Universality in metallic nanocohesion: a quantum chaos approach

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Convergent semiclassical trace formulae for the density of states and 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 nano-Newton, in agreement with recent experiments. Interestingly, quantum tunneling is shown to be described quantitatively in terms of the instability of the classical periodic orbits.

An intriguing question posed by Kac [1] is, “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 $\varepsilon_F/\lambda_F$ to the cohesion, where $\lambda_F$ is the de Broglie wavelength at the Fermi energy $\varepsilon_F$. 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 r.m.s. 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 formulæ 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 [12–16] to describe the quantum mechanics of such an open system. It is found that Gutzwiller-type trace formulæ [12–16], 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 $\delta F$ 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 r.m.s. value which is independent of the conductance $G$ of the contact and depends only on a scaling parameter $\alpha$ which describes the crossover from chaotic to integrable motion, and (iii) are proportional to the charge oscillations induced on the contact by the quantum confinement. Furthermore, we show (iv) that quantum tunneling through the constriction is determined by the instability of the classical periodic orbits within the constriction, and that the force and charge oscillations are suppressed only weakly (algebraically) by tunneling, 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 r.m.s $\delta F \propto G^{-1/2}$. 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. Here we take the confinement potential to be a hard wall; the effects of interest to us are virtually unchanged when one considers a more realistic confinement potential [7]. The grand canonical potential $\Omega$ is the appropriate thermodynamic potential describing the energetics of the electron gas in the nanocontact [4], and
\[ \Omega = -\frac{1}{\beta} \int dE \, g(E) \ln \left( 1 + e^{-\beta(E-\mu)} \right), \] (1)

where \( g(E) \) is the electronic density of states (DOS) and \( \beta \) is the inverse temperature [17]. The total number of electrons in the system is

\[ N_- = \int dE \, f(E)g(E), \] (2)

where \( f(E) \) is the Fermi-Dirac distribution function. The DOS of an open quantum system, such as that shown in Fig. 1 (inset), is given in terms of the electronic scattering matrix \( S(E) \) by [18] \( g(E) = (2\pi)^{-1}\text{Tr}\{S^\dagger(E)\partial S/\partial E - \text{H.c.}\} \), where a factor of 2 for spin has been included.

The DOS can be decomposed [13,14] in terms of a smooth Weyl contribution \( g(E) \) and a fluctuating term \( \delta g(E) \),

\[ g(E) = \frac{k_F^3 V}{2\pi^2 E} \frac{k_F^2 S}{8\pi E} + \frac{k_F C}{6\pi^2 E} + \delta g(E), \] (3)

where \( k_F = (2mE/\hbar^2)^{1/2}, V \) 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 \( \delta g \) 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

\[ \frac{\Omega}{\epsilon_F} = -\frac{2k_F^3 V}{15\pi^2} - \frac{k_F^2 S}{16\pi} - \frac{2k_F C}{9\pi^2} + \frac{\delta \Omega}{\epsilon_F}, \] (4)

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

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

The cohesive force of the nanocontact is given by the derivative of the grand canonical potential with respect to the elongation, \( F = -\partial \Omega/\partial L \). Under elongation, the contact narrows and its surface area \( S \) increases. The increase of \( S \) under elongation would lead to a macroscopic surface charge by Eq. (5). 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 [19]. The macroscopic incompressibility of the electron gas can be included by imposing the constraint \( \delta N_- = \text{const.} \) [20], where \( \delta N_- \) is given by the first three terms in Eq. (5). The macroscopic electronic charge \(-e\delta N_-\) 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 \( \delta N_- = \text{const.} \), one finds

\[ F = -\frac{\partial \Omega}{\partial L} \bigg|_{\delta N_-} = -\frac{\sigma_V}{5} \frac{\partial S}{\partial L} + \frac{2}{5} \frac{\partial(C/\pi)}{\partial L} \Delta F_{\text{top}} + \delta F, \] (6)

where \( \sigma_V = \xi_F k_F^2/16\pi \) is the surface energy of a noninteracting electron gas [4] at fixed \( V \) and \( \Delta F_{\text{top}} = 4\pi e_F/9\lambda_F \). The reduction of the surface energy by a factor of 5 has been discussed by Lang [19]. 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 \( \delta N_- = \text{const.} \) differs from the constraint \( V = \text{const.} \) used in previous work [4–6,8–10] only by terms of order \( (k_F D^*)^{-1} \), the mesoscopic fluctuations \( \delta F \) and \( \delta N_- \) are quite insensitive to the choice of constraint.

The fluctuating part of the DOS \( \delta g \) may be evaluated in the semiclassical (stationary-phase) approximation as a sum over the periodic classical orbits of the system [12–16]. 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

\[ \delta g_{\text{sc}}^{2D}(E) = \frac{2mD^*}{\pi\hbar^2 k_F} \sum_{n=1}^{\infty} \frac{\cos(2nk_F D^*)}{\sinh(n\chi)} , \] (7)

where the Lyapunov exponent \( \chi \) of the primitive periodic orbit satisfies \( \exp(\chi) = 1 + D^*/R + \sqrt{(1 + D^*/R)^2 - 1} \). Eq. (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 [15] 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 \( R \):

\[ \delta g_{\text{int}}^{2D}(E) = \frac{\sqrt{2mD^*}}{\pi\hbar^2 k_F} \sum_{n=1}^{\infty} \frac{C(2nk_F D^* - \frac{\pi}{4}\sqrt{\frac{2nk_F D^*}{\pi R}})}{\sinh(n\chi)} , \] (8)

where \( C(x,y) \equiv \cos(x)C(y) - \sin(x)S(y) \), 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 formulae, see Ref. [16]. Classically, only the case \( R = \infty \) is integrable. But semiclassically, there is a smooth crossover between the strongly chaotic \((R \to 0)\) and the nearly integrable \((R \to \infty)\) regimes. The scaling parameter describing this crossover is

\[
\alpha = L/\sqrt{\lambda FR}.
\]

We refer to \( \alpha \) 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 a quasi-integrable system when \( \alpha \ll 1 \).

Fig. 1 shows a comparison of the semiclassical result \( g_{sc} = \bar{g} + \delta g_{2D} \) 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 \( \sinh \chi \) in Eqs. (7) and (8) describes the effects of tunneling. 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 \( \delta g \) is suppressed relative to the value expected in the WKB approximation (which neglects tunneling) by a factor of \( \sqrt{2R/D^*} \). In the adiabatic approximation, the energies of the transverse modes in the point contact are \( \varepsilon_n(z) = (\hbar^2/2m)(\pi n/D(z))^2 = \varepsilon_n(0) - m\omega^2 z^2/2 + \cdots \) 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 \( \delta \gamma \) are suppressed only inversely proportional to this parameter. The fact that the suppression in each case depends only on the ratio \( D^*/R \) implies that the suppression of \( \delta \gamma \), like the degradation of conductance quantization, is a consequence of tunneling. Indeed, it is the rounding of the DOS due to tunneling that causes the sums over \( n \) in Eqs. (7) and (8) to converge. That quantum tunneling through a point contact can be expressed purely in terms of the instability \( \chi \) of the classical periodic orbits within the contact is remarkable.

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 [13,9], 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 \( \delta g \), describing the crossover from the chaotic regime \( \alpha \gg 1 \) to the integrable regime \( \alpha \ll 1 \), is

\[
\delta g_{3D}(E) = \frac{m}{\hbar^2 \pi k_F} \sum_{w=1}^{\infty} \sum_{v=2w}^{\infty} f_{vwL_{vw}}^{3/2} \frac{L_{vw}^{3/2}}{v^2 \sinh(v\chi_{vw}/2)} \times C(k_F L_{vw} - 3\pi \alpha \sqrt{v \sin \phi_{vw} k_F / k_F}),
\]

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

\[
\exp(\chi_{vw}) = 1 + L_{vw} \sin \phi_{vw} \sqrt{\frac{L_{vw} \sin \phi_{vw}}{v R} + \left( 1 + L_{vw} \sin \phi_{vw} \right)^2} - 1,
\]

with \( L_{vw} = vD^* \sin \phi_{vw} \) 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 \( \chi_{vw} \). In Eq. (10), higher-order terms in the small parameter \( 1/k_F D^* \) (\( D^* / k_F \) (\( D^* < 0.21 \) for contacts of nonzero conductance) 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 \( D^* 2L \approx \text{const.} \). 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 $\delta F$ is rather lengthy, and will be presented elsewhere. Here we give only the limiting behavior of the leading-order semiclassical results:

$$\delta F \sim \frac{\varepsilon_F}{\lambda_F} \sum_{w=1}^{\infty} \sum_{v=2w}^{\infty} \sqrt{f_{vw} f_{wu} \sin(k_F L_{vw} - b_w)}.$$  \hspace{1cm} (11)

$$\delta F \sim \frac{-2 \varepsilon_F}{\lambda_F} \sum_{w=1}^{\infty} \sum_{v=2w}^{\infty} \frac{f_{vw}}{v^2} \sin(k_F L_{vw} - 3v\pi/2).$$  \hspace{1cm} (12)

where $b_v = 3v\pi/2 - \pi/4$. $\delta F$ is an oscillatory function of $k_F D^*$; the conductance of the contact is also determined by $k_F D^*$, indicating that the force oscillations are synchronized with the conductance steps, as shown in Ref. [4] and observed experimentally [3].

The rms amplitude of the force oscillations may be readily calculated from Eqs. (11) and (12). We find that $\text{rms} \delta F$ is independent of $D^*$, and, apart from small corrections due to tunneling when $R \ll D^*$, depends only on the quantum chaos parameter $\alpha$:

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

The result for $\alpha \ll 1$ agrees with the result for a straight wire ($\alpha = 0$) derived previously by Höppler and Zwerger [9]. Eq. (13) is also consistent with previous results based on the WKB approximation [4]. For a realistic geometry of the nanowire [3], one expects both the radius of curvature and the elongation to be on the scale of $\lambda_F$, implying $\alpha \sim 1$. There is also experimental evidence [21] of exceptional geometries with $R \gg \lambda_F$, implying $\alpha \ll 1$. Thus the mesoscopic oscillations of the cohesive force are expected to be universal $\text{rms} \delta F \sim \varepsilon_F/\lambda_F \approx \frac{1}{2} N_2$ in monovalent metals, in agreement with all available experimental data [3].

In nanowires lacking axial symmetry, e.g., with an aspect ratio $a \gg 1$, one can show that $\text{rms} \delta F \sim a \varepsilon_F/\lambda_F$. However, such shapes are energetically highly unfavorable due to the increased surface energy. Eq. (13) is therefore expected to describe all spontaneously occurring nanocontacts.

Eq. (10) and the assumption $D^2 L = \text{const.}$ imply that the force and charge oscillations are proportional to each other in 3D nanocontacts: $\delta F = -\varepsilon_F \delta N_2/L + O(1/k_F D^*)$. In an interacting system, the charge oscillations are screened [8], and the Hartree correction to the grand canonical potential is bounded by $\Delta \Omega < \delta N_2^2/2g(\varepsilon_F)$. Evaluating the elementary sums over periodic orbits, we find that the average interaction correction $\langle \Delta \Omega \rangle$ is small compared to the mesoscopic oscillations of $\Omega$:

$$\frac{\langle \Delta \Omega \rangle}{\text{rms} \delta \Omega} \leq \frac{1.36791}{k_F D^*},$$  \hspace{1cm} (14)

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 formulæ 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 $\alpha$ characterizing the degree of quantum chaos. Our prediction of universality is consistent with all experiments performed to date [3].

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In Eq. (1), we have neglected a contribution $\Delta \Omega$ due to electron-electron interactions, which will be shown to be unimportant for mesoscopic effects.

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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.

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