Nanomechanics – Quantum Size Effects, Contacts, and Triboelectricity

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To my parents
Abstract

Nanomechanics is different from the mechanics that we experience in everyday life. At the nano-scale, typically defined as 1 to 100 nanometers, some phenomena are of crucial importance, while the same phenomena can be completely neglected on a larger scale. For example, the feet of a gekko are covered by nanocontacts that yield such high adhesion forces that the animal can run up on walls and even on the ceiling. At small enough distances, matter and energy become discrete, and the description of the phenomena occurring at this scale requires quantum mechanics. However, at room temperature the transitions between quantized energy levels may be concealed by the thermal vibrations of the system. As two surfaces approach each other and come into contact, electrostatic forces and van der Waals forces may cause redistribution of matter at the nano level. One effect that may occur upon contact between two surfaces is the triboelectric effect, in which charge is transferred from one surface to the other. This effect can be used to generate electricity in triboelectric nanogenerators (TENGs), where two surfaces are repeatedly brought in and out of contact, and where the charge transfer is turned into electrical energy.

This thesis concerns nanomechanics addressing whether quantum mechanics play a role in elastic deformation, as well as various mechanical aspects of nanocontacts including electric charging. The objectives are to contribute to the understanding when quantum effects are of importance at the nanolevel, increase the fundamental understanding of the mechanisms responsible for triboelectric phenomena and apply the triboelectric effect to a wind harvesting device.

For more insight into whether quantum effects are of importance in nanomechanics, we use a one dimensional jellium model and the standard beam theory allowing the spring constant of an oscillating nanowire cantilever to be calculated. As the nanowire bends, more electron states fit in its cross section, giving rise to an amplitude dependent resonance frequency of the nanowire oscillations.

Furthermore, a model for electric field induced surface diffusion of adatoms was developed. The model takes electrostatic forces and van der Waals forces into account as a voltage is applied between a scanning tunneling microscope tip and a sample. The calculated force on the adatoms at the surface of the sample, which is stemming from the inhomogeneous electric field and the dipole moment of the adatoms, is relatively small, but due to thermal vibrations adatoms diffuse and form mounds at the sample.
When bringing two different materials into contact, the difference in triboelectric potentials between the materials results in electric charging. To increase the understanding of triboelectricity, a two-level Schottky model, assuming ion transfer, was developed to describe the temperature dependence of the triboelectric effect for a TENG. The two levels correspond to the binding energy for ions on the two surfaces that are brought into contact, where the difference in binding energy enters the Boltzmann distribution. The model describes the decreasing triboelectric effect in TENGs with increasing temperature as described in the literature, and results in a separation energy, which is of the right order of magnitude for physically adsorbed atoms.

It was recently demonstrated that TENGs can convert wind energy into electrical energy. Here, a TENG based on a plastic film fluttering between two copper electrodes was constructed. It was found that the frequency of the the fluttering film increases linearly with the wind speed. TENG:s designed in this way generate electricity already at low wind speed, and we therefore expect such TENGs to be useful both as generators and speed sensors in the future.

While quantum mechanics is of importance in a limited number of nanomechanical systems, nanocontacts have a broader meaning, and are crucial for the understanding of triboelectric phenomena. We anticipate that the findings in this thesis will contribute to a better understanding of nanomechanics, in particular the mechanism of triboelectricity.
Sammanfattning

Nanomekanik är annorlunda än den mekanik vi upplever i vardagen. I nanoskalan, som definieras som storleksområdet 1 -100 nanometer, är vissa fenomen viktiga medan dessa helt kan försummas i den större skalan i vardagslivet. Till exempel har evolutionen på nanoskalan designat en gekkoödlas fotter så att de har en så kraftig vidhäftning till omgivningen att gekkon kan gå omkring i taket. Tittar man på den lilla skalan finner man att materien är diskret och att beskrivning av fenomen i denna skala kräver kvantmekanik. Övergångar mellan kvantnivåer döljs dock ofta vid rumstemperatur av termiska vibrationer hos systemet. När två ytor närmar sig varandra och kommer i kontakt kan elektrostatiska krafter och van der Waalskrafter orsaka omfördelning av materi på nanonivå. En effekt som kan uppstå vid kontakt mellan två ytor är den triboelektriska effekten vid vilken det sker överföring av laddning från den ena ytan till den andra. Denna effekt kan användas för att generera elektrisk energi i triboelektriska nanogeneratorer (TENG:s) där två ytor omväxlande förs ihop och dras isär.

Denna avhandling behandlar nanomekanik med fokus på om kvantmekaniken spelar en viktig roll vid elastisk deformation och även olika mekaniska aspekter hos nanokontakter inklusive elektrisk uppladdning. Målsättningen är att bidra till kunskap om när kvanteffekter är viktiga i nanoskalan och att öka den grundläggande förståelsen för triboelektriska fenomen samt att tillämpa den triboelektriska effekten för en vinddriven energiutvinande apparat.

För att få bättre förståelse om kvanteffekter är betydelsefulla i nanomekanik har vi gjort en endimensionell fri elektronmodell och använder vanlig balkteori för att beräkna fjäderkonstanten för en nanotråd utgörande en svängande bladljär. När nanotråden böjs kommer fler elektron tillstånd att passa i trådens tvåsiffrigt vilket ger upphov till en amplitudberobande resonansfrekvens hos tråden.

Dessutom har vi utvecklat en modell för elektriskt fältinducerad ytdiffusion av adatomer. Modellen tar hänsyn till elektrostatiska krafter samt till van der Waalskrafter när en spännning pålaggs mellan en spets i ett sveisnålmikroskop och en provyta. Den beräknade krafterna på adatomerna på provets yta - vilken kommer av det inhomogena elektriska fältet och adatomernas dipolmoment - är relativt liten, men på grund av de termiska vibrationerna kan adatomerna ändå diffundera och bilda en kulle under tippen.
När man sammanför två olika material kommer skillnaden i deras triboelektriska potentialer att orsaka uppladdning. För att öka förståelsen av triboelektriciteten har vi utvecklat en två-nivå Schottkymodell som antar joner som laddningsbärare för att beskriva den triboelektriska uppladdningens temperaturberoende för en TENG. De två nivåerna motsvarar de två kontaktande ytorna. Skillnaden i bindningsenergi mellan joner på ytorna kommer därför in i Boltzmannfaktorn. Modellen beskriver den minskande triboelektriska effekten vid ökande temperatur som rapporterats i litteraturen, och stöds av att den separationsenergi man finner vid anpassning av modellen till data är av samma storleksordning som skillnaden i bindningsenergi för fysikaliskt ytadsorberade atomer (adatomer).

Nyligen visades det att TENG:s kan omvandla vindenergi till elektrisk energi. Vi har konstruerat en TENG baserad på ett flappande plastband löst inspänt mellan två kopparelektroder. Vi fann att frekvensen hos det flappande plastbandet ökar linjärt med vindhastigheten. TENG designade på detta sätt alstrar elektrisk energi redan vid låga vindhastigheter vilket gör att apparaten kan komma att användas både som generator och som vindhastighetsmätare i framtiden.

Medan kvantmekanik bara är betydelsefull i ett begränsat antal nanomekaniska system har nanokontakter en mer allmän tillämpning och är viktig för förståelsen av triboelektriska fenomen. Vi förutser att resultaten i denna avhandling kan komma att bidra till en bättre förståelse för nanomekanik i allmänhet och för mekanismen för triboelektricitet i synnerhet.
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Contents

Abstract v

Sammanfattning vii

Acknowledgements ix

List of papers xiii

Terminology xvii

1 Introduction 1
  1.1 Nanomechanics and nanocontacts ............................. 1
  1.2 Quantum effects at the nanoscale ............................. 2
  1.3 Friction is due to nanocontacts ............................... 6
  1.4 Charged nanocontacts ......................................... 7
  1.5 Triboelectricity – Friction with charge transfer .......... 8
  1.6 Triboelectric nanogenerators ................................. 10
  1.7 Objectives ...................................................... 12

2 Results 15
  2.1 Quantum effects in nanomechanics ............................. 15
  2.2 Electrically charged nanocontacts .............................. 19
  2.3 Temperature dependence of triboelectricity ................ 22
  2.4 A wind-driven triboelectric nanogenerator ................. 25

3 Discussion 31
  3.1 Future works .................................................. 34
Bibliography

A  Number of electrons in square cross-section  43

B  Metallic nanowires: differences between stretching and bending  45
List of papers

This thesis is mainly based on the following papers, herein referred by their Roman numerals:

I Martin Olsen, Per Gradin, Ulf Lindefelt, and Håkan Olin *Nonharmonic oscillations of nanosized cantilevers due to quantum-size effects*. Physical Review B (2010), volume 81, issue 5, article id. 054304

II Martin Olsen, Magnus Hummelgård, and Håkan Olin *Surface modifications by field induced diffusion*. PLoS ONE (2012), volume 7, issue 1, article id. e30106

III Martin Olsen, Jonas Örtegren, Renyun Zhang, Salim Reza, Henrik Andersson and Håkan Olin *Schottky model for triboelectric temperature dependence*. Scientific Reports (2018), volume 8, issue 1, article id. 5293

IV Martin Olsen, Renyun Zhang, Jonas Örtegren, Henrik Andersson, Ya Yang and Håkan Olin *Frequency and voltage response of a wind-driven fluttering triboelectric nanogenerator*. Scientific Reports (2019), volume 9, issue 1, article id. 5543

Contributions Paper I: This was my second project as a Ph.D. student although this was the paper that was first completed and published. Håkan Olin had previously written a paper about quantum-size effects in nanowires when stretching them, and he suggested that we may be able to produce this effect even when bending a nanowire cantilever, affecting its resonance frequency. I carried out most of the calculations in this article, the exception being the cross sectional area calculation carried out by Per Gradin, finding that an approximately analytical solution existed. Ulf Lindefelt did interesting simulations for the energy levels of the cross section, which added to the understanding. I wrote the paper and made the figures.

Contributions Paper II: This was my first project as a PhD student. Håkan Olin introduced me to the subject of surface modification when two nanosized tips came close together. I carried out the calculations and made most of the figures. The literature suggested that the surface induced dipole moment of a surface adsorbed atom always pointed away from the surface indicating a threshold field for mound formation by diffusion. Magnus Hummelgård did interesting simulations that supported the analytical calculations and he is responsible for two figures in this paper. I wrote the paper together with Håkan Olin.
Contributions Paper III: This was the third published paper with me as the first author. Renyun Zhang did experiments on triboelectric nanogenerators (TENGs) and I became interested in how they worked. The temperature dependence for the charging at contact had just recently been investigated for a generator using Al and PTFE (teflon) as contact materials, but the charging mechanism for triboelectric systems containing non-metals was disputed: electron transfer or ion transfer? I made a two-level Schottky ion transfer model for this system comparing it to experimental data found in three references. The characteristic temperature for the transition between the two levels obtained from fitting the Schottky model to the data was of the right magnitude for physically adsorbed atoms. I was the main writer of the paper with support of Jonas Örtegren, Salim Reza, Henrik Andersson and Håkan Olin who commented on the text.

Contributions Paper IV: This was the fourth published paper and my second about triboelectricity. Renyun Zhang made a wind-driven triboelectric nanogenerator consisting of a plastic ribbon that could flutter between two copper electrodes. He tested it in a table-top sized wind tunnel studying the frequency and voltage response at different wind speeds and gave me the data to analyze. Behind an obstacle in a flowing fluid, a von Karman vortex street is generated and I fitted this model to data and found that the fluttering frequency of the plastic ribbon was proportional to the von Karman frequency. The result of the analysis indicated that different harmonics could be excited in the plastic ribbon depending on the electrode distance. I wrote the paper with the support of Jonas Örtegren, Henrik Andersson, Ya Yang and Håkan Olin. Renyun and I made two figures each in the paper.

List of papers not included in the thesis:


C. Renyun Zhang, Magnus Hummelgård, Martin Olsen, Jonas Örtegren and Håkan Olin Nanogenerator made of ZnO nanosheet networks. Semiconductor Science and Technology (2017), volume 32, nr 5, article id. 054002


Terminology

Abbreviations and acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>NEMS</td>
<td>Nanoelectromechanical systems</td>
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<tr>
<td>TENG</td>
<td>Triboelectric nanogenerator</td>
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Chapter 1

Introduction

1.1 Nanomechanics and nanocontacts

At the nanoscale a number of phenomena occur that could be neglected at the macroscale. The below will provide examples of nanostructures and how they are influenced by nanomechanical forces due to quantum size-effects, adhesion, and electrical fields. In particular the nanocontact – a small contact that forms when two materials are brought close to each other and make contact – is of importance, and under the influence of nanomechanical forces it permits a way to start understanding a number of phenomena at the nanoscale including elastic beams, friction, charged nanocontacts, and triboelectricity.

Also of importance is that matter cannot be treated as a continuum. Instead, matter is discrete with atomic building blocks and loosely bound atoms, so-called adatoms [1], which can diffuse under the influence of weak nanomechanical forces due to the thermal vibration of the lattice [2].

That the nanoscale is different from the macroscale, can easily be seen by changing the scale of an object, permitting simple estimations of which physical phenomena are important, and which can safely be ignored. For example, say that an object has a lateral extension of \( L \), then the area will be \( L^2 \) and the volume \( L^3 \). The area-volume ratio will then be \( 1/L \). If \( L \) decreases from 1 m to 1 nm, then this ratio will grow with the factor \( 10^9 \). This is the reason one sometimes hear that at the nanoscale everything is surface.

If "everything" is surface, adhesion will be important for nanoscale objects. Adhesion is of importance to nanoscale phenomena including friction and triboelectricity. In practice the contact between two surfaces is between several nanocontacts. As explained below, this is the origin of the apparent area independency of friction forces.

One particularly clear example of how nanocontacts are used to enhance the adhesion is how evolution has given some small animals the advantage that allow them
to run up on smooth walls and even ceilings. Instead of having feet with one large contact area, which in practice will only make true contact between a smaller number of nanocontacts, the feet are designed with nanosized hair allowing a large number of nanocontacts and thereby increasing the adhesion force, see Figure 1.1.

The inventions of the scanning tunneling microscope and the atomic force microscope added key laboratory tools to investigate the nano-mechanical area. These microscopes are not only used for imaging, instead since the sensing tip is just a single nanocontact, detailed investigations have been done for many of the above mentioned systems.

Electrical charge will give rise to electric fields that should be considered enormous if present at the macroscale. For example, a voltage of 1 V over a distance of 1 nm, will give an electric field of 1 GV/m. This means that strong electrostatic forces could be present at nanocontacts moving around atoms on the surface. Because atoms or molecules could have dipole moments they are affected by inhomogeneous electric fields [3]. Sometimes they have a net charge making them able to contribute to, for example, the triboelectric charging when two different materials come in contact [4]. Charge transfer can also cause strong adhesive forces [5].

Quantum mechanics tell us that a particle could also be described as a wave, and when its wavelength is of the size of the object we need to consider quantum effects. At the atomic scale the system is always governed by quantum mechanics but at the nanoscale it depends on the particular system, geometry, and the wavelength of the active particles.

### 1.2 Quantum effects at the nanoscale

What decides if a system is in the quantum regime or in the classical regime? Every particle in motion has a wavelength associated with it called the de Broglie wavelength $\lambda$. It is given by

$$\lambda = \frac{h}{p},$$  \hspace{2cm} (1.1)

where $p = mv$ is the linear momentum. Here $m$ is the particle mass and $v$ is the particle speed. The particle speed is related to the temperature $T$ by $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$ so we obtain

$$\lambda = \frac{h}{\sqrt{3mk_B T}}.$$ \hspace{2cm} (1.2)

This is the thermal de Broglie wavelength. We see that a low temperature $T$ and a small particle mass $m$ make $\lambda$ large. If the distances between the particles are small so that the de Broglie waves of the individual particles overlap, we are in the quantum regime. If the distances between particles are large compared with the de Broglie wavelength, we are in the classical regime. In the nanometer scale, electrons
1.2 Quantum effects at the nanoscale

Figure 1.1: Examples of small animals that have their feet covered by nano-sized hair with terminal elements (circles) to ensure high adhesion. Feet with a larger area would only have a true contact area from a small number of nanocontacts, whereas if there is a large number of nanocontacts, all of them could potentially adhere to the target surface. The heavier the animal the smaller is the diameter of the top of the hair. From ref [6]. ©2003 by National Academy of Sciences

are usually in the quantum regime while the much heavier atoms are in the classical regime.

If we are in the classical regime the law of equipartition is valid. It tells us that for each excited degree of freedom, like the kinetic energy in the three translation directions, rotation or vibration kinetic energy components or potential energy components, there will be an equal contribution to the internal energy. If the dependence is quadratic like in $\frac{1}{2}mv^2$ or $\frac{1}{2}kx^2$, then the contribution for each such term will be $\frac{1}{2}k_BT$. New degrees of freedom become excited as the temperature rises and we are leaving the quantum regime for this degree of freedom.

The law of equipartition is also valid for a nanowire cantilever. If its potential energy is given by $\frac{1}{2}kA^2$ where $A$ is the amplitude of oscillation and $k$ is the spring constant, the cantilever has the energy $\frac{1}{2}k_BT$. This means that we can calculate the thermally excited oscillation amplitude from $kA^2 = k_BT$. At room temperature this amplitude has been observed, see Figure 1.3 (2A).

The de Broglie relation $\lambda = \frac{h}{p}$ between wavelength $\lambda$ and linear momentum $p$ as well as the relation between energy $E$ and frequency $f$, $E = hf$ are universally valid for all particles and quasi particles: for photons (light), electrons, phonons (vibration quanta) and even nanowire cantilevers [7]. We can thus write its energy, assuming that the cantilever is an harmonic oscillator, as $\frac{1}{2}kA^2 = (n + \frac{1}{2})hf$ where the integer $n$ is the quantum number. For a cantilever, however $n$ is very large, so the difference in amplitude $A$ for different $n$ can not be observed as it could be in the thermal
Introduction

\[ \lambda = \frac{h}{mv} \]

\[ E = \frac{mv^2}{2} \]

**\( \lambda \)** = de Broglie wavelength

**\( h \)** = Plank’s constant

**\( m \)** = electron mass

**\( v \)** = velocity

**\( E \)** = kinetic energy

**\( d \)** = box diameter

**Figure 1.2:** Standing waves corresponding to an integer number of half wavelength will fit.

excitation case above. Through the existing quantum-size effect in the electron gas even a metallic nanosized cantilever will indirectly be in the quantum regime. The electrons in a metal can either be bound to individual atoms or be delocalized and free to move in the entire volume of the metal. These free electrons form the gas that makes electrical conduction possible. An electron in motion has a de Broglie wavelength associated with it. In a given direction, this wavelength depends on the electron velocity component in this particular direction. The higher the velocity of the electron, the shorter the de Broglie wavelength becomes (electron size). Because an electron in a volume is described by standing waves between the walls of the volume, only certain wavelengths will fit, see Figure 1.2. For a wire of length \( L \) with a rectangular cross section we have the energies

\[ E_n = \frac{\hbar^2 \pi^2}{2m} \left[ \frac{n_1}{d_1} \right]^2 + \frac{n_2}{d_2}^2 + \frac{n_3}{L}^2 \]  

(1.3)

where \( d_1 \) and \( d_2 \) are the sides in the rectangle, \( m \) is the electron mass and \( n_1, n_2 \) and \( n_3 \) are the quantum numbers = 1, 2, 3, \ldots. There is thus a minimum energy the electron can have when it is confined to move between the walls. The smaller the volume the larger this minimum energy. If one dimension is much smaller than the other two this distance will determine the electron minimum energy, see Eq. (1.3).

Electrons also have a maximum energy depending on the metal used. This maximum energy is called the Fermi energy. If we then make a wire of the metal and reduce its diameter the minimum energy of the electrons will increase. When this minimum energy exceeds the Fermi energy of the metal, the wire will no longer be able to contain any free electrons and would no longer be a conductor.

What will then happen if we stretch a nanowire? This has been calculated by Stafford *et al.* and Blom *et al.* [10, 8]. When a nanowire is stretched, its cross section decreases. All electron energy levels are then shifted to higher energies, see Figure
1.2 Quantum effects at the nanoscale

Figure 1.3: (1): When a nanowire is stretched, its cross section decreases. All electron energy levels are then shifted to higher energies. Then the top states can be pushed over the Fermi level and the corresponding electrons leave the wire. This will then decrease the energy due to fewer electrons in the wire. However, stretching the nanowire further without pushing out any new electron state will increase the energy of the remaining electrons until another state is pushed out and so on. The energy of the electrons and thus the tensile force will thus oscillate with the elongation. From Blom et al. [8]. © The American Physical Society. (2 A): Nanotube (hollow nanowire) oscillation driven by thermal excitation. (2 B): Nanotube driven by an external electric field to the first harmonic at 530 kHz. (2 C): Nanotube driven by an external electric field to the second harmonic at 3.01 MHz. From Poncharal et al. [9]. © American Association for the Advancement of Science.

1.3. Then the top states can be pushed over the Fermi level and the corresponding electrons leave the wire. This will then decrease the energy due to fewer electrons in the wire. However, stretching the nanowire further without pushing out any new electron state will increase the energy of the remaining electrons until another state is pushed out and so on. The energy of the electrons and thus the tensile force will thus oscillate with the elongation as reported by ref. [11]. The electrical conduction also decreases in steps as electron states are pushed over the Fermi level. This has been experimentally confirmed [12].
1.3 Friction is due to nanocontacts

Coulomb’s law of friction states that the friction force $F$ is proportional to the perpendicular normal loading force $N$:

$$F = \mu N,$$

(1.4)

where $\mu$ is the coefficient of friction and $N$ is the loading force [13]. Surprisingly, the coefficient of friction is independent of contact area, surface roughness, and sliding velocity. The correct explanation of why friction is independent of contact area was not understood until around 1940 when Bowden and Tabor [14] pointed out that the real contact area is due to asperities, or nanocontacts, and it is the adhesion forces of this real contact area that is of importance. Such small contacts can be elastically or plastically deformed and by increasing the loading force the contact area will increase, explaining the loading dependency and at the same time the apparent contact-area independence of the Coulomb’s friction law. In 1987 the newly invented scanning tunnelling microscopes (STM) and atomic force microscopes (AFM) allowed studies of single nanocontacts making further progress possible. The velocity independence is perplexing since according to Stokes law the friction force of a particle in a fluid is proportional to the velocity of the particle. This problem was solved when it was understood that at the nanocontacts during sliding, there are very rapid processes occurring that are independent of the macroscopic speed [13].

![Figure 1.4: The friction force $F$ is proportional to the normal force $N$ due to an increase of contact area as the normal force increase.](image-url)
1.4 Charged nanocontacts

As we have seen above, usually quantum effects do not play any substantial role in nanomechanics except in special cases.

If a voltage is applied between a scanning tunneling microscope tip and a substrate plane, a mound or a pit will be formed on the plane if the voltage is high enough. Many explanations of this effect have been proposed. Below the formation of the mound (another explanation for the pit), as a result of electric field induced diffusion of free surface atoms, so-called adatoms, towards the tip forming the mound under it, is discussed.

The force that attracts the adatoms is the electrostatic force on a neutral particle with dipole moment in an inhomogeneous (position dependent) electric field. This force is the same as the one which deflects a thin water ray when holding an electrically charged hair brush close to the ray. This happens because the water molecule has a dipole moment and the electric field around the hair brush is inhomogeneous, that is the field is stronger near the brush and weaker further away from it. If the adatom or molecule is free to rotate or the dipole moment is induced by the electric field, the dipole force is always attractive. But for the adatoms on the plane substrate surface, a part of the dipole moment is surface induced. This component of the dipole moment of the atom always points away from the surface that it sits on. The total dipole force on the adatoms may, in this case, be either attractive or repulsive depending on the strength of the electric field, that is, on the applied voltage.

Depending on the tip polarity and tip-to-surface distance, different things will occur. Studying the literature, the phase diagram shown in Figure 1.5 will emerge, discussed below.

In area A, with positive tip, we obtain a mound, made up of sample material most likely created by field enhanced surface diffusion of adatoms. The mounds created using a positive tip are unstable, lasting only an hour in the experiment of Hsiao et al. [15]. Mayer et al. [19] made a computer simulation of such a field enhanced diffusion of adatoms under an STM tip.

In area B, at short distances and negative tip voltage, mounds made of tip materials are formed as found by Hsiao et al. [15]. The transport of tip material is due to field enhanced diffusion on the tip toward the gap, leading to a neck formation, which results in a mound when retracting the tip [15]. If the voltage applied is increased sufficiently, field evaporation of tip material will occur instead [15].

In area C, the experiments by Kondo et al. [17, 20], show a strong correlation between the threshold voltage for pit formation and the binding energy for ten different materials: for example gold (Au) with a binding energy of 3.8 eV, has a threshold voltage of $U = 3.5$ V, while tungsten (W) with a binding energy of 8.8 eV, has $U = 8.7$ V. Their explanation for this mechanism is sublimation induced by tunneling electrons.

In area D, for short distances and low electric fields, Erts et al. [18] measured the force between a gold coated atomic force microscope (AFM) tip and a gold tip.
Figure 1.5: Phase diagram showing STM induced surface modifications at different tip voltage $U$ and different tip-to-surface distance $D$ mainly constructed using ref. [15, 16] and ref. [17]. In drawing the lines for mound formation, we have assumed that it is the electric field $E = U/D$ that decides if a particular kind of mound will be formed. Mounds will form at positive voltages, area A. Based on our model assuming field induced diffusion of adatoms we are able to calculate the threshold electric field for mound formation for area A to $E_0 = \mu/\alpha \approx 2$ V/nm. In area B we have transfer of tip materials to the surface making a mound of tip material on the surface. For pits, area C, we have assumed that they are formed at constant $U$ independently of the tip-to-surface distance $D$ in agreement with Kondo et al. [17]. At short distances and low electric fields, area D, the van der Waals force will contribute in creating a mound [18].

using an AFM cantilever placed inside a transmission electron microscope (TEM). In this way, they were able to image the system while manipulating it. They found an anomalously high value of the jump-to-contact distance indicating a larger force than expected from the distance between the tips using the van der Waals force. Closer inspection revealed a thin neck formed between the tip and sample. Their interpretation was that the van der Waals force caused field induced surface diffusion leading to a shorter gap, which in turn increased the van der Waals force, and this avalanche of adatoms quickly formed the neck.

1.5 Triboelectricity – Friction with charge transfer

Tribology is the science of friction, lubrication, and wear. Triboelectricity concerns studies of the charging due to contacts between materials. When two different materials come in contact, charge is transferred so that one material becomes positively charged and the other material becomes negatively charged [21]. By comparing two
materials at a time, a triboelectric series can be established. If one chooses two materials far apart in a linear series, the created charge difference will be larger than if one chooses materials that are closer to each others in the series.

The mechanism for triboelectricity is not fully clear, except when contacting two metals. In the metallic case, the difference between the work functions of the two metals determine the amount of transferred charge [22, 23]. All metals are expected to be in a linear series in this way: that is if three materials A, B and C charge more negatively according to $A \rightarrow B$ and $B \rightarrow C$ then we know that $A \rightarrow C$.

The triboelectric mechanism for non-metals is not fully understood, but in several cases it is clear that motion of ions is involved. Many studies [4] show that materials, that are known to contain ions, give consistent charging results if the mechanism is modelled as motion of ions. Further, a cyclic series may in some cases be created indicating the existence of more than one charging mechanism. For a cyclic series we may have $A \rightarrow B$ and $B \rightarrow C$, as in the standard linear series, however, then $C \rightarrow A$ (see Fig. 1.6) making the series cyclic. This cyclic mechanism cannot be explained using only one mechanism, instead several mechanisms might be involved with ion transfer or electron transfer between potential wells of atoms, or by both mechanisms.

![Triboelectric series](image)

Figure 1.6: Triboelectric series are of two kinds: a linear triboelectric series is shown to the left, and a cyclic triboelectric series to the right. These two types of series indicate two different charging mechanisms: with the exception of bulk electron transfer we seems to have ion transfer [4] or transfer of localized electrons [24]. Figure adapted from McCarty and Whitesides [4].
1.6 Triboelectric nanogenerators

Triboelectric nanogenerators (TENG), that were invented by Zhong Lin Wang and co-workers in 2012 [25], utilize the contact electrification described above. In principle the devices are capacitors, charged by the triboelectric effect, that change their energies as the plates are separated. Many modes are possible, some of them are shown in Figure 1.8. The energy of a capacitor is given by

\[
W = \frac{Q^2}{2C} = \frac{Q^2 d}{2\epsilon_0 A}. \tag{1.5}
\]

Here \(Q\) is the fixed capacitor charge, \(d\) is the distance between the plates, \(A\) is the contact area between the plates and \(\epsilon_0\) is the permittivity of vacuum. We see that we can increase the energy \(W\) by increasing the charge \(Q\) by selecting the right contact materials, by increasing the plate distance \(d\), or by decreasing the contact area \(A\). The open circuit voltage of the triboelectric nanogenerator is given by

\[
u = \frac{Q}{C} = \frac{Qd}{\epsilon_0 A}, \tag{1.6}
\]

and is independent of operating frequency \(f\). The current becomes \(i = dQ/dt\) and is thus proportional to \(f\). This means that the power \(P = ui\) generated is proportional to the frequency. This can be compared with an electromagnetic generator where the voltage is proportional to speed and thus is proportional to the operating frequency. Using a constant resistance as a load, also the current in an electromagnetic generator will become proportional to frequency. Thus, for an electromagnetic generator the
power will be proportional to the frequency squared. Here the triboelectric generator has an advantage over the electromagnetic generator, it works already at low frequencies. This is important since there is a large untapped source of low-frequency vibrations available from the environment and human activity. Many different kinds of applications of the triboelectric nanogenerators have been suggested and demonstrated, see Figure 1.10, from sensors to large scale energy harvesting [26].

Figure 1.8: Examples of the different working modes of triboelectric generators. The insulators in the figures must be of different materials to get the triboelectric effect.

Figure 1.9: Current and voltage as a function of operating frequency of an electromagnetic generator and a triboelectric generator.
1.7 Objectives

The electromagnetic force governs nanomechanics and important nanocontact phenomena such as the triboelectric effect. Consequently, the electromagnetic force is the origin behind the interactions that we call adhesion forces, electrostatic forces, van der Waals forces, etc. At the nanoscale, the quantum nature of the electromagnetic force may be detected in some cases, whereas thermal fluctuations may conceal the quantum effects in others. This thesis aims at a fundamental understanding of some of the mechanisms occurring in the case of nanocontact, that governs important phenomena such as the triboelectric effect. The triboelectric effect may find use in energy harvesting devices such as TENGs. Such devices may be driven by mechanical vibrations, excited for example by a flowing medium, and may be used for conversion of energy sources that are not utilized today.

The objectives of this thesis concerns nanomechanics towards a better understanding of the fundamental mechanism of charged nanocontacts:

1. Increase the fundamental understanding of the mechanisms responsible for charged nanocontacts and in particular triboelectric phenomena by
1.7 Objectives

i. Investigating whether quantum effects are of importance at the nano level. For example, as one or more dimensions in a material having free electrons become very small, the electron states are affected. To be specific we choose to model the bending of a metallic nanowire. If the nanowire can freely oscillate, will the oscillation frequency be quantized as the nanowire is bent? To answer this we have made a model of a free electron gas confined in the volume of a nanowire.

ii. Modeling charged matter at nanocontact. Here, a model was made of adsorbed atoms (adatoms) affected by the electric field from a charged nanosized tip. The adatoms are uncharged but have a dipole moment, which affects how the adatoms move in this inhomogeneous electric field.

iii. Modeling the temperature dependency and propose charge transfer mechanisms. Here a two-level Schottky ion model was made, where the two energy levels correspond to the two surfaces that are brought in and out of contact.

2. Demonstrate and describe low speed wind energy conversion using a wind driven TENG. An experiment with a generator in a table-top sized wind tunnel was performed, and a von Karman vortex model was developed and fitted to experimental data.
Chapter 2

Results

2.1 Quantum effects in nanomechanics

How will the quantum-size effect in the electron gas in a metallic nanowire affect its mechanical and electrical properties? By modeling a free electron gas confined in the volume of a nanowire Blom et al. [8] showed that stretching a nanowire has an effect on tensile force. It was found to oscillate with the elongation as electron states were pushed over the Fermi level of the metal as the cross section decreases at elongation. One of our objectives was to increase our understanding of a nanosized system like this. How will, for example, the quantum-size affect the transverse force in a metallic nanowire cantilever when it is bent? If it does affect it, how will the oscillating wires resonance frequency be affected? To investigate this we made a model like the one in Blom et al. but bending the wire instead of stretching. We find that there is an effect, which is presented in this section.

When a metallic nanowire is bent, its cross section increases which lowers the minimum energy. This can sometimes allow the addition of a new electron to the wire, which will increase the energy in the electron gas due to more electrons in wire. This makes it difficult to bend the wire further. However, bending it even further without any new added electrons will decrease the energy of each electron making the spring softer until it is so bent that a new electron is added and the spring becomes harder again and so on. We obtain a bending dependent spring “constant”, which make the wires resonance frequency dependent on the amplitude of oscillation.

We are starting from the grand canonical potential given by [10, 8] for the $T = 0$ case

$$
\Omega = - \sum_n \int_0^L \frac{4}{3} \sqrt{\frac{2m}{\pi^2 \hbar^2}} (E_F - E_n(x))^{3/2} \, dx,
$$

(2.1)

where $L$ is the length of the wire. This equation is the starting point of Paper I. We then need an expression for the energy eigenvalues $E_n(x)$ of the waves that fits the
cross section. For a wire with a quadratic cross section we have

\[ E_n = \frac{\hbar^2 \pi^2}{2md_0^2} \left(n_1^2 + n_2^2\right), \quad (2.2) \]

where \(n_1\) and \(n_2\) is the quantum numbers \(= 1, 2, 3, \ldots\). The side in the square is denoted \(d_0\), and \(m\) is the electron mass. The degeneration is twofold (not counting spin) unless \(n_1 = n_2\). We bend a nanowire, which initially has a square cross section. This leads to the deformation of the nanowire cantilever cross section as shown in Figure B.1. To calculate \(\Omega\) we must sum over all energy levels, from the ground level up to just below the Fermi level \(E_F\). The dependency of the two quantum numbers are somewhat complicated because their sum \(n_1^2 + n_2^2\) is restricted so that the energy of the wave does not exceed \(E_F\). Also, after its deformation, due to the wire bending, the shape of the cross section is no longer square. To be able to proceed analytically we use the formula for the asymptotic eigenenergies for high eigenvalues of confined waves on a two-dimensional flat surface of area \(S\), which may have any shape. We have [28]

\[ E_n(x) = \frac{\hbar^2}{2m} \frac{4\pi}{S(x)} n, \quad (2.3) \]

where \(n\) is now the only "quantum number" in this approximation. The higher \(n\) becomes, the better the approximation. \(S(x)\) is given in Paper I by

\[ S(x) = d_0^2 \left(1 + \frac{9\nu^2d_0^2}{8L^4} (L - x)^2 Z^2 \right), \quad (2.4) \]

where \(\nu\) is the Poisson’s ratio of the metal in the wire. \(S\) thus varies along the wire: if the cross section is allowed to expand and contract freely, the most deformed part of the cross section is closer to the fixed end at \(x = 0\). At the free tip at \(x = L\) it assumes its undeformed value \(S = d_0^2\). Calculating, this leads to a bending dependent spring constant given by

\[ k = \sum_{n=1}^{N} \sqrt{E_F - E_0 n} \sqrt{\frac{2\pi \hbar^2}{m} n E_0 \frac{6\nu^2 d_0^2}{4L^4} \left[1 + \frac{9\nu^2 d_0^2 Z^2}{8L^4}\right]^2}, \quad (2.5) \]

using \(E_0 = 2\pi \hbar^2 / (md_0^2)\) and

\[ N = \frac{E_F}{E_0} \left(1 + \frac{9\nu^2 d_0^2 Z^2}{8L^4}\right). \quad (2.6) \]

To illustrate the changes in equation (2.5) with different values of \(N = E_F / E_0\) we made plots. The function to be plotted is

\[ k'(Z) = \sum_{n=1}^{N(1+CZ^2)} \sqrt{N - \frac{n}{1+CZ^2}} \times \frac{n}{(1+CZ^2)^2}, \quad (2.7) \]
2.1 Quantum effects in nanomechanics

Figure 2.1: Spring constant \( k \) as a function of normalized bending \( Z' \) obtained from our model for \( T = 0 \). For the curve with \( \frac{E_F}{E_0} = 5.9 \) no electron state will be added for small bending. Bending will instead decrease all energy levels making the spring softer to bend further. For the curve with \( \frac{E_F}{E_0} = 6.1 \) bending the wire will add an electron state making the spring harder to bend further at small bending. For small \( Z \) we have approximately \( k = k_0 + K \times Z^2 \) for the upper and lower curve with different signs of the constant \( K \).

where \( C = 9 \nu^2 d_0^2/(8L^4) \), which has the same type of dependency on \( n \) and \( Z \) as equation (2.5) has. We then obtain curves as shown in Figure 2.1. Taylor expansion for small bending \( Z \) yields

\[
k' (Z) = \sum_{n=1}^{N} n \sqrt{N - n} + CZ^2 \sum_{n=1}^{N} \left( \frac{5n^2 - 4Nn}{2\sqrt{N - n}} \right) + \ldots .
\]  

(2.8)

Because of the weak non-linearity the resonance frequency of the oscillation is shifted from \( \omega_0 \) to \( \sqrt{\omega_0^2 + \frac{1}{4}\beta A^2} \), see ref. [29]. A shift in the amplitude maximum is obtained, towards a higher frequency for positive \( \beta \) and towards a lower frequency for negative \( \beta \). For small \( Z \) we have that \( k = k_0 + K \times Z^2 \) except for the case when \( N = \text{integer} \). The constant \( K \) may be positive as in the upper curve in Figure 2.1, or negative as in the lower curve. We may then rewrite the harmonic equation with a bending dependent spring constant. The Duffing equation reads

\[
\frac{d^2 Z}{dt^2} + \omega_0^2 Z + \beta Z^3 + 2\gamma \frac{dZ}{dt} = F \sin (\omega t),
\]

(2.9)

where \( \omega_0^2 = k_0/M \) and the effective mass \( M \) is about 0.24 of the cantilever mass for an evenly thick cantilever, see [30, 31]. We show that the relative frequency shift \( \Delta f/f_0 \) would be given by

\[
\frac{\Delta f}{f_0} \approx \frac{27}{64} \xi \nu^2 \left( \frac{d_0}{L} \right)^2 \left( \frac{A}{L} \right)^2.
\]

(2.10)
Figure 2.2: Spring constant as a function of normalized bending for four temperatures $T$ from our model with $E_F/E_0 = 6.17$. Curve (a): $k_B T = 0.0001$ eV. Curve (b): $k_B T = 0.01$ eV. Curve (c): room temperature $k_B T = 0.025$ eV. Curve (d): $k_B T = 0.05$ eV. The plot is made using $\mu = 2.9$ eV, $E_0 = 0.47$ eV that is wire is made of gold and with a diameter $d_0 = 1$ nm. We see that the effect of an increased temperature is to smooth and reduce the oscillations.

where the constant $\xi$ can be calculated from our model. We find

$$\xi = \frac{\beta}{C \omega_0^2} = \sum_{n=1}^{N'} \left( \frac{5n^3 - 4nn}{2\sqrt{N-n}} \right)$$

(2.11)

What is the effect of a finite temperature? Our new function should reduce to Eq. (2.5) when $T$ becomes low. We argue that it should be given by

$$k = \sum_{n=1}^{N'} \left\{ \frac{2n^2}{\pi^2 k_n B_n E_0} \frac{dE_n}{dE} \times \right.$$

$$\times \int_{E_n'}^{E_{cut}} \frac{1/2}{\sqrt{E - \frac{E_n}{1 + \frac{9\mu^2 d_0^2 Z^2}{8L^4}}}} \frac{dE}{(e(E-\mu)/k_B T + 1)} \right\},$$

(2.12)

where

$$N' = \frac{E_{cut}}{E_0} \left( 1 + \frac{9\mu^2 d_0^2 Z^2}{8L^4} \right),$$

(2.13)

$$E_n' = \frac{E_0 n}{\left( 1 + \frac{9\mu^2 d_0^2 Z^2}{8L^4} \right)},$$

(2.14)
and the upper integration limit $E_{cut} \to \infty$. Eq. (2.12) reduces to Eq. (2.5) when $T \to 0$. A plot of Eq. (2.12) for different temperatures is shown in Figure 2.2. Due to the finite temperature, more states becomes available for the electrons from $E_F$ up to about $E_F + k_BT$; decreasing the number of occupied states between $E_F$ and about $E_F - k_BT$. Figure 2.2 demonstrates that at room temperature the curve follows the zero temperature curve well, except around the minima where a new state is added due to bending. Here the room temperature curves are smoothed.

In this section we have found that the spring constant oscillates with the bending – an effect that, however, is slightly reduced due to thermal effects. For small bending the spring softens or hardens as the amplitudes increases. If we have softening or hardening is dependent on the proximity of electron states to the Fermi level at the actual nanowire diameter. This softening or hardening of the spring has an influence on the resonance frequency, which becomes amplitude dependent.

### 2.2 Electrically charged nanocontacts

We want to increase the fundamental understanding of the triboelectric effect. A phenomenon related to this contact electrification is the formation of mounds under a charged nanosized tip. Under a charged nanosized metallic tip, mounds can be formed by electrostatic forces and van der Waals forces acting on the adsorbed atoms on the surface. This can then contribute to making a contact.

If we have a nanosized charged tip over a conducting surface we can model the electric field at the surface as the field from a point charge located inside the volume of the tip and its charge mirror located under the surface. We obtain [Paper II] close to the surface

$$E_z \approx -\frac{q}{4\pi \varepsilon} \left[\frac{2d}{(d^2 + r^2)^{3/2}} + \frac{15d^2 z^2}{(d^2 + r^2)^{7/2}}\right],$$

(2.15)

$$E_r \approx \frac{6qdr}{4\pi \varepsilon (d^2 + r^2)^{5/2} z}.$$

(2.16)

Here the charge $q$ can be expressed in terms of the voltage between the conducting tip and the surface:

$$\frac{q}{4\pi \varepsilon} = \frac{U}{2D} \left(R^2 + 2DR\right).$$

(2.17)

The dipole moment $\vec{p}$ for an adatom in an electric field $\vec{E}$ is given by Tsong and Kellogg [1]:

$$\vec{p} = \vec{\mu} + \alpha \vec{E} + \frac{1}{6}\gamma \vec{E}^3 + \cdots,$$

(2.18)

where $\vec{\mu}$ is the surface-induced dipole moment of the adatom, $\alpha$ is its polarizability and $\gamma$ is its hyperpolarizability. $\vec{\mu}$ always points away from the surface that it sits on, see ref. [32, 33], so $\mu$ is always positive in our calculations regardless of the polarity.
of the voltage \( U \). For the \( z \)– and \( r \)–components of the dipole moment \( \mathbf{p} \), we have neglected the hyperpolarizability term:

\[
p_z = \mu + \alpha E_z \\
p_r = \alpha E_r,
\]

(2.19) (2.20)

where \( \mu \) is positive. \( p_z \) and \( p_r \) may therefore be positive or negative. The force on a dipole in an electric field is

\[
\mathbf{F} = (\mathbf{p} \cdot \nabla) \mathbf{E}.
\]

(2.21)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3.png}
\caption{Adatoms with dipole moments on the surface for \( U > U_0 \). The dipole moment \( \mathbf{p} = \mathbf{\pi} + \alpha \mathbf{E} \) tends to align to the strong field inside \( r_0 \) on the surface and points away from the surface outside \( r_0 \) where the field is weaker. The radial force on the dipole on the surface is due to this effect, attractive inside \( r_0 \) and repulsive outside, tending to create a mound made of surface material with maximum radius \( r_0 \).}
\end{figure}

Combining our expressions and their derivatives we obtain to order \( z \)

\[
F_z \approx \alpha \left[ \frac{U}{2D} (R^2 + 2DR) \right]^2 \frac{60d^4 + 36d^2r^2}{(d^2 + r^2)^5} z \\
- \mu \left[ \frac{U}{2D} (R^2 + 2DR) \right] \frac{30d^2}{(d^2 + r^2)^{7/2}} z, \\
F_r \approx -\alpha \left[ \frac{U}{2D} (R^2 + 2DR) \right]^2 \frac{12d^2r}{(d^2 + r^2)^3} z \\
+ \mu \left[ \frac{U}{2D} (R^2 + 2DR) \right] \frac{6dr}{(d^2 + r^2)^{5/2}}. 
\]

(2.22) (2.23)
2.2 Electrically charged nanocontacts

Figure 2.4: Radial dipole force on an adatom using $D = 1.5$ nm and $R = 3.0$ nm and our values of $\mu$ and $\alpha$ for two different voltages $U$, one above and one below $U_0 = 3.7$ V. The van der Waals force has been calculated and plotted in the figure using $D = 1.5$ nm. For $D < 1.5$ nm the van der Waals force becomes important for the radial force on the adatoms.

where $z$ is the height over the surface for the center of the adatom, about one adatom radius. We see that the distance $z$ only affects $F_z$, not $F_r$. We are now able to calculate the electrostatic forces on the adatom on the surface under the tip. The calculation above is valid for the first step in the mound formation where the surface still may be considered as flat. Setting $F_r = 0$ in the expression above then yields

$$r_0 = (D + R) \sqrt{ \left( \frac{U}{U_0} \right)^{2/3} - 1}, \quad (2.24)$$

where

$$U_0 = \frac{\mu D (D + R)^2}{\alpha R (2D + R)}. \quad (2.25)$$

Inserting the equation for the threshold voltage $U_0$ into the equation for the electric field $E \approx E_z$ yields for $r = 0$ where a mound of radius zero will form the threshold field for mound formation $E_0 = \mu / \alpha \approx 2$ V/nm.

What about the van der Waals force? We find that it can be neglected compared to the electric dipole force for tip-to-surface distance $D$ larger than 1.5 nm.

In this section we have seen that due to the competition between the surface induced dipole moment and the electric field induced dipole moment of the adatom, the sign of the dipole vector depends on the electric field strength for a positive tip.
This sign determines in turn if the force on an adatom on the surface is attractive towards the tip or repulsive. Thus there exist a threshold field $E_0$ for mound formation that we can calculate from our model.

### 2.3 Temperature dependence of triboelectricity

The existence of cyclic triboelectric series, as we saw in the introduction chapter, indicates more than one charging mechanism. For metals it is clear that electrons are transferred, but for non-metals the charge carriers could be electrons or ions.

McCarty and Whitesides [4] have developed a model where the charge of the ions on a dielectric plate is neutralized by bound counter ions close to the surface of this material. The ions thus “belong” to this plate making it neutral. When another plate is brought in contact, some of the ions are transferred to the other plate. The ion transfer then creates an electric field between the plates which counteract more ion transfer. In this way the number of ions on the two surfaces can be calculated and hence the net charge on the plates.

We have developed a model [Paper III] that does not assume that the ions belong to one plate: we are assuming that they come from both plates. They are then distributed between the plates depending on the difference in work function for ions for the two plates creating a charge difference between the electrodes. Because this model then has two constant energy levels that do not change as the charging takes place we call it a two-level Schottky model in analogy with the Schottky model for heat capacity that gives rise to the Schottky anomaly.

A two-level Schottky system [37] is a well known model with only two energy levels, 1 and 2, separated by the energy $E$. The ratio of the number of particles on the two levels is given by the Boltzmann factor

$$\frac{N_2}{N_1} = e^{-E/k_BT}. \quad (2.26)$$

If the number of particles is fixed to $N = N_1 + N_2$ the number of particles on the lower energy level is given by

$$N_1 = \frac{N}{1 + e^{-E/k_BT}}. \quad (2.27)$$

We see that at low temperatures $T$ all the particles are on the lowest level $N_1 = N$, $N_2 = 0$ and at high temperatures they are equally distributed $N_1 = N_2 = N/2$. From the partition function $Z = 1 + \exp(-E/k_BT)$ for the two-level system many thermodynamical functions of state like internal energy, heat capacity and entropy can be calculated [38]. When two materials with a difference $E$ in binding energy for ions are brought into contact, a two-level system will develop. We assume that the materials have $N$ ions in common that can be distributed between them. The net charge of the capacitor is then $Q = q(N_1 - N_2)$, see Fig. 2.5. We obtain

$$Q = qN \left( \frac{2}{1 + e^{-E/k_BT}} - 1 \right). \quad (2.28)$$
2.3 Temperature dependence of triboelectricity

The capacitor voltage is given by $U = Q/C$ where $C = \epsilon_0 A/d$ is the capacitance so

$$U = \frac{qN}{C} \left( \frac{2}{1 + e^{-E/k_B T}} - 1 \right).$$  \hspace{1cm} (2.29)

The energy of a capacitor is $W = Q^2/(2C)$. The power density $P = W f/A$ becomes

$$P = \frac{N^2 q^2 f}{2CA} \left( \frac{2}{1 + e^{-E/k_B T}} - 1 \right)^2,$$

where $f$ is the charging/discharging frequency. The power density $P$ is thus proportional to the frequency while the maximum output power from the device to the
load resistance $R$ given by $U^2/R$ is independent of the frequency. For low temperatures Eq. (2.30) becomes $P \approx N^2 q^2 f/(2CA)$ independent of temperature, and for high temperatures $T$ Eq. (2.30) reduces to

$$P \approx \frac{N^2 q^2 f}{2CA} \left( \frac{E}{2k_B T} \right)^2.$$  

(2.31)

We have fitted our model of the power density or voltage of a triboelectric nanogenerator made of Al-PTFE-Cu to data from Wen et al. [35], Su et al. [34] and Lu et al. [36]. For the three curves we obtained three least square fits for a separation energy corresponding to temperatures of 374 K, 451 K and 269 K, respectively. The average temperature is 365 K. All three fitted values above are in the interval $365 \pm 96$ K.

$
\begin{array}{|c|c|c|c|}
\hline
\text{Ar} & \text{Kr} & \text{Xe} \\
\text{Au(111) substrate} & 0.38 \pm 0.03 \text{ eV} & 0.42 \pm 0.02 \text{ eV} & 0.53 \pm 0.03 \text{ eV} \\
\text{Ag(111) substrate} & 0.40 \pm 0.03 \text{ eV} & 0.46 \pm 0.02 \text{ eV} & 0.59 \pm 0.03 \text{ eV} \\
\text{Cu(111) substrate} & 0.42 \pm 0.03 \text{ eV} & 0.49 \pm 0.03 \text{ eV} & 0.62 \pm 0.03 \text{ eV} \\
\hline
\end{array}$

Table 2.1: Average of measured work function differences for Ar, Kr and Xe atoms adsorbed to substrates of Au, Ag and Cu from Hückstädt et al. [39]. The work function difference is for a mono layer of adsorbate compared to a clean substrate surface.

Table 2.1 shows work function differences for three kinds of noble gases adsorbed to three different noble metals. We see that for example the difference in work function for an Ar atom when it sits on an Au surface, compared to when it sits on an Ag surface, is 20 meV corresponding to a temperature of 232 K. This energy should correspond to the separation energy $E$. The energy difference between different substrates for an adsorbed atom seems then to be of the right magnitude to support an ion Schottky model, see legends of Figure 2.5.

Can the Schottky model be applied to all nanogenerators containing non-metals so that ion transfer may be the dominating source of triboelectric charging? No. For a generator with one sheet covered with TiO$_2$-nanotubes the reverse temperature behavior was found with increasing charging with temperature [34].

What about another new charging model which assumes electron transfer between potential wells of surface atoms proposed by Xu et al. [24]? This paper was published at about the same time as our ion Schottky model was published. This model by Xu et al. should, however, be equivalent to our model because it should not matter energy-wise if a whole ion moves to the other surface or if it is just its charge that moves to an uncharged atom on the other surface. At least not as long as the electron is transferred to an atom of the same kind as the one it comes from. We believe that the temperature dependence should be the same. It is possible that a high frequency experiment could distinguish between the models because electrons move more easily than ions.

In this section we have described a two-level ion Schottky model for the triboelectric charging of a nanogenerator. The energy difference for ions on the two surfaces
then enters the derived equation for charging. We compare this energy with adsorption energy differences for adatoms on different surfaces found in the literature. The energies are of the same order, which makes the model reasonable.

### 2.4 A wind-driven triboelectric nanogenerator

Triboelectric nanogenerators (TENG:s) are used as efficient energy transducers in energy harvesting to replace the need for batteries for small electronic devices, or as sensors for different physical properties. One of our objectives was to demonstrate and describe low speed wind energy conversion using a wind-driven TENG. This will be described below. We made an experiment with a generator in a table-top-sized wind tunnel and tried to explain the observed frequency and voltage response at different wind speeds with a von Karman vortex model for the frequency and a capacitor model for the voltage.

We have studied a triboelectric nanogenerator driven by air flow. The working principle is shown in in Figure 2.6. How should such a nanogenerator be designed and what will be its characteristics? Many designs of a wind generator are possible, the most straightforward idea is to use an ordinary wind turbine and just replace the electromagnetic generator with a triboelectric generator [27]. Some more elaborate designs are given by Yong et al.: They considered a dielectric ball rolling inside a vortex chamber with one tangential air inlet and a central air outlet, generating triboelectricity as the ball make contacts with the walls [40]. However, a triboelectric generator harvester can also be designed to include the turbine function in the generator part itself, allowing a considerable simpler design. For example Bae et al. [41] studied a triboelectric generator in the form of a flag fluttering in the air stream close to an electrode. Wang et al. [42] made a wind-driven triboelectric nanogenerator device constituting of a two-sided clamped kapton film that was fluttering between two copper electrodes. They measured the frequency and voltage as a function of length, width and thickness of the fluttering film and as a function of the electrode distance, with emphasis on the generator part.

We made a wind nanogenerator similar to that of Wang et al., however, we also made a detailed study of the fluid dynamics using a table-top sized wind tunnel, allowing measurements of the frequency and voltage response as a function of wind speed [Paper IV]. Our nanogenerator device, Figure 2.6, even simpler than the one reported by Wang et al., consisted of a two-sided clamped fluorinated ethylene-propylene (FEP) plastic ribbon placed between two parallel or two outwardly bent copper electrodes. At the start of the experiments, the FEP plastic ribbon is mildly stretched and then clamped at the ends 10 cm apart, see inset of Figure 2.7.

However, because the clamping is not perfect and because the ribbon is elastic it can move a little. After a while the ribbon becomes relaxed and so becomes about 1 cm longer (i.e. 11 cm) between the clamps so that it can touch the electrodes when fluttering. This state is then stable generating a stable voltage signal. The device was placed in a table-top sized wind tunnel (Omega mini wind tunnel, model WTM-1000) to let the air flow drive the FEP plastic film motion. The fluttering of the FEP
plastic ribbon between the two copper electrodes generated alternating voltage and current with positive and negative maximum values. The raw signal was then fed into a bridge rectifier (GJB2508 from Diodes Incorporated) and the rectified signal data was recorded, giving frequency and voltage as a function of wind speed on which the plots in Figure 2.7 and Figure 2.8 are based. The wind speed was measured with an air speed meter belonging to the wind tunnel. In this paper, we carry out a detailed study of the frequency and voltage response to wind speed using the three half electrode distances $d = 3$ mm, 5 mm and 7 mm (electrode distances 6 mm, 10 mm and 14 mm). We find that the frequency increases linearly with air speed, with a cutoff at a low speed for each $d$. The generated power of our device is enough to power a battery of LEDs. In our device, power started to be generated at wind speeds as low as 1.6 m/s. We also find that the voltage is proportional to the frequency at each $d$. We seem able to explain the main features of the data assuming the presence of von Karman vortices exciting the plastic FEP ribbon into different harmonics of vibration. We anticipate that this design could be useful because it works at low wind speeds, suitable both as air speed meters and power generators.
When investigating oscillations in fluids, the Strouhal number \( St = \frac{fd}{U} \) where \( U \) is a characteristic fluid speed and \( d \) is a characteristic distance perpendicular to the fluid flow, is found to be of importance [43]. It is thus reasonable to assume that the frequency of fluttering of the plastic FEP film could be given by

\[
f = \frac{StU}{d},
\]

for some \( St \). In our case we take the characteristic distance to be the triboelectric generator half width \( d \) in the air stream. The relation between the Strouhal number \( St \) and the Reynolds number \( Re = Ud/\nu \), where \( \nu = 1.5 \times 10^{-5} \) m\(^2\)/s is the kinematic viscosity of air, can be deduced from the vorticity transport equation: [44]

\[
St = A - \frac{B}{Re}.
\]

The dimensionless constants \( A \) and \( B \) would be of the order unity. For a circular cylinder with diameter \( d \) as the obstacle generating the vortices, \( A = 0.21, B = 5.4 \) was experimentally found. In our case we do not have this geometry, so the constants \( A \) and \( B \) would probably be different in our case [45, 46]. Combining these two equations we obtain

\[
f = \frac{A}{d}U - \frac{B\nu}{d^2}.
\]

<table>
<thead>
<tr>
<th>Half width ( d ) (mm)</th>
<th>Calculated ( A )</th>
<th>Calculated ( B )</th>
<th>Ratio ( A/B )</th>
<th>Harmonic ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.062</td>
<td>23</td>
<td>0.0027</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>0.058</td>
<td>22</td>
<td>0.0026</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>0.093</td>
<td>34</td>
<td>0.0027</td>
<td>3</td>
</tr>
<tr>
<td>Average</td>
<td>0.071</td>
<td>26</td>
<td>0.0027</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.2: Calculated values of the constants \( A \) and \( B \) in Eq. (2.34) using the three fitted curves in Figure 2.7. If the model Eq. (2.34) is correct, all three fitted values of \( A \) and \( B \) respectively in the table should be the same. The three equations for the fitted curves are for the \( d = 3 \) mm case \( f = 20.67U - 38.10 \), for the \( d = 5 \) mm case we have \( f = 11.55U - 13.38 \) and for the \( d = 7 \) mm case we have \( f = 13.33U - 10.42 \). The constants \( A \) and \( B \) are not the same for all \( d \) but the ratios \( A/B \) are the same. To the rightmost in the table are the different vibrational harmonics showed suggested to explain the differences in \( A \) and \( B \).

We see that the frequency increase linearly with \( U \) and has a cutoff at low air speeds given by \( U_{cut} = B\nu/(Ad) \). Using our calculated constants \( A \) and \( B \) we can then write Eq. (2.34) for our three curves as

\[
f = \xi \left( \frac{0.060}{d}U - \frac{22\nu}{d^2} \right),
\]

where \( \xi = 1.0 \) for \( d = 3 \) mm and 5 mm and \( \xi = 1.5 \) for \( d = 7 \) mm.

Analytical calculation of charge and voltage of a triboelectric generator in contact-mode can be found in Yang et al. [47]. The voltage is in this reference found to increase linearly, with the frequency which our experiments confirm, see Fig 2.8. For
Results

Figure 2.7: Fluttering frequency $f$ as a function of wind speed $U$ in the table-top-sized wind tunnel for three different half electrode distances $d = 3$ mm, 5 mm and 7 mm. When the wind blows the FEP film is fluttering between the two copper electrodes placed at $d = 3$ mm away (parallel electrodes), $d = 5$ mm away (electrodes slightly bent outward) or $d = 7$ mm away (electrodes more bent outward) respectively. Inset: Drawing of the TENG.

$d = 3$ mm, 5 mm and 7 mm we found $u = 0.401248 \times f$, $u = 0.602743 \times f$ and $u = 0.352747 \times f$ respectively. The fitted lines for $d = 3$ mm and $d = 7$ mm almost coincide. Given the frequency $f$ the voltage thus becomes largest at $d = 5$ mm.

Why is there an optimum $d$ giving the voltage $u$ a maximum at constant frequency? We could give two reasons: (i): approximating the fluttering film and electrode as a capacitor of capacitance $C$ one would expect the voltage $u$ to increase with the half width $d$ as

$$u = \frac{Q}{C} = \frac{2Qd}{\epsilon_0 S},$$

(2.36)

where $Q$ is the charge, $S$ is the capacitor area, $2d$ is the distance between the ”plates” and $\epsilon_0$ is the permittivity of air. (ii): The impact speed $v$ of the plastic ribbon fluttering between the two copper electrodes is approximately

$$v = \frac{2d}{P/2} = 4df,$$

(2.37)
We see that the voltage becomes larger for $d = 5$ mm than for $d = 3$ mm and $d = 7$ mm at the same frequency. Inset: photography of the triboelectric nanogenerator mounted inside the table-top-sized wind tunnel at work, generating enough power to light up the LED:s on the circuit board.

Figure 2.8: Voltage $u$ as a function of vibration frequency $f$ for the three different half electrode distances. We see that the voltage becomes larger for $d = 5$ mm than for $d = 3$ mm and $d = 7$ mm at the same frequency. Inset: photography of the triboelectric nanogenerator mounted inside the table-top-sized wind tunnel at work, generating enough power to light up the LED:s on the circuit board.

where $P = 1/f$ is the period time for one oscillation. The charge transfer $Q$ increases with contact force [48, 49]. The contact force $F$ in turn increases with the impact speed $v$ because the impulse $I = Ft = 2mv$ where $t$ is the contact time. These two reasons, (i) and (ii), suggest that the voltage should increase with the half width $d$. We see that as $d$ increases from 3 mm to 5 mm the voltage increases in qualitatively agreement with this.

However, for the larger $d = 7$ mm, the voltage decrease compared to the 5 mm case, see Figure 2.8. This effect can be due to that for this $d$, higher harmonic $n = 3$ is excited instead of the lower harmonic $n = 2$ which may be excited at $d = 3$ mm and 5 mm. Different harmonics has different geometrical shapes affecting the contact area with the electrodes, and can thus change the charge transferred and the voltage.

In this section, we have presented an experiment with a triboelectric nanogenerator in a wind tunnel and tried to explain the result. The nanogenerator consists of two copper electrodes with a plastic ribbon in between that is fluttering as the wind blows. We measured the frequency and voltage response of the nanogenerator
for different wind speeds. We found that the frequency is proportional to the von Karman vortex frequency and that the proportionality constant is the same for two out of our three electrode distances. This seems to indicate excitation of the plastic ribbon by the von Karman vortices into two different harmonics. The different harmonics have different geometry affecting the contact area with the electrodes and thus the charging.
Chapter 3

Discussion

To increase the understanding of the mechanisms responsible for charged nanocontacts and in particular triboelectric phenomena we have investigated quantum-size effects, electric field induced adatom diffusion, and thermodynamics of triboelectricity. The quantum nature of the elastic force may be of importance as the dimensions become very small, or as thermal vibrational energy diminishes, or both. As two approaching surfaces come into contact, electromagnetic forces may cause redistribution of matter and charges at the nano level. A fundamental understanding of the electromagnetic forces between two surfaces in close proximity will give insight into important nanomechanics phenomena such as triboelectricity. The triboelectric effect can in turn be useful for energy conversion in triboelectric nanogenerators, in which mechanical vibrations are converted into electrical energy upon contact between two surfaces.

To address the question whether quantum-size effect on elastic forces is relevant in nanomechanics, we combined a one-dimensional jellium model and standard beam theory allowing the spring constant of a vibrating nanowire cantilever to be calculated. By using the asymptotic energy eigenvalues of the standing electron waves over the nanometer sized cross section area, the change in the grand canonical potential was calculated and hence the force and the spring constant. As the wire is bent more electron states fit in its cross section. This has an impact on the spring "constant" which oscillates slightly with the bending of the wire. In this way an amplitude dependent resonance frequency of the oscillations is obtained. Because of the weak non-linearity, the resonance frequency becomes amplitude dependent. For certain geometries and temperatures this shift of resonance frequency should be detectable experimentally.

Triboelectric systems, that are of special interest in this thesis, will however not have any important influence from quantum-size effects. There are almost certainly quantum-size effects in the individual nanocontacts in a metallic TENG during the final breaking of the nanocontacts, both quantized conductance and quantum-size influenced forces. Such observations have been reported in the literature for single contacts using STM [12] and AFM [11]. However, these effects will not be detectable
because in a TENG there are many contacts and the current from each individual nanocontact will be averaged out. The temperature might also wash out the quantum effects. Stretching a nanocontact will give a large change in the diameter and consequently large differences in the quantum level that is readily detectable at room temperature as shown for example in the AFM experiments by Rubio et al. [11]. However, the nanowire cantilever studied in this thesis has a smaller shift in the levels during the bending because the change in the cross section due to bending is small.

The mechanics of bending and stretching nanosized wire resembles nano contacting during triboelectrification as two surfaces are approaching or departing from each other. When the two surfaces are in close proximity, variations in the distribution of charges, dipole-moments and induced dipole-moments, will create electric fields affecting neighbouring surfaces. This may lead to redistribution of charges and atoms at the neighboring surface in the event of nanocontact.

A model of field induced surface diffusion of adatoms including electrostatic forces and van der Waals forces was developed. The electric field is analytically modelled as a point charge over an infinite conducting flat surface. The force acting on the adatoms is small for voltages commonly used, but due to thermal vibrations, adatoms are hopping on the surface. Under these circumstances even a small net force can be significant in the drift of adatoms. A novel formula for a polarity dependent threshold voltage for mound formation on the surface for a positively charged tip was developed. Knowing the voltage of the pulse, the radius of the formed mound could be calculated. A threshold electric field for mound formation of about 2 V/nm was also calculated. In addition, we found that the van der Waals force is of importance for shorter distances and its contribution to the radial force on the adatoms has to be considered for distances smaller than 1.5 nm for low voltages.

Although this model of field induced matter transport was compared with surface modifications experiments using STM, the model has implications for the fundamentals of triboelectricity. In the triboelectric system there is no STM tip, but each nanocontact formed during contact will be broken during detachment. During this breaking moment the remains from the broken nanocontact will form sharp protrusions effectively acting as STM tips. The relevant voltage is different for the two cases: the typical voltage in the STM case is about 1 V, while it is 1-3 orders higher in the triboelectric case. One immediate observation concerns the wear of the contact areas of a triboelectric generator. Our field induced modification model show that material could be transferred from one electrode to the other one, potentially diminishing the triboelectric effect. This process is polarity dependent as shown in the phase diagram Figure 1.5 in the introduction. The phase diagram seems to indicate that stable material transfer mainly occurs from a negative to a positive surface.

As two different materials are brought into contact, the difference in triboelectric potentials between the materials results in electric charges transferred from one surface to the other. These mechanisms are not fully understood in the cases where one or both of the surfaces are non-metals. Charge transfer may then in some cases include transfer of both electrons and ions. The dependency of charge transfer on variables such as frequency and temperature should give valuable information about
these mechanisms.

A two-level Schottky model, assuming ion transfer, was developed to describe the temperature dependence of the triboelectric effect for a TENG. It was assumed that a number of the adatoms shared between two contacting surfaces of different materials are ionized. The two levels are characterized by the different energies that the ions have as they are attached to one surface or the other. This means that the Boltzmann distribution can be used to calculate the ratio of the number of ions at the two surfaces at any temperature. The model describes the decreasing triboelectric effect in TENGs with increasing temperature as described in the literature, and results in a separation energy which is of the right order of magnitude for physically adsorbed atoms when the model is compared with experiments reported in the literature.

Another charging model was suggested by Xu et al. [24], published at about the same time as our Schottky paper. Xu propose that a charging mechanism could be transfer of electrons between potential wells of atoms. How does this model compare to our ion Schottky model? We believe that the two models should be equivalent for the following reasons: We know that ions follow the Maxwell-Boltzmann distribution because there are many unoccupied states on the surfaces. Even localized electrons should approximately follow this distribution because the electrons in this system are not part of a Fermi gas: there are a lot of unoccupied states for the electrons to go between at the surfaces. It should thus not matter energy-wise if an entire ion moves to the other surface or if it is just the charge of the ion that moves to an uncharged atom on the other surface as long as the transfer is made between atoms of the same kind. High frequency experiments might distinguish between the models because electrons move more easily than heavy ions.

The triboelectric effect can be used to generate electricity in TENGs, where two surfaces are repeatedly brought in and out of contact, and where the charge transfer is turned into electrical energy. It was recently demonstrated that TENGs can convert wind energy into electrical energy. In our work, a plastic ribbon fluttering in the wind between two copper electrodes was used to produce electric power. We find that the fluttering is proportional to the von Karman frequency, making them suitable both as air speed sensors as well as power generators. The data seems to suggest that different harmonics of oscillations in the plastic ribbon can be excited in response to the von Karman vortices depending on electrode distance. We do furthermore anticipate that a wind driven triboelectric nanogenerator of this design can be useful because it can generate power already at air speeds as low as 1.6 m/s. There are two features that make a TENG wind generator interesting for large-scale implementation in society. Firstly, the very simple design of the TENG compared to standard electromagnetic generators might make the manufacturing cost an order of magnitude lower. Secondly, the finding that it is operational at very low wind speed should allow placement of TENG wind generators inside cities and other places that do not suit todays wind power systems.
We can summarize with the following conclusions

1. Several findings on the nanomechanical forces, due to quantum size-effects, electrical fields, and van derWaals, showed that

   i. Quantum effects are not of general importance in nanomechanics, except in special systems.
   
   ii. Field-induces matter transport, both by electric field and van derWaals forces, is of importance to understand phenomena in nanocontacts including triboelectric contacts.
   
   iii. Thermodynamics might be an important tool to investigate the triboelectric mechanism.

2. We anticipate that the triboelectric wind generator with its simple design and low wind speed capability should allow development of large-area wind power systems in the future.

3.1 Future works

A better understanding of the triboelectric mechanism is desired and the two models presented in this thesis, if developed further, could contribute towards this. Firstly, the field-induced matter transport model could be more specifically modelled towards triboelectricity in order to be useful to understand the wear of the electrodes in TENG. Such a model might also contribute to design rules for a proper choice of materials. It would then be desired to include also insulators in the model - our field induced model assume a conducting surface under the charged tip - since the majority of practical TENGs are made of non-metals. Secondly, the Schottky model for studies of the temperature dependency could be useful to interpret new tailor-made experiments.

In particular it would be interesting to experimentally show if we have ion transfer or transfer of electrons between potential wells of atoms as charge carriers in triboelectric nanogenerators containing non-metals but not nanomaterials. Perhaps a high frequency experiment could answer this question because electrons move more easily than heavy ions. Dielectric spectroscopy measurements could give valuable information about what kind of charge carrier that is active in triboelectric nanogenerators.

The development of TENG:s are done along several lines, for example, they are used in self-powered sensors which already have been demonstrated in a number of systems [27]. Our wind-driven TENG have many desired properties; they are simple, efficient, cheap and are working already at low wind speeds with potential to scale up to large-area coverage for contribution to the need of energy in the future society. This might also be valid for other kinds of renewable energy including thermal waste heat and solar energy that might use thermoacoustic principles [50] for
3.1 Future works

converting thermal gradients to mechanical vibrations. Another large source of renewable energy is water power and Zhong Lin Wang et al. have already shown [51] such an application for wave energy. Because of this we anticipate that TENG based energy converters could have many applications for large-scale energy harvesting in the future.
Bibliography


Appendix A

Number of electrons in square cross-section

For a wire with quadratic cross section, like in Paper I, we have standing waves in the cross section with eigenenergies

\[ E_n = \frac{\hbar^2 \pi^2}{2md_0^2} (n_1^2 + n_2^2) = E_0 (n_1^2 + n_2^2), \quad (A.1) \]

where \( n_1 \) and \( n_2 \) is the quantum numbers = 1, 2, 3, ..., and \( d_0 \) is the side in the square cross section. \( m \) is the electron mass. The degeneration is twofold (not counting spin) unless \( n_1 = n_2 \). Note that \( E_0 \) here is not the same as the one used in Paper I.

To obtain the number of electrons under the Fermi level \( E_F \) from this equation we use the Matlab/Octav code shown below.

We will in the code let both \( n_1 \) and \( n_2 \) go from 1 to \( N_{\text{max}} > \sqrt{E_F/E_0} \). The double loop then gets all possible energy levels the correct number of times so that we obtain the correct number of electrons below Fermi level directly and no special care must be taken in the program to account for different degeneration of different energy levels. We can see this by making a table with \( n_1 = 1, 2, 3, ... \) horizontal and \( n_2 = 1, 2, 3, ... \) vertical. Every position in the matrix can then add one electron to the sum, if \( E_n < E_F \). The of-diagonal elements like \( E(1, 2) \) and \( E(2, 1) \) then each give one electron to the sum so we have here twofold degeneracy of this energy value \( E(1, 2) = E(2, 1) \). This in contrast to an on-diagonal element like \( E(2, 2) \) which only yields one single electron.

If we instead would have made the outer loop for \( n_1 \) go from 1 to \( N_{\text{max}} \) but letting the inner loop for \( n_2 \) go from 1 to \( n_1 \), care would have to be taken to get the degeneration right.
% The program calculates the number of electrons below Fermi level EF for standing electron waves on a square cross section d0 x d0 with energy E = E0*(n1^2 + n2^2) where n1,n2 = 1,2,3,... and E0 is given by E0 = hbar^2 Pi^2/(2 m d0^2).

Nmax = 50; % Nmax > sqrt(EF/E0)
N = 0; % The number of electrons
E0 = 0.02348; % 4 x 4 nm cross section
%E0 = 0.3757; % 1 x 1 nm cross section
EF = 5.5; % Fermi energy for gold in eV

% Sum over all energy levels that can contribute:
for n1=1:Nmax
  for n2=1:Nmax
    % Calculate energy using n1 and n2:
    E = E0*(n1*n1+n2*n2);
    % Add electrons only if energy is below EF:
    if (E < EF)
      % Add one electron at this level:
      N = N + 1;
    end
  end
end

% Print the result:
N

Using d0 = 1 nm in the program we obtain N = 8 electrons below Fermi level and from d0 = 4 nm we obtain N = 172 electrons. This is to be compared with the more simple asymptotic formula used in Paper I:

\[ E_n = \frac{\hbar^2}{2m} \frac{4\pi}{S} n, \]

(A.2)

where S = d0^2. This one yields N = 11 and N = 183 electrons respectively.
Appendix B

Metallic nanowires: differences between stretching and bending

In this appendix we compare stretching and bending of a nanowire. We calculate Young’s modulus for both cases and show that while the dependency of the Fermi energy are the same the dependency on Poisson’s ratio is different. First we calculate for the bending case and thereafter for the stretching case.

Because the cross section of a nanowire is small, about 1 to 10 nm, but the wire may be at least ten times its diameter in length, we use the one dimensional free electron model. We have

\[ N_{tot} = \sum_n \int_0^L \int_{E_n}^\infty g(E - E_n) f(E) \, dE \, dx, \]  
(B.1)

\[ E_{tot} = \sum_n \int_0^L \int_{E_n}^\infty g(E - E_n) f(E) \, dE \, dx, \]  
(B.2)

where \( E_n \) is the energy of the \( n \):th energy level for waves that fits the cross section, \( N_{tot} \) is the total number of free electrons in the wire and \( E_{tot} \) is their total energy. \( L \) is the wire length. \( g(E) \) is the one dimensional density of states given by ref. [8]:

\[ g(E) = \sqrt{\frac{2m}{\pi \hbar^2}} \frac{1}{\sqrt{E}}. \]  
(B.3)

\( f(E) \) is the Fermi-Dirac distribution function:

\[ f(E) = \frac{1}{e^{(E - \mu)/k_B T} + 1}. \]  
(B.4)

We have at finite temperature \( T \) the grand canonical potential of the electron gas

\[ \Omega(\mu, T, Z) = E_{tot}(N_{tot}, S_{tot}, Z) - \mu N_{tot} - TS_{tot}. \]  
(B.5)
using Legendre transforms [52] of the energy to get $\Omega$ were $S_{tot}$ is the entropy of the electron gas. We have for the electron gas the heat capacity $C_v$ [53]

$$C_v = \frac{\pi^2}{2} N_{tot} k_B \frac{T}{T_F}, \quad (B.6)$$

where $E_F = k_B T_F$. By using $dS_{tot} = dQ/T = C_v dT/T$ and integrating we obtain

$$S_{tot} = \frac{\pi^2}{2} N_{tot} k_B \frac{T}{T_F}, \quad (B.7)$$

so using $\mu \approx E_F$ at room temperature we find

$$TS_{tot} = \mu N_{tot} \frac{\pi^2}{2} \left( \frac{T}{T_F} \right)^2. \quad (B.8)$$

Because $T/T_F \approx 1/100$ at room temperature, the contribution from the entropy term $TS_{tot}$ to $\Omega$ may be neglected and we obtain using Eq. (B.5) the grand canonical potential given by [10, 8] for the $T = 0$ case

$$\Omega = - \sum_n \int_0^L \frac{4}{3} \sqrt{\frac{2m}{\pi^2 \hbar^2}} \left( E_F - E_n(x) \right)^{3/2} dx, \quad (B.9)$$

where $L$ is the length of the wire. This equation is the starting point of Paper I and also of Blom et al. [8].
We then need an expression for the energy eigenvalues \( E_n(x) \) of the waves that fits the cross section. For a wire with quadratic cross section we have

\[
E_n = \frac{\hbar^2 \pi^2}{2m d_0^2} (n_1^2 + n_2^2),
\]

where \( n_1 \) and \( n_2 \) is the quantum numbers \( = 1, 2, 3, \ldots \). \( d_0 \) is the side in the square and \( m \) is the electron mass. The degeneration is twofold (not counting spin) unless \( n_1 = n_2 \).

We now bend a nanowire which initially has a square cross section. This leads to the deformation of the nanowire cantilever cross section as shown in fig B.1. To calculate \( \Omega \) we must sum over all energy levels, from the ground level up to just below the Fermi level \( E_F \). The dependency of the two quantum numbers are somewhat complicated because their sum \( n_1^2 + n_2^2 \) is restricted so that the energy of the wave is not exceeding \( E_F \). Also, after its deformation due to the wire bending, the shape of the cross section is no longer square. To be able to proceed analytically we use the formula for the asymptotic eigenenergies for high eigenvalues of confined waves on a two-dimensional flat surface of area \( S \), which may have any shape. We have [28]

\[
E_n(x) = \frac{\hbar^2}{2m} \frac{4\pi}{S(x)} n,
\]

where \( n \) is now the only "quantum number" in this approximation. The higher \( n \) becomes, the better the approximation. \( S(x) \) is given in Paper I by

\[
S(x) = d_0^2 \left( 1 + \frac{9\nu^2 d_0^2 (L - x)^2 Z^2}{8L^4} \right),
\]

where \( \nu \) is the Poisson’s ratio of the metal in the wire. \( S \) thus varies along the wire: if the cross section is allowed to expand and contract freely, the most deformed part of the cross section is closer to the fixed end at \( x = 0 \). At the free tip at \( x = L \) it assumes its undeformed value \( S = d_0^2 \). Calculating, this leads to a bending dependent spring constant given by

\[
k = \sum_{n=1}^{N} \sqrt{E_F - \frac{E_0 n}{1 + \frac{9\nu^2 d_0^2 Z^2}{8L^4} \left[ 1 + \frac{9\nu^2 d_0^2 Z^2}{8L^4} \right]^2}},
\]

using \( E_0 = \frac{2\pi \hbar^2}{(md_0^2)} \) and

\[
N = \frac{E_F}{E_0} \left( 1 + \frac{9\nu^2 d_0^2 Z^2}{8L^4} \right).
\]

To illustrate the changes in this equation with different values of \( N = E_F/E_0 \) we made plots. The function to be plotted is

\[
k'(Z) = \sum_{n=1}^{N} \sqrt{N - \frac{n}{1 + CZ^2}} \times \frac{n}{(1 + CZ^2)^2},
\]
where \( C = \frac{9\nu^2 d_0^2}{8L^4} \), which has the same type of dependency on \( n \) and \( Z \) as Eq. (B.13) has. Then we obtain curves as in fig 2.1. For small bending \( Z \) we obtain

\[
k'(Z) = \sum_{n=1}^{N} n\sqrt{N-n} + CZ^2 \sum_{n=1}^{N} \left( \frac{5n^2 - 4Nn}{2\sqrt{N-n}} \right) + \ldots .
\]  

(B.16)

The spring constant \( k \) and hence Young’s modules \( E \) in our model is proportional to this sum yielding a size effect lowering \( E \) for small cantilevers. \( E \) is found to have the ability to increase as well as decrease with diameter depending on the temperature [54]. Setting the sum equal to zero using \( N = E_F/E_0 \) and \( E_0 = \frac{2\pi\hbar^2}{md_0^2} \) we find using \( D_0 = d_0(E = 0) \) the size effect

\[
D_0 = \sqrt{\frac{2\pi\hbar^2}{mE_F}}.
\]  

(B.17)

For wires with diameter less than this the Young’s modulus is zero in the model. For gold we obtain from this formula \( D_0 = 0.3 \text{ nm} \). Replacing a sum by an integral we have

\[
\sum_{n=1}^{N} n\sqrt{N-n} \approx \frac{4}{15} \left( N^{5/2} - N \right).
\]  

(B.18)

Using this approximation we then obtain the spring constant of the unbent wire including the size effect as

\[
k_0 = \sqrt{\frac{2\nu^2}{5\pi^2}} \sqrt{\frac{d_0^2 m^3 E_F^5}{\hbar^6}} \left( \frac{d_0}{L} \right)^3 \left( 1 - \frac{D_0^3}{d_0^3} \right).
\]  

(B.19)

We see that if \( \nu = 0 \) this formula yields \( k_0 = 0 \). This because of that the cross sectional area then does not change when the wire bends. A beam of length \( L \) with a perpendicular force \( F \) applied at the end bends the distance \( Z \):

\[
Z = \frac{F_{bend} L^3}{3E_{bend} I} = \frac{k_0 Z L^3}{3E_{bend} I},
\]  

(B.20)

where \( E_{bend} \) is the Young’s modulus for the cantilever and \( I \) is the moment of inertia of the beams cross section. \( I = d_0^4/12 \) for a beam of square cross section. \( F = k_0 Z \), and \( k \) is in turn the transverse spring constant of the wire. Eqs. (B.19) and (B.20) yields an expression for \( E_{bend} \) neglecting the size effect:

\[
E_{bend} = \frac{4\sqrt{2\nu^2}}{5\pi^2} \sqrt{\frac{m^3 E_F^5}{\hbar^6}}.
\]  

(B.21)

This formula yields a value of Young’s modulus for a cantilever wire which may differ from the value obtained by stretching the wire due to the different mechanisms that changes the cross sectional area. Because \( D_0 \) is very small, the size effect may be neglected for most nanowires.
Next we try calculating the stretching of a nanowire. Blom et al. [8] calculated the force using a free electron model when stretching out a wire with the same cross section area along the wire using Poisson’s ratio $\nu = \frac{1}{2}$. For such a wire but with an arbitrary $\nu$ we have the volume $V$ at length $L$ (and cross sectional area $S$) starting from the volume $V_0$ at length $L_0$ (and area $S_0$):

$$V = V_0 \left( \frac{L}{L_0} \right)^{1-2\nu}. \quad (B.22)$$

To obtain this we have used $V/V_0 = LxLyLz/(Lx_0Ly_0Lz_0)$ and taking the logarithm.

Using the strain $\varepsilon = \ln(L/L_0)$ for every component and $\varepsilon_x = \varepsilon_y = -\nu \varepsilon_z$ we obtain Eq. (B.22). Starting from Eq. (B.9) using $F = \frac{\partial \Omega}{\partial L}$ and performing the calculations in Blom et al. for an arbitrary $\nu$ we find (for voltage $U = 0$ over the wire, see ref. [55] when $U$ is not zero)

$$F_{\text{stretch}} = -\sum_{n=1}^{N} \sqrt{\frac{2m}{\pi^2 \hbar^2}} \left( \frac{4}{3} (E_F - E_n)^{3/2} - 4\nu E_n \sqrt{E_F - E_n} \right), \quad (B.23)$$

where we have used the asymptotic energy eigenvalues

$$E_n = \frac{\hbar^2}{2m} \frac{4\pi}{S_n} = \frac{\hbar^2}{2m} S_0 \left( \frac{L}{L_0} \right)^{2\nu} n. \quad (B.24)$$

Replacing the sums in (B.23) by integrals for not too small $N$ we find

$$F_{\text{stretch}} = -\frac{4\sqrt{2}}{15\pi^2} S_0 \left( \frac{L_0}{L} \right)^{2\nu} (1 - 2\nu) \sqrt{\frac{m^3 E_F^2}{\hbar^6}}. \quad (B.25)$$

We see that $F_{\text{stretch}}$ decreases when $L$ increases. Using $\Delta L = L - L_0$ we can write

$$\left( \frac{L_0}{L} \right)^{2\nu} = \left( \frac{L_0}{L_0 + \Delta L} \right)^{2\nu} \approx 1 - 2\nu \frac{\Delta L}{L_0}, \quad (B.26)$$

for $\Delta L/L_0$ much less than one, that is for small strain. The strain $\varepsilon = \ln(L/L_0)$ yields

$$L = L_0 e^{\varepsilon} \approx L_0 e^{\frac{\Delta L}{L_0}} \approx L_0 \left( 1 + \frac{\Delta L}{L_0} \right), \quad (B.27)$$

for small strain. We have $\sigma = E_{\text{stretch}} \varepsilon$ and $F_{\text{stretch}} = \sigma S$, so for a small $\Delta L/L_0$

$$F_{\text{stretch}} \approx F_0 + E_{\text{stretch}} S_0 \frac{\Delta L}{L_0}. \quad (B.28)$$

Using Eqs. (B.25), (B.26), (B.27) and (B.28) we identify the Young’s modulus for the Blom wire

$$E_{\text{stretch}} = 2\nu \frac{4\sqrt{2}}{15\pi^2} (1 - 2\nu) \sqrt{\frac{m^3 E_F^2}{\hbar^6}}. \quad (B.29)$$
Table B.1: Poisson’s ratio $\nu$, Fermi energy $E_F$ and calculated Young’s modulus for different metals. Using $\nu$ and $E_F$ in the table, we calculate using the free electron model Young’s modulus when stretching the wire $E_{\text{stretch}}$ and $E_{\text{bend}}$ when bending the cantilever wire, from Eqs. (B.29) and (B.21) respectively. Free electron bulk values $E_{\text{bulk}}$ from Eq. (B.31).

<table>
<thead>
<tr>
<th></th>
<th>$\nu$</th>
<th>$E_F$ (eV)</th>
<th>$E_{\text{stretch}}$ (GPa)</th>
<th>$E_{\text{bend}}$ (GPa)</th>
<th>$E_{\text{bulk}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.37 [56]</td>
<td>5.48 [57]</td>
<td>3.94</td>
<td>8.41</td>
<td>26.6</td>
</tr>
<tr>
<td>Al</td>
<td>0.35 [56]</td>
<td>11.6 [57]</td>
<td>28.0</td>
<td>49.1</td>
<td>200</td>
</tr>
<tr>
<td>Au</td>
<td>0.44 [56]</td>
<td>5.51 [57]</td>
<td>2.20</td>
<td>12.1</td>
<td>12.5</td>
</tr>
<tr>
<td>Be</td>
<td>0.032 [56]</td>
<td>14.3 [53]</td>
<td>13.5</td>
<td>0.692</td>
<td>1054</td>
</tr>
<tr>
<td>Bi</td>
<td>0.33 [56]</td>
<td>1.58 [53]</td>
<td>0.205</td>
<td>0.299</td>
<td>1.56</td>
</tr>
<tr>
<td>Ca</td>
<td>0.31 [56]</td>
<td>4.68 [57]</td>
<td>3.25</td>
<td>3.98</td>
<td>26.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.30 [56]</td>
<td>7.46 [57]</td>
<td>10.7</td>
<td>12.0</td>
<td>88.9</td>
</tr>
<tr>
<td>Cu</td>
<td>0.34 [56]</td>
<td>7.00 [57]</td>
<td>8.22</td>
<td>13.1</td>
<td>60.4</td>
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<tr>
<td>Fe</td>
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<td>11.1 [53]</td>
<td>29.2</td>
<td>30.2</td>
<td>251</td>
</tr>
<tr>
<td>Mg</td>
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<td>7.13 [57]</td>
<td>9.64</td>
<td>9.98</td>
<td>83.1</td>
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<tr>
<td>Nb</td>
<td>0.40 [56]</td>
<td>5.32 [53]</td>
<td>1.83</td>
<td>9.13</td>
<td>19.0</td>
</tr>
<tr>
<td>Pb</td>
<td>0.44 [56]</td>
<td>9.37 [57]</td>
<td>8.27</td>
<td>45.5</td>
<td>47.0</td>
</tr>
<tr>
<td>Sn</td>
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<td>10.0 [57]</td>
<td>18.6</td>
<td>35.8</td>
<td>129</td>
</tr>
<tr>
<td>Sr</td>
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<td>3.95 [57]</td>
<td>2.23</td>
<td>2.13</td>
<td>19.9</td>
</tr>
<tr>
<td>Tl</td>
<td>0.45 [56]</td>
<td>8.15 [53]</td>
<td>4.98</td>
<td>33.6</td>
<td>27.7</td>
</tr>
<tr>
<td>Zn</td>
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<td>9.39 [57]</td>
<td>19.7</td>
<td>14.8</td>
<td>197</td>
</tr>
</tbody>
</table>

Comparing (B.21) with (B.29) we see that the dependency on $E_F$ are the same in the two formulas but the dependency on Poisson’s number $\nu$ are different. In the cantilever case Young’s module increases as $\nu^2$, but in the elongation due to stretching case Young’s modulus is proportional to $\nu (1 - 2\nu)$. For metal in bulk we have the well known free electron bulk modulus $B$, see ref. [53, 57].

$$B = \frac{4\sqrt{2}}{9\pi^2} \sqrt{\frac{m^3 E_F^5}{\hbar^6}}, \quad \text{(B.30)}$$

We then obtain

$$E_{\text{bulk}} = \frac{4\sqrt{2}}{3\pi^2} (1 - 2\nu) \sqrt{\frac{m^3 E_F^5}{\hbar^6}}, \quad \text{(B.31)}$$

using $E_{\text{bulk}} = 3B (1 - 2\nu)$, see ref. [58]. For macroscopical materials we have $E_{\text{stretch}} = E_{\text{bend}} = E_{\text{bulk}}$. For our nanowires we have found

$$E_{\text{stretch}} = \frac{18}{15} B\nu (1 - 2\nu), \quad \text{(B.32)}$$

$$E_{\text{bend}} = \frac{9}{5} B\nu^2. \quad \text{(B.33)}$$

When $\nu = \frac{2}{7} \approx 0.286$ the two formulas yields the same result. Note the large differences in $E$ for beryllium (Be) in Table B.1 due to the metal’s low Poisson’s ratio $\nu = 0.032$. 

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50 Metallic nanowires: differences between stretching and bending