Jellium Model of Metallic Nanocohesion

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A unified treatment of the cohesive and conducting properties of metallic nanostructures in terms of the electronic scattering matrix is developed. A simple picture of metallic nanocohesion in which conductance channels act as delocalized chemical bonds is derived in the jellium approximation. Universal force oscillations of order ε_F/λ_F are predicted when a metallic quantum wire is stretched to the breaking point, which are synchronized with quantized jumps in the conductance. [S0031-9007(97)04243-9]

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Cohesion in metals is due to the formation of bands, which arise from the overlap of atomic orbitals. In a metallic constriction with nanoscopic cross section, the transverse motion is quantized, leading to a finite number of subbands below the Fermi energy ε_F. A striking consequence of these discrete subbands is the phenomenon of conductance quantization [1]. The cohesion in a metallic nanoconstriction must also be provided by these discrete subbands, which may be thought of as chemical bonds which are delocalized over the cross section. In this Letter, we confirm this intuitive picture of metallic nanocohesion using a simple jellium model. Universal force oscillations of order ε_F/λ_F are predicted in metallic nanostructures exhibiting conductance quantization, where λ_F is the Fermi wavelength. Our results are in quantitative agreement with the recent pioneering experiment of Rubio, Agraït, and Vieira [2], who measured simultaneously the force and conductance during the formation and rupture of an atomic-scale Au contact. Similar experimental results have been obtained independently by Stalder and Dürig [3].

Quantum-size effects on the mechanical properties of metallic systems have previously been observed in ultrasmall metal clusters [4], which exhibit enhanced stability for certain *magic numbers* of atoms. These magic numbers have been rather well explained in terms of a shell model based on the jellium approximation [4]. The success of the jellium approximation in these closed nanoscopic systems motivates its application to open (infinite) systems, which are the subject of interest here. We investigate the conducting and mechanical properties of a nanoscopic constriction connecting two macroscopic metallic reservoirs. The natural framework in which to investigate such an open system is the scattering approach developed by Landauer [5] and Büttiker [6]. Here, we extend the formalism of Ref. [6], which describes electrical conduction, to describe the mechanical properties of a confined electron gas as well.

For definiteness, we consider a constriction of length L in an infinitely long cylindrical wire of radius R, as shown in Fig. 1. We neglect electron-electron interactions, and assume the electrons to be confined along the z axis by a hard-wall potential at $r = r(z)$. This model is considerably simpler than a self-consistent jellium calculation [4], but should suffice to capture the essential physics of the problem. Outside the constriction, the Schrödinger equation is separable, and the scattering states can be written as

$$\psi^{\pm}_{kmn}(\phi, r, z) = e^{\pm ikz + im\phi} J_m(\gamma_{mn} r/R)\,, \qquad (1)$$

where the quantum numbers γ_{mn} are the roots of the Bessel functions $J_m(\gamma_{mn}) = 0$. These scattering states may be grouped into subbands characterized by the quantum numbers m and n, and we shall use the notation $\nu = (m, n)$. The energy of an electron in subband ν is $\varepsilon(k) = \varepsilon_\nu + \hbar^2 k^2/2m$, where

$$\varepsilon_\nu = \frac{\hbar^2 \gamma_\nu^2}{2mR^2}\,. \qquad (2)$$

The fundamental theoretical quantity is the scattering matrix of the constriction $S(E)$, which connects the incoming and outgoing scattering states. For a two-terminal device, such as that shown in Fig. 1, $S(E)$ can be decomposed into four submatrices $S_{\alpha\beta}(E)$, $\alpha, \beta = 1, 2$, where 1 (2) indicates scattering states to the left (right) of the constriction. Each submatrix $S_{\alpha\beta}(E)$ is a matrix in the scattering channels $\nu\nu'$.

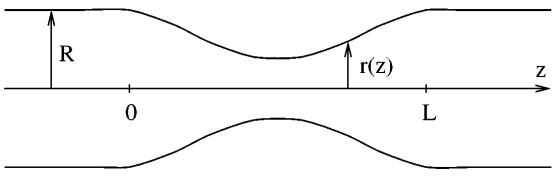

FIG. 1. Schematic diagram of a constriction in a cylindrical quantum wire. Electrons are confined along the z axis by a hard-wall potential at $r = r(z)$. Two different geometries are considered: $r(z) = (R + R_{\min})/2 + (R - R_{\min})\cos(2\pi z/L)/2$ (cosine constriction) and $r(z) = R_{\min} + (R - R_{\min})(2z/L - 1)^2$ (parabolic constriction), with $r(z) = R$ for $z < 0$ and $z > L$. The minimum radius of the neck $R_{\min}$ as a function of the elongation $\Delta L/L_0$ is determined by a constant volume constraint $\int_0^L r(z)^2\, dz = R^2 L_0$.

In terms of the scattering matrix, the electrical conductance is given by [6]

$$G = \frac{2e^2}{h} \int dE \, \frac{-df}{dE} \, \mathrm{Tr}\{S_{12}^{\dagger}(E) S_{12}(E)\}, \qquad (3)$$

where $f(E) = \{\exp[\beta(E - \mu)] + 1\}^{-1}$ is the Fermi distribution function and a factor of 2 has been included to account for spin degeneracy. The grand canonical potential of the system is

$$\Omega = -k_B T \int dE \, D(E) \ln(1 + e^{-\beta(E-\mu)}), \qquad (4)$$

where the density of states in the constriction may be expressed in terms of the scattering matrix as [7,8]

$$D(E) = \frac{1}{2\pi i} \sum_{\alpha,\beta} \mathrm{Tr}\left\{ S_{\alpha\beta}^{\dagger}(E) \frac{\partial S_{\alpha\beta}}{\partial E} - S_{\alpha\beta}(E) \frac{\partial S_{\alpha\beta}^{\dagger}}{\partial E} \right\}. \qquad (5)$$

Equations (3)–(5) allow one to treat the conducting and mechanical properties of a confined electron gas on an equal footing, and provide the starting point for our calculation.

We are interested in the mechanical properties of a metallic nanoconstriction in the regime of conductance quantization. The necessary condition to have well-defined conductance plateaus in a three-dimensional constriction was shown by Torres, Pascual, and Sáenz [9] to be $(dr/dz)^2 \ll 1$. In this limit, Eqs. (3)–(5) simplify considerably because one may employ the adiabatic approximation [10]. In the adiabatic limit, the transverse motion is separable from the motion parallel to the z axis, so Eqs. (1) and (2) remain valid in the region of the constriction, with R replaced by $r(z)$. The channel energies thus become functions of z, $\varepsilon_\nu(z) = \hbar^2 \gamma_\nu^2 / 2m r(z)^2$. In this limit, the scattering matrices $S_{\alpha\beta}(E)$, $\alpha, \beta = 1, 2$ are diagonal in the channel indices, leading to an effective one-dimensional scattering problem. The condition $(dr/dz)^2 \ll 1$ and the requirement that the radius of the wire outside the constriction not be smaller than an atomic radius (i.e., $k_F R > 1$) automatically imply the validity of the WKB approximation.

Since the energy differences between the transverse channels in an atomic-scale constriction are large compared to $k_B T$ at ambient temperature, we restrict consideration in the following to the case $T = 0$. In the adiabatic approximation, the conductance becomes

$$G = \frac{2e^2}{h} \sum_{\nu} T_\nu, \qquad (6)$$

where the transmission probability for channel ν may be calculated using a variant of the WKB approximation [11,12], which correctly describes the rounding of the conductance steps at threshold. The density of states in the constriction in the adiabatic approximation is

$$D(E) = \frac{2}{\pi} \sum_{\nu} \frac{d\Theta_\nu}{dE}, \qquad (7)$$

where the total phase shift is given in the WKB approximation by

$$\Theta_\nu(E) = (2m/\hbar^2)^{1/2} \int_0^L dz [E - \varepsilon_\nu(z)]^{1/2}, \qquad (8)$$

the integral being restricted to the region where $\varepsilon_\nu(z) < E$. The grand canonical potential of the system is thus

$$\Omega = -\frac{8\varepsilon_F}{3\lambda_F} \int_0^L dz \sum_{\nu}{}' \left(1 - \frac{\varepsilon_\nu(z)}{\varepsilon_F}\right)^{3/2}, \qquad (9)$$

the sum being over channels with $\varepsilon_\nu(z) < \varepsilon_F$. Under elongation, the tensile force is given by $F = -\partial\Omega/\partial L$. It is easy to show that F is invariant under a stretching of the geometry $r(z) \to r(\lambda z)$, i.e.,

$$F = \frac{\varepsilon_F}{\lambda_F} f(\Delta L / L_0, k_F R), \qquad (10)$$

where $f(x, y)$ is a dimensionless function. Nonuniversal corrections to F occur in very short constrictions, for which the adiabatic approximation breaks down. The leading order correction to the integrand in Eq. (9) is $-(3\pi/64) k_F r(z) (dr/dz)^2$, leading to a relative error in F of $\sim 2 \sin^2 \theta/4$, where θ is the opening angle of the constriction. Using a modified Sharvin equation [9] to estimate the diameter of the contact versus elongation for the experiment of Ref. [2] indicates an opening angle $\theta \lesssim 45°$, for which the nonuniversal corrections are $\lesssim 8\%$, justifying the above approach.

Figure 2 shows the conductance and force of a metallic nanoconstriction as a function of the elongation, calculated from Eqs. (6) and (9). Here an ideal plastic deformation was assumed, i.e., the volume of the constriction was held constant [13]. The correlations between the force and the conductance are striking: $|F|$ increases along the conductance plateaus, and decreases sharply when the conductance drops. The constriction becomes unstable when the last conductance channel is cut off. Some transverse channels are quite closely spaced, and in these cases, the individual conductance plateaus [e.g., $G/(2e^2/h) = 14, 15, 19, 21$] and force oscillations are difficult to resolve. Figure 2 is remarkably similar to the experimental results of Refs. [2] and [3], both qualitatively and quantitatively. Inserting the value $\varepsilon_F/\lambda_F \simeq 1.7$ nN for Au, we see that both the overall scale of the force for a given value of the conductance and the heights of the last two force oscillations are in quantitative agreement with the data shown in Fig. 1 of Ref. [2]. We wish to emphasize that the calculation of F presented in our Fig. 2 contains no adjustable parameters [14]. The increase of $|F|$ along the conductance plateaus and the rapid decrease at

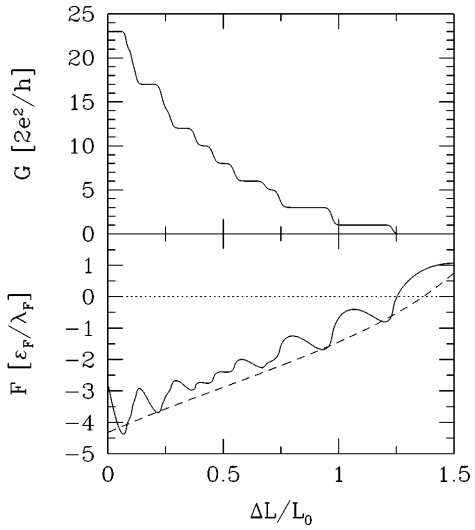

FIG. 2. Electrical conductance G and tensile force F of a cosine constriction in a cylindrical quantum wire of radius $k_F R = 11$ versus the elongation $\Delta L/L_0$. For the calculation of G, an initial length $k_F L_0 = 50$ was assumed. The dashed line indicates the contribution to the force due to the macroscopic surface tension $F_S = -\sigma \partial S/\partial L$, where S is the surface area of the system and $\sigma = \varepsilon_F k_F^2/16\pi$. F_S determines the overall slope of F, on which are superimposed the quantum oscillations due to the discrete transverse channels.

the conductance steps were described in Ref. [2] as "elastic" and "yielding" stages, respectively. With our intuitive picture of a conductance channel as a delocalized metallic bond, it is natural to interpret these elastic and yielding stages as the stretching and breaking of these bonds.

The fluctuations in F due to the discrete transverse channels may be thought of as arising from finite-size corrections to the surface tension σ. However, as in the case of universal conductance fluctuations [15], it is more instructive to consider the extensive quantity F itself, rather than the intensive quantity σ. Approximating the sum in Eq. (9) by an integral, and keeping the leading order corrections, one obtains

$$\Omega = \omega V + \sigma S - \frac{2\varepsilon_F}{3\lambda_F} L + \delta\Omega , \tag{11}$$

where V is the volume of the system, S is the surface area, $\omega = -2\varepsilon_F k_F^3/15\pi^2$ is the macroscopic free energy density, and $\sigma = \varepsilon_F k_F^2/16\pi$ is the macroscopic surface energy. The remaining term $\delta\Omega$ is a quantum correction due to the discrete transverse channels, and may be either positive or negative. Under an ideal plastic deformation, the volume of the system is unchanged, and the tensile force is

$$F = -\sigma \frac{\partial S}{\partial L} + \frac{2\varepsilon_F}{3\lambda_F} + \delta F , \tag{12}$$

where $\delta F = -\partial(\delta\Omega)/\partial L$. The first term in Eq. (12) is the contribution to the force due to the macroscopic surface tension. This is plotted as a dashed line in Fig. 2, for comparison. The macroscopic surface tension determines the overall slope of F. The quantum corrections to F due to the discrete transverse channels consist of a constant term plus the fluctuating term δF. Figure 3 shows δF for three different geometries and for values of $k_F R$ from 6 to 1200, plotted versus the corrected Sharvin conductance [9]

$$G_s = \frac{k_F^2 A_{\min} - k_F C_{\min}}{4\pi} , \tag{13}$$

where $A_{\min}$ and $C_{\min}$ are the area and circumference of the constriction at its narrowest point. G_s gives a smooth approximation to G. As shown in Fig. 3(a), the force oscillations obey the approximate scaling relation

$$\delta F(\Delta L/L_0, k_F R) \simeq \frac{\varepsilon_F}{\lambda_F} Y(G_s) , \tag{14}$$

where Y is a dimensionless scaling function which is independent of the precise geometry $r(z)$. Equation (14) indicates that the force fluctuations, like the conductance, are dominated by the contribution from the narrowest part of the constriction, of radius $R_{\min}$. The scaling relation (14) breaks down when $R_{\min}/R \gtrsim 0.8$.

Figure 3 shows that the amplitude of the force fluctuations persists essentially unchanged to very large values of G_s. It was found to be

$$\Delta Y = (\overline{Y^2} - \overline{Y}^2)^{1/2} \sim 0.3 \tag{15}$$

for $0 < G_s \leq 10^4$. The detailed functional form of $Y(G_s)$, like the distribution of widths of the conductance plateaus, depends on the sequence of quantum numbers γ_ν, which is determined by the shape of the cross section. However, the amplitude of the force fluctuations ΔY was found to be the same for both circular and square cross sections. Both these geometries are integrable, and hence have Poissonian distributions of transverse modes. It is clearly of interest to investigate the force fluctuations for nonintegrable cross sections, with non-Poissonian level statistics.

The experiments of Refs. [2,3] observed well-defined conductance steps, but found no clear evidence of conductance quantization for $G/(2e^2/h) > 4$ [16]. Deviations of the conductance plateaus from integer values in metallic point contacts are likely to be due to backscattering from imperfections in the lattice or irregularities in the shape of the constriction [12]. We find that such disorder-induced coherent backscattering leads to noise-like fine structure [17] in the conductance steps and force oscillations, with a reduction of the conductance on the plateaus, but no shift of the overall force oscillations [18]. Our prediction of universal force oscillations is consistent with the experiments of Refs. [2] and [3], which found force oscillations with an amplitude comparable to our theoretical prediction for $G/(2e^2/h)$ up to 60.

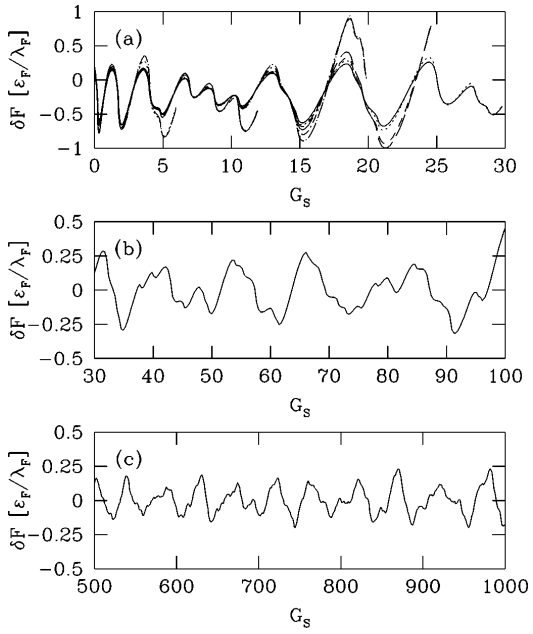

FIG. 3. Force fluctuations versus the corrected Sharvin conductance. (a) Results for cosine and parabolic constrictions in cylindrical quantum wires with radii $k_F R = 6$, 8, 10, 11, and 12 (left to right). The results for the cosine and parabolic constrictions are almost indistinguishable when plotted as a function of G_s, despite the fact that the total elongation and total work done differ by roughly a factor of 2 in the two cases. The dependence on R is also very weak, except for $R_{\min} \approx R$ (the rightmost portion of each curve). (b) Force fluctuations for a cosine constriction in a square quantum wire with 120 conductance channels, and (c) for a wire with 1200 conductance channels.

Molecular dynamics simulations by Landman *et al.* [19], Todorov and Sutton [20], and Brandbyge *et al.* [12] have suggested that the conductance steps and force oscillations observed in Refs. [2] and [3] may be due to a sequence of abrupt atomic rearrangements. While the discreteness of the ionic background is not included in the jellium model, our results nevertheless suggest that such atomic rearrangements may be caused by the breaking of the extended metallic bonds formed by each conductance channel. However, it should be emphasized that our prediction of universal force fluctuations of order ε_F/λ_F is not consistent with the simulations of Refs. [19] and [20], which predict force fluctuations which increase with increasing contact area. This discrepancy may arise because we consider the equilibrium deformation of a system with extended electronic wave functions, while Refs. [12,19,20] use a purely local interatomic potential and a fast, nonequilibrium deformation [21].

In conclusion, we have presented a simple jellium model of metallic nanocohesion in which conductance channels act as delocalized metallic bonds. This model predicts universal force oscillations of order ε_F/λ_F in metallic nanostructures in the regime of conductance quantization, and is able to explain quantitatively recent experiments on the mechanical properties of nanoscopic metallic contacts [2,3]. The formalism developed here based on the electronic scattering matrix should be applicable to a wide variety of problems in the rapidly evolving field of nanomechanics.

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