Universality in Metallic Nanocohesion: A Quantum Chaos Approach

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(Received 7 July 1999)

Convergent semiclassical trace formulas for the density of states and the cohesive force of a narrow constriction in an electron gas, whose classical motion is either chaotic or integrable, are derived. It is shown that mode quantization in a metallic point contact or nanowire leads to universal oscillations in its cohesive force: the amplitude of the oscillations depends only on a dimensionless quantum parameter describing the crossover from chaotic to integrable motion, and is of order 1 nN, in agreement with recent experiments.

PACS numbers: 73.40.Jn, 03.65.Sq, 05.45.Mt, 73.23.–b

An intriguing question posed by Kac [1] is the following: "Can one hear the shape of a drum?" That is, given the spectrum of the wave equation [1] or Schrödinger's equation for free particles [2] on a domain, can one infer the domain's shape? This question was answered in the negative [1,2]; nevertheless there is an intimate relation between the two. In the context of metallic nanocohesion [3–10], a related question has recently emerged: "Can one feel the shape of a metallic nanocontact?" It was shown experimentally [3] that the cohesive force of Au nanocontacts exhibits mesoscopic oscillations on the nano-Newton scale, which are synchronized with steps of order $2e^2/h$ in the contact conductance. In a previous article [4], it was argued that these mesoscopic force oscillations, like the corresponding conductance steps [11], 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 [11] and a force of order ε_F/λ_F to the cohesion, where λ_F is the de Broglie wavelength at the Fermi energy ε_F. It was shown by comparing various geometries [4] that the force oscillations were determined by the area and symmetry of the narrowest cross section of the contact, and depended only weakly on other aspects of the geometry. Subsequent studies confirmed this observation, both for generic geometries [5,7,8,10], whose classical dynamics is *chaotic*, and for special geometries [6,9], whose classical dynamics is *integrable*. The insensitivity of the force oscillations to the details of the geometry, along with the approximate independence of their rms size on the contact area, was termed *universality* in Ref. [4]. A fundamental explanation of the universality observed in both the model calculations [4–10] and the experiments [3] has so far been lacking.

In this Letter, we derive semiclassical trace formulas for the force and charge oscillations of a metallic nanocontact, modeled as a constriction in an electron gas with hard-wall boundary conditions (see Fig. 1, inset), by adapting methods from quantum chaos [12–15] to describe the quantum mechanics of such an open system. It is found that Gutzwiller-type trace formulas [12–15], which typically do not converge for closed systems, not only converge but give quantitatively accurate results for open quantum mechanical systems, which are typically more difficult to treat than closed systems by other methods. Using these techniques, we demonstrate analytically that the force oscillations δF of a narrow constriction in a three-dimensional (3D) electron gas (i) depend only on the diameter D^* and radius of curvature R of the neck, (ii) have an rms value which is independent of the conductance G of the contact and depends only on a scaling parameter α which describes the crossover from chaotic to integrable

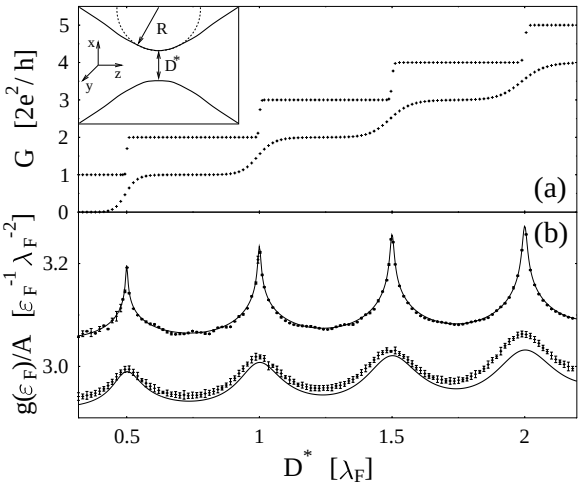

FIG. 1. Inset: Schematic diagram of a metallic nanocontact. (a) Conductance G and (b) DOS $g(\varepsilon_F)$ for 2D nanocontacts with $\alpha \approx 5$ versus the contact diameter D^*. g is normalized to the area A of the region. Solid curves: semiclassical result based on Eq. (8); crosses with error bars: numerical results using the method of Ref. [10]. Lower curves in (a) and (b): $R \approx \lambda_F$; upper curves (offset vertically): $R \approx 170\lambda_F$.

 0031-9007/99/83(23)/4836(4)$15.00

motion, and (iii) are proportional to the charge oscillations induced on the contact by the quantum confinement. Furthermore, we show (iv) that the force and charge oscillations are suppressed only weakly (algebraically) in short contacts, unlike conductance quantization, which is suppressed exponentially [11]. Conclusion (ii) is specific to 3D contacts, and breaks down for, e.g., two-dimensional (2D) nanowires, where rms $\delta F \propto G^{-1/2}$. Conclusions (i), (ii), and (iv) are unchanged when electron-electron interactions are included within the Hartree approximation.

The properties of simple metals are determined largely by the conduction electrons, the simplest model of which is a free-electron gas confined within the surface of the metal. We take the confinement potential to be a hard wall; the mesoscopic effects are virtually unchanged when one considers a more realistic confinement potential [7]. The grand canonical potential Ω is the appropriate thermodynamic potential describing the energetics of the electron gas in the nanocontact [4], and is

$$\Omega = -\frac{1}{\beta}\int dE\, g(E)\ln(1 + e^{-\beta(E-\mu)}), \qquad (1)$$

where $g(E)$ is the electronic density of states (DOS) and β is the inverse temperature [16]. The total number of electrons in the system is

$$N_- = \int dE\, f(E)g(E), \qquad (2)$$

where $f(E)$ is the Fermi-Dirac distribution function.

The DOS can be decomposed [12,13] in terms of a smooth Weyl contribution and a fluctuating term $\delta g(E)$,

$$g(E) = \frac{k_E^3 \mathcal{V}}{2\pi^2 E} - \frac{k_E^2 S}{8\pi E} + \frac{k_E C}{6\pi^2 E} + \delta g(E), \qquad (3)$$

where $k_E = (2mE/\hbar^2)^{1/2}$, $\mathcal{V}$ is the volume of the electron gas, S is its surface area, and $C = \frac{1}{2}\int d\sigma(1/R_1 + 1/R_2)$ is the mean curvature of its surface, $R_{1,2}$ being the principal radii of curvature. The first three terms in Eq. (3) are macroscopic, while δg determines the mesoscopic fluctuations of the equilibrium properties of the system. Inserting Eq. (3) into Eqs. (1) and (2), and taking the limit of zero temperature, one finds

$$\frac{\Omega}{\varepsilon_F} = -\frac{2k_F^3 \mathcal{V}}{15\pi^2} + \frac{k_F^2 S}{16\pi} - \frac{2k_F C}{9\pi^2} + \frac{\delta\Omega}{\varepsilon_F}, \qquad (4)$$

$$N_- = \frac{k_F^3 \mathcal{V}}{3\pi^2} - \frac{k_F^2 S}{8\pi} + \frac{k_F C}{3\pi^2} + \delta N_-, \qquad (5)$$

where $k_F = 2\pi/\lambda_F$ is the Fermi wave vector. The corrections to Eqs. (4) and (5) at finite temperature may be evaluated straightforwardly [13], and are quite small at room temperature, since $\varepsilon_F/k_B > 10^4$ K.

The cohesive force of the nanocontact is given by the derivative of the grand canonical potential with respect to elongation, $F = -\partial\Omega/\partial L$. Under elongation, the contact narrows and its surface area S increases, which would lead to a macroscopic surface charge by Eq. (5) if $\mathcal{V}$ were held fixed. This is due to the hard-wall boundary condition, which leads to a depletion of negative charge in a layer of thickness $\sim\lambda_F$ at the boundary [17]. The macroscopic incompressibility of the electron gas can be included by imposing the constraint $\bar{N}_- = \text{const}$ [18], where $\bar{N}_-$ is given by the first three terms in Eq. (5). The macroscopic electronic charge $-e\bar{N}_-$ is neutralized by the equal and opposite positive charge of the jellium background. The net charge imbalance on the nanocontact (neglecting screening) is thus $\delta Q_0 = -e\,\delta N_-$, which we will show to be quite small—on the order of a single electron charge. Differentiating Eq. (4) with respect to L with the constraint $\bar{N}_- = \text{const}$, one finds

$$F = -\frac{\partial\Omega}{\partial L}\bigg|_{\bar{N}_-} = -\frac{\sigma\mathcal{V}}{5}\frac{\partial S}{\partial L} + \frac{2}{5}\frac{\partial(C/\pi)}{\partial L}\Delta F_{\text{top}} + \delta F, \qquad (6)$$

where $\sigma\mathcal{V} = \varepsilon_F k_F^2/16\pi$ is the surface energy of a noninteracting electron gas [4] at fixed $\mathcal{V}$, and $\Delta F_{\text{top}} = 4\varepsilon_F/9\lambda_F$. The reduction of the surface energy by a factor of 5 has been discussed by Lang [17]. The second term on the right-hand side of Eq. (6), termed the "topological force" by Höppler and Zwerger [5] since it depends only on the topology of the cross section in the adiabatic limit, is reduced by a factor of 2.5. Importantly, since the constraint $\bar{N}_- = \text{const}$ differs from the constraint $\mathcal{V} = \text{const}$ used in previous work [4–6,8–10] only by terms of order $(k_F D^*)^{-1}$, the mesoscopic fluctuations δF and δN_- are quite insensitive to the choice of constraint.

The fluctuating part of the DOS δg may be evaluated in the semiclassical (stationary-phase) approximation as a sum over the periodic classical orbits of the system [12–15]. For closed systems, the sum over periodic orbits is generically not convergent, and a broadening of the energy structure in $\delta g(E)$ must be introduced by hand [13]. However, we shall see that for an open system, such as a nanocontact, the periodic orbit sum converges; the finite dwell time of a particle in an open system introduces a natural energy broadening.

Let us first consider the case of a 2D nanocontact. For a finite radius of curvature R, there is only one unstable periodic classical orbit (plus harmonics), which moves up and down at the narrowest point of the neck. One obtains

$$\delta g_{\text{sc}}^{\text{2D}}(E) = \frac{2mD^*}{\pi\hbar^2 k_E}\sum_{n=1}^{\infty}\frac{\cos(2nk_E D^*)}{\sinh(n\chi)}, \qquad (7)$$

where the Lyapunov exponent χ of the primitive periodic orbit satisfies $\exp(\chi) = 1 + D^*/R + \sqrt{(1 + D^*/R)^2 - 1}$. Equation (7) diverges when $\chi \to 0$, i.e., when $R \to \infty$. In that limit, the nanocontact acquires translational symmetry along the z axis, so that a generalization of the Gutzwiller formula obtained by Creagh and Littlejohn [14] must be used, which gives a finite result. In this limit, the motion is classically *integrable*. One can treat small deviations from translational symmetry via perturbation theory in $1/R$. The resulting asymptotic behavior for large R may be combined with

the result [Eq. (7)] valid for small R to construct the following interpolation formula, valid for arbitrary R:

$$\delta g_{\rm int}^{\rm 2D}(E) = \frac{\sqrt{8}\, mD^*}{\pi\hbar^2 k_E} \times \sum_{n=1}^{\infty} \frac{C\left(2nk_E D^* - \frac{\pi}{4}, \sqrt{\frac{nk_E L^2}{\pi R}}\right)}{\sinh(n\chi)}, \quad (8)$$

where $C(x,y) \equiv \cos(x)\mathrm{C}(y) - \sin(x)\mathrm{S}(y)$, with C and S Fresnel integrals. In Eq. (8), the specific shape of the nanocontact was taken to be $D(z) = D^* + z^2/R$. For a discussion of related interpolation formulas, see Ref. [15]. There is a smooth crossover between the strongly chaotic ($R \to 0$) and the nearly integrable ($R \to \infty$) regimes, described by the scaling parameter

$$\alpha = L/\sqrt{\lambda_F R}\,. \quad (9)$$

We refer to α as the *quantum chaos parameter*, since the quantum fluctuations of the system correspond to those of a chaotic system when $\alpha \gg 1$ and correspond to those of an integrable system when $\alpha \ll 1$.

Figure 1 shows a comparison of the semiclassical result [Eq. (8) + Weyl term] and a numerical calculation of g using a recursive Green's function technique [10]. The agreement of the semiclassical result and the numerical calculation is quite good, even in the extreme quantum limit $G \lesssim 2e^2/h$. The small discrepancy is of the size expected due to diffractive corrections [13] from the sharp corners present in the geometry studied numerically, where the nanocontact was connected to straight wires of width $k_F D = 52$ for technical reasons.

The denominator $\sinh n\chi$ in Eqs. (7) and (8) describes the rounding of the peaks in the DOS due to the finite dwell time of an electron in the neck. In the limit $R \gg D^*$, the Lyapunov exponent $\chi \to \sqrt{2D^*/R}$, and one recovers the WKB approximation of Ref. [4]. In the opposite limit $R \ll D^*$, $\sinh\chi \to D^*/R$, so δg is suppressed relative to the value expected in the WKB approximation (which neglects finite dwell-time effects) by a factor of $\sqrt{2R/D^*}$. In the adiabatic approximation, the energies of the transverse modes in the point contact are $\varepsilon_n(z) = (\hbar^2/2m)[\pi n/D(z)]^2 = \varepsilon_n(0) - m\omega_n^2 z^2/2 + \cdots$ and the probability that an electron of energy E in mode n will be transmitted through the point contact is [11] $T_n(E) \simeq (1 + \exp\{-2\pi[E - \varepsilon_n(0)]/\hbar\omega_n\})^{-1}$. The quality of the conductance quantization thus decreases *exponentially* with the parameter $\hbar\omega_n/\Delta\varepsilon_n \simeq \pi^{-1}\sqrt{2D^*/R}$, where $\Delta\varepsilon_n = \varepsilon_n - \varepsilon_{n-1}$, while the DOS fluctuations δg are suppressed only *inversely proportional* to this parameter.

Let us now consider the experimentally relevant case of an axially symmetric 3D nanocontact. For finite R, all classical periodic orbits lie in the plane of the narrowest cross section of the contact; however, there are now countably many distinct families of singly degenerate periodic orbits [9,13], labeled by their winding number w about the axis of symmetry z and by the number of vertices $v \geq 2w$. The interpolation formula for δg, describing the crossover from the chaotic regime $\alpha \gg 1$ to the integrable regime $\alpha \ll 1$, is

$$\delta g_{\rm int}^{\rm 3D}(E) = \frac{m}{\hbar^2\sqrt{\pi k_E}} \sum_{w=1}^{\infty}\sum_{v=2w}^{\infty} \frac{f_{vw} L_{vw}^{3/2}}{v^2 \sinh(v\chi_{vw}/2)} \times C(k_E L_{vw} - \tfrac{3v\pi}{2}, \alpha\sqrt{v\sin\phi_{vw} k_E/k_F}), \quad (10)$$

where $\phi_{vw} = \pi w/v$, $f_{vw} = 1 + \theta(v - 2w)$, and

$$e^{\chi_{vw}} = 1 + \frac{L_{vw}\sin\phi_{vw}}{vR} + \sqrt{\left(1 + \frac{L_{vw}\sin\phi_{vw}}{vR}\right)^2 - 1},$$

where $L_{vw} = vD^*\sin\phi_{vw}$ is the length of a periodic orbit. We emphasize that the double sum over w and v in Eq. (10) converges due to the finite Lyapunov exponent χ_{vw}. In Eq. (10), higher-order terms in the small parameter $1/k_E D^*$ have been omitted.

The mesoscopic force and charge fluctuations are calculated by inserting Eq. (10) into Eqs. (1), (2), and (6). In order to demonstrate the *universality* of the force oscillations, it is necessary to make some physically reasonable assumptions regarding the scaling of the geometry when the nanowire is elongated. It is natural to assume that the deformation occurs predominantly in the narrowest section, where the wire is weakest. This assumption, combined with the constraint of incompressibility $\bar{N}_- = \text{const}$, implies $D^{*2}L \approx \text{const}$. Furthermore, the radius of curvature $R \propto L^2/(D - D^*)$, where D is the diameter at $\pm L/2$, which implies $\partial\ln R/\partial\ln L = 2 + (\partial\ln D^*/\partial\ln L)/(D/D^* - 1) \approx 2$. Thus the quantum chaos parameter $\alpha \approx \text{const}$ under elongation.

Using these assumptions about the scaling of the geometry with elongation, the derivative with respect to L in Eq. (6) can be evaluated; the general formula for δF is rather lengthy, and will be presented elsewhere. Here we give only the limiting behavior of the leading-order semiclassical results:

$$\delta F \underset{\alpha\gg 1}{\simeq} -\frac{\varepsilon_F}{L}\sum_{w=1}^{\infty}\sum_{v=2w}^{\infty}\sqrt{\frac{L_{vw}}{\lambda_F}}\,\frac{f_{vw}\sin(k_F L_{vw} - b_v)}{v^2\sinh(v\chi_{vw}/2)}, \quad (11)$$

$$\delta F \underset{\alpha\ll 1}{\simeq} -\frac{2\varepsilon_F}{\lambda_F}\sum_{w=1}^{\infty}\sum_{v=2w}^{\infty}\frac{f_{vw}}{v^2}\sin(k_F L_{vw} - 3v\pi/2), \quad (12)$$

where $b_v = 3v\pi/2 - \pi/4$. δF is an oscillatory function of $k_F D^*$, and is plotted in Fig. 2 for $R \gg D^*$.

The rms amplitude of the force oscillations may be readily calculated from Eqs. (11) and (12). We find that rms δF is independent of D^*, and, apart from small

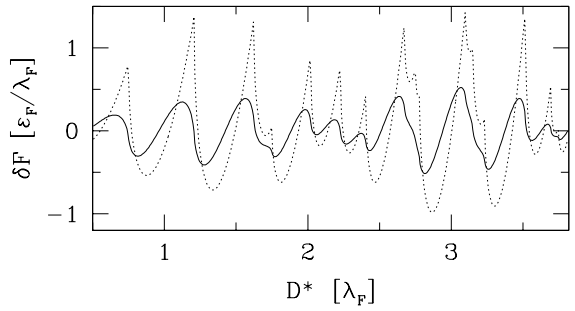

FIG. 2. Force oscillations δF versus the minimum contact diameter D^*: dashed curve: $\lim_{\alpha\to 0}\{\delta F\}$; solid curve: $\lim_{\alpha\to\infty}\{\alpha\,\delta F\}$. The result for $\alpha \gg 1$ (chaotic motion) is consistent with previous results based on the WKB approximation [4], while the result for $\alpha \to 0$ (integrable limit) agrees with the result [6,9] for a straight wire.

corrections due to tunneling when $R \ll D^*$, depends only on the quantum chaos parameter α:

$$\text{rms}\,\delta F = \frac{\varepsilon_F}{\lambda_F} \times \begin{cases} 0.58621 & \alpha \ll 1 \\ 0.36208\alpha^{-1} & \alpha \gg 1\,. \end{cases} \tag{13}$$

The quantum fluctuations in the chaotic regime $\alpha \gg 1$ are suppressed relative to those in the integrable limit $\alpha \ll 1$ due to the reduced measure of the periodic orbits in phase space [19]. For a realistic geometry of the nanowire [3], one expects both the radius of curvature and the elongation to be on the scale of λ_F, implying $\alpha \sim 1$. There is also experimental evidence [20] of exceptional geometries with $R \gg \lambda_F$, implying $\alpha \ll 1$. Thus the mesoscopic oscillations of the cohesive force are expected [21] to be universal $\text{rms}\,\delta F \sim \varepsilon_F/\lambda_F \approx 1$ nN in monovalent metals.

Equation (10) and the assumption $D^{*2}L = \text{const}$ imply that the force and charge oscillations are proportional to each other in 3D nanocontacts: $\delta F = -\varepsilon_F \delta N_-/L + \mathcal{O}(1/k_F D^*)$. In an interacting system, the charge oscillations are screened [8], and the Hartree correction to the grand canonical potential is bounded by $\Delta\Omega < \delta N_-^2/2g(\varepsilon_F)$. Evaluating the sums over periodic orbits, we find that the average interaction correction $\langle\Delta\Omega\rangle$ is small compared to the mesoscopic oscillations of Ω: $\langle\Delta\Omega\rangle/\text{rms}\,\delta\Omega < 1.36791/k_F D^*$, where $k_F D^* > 4.81$ for a contact with nonzero conductance. This result justifies the use of the independent-electron approximation [4–6,8–10].

In conclusion, we have shown that trace formulas à la Gutzwiller converge and give quantitatively accurate results for the equilibrium quantum fluctuations in point contacts and nanowires. Using this approach, we have shown that the cohesive force of a metallic nanocontact, modeled as a hard-wall constriction in an electron gas, exhibits universal mesoscopic oscillations, whose size $\text{rms}\,\delta F \sim \varepsilon_F/\lambda_F$ is independent of the conductance and shape of the contact, and depends only on a dimensionless parameter α characterizing the degree of quantum chaos. Our prediction of universality is consistent with all experiments performed until now [3].

We thank R. Blümel, J. Morris, R. Prange, and H. Primack for useful discussions. This work was supported in part by NSF Grant No. PHY94-07194. F. K. acknowledges support from Grant No. SFB 276 of the Deutsche Forschungsgemeinschaft. J. B. acknowledges support from Swiss National Foundation PNR 36 "Nanosciences" Grant No. 4036-044033.

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[18] One should not impose the constraint $N_- = \text{const}$, which would require the positive background to be infinitely soft, to adapt to every mesoscopic variation in the electron density.
[19] The suppression of $|\delta F|$ in the chaotic regime arises because $\delta\Omega$ is dominated by a region of length $\sim\sqrt{\lambda_F R}$ at the narrowest point of the neck [cf. Eqs. (8) and (10)]; if the deformation of the system is distributed over a much longer region ($\alpha \gg 1$), then $\delta F = -\partial[\delta\Omega]/\partial L \propto \alpha^{-1}$.
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[21] In nanowires lacking axial symmetry, i.e., with an aspect ratio $a \gg 1$, one finds $\text{rms}\,\delta F \sim a\varepsilon_F/\lambda_F$. However, such shapes are energetically highly unfavorable due to the increased surface energy. Equation (13) is therefore expected to describe all spontaneously occurring nanocontacts.