On the Stability and Structural Dynamics of Metal Nanowires

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Abstract

This article presents a brief review of the nanoscale free-electron model, which provides a continuum description of metal nanostructures. It is argued that surface and quantum-size effects are the two dominant factors in the energetics of metal nanowires, and that much of the phenomenology of nanowire stability and structural dynamics can be understood based on the interplay of these two competing factors. A linear stability analysis reveals that metal nanocylinders with certain magic conductance values $G = 1, 3, 6, 12, 17, 23, 34, 42, 51, 67, 78, 96, \ldots$ times the conductance quantum are exceptionally stable. A non-linear dynamical simulation of nanowire structural evolution reveals a universal equilibrium shape consisting of a magic cylinder suspended between unduloidal contacts. The lifetimes of these metastable structures are also computed.

1 Introduction

A macroscopic analysis of the mechanical properties of thin metal wires suggests that it might be difficult to fabricate wires thinner than a few thousand atoms in cross section: Consider a cylindrical wire of radius $R$ and length $L$. The maximum stress that the wire can sustain before the onset of plastic flow is $\sigma_Y$, the yield strength. On the other hand, the surface-induced stress in a thin wire is $\sigma_s/R$, where $\sigma_s$ is the surface tension. If $\sigma_s/R > \sigma_Y$, one would expect the wire to undergo plastic flow and, if $L > 2\pi R$, to break up under surface tension, as in the Rayleigh instability of a column of fluid [1]. This estimate gives a minimum radius for solidity, $R_{\text{min}} = \sigma_s/\sigma_Y$. The parameters for several simple metals are given in Table 1. Plateau realized as early as 1873 that this surface-tension driven instability of a cylinder is unavoidable if cohesion is due solely to classical pairwise interactions between atoms [2].

A great deal of experimental evidence has accumulated over the past decade, however, indicating that metal wires considerably thinner than the above estimate can be fabricated by a number of different techniques [3,4,5,6,7,8,8,9,10,11,12,13,14,15,16,17,18,19,20]. Even wires with lengths significantly exceeding their circumference were found to be remarkably stable [3,4,5,6,7,8,9,17,18,19], indicating that some new mechanism must intervene to prevent their breakup.

A clue to the resolution of this problem was provided by the observation of electron-shell structure in conductance histograms of alkali metal point contacts [11,14,15,16]. Like the surface tension, quantum-size effects arising from the confinement of the conduction electrons within the cross-section of the wire become increasingly important as the wire is scaled down to atomic dimensions. In fact, a linear stability analysis [21,22] of ultrathin metal wires within the free-electron model found that the Rayleigh instability can be completely suppressed in the vicinity of certain magic radii.

In this article, we argue that surface and quantum-size effects are the two dominant factors in the energetics of metal nanowires, and that much of the phenomenology of nanowire stability and structural dynamics can be understood based on the interplay of these two competing factors. A linear stability analysis reveals that metal nanocylinders with certain magic conductance values $G = 1, 3, 6, 12, 17, 23, 34, 42, 51, 67, 78, 96, \ldots$ times the conductance quantum are exceptionally stable. A non-linear dynamical simulation of nanowire structural evolution reveals a universal equilibrium shape consisting of a magic cylinder suspended between unduloidal contacts. The lifetimes of these metastable structures are also computed.

### Table 1

| Metal | $\sigma_Y$ (MPa) | $\sigma_s$ (N/m) | $\gamma_s$ (pN) | $R_{\text{min}}$ (nm) | $G_{\text{min}}/G_0$ |
|-------|-----------------|------------------|-----------------|-------------------|------------------|
| Cu    | 210             | 1.5              | 190             | 7.1               | 2300             |
| Ag    | 140             | 1.0              | 154             | 7.4               | 1900             |
| Au    | 100             | 1.3              | 257             | 13                | 5600             |
| Li    | 15              | 0.44             | 99              | 29                | 26000            |
| Na    | 10              | 0.22             | 39              | 22                | 10000            |

Table 1 The yield strength $\sigma_Y$ [3], surface tension $\sigma_s$ [4], and curvature energy $\gamma_s$ [5] of various monovalent metals. For a wire of radius $R < \sigma_s/\sigma_Y$, the stress due to surface tension exceeds $\sigma_Y$, signalling a breakdown of macroscopic elasticity theory. The electrical conductance $G_{\text{min}}$ of a ballistic wire of radius $R_{\text{min}} = \sigma_s/\sigma_Y$ is shown in the rightmost column, in units of the conductance quantum $G_0 = 2e^2/h$. Note that $G/G_0$ is approximately equal to the number of atoms that fit within the cross section for monovalent metals.
of metal nanowires, that is, metal wires with $R < R_{\text{min}}$. We show that much of the phenomenology of nanowire stability and structural dynamics can be understood based on the interplay of these two competing factors.

This article is organized as follows: In Sec. 2, we describe our continuum structural model for metal nanowires. A linear stability analysis of metal nanowires is presented in Sec. 3. Section 4 describes the structural evolution of a metal nanowire from a random initial configuration to a universal equilibrium shape. The thermally-activated decay of metal nanowires is discussed in Sec. 5. Some concluding remarks are given in Sec. 6.

## 2 The Nanoscale Free-Electron Model

Guided by the importance of conduction electrons in the cohesion of metals, and by the success of the jellium model in describing metal clusters [23], the nanoscale free-electron model (NFEM) [24] replaces the metal ions by a uniform, positively charged background that provides a confinement potential for the electrons. The electron motion is free along the wire, and confined in the transverse directions. Due to the excellent screening [25] in metal wires with $G > G_0$, electron-electron interactions can in most cases be neglected. The surface properties of various metals can be fit by using appropriate surface boundary conditions [27,28].

The NFEM is especially suitable for alkali metals, but is also adequate to describe shell effects due to the conduction-band $s$-electrons in other monovalent metals, such as gold. The experimental observation of a crossover from atomic-shell to electron-shell effects with decreasing radius in both metal clusters [24] and nanowires [15,16] justifies $a$ posteriori the use of the NFEM in the later regime.

A nanowire connecting two macroscopic electrodes is an open quantum system, for which the Schrödinger equation is most naturally formulated as a scattering problem. Transport properties can be obtained from the scattering matrix using Landauer-type formulas [24,30,31], while cohesive properties require the computation of the grand canonical potential of the electrons. The latter can also be expressed in terms of the scattering matrix [24], or calculated semiclassically [32] in terms of geometrical quantities and a sum over classical periodic orbits, as presented in Sect. [24].

Motivated by the argument presented in Table 1, the electronic degrees of freedom in the wire are modeled as an incompressible, irrotational fluid. In the Born-Oppenheimer approximation, the electronic free energy serves as the potential energy for the ions. The ionic dynamics may then be modeled via a surface self-diffusion equation [33], as presented in Sec. [24,31] or, taking thermal fluctuations into account, via a classical Ginzburg-Landau stochastic field theory [34], as presented in Sec. [24,29].

### 2.1 Electronic Energy Functional

Restricting ourselves to axisymmetric structures, the grand canonical potential for the electrons $\Omega_e$ becomes a functional of the radius $R(z)$ of the wire. Using the Weyl expansion [35], $\Omega_e$ can be expressed in terms of geometrical quantities such as the volume $V$, surface area $S$, and integrated mean curvature $C$ of the wire’s surface, plus an electron-shell correction,

$$\Omega_e[R(z), T] = -\omega V + \sigma_s S - \gamma_s C + \int_0^L dz V_{\text{shell}},$$  

(1)

where $-\omega$ is the bulk value per unit volume, $\sigma_s$ is the surface tension, $\gamma_s$ is a curvature-energy density, and $V_{\text{shell}}(R(z), T)$ is a mesoscopic electron-shell potential, shown in Fig. 1. The parameters $\sigma_s$ and $\gamma_s$, tabulated for various metals in Table 1, depend on the details of the interaction-dependent surface confinement potential [27,28,32], but can be taken as phenomenological material-dependent parameters (along with $\omega$) in our model. The leading-order electron-shell correction is, however, independent of the Coulomb interaction [24,26,32] and therefore insensitive to the details of the confinement potential.

The geometrical quantities $S = \int_0^L dz \partial S$ and $C = \int_0^L dz \partial C$ are given by

$$\partial S[R(z)] = 2\pi R(z)\sqrt{1 + (\partial_z R)^2},$$  

(2)

and

$$\partial C[R(z)] = \pi \left(1 - \frac{R \partial_z R}{1 + (\partial_z R)^2}\right),$$  

(3)

where $\partial_z = \partial / \partial z$.

Approximating the confining potential by a hard wall at the surface of the wire, the electron-shell potential $V_{\text{shell}}(R, T)$ at zero and two finite temperatures, which correspond respectively to 1000K and 2500K for Na. The electrical conductance values of the magic cylindrical wires are indicated on the upper axis.
\[ V_{\text{shell}}(R, T) = \frac{2 \varepsilon_F}{\pi} \sum_{w=1}^{\infty} \sum_{v=2w}^{\infty} a_{wv}(T) f_{wv} \cos \theta_{wv} \frac{v^2}{L_{vw}^2}, \]

where the sum includes all classical periodic orbits \((v, w)\) in a disk billiard \(35\), characterized by their number of vertices \(v\) and winding number \(w\), \(L_{vw} = 2vR \sin(\pi w/v)\) is the length of orbit \((v, w)\), and \(\theta_{wv} = k_F L_{vw} - 3\pi/2\). The factor \(f_{wv} = 1\) for \(v = 2w, 2\) otherwise, accounts for the invariance under time-reversal symmetry of some orbits, and \(a_{wv}(T) = \tau_{wv}/\sinh \tau_{wv}\) (\(\tau_{wv} = \pi k_F L_{vw} T/2T_F\)) is a temperature-dependent damping factor.

\(V_{\text{shell}}(R)\) exhibits deep minima as a function of \(R\) (see Fig. 14), suggesting that some radii are strongly favored, which is confirmed by the stability analysis of Sec. 13. Note that room temperature is small compared to the Fermi temperature \(T_F = \varepsilon_F/k_B\), (in particular, \(T/T_F = 0.008\) at \(T = 300\text{K}\) for Na), so that the finite-temperature electron-shell potential is essentially indistinguishable from its zero-temperature limit at experimental temperatures.

### 2.2 Ionic Energetics

In the Born-Oppenheimer approximation, the electronic energy 11 acts as a potential energy for the ionic background. The wire can exchange atoms with the macroscopic contacts via surface self-diffusion, so the grand canonical ensemble has to be used for the ionic back-soscopic contacts as well, leading to an ionic grand canonical potential

\[ \Omega_a = \Omega_e - \mu_a N_a, \]

where \(N_a = V/V_a\) is the number of positive ions in the wire \((V_a = 3\pi^2/v_F^2\) is the volume of an atom), and \(\mu_a\) is the chemical potential for a surface atom in the wire. Using Eqs. (11–4), the ionic free energy 11 becomes

\[ \Omega_a = \int dz \left[ 2\pi \sigma_s R(z, t) \sqrt{1 + (\partial_z R)^2} - \pi \gamma_s + V_{\text{shell}}(R, T) \right] - (\omega + \mu_a/V_a) V, \]

where only the leading-order term in the curvature energy is included. The chemical potential \(\mu_a\) is obtained by calculating the change in the energy 11 with the addition of an atom at point \(z_0\), \(\mu_a(z_0) = \Omega_e [R(z) + \delta(z - z_0), T] - \Omega_e [R(z), T]\), where \(c = V_a/2\pi R(z)\) is chosen so that the volume of an atom is added:

\[ \mu_a(z) = -\omega V_a + \frac{V_a}{2\pi R} \left( \frac{2\sigma_s \partial C[R(z)]}{\sqrt{1 + (\partial_z R)^2}} + \partial V_{\text{shell}}/\partial R \right). \]

### 2.3 Structural Dynamics

#### 2.3.1 Surface self-diffusion

Since a large fraction of the atoms in a nanowire are on the surface, surface self-diffusion is the dominant mechanism of ionic motion 33. The dynamics derive from ionic mass conservation:

\[ \frac{\pi}{V_a} \frac{\partial R^2(z,t)}{\partial t} + \frac{\partial}{\partial z} \left[ 2\pi R(z,t) J_z(z,t) \right] = 0, \]

where the \(z\)-component of the surface current density is given by Fick’s law:

\[ J_z = -\frac{\rho_s D_S}{k_B T} \frac{1}{\sqrt{1 + (\partial_z R)^2}} \frac{\partial \mu_a}{\partial z}. \]

Here \(\rho_s\) and \(D_S\) are the surface density of ions and the surface self-diffusion coefficient, respectively. The precise value of \(D_S\) for most metals is not known, but it can be removed from the evolution equation by rescaling time to the dimensionless variable \(\tau = (\rho_s D_S T_F/k_B T) t\). For comparison to experimental time scales, one can estimate that for quasi-one-dimensional diffusion \(D_s \approx \nu_D a^2 \exp(-E_s/k_B T)\), where \(\nu_D\) is the Debye frequency, \(a\) is the lattice spacing, and \(E_s\) is an activation energy comparable to the energy of a single bond in the solid. Our non-linear dynamical model, Eqs. 10–9, differs from previous studies of axisymmetric surface self-diffusion 37,38 by the inclusion of electron-shell effects [last term of Eq. 1], which fundamentally alter the dynamics.

#### 2.3.2 Thermal fluctuations

The diffusive dynamics of the previous subsection describe relaxation toward structures of lower free energy. Once an equilibrium configuration (i.e., a local minimum of the free energy) is attained, however, fluctuations about this configuration will dominate the dynamics, limiting the dwell time of the system in this local minimum. As shown in Sec. 4, the equilibrium configurations consist of stable cylindrical nanowires in diffusive equilibrium with unchuloid-like contacts 33,39. We therefore study fluctuations of the form

\[ R(z, t) \equiv R_0 + \phi(z, t), \]

where \(R_0\) is the radius of a stable cylinder of length \(L\).

The energy 10 can be expanded as a series in \(\phi\). For the magic cylinders, corresponding to minima of \(V_{\text{shell}}(R_0)\) (c.f. Fig. 11), the chemical potential for the exchange of atoms between the wire and the contacts reduces to

\[ \frac{\mu_a}{V_a} = \frac{\sigma_s}{R_0} - \omega. \]

Keeping only the leading-order terms in \(\partial_z \phi\), one gets \(\Omega_a = \Omega_a(R_0) + \mathcal{H}[\phi]\), where \(\Omega_a(R_0)\) is the energy of an unperturbed cylinder of radius \(R_0\) and

\[ \mathcal{H}[\phi] = \int_0^L dz \left[ \frac{\kappa}{2} (\partial_z \phi)^2 + V(\phi) \right]. \]
Here $\kappa = 2\pi \sigma_s R_0$ and

$$V(\phi) \equiv V_{\text{shell}}(R_0 + \phi) - V_{\text{shell}}(R_0) - \frac{\pi \sigma_s}{R_0} \phi^2. \quad (13)$$

The problem of stability of nanowires against thermal fluctuations can be studied as a one-dimensional Ginzburg–Landau scalar field theory, perturbed by weak spatiotemporal noise, in a domain of finite extent (see [24] and references therein): The fluctuations of the nanowire radius $\phi$ are treated as a classical field on a one-dimensional spatial domain [0, L]. Its dynamics are governed by the stochastic Ginzburg–Landau equation

$$\frac{\partial \phi(z, t)}{\partial t} = \kappa \frac{\partial^2 \phi}{\partial z^2} - \frac{\partial V}{\partial \phi} + (2T)^{1/2} \xi(z, t), \quad (14)$$

where $\xi(z, t)$ is unit-strength spatiotemporal white noise, satisfying $\langle \xi(z_1, t_1) \xi(z_2, t_2) \rangle = \delta(z_1 - z_2) \delta(t_1 - t_2)$. In Eq. (14), time is measured in units of a microscopic timescale describing the short-wavelength cutoff of the surface dynamics [22], which is given to within a factor of order unity by the inverse Debye frequency $\nu_D^{-1}$. The zero-noise dynamics is “gradient,” that is, at zero temperature $\phi = -\delta \mathcal{H}/\delta \phi$, where $\mathcal{H}[\phi]$ is given by Eq. (12). Eq. (14) represents a considerable simplification compared to the volume-conserving dynamics of Eq. (8) (which involves derivatives up to $\partial^2 R$), and makes possible an analytical treatment of thermal fluctuations.

### 3 Linear Stability of Cylinders

The linear stability of a structure is determined by studying the change of energy induced by a small perturbation: If any one perturbation decreases the energy, the structure is unstable, while it is stable if all perturbations increase the energy.

The most general perturbation of a cylinder of radius $R_0$ and length $L$ is

$$R(z, \phi) = R_0 + \lambda \sum_{m} \sum_{q} b_m(q)e^{i(qz + m\phi)}, \quad (15)$$

where $b_m(q) = b_{-m}(-q)^*$. For simplicity, we impose periodic boundary conditions, so that $q$ is an integer multiple of $2\pi/L$. Since the total number of atoms in the system is unchanged by the perturbation, $b_0(0)$ is related to the other coefficients by volume conservation

$$b_0(0) = -\frac{\lambda}{R_0} \sum_{m > 0} |b_m(q)|^2 + \mathcal{O}(\lambda^2), \quad (16)$$

and may be eliminated. Other constraints [28] may be utilized to account for confinement potentials more general [21] than the hard walls considered in the present article, but do not lead to a qualitative change in the stability analysis.

The energy change (per unit length) under such a perturbation is found to be

$$\frac{\Delta \Omega}{L} = \lambda^2 \sum_m \sum_{q > 0} \alpha_m(q; R_0, T)|b_m(q)|^2 + \mathcal{O}(\lambda^3), \quad (17)$$

where the mode stiffness $\alpha_m(q)$ is given by

$$\alpha_m(q; R, T) = (m^2 - 1)\frac{2\pi \sigma_s}{R} + 2\pi (\sigma_s R - \gamma_s)q^2 + \delta \alpha_m(q; R, T), \quad (18)$$

and $\delta \alpha_m$ is a mesoscopic electron-shell correction.

Neglecting for the moment the mesoscopic correction $\delta \alpha_m(q)$, we find that the perturbation can only lead to an instability for $m = 0$ and $q R_0 < (1 - \gamma_s/\sigma_s R_0)^{-1/2} \approx 1$, which is the criterion for the classical Rayleigh instability [1]. Note that $\sigma_s R > \gamma_s$ for all physically meaningful radii (c.f. Table 1). Any perturbation breaking axial symmetry is classically unfavorable, and we will therefore consider only axisymmetric perturbations $(m = 0)$ in the rest of this paper.

Using semiclassical perturbation theory, the electron-shell correction to the mode stiffness for axisymmetric deformations was found to be independent of $q$ [21][22].

$$\delta \alpha_0(R, T) = \left( \frac{\partial^2}{\partial R^2} - \frac{1}{R} \frac{\partial}{\partial R} \right) V_{\text{shell}}(R, T). \quad (19)$$

This turns out to be true only in the semiclassical approximation: A fully quantum-mechanical stability analysis [10] reveals that long wires undergo a Peierls-type instability at $q = 2k_F^{(\nu)}$, where $k_F^{(\nu)}$ is the Fermi wavevector for subband $\nu$. However, the semiclassical results are found to provide a good approximation as long as the temperature is not too low, and the wires are not too long [10]. The total mode stiffness $\alpha_0(q = 1/R_0)$ in the semiclassical approximation is shown in Fig. 2, together with the density of states $g(\varepsilon_F)$. The perturbation wavevector was chosen so that the surface contribution to $\alpha_0$ (dashed curve) is nearly zero. Fig. 2 shows that near the thresholds to open new conducting channels, where the density of states is large, the wire is very unstable ($\alpha_0 < 0$). However, in between the subband thresholds, the shell correction stabilizes the wire ($\alpha_0 > 0$).

According to Eqs. (18) and (19), the most unstable mode is $m = 0$, $q = 0$. The stability of the wire is thus determined by the sign of the stability coefficient $A(R_0, T) \equiv \alpha_0(q = 0; R_0, T)$,

$$A(R, T) = -2\pi \sigma_s \left( \frac{\partial^2}{\partial R^2} - \frac{1}{R} \frac{\partial}{\partial R} \right) V_{\text{shell}}(R, T). \quad (20)$$

For $A > 0$, the wire is stable with respect to all small perturbations, while the wire is unstable for $A < 0$. The stability diagram so determined is shown in Fig. 3. Competition between surface tension and electron-shell effects leads to a complex landscape of stable fingers and
rather by the magnitude smaller than the surface energy! Stability to the shell-correction to the energy is thus two orders of magnitude smaller than the surface energy. For a cylinder is rather remarkable. The surface contribution to the stability coefficient \( \sigma \) is a rapidly oscillating function of \( R \), its second derivative actually has the same characteristic size as the surface contribution to the stability coefficient [first term on the r.h.s. of Eq. (20)].

Cylinders are special in this respect, because the term \( \delta \) in Eq. (17) vanishes exactly by symmetry. For a typical radius \( k_F R_0 = 10 \), the shell-correction to the energy is thus two orders of magnitude smaller than the surface energy! Stability is not determined by the energy directly, however, but rather by the convexity (or lack thereof) of the energy functional, which involves the second derivative with respect to \( R_0 \) [c.f. Eq. (20)]. Because \( V_{\text{shell}} \) is a rapidly oscillating function of \( R_0 \), its second derivative actually has the same characteristic size as the surface contribution to the stability coefficient [first term on the r.h.s. of Eq. (20)].

In this section, we use the diffusion equation \( \delta \) to study the equilibrium shapes of metal nanowires, as well as the approach to equilibrium. Figure 4 shows three stages of the typical evolution of an initially random (a) nanowire: After a relatively short time (b), the short-wavelength surface roughness is smoothed out, leaving a few cylindrical segments, connected by kinks. Eventually, all kinks propagate outward and coalesce, yielding an equilibrium shape (c) consisting of a cylindrical wire suspended between two thicker contacts.

Several such simulations starting from various initial configurations, with conductance ranging from 1 to...
Fig. 4 Equilibration of an initially random nanowire: (a) initial shape; (b) $\tau = 2 \times 10^4$; (c) $\tau = 3 \times 10^7$, equilibrium structure with $G = 12G_0$.

200 $G_0$, and lengths $200 \leq k_F L \leq 600$, all evolved to equilibrium structures consisting of one of the stable cylinders found in Sec. 3 connecting two quasi-spherical contacts (see Fig. 5(a)). The shape of the contact is actually a close approximation to a Delaunay unduloid of revolution [38], which is a surface of constant mean curvature, and is an unstable steady state of diffusion equation (8) without the shell-effect term. This is illustrated in Fig. 5 comparing the equilibrium wires, rescaled (b) by their maximum radius $R_{\text{max}}$ to a series of unduloids (c) of various mean curvature. The curvature of the unduloid is determined solely by the ratio of the radius of the cylindrical part to $R_{\text{max}}$, and not by the conductance of the wire, or its length. In our case, the deep minima of the electron-shell potential, Fig. 1 pin the unduloid at its connection with the cylindrical part, thus stabilizing it. In fact, if one switches off the electron-shell potential in the simulations, the equilibrated wires break apart, as expected from the Rayleigh instability. The breaking is found to happen first at the junction between the cylinder and the lead, suggesting that it is the weak point of the equilibrium structure.

This suggests that the natural evolution of a nanowire, at a temperature sufficient for surface atoms to diffuse, is to form a cylinder, thus providing an explanation of the observation of long, almost perfect cylindrical Au nanowires in transmission electron microscope (TEM) experiments [8,12,13,18]. The same type of simulation can be used to understand the thinning process observed in TEM experiments [19], where the wire diameter is seen to decrease step by step through the propagation of kinks along the wire.

5 Lifetimes of Metastable Cylinders

The equilibrium nanowire structures determined in the preceding sections are stable with respect to small perturbations, and represent local minima of the free energy functional [18]. However, large perturbations induced e.g. by thermal fluctuations can drive the nanowire out of such a minimum, leading to a finite lifetime of these metastable structures. In this section, we use the stochastic model [34] derived in Sec. 2.3.2 to study this process.

The statistical properties of the stochastically evolving field $\phi$, Eq. (10), are described by equilibrium statistical mechanics. At nonzero temperature, thermal fluctuations can induce transitions between stable states (i.e., local minima) of the potential $V(\phi)$, Eq. (13). Such transitions occur via nucleation of a “droplet” of one stable configuration in the background of the other, subsequently quickly spreading to fill the entire spatial domain. When the noise is weak, i.e., at low temperatures (compared to the barrier height) most fluctuations will not succeed in nucleating a new phase; it is far more likely for a small droplet to shrink and vanish.

A transition state must go “uphill” in energy from each stable field configuration, because of exponential suppression of fluctuations as their energy increases, there is at low temperature a preferred transition configuration (saddle) that lies between adjacent minima. These are the nucleation pathways. By time-reversal invariance, they are time-reversed zero-noise “downhill” trajectories [12]. At low temperatures, the expected waiting time of the order parameter $\phi$ in a basin of attraction is an exponential random variable, as is typical.

Fig. 5 (a) Radius $R(z)$ of the equilibrium shapes for 14 simulations starting from random initial shapes; the equilibrium shapes being symmetric (although the initial shapes are not), we only show $R(z)$ for $z \in [0, L/2]$. (b) Same shapes rescaled by their maximum radius $R_{\text{max}}$. (c) Series of Delaunay unduloids of various curvature.
of slow rate processes. The activation rate is given in the $T \to 0$ limit by the Kramers formula

$$\Gamma \sim \Gamma_0 \exp(-\Delta E/T).$$  \hspace{1cm} (22)

Here the activation barrier $\Delta E$ is the energy of the transition state minus that of the stable state, and $\Gamma_0$ is the rate prefactor. The quantities $\Delta E$ and $\Gamma_0$ depend on the details of the potential, on the length $L$, and on the choice of boundary conditions at the endpoints $z = 0$ and $z = L$. Based on the equilibrium structures found in Sec. [4] we employ Neumann boundary conditions, $0 = \partial_z \phi(z, t)|_{z=0,L}$. These boundary conditions force nucleation to begin, preferentially, at the endpoints, consistent with experimental observations [19].

Equation (14) with the potential (13) can not in general be solved analytically, but most minima of the potential $V(\phi)$ can be locally approximated by a cubic potential

$$V^{(\pm)}(\phi) = -\tilde{\alpha}\phi^{\pm} + \frac{\beta}{3}\phi^{3},$$  \hspace{1cm} (23)

where $\tilde{\phi} = \sqrt{\alpha/\beta} \mp \phi$ ($\alpha, \beta > 0$). The potential $V^{(-)}$ ($V^{(+)}$) biases fluctuations toward smaller (larger) radii.

Fig. 6 shows the escape barrier $\Delta E$ as a function of the wire length $L$ [34]: Below a critical length $L_c$, the transition state is a spatially constant field configuration, and the escape barrier grows linearly with the wire length $L$. However, at $L = L_c$ it bifurcates into a spatially varying instanton configuration with characteristic size $\sim L_c$, so that $\Delta E$ becomes length-independent for $L \gg L_c$.

Our continuum dynamical model thus predicts that the lifetime $\tau$ of a metastable cylindrical nanowire of length greater than the critical length $L_c$, saturates with an escape barrier given by $\Delta E_\infty = \lim_{L \to \infty} \Delta E$. In terms of the physical parameters defining the cubic potential (13), the critical length $L_c = \sqrt{\frac{\alpha}{\beta} k_{B} T}$ and $\Delta E_\infty = \frac{12\sqrt{2}}{5} k_{B} T \alpha^{1/2} \beta^{3/4} / \beta^{1/4}$. The lifetimes $\tau = 1/\Gamma$ for several cylindrical sodium nanowires, calculated using the best cubic-polynomial fits to the potential (13), are tabulated in Table 2. Note that for a wire with $G/G_0 > 1$, the lifetime $\tau$ may not be the typical time before the wire breaks, but rather a switching time between two different metastable wires with different conductance values.

An important prediction given in Table 2 is that the lifetimes of the most stable nanowires, while they do exhibit significant variations from one conductance plateau to another, do not vary systematically as a function of radius; the activation barriers in Table 2 vary by only about 30% from one plateau to another, and the wire with a conductance of $G_0$ has essentially the same lifetime as that with a conductance of $3G_0$. In this sense, the activation barrier is found to be universal in any conductance interval, there are very short-lived wires (not shown in Table 2) with very small activation barriers, while the longest-lived wires have activation barriers of a universal size

$$\Delta E_\infty \simeq 0.6 \left( \frac{h^2 \kappa}{m_e} \right)^{1/2},$$  \hspace{1cm} (24)

depending only on the surface tension of the material. Here $m_e$ is the conduction-band effective mass, which is comparable to the free-electron rest mass. A comparison of the lifetimes of sodium and gold nanowires [34] indicates that gold nanowires are much more stable, as expected from the larger value of the surface tension $\sigma_s(Au) = 5.9 \sigma_s(Na)$. This is consistent with the observation that gold nanowires in particular, and noble metal nanowires in general, are much more stable than alkali metal nanowires.

The fact that the typical activation energy (21) is independent of $R_0$ may be understood as follows: The instanton is a stationary state of Eq. (12); as such, the Virial theorem implies that the bending energy ($\frac{1}{2} (\partial_z \phi)^2$) is proportional to $\langle V(\phi) \rangle$. Since $\kappa \sim \sigma_s R_0$.
and $V \sim 1/R_0$, this implies that the characteristic size of the instanton $L_c \sim \sqrt{\sigma_z R_0}$ and $\Delta E_\infty \sim \sqrt{\sigma_z}$.

The lifetimes tabulated for sodium nanowires in Table 2 exhibit a rapid decrease in the temperature interval between 75K and 125K. This behavior can explain the observed temperature dependence of conductance histograms for sodium nanowires [11,14,15], which show clear peaks at conductances near the predicted values at temperatures below 100K, but were not reported at higher temperatures.

6 Conclusions

The NFEM is the simplest possible model of metal nanostructures. Nonetheless, it is a remarkably rich model, which provides a unified description of quantum transport, stability, and structural dynamics of simple metal nanowires. It is hoped that the generic properties of metal nanostructures elucidated by the NFEM can guide the exploration of more elaborate, material-specific models, in the same way that the free-electron model provides an important theoretical reference point from which to understand the complex properties of real bulk metals.

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