PHYSICAL REVIEW B VOLUME 56, NUMBER 19 15 NOVEMBER 1997-I

Conductance quantization in metals: The influence of subband formation on the relative stability of specific contact diameters

J. M. van Ruitenbeek
Kamerlingh Onnes Laboratorium, Leiden University, P.O. Box 9506, NL-2300 RA Leiden, The Netherlands

M. H. Devoret, D. Esteve, and C. Urbina
Service de Physique de l'Etat Condensé, Centre d'Etudes de Saclay, CEA, Orme de Merisiers, F-91191 Gif-sur-Yvette Cedex, France

(Received 24 April 1997; revised manuscript received 7 July 1997)

We consider a simple model of a metallic nanowire, consisting of a free electron gas confined within hard-wall boundaries and connected to banks on either side. Similar models have been widely used to discuss conductance properties of nanowires and point contacts. Here we show that the same model has implications for the mechanical stability of the wire and its work function, and that it possibly induces Jahn-Teller-type distortions in the wire cross section. [S0163-1829(97)02243-1]

I. INTRODUCTION

Metallic contacts of atomic dimensions are routinely obtained by pressing two electrodes together in a controlled way.[1–13] As the contacts are elongated, they change size in a stepwise fashion due to atomic structural rearrangements which are revealed by an irregular staircase variation of both the force between electrodes and the electrical conductance of the contact. Although the conductance staircase is different for each elongation process, a statistical analysis over a large number of runs, for simple free electronlike metals, results in conductance histograms that usually display several distinct peaks. The exact histogram depends on the particular metal and on the experimental conditions but one fact is quite general: For most metals measured up to now, and especially for monovalent ones, there exist certain favored values for the conductance. In particular, the most prominent peak corresponds to one conductance quantum $G_0 = 2e^2/h$ (to within 10% or better). This suggests that the conductance in atom size metallic contacts shows a tendency for quantization.[14] However, the problem is intimately connected to the distribution of atomic configurations which are visited in the experiments. When particular atomic configurations are preferred over others, this by itself would lead to peaks in the histograms. The question then arises as to why these configurations are preferred.

Theoretical descriptions of conductance quantization in metallic contacts have been given in terms of free electron waves, confined within a boundary which was fixed by the positions of the atoms at the surface.[8,6,15] Alternatively the electron waves have been described in terms of a tight binding model,[15–17] but in each case the problem of finding the electronic wave functions was separated from the problem of determining the atomic configuration of the contact, for which molecular dynamics simulations were employed or fixed convenient geometries were chosen. The question we want to investigate below, is whether this separation is allowed: are the contributions of the wave functions of the conduction electrons sufficiently small (or sufficiently smooth) that they can be ignored in searching for the minimum-energy configurations of the atoms in the contact? Is an effective nearest-neighbor interaction valid in the calculation of the interatomic forces?

The nearly free electron approximation has proven its value for the calculation of various properties of metals.[18] It works best for simple, monovalent metals, in particular the alkali metals, for which the Fermi surface is nearly spherical. One of the most convincing implications of the free electron approximation is the shell structure in metal clusters.[19] In vapor jets of potassium, the metal atoms cluster together, and clusters composed of specific ''magic'' numbers of atoms (2, 8, 18, 20, 40, 58, ...) are more frequently detected than others.[20] This observation was explained, in analogy to the magic numbers in nuclear structure, by the favorable binding energy for clusters having ''closed'' electronic shells. The electronic wave functions can be approximated as free electrons confined inside a spherical potential well, given by the spherical Bessel functions. The total energy per atom of the occupied electronic states decreases with cluster size as long as the set of states for a given l quantum number (a shell) is partially filled. The addition of one atom to a filled-shell cluster requires occupying a higher-energy level, and the total energy per atom of the cluster increases again. Therefore, the cluster energy finds itself at a minimum when the shell is just completed. The magic numbers are found from the degeneracy of the levels, $(2s+1)(2l+1)$, with spin $s = \frac{1}{2}$. The order in which the l quantum numbers are filled can be read from the order of the zero's of the Bessel functions.

A proper calculation of the cluster abundance spectrum requires including exchange and correlation effects as well as a realistic shape of the confining potential.[19] However, the principle of the magic numbers can be demonstrated using a hard-wall boundary and ignoring exchange and correlation contributions.[20] We will use this simple approach below in a calculation for a wire connected to bulk reservoirs, and discuss the question of whether specific wire diameters have a higher relative stability due to the electronic degrees of freedom, in analogy to the shell-filling effects in clusters. In contrast to the clusters, the wire is not isolated, and the connection of the wire to the reservoirs results in an equilibrium electric charge in the wire, which may be observed as fluc-

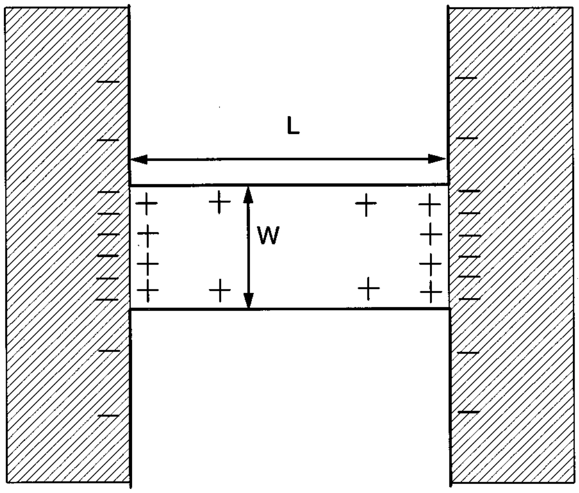

FIG. 1. As the geometry of the model nanowire we choose a conductor of uniform square cross section $W\times W$ and length L, connected to reservoirs at both ends (dashed).

tuations in the work function with the wire diameter.

We are aware of the serious limitations of the approximations, but we want to point out some of the interesting consequences of the model, which may stimulate more realistic model calculations. Furthermore, similar approximations have been widely used in the calculation of the conductance of nanowires, while the implications of this model for the total energy and electric potential of the wire have generally been ignored. In Sec. II the problem is introduced and it is shown that screening effects should be taken into account. The calculation preserving charge neutrality is presented in Sec. III, and in Sec. IV electron energy induced deviations from a symmetric square cross section are considered. The relevance to experimental results is briefly discussed in Sec. V.

II. THE TOTAL ENERGY OF A NANOWIRE

Since we are only interested in demonstrating the principle we can choose convenient boundary conditions. Our wire consists of a uniform conductor of square cross section $W\times W$ and length L, with free and independent electrons confined within hard-wall boundaries, connected to free electron gas reservoirs (Fig. 1). We consider wires sufficiently long that the contribution of tunneling electrons (evanescent modes) can be ignored. It poses no great difficulty to extend the calculations to include such contributions, but for the sake of clarity we limit ourselves to a brief discussion of this aspect in Sec. V. When it is necessary to choose values for the parameters we will use those appropriate for sodium.

The density of states (DOS) in the wire can be expressed as

$$\mathcal{N}(W,\epsilon_F)=\frac{2m}{W\pi^2\hbar^2}\sum_{n_1,n_2}^{+}\frac{1}{\sqrt{w^2-n_1^2-n_2^2}}, \tag{1}$$

where $w=2W/\lambda_F$, $\lambda_F=2\pi\hbar/\sqrt{2m\epsilon_F}$, and λ_F, ϵ_F, and m are the Fermi wavelength, Fermi energy, and the free electron mass, respectively. The $+$ on the summation indicates that n_1 and n_2 run from 1 to the maximum value for which the expression under the square root in Eq. (1) is positive. In Fig. 2 the DOS of the wire is compared to that of a bulk electron gas. The figure illustrates that the total energy of the occupied states is very sensitive to the actual position of the Fermi energy relative to the positions of the peaks in the DOS. This particular DOS is a consequence of the quantization of the transverse degrees of freedom of the electron wave function in a contact and results in a finite number of subbands, each of which contributes a quantum to the conductance of the contact. Perfect quantization is only obtained when (1) the contact length L is much larger than the width W of the contact and the Fermi wavelength λ_F, (2) the width of the contact is a smooth function of the longitudinal coordinate (adiabatic approximation), and (3) the total mean free path $l\gg L$. Further, all energies (k_BT,eV) should be much smaller than the subband splitting. This is the explanation for the phenomenon of conductance quantization observed in

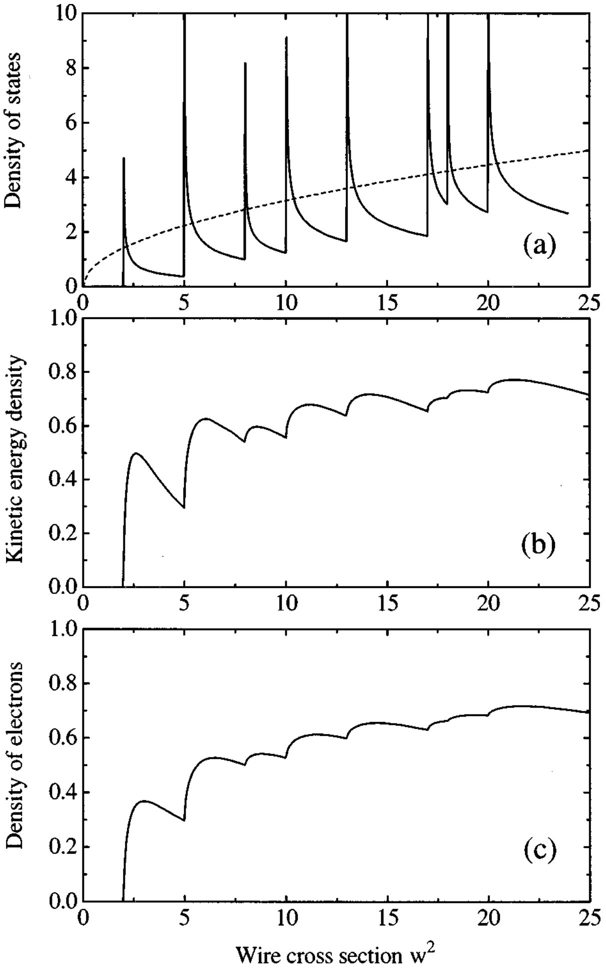

FIG. 2. Density of states, $\mathcal{N}$, of the wire (a, solid curve) compared to the bulk (a, dashed curve), in units $m/\pi\hbar^2W$, as a function of $w^2=(2W/\lambda_F)^2$. Also the total kinetic energy density, $\mathcal{K}$, (b) and the density of electrons, $n(w)$, (c), are shown, both normalized to the bulk value. These are obtained by integrating the DOS and the product of the DOS and the energy, respectively, over all states up to the Fermi energy.

semiconducting point contacts, for which the free electron model is applicable. The adiabatic approximation (2) is clearly not applicable for the model geometry of Fig. 1, and additional resonances of the conductance on the plateaus appear as a result of the interference of waves scattered from the two interfaces. However, globally the conductance can still be seen to increase by quantum units for this model.[21]

The total kinetic energy of the occupied states can be found by integrating the energy over this DOS. Expressing the total energy normalized to the bulk value, $\mathcal{K}_0 = \hbar^2 k_F^5/10\pi^2 m$, we obtain,

$$\mathcal{K}(w) = \frac{10}{3\pi}\frac{1}{w^5}\sum_{n_1,n_2}^{+} (w^2 + 2n_1^2 + 2n_2^2)\sqrt{w^2 - n_1^2 - n_2^2}. \tag{2}$$

Similarly, the density of electrons normalized to the bulk value $n_0 = k_F^3/3\pi^2$ is

$$n(w) = \frac{6}{\pi}\frac{1}{w^3}\sum_{n_1,n_2}^{+} \sqrt{w^2 - n_1^2 - n_2^2}. \tag{3}$$

These functions are also plotted in Fig. 2.

The figure clearly demonstrates three important features: (a) the total energy density and (b) the electron density are much lower than the bulk values, and (c) there are strong fluctuations in both quantities as a function of the width of the wire. The first, (a), is the result of the strong confinement imposed by the hard-wall potential. A realistic potential allows spillout of the wave function beyond the boundaries. There is a simple solution to this problem, since the energy levels for a finite potential well can be described to a very good approximation by those of an infinite potential well of larger width. Using parameters appropriate for sodium, the width should be increased by an amount $dw = 0.688$. Using this value in the calculation of the total energy, we find that $\mathcal{K}$ fluctuates properly around 1. The second feature, (b), is also a consequence of the hard-wall potential. The distribution of states in momentum space is not uniform, since states with $k_x = 0$ or $k_y = 0$ are excluded. This is a well known problem which was already treated by Weyl.[22] The bulk density of electrons to which Eq. (3) should be normalized receives surface corrections, which can be expressed as $n_0 = (k_F^3/3\pi^2)(1 - 3/2w + 3/2\pi w^2)$.[23] When the density is recalculated and normalized using this correction, we find that it fluctuates around the proper bulk limit. Both features, (a) and (b), have recently been discussed in the context of conductance quantization by García-Martín *et al.*[24] They showed how the semiclassical Sharvin limit can be obtained by including these corrections, and that the actual diameter of the wires required for a specific number of modes is smaller than obtained from the standard calculations.

The third feature, (c), is the one that we are particularly interested in. The strong fluctuations in the total energy may contribute to the relative stability of specific wire widths. Although the details will also be sensitive to the artificial boundary conditions that we use, the general features should be present for any choice of potential. They can be understood as follows. When the diameter of the wire increases to $w = \sqrt{2}$ the Fermi energy touches the bottom of the first subband. From this point onward the subband starts to be filled and the electron density and kinetic energy per volume start rising rapidly as a result of the peak in the DOS. For further increase of w the DOS decreases leading to a slowdown in the increase of the number of electrons and the kinetic energy, while the volume keeps increasing as W^2 resulting in a maximum in the densities of electrons and energy, followed by a decrease in these densities until the next subband is reached. As a result, $n(w)$ and $\mathcal{K}(w)$ show oscillations as a function of w, with the amplitude decreasing for increasing w. The deviations from the bulk values are largest for small W, and amount up to tens of percents.

Such deviations from the bulk density are not realistic. The most dramatic consequence is that the electron density is found to drop to zero for small widths when the last channel is closed, whereas in practice every atom will continue to be surrounded, on average, by one electron (for a monovalent metal). The screening in metals is very effective down to a scale ~1 Å, and the positive background charge density will tend to be compensated. This shortcoming is generally ignored in free-electron calculations of conductance in nanowires.

III. SCREENING: CONSTANT ELECTRON DENSITY

The main effect of the electron screening can be taken into account by fixing the electron density in the wire at the bulk value.[26] This can be done by adjusting the electrochemical potential μ of the wire such that

$$n(w,\mu) = \frac{6}{\pi}\frac{\displaystyle\sum_{n_1,n_2}^{+}\sqrt{\left(\frac{w+dw}{w_\mu}\right)^2 - n_1^2 - n_2^2}}{(w+dw)^3 - \frac{3}{2}(w+dw)^2 + \frac{3}{2\pi}(w+dw)} = 1, \tag{4}$$

with $w_\mu = \lambda/\lambda_F = \sqrt{\epsilon_F/\mu}$. The corrections for the effects of the hard-wall potential discussed above have been incorporated in this expression. The total kinetic energy is then calculated for the value of μ obtained by solving Eq. (4), which needs to be reevaluated for each width W of the wire:

$$\mathcal{K}(w,\mu) = \frac{10}{3\pi}\frac{\displaystyle\sum_{n_1,n_2}^{+}\left[\left(\frac{w+dw}{w_\mu}\right)^2 + 2n_1^2 + 2n_2^2\right]\sqrt{\left(\frac{w+dw}{w_\mu}\right)^2 - n_1^2 - n_2^2}}{w^2(w+dw)^3}. \tag{5}$$

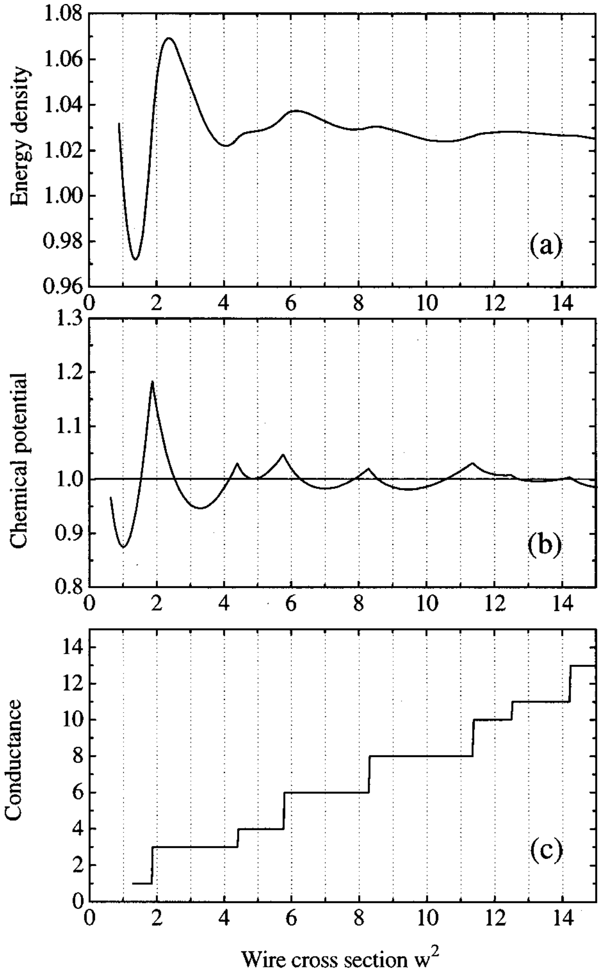

FIG. 3. Kinetic energy density, $\mathcal{K}$, (a) of the wire normalized to the bulk value calculated while keeping density of electrons constant, plotted as a function of $w^2=(2W/\lambda_F)^2$. The electron density is held constant by adjusting the chemical potential, shown in (b) as μ/ϵ_F, normalized to the bulk Fermi energy. The cusps in the chemical potential are found at the steps in the conductance (c).

The result is given in Fig. 3, together with the variation of the chemical potential μ/ϵ_F. The conductance has also been calculated, using $G(w)=\Sigma^{+}_{n_1,n_2}1$, in units $G_0=2e^2/h$ and ignoring reduction of the transmission probability due to reflections at the interface with the reservoirs. The consequences of this scenario are the following:

(a) The width at which a new channel is opened, and at which the conductance jumps by one or two units, is considerably smaller than in the case discussed above with $\mu=\epsilon_F$, even smaller than that obtained after correction for the effects of the hard-wall potential. In particular, the jump from zero to 1 G_0 is displaced to $w=0$ in this model. In reality the electrochemical potential and the kinetic energy density (Fig. 3) cannot be raised indefinitely, and the density would still drop to zero at some point. A density of states equal to zero in the wire corresponds to ionization of the atom(s) which make up the wire. The energy cost involved is so large that the wire will most likely break before this happens. This suggests that a contact having no conducting modes and only tunneling contributions to the conductance, is not stable. Note that this applies to metals, and need not hold, e.g., for semimetals, where the contribution to the total energy of the conduction electrons is extremely small.

(b) The difference between the bulk Fermi energy and the chemical potential in the wire can be maintained only by adjusting the electric potential of the wire with respect to the bulk by an amount $V=+(\mu-\epsilon_F)/e$; i.e., the electrochemical potential matches the Fermi energy. The fluctuations of the electrical potential can be read from Fig. 3(b) in units ϵ_F/e. For the narrowest wires the potential can reach values up to 0.6 V, but even for much larger diameters excursions up to 0.1 V are obtained. Similar effects have been considered by Moskalets for two-dimensional electron gas quantum point contacts, where the quantum-size induced potential should modify the applied gate potential.[25] For the metallic 3D nanowires the effects are more pronounced and may be observable as fluctuations in the work function.

(c) In order to set up the electrical potential difference between the wire and the bulk electrodes a charged dipole layer will be formed at the interfaces (see Fig. 1), and also some charge will accumulate at the surface of the wire and electrodes. The electrostatic energy involved needs to be taken into account in the evaluation of the total energy of the wire configuration, and it should be small compared to the total kinetic energy, otherwise we must accept that the electron density deviates from the bulk value. We estimate the electrostatic energy as that of the capacitance of an isolated wire end of length L, $C\simeq 2\pi\varepsilon_0 L$, and charged to a potential $V=+(\mu-\epsilon_F)/e$. In units of the bulk energy density $\mathcal{K}_0$, the electrostatic energy per unit volume of the wire can be expressed as

$$\mathcal{E}_C=\frac{5}{6}C'\left(\frac{\mu}{\epsilon_F}-1\right)^2, \tag{6}$$

where C' is the capacitance in dimensionless units, $C'=(6\pi^2\varepsilon_0\hbar^2/me^2\lambda_F w^2)$, and ε_0 is the vacuum dielectric constant for SI units. With $\lambda_F=0.683$ nm, we obtain $\mathcal{E}_C=(0.305/w^2)(\mu/\epsilon_F-1)^2$. For the larger wire diameters this is a minor correction to the energy, but for small w^2 the charging energy cannot be ignored. At small diameters neither a constant electron density, nor a constant chemical potential forms a good approximation, and the truth is somewhere in between. The balance is determined by the charging energy, expressed by the relation,

$$\frac{n-1}{\mu/\epsilon_F-1}=C'.$$

With $C'=0.366/w^2$ we find that the deviations from the bulk density are smaller than the deviations from the bulk chemical potential down to $w^2=1$. Keeping n constant is thus a better approximation, but corrections are only negligible for $w^2>3$.

There are a number of other corrections to the energy, such as an increased spillout of the wave function for a higher chemical potential and a tendency for the charge to accumulate at the surface due to electron-electron repulsion, resulting in a nonhomogeneous density profile. Estimating such corrections goes beyond the validity of the model, but we believe they are smaller than the terms we have considered here.

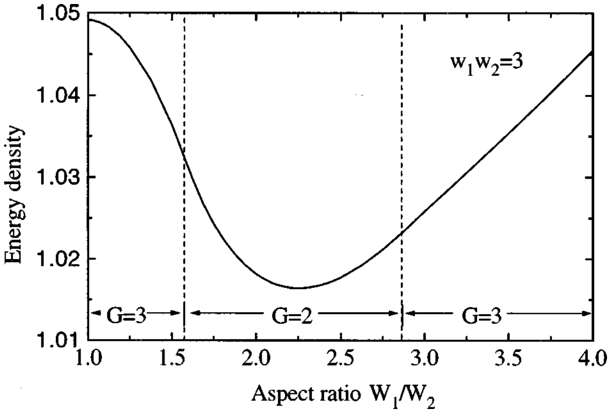

FIG. 4. Kinetic energy density, $\mathcal{K}$, of a rectangular wire for fixed cross-sectional area $w_1w_2=4W_1W_2/\lambda_F^2=3$, plotted as a function of the ratio of the two widths, W_1/W_2. The energy density is normalized to the bulk value and the density of electrons is held constant at the bulk value.

(d) The total energy density in Fig. 3(a) shows distinct local minima, notably near $w^2=1.4, 4, 8, 10.5, \ldots$. This suggests that the formation of quantum modes in the contact has a significant influence on the stability of specific wire diameters. In contrast to the calculation in the previous section, which ignored screening effects, the minima in the energy do not coincide with the steps in the conductance, but are found on the plateaus. Near the steps deviations from quantized values are most pronounced due to tunneling and backscattering contributions. This suggests that the minima in the total energy may play a role in explaining the fact that quantized values of the conductance are more frequently observed in experiment, compared to nonquantized values.[7,8,9,10]

To this point we have considered the width of the wire as a continuous parameter. In fact, the finite size of the atomic building blocks restricts the accessible values for W. In the metal-cluster calculations the radius of the cluster is taken to be $R=Zr_s$, with Z the number of (monovalent) atoms, and r_s the Wigner-Seitz radius. In Ref. 7 the cross-sectional area of point contacts was estimated as $\alpha(\lambda_F/2)^2$, with α a constant depending on the crystal structure, being slightly smaller than unity. All estimates give contact areas of $w^2 \simeq 1$ per atom. The integer contact areas are marked by the grid lines in Fig. 3. However, stacking patterns of atoms can exist which correspond to noninteger effective cross sections. The grid mainly illustrates the typical jump in cross section which will be made between successive configurations. As a final step in refinement of the problem we will now consider deviations from symmetric square shapes of the wire cross section.

IV. LIFTING OF THE DEGENERACY OF THE MODES

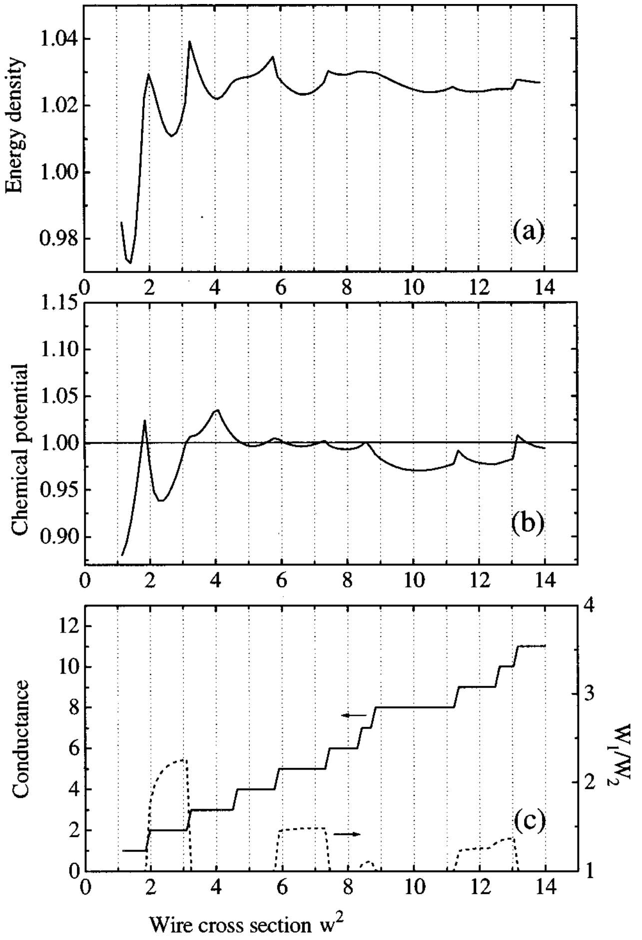

FIG. 5. Kinetic energy density, $\mathcal{K}$, (a) of the wire normalized to the bulk value for constant density of electrons, as a function of the area $w^2=4W_1W_2/\lambda_F^2$. The electron density is held constant by adjusting the chemical potential, μ/ϵ_F, shown in (b). The energy is minimized at each point as a function of the ratio W_1/W_2, which is also plotted (c) together with the conductance, G.

For the symmetric wire of square cross section which we have considered here, the conductance shows double jumps between 1 and 3 G_0, between 4 and 6, 6 and 8, etc. The double jumps are the result of the degeneracy of the modes.[27] When we distort the wire under volume conservation, one expects that the energy can be lowered by lifting of the degeneracy of the modes, in analogy to the Jahn-Teller effect. Similar electron wave induced distortions have been shown to be relevant for the description of cluster abundance spectra.[28] In Fig. 4 we plot the energy density as a function of the ratio W_1/W_2 of the wire widths in the two perpendicular directions, for a rectangular wire of fixed cross section $4W_1W_2/\lambda_F^2=w^2=3$. At $W_1/W_2=1$ the calculation starts from a square wire and a conductance of 3 G_0. The figure shows that the energy indeed decreases with distortion, and a minimum is found for $W_1/W_2=2.22$. For $1.57 < W_1/W_2 < 2.86$ the conductance drops to 2 G_0, carried by two modes in one direction and a single in the other direction. At the minima in Fig. 3(a) near $w^2=4$ and 1.36 the energy *increases* with distortion from square symmetry. In Fig. 5 we replot the curves from Fig. 3, where at each point the ratio W_1/W_2 has been optimized for minimum energy. In Fig. 5(c) it is shown that between the plateaus of 1 and 3 G_0 of Fig. 3, a new plateau at 2 has been created by increasing W_1/W_2 to 2.2. Similarly, we find that all double steps are removed by distortion of the shape of the wire. Often we find slightly lower-energy minima at very large distortions. We discard these because of the small gain in energy, and because in practice other contributions to the surface tension, which have been ignored here, are probably more important.

V. RELEVANCE TO EXPERIMENTS

We stress again that the results of the calculations presented should be interpreted with some precautions because the model is oversimplified. However, it is a useful exercise for two reasons. First, free electron calculations with hard-wall boundaries have been widely employed in the context of conductance quantization in metals, where the consequences discussed here have been ignored. Second, the effects on the work function of the nanowire, and on the relative stability of specific wire diameters may survive in more realistic calculations, and have some relevance for the interpretation of the experiments.

One of the features that have been neglected in the discussion above is the contribution of evanescent modes (tunneling) to the total energy. The importance of such corrections depends sensitively on the effective length of the wire. Including the occupation of tunneling modes will round-off the cusps in the energy density and electron density in Fig. 2. However, after including screening contributions, the minima in the energy density are repelled from the maxima in the density of states (Fig. 3), and will be less sensitive to the rounding introduced by tunneling modes. On the other hand, the cusps in the chemical potential in Fig. 3(b) will be rounded-off, as will be the steps in the conductance in Fig. 3(c).

Regarding the relative stability, we have found that minima in the energy are situated near the middle of the conductance plateaus, which would provide a mechanism to stabilize those wire geometries which have a quantized value of the conductance. It is interesting to note that in the experiment of Muller *et al.*[10] the contact was not strained, but it was allowed to evolve spontaneously. Sharp steps between very horizontal plateaus are observed, while other experiments generally measure the conductance during continuous elongation of the contact where the conductance at the plateaus is generally seen to decrease with increasing elongation until a new step is encountered. Thus, the experiment of Ref. 10 allows the contact to find its equilibrium configuration. Also the fact that it is performed at room temperature is of importance, since the mobility of the atoms is sufficiently high that the contact can explore various configurations.

On the other hand, equally horizontal plateaus at noninteger conductance values are regularly observed, as can also be seen in Ref. 10. Such plateaus seem to contradict the mechanism discussed here. We should keep in mind, however, that the wire diameter is not a continuous parameter in reality. Molecular dynamics simulations[16,8,29] clearly show that the contact diameter jumps between atomic scale configurations corresponding to cross-section jumps Δw^2 of order unity. The true minimum-energy configurations of the contact are, therefore, not all accessible due to atomic size constraints.

The same constraints may explain the observation of degenerate conductance modes in sodium.[7] In that experiment histograms of conductance values showed clear peaks at 1, 3, 5, and 6 G_0, exactly the series expected for a circularly symmetric contact. The Jahn-Teller-type distortion considered here would prevent the absence of conductance peaks at 2, 4, and 7 G_0. Surface tension may prohibit the distortion, but further work is needed to clarify this point.

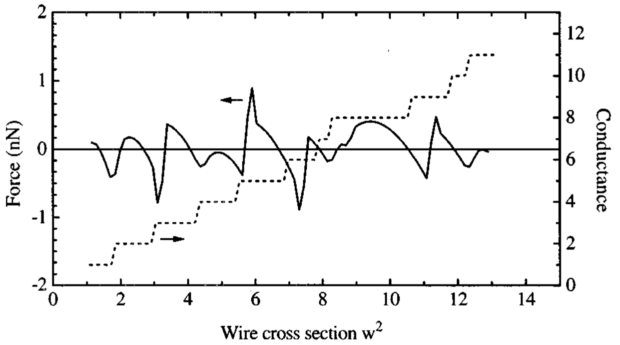

FIG. 6. Force acting in the longitudinal direction of the wire as a consequence of the fluctuations in the total energy, calculated using parameters appropriate for sodium. The electron density is held constant at the bulk value and the rectangular distortion is adjusted to minimize the energy. The force is plotted as a function of the wire cross section $w^2 = 4W_1W_2/\lambda_F^2$.

A very surprising consequence of the mechanism considered here is that a nanowire may prefer to split into parallel wires, each carrying a single quantum of conductance. A deep minimum in energy is found at $w^2 = 1.36$, where the conductance corresponds to one quantum. Comparing the energy density for this contact area to that at twice the area, and multiplying by the volume of the wire, we find using $\epsilon_F = 3.23$ eV, that the total energy for two parallel one-quantum wires is 0.21 eV lower than for a single wire of double cross section, per $\lambda_F/2$ of length of the wire. The energy gain is clearly not negligible, and such parallel wires would offer an alternative explanation for the observation of quantized conductance values 1,2,3, ... On the other hand, the energy barrier encountered between the two topologically different configurations may be too large. Also, the low energy for the one-mode wire may be sensitive to the boundary conditions of the model. Again, more sophisticated calculations should be made to test these ideas.

The rapid variation in the total energy as a function of wire diameter can be translated into a force $\mathcal{F}$ acting in the longitudinal direction of the wire. In hydrostatic approximation, and assuming conservation of volume of the wire, it follows that

$$\mathcal{F} = -\frac{2\pi}{5}\frac{w^4}{\lambda_F}\epsilon_F\frac{d\mathcal{K}}{dw^2}. \qquad (7)$$

Applying this to the result of Fig. 5(a) we obtain the force plotted in Fig. 6, expressed in nanoNewtons, using parameters appropriate for sodium. The (negative) peaks in the force are somewhat smaller than those measured for gold nanocontacts at room temperature[11] and at larger contact diameters the experimental forces are much larger. We stress that no quantitative predictions can be made based on this model. Qualitatively, the quantum-mode induced force jumps offer an alternative explanation for the observations in the experiment for small contacts. The model does not treat in detail the interaction between all the atoms of the contact. The force calculated here is just the average contribution originating from the conduction electrons to the force between atoms. If the atoms can move in response to this force, arrangements that accommodate the quantum modes will be preferred.

In conclusion, a simple model of free electron waves confined by a hard-wall potential has some unexpected and observable consequences for the properties of metallic nanowires. The three main conclusions are (1) the work function is expected to fluctuate with the cross section of the wire, (2) the total energy has minima on the conductance plateaus which may help to favor the corresponding wire geometry, and (3) a Jahn-Teller type of distortion of wire is expected, which would lift the degeneracy of the modes and remove double quantum steps in the conductance.

After completing this work we have received a preprint ‘‘Jellium model of metallic nanocohesion’’ by C. A. Stafford, D. Baeriswyl, and J. Bürki. These authors also calculate the total energy for free electrons confined by hard-wall boundaries, and discuss the resulting force on the wire. Their wire geometry is taken as circularly symmetric, having an adiabatic constriction. Compared to the present work, they have not considered surface corrections and electron screening. Tunneling contributions are included in their approach, and they obtain similar force fluctuations as in Fig. 6.

ACKNOWLEDGMENTS

J.M.vR. acknowledges the stimulating support of L. J. de Jongh, as well as informative discussions with J. M. Krans. This work is part of the research program of the ‘‘Stichting FOM,’’ which is financially supported by NWO.

---

[1] C. J. Muller, J. M. van Ruitenbeek, and L. J. de Jongh, Phys. Rev. Lett. **69**, 140 (1992).

[2] N. Agrait, J. G. Rodrigo, and S. Vieira, Phys. Rev. B **47**, 12 345 (1993).

[3] J. I. Pascual, J. Méndez, J. Gömez-Herrero, A. M. Baró, and N. García, Phys. Rev. Lett. **71**, 1852 (1993).

[4] J. M. Krans, C. J. Muller, I. K. Yanson, Th. C. M. Govaert, R. Hesper, and J. M. van Ruitenbeek, Phys. Rev. B **48**, 14 721 (1993).

[5] J. M. Krans and J. M. van Ruitenbeek Phys. Rev. B **50**, 17 659 (1994).

[6] L. Olesen, E. Lægsgaard, I. Stensgaard, F. Besenbacher, J. Schiøtz, P. Stoltze, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **72**, 2251 (1994).

[7] J. M. Krans, J. M. van Ruitenbeek, V. V. Fisun, I. K. Yanson, and L. J. de Jongh, Nature (London) **375**, 767 (1995).

[8] M. Brandbyge, J. Schiøtz, M. R. Sørensen, P. Stoltze, K. W. Jacobsen, J. K. Nørskov, L. Olesen, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. B **52**, 8499 (1995).

[9] J. L. Costa-Krämer, N. García, P. García-Mochales, and P. A. Serena, Surf. Sci. **342**, L1 144 (1995).

[10] C. J. Muller, J. M. Krans, T. N. Todorov, and M. A. Reed, Phys. Rev. B **53**, 1022 (1996).

[11] G. Rubio, N. Agraït, and S. Vieira, Phys. Rev. Lett. **76**, 2302 (1996).

[12] E. Scheer, P. Joyez, D. Esteve, C. Urbina, and M. H. Devoret, Phys. Rev. Lett. **78**, 3535 (1997).

[13] For a recent review, see J. M. van Ruitenbeek, in *Mesoscopic Electron Transport*, edited by L. L. Sohn, L. P. Kouwenhoven, and G. Schön, NATO Advanced Study Institute, Series E, Applied Sciences (Kluwer, Dordrecht, to be published).

[14] For a review, see C. W. J. Beenakker and H. van Houten, *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich and D. Turnbull (Academic Press, New York, 1991), Vol. 44, p. 1.

[15] A. M. Bratkovsky, A. P. Sutton, and T. N. Todorov, Phys. Rev. B **52**, 5036 (1995).

[16] T. N. Todorov and A. P. Sutton, Phys. Rev. Lett. **70**, 2138 (1993).

[17] A. Levy Yeyati, A. Martín-Rodero, and F. Flores (unpublished).

[18] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1976).

[19] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).

[20] W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[21] E. Tekman and S. Ciraci, Phys. Rev. B **43**, 7145 (1991).

[22] H. Weyl, Kgl. Ges. d. Wiss. Nachrichten. Math. Phys. Klasse Heft **2**, 110 (1911).

[23] D. B. Bivin and J. W. McClure, Phys. Rev. B **16**, 762 (1977).

[24] A. García-Martín, J. A. Torres, and J. J. Sáenz, Phys. Rev. B **54**, 13 448 (1996).

[25] M. V. Moskalets, Pis'ma Zh. Eksp. Teor. Fiz. **62**, 702 (1995) [JETP Lett. **62**, 719 (1995)].

[26] Note that a similar approximation has been adopted in a recent preprint by A. Levy Yeyati, A. Martín-Rodero, and F. Flores, Ref. 17, for a tight binding model of atom size contacts.

[27] Note that the series of conductance values for a circularly symmetric contact is different: 1, 3, 5, 6, 8, . . . ,G_0.

[28] O. B. Christensen, K. W. Jacobsen, J. K. Nørskov, and M. Manninen, Phys. Rev. Lett. **66**, 2219 (1991).

[29] U. Landman, W. D. Luedtke, B. E. Salisbury, and R. L. Whetten, Phys. Rev. Lett. **77**, 1362 (1996).