COHESION, CONDUCTANCE, AND CHARGING EFFECTS IN A METALLIC NANOCONTACT [a]

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The conducting and thermodynamic properties of ballistic metallic nanocontacts with smooth shapes are investigated. All properties are related to the electronic scattering matrix, which is evaluated in the WKB approximation for independent electrons and in the self-consistent Hartree approximation for interacting electrons. Mesoscopic oscillations of order 1nN in the cohesive force and of order e in the contact charge are predicted when a metallic nanocontact is pulled apart, which are synchronized with quantized jumps in the conductance.

1 Introduction

In a seminal experiment published in 1996, Rubio, Agraït, and Vieira [1] measured simultaneously the electrical conductance and cohesive force of Au–Au contacts with diameters ranging from several Ångstroms to several nanometers. They observed oscillations in the cohesive force of order 1nN as the contact was pulled apart, which were synchronized with jumps of order $G_0 = 2e^2/h$ in the conductance G. Similar results were obtained independently by Stalder and Dürig.[2] In a previous article,[3] it was argued that the mesoscopic force oscillations, like the corresponding conductance steps, can be understood by considering the nanocontact as a waveguide for the conduction electrons (which are responsible for both conduction and cohesion in simple metals): each quantized mode transmitted through the contact contributes $2e^2/h$ to the conductance,[4] and a force of order E_F/λ_F to the cohesion,[3] where λ_F is the de Broglie wavelength at the Fermi energy E_F. Recent experiments [5] suggest that mode quantization plays an important role in the cohesion of Na nanocontacts for $G \leq 120G_0$. In Ref. 3 and several subsequent works,[6–9] an independent-electron model was used to describe the cohesion and conductance of metallic nanocontacts within the grand canonical ensemble. Recently, several attempts have been made to include the effects of electron-electron interactions in the extended Thomas-Fermi approximation [10] and in the local density approximation; [11] however, these calculations have utilized the canonical ensemble, which is not appropriate for an open mesoscopic system, such as a metallic nanocontact.

In this article, we show how to treat electron-electron interactions self-consistently in open mesoscopic systems via a generalization of the scattering-matrix approach of Ref. 3. In Sec. 2, we describe the scattering-matrix formalism for independent electrons, and show that the bare mesoscopic charge oscillations induced by the quantum confinement are small, of order e in nanometer scale contacts. In Sec. 3, we derive the self-consistent Hartree approximation using the electronic scattering matrix, and obtain integral equations for the screened charge and grand canonical potential within linear response. The Hartree equations are solved for the case of a discrete-potential model, and it is shown that the Hartree correction to the cohesive force is small, justifying the use of the independent-electron model. [3,6–9]

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2 Independent electron model of a metallic nanocontact

We first model the metallic nanocontact as a system of noninteracting electrons confined along the z-axis by a potential $U_0(\mathbf{x})$ with a saddle-point at $\mathbf{x} = 0$, and assume U_0 varies slowly, i.e., $\partial U_0/\partial z \ll E_F/\lambda_F \; \forall \, \mathbf{x} = (x, y, z)$. Neglecting small terms of order $\partial U_0/\partial z$, the Schrödinger equation is separable into a series of one-dimensional scattering problems with effective potential barriers $\varepsilon_\nu(z)$, the eigenvalues of the two-dimensional Schrödinger equation in planes of constant z. The scattering matrix is then diagonal, and for a system with inversion symmetry about $z = 0$, it is found in an extended WKB approximation to be [3]

$$S_{\mu\nu}(E) = \delta_{\mu\nu}\, e^{i\Theta_\nu(E)} \begin{pmatrix} iR_\nu^{1/2}(E) & T_\nu^{1/2}(E) \\ T_\nu^{1/2}(E) & iR_\nu^{1/2}(E) \end{pmatrix}, \tag{1}$$

where

$$\Theta_\nu(E) = (2m/\hbar^2)^{1/2} \int_{\varepsilon_\nu(z)<E} dz\, [E - \varepsilon_\nu(z)]^{1/2} \tag{2}$$

is the scattering phase shift, and $R_\nu(E)$ and $T_\nu(E)$ are the reflection and transmission probabilities for mode ν, which satisfy $R_\nu(E) + T_\nu(E) = 1$. The transmission probability for mode ν may be expressed [12] as $T_\nu^{-1}(E) = 1 + \mathcal{T}_\nu(E)^{-1}$, where

$$\ln \mathcal{T}_\nu(E) = \begin{cases} -2(2m/\hbar^2)^{1/2} \displaystyle\int_{\varepsilon_\nu(z)>E} dz\, [\varepsilon_\nu(z) - E]^{1/2}, & E < \varepsilon_\nu(0), \\[2ex] 2(2m/\hbar^2)^{1/2} \displaystyle\int_{\varepsilon_\nu(z)>2\varepsilon_\nu(0)-E} dz\, [\varepsilon_\nu(z) + E - 2\varepsilon_\nu(0)]^{1/2}, & E > \varepsilon_\nu(0). \end{cases} \tag{3}$$

Given the scattering matrix (1)–(3), the electrical conductance of the nanocontact may be obtained from the Landauer formula,[4] and all equilibrium thermodynamic properties of the system may be obtained from the density of states $g(E)$,

$$G = \frac{2e^2}{h} \sum_\nu T_\nu(E_F), \qquad g(E) = \frac{1}{2\pi i} \mathrm{Tr} \left\{ S^\dagger \frac{\partial S}{\partial E} - S \frac{\partial S^\dagger}{\partial E} \right\} = \frac{2}{\pi} \sum_\nu \frac{\partial \Theta_\nu}{\partial E}. \tag{4}$$

The grand canonical potential, which governs the energetics of the nanocontact is [3]

$$\Omega = \int_0^{E_F} dE\, g(E)(E - E_F) = -\frac{8E_F}{3\lambda_F} \sum_\nu \int_{\varepsilon_\nu(z)<E_F} dz \left(1 - \frac{\varepsilon_\nu(z)}{E_F}\right)^{3/2}. \tag{5}$$

The total number of electrons in the nanocontact is

$$N_- = \int_0^{E_F} dE\, g(E) = \frac{4}{\lambda_F} \sum_\nu \int_{\varepsilon_\nu(z)<E_F} dz \left(1 - \frac{\varepsilon_\nu(z)}{E_F}\right)^{1/2}. \tag{6}$$

Eqs. (4), (5), and (6) are given at zero temperature for simplicity. When the nanocontact is elongated, the contact area decreases, steepening the saddle in the confining potential, and hence increasing the mode energies $\varepsilon_\nu(z)$. The cohesive force is given by $F = -\partial\Omega/\partial L$.

2.1 Hard-wall confinement

We now specialize to the case where electrons are confined within the nanocontact by impenetrable walls, with $U_0 = 0$ on the interior. In this case, the condition for the validity of Eqs. (5) and (6) is $|dD(z)/dz| \ll 1$, where $D(z)$ is the diameter of the contact.[3] In order to separate the macroscopic contributions to Ω and N_- from the quantum fluctuations, it is useful [6] to express the sum over transverse modes ν in Eqs. (5) and (6) in terms of an integral over a local transverse density of states $\sum_\nu \int dz\,(\cdots) \rightarrow \int dE \int dz\, \partial N_\perp(E,z)/\partial E\,(\cdots)$. The total number of transverse modes $N_\perp(E,z)$ with $\varepsilon_\nu(z) < E$ may be determined with the aid of the Weyl expansion [6]

$$N_\perp(E,z) = \frac{k_E^2 \mathcal{A}(z)}{4\pi} - \frac{k_E \partial\mathcal{A}(z)}{4\pi} + \frac{1}{6} + \delta N_\perp(E,z), \tag{7}$$

where $\mathcal{A}(z)$ and $\partial\mathcal{A}(z)$ are the cross-sectional area, and circumference, respectively, of the contact as function of z, and $\delta N_\perp(E,z)$ is a fluctuating correction determined by the spectrum of quantized transverse modes, whose average is zero. Using Eq. (7), Eqs. (5) and (6) may be rewritten as

$$\frac{\Omega}{E_F} = -\frac{2k_F^3\mathcal{V}}{15\pi^2} + \frac{k_F^2\mathcal{S}}{16\pi} - \frac{2k_F L}{9\pi} + \frac{\delta\Omega}{E_F}, \qquad N_- = \frac{k_F^3\mathcal{V}}{3\pi^2} - \frac{k_F^2\mathcal{S}}{8\pi} + \frac{k_F L}{3\pi} + \delta N_-, \tag{8}$$

where $\mathcal{V}$ is the volume of the nanocontact, $\mathcal{S}$ is its surface area, L is its length, and $\delta\Omega$ and δN_- are oscillatory quantum corrections whose average is zero.

During elongation, it is assumed that the positive background charge density remains constant, i.e., that the system is incompressible.[7] Hard-wall boundary conditions impose a node of the electron wavefunction at the boundary, and lead to a depletion of electrons within a distance of order λ_F from the boundary [second term on the right of Eq. (8)]. To reconcile the constraint of incompressibility and the Dirichlet boundary conditions, we assume that the shape $D(z)$ of the nanocontact evolves during elongation in such a way that the macroscopic part $\bar{N}_-$ of the electron number of the system [first three terms on the right of Eq. (8)] remains constant,[13] and is neutralized by an equal and opposite positive background charge. The net charge imbalance on the nanocontact (neglecting screening) is thus $\delta Q_0 = -e\delta N_-$, which we show to be small. Differentiating Ω with respect to L with the constraint $\bar{N}_- =$ const., and using Eq. (8), one finds

$$F = -\left.\frac{\partial\Omega}{\partial L}\right|_{\bar{N}_-} = -\frac{\sigma_\mathcal{V}}{5}\frac{\partial\mathcal{S}}{\partial L} + \frac{2}{5}\Delta F_{\rm top} + \delta F, \tag{9}$$

where $\sigma_\mathcal{V} = E_F k_F^2/16\pi$ is the surface energy [3] of a noninteracting electron gas at fixed $\mathcal{V}$ and $\Delta F_{\rm top} = 4E_F/9\lambda_F$ is the mean mesoscopic suppression [6] of the cohesive force at fixed $\mathcal{V}$. The reduction of the surface energy by a factor of 5 has been discussed by Lang.[14] Importantly, since the constraint $\bar{N}_- =$ const. differs from the constraint $\mathcal{V} =$ const. only by terms of order $(k_F D_{\rm min})^{-1}$, the mesoscopic fluctuations δF and δN_- are quite insensitive to the choice of constraint.

Figure 1 shows the electrical conductance G of a metallic nanocontact, calculated from Eqs. (3) and (4), and its cohesive force F, calculated from Eqs. (5) and (9). The conductance decreases in steps of $2e^2/h$ and $4e^2/h$ (depending on whether the transverse mode involved is singly or doubly degenerate) as the contact is elongated, and the force exhibits oscillations of amplitude $\sim E_F/\lambda_F$, which are synchronized with the conductance steps. The overall magnitude of the force is reduced relative to that obtained in a previous calculation [3] using a constraint of constant volume, but the force oscillations δF are *virtually identical* to those obtained in Ref. 3. Noting that $E_F/\lambda_F \simeq 0.76$nN for Na, one finds that the force shown in Fig. 1(b) is also virtually identical to that calculated for a Na nanowire by Yannouleas et al.,[10] suggesting that the more realistic jellium confinement potential they utilized does not significantly modify the cohesion.

The net charge δQ_0 on the nanowire (neglecting screening) is also shown in Fig. 1. Interestingly, we find that $\delta Q_0/L_0 \simeq e\delta F/E_F$, where L_0 is the initial length of the (initially cylindrical) nanocontact. This result is consistent with the result of Kassubek et al.[7] for an abrupt geometry, and will be discussed in more detail elsewhere. Here it suffices to note that since $|\delta Q_0| \ll e\bar{N}_-$, the electron-electron interactions in the nanowire may be treated using linear-response theory.

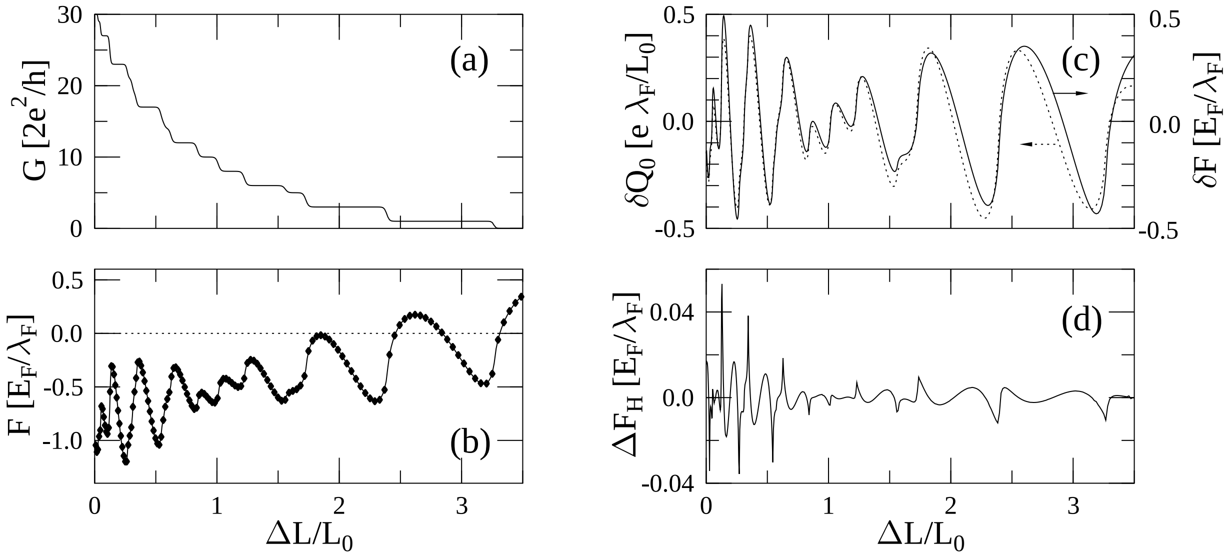

Figure 1: Properties of an axially symmetric nanocontact with diameter $D(z) = D_{\min} + (D_{\max} - D_{\min})(2z/L)^2$ as a function of the relative elongation $\Delta L/L_0$, where $k_F D_{\max} = 24$ and $k_F L_0 = 40$: (a) Electrical conductance G; (b) cohesive force F in the independent-electron model (solid curve) and in the self-consistent Hartree approximation (points); (c) mesoscopic charge oscillations δQ_0 (neglecting screening) and force oscillations δF; (d) self-consistent Hartree correction to the cohesive force in the constant interaction model [Eq. (15)].

3 Interacting electron model

3.1 Self-consistent Hartree approximation

In an interacting model, the confinement potential of the nanocontact is determined self-consistently via the Coulomb interaction: $U_0(\mathbf{x}) \to U(\mathbf{x}) = \int d^3y\, V(\mathbf{x}-\mathbf{y})\delta\rho(\mathbf{y})$ (Hartree approximation), where $\delta\rho(\mathbf{x}) \equiv \rho_-(\mathbf{x}) + \rho_+(\mathbf{x})$ is the net charge density, $V(\mathbf{x})$ is the Coulomb interaction, and $\rho_+(\mathbf{x})$ describes the fixed positive background. The grand canonical potential becomes

$$\Omega = \Omega_0[U(\mathbf{x})] - \frac{1}{2}\int d^3x\, [\rho_-(\mathbf{x}) - \rho_+(\mathbf{x})]\, U(\mathbf{x}), \tag{10}$$

where $\Omega_0[U(\mathbf{x})]$ is given by Eq. (5) with $U_0(\mathbf{x})$ replaced by $U(\mathbf{x})$. The second term in Eq. (10) corrects for the double counting of electron-electron interactions in $\Omega_0[U(\mathbf{x})]$. The charge density of the conduction electrons is

$$\rho_-(\mathbf{x}) = \frac{\delta\Omega_0}{\delta U(\mathbf{x})} = -\frac{1}{2\pi i}\int_0^{E_F} dE\, \mathrm{Tr}\left\{S^\dagger \frac{\delta S}{\delta U(\mathbf{x})} - S\frac{\delta S^\dagger}{\delta U(\mathbf{x})}\right\}. \tag{11}$$

3.2 Linear response

Motivated by the smallness of the bare charge fluctuations $\delta Q_0 = \int d^3x\, \delta\rho_0(\mathbf{x})$, we expand Eq. (11) to linear order in $U(\mathbf{x})$, obtaining a self-consistent equation for the screened charge density

$$\int d^3y\, \epsilon(\mathbf{x},\mathbf{y})\delta\rho(\mathbf{y}) = \delta\rho_0(\mathbf{x}), \qquad \epsilon(\mathbf{x},\mathbf{y}) = \delta(\mathbf{x}-\mathbf{y}) - \int d^3z\, \left.\frac{\delta\rho(\mathbf{x})}{\delta U(\mathbf{z})}\right|_{U=0} V(\mathbf{z}-\mathbf{y}), \tag{12}$$

where $\epsilon(\mathbf{x},\mathbf{y})$ is the nonlocal Hartree dielectric function and

$$\frac{\delta\rho(\mathbf{x})}{\delta U(\mathbf{y})} = -\frac{1}{2\pi i}\int_0^{E_F} dE\, \mathrm{Tr}\left\{\frac{\delta S^\dagger}{\delta U(\mathbf{y})}\frac{\delta S}{\delta U(\mathbf{x})} + S^\dagger \frac{\delta^2 S}{\delta U(\mathbf{y})\delta U(\mathbf{x})} - \mathrm{H.c.}\right\}. \tag{13}$$

Expanding Eq. (10) in powers of $U(\mathbf{x})$ and using Eq. (12), one finds

$$\Omega = \Omega_0[0] + \frac{1}{2}\int d^3x \int d^3y \;\; \delta\rho_0(\mathbf{x})\tilde{V}(\mathbf{x},\mathbf{y})\delta\rho_0(\mathbf{y}) + \mathcal{O}(\delta\rho_0^3), \tag{14}$$

where the screened interaction is given by $\tilde{V}(\mathbf{x},\mathbf{y}) = \int d^3z \; V(\mathbf{x}-\mathbf{z})\epsilon^{-1}(\mathbf{z},\mathbf{y})$ and the inverse dielectric function ϵ^{-1} satisfies $\int d^3z \; \epsilon^{-1}(\mathbf{x},\mathbf{z})\epsilon(\mathbf{z},\mathbf{y}) = \int d^3z \; \epsilon(\mathbf{x},\mathbf{z})\epsilon^{-1}(\mathbf{z},\mathbf{y}) = \delta(\mathbf{x}-\mathbf{y})$. Eq. (14) is a familiar result of linear-response theory; the new element here is that the dielectric function is calculated from the scattering matrix [Eqs. (12) and (13)] and is nonlocal due to quantum confinement.

3.3 Constant interaction model

A simple case for which Eqs. (12) and (14) can be solved easily is the so-called constant interaction model, $V(\mathbf{x},\mathbf{y}) = C^{-1}$ if $\mathbf{x},\mathbf{y} \in \mathcal{V}$ and 0 otherwise. C plays the role of the capacitance of the nanocontact to its environment, and Eqs. (12) and (14) become:

$$\delta Q = \frac{\delta Q_0}{1+e^2 g(E_F)/C}, \qquad \Omega = \Omega_0[0] + \frac{1}{2}\frac{\delta Q_0^2}{C + e^2 g(E_F)} + \mathcal{O}(\delta Q_0^3). \tag{15}$$

The result (15) confirms a previous conjecture [7] based on simple physical arguments. An upper bound on the magnitude of $\Delta\Omega_H = \Omega - \Omega_0[0]$ is obtained by setting $C = 0$, which enforces global charge neutrality. The Hartree correction to the cohesive force $\Delta F_H = -\partial\Delta\Omega_H/\partial L$ is plotted in Fig. 1 for $C = 0$. ΔF_H is over an order of magnitude smaller than δF, and gives an indiscernible correction to the total force, suggesting that the independent electron model of metallic nanocohesion [3,6–9] is well justified.

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References

[1] C. Rubio, N. Agraït, and S. Vieira, Phys. Rev. Lett. **76**, 2302 (1996).
[2] A. Stalder and U. Dürig, Appl. Phys. Lett. **68**, 637 (1996).
[3] C. A. Stafford, D. Baeriswyl, and J. Bürki, Phys. Rev. Lett. **79**, 2863 (1997).
[4] For a review, see C. W. J. Beenakker and H. van Houten, Solid State Phys. **44**, 1 (1991).
[5] A. I. Yanson, I. K. Yanson, and J. M. van Ruitenbeek, Nature **400**, 144 (1999).
[6] C. Höppler and W. Zwerger, Phys. Rev. Lett. **80**, 1792 (1998).
[7] F. Kassubek, C. A. Stafford, and H. Grabert, Phys. Rev. B **59**, 7560 (1999).
[8] C. Höppler and W. Zwerger, Phys. Rev. B **59**, R7849 (1999).
[9] J. Bürki, C. A. Stafford, X. Zotos, and D. Baeriswyl, Phys. Rev. B **60**, 5000 (1999).
[10] C. Yannouleas, E. N. Bogachek, and U. Landman, Phys. Rev. B **57**, 4872 (1998).
[11] H. Hakkinen and M. Manninen, Europhys. Lett. **44**, 80 (1998); N. Zabala, M. J. Puska, and R. M. Nieminen, Phys. Rev. Lett. **80**, 3336 (1998); A. Nakamura, M. Brandbyge, L. B. Hansen, and K. W. Jacobsen, ibid. **82**, 1538 (1999).
[12] L. I. Glazman, G. B. Lesovik, D. E. Khmel'nitskii, and R. I. Shekhter, JETP Lett. **48**, 238 (1988).
[13] It should be emphasized that one should not impose the constraint $N_- =$ const. This would require that the positive background be infinitely soft, in order to adapt to every mesoscopic variation in the electron density, which is unrealistic.
[14] N. D. Lang, Solid State Phys. **28**, 225 (1973).