupied. This implies that only a single resonance peak appears in the differential conductance at

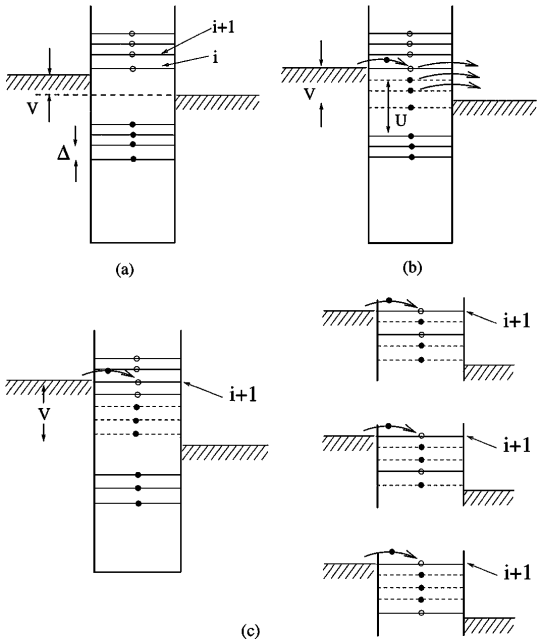

FIG. 2. An illustration of transport through the metal particle at various values of the source-drain voltage V. Filled single-particle levels are indicated by full circles and empty ones by open circles. U is the charging energy, and Δ is the single-particle mean level spacing. (a) The system at small bias voltage within the Coulomb blockade regime. (b) V corresponding to the first resonance in Figs. 1(a) and 1(b). The thin dashed lines indicate the energy of a level after an electron has tunneled into the dot. (c) V near the first cluster of resonances in Figs. 1(a) and 1(b). The splitting within the first cluster originates from the sensitivity of level $i + 1$ to the different possible occupation configurations as shown.

the onset of the current flow through the system (broken spin degeneracy would cause splitting of this peak).

The situation changes when V increases such that electrons can tunnel from the left lead into the next higher available state $i + 1$, as shown in Fig. 2(c). In this case, there are several possible occupancy configurations, on which the exact energy of level $i + 1$ depends. The several possible energies of level $i + 1$ lead to a cluster of resonances in the differential conductance of the grain. The scenario described above holds provided that inelastic processes are too slow to maintain equilibrium in the particle.

To explicitly demonstrate the splitting of resonances induced by fixed fluctuations in the interaction energy δU, model detailed-balance equations [12] were solved numerically and the corresponding differential conductance plotted in Fig. 1(c) by the solid line. The model system consists of seven equally spaced levels, occupied alternately by four or five electrons, in a current-carrying steady state. For simplicity, the tunneling rate into each level, $1/\tau_{\rm tun}$ [$\Gamma_{L(R)}(\epsilon_l)$ in the notation of Ref. [12]], is chosen to be uniform, and the voltage is applied by increasing the left chemical potential. The temperature is 1% of the mean level spacing Δ, and the variance of the fluctuations δU in the interaction energy is $\Delta/5$. [In the absence of fluctuations ($\delta U = 0$), dI/dV consists of single resonances spaced by Δ.]

To estimate the fluctuations in the interaction energy consider the Hartree term of the interaction energy, U_H. We wish to calculate the interaction energy difference associated with different occupation configurations of low energy states. Suppose that, as illustrated in Fig. 2(c), these differ by a single occupation number, namely, in one configuration the state j is empty and j' is full while in the other j' is empty and j is full. Then

$$\delta U_H = \int dr_1 dr_2 |\psi_i(\mathbf{r}_1)|^2 U(\mathbf{r}_1, \mathbf{r}_2) \times [|\psi_{j'}(\mathbf{r}_2)|^2 - |\psi_j(\mathbf{r}_2)|^2], \quad (4)$$

where the index i labels an electron state other than j or j', $U(\mathbf{r}_1, \mathbf{r}_2)$ is the interaction potential. Clearly $\langle \delta U_H \rangle = 0$, where $\langle \cdots \rangle$ denotes ensemble or energy averaging. We are therefore interested in fluctuations of δU_H which emerge from the nonuniform probability distributions of the single-particle eigenstates in real space. To calculate $\langle \delta U_H^2 \rangle$ we approximate the interaction by $U(\mathbf{r}_1, \mathbf{r}_2) \simeq \nu^{-1} \delta(\mathbf{r}_1 - \mathbf{r}_2)$, where ν is the density of states, then

$$\langle \delta U_H^2 \rangle = 2\nu^{-2} \int d^d r d^d r' C^2(\mathbf{r}, \mathbf{r}'), \quad (5)$$

where $C(\mathbf{r}, \mathbf{r}') = \langle |\psi(\mathbf{r})\psi(\mathbf{r}')|^2 \rangle - \langle |\psi(\mathbf{r})|^2 \rangle \langle |\psi(\mathbf{r}')|^2 \rangle$ is the probability-density correlation function. For disordered systems it takes the form (see, e.g., [7])

$$C(\mathbf{r}, \mathbf{r}') = \frac{\alpha \Delta}{\pi \hbar \Omega} \sum_{\mathbf{n} \neq \mathbf{0}} \frac{\phi_{\mathbf{n}}^*(\mathbf{r}) \phi_{\mathbf{n}}(\mathbf{r}')}{D \mathbf{q}_{\mathbf{n}}^2}, \quad (6)$$

where α is a symmetry factor (2 for Gaussian orthogonal ensemble systems and 1 for Gaussian unitary ensemble), Ω is the volume of the grain, D is the diffusion constant, and the sum is over the diffusion modes $\phi_{\mathbf{n}}(\mathbf{r})$. Introducing the dimensionless conductance $g = \hbar \pi^2 D / L^2 \Delta = E_c / \Delta$, where L is the linear size of the system we obtain from (5) and (6) [13]

$$\langle \delta U_H^2 \rangle = \left(c \frac{\Delta}{g} \right)^2, \quad (7)$$

where $c = \sqrt{2}\, \alpha \sum_{\mathbf{n}} |\mathbf{n}|^{-4} / \pi$ is a constant of order unity. Equation (7) also applies for general chaotic systems, with $g \simeq \gamma_1 / \Delta$, where γ_1 is the first nonvanishing Perron-Frobenius eigenvalue [14]. In essence, smaller g implies less uniform wave functions, so fluctuations in the interaction energy increase as g decreases. Experimentally we find $g \approx 5$. Unfortunately, an analytical estimate of g requires precise knowledge of the shape and disorder of the particle which we lack [15].

Within our approximation for the interaction potential the Fock term, δU_F, is equal to $-\delta U_H$; thus apparently $\delta U_F + \delta U_H = 0$. However, for a more realistic interaction potential $\delta U_F \neq -\delta U_H$, and, moreover, the Fock term exists only for electrons with parallel spins. δU_H is therefore the typical single-electron level splitting due to interaction.

More generally, when M available states below the highest accessible energy level (including spin) are occupied by $M' < M$ electrons, there are $\binom{M}{M'}$ different occupancy configurations. The typical width of a cluster of resonances in this case is $W^{1/2} c \Delta / g$, where $W = \min(M - M', M')$. The width of a cluster of resonances therefore *increases* with the source-drain voltage. The distance between nearby peaks of the cluster, on the other hand, *decreases* as $W^{1/2} / \binom{M}{M'}$. This behavior can be seen in Fig. 1(c).

Central to our analysis is the assumption that the steady-state occupation configurations of the electrons in the dot are far from equilibrium. This condition holds when the rate $1/\tau_{\rm in}$ of inelastic relaxation processes is smaller than the tunneling rate of an electron into and out of the dot, $1/\tau_{\rm tun}$. In the opposite limit, $1/\tau_{\rm in} > 1/\tau_{\rm tun}$, the system relaxes to equilibrium between tunneling events, and the electrons effectively occupy only one configuration. In this case one expects each resonance cluster to collapse to a single peak. This behavior is illustrated by the dashed line in Fig. 1(c) where a large inelastic relaxation rate $1/\tau_{\rm in} = 5/\tau_{\rm tun}$ was included in the detailed-balance equations.

The results shown in Fig. 1 indicate that the metal particle in the experimental system is indeed in a strongly nonequilibrium state. It is useful, however, to consider the various relaxation processes in our system in order to delimit the expected nonequilibrium regime. Relaxation of excited Hartree-Fock states may occur due to (1) electron-electron interaction in the dot beyond Hartree-Fock, (2) electron-phonon interaction, (3) Auger processes in which an electron in the dot relaxes while another one

in the lead is excited, (4) relaxation of an electron in the dot as another electron tunnels out to the lead, and (5) thermalization with the leads via tunneling. The last two processes are small corrections since they clearly happen on time scales larger than the tunneling time.

In Ref. [8] it was shown that excited many-body states of closed systems with energy ϵ smaller than $(g/\ln g)^{1/2}\Delta$ are merely slightly perturbed Hartree-Fock states. In other words, the overlap between the true many-body state and the corresponding Hartree-Fock approximation is very close to unity. This justifies the use of our model for the low energy resonances since $g \approx 5$; therefore the energy interval $0 < \epsilon < (g/\ln g)^{1/2}\Delta$ contains at least the first few excited states. At high source-drain voltage, however, when the dot is excited to energy $g^{1/2}\Delta < \epsilon < g\Delta$, tunneling takes place into quasiparticle states of width $\epsilon^2/(g^2\Delta)$ [7]. This width is larger than the typical separation between nearby resonances but smaller than Δ. Therefore, electron-electron scattering will obliterate the fine structure of resonances for high energy excitations of the dot.

Consider now the electron-phonon interaction. The temperature, 30 mK, is much smaller than the mean level spacing; therefore, the probability of phonon absorption is negligible, and only emission may take place. The sound velocity in aluminum is $v_s = 6420$ m/sec, therefore the wavelength of a phonon associated with relaxation of energy $\omega \sim \Delta = 1$ meV is approximately 50 Å, the same as the system size. In this regime, we estimate the phonon emission rate to be

$$\frac{1}{\tau_{e\text{-}ph}} \sim \left(\frac{2}{3}\epsilon_F\right)^2 \frac{\omega^3 \tau \Delta}{2\rho\hbar^4 v_s^5}, \tag{8}$$

where ϵ_F is the Fermi energy (11.7 eV in Al), and ρ is the ion mass density (2.7 g/cm^3 in Al). This rate is that of a clean metal but reduced by a factor of $\tau\Delta/\hbar$ where τ is the elastic mean free time [16]. In ballistic systems, τ is the traversal time across the system of an electron at the Fermi level. Assuming ballistic motion this factor is of order 10^{-3}. The resulting relaxation rate for $\omega = \Delta$ is therefore of order $1/\tau_{e\text{-}ph} \approx 10^8$ sec^{-1} which is similar to the tunneling rate $1/\tau_{\text{tun}} \approx 6 \times 10^8$ sec^{-1} (corresponding to a current of 10^{-10} A through the particle). Thus, by increasing the resistance of the tunnel junctions one should be able to cross over to the near-equilibrium regime shown by the dashed line in Fig. 1(c).

Relaxation due to the Auger process is estimated to be negligible. Two factors reduce this rate considerably: (1) it is exponentially small in w/χ where w is the width of the tunnel junction and χ is the screening length, and (2) interaction between electrons on both sides of the tunnel junction can take place only within a very limited volume.

In conclusion, we have shown that the low-voltage tunneling-resonance spectrum of an ultrasmall metallic grain reflects nonequilibrium electron configurations each of which leads to a different energy of the single-electron level used for tunneling. Consequently, the tunneling resonances appear in clusters of width Δ/g. This phenomenon is a result of electron-electron interaction beyond the orthodox model [11]. Relaxation due to electron-phonon interaction, which becomes important for high resistance tunnel barriers, will collapse the clusters. This effect can be used to probe the electron-phonon relaxation rate in nanometer size metal particles.

The research at Harvard was supported by NSF Grant No. DMR-92-07956, ONR Grant No. N00014-96-1-0108, and JSEP Grant No. N00014-89-J-1023. The research at Cornell was supported by the Sloan Foundation, and was performed at the Cornell Nanofabrication Facility, funded by the NSF (Grant No. ECS-9319005), Cornell University, and industrial affiliates.

[1] M. L. Mehta, *Random Matrices* (Academic Press, New York, 1991).
[2] G. Casati, F. Valz-Gris, and I. Guarnery, Lett. Nuovo Cimento **28**, 279 (1980).
[3] O. Bohigas, M. J. Giannoni, and C. Schmidt, Phys. Rev. Lett. **52**, 1 (1984).
[4] K. B. Efetov, Adv. Phys. **32**, 53 (1983).
[5] A. V. Andreev, O. Agam, B. D. Simons, and B. L. Altshuler, Phys. Rev. Lett. **76**, 3947 (1996).
[6] U. Sivan, F. P. Milliken, K. Milkove, S. Rishton, Y. Lee, J. M. Hong, V. Boegli, D. Kern, and M. deFranza, Europhys. Lett. **25**, 605 (1994).
[7] U. Sivan, Y. Imry, and A. G. Aronov, Europhys. Lett. **28**, 115 (1994).
[8] B. L. Altshuler, Y. Gefen, A. Kamenev, and L. S. Levitov, Report No. cond-mat/9609132.
[9] D. C. Ralph, C. T. Black, and M. Tinkham, Physica (Amsterdam) **218B**, 258 (1996).
[10] J. von Delft, A. D. Zaikin, D. S. Golubev, and W. Tichy, Phys. Rev. Lett. **77**, 3189 (1996); R. A. Smith and V. Ambegaokar, Phys. Rev. Lett. **77**, 4962 (1996).
[11] D. V. Averin and K. K. Likharev, in *Mesoscopic Phenomena in Solids*, edited by B. L. Altshuler, P. A. Lee, and R. A. Webb (Elsevier, New York, 1991), pp. 173–271.
[12] D. V. Averin and A. N. Korotkov, Zh. Eksp. Teor. Fiz. **97**, 1661 (1990) [Sov. Phys. JETP **70**, 937 (1990)]. This work neglects fluctuations of the interaction energy ($\delta U = 0$).
[13] Ya. M. Blanter, Phys. Rev. B **54**, 12 807 (1996).
[14] O. Agam, B. L. Altshuler, and A. V. Andreev, Phys. Rev. Lett. **75**, 4389 (1995).
[15] A naive estimate of g in ballistic systems is $\hbar/\tau\Delta$, where τ is the time for an electron at the Fermi energy to cross the system. The metallic grains of the experiment, however, have a roughly pancake shape. Assuming diffusive dynamics one can show that $g\tau\Delta/\hbar \propto (z/r)^2$, where z is the pancake thickness and r is its radius. g is therefore much smaller than $\hbar/\tau\Delta$.
[16] M. Yu Reizer and A. V. Sergeyev, Zh. Eksp. Teor. Fiz. **90**, 1056 (1986) [Sov. Phys. JETP **63**, 616 (1986)].