

Title

Subtitle

by

Mikkel Metzsch Jensen

THESIS

for the degree of

MASTER OF SCIENCE



Faculty of Mathematics and Natural Sciences
University of Oslo

Spring 2023

Title

Subtitle

Mikkel Metzsch Jensen

© 2023 Mikkel Metzsch Jensen

Title

<http://www.duo.uio.no/>

Printed: Reprosentralen, University of Oslo

Abstract

Abstract.

Acknowledgments

Acknowledgments.

Contents

List of symbols?	vii
Introduction	1
0.1 Motivation	1
0.1.1 Friction	1
0.1.2 Thesis	1
0.2 Approach	1
0.3 Objective of the study	2
0.4 Contributions	2
0.5 Thesis structure	2
1 Background Theory and Method	3
1.1 Tribology - friction	3
1.1.1 Macroscale	3
1.1.1.1 Amontons' law	3
1.1.2 Microscopic scale	4
1.1.2.1 Surface roughness - Asperity theories	4
1.1.3 Nanotribology - Atomic scale	5
1.1.3.1 Tomlinson model	5
1.1.3.2 Frenkel-Kontorova (FK)	6
1.1.3.3 FK extension: Frenkel-Kontorova-Tomlinson (FKT)	8
1.1.3.4 Other stuff	8
1.1.4 Multi scale models?	9
1.1.5 Summary of expected frictional properties	9
1.1.6 Graphene friction	9
1.1.6.1 Experimental procedures	9
1.2 Molecular Dynamics	10
1.2.1 Potentials	10
1.2.1.1 General formulation of potentials...?	10
1.2.2 Lennard Jones	10
1.2.3 Stillinger weber	11
1.2.4 Tersoff	12
1.2.5 LAMMPS	13
1.2.6 Integration	13
1.2.6.1 Velocity Verlet	13
1.2.7 Thermostats	14
1.2.7.1 Implementing Langevin	17
1.2.7.2 MD limitations	17
1.3 Defining the system	17
1.3.1 Groups: Sheet, pullblocks and substrate	17
1.3.1.1 Pressure reference	19
1.3.2 Creating sheets	19
1.3.2.1 Grapheme	19
1.3.2.2 Indexing	20

1.3.2.3	Removing atoms	21
1.3.3	Pull blocks	22
1.3.4	Kirigami inspired cut out patterns	22
1.3.4.1	Pop-up pattern	22
1.3.4.2	Honeycomb	22
1.3.4.3	Random walk	22
1.4	Fourier Transform (light)	22
1.4.1	Real life experimental procedures	23
1.5	Machine Learning (ML)	23
1.5.1	Feed forward network / Neural networks	23
1.5.2	CNN for image recognition	23
1.5.3	GAN (encoder + deoder)	23
1.5.4	Inverse desing using machine learning	23
1.5.5	Prediction explanation	23
1.5.5.1	Shapley	23
1.5.5.2	Linearariations	23
1.5.5.3	LRP	23
1.5.5.4	t-SNE	23

List of symbols?

Maybe add list of symbols and where they are used like Trømborg.

Introduction

0.1 Motivation

0.1.1 Friction

Friction is a fundamental force that takes part in almost all interactions with physical matter. Even though the everyday person might not be familiar with the term “friction” we would undoubtedly notice its disappearance. Without friction, it would not be possible to walk across a flat surface, lean against the wall or secure an object by the use of nails or screws (Static friction allows us to join objects together using screws [1][p. 5]). Similarly, we expect a moving object to eventually come to a stop if not supplied with new energy, and we know intuitively that sliding down a snow covered hill is much more exciting than its grassy counterpart. It is probably safe to say that the concept of friction is well integrated in our everyday life to such an extent that most people take it for granted. However, the efforts to control friction dates back to the early civilization (3500 B.C.) with the use of the wheel and lubricants to reduce friction in translational motion [2]. Friction is a part of the wider field tribology derived from the Greek word *Tribos* meaning rubbing and includes the science of friction, wear and lubrication [2].

The most important motivation to study tribology is ultimately to gain full control of frictional and wear for various technical applications. Especially, reducing friction is of great interest as this has tremendous advantages regarding energy efficiency. It has been reported that the monetary value of tribological problems has significant potential for economic and environmental improvements [3]:

“On global scale, these savings would amount to 1.4% of the GDP annually and 8.7% of the total energy consumption in the long term.” [4].

The reduction of friction is not the only sensible application as a controlled increase in friction might be of interest in the development of grasping robots or perhaps breaking system (get some sourced examples maybe...).

0.1.2 Thesis

In this thesis we investigate the possibility to control the frictional properties of a graphene sheet by applying strategically positioned cuts to the sheet inspired by kirigami. Kirigami is a variation of origami where the paper is cut additionally to being folded. Hanakata et al. [5] has shown that kirigami inspired cuts on a graphene sheet can be used to alter the yield strain and yield stress of the sheet. They observed that the stretching of the cutted sheet induced a out-of-plane buckling which serves as a key observation for the motivation of this thesis. It is currently well established/believed that the friction between two surfaces is proportional to the real microscopic contact area (source here?). Hence, one can hypothesize that the buckling of the sheet will affect the contact area and consequently the frictional properties.

0.2 Approach

In the study by Hanakata et al. [5] they used a machine learning (ML) approach to overcome the complexity of the nonlinear effects arising from the out-of-plane buckling which made them successfully map the cutting patterns to the mechanical properties of yield and stress. The dataset used for the ML training was generated by molecular dynamics (MD) simulations for a limited set of cut configuration. By training the network the MD simulations could effectively be skipped all together making for an accelerated search through new cut configurations for certain mechanical properties. By setting up a MD simulation that quantifies the frictional

properties of the graphene sheet we aim to make an analog study regarding the search for certain frictional properties.

We will take this one step further by creating a GAN network that utilises the latter network for creating an inverse design framework. That is, a network that takes frictional properties as input and return the corresponding cut configuration. By having such a tool we can execute a targeted search for exotic frictional properties. Particularly, we are interested in nonlinear and possibly even negative friction coefficients. Friction is essentially observed to increase with increasing load on the frictional surface, and we often describe this as having a positive friction coefficient. However, if we are able to couple the stretching of the sheet with friction we might be able to break this barrier for the coefficient. By imagining some nanomachine which translates downward pressure into either compression or expansion of the altered graphene, we could have a coupling between downward pressure and stretch of the sheet. In that case, a friction force depending on stretch could effectively be made to decrease with increasing load which would correspond to a negative friction coefficient following this definition (formulate such that we do not imply free acceleration from nothing).

One of the features from inverse design, separating it from the general class of ML approaches, is that we do not depend on trusting the ML predictions. While a standard neural network might be extremely efficient on a certain prediction task we have usually no information on how these predictions are based. We say that the internal workings of the network is a black box beyond our capacity of interpretation. However, for the inverse design problem we are prompted with a few promising design proposals which can immediately be tested in the MD simulations which we will regard as the most reliable predictor in this setting. Hence, if arriving at a successful design in alignment with our search prompt, we can disregard any uncertainty in the network. In that case the remaining gap to bridge is that of the MD simulation and real life implementations.

0.3 Objective of the study

1. Design a MD simulation to evaluate the frictional properties of the graphene sheet under different variations of cut patterns, stretching and loading, among other physical variables.
2. Train a network to replace the MD simulation completely.
3. (Variation 1) Do an accelerated search using the ML network for exotic frictional properties such as low friction coefficients and a strong coupling between stretch and friction.
4. (Variation 2) Make a GAN network using the first network and predict cut configurations for some of the above mentioned frictional properties.
5. (If I have time) Make a nanomachine that couples load and stretch (perhaps just artificially without any molecular mechanism) to test the hypothesis of a negative friction coefficient.

0.4 Contributions

What did I actually achieve

0.5 Thesis structure

How is the thesis structured.

Chapter 1

Background Theory and Method

Small introtext to motivate this chapter. What am I going to go over here.

1.1 Tribology - friction

Friction is a part of the wider field tribology which includes the study of friction, wear and lubrication between two surfaces in relative motion [1, p. 1]. In this thesis we will only concern ourselves with dry friction (no lubrication) without any wear. Tribological systems take place across a broad range of time and length scales, ranging from geological stratum layers involved in earthquakes [3] to microscopic atomistic processes, as in the gliding motion of nanocluster of a nanomotor [6].

This vast difference in scale gives rises to different frictional mechanism being dominating at different scale. On a macro scale the system is usually (tested) under large loads and speeds leading to high contact stresses and wear, while the micro/nano-scale systems on the other hand operate under relatively low loads and speeds with negligible wear [3] [2, p. 5]. While macroscale friction is often reduced into a few variables such as normal load, material type, speed and surface roughness it is clear that micro/nanoscale friction cannot be generalized under this simple representation. On a micro/nano scale the surface properties dominate the tribological properties and the systems will additionally be sensitive to temperature, humidity and even sliding history. The works of Bhushan and Kulkarni (1996)[7] showed that the friction coefficient decreased with scale, revealing the change in the mechanism of friction as the contact condition was altered, even for the same type of material used.

The phenomenological descriptions of macroscale friction cannot yet be derived from the fundamental atomic principles and bridging the gap between different length scales in tribological systems remains an open challenge [6]. Hence, the following sections will be divided into macro, micro and nanoscale representing the different theories at each scale governing the understanding of friction. Our study is going to take place at the nanoscale, but since any application will eventually take action on a macroscopic level, the multi scale understanding serves as useful way to bridge expectations into real life (does this make sense?)

1.1.1 Macroscale

Our working definition of macroscale is everything on the scale of visible everyday objects. We want to make a distinction to microscopic where the prefix indicates the size of micrometers m^{-6} and hence essentially assign everything larger than that into the term macroscale¹.

1.1.1.1 Amontons' law

In order to start and keep a solid block moving against a solid surface we must overcome certain frictional forces F_{fric} [1]. The static friction force F_s corresponds to the minimum tangential force required to initiate the sliding while the kinetic friction force F_k corresponds to the tangential force needed to sustain such a sliding at steady speed. The work of Leonardo da Vinci (1452–1519), Guillaume Amontons (1663–705) and Charles de Coulomb (1736–1806) all contributed to the empirical law, commonly known Amontons' law, which states these frictional

¹The width of a human hair is on the length scale 10^{-5} to 10^{-4} m which constitute a reasonable boundary between macro- and microscale as this is at the lower boundary of what we can perceive.

forces is entirely independent of contact area and sliding velocity (at ordinary sliding velocities). Instead, it relies only on the normal force F_N , acting perpendicular to the surface, and the material specific friction coefficient μ as

$$F_{\text{fric}} = \mu F_N.$$

The friction coefficient is most often different for the cases of static μ_s and kinetic μ_k friction, usually with values lower than one and $\mu_s \geq \mu_k$ in all cases [p. 6][1].

Statistical mechanics provides a general explanation for the phenomena of friction [6]: A system in equilibrium has its kinetic energy uniformly distributed among all its degrees of freedom (equipartition of energy).

When a macroscale object is sliding in a given direction it is clearly not in equilibrium since one of its degrees of freedom carries considerable more kinetic energy. Thus, the system will have a tendency to transfer the kinetic energy to the remaining degrees of freedom as heat while slowing down as a result. Hence friction is really the tendency of systems toward equilibrium energy equipartitioning among many interacting degrees of freedom. When friction occurs under an external force energy is reversed into the system in the form of frictional heat which will dissipate. [6]

Although Amontons' law is a common base for understanding friction on a macroscopic it has its limitations. For instance, it turns out that static friction is not time independent, but depends on the so-called contact history with increasing friction as the logarithm of time of stationary contact [8]. For the kinetic friction the independency of sliding velocity disappears at low velocities as thermal effects becomes important and for high velocities due to inertial effects. [1][pp. 5-6]. Additionally, this simple macroscale perspective disguises (better word) the underlying mechanism behind the friction phenomena arising from a more complicated contact interface. This includes taking the microscopic roughness into account together with surface chemistry. This more complex perspective introduces new (...) as real contact area, contact stresses, surface adhesion which makes frictional properties dependent on sliding speed, temperature and environment in general [3].

Friction phenomena take place across a broad range of time and length scales, from microscopic atomistic processes, as in the gliding motion of a nanocluster or a nanomotor [1]

The conclusion is that the friction coefficient is not an intrinsic physical property [9].

1.1.2 Microscopic scale

Going beyond a macroscopic perspective to the microscopic scale we realise that most surfaces is in fact rough (Bowden, F. P. & Tabor, D. The Friction and Lubrication of Solids (Clarendon, 1950).). The contact between two surfaces consist of numerous smaller contact point, so-called asperities, for which the friction between two such opposing surfaces involves interlocking of those asperities. Additionally, the adhesion between surfaces is taken to be a dominant factor, for which the chemical state of the surfaces has to be considered.

1.1.2.1 Surface roughness - Asperity theories

Asperity theories is based on the observation that microscopic rough surfaces with contacting asperities, each with a contact area of A_{asp} , will have a true contact area $\sum A_{\text{asp}}$ which is found to be much smaller than the apparent macroscopic area A_{macro} . The friction force was shown to be proportional (extra source on this) to this true contact area as

$$F_{\text{fric}} = \tau \sum A_{\text{asp}},$$

where τ is an effective shear strength of the contacting bodies. This is still compatible with Amontons' law for the cases where the real contact area dependt linearly on the applied normal force F_N .



Figure 1.1: Example figure showing asperity deformation as the load is increased from top to bottom. Source: [`https://en.wikipedia.org/wiki/Asperity_\(materials_science\)`](https://en.wikipedia.org/wiki/Asperity_(materials_science)) Put in reference list? Find better picture?

Thus, many studies have focused on the individual single asperity contact to reveal the relationship between the contact area and F_N (13–15 from [10]). By assuming perfectly smooth asperities with radii of curvature from nanometers to micrometres continuum mechanics can be used to predict the deformation of asperities as normal force is applied. A model for non-adhesive contact between homogeneous, isotropic, linear elastic spheres was first developed by Hertz (17 [10]), which predicted $A_{asp} \propto F_N^{2/3}$. Later adhesion effects were included in a number of subsequent models, including Maugis-Dugdale theory (18 from [10]), which also predicts a sublinear relationship between A_{asp} and f_N , leading to a similar sublinear relationship for $F_{fric}(F_N)$. (Address that this deviates with the macroscale).

What about multi asperity theory?

However, even though the successes of continuum mechanics there is no reason to believe that it will be capable of reproducing tribological behaviour at the nanometre length scale where the discreteness of atoms often has a direct effect on physical properties [9].

This approach enables the bottom-up derivation of the linear scaling laws of macroscopic friction with size, and their transition to the sublinear ones for incommensurate nanosized contacts. We can now understand that such transition takes place when the contact roughness becomes large compared to the range of interfacial interactions [162] [6].

1.1.3 Nanotribology - Atomic scale

On the smallest possible scale, atomic scale, the surfaces does not have structural asperities. Instead, atomic level friction is being modelled as a consequence of the rough potential of the atomic landscape and real contact area defined in terms of atomic bonding.

1.1.3.1 Tomlinson model

One of the first atomic scale models. Here we have no asperities but it is based on the assumptions that the atomic surface is not completely smooth. Since atoms was modelled as spheres the surface topography would not be completely flat. The idea is shown in figure 1.2 where the moving body is connected the atom with springs.

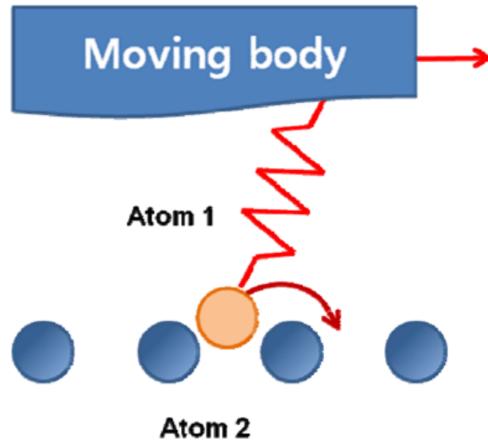


Figure 1.2: Temporary figure from [3]

This model gives an explanation to the stick-slip behaviour. This layed the foundation for the Frenkel-Kontorova model so maybe go straight to that?

1.1.3.2 Frenkel-Kontorova (FK)

The FK model builds upon the time-honored PT model describing a point-like tip sliding over a space-periodic crystalline surface. The FK model extents this description to hat of two 1D crystalline surfaces sliding on top of eahc other. The standard FK model consists of a 1D chain of N classical particles, representing atoms, interacting via a hamornic forces and movig in a sinusoidal potential as sketched in figure 1.3. The hamiltonian is

$$H = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + \frac{1}{2}K(x_{i+1} - x_i - a_c)^2 + \frac{1}{2}U_0 \cos\left(\frac{2\pi x_i}{a_b}\right) \right], \quad (1.1)$$

where the first term $p_i^2/2m$ represents the kinetic energy with momentum p and mass m . The next term describes the harmonic interaction with elastic constant K , nearest neighbour distance $\Delta x = x_{i+1} - x_i$ with a correspnding equilibrium distance a_c . The final term represents the periodic substrate potential with amplitude U_0 and period a_b .

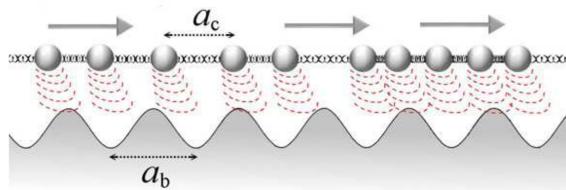


Figure 1. A sketch of the FK model, showing the two competing lengths: the average interparticle spacing and the lattice periodicity of the substrate.

Figure 1.3: Temporary figure from [6]

By applying an external force to the chain one can use the FK model to investigate static friction. The sliding properties are entirely governed by its topological excitations referred to as so-called kinks and anti-kinks

Commensurability We can describe the interactions of the model in a commensurate or incommensurate case. Let us begin with the commensurate case where the spacing of the atoms matches perfectly the substrate potential periodicity, i.e. $a_c = a_b$. The ground state (GS) is the configuration where each atom fits in one of

the M minima in the substrate potential such that the coverage, $\Theta = N/M = a_b/a_c$, equals 1. By adding an atom we would excite the system with a so-called kink excitation (two atoms share the same potential well) while subtracting an atom results in an antikink excitation (one potential well becomes atomless). In order to reach a local minimum the kink (antikink) will expand in space over a finite length such that the chain is imposed a local compression (expansion). When applying a tangential force to the chain it is much easier for a kink to move along the chain than it is for atoms since the activation energy ϵ_{PN} for a kink displacement is systematically smaller (often much smaller) than the potential barrier U_0 . Thus the motion of kinks (antikinks), i.e. the displacement of extra atoms or vacancies, is representing the fundamental mechanism for mass transport. In the ideal zero temperature case with adiabatically (right term?) increase in force all atoms would be put into an accelerating motion as soon as the energy NU_0 is present. However, in reality any thermal excitation would excite the system with the creation of kink-antikink pairs that would travel down the chain. For a chain of finite length these often occur at the end of the chain running in opposite direction. As the kinks travels by the atoms is advanced by one atom spacing a_b along the force direction. This cascade of kink-antikink excitations is shown in figure 1.4

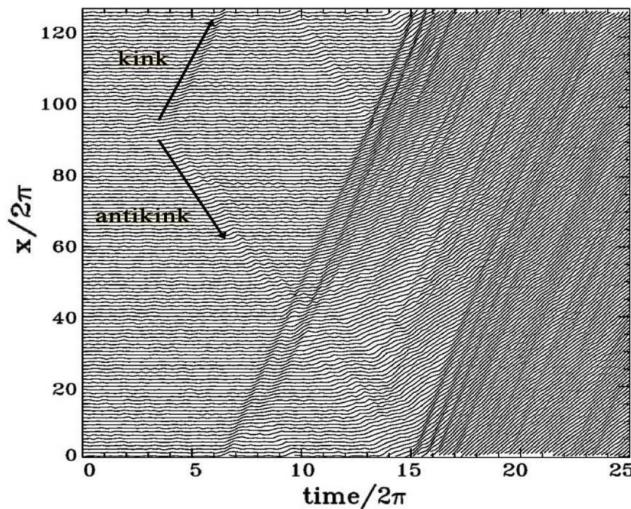


Figure 2. Time dependence of the atomic trajectories for the fully matched ($\theta = 1$) FK model at the (low-temperature) onset of depinning. Motion starts with the nucleation of a kink-antikink pair. The kink and the antikink depart in opposite directions cross the periodic boundary conditions, and collide quasielastically. A second kink-antikink pair forms in the wake of the initial kink. Further kink-antikink pairs are generated, with an avalanche-like increase of the kink-antikink concentration, eventually leading to a sliding state. Adapted from Ref. [21], Copyright (1997) by The American Physical Society.

Figure 1.4: **Temporary** figure from [6]

For the 2D case where an island is deposited on a surface, in our case the graphene sheet on the Si substrate, we generally expect the sliding to be initiated by kink-antikink pairs at the boundary.

For the case of incommensurability, i.e. $\theta = a_b/a_c$ is irrational, the GS is characterized by a sort of ‘‘staircase’’ deformation. That is, the chain will exhibit regular periods of regions where the chain is slightly compressed (expanded) to match the substrate potential, separated by kinks (antikinks), where the increased stress is eventually realized through a localized expansion (compression) as illustrated in figure 1.5.



Figure 1.5: **Temporary** figure from url`http://www.iop.kiev.ua/obraun/myreprints/surveyfk.pdf` p. 14. Incommensurable case ($\theta = ?$) where atoms sits slightly closer than otherwise dictated by the substrate potential for which this regularly result in a kink here seen as the presence of two atoms closeæy together in on of the potential wells.

The incommensurable FK model contains a critical elastic constant K_c , such that for $K > K_c$ (infinite chain, right?) the static friction F_s drop to zero (article says low-velocity kintetic friction as well which I do not get for no temperature?), making the chain able to slide at no energy cost. This can be explained by the fact that the displacement accouring in the incommensurable case will yield one atom climbing up a corrugation (introduce this word earlier) for every atom clibing down on. In turns out that this will exactly balance the energy making it non-resistant to sliding. Generally, incommensurability guarantees that the total energy (for $T = 0$) is independent of the relative position to the potential. However, when sliding freely a single atom will eventually occupy a maximum of the potential. When increasing the potential magnitude U_0 of softning the chain stiffness, lowering K , (the probability for a particle to occupy that position drops from a finite value to exactly zero, how can this work for zero temp?) this is no longer possible, which is described by the Aubry transition. The phase transistion is marked by the critical elastic constant $K = K_c$ where the chain goes from free sliding to a pinned state with a nonzero static friction. K_c is a discontinuous function of the ratio θ , due to the reliance on irrational numbers for incommensurability (?), get plot of this?). The minimal value $K_c \simeq 1.0291926$ in units $[2U_0(\pi/a_b)^2]$ is achieved for the golden-mean ratio $\theta = (1 + \sqrt{5}/2)$ (compare to my model?). The pinning is provided despite translational invariance by the inaccessibility to move past the energy barrier which act as dynamical constraint. The Aubry transistion can be invistigated as ?-order phase transistion for which power laws can be defined for the order parameter (beyond the scope of this thesis).

The phenonema of non pinned configurations is named *superlubricity* in trobological context. Despite the misleading name this refers to the case where the static friction is zero while the kinetic friction is only reduced but nonzero.

Experimentally superlubricity has been studied for a graphene flake (single layer) sliding over a graphite surface (multiple layers) where the friction force was extremely weak (50 pN) for orientations between flake and substrate yielding incommensurability.

When considering the nonzero temperature case for the FK model one would have to add a thermostat such as the Langevin thermostat (see theory section ?). Thermal fluctuations can then overcome pinning effects even in fully commensurate cases. This also give rise to a damping force proportional to sliding velcoty as a mean of modelling the dissipitive force accouring.

By applying a finite driving force it is known that a pinned configuration will go through several first-order dynamical pahse transistions as the system transfers from a pinned to a sliding state.

1.1.3.3 FK extension: Frenkel-Kontorova-Tomlinson (FKT)

Several extensions has been provided for the FK model with modifications of the interactions or system dimensionality. Anharmonicity of the chain

However, Weiss and Elmer (1995) proposed that the model had a deficiency. They suggested that in the FK model, there was no connection between the atoms and the sliding body. Therefore, Frenkel-Kontorova-Tomlinson (FKT) model that combines the FK model with the Tomlinson model was proposed. [3]

1.1.3.4 Other stuff

At nanoscales things get a bit more unclear. SFM (explain) experiments have reported (copy sources 5, 6, 21 from [10]) where $F_f \propto F_N$ or even with these quantities being nearly independent of each other.

Physically relevant quantities, including the average friction force, the slider and the lubricant mean velocities, several correlation functions, and the heat flow can be evaluated numerically by carrying out suitable averages over the model dynamics of a sliding interface, as long as it is followed for a sufficiently long time. The modeling of friction must first of all address correctly ordinary equilibrium and near-equilibrium phenomena, where the

fluctuation-dissipation theorem (Sec. 2) governs the smooth conversion of mechanical energy into heat, but most importantly it must also deal with inherently nonlinear dissipative phenomena such as instabilities, stick-slip, and all kinds of hysteretic response to external driving forces, characteristic of non-equilibrium dynamics. [6]

In several works by J. Fineberg's group [2–4] the transition from sticking to sliding is characterized by slip fronts propagating along the interface. [11][p. 2].

1.1.4 Multi scale models?

[6] p. 24.

1.1.5 Summary of expected frictional properties

1. Smooth kinetic friction generally increase with speed [6]. so-called velocity strengthening. Logarithmic with speed
2. Friction coefficients on the scale 0.01 to 0.03.
3. Occurrence of stick slip (also in MD) [3] (p. 146)

Should period match the lattice spacing as described in [3][p. 144]

Maybe talk about the slip line as shown in figure 1.6

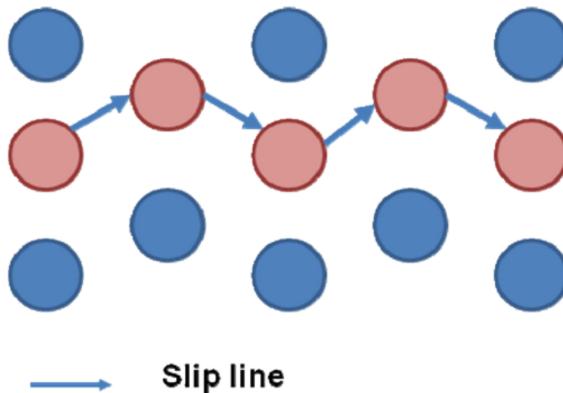


Fig. 5 Schematic of zigzag motion of the AFM tip in 2-dimensional atomic-scale stick-slip model [adapted from 32]

Figure 1.6: Temporary figure from [3][p. 144]

1.1.6 Graphene friction

Theory of friction experiment involving graphene.

Because of this frictional reduction, many studies indicate graphene as the thinnest solid-state lubricant and anti-wear coating [104–106]. (Current trends in the physics of nanoscale friction)

Accurate FFM measurements on few-layer graphene systems show that friction decreases by increasing graphene thickness from a single layer up to 4–5 layers, and then it approaches graphite values [97, 99, 101, 107, 108]. (Current trends in the physics of nanoscale friction)

1.1.6.1 Experimental procedures

- Atomic Force Microscope (AFM)

1.2 Molecular Dynamics

Maybe also ‘‘Computer Simulations 7 of Nanometer-Scale Indentation and Friction’’ from [12]

Read [6][p. 18]

A promising compromise could possibly be provided by the so-called reactive potentials [120–122], capable of describing some chemical reactions, including interface wear with satisfactory computational efficiency in large-scale atomic simulations, compared to semi-empirical and first-principles approaches. [6]

- MD simulation (classical or ab initio)
- Basics of classical MD simulations: Integration and stuff
- Ab initio simulation (quantum mechanics, solving schrödinger)

1.2.1 Potentials

The choices of potentials used in the MD simulation is mainly based on the on [13] which have a somewhat similar MD friction simulation, the difference being that they impose a Si-tip on the graphene sheet supported by a Si-substrate where we impose drag the whole sheet upon the substrate. Nonetheless this serves as a good anchor for the methodology of the setup. The covalent bonds of C-C in graphene and Si-Si in the substrate is described by the Tersoff and Stillinger–Weber potentials, respectively. A typical 12-6 Lennard–Jones potential is used to describe the van der Waals adhesive interaction between graphene and the substrate.

1.2.1.1 General formulation of potentials...?

On a general note we can generalize the n-body potential as the expansion in orders of participating atoms as

$$E = \sum_i V_1(\mathbf{r}_i) + \sum_{\substack{i,j \\ i < j}} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{\substack{i,j,k \\ i < j < k}} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots$$

where \mathbf{r}_n is the position of the n th particle and V_m is called an m -body potential [14]. The first one-body term corresponds to an external potential, followed by the two-body term, the three-body term and so on. The simplest model that includes particle interaction is the pair potential truncating the expansion after the two-body term. A general feature of the pair potentials is that they favor close-packed structures which is unsuited to describe covalent bonds that take more open structures. In particular, pair potentials are completely inapplicable to strongly covalent systems such as semiconductors [14]. In order to accomodate the description of covalent bonds the natural step is thus to include the next step of the expansion, the three-body terms, as we will see for the modeling of the graphene sheet C-C bonds and the Silicon sheet Si-Si bonds. For the interaction between the sheet and the substrate we can nojes med a Lennard Jones pair potential describing the non-bonded van der Waals interaction.

1.2.2 Lennard Jones

This sections is based on [[15], [16], [17]].

The Lennard-Jones (LJ) model is probably one of the most famous pair potentials used in MD simulations. LJ models the potential energy between two non-bonding atoms based solely on interatomic distance r . The model accounts for attractive forces arising from dipole-dipole, dipole-induced dipole and London interactions, and repulsive forces that capture the hard core (is this safe to say?) of overlapping wave functions at small distances. Thus it is assumed neutrally charged atoms and was originally proposed for noble gases. The classical 12-6 version of the model (refering to the power law of the repulsive and attractive forces respectively) reads

$$E = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad r < r_c, \quad (1.2)$$

where r is the interatomic distance with cut-off r_c , ϵ is the depth of the potential well and σ the distance where the potential is zero. By solving for the potential minimum ($dE/dr = 0$) we find the equilibrium distance to

be $r_0 = \sigma 2^{1/6}$. This makes for an even clear interpretation of σ which effectively sets the equilibrium distance between atoms, i.e. the dividing line for which the net force is repulsive or attractive. While the LJ model in many ways is an oversimplified model that is insufficient in its description of ... (get source and concrete examples) it is commonly used as a model for intermaterial interactions (between moving object and substrate) in friction studies [[13], [18], [3]].

1.2.3 Stillinger weber

This section is based on [[19], [20]]

The stillinger weber potential takes the form of a three body potential

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}),$$

where r_{ij} denotes the distance between atom i and j and θ_{ijk} the angle between bond ij and jk . The summations is over all neighbours j and k of atom i within a cut-off distance $r = a\sigma$.

The two-body term ϕ_2 builds from the LJ model with the addition of an exponential cutoff term

$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right). \quad (1.3)$$

The model parameters A , ϵ , B , σ , p , q and a comes with i, j indices to indicate that these parameters should be specified for each unique pair of atom types. However, in our case we will only provide a single value for each model parameter as we are exclusively dealing with Si-Si bonds. We see that the first term in eq. (1.3) is reminiscent of the LJ model in eq. (1.2) while the last term effectively drives the potential to zero at $r = a\sigma$, which is thus the chosen cut-off distance for the potential evaluation. With the model parameters for the Si-Si modelling (see table 1.1) the cut-off becomes ~ 3.8 Å.

The three body term includes an angle dependency as

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \epsilon_{ijk} \left[\cos \theta_{ijk} - \cos \theta_{0,ijk} \right]^2 \exp\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right) \exp\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}}\right), \quad (1.4)$$

where $\theta_{0,ijk}$ is the equilibrium angle. The first term of eq. (1.4) includes an angle dependency analog to a harmonic oscillator based on a cosine angle distance from the equilibrium angle. The final two terms act again as a cut-off function by driving the potential to zero at $r_{ij} = a_{ij}\sigma_{ij}$ and $r_{ik} = a_{ik}\sigma_{ik}$ respectively.

The parameters used for the Si-Si bond modeling is displayed in table 1.1 along with an interpretation of each model parameter.

Table 1.1: Parameters for the stillinger weber potential used for intermolecular interactions in the silicon substrate.

Parameter	Value	Description
ϵ	2.1683	Individual depth of the potential well for each atom type pair/tiplets.
σ	2.0951	Distance for which the individual pair interactions has zero potential (analog to the LJ model).
a	1.80	The individual cut-off distance for each atom type pair.
λ	21.0	The overall depth of the three-body potential well.
γ	1.20	The shape of the three-body cut-off terms.
$\cos(\theta_0)$	-1/3	Cosine of equilibrium angle.
A	7.049556277	The overall depth of the two-body potential well.
B	0.6022245584	Scales the repulsion part of the two-body term.
p	4.0	The power dependency for the repulsion part of the two-body term.
q	0.0	The power dependency for the attraction part of the two-body term.
tol	0.0	LAMMPS: Option to define a different cut-off than the theoretical of $r = a\sigma$. tol = 0 refers to the theoretical being used.

1.2.4 Tersoff

This section is based on [[21], [14]].

The tersoff potential abandon the idea of a general n -body form and attempts instead to build the model on a more physics informed approach; The more neighbours an atom has the weaker the bonds will be. Thus it introduces the bond order (bond strength), that is environment specific and decrease with increasing bond coordination (number of neighbours for a given atom). The potential energy is taken to have the form

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij},$$

$$V_{ij} = f_C(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})],$$

where the total potential energy is decomposed into a bond energy V_{ij} . The indices i and j run over the atoms of the system with r_{ij} denoting the distance between atom i and j . Notice that the sum includes all combinations of i, j where $i \neq j$ meaning that the same bond is double counted which is the reason for the additional factor $1/2$. The reasoning behind comes from the asymmetry of the bond order $b_{ij} \neq b_{ji}$ leading to a $V_{ij} \neq V_{ji}$. The bond energy is composed of a repulsive term f_R , arising from overlapping wave functions, and an attractive term f_A associated with bonding. f_C is simply a smooth cut-off function to increase computational efficiency. b_{ij} represent the bond order, i.e. the strength of the bonds, which depends inversely on the number of bonds, the bond angles (θ_{ijk}) and optionally the relative bonds lengths (r_{ij}, r_{jk}). Notice that an additional cut-off term a_{ij} was originally multiplied to f_R as a way of including terms that limit the range of the interactions to the first neighbour shell. These kind of limitations is already included in b_{ij} for the attractive term f_A but is often omitted for the repulsive term f_R , and we do so to by setting $a_{ij} = 1$.

The cut-off function f_C goes from 1 to 0 over a small interval range $R \pm D$ as

$$f_C(r) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \frac{r-R}{D}\right) & R - D < r < R + D \\ 0 & r > R + D \end{cases}$$

which is continuous and differentiable for all r . R is usually chosen to include only the first neighbour shell. The repulsive and attractive terms f_R and f_A is modelled as an exponential function, similar to a morse potential,

$$f_R(r) = A \exp(-\lambda_1 r),$$

$$f_A(r) = -B \exp(-\lambda_2 r).$$

The novel feature of the model lies in modeling of the bond order b_{ij} which includes three-body interactions by summing over a third atom $k \neq i, j$ within the cut-off $r_{ik} < R + D$ as shown in the following.

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}} \quad (1.5)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) g(\theta_{ijk}(r_{ij}, r_{ik})) \exp(\lambda_3 m (r_{ij} - r_{ik})^m) \quad (1.6)$$

$$g(\theta) = \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (\cos \theta - \cos \theta_0)^2]} \right). \quad (1.7)$$

In eq. (1.7) $\zeta_{i,j}$ is an effective coordination and $g(\theta)$ captures angle dependency as it is minimized at the equilibrium angle $\theta = \theta_0$.

The parameters used to model the graphene C-C bonds is summarized in table 1.2

Table 1.2: Parameters for the tersoff potential used for intermolecular interactions in the graphene sheet

Parameter	Value	Description
m	3.0	Default (not used since $\lambda_3 = 0$)
γ	1.0	...
λ_3	0.0 \AA^{-1}	...
c	3.8049×10^4	Strength of the angular effect
d	4.3484	Determines the “sharpness” of the angular dependency
$\cos(\theta_0)$	-0.57058	Cosine of the equilibrium angle
n	0.72751	Power law exponent for the bond order dependency
β	1.5724×10^{-7}	...
λ_2	2.2119 \AA^{-1}	Decay of repulsion potential term
B	346.74 eV	Attractive potential term minimum at core ($r_{ij} = 0$).
R	1.95 Å	Center distance for cut-off
D	0.15 Å	Thickness of cut-off layers
λ_1	3.4879 \AA^{-1}	Decay of repulsion potential term
A	1393.6 eV	Repulsion potential term at core ($r_{ij} = 0$)

1.2.5 LAMMPS

1.2.6 Integration

Having defined a system of particles governed by interatomic potentials we need to move the system forward in time. By solving Newtons equations of motion we effectively do so by sampling the microcanonical ensemble characterized by a constant number of particles N , volume V and energy E , hence denoted NVE. Newtons equaitons of motion read

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i = -\nabla U_i \quad (1.8)$$

where i is the particle index and m_i its mass, $\mathbf{r}_i = (x_i, y_i, z_i)$ the position, t is time, $\nabla_i = (\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i})$ and U_i the potential energy. In system the potential energy is a function of the particle positions of nearby particles depending on the specefic potential in use. Since the forces defined by the potentials is conservative we expect the energy of the solution to be conserved. We redefine eq.(1.8) in terms of two coupled first order differential equations

$$\dot{\mathbf{v}}_i(t) = \frac{\mathbf{F}}{m_i}, \quad \dot{\mathbf{r}}_i(t) = \mathbf{v}_i(t), \quad (1.9)$$

where $\dot{x} = dx/dt$ (Newton's notation) and $\mathbf{v} = (v_x, v_y, v_z)$ is velocity. Numerically we can solve the coupled equations (eq.(1.9)) by integrating over discrete timnesteps. That is, we discretize the solution into temporal steps $t_k = t_0 + k \cdot \Delta t$ with time-step Δt .

1.2.6.1 Velocity Verlet

A common algorithm to integrate Newtons equation of motion (as formulated in eq.(1.9)) is the *velocity verlet*. We can derive the algorithm by the use of Taylor expansions. We begin by expanding the next-step position vector $\mathbf{r}_i(t + \Delta t)$ at time t

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\Delta t + \frac{\ddot{\mathbf{r}}_i(t)}{2}\Delta t^2 + \mathcal{O}(\Delta t^3), \quad (1.10)$$

where $\ddot{\mathbf{r}} = d^2\mathbf{r}/dt^2$ and Δt^n is simply the relaxed notation for $(\Delta t)^n$. Similar we take the expansions of the next-step velocity vector $\mathbf{v}_i(t + \Delta t)$ at time t

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \dot{\mathbf{v}}_i(t)\Delta t + \frac{\ddot{\mathbf{v}}_i(t)}{2}\Delta t^2 + \mathcal{O}(\Delta t^3). \quad (1.11)$$

Finnally, by taking the expansion of $\dot{\mathbf{v}}_i(t + \Delta t)$ we can eliminate the $\ddot{\mathbf{v}}_i$ -term in eq. (1.11) and simplify it as shown in the following.

$$\begin{aligned}
\dot{\mathbf{v}}_i(t + \Delta t) &= \dot{\mathbf{v}}_i(t) + \ddot{\mathbf{v}}_i(t)\Delta t + \mathcal{O}(\Delta t^2) \\
\frac{\ddot{\mathbf{v}}_i(t)}{2}\Delta t^2 &= \frac{\Delta t}{2}(\dot{\mathbf{v}}(t + \Delta t) - \dot{\mathbf{v}}_i(t)) + \mathcal{O}(\Delta t^3) \\
&\Downarrow \\
\mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \dot{\mathbf{v}}_i(t)\Delta t + \frac{\Delta t}{2}(\dot{\mathbf{v}}_i(t + \Delta t) - \dot{\mathbf{v}}_i(t)) + \mathcal{O}(\Delta t^3) \\
&= \mathbf{v}_i(t) + \frac{\Delta t}{2}(\dot{\mathbf{v}}_i(t) + \dot{\mathbf{v}}_i(t + \Delta t)) + \mathcal{O}(\Delta t^3).
\end{aligned} \tag{1.12}$$

By combining eq. (1.10) and eq. (1.12) and using Newton's second equation $\dot{\mathbf{v}} = \mathbf{F}_i(t)/m_i$ and $\mathbf{v} = \dot{\mathbf{r}}$ we arrive at the final scheme

$$\begin{aligned}
\mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{F}_i(t)}{2m_i}\Delta t^2 + \mathcal{O}(\Delta t^3), \\
\mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \frac{\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)}{2m_i}\Delta t + \mathcal{O}(\Delta t^3).
\end{aligned}$$

The scheme will give a local error of order Δt^3 corresponding to a global error of Δt^2 . One of the most popular ways to implement this numerically is as stated in the following steps.

1. Calculate $v_{k+\frac{1}{2}} = v_k + \frac{F_k}{2m}\Delta t$.
2. Calculate $r_{k+1} = r_k + v_{k+\frac{1}{2}}\Delta t$.
3. Evaluate the force $F_{k+1} = F(r_{k+1})$.
4. Calculate $v_{k+1} = v_{k+\frac{1}{2}} + \frac{F_{k+1}}{2m}\Delta t$

1.2.7 Thermostats

As we already mentioned above in Sec. 2, any kind of sliding friction involves mechanical work, some of which is then transformed into heat (the rest going into structural transformations, wear, etc.). The heat is then transported away by phonons (and electrons in the case of metallic sliders) and eventually dissipated to the environment [6].

Likewise all excitations generated in the simulations should be allowed to propagate in the system and disperse in the bulk of both sheet and substrate. Due to small simulation size theese is likely to reflect back and ‘pile up’ unphysically. Thus in order to avoid continuous heating and attain a steady state the (Joule) heat must be removed at a steady state. This is very the viscous damping of the langevin equations enter the picture. It can be difficult to set the value γ for the magnitude of this damping. The unphysical introduction of heat sink can be mitigated by some modifications he mention, which is kind of next level I guess.

Langevin thermostat

In order to control the temperature of the system we introduce the so-called Langevin thermostat. This is a stochastic thermostat that modifies Newtons equation of motion such that solution lies in the canonical ensemble characterized by a constant number of particles N , constant volume V and constant temperature T , hence denoted NVT. The canonical ensemble system is represented by the finite system being in contact with an infinite heat bath of temperature T . The NVT ensemble is equivalent to sampling a system in thermodynamic equilibrium where the weight of each microscopic state is given by the boltzmann factor $\exp[-E/(k_B T)]$.

The Langevin equation is the modified version of Newtons second law for a Brownian particle. A brownian particle is a small particle suspendend in liquid, e.g. pollen or dust, named after Robert brown (1773–1858) who was the first to observe its jittery motion. The Langevin equation describes this motion as the combination

of viscous drag force $-\gamma\mathbf{v}$, where γ is a positive friction coefficient and \mathbf{v} the velocity vector, and a random fluctuation force \mathbf{R} . The langevin equation reads

$$m \frac{d\mathbf{v}}{dt} = -\gamma\mathbf{v} + \mathbf{R} \quad (1.13)$$

where m is the particle mass. This effectively describes the particle of interest, the brownian particle, as being suspendend in a sea of smaller particles. The collision with these smaller particles is modelled by the drag force and the fluctuation force. We notice that if the fluctuation force is excluded eq. (1.13) becomes

$$m \frac{d\mathbf{v}}{dt} = -\gamma\mathbf{v} \Rightarrow \mathbf{v}_i(t) = v(0)e^{-\frac{\gamma t}{m}},$$

where the solution shows that the brownian particle will come to a complete stop after a long time $\mathbf{v}_i(t \rightarrow \infty) \rightarrow \mathbf{0}$. This is in violation with the equipartition theorem

$$\frac{1}{2}m\langle v^2 \rangle_{eq} = \frac{k_B T}{2},$$

and hence the fluctuation force is nessecary to obtain the correct equilibrium.

The following calculations are done in one dimension in order to simplify the notation. We describe the statistical nature of the collisions as a sum of independent momentum transfers

$$\Delta P = \sum_i^N \delta p_i$$

where ΔP denotes the change of momentum after N momentum transfers δp_i from the environment to the brownian particle. We assume the first and second moments $\langle \delta p \rangle = 0$ and $\langle \delta p^2 \rangle = \sigma^2$. When N is large the central limit theorem states that the random variable ΔP has a gaussian distribution with $\langle P \rangle = 0$ and $\langle \Delta P^2 \rangle = N\sigma^2$. If we consider the momentum change ΔP over a discrete time Δt , where the number of collisiosn is proportional to time $N \propto \Delta t$, the corresponding fluctuation force $R = \Delta P/\Delta t$ will have a variance

$$\langle R^2 \rangle = \frac{\langle \Delta P^2 \rangle}{\Delta t^2} = \frac{N\sigma^2}{\Delta t^2} \propto \frac{1}{\Delta t}.$$

In a computer simulation we need to pick a random force $R(t)$ from a Gaussian distribution every time-step Δt . These forces will not be correlated as long as Δt is larger than the correlation time of the forces from the molecules which we will assume for this model (I think there exist corrections for this to refer to here). With this assumption we can write the correlation function as

$$\langle R(t)R(0) \rangle = \begin{cases} \frac{a}{\Delta t}, & |\Delta t| < \Delta t/2 \\ 0, & |\Delta t| > \Delta t/2, \end{cases} \quad (1.14)$$

where a is some strength of (...?). In the limit $\Delta t \rightarrow 0$ the correlation function becomes

$$\langle R(t)R(0) \rangle = a\delta(t), \quad (1.15)$$

where δ denotes the dirac delta function. This is valid for all spatial coordinates which will all be independent of each other. Since both the drag force and the fluctuation force originate from the molecular fluid, where the drag force $-\alpha\mathbf{v}$ is velocity dependent it is reasonable to assume that fluctuation force is independent of velocity, i.e. $\langle R_i v_j \rangle = 0$ for all cartesian indices i and j .

In the following we will attempt justify the Langevin equaiton (why it is like it is) and determine the relationship between the drag coefficient γ and the random force R .

From the Langevin equation eq. (1.13) we can compute the velocity autocorrelation function (Move to appendix?). We do this in one dimension for simplicity. We begin by multiplying by $(e^{\gamma t/m})/m$

$$\dot{v}(t)e^{\gamma t/m} + \frac{\gamma}{m}v(t)e^{\gamma t/m} = \frac{F}{m}e^{\gamma t/m},$$

and integrate from $t = -\infty$. By the use of integration by parts on the latter term on the left hand side we calculate the velocity

$$\begin{aligned} \int_{-\infty}^t dt' \dot{v}(t') e^{\frac{\gamma t'}{m}} + \frac{\gamma}{m} v(t) e^{\frac{\gamma t}{m}} &= \int_{-\infty}^t dt' e^{\frac{\gamma t'}{m}} \frac{F(t')}{m} \\ \int_{-\infty}^t dt' \dot{v}(t') e^{\frac{\gamma t'}{m}} + \left(\left[v(t') e^{\frac{\gamma t'}{m}} \right]_{-\infty}^t - \int_{-\infty}^t dt' \dot{v}(t') e^{\frac{\gamma t'}{m}} \right) &= \int_{-\infty}^t dt' e^{\frac{\gamma t'}{m}} \frac{F(t')}{m} \\ v(t) &= \int_{-\infty}^t dt' e^{\frac{-\gamma(t-t')}{m}} \frac{F(t')}{m}, \end{aligned}$$

where $e^{\frac{-\gamma t}{m}}$ plays the role of a response function. We can then calculate the autocorrelation

$$\begin{aligned} \langle v(t)v(0) \rangle &= \int_{-\infty}^t dt_1 \int_{-\infty}^0 dt_2 e^{\frac{t-t_1-t_2}{m}} \frac{\langle F(t_1)F(t_2) \rangle}{m^2} \\ &= \int_{-\infty}^t dt_1 \int_{-\infty}^0 dt_2 e^{\frac{t-t_1-t_2}{m}} \frac{a\delta(t_1-t_2)}{m^2} \\ &= \int_{-\infty}^0 dt_2 e^{\frac{t-2t_2}{m}} \frac{a}{m^2} = \frac{a}{2m\gamma} e^{-\frac{\gamma t}{m}}, \end{aligned}$$

where we used eq. (1.15) and the fact that the integration commutes with the average (we are allowed to flip the order). By comparing this with the equipartition theorem we get

$$\begin{aligned} \frac{1}{2}m\langle v^2 \rangle &= \frac{k_B T}{2} \\ \frac{1}{2}m\langle v(0)v(0) \rangle &= \frac{a}{4\gamma} = \frac{k_B T}{2} \\ a &= 2\gamma k_B T \end{aligned}$$

We notice the appearance of γ meaning that the magnitude of the fluctuations increase both with friction and temperature. Further we can integrate the velocity over time to get displacement $x(t)$ and show that the variance (show this? In appendix maybe?) is

$$\langle x^2(t) \rangle = \frac{2k_B T}{\gamma} \left(t - \frac{m}{\gamma} \left(1 - e^{-\gamma t/m} \right) \right),$$

where for $t \gg m/\gamma$ only the t -term survives yielding

$$\langle x^2(t) \rangle = 2k_B T t / \gamma.$$

In 1D, the diffusion constant D is related to the variance as $\langle x^2 \rangle = 2Dt$, meaning that this represents the einstein relation $D = \mu k_B T$ with the mobility $\mu = 1/\gamma$.

when $t \ll m/\gamma$ we use the Taylor expansion $1 - e^{-x} \approx x - x^2/2$ for $x \ll 1$ to get

$$\langle x^2(t) \rangle = \frac{k_B T}{m} t^2$$

which exactly matches the thermal velocity

$$v_{\text{th}} \frac{\langle x^2(t) \rangle}{t^2} = \frac{k_B T}{m}$$

which follows from the equipartition theorem. The finite correlation time γ/m hence describe the crossover from the ballistic regime $\sqrt{\langle x^2(t) \rangle} \propto t$ to the diffusive regime $\sqrt{\langle x^2(t) \rangle} \propto \sqrt{t}$.

Introduce the fluctuation-dissipation theorem concept earlier since this is a motivation for the Langevin equation.

1.2.7.1 Implementing Langevin

The implementation of the Langevin equation into LAMMPS follows [22] and updates the force vector for each particle as

$$\begin{aligned}\mathbf{F} &= \mathbf{F}_c + \mathbf{F}_f + \mathbf{F}_r \\ &= -\nabla U - \gamma m \mathbf{v} + \sqrt{\frac{2k_B T m \gamma}{\Delta t}} \mathbf{h}(t)\end{aligned}\quad (1.16)$$

where \mathbf{F}_c is the conservative force computed via the usual inter-particle interactions described by the potential U , \mathbf{F}_f is the drag force and \mathbf{F}_r is the random fluctuation force where \mathbf{h} is a random vector drawn from a normal distribution with zero mean and unit variance. Notice that this generalized description of the Langevin equation deviates from the presentation in eq. (1.13) since we have added the conservative force \mathbf{F}_c , but also by the appearance of the mass in both the drag force and the fluctuation force due to the introduction of damping. It is beyond our scope to comprehend this. However, the fact that Δt now appears in the denominator for the random force variance $2k_B T m \gamma / \Delta t$ is due to the fact that we have discretized time. This is in agreement with the formulation in eq. (1.14). By applying eq. (1.16) we get the refined velocity verlet scheme

$$\begin{aligned}\mathbf{v}_i(t + \Delta t/2) &= \mathbf{v}_i(t) - \frac{\Delta t}{2} \left(\frac{\nabla_i U(t)}{m_i} + \gamma \mathbf{v}_i \right) + \sqrt{\frac{k_B T \gamma \Delta t}{2m_i}} \mathbf{h}_i \\ \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t + \Delta t/2) \Delta t \\ \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t + \Delta t/2) - \frac{\Delta t}{2} \left(\frac{\nabla_i U(t + \Delta t)}{m_i} + \gamma \mathbf{v}_i(t + \Delta t/2) \right) + \sqrt{\frac{k_B T \gamma \Delta t}{2m_i}} \mathbf{h}_i\end{aligned}$$

with new random vector \mathbf{h}_i for each particle and each update. Notice however, that LAMMPS only apply this scheme to the particle groups with the thermostat on.

1.2.7.2 MD limitations

1.3 Defining the system

1.3.1 Groups: Sheet, pullblocks and substrate

Include figure of system to point out thermo layers and freeze layers.

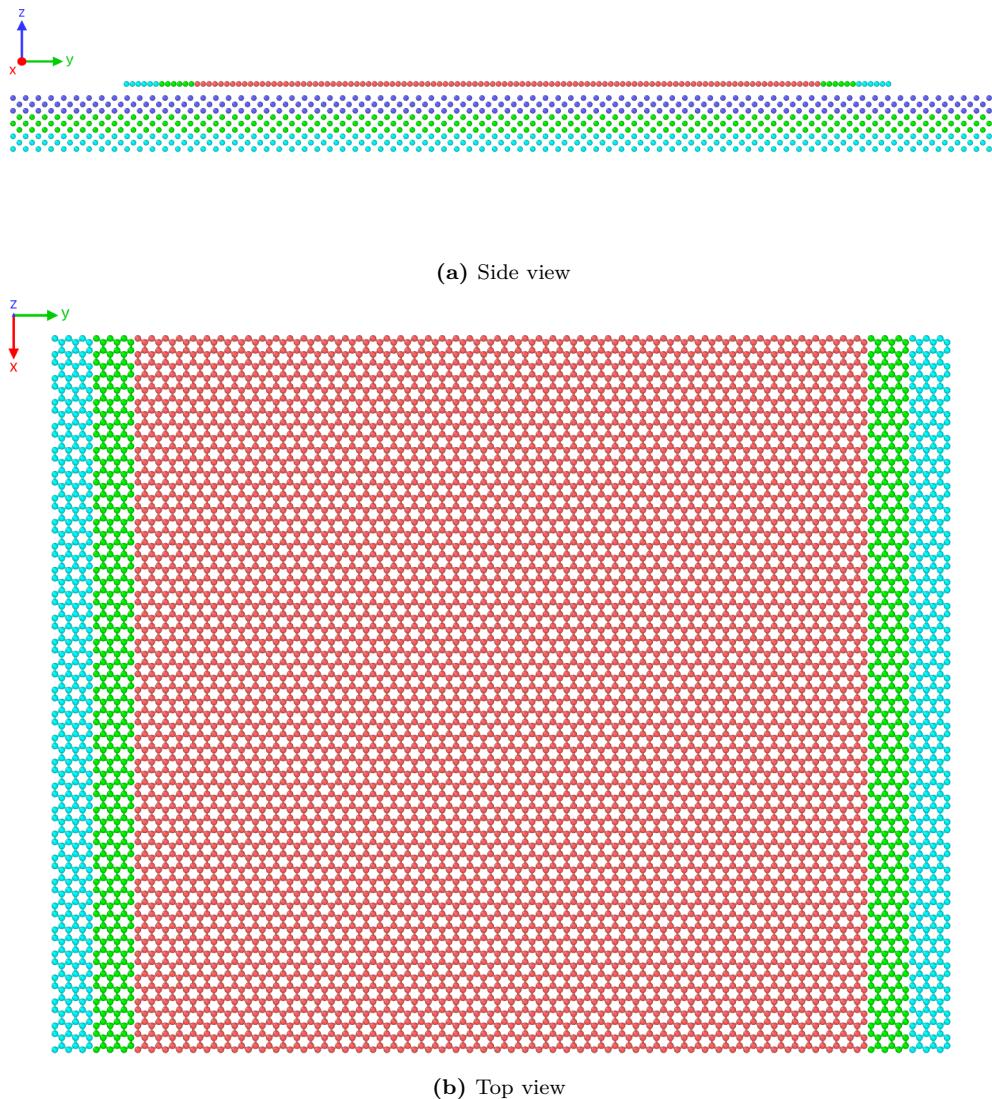


Figure 1.7: System. 27456 atoms in total: 7272 with thermostat (orange), 7272 is locked (light blue) and the remaining 12912 just with NVE. (Get better colors)

Table 1.3: System atom count and region division.

Region	Total	Sub region	Sub total	NVE	NVT	Locked
Sheet	7800	Inner sheet	6360	6360	0	0
		Pull blocks	1440	0	720	720
Substrate	19656	Upper	6552	6552	0	0
		Middle	6552	0	6552	0
		Bottom	6552	0	0	6552
All	27456			12912	7272	7272

The sheet dimensions is

Table 1.4: Sheet dimensions

Group	x, y -dim	dim [Å]	Area [Å ²]
Full sheet	$x_S \times y_S$	$130.029 \times 163.219 \text{ Å}$	$21,223.203$
Inner sheet	$x_S \times 81.40 \%_{y_s}$	$130.029 \times 132.853 \text{ Å}$	$17,274.743$
Pull blocks	$2 \times x_S \times 9.30 \%_{y_s}$	$2 \times 130.029 \times 15.183 \text{ Å}$	$2 \times 1,974.230$

1.3.1.1 Pressure reference

Find place to put this.

In order to relate the magnitude of the normal force in our friction measurement we will use the pressure as a reference. We will use the pressure underneath a stiletto shoe as a worst case for human pressure execution underneath the shoes. From (source 1) it is reported that the diameter of a stiletto heeled shoe can be less than 1 cm. Hence a 80 kg man² standing on one stiletto heel (with all the weight on the heel) will result in a pressure corresponding diameter of

$$P = \frac{F}{A} = \frac{mg}{r^2\pi} = \frac{80 \text{ kg} \cdot 9.8 \frac{\text{m}}{\text{s}^2}}{\left(\frac{1 \times 10^{-2} \text{ m}}{2}\right)^2\pi} = 9.98 \text{ MPa}$$

While this is in itself a spectacular realization that is often used in introduction physics courses (source 2) to demonstrate the rather extreme pressure under a stiletto heel (greater than the foot of an elephant) (how many Atmos) this serves as a reasonable upperbound for human executed pressure. With a full sheet area of $\sim 21 \times 10^3 \text{ Å}^2$ we can achieve a similar pressure of $\sim 10 \text{ MPa}$ with a normal force

$$F_N = 10 \text{ MPa} \cdot 21 \times 10^{-17} \text{ m}^2 = 2.10 \text{ nN}$$

Of course this pressure might be insufficient for various industrial purposes, but with no specific procedure in mind this serves as a decent reference point. Notice that if we consider a human foot with area 113 cm^2 the pressure drops to a mere 70 kPa corresponding to $\sim 0.01 \text{ nN}$.

1.3.2 Creating sheets

We are going to create a 2D sheet graphene sheet.

1.3.2.1 Graphene

Graphene is a single layer of carbon atom, graphite is the bulk, arranged in a hexagonal lattice structure. We can describe the 2D crystal structure in terms of its primitive lattice vector and a basis. That is we populate each lattice site by the given basis and translate it to fill the whole plane by any linear combination of the lattice vectors

$$\mathbf{T}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2, \quad m, n \in \mathbb{N}.$$

For graphene we have the primitive lattice vectors

$$\mathbf{a}_1 = a \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right), \quad \mathbf{a}_2 = a \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right), \quad |\mathbf{a}_1| = |\mathbf{a}_2| = 2.46 \text{ Å}.$$

Notice that we deliberately excluded the third coordinate as we only consider a single graphene layer or not the bulk graphite consisting of multiple layers stacked on top of each other. The basis is

$$\left\{ \left(0, 0 \right), \frac{a}{2} \left(\frac{1}{\sqrt{3}}, 1 \right) \right\}$$

²Yes, a man can certainly wear stiletto heels.

It turns out that the spacing between atoms is equal for all pairs with an interatomic distance

$$\left| \frac{a}{2} \left(\frac{1}{\sqrt{3}}, 1 \right) \right| \approx 1.42 \text{ \AA}.$$

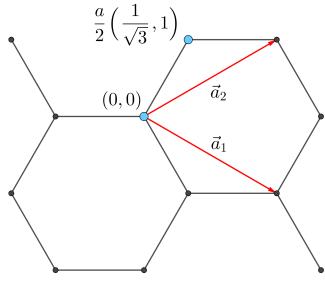


Figure 1.8: Graphene crystal structure with basis.

1.3.2.2 Indexing

In order to define the cut patterns applied to the graphene sheet we must define an indexing system. We must ensure that this gives an unique description of the atoms as we eventually want to pass a binary matrix, containing 0 for removed atom and 1 for present atom, that uniquely describes the sheet. We do this by letting the x-coordinate point to zigzag chains and the y-coordinate to the position along that chain. This is illustrated in figure 1.9. Other solutions might naturally involve the lattice vectors, but as these only can be used to translate to similar basis atoms a unfortunate duality is introduced as ones need to include the basis atom of choice into the indexing system. With the current system we notice that locality is somewhat preserved. That is, atom (i, j) is in the proximity of $\{(i+1, j), (i-1, j), (i, j+1), (i, j-1)\}$, but only three of them is categorized as nearest neighbours due to the hexagonal structure of the lattice. While $(i, j \pm 1)$ is always nearest neighbours the neighbour in the x-direction flip sides with incrementing y-coordinate. That is the nearest neighbours (NN) is decided as

$$\begin{aligned} j \text{ is even} &\rightarrow \text{NN} = \{(i+1, j), (i, j+1), (i, j-1)\}, \\ j \text{ is odd} &\rightarrow \text{NN} = \{(i-1, j), (i, j+1), (i, j-1)\}. \end{aligned}$$

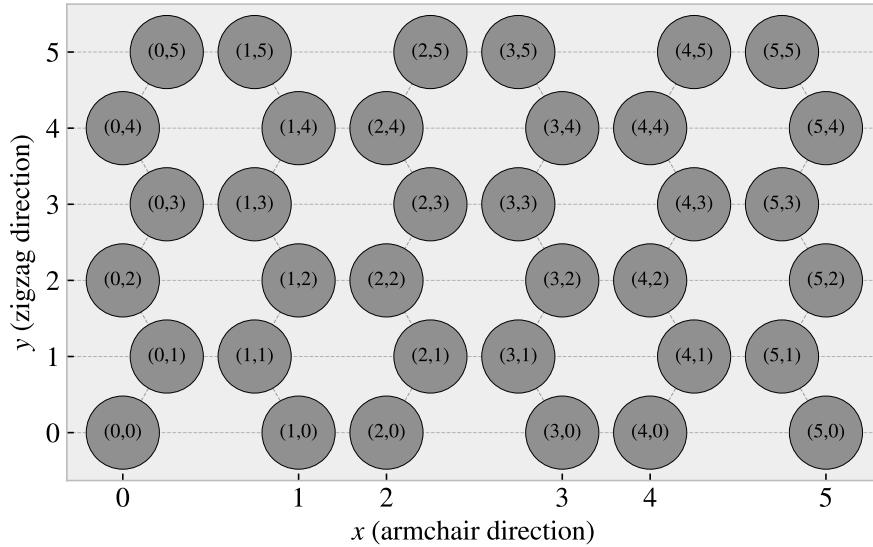


Figure 1.9: Graphene atom indexing

1.3.2.3 Removing atoms

As a mean to ease the formulation of cut patterns we introduce pseudo center element in each gap of the hexagonal honeycombs, see figure 1.10.

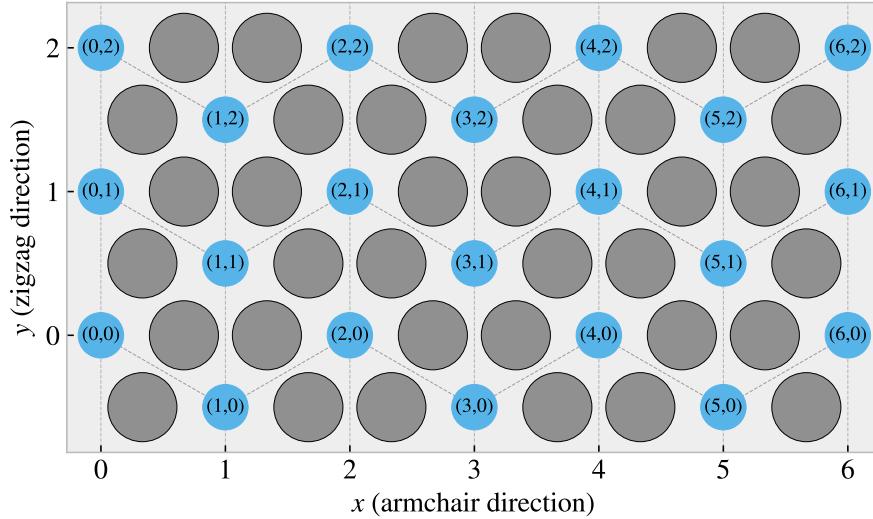


Figure 1.10: Graphene center indexing

Similar to the case of the indexing for the carbon atoms themselves the nearest neighbour center elements alternate with position, this time along the x-coordinate. Each center element has six nearest neighbours, in clock wise direction we can denote them: “up”, “upper right”, “lower right”, “down”, “lower left”, “upper left”. The “up” and “down” is always accessed as $(i, j \pm 1)$, but for even i the $(i + 1, j)$ index corresponds to the “lower right” neighbour while for odd i this corresponds to the “upper right” neighbour. This shifting applies for all left or right neighbours and the full neighbour list is illustrated in figure 1.11.

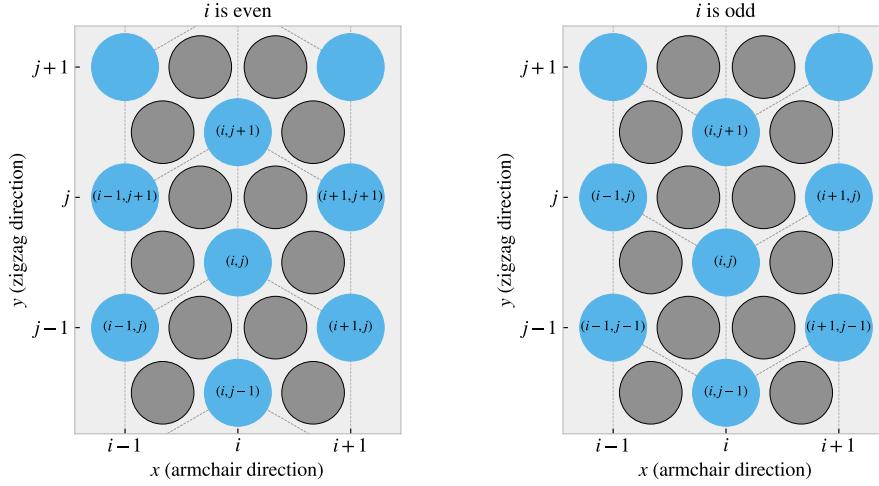


Figure 1.11: Graphene center elements directions

We define a cut pattern by connecting center elements into connected paths. As we walk element to element we remove atoms according to one of two rules

1. Remove intersection atoms: We remove the pair of atoms placed directly in the path we are walking. That is, when jumping to the “up” center element we remove the two upper atoms located in the local hexagon of atoms. This method is sensitive to the order of the center elements in the path.
2. Remove all surrounding atoms: We simply remove all atoms in the local hexagon surrounding each center element. This method is independent of the ordering of center elements in the path.

We notice that removing atoms using either of these rules will not guarantee an unique cut pattern. Rule 1 is the more sensitive to paths but we realize that, for an even i , we will remove the same five atoms following either of the following paths.

$$\begin{aligned}
 & (i, j) \rightarrow \underbrace{(i + 1, j + 1)}_{\text{upper right}} \rightarrow \underbrace{(i, j + 1)}_{\text{up}} \rightarrow \underbrace{(i + 1, j + 2)}_{\text{upperright + up}} \rightarrow \underbrace{(i + 1, j + 1)}_{\text{upper right}} \\
 & (i, j) \rightarrow \underbrace{(i + 1, j + 1)}_{\text{upper right}} \rightarrow \underbrace{(i + 1, j + 2)}_{\text{upperright + up}} \rightarrow \underbrace{(i, j + 1)}_{\text{up}}
 \end{aligned}$$

For rule 2 it is even more obvious that different paths can result in the same atoms being removed. This is the reason that we needed to define and indexing system for the atom position itself even though that all cuts generated manually will use the center element path as reference.

Illustrate some delete path?

1.3.3 Pull blocks

1.3.4 Kirigami inspired cut out patterns

1.3.4.1 Pop-up pattern

1.3.4.2 Honeycomb

1.3.4.3 Random walk

1.4 Fourier Transform (light)

Find out where to put this if necessary.

Fourier transform is a technique where we transform a function $f(t)$ of time to a function $F(k)$ of frequency. The Forward Fourier Transform is done as

$$F(k) = \int_{-\infty}^{\infty} f(t)e^{-2\pi i k x} dx$$

For any complex function $F(k)$ we can decompose it into magnitude $A(k)$ and phase $\phi(k)$

$$F(k) = A(k)e^{i\phi(k)}$$

Hence when performing a Forward Fourier transform on a time series we can determine the amplitude and phase as a function of frequency as

$$A(k) = |F(k)|^2, \quad \phi(k) = \Im \ln F(k)$$

1.4.1 Real life experimental procedures

From Introduction to Tribology, Second Edition, p. 526:

The surface force apparatus (SFA), the scanning tunneling microscopes (STM), and atomic force and friction force microscopes (AFM and FFM) are widely used in nanotribological and nanomechanics studies.

- Real life procedures to mimic in computation, for instance Atomic Force Microscopy (AFM) for friction measurements.
- Available technology for test of my findings if successful (possibilities for making the nano machine)

1.5 Machine Learning (ML)

- Feed forward fully connected
- CNN
- GAN (encoder + decoder)
- Genetic algorithm
- Using machine learning for inverse designs partly eliminate the black box problem. When a design is produced we can test it, and if it works we not rely on machine learning connections to verify its relevance.
- However, using explanations techniques such as maybe t-SNE, Deep dream, LRP, Shapley values and linearizations, we can try to understand why the AI chose as it did. This can lead to an increased understanding of each design feature. Again this is not dependent on the complex network of the network as this can be tested and verified independently of the network.

1.5.1 Feed forward network / Neural networks

1.5.2 CNN for image recognition

1.5.3 GAN (encoder + decoder)

1.5.4 Inverse design using machine learning

1.5.5 Prediction explanation

1.5.5.1 Shapley

1.5.5.2 Linearizations

1.5.5.3 LRP

1.5.5.4 t-SNE

Bibliography

- [1] E. Gnecco and E. Meyer, *Elements of Friction Theory and Nanotribology*. Cambridge University Press, 2015, 10.1017/CBO9780511795039.
- [2] Bhushan, *Introduction*, ch. 1, pp. 1–? John Wiley & Sons, Ltd, 2013.
<https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781118403259.ch1>.
<https://doi.org/10.1002/9781118403259.ch1>.
- [3] H.-J. Kim and D.-E. Kim, *Nano-scale friction: A review*, .
- [4] K. Holmberg and A. Erdemir, *Influence of tribology on global energy consumption, costs and emissions*, .
- [5] P. Z. Hanakata, E. D. Cubuk, D. K. Campbell and H. S. Park, *Forward and inverse design of kirigami via supervised autoencoder*, *Phys. Rev. Res.* **2** (Oct, 2020) 042006.
- [6] N. Manini, O. M. Braun, E. Tosatti, R. Guerra and A. Vanossi, *Friction and nonlinear dynamics*, *Journal of Physics: Condensed Matter* **28** (jun, 2016) 293001.
- [7] B. Bhushan and A. V. Kulkarni, *Effect of normal load on microscale friction measurements*, *Thin Solid Films* **278** (1996) 49–56.
- [8] J. H. Dieterich, *Time-dependent friction in rocks*, *Journal of Geophysical Research (1896-1977)* **77** (1972) 3690–3697, [<https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/JB077i020p03690>].
- [9] I. Szlufarska, M. Chandross and R. W. Carpick, *Recent advances in single-asperity nanotribology*, *Journal of Physics D: Applied Physics* **41** (may, 2008) 123001.
- [10] Y. Mo, K. T. Turner and I. Szlufarska, *Friction laws at the nanoscale*, .
- [11] N. Manini, G. Mistura, G. Paolicelli, E. Tosatti and A. Vanossi, *Current trends in the physics of nanoscale friction*, *Advances in Physics: X* **2** (may, 2017) 569–590.
- [12] B. Bhushan, *Nanotribology and nanomechanics*, *Wear* **259** (2005) 1–?
- [13] S. Li, Q. Li, R. W. Carpick, P. Gumbsch, X. Z. Liu, X. Ding et al., *The evolving quality of frictional contact with graphene*, .
- [14] J. Tersoff, *New empirical approach for the structure and energy of covalent systems*, *Phys. Rev. B* **37** (Apr, 1988) 6991–7000.
- [15] S. Corporation, “pair_style lj/cut command.”
- [16] X. Wang, S. Ramírez-Hinestrosa, J. Dobnikar and D. Frenkel, *The lennard-jones potential: when (not) to use it*, *Phys. Chem. Chem. Phys.* **22** (2020) 10624–10633.
- [17] R. Naeem, “Lennard-jones potential.”
- [18] Q. Zhang, D. Diao and M. Kubo, *Nanoscratching of multi-layer graphene by molecular dynamics simulations*, *Tribology International* **88** (2015) 85–88.
- [19] S. Corporation, “pair_style sw command.”
- [20] F. H. Stillinger and T. A. Weber, *Computer simulation of local order in condensed phases of silicon*, *Phys. Rev. B* **31** (Apr, 1985) 5262–5271.
- [21] S. Corporation, “pair_style tersoff command.”
- [22] T. Schneider and E. Stoll, *Molecular-dynamics study of a three-dimensional one-component model for distortive phase transitions*, *Phys. Rev. B* **17** (Feb, 1978) 1302–1322.