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Robin Sam Vacher

Nanoscale tribological simulations of a semi-crystalline polymer

NTNU

Norwegian University of Science and Technology Thesis for the Degree of Philosophiae Doctor Faculty of Engineering Department of Mechanical and Industrial Engineering



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Trondheim, March 2022

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Abstract

Many of the objects surrounding us are made of polymers. Those polymers are often used for their tribological properties, for example, shoes with rubber soles or car tyres. Polymers materials become more and more presents, and their frictional behaviour is often a significant issue. Macroscopic properties of those materials such as friction and wear have been intensely studied in the past. Those studies have shown that there are nontrivial effects in friction and wear specific to polymers, such as non-linearity and nontrivial temperature dependence. Much remains to be understood, as there are many additional complications in many realistic polymers that can affect the structure and friction, such as the strength of the interatomic interactions, cross-linking, or the presence of water and other contaminants.

We want to identify and investigate some of the main mechanisms of semicrystalline polymer friction. In that regard, molecular dynamic simulations are used to create semi-crystalline solid polymer substrates at the nanoscopic scale. We modelled a friction force microscope experiment. The polymer tends to coaxially align and form a layered structure during rubbing simulations directly under the tip. Over time, the plastic deformation on and near the surface builds up, the friction decreases, and the polymers in the top layer align with each other in the sliding direction.

A small amount of friction is often wanted in tribological systems because high friction is linked to high wear and large energy consumption. A way to reduce friction is to apply lubricants. We have put the focus of our study on graphene lubricant. One of our goals is to identify how adding a graphene layer helps reduce friction and wear. We found that the stiffness of the graphene membrane linked to the boundary condition has a substantial impact on the indentation depth.

The surface profiles are directly affecting the friction. We investigate the emergence of the roughness of a polymer material. We found that by compressing a solid PVA substrate, the roughness of the polymer self-affinity continues to change with increasing strain. We associate this phenomenon with the viscoelastic properties of the polymer.

While our simulations are for a specific polymer, the qualitative behaviour is likely to be general and present in other polymers.

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Chapter 1

Introduction

In many engineering applications, the role of polymer friction is crucially important. Soft material friction is present in healthcare, biomedical, food, seals, etc [1]. Polymers are often used because of their mechanical properties; however, some challenges remain. Studying tribological systems is often a difficult task by itself. For example, the coefficient of friction can depend on many parameters (load, sliding speed, temperature, chemicals, the history of the surface, etc.). Studying polymer tribology, in particular, is a difficult task. Such systems are often more complex to analyse, and polymer friction is still poorly understood. The glassy behaviour of polymers and their viscoelastic properties are qualitatively different from what can be seen in other materials (metals, ceramics, gases). Since polymer tribology is found everywhere, it is scientifically relevant to understand the underlying mechanisms of such systems. This would increase innovation, and it would help build better solutions with tribological systems having less wear, less energy consumption, less noise, etc.

Friction is a multiscale phenomenon where macroscopic friction often arises from a multitude of individual nanoscale contacts. Studying such materials at a nanoscale level is a way to gain knowledge on their tribological behaviours. FFM experiments have in recent years been used to study phenomena at that scale. Some effects observed with that method of analysis are, for example, the stickslip effect [2], super-lubricity [3], anisotropy [4], etc.

One of the challenges of such laboratory experiments is the lack of knowledge about the dynamics of the molecules and the structural changes that happen underneath the tip of the AFM. Molecular dynamics is a simulation technique that can be used to obtain such type of information. The positions of the particles are registered, and this information can then be used to see structural changes and compute average properties. In this thesis, we have used this MD technique with a simple model which aims to reproduce the frictional behaviour of polyvinyl alcohol material. The material changes are often occurring in the first few micrometres close to the surface, and this is where we have focused our investigation.

Three articles have been produced during this PhD. The primary purpose of the present document is to be used as a guide for the reader. The first chapter is the

introduction. The second chapter is a short review of friction. The third focus more in detail on polymer and polymer friction. The fourth chapter explains in a general way how molecular dynamics simulations are working. The fifth chapter provides the results found in each article. The last chapter is the general conclusion and discussion.

Chapter 2

General introduction to friction

This chapter summarises some of the critical concepts associated with friction. First, we will describe what a dry tribological contact is, then we explain the main phenomenological laws of friction that are commonly used. It is followed by some explanations about what is happening at a lower scale, which is the scale investigated in this thesis.

2.1 The importance of friction

Friction is a force resisting the relative motion of an object. When there is movement, friction is a process that dissipates energy. Investigating it is interesting because it is a complex phenomenon that is happening everywhere in our daily life. Many applications use friction to their advantage (braking, walking, drilling, keeping an object stationary, etc.). Studies have shown that around 23% of the energy produced by human activity is spent on tribological contacts [5, 6].

In many other applications, friction is something unwanted. A grain of sand in a gear system can be a considerable problem! High friction can lead to high material wear, excessive energy consumption, and prevent motion. Using available methods to reduce friction could save a substantial amount of money.

2.2 What is a tribological contact?

We can not speak about friction without speaking about surface contacts. Understanding what friction is and where it physically comes from is a difficult task. Many theories have been developed over the years, and it is relatively hard to navigate and understand the relations between the laws and theories that exist. Friction is a multiscale problem where a lot of branches of physics and chemistry are involved. In our study, we are focused on dry friction. In dry friction, surfaces are in direct contact. It is essential to understand what this means because the frictional forces are located at the contact.

While to our eyes on macroscopic scales, the surfaces appear to have a big



Figure 2.1: Macroscopic contact is made of multiple micro or nanoscopic contacts (multi-asperity contact) that are often modelled by single contact asperity. In reality, the contact is done via the atoms.

area of contact, in reality, the actual contact consists only of the small areas where the asperities meet. There is a distinction between the apparent area of contact and the true area of contact. The first one depends only on the dimension and geometry of the objects in contact. For example, if we consider a cube of dimensions $1 \times 1 \times 1 \text{ cm}^2$ put on a surface, the apparent contact area would be 1 cm^2 . The true area, however, is the sum of all individual microcontacts. The result of this sum is usually much smaller than the apparent contact area. It is the value of the true contact area that is mostly governing the amount of friction.

As a first approximation, a macroscopic contact can be seen as a continuous and smooth surface (Fig. 2.1). However, when we zoom in, we can see that the surfaces are made of multiple asperities. Those asperities are responsible for the roughness of the surface. Only a few asperities are in contact with one another. When the magnification is increased, only one asperity is visible. Zooming, even more, we can see that the single asperity is made of molecules and atoms; the system becomes discrete. At this scale, the notion of the contact area is becoming a bit more difficult to apprehend because the system is noncontinuous. If the atom positions are known at this scale, there are different ways to compute the contact area (counting the atoms, looking at the potential energy between particles, looking at the radial distribution function, etc.) [7].

2.3 The three laws of friction

Leonardo da Vinci was the first to study this phenomenon via thorough experiments on dry wood 500 years ago. He understood that friction is dependent on the normal load. Two hundred years later, three main laws of friction have been described by Amontons and Coulomb. Amontons rediscovered what Da Vinci had already discovered. Those phenomenological laws are widely used by engineers today because they are simple to apply. The main assumptions of those laws are that the frictional force is proportional to the normal load, independent of the apparent area of contact and independent of the sliding velocity. In a lot of applications, those approximations are sufficient. However, those laws should be used



Figure 2.2: The Friction is independent of the contact area. The two objects of the same mass *m* that are shown in the picture would experience the same friction.



Figure 2.3: The Friction is independent of the velocity. Objects of the same mass m moving at different speeds v would experience the same friction.

with care because they are reductive and mask the complexity of the underlying friction mechanisms (see for example [8]).

2.3.1 Amontons' and Coulomb's laws

The first law stipulates that the frictional force is proportional to the normal load:

$$F_t \le F_n \mu, \tag{2.1}$$

where F_t is the tangential force and F_n is the normal force (perpendicular to the contact). It assumes that the tangential force can never be higher than μF_n . Sliding occurs when the tangential force F_t is equal to μF_n ; before that, the friction is whatever it needs to be to keep the objects still relative to one another. The ratio between those two forces (when there is sliding) is called the Coefficient Of Friction (COF) μ and is a system property that depends on the surface in contacts.

The second law stipulates that friction is independent of the apparent area of contact (Fig. 2.2). Coulombs's law specifies that the friction is independent of the sliding velocity (Fig. 2.3).

2.3.2 General remarks on the laws of friction

A simple example to illustrate the first law is to perform an experiment where we put an object of mass *m* on a horizontal surface and slowly tilt the surface (Fig. 2.4). It is only at a given angle α called the resting angle that sliding occurs. Before that, the frictional forces prevent the object from moving. We can find the relationship between the resting angle α and the static COF μ by substituting F_t and F_n by their components:

$$F_n = mg\cos\alpha,\tag{2.2}$$

$$F_t = mg\sin\alpha, \tag{2.3}$$

$$\mu = \tan \alpha. \tag{2.4}$$



Figure 2.4: Simple experiment to find the resting angle α , the cone of friction is also represented in the picture. During sliding, F_t becomes equal to μF_n . Before that, the friction remains in the cone of friction, and there is no relative movement.

During sliding, F_t becomes equal to μF_n . Before that, the friction remains in the cone of friction, and there is no relative movement.

One of the implications of Amontons' first law is that the real contact area should increase proportionally to the pressure, which in return increases the friction. This works well only for relatively low or medium contact pressure. For high or extremely high contact pressure, the real contact area tends to approach the apparent contact area (except for soft materials on hard surfaces where the soft material can accommodate the roughness of the hard material). In that case, the frictional force remains constant when the pressure is increased. In 1950, Bowden and Tabor assumed that the true contact area was really small compared to the apparent contact area. When the load is increased, it increases the amount of asperity in contact and the average size of the contacts.

It is pretty common to see the frictional force changing with the velocity in experiments, so Coulombs's law is inaccurate. Often, the static friction is higher than the dynamic friction. Surfaces are rough, and when they are stationary, the material has the time to deform, and the asperities accommodate the roughness of the other surface (the potential energy is reduced). The number of atomistic interactions between the surfaces is high (the true contact area increases). When the sliding speed is high, the amount of atomistic interaction between the surfaces is reduced because the top of the asperities does not have time to fit in the valleys of the other surface (Fig. 2.5). Other mechanisms can lead to velocity-dependent friction. When the atoms have more kinetic energy, the impact of the atoms can trigger more chemical reactions and structural changes in the materials (deformation).

2.4 Friction's mechanisms

Because of their simplicities, Amontons-Coulomb's laws are widely used by engineers. However, those laws do not necessarily capture all subtleties, for example, roughness, presence of tribological film, sliding speed, temperature effect, wear,



Figure 2.5: Schematic representation of two objects sliding on one another for low speed and high speed. The circles represent atoms, and the colour is here to distinguish to which object the atoms belong. At low velocity v, the atoms have time to accommodate the roughness of the other surface. This is not the case when the velocity v is high. This phenomenon often involves that the kinetic friction is lower than the static friction.

etc.

For simplicity, it is sometimes assumed that the frictional force can be split into two components, adhesion (shearing of junctions) and deformation (force required to deform the material) [9]. For simplicity, it is often assumed that those components are independent of one another and therefore can be summed up:

$$F_T = F_{adhesion} + F_{deformation}.$$
 (2.5)

However, in reality, their relation is often complicated, and classifying phenomena like this does not necessarily make sense.

Adhesion component of friction

The adhesion theory has been developed to consider the fact that an attractive force is generated when two surfaces are placed close to one another. The surfaces bond to one another via adhesion at an atomic level, and junctions are formed. It is often the case that the atoms at the surface chemically react with one another and form strong covalent bonds, which can, in some cases, drastically increase the friction. But even the forces coming from electrostatic interactions (hydrogen bonding, Van der Waals) are enough to create high adhesion.

For an object to slide on one another, some of the inter-atomic interactions (electrostatic, Van der Waals) must break (slip). This breaking occurs at the weakest spots in the materials. The spot where the slip occurs is often located at the junctions (interface) between the two materials. In that case, once the object has moved, new junctions are created, and the friction is determined mainly by the amount of real contact area. However, if the junctions are too hard to break (strong link between the atoms) or one of the materials is not strong enough to withstand the stresses, slip occurs in the substrate. In that case, the breaking happens on the weakest material, which is the material that has the lowest shear strength. The strength of a material is defined as the maximum stress a material can withstand before plastic deformation or failure occur. In systems with high adhesion, it is often the case where one material (usually the softest) deposit on the other surface. For a dry contact, Bowden and Tabor in 1950 [10–12] built an adhesion theory that allows calculating friction coming from adhesion:

$$f_d = \tau_d A_r, \tag{2.6}$$

where f_d is the dynamic friction, A_r is the true area of contact and τ_d is an interfacial shear strength representing the quality of the contact. The interfacial shear strenght τ_d is varying with the temperature and the sliding velocity, it depends on the pressure through:

$$\tau_d = \tau_0 + \alpha P, \tag{2.7}$$

where α and τ_0 are material constants and *P* is the mean contact pressure expressed as:

$$P = \frac{F_N}{A_r}.$$
 (2.8)

This adhesion theory works relatively well for plastic film material [13]. However, the adhesion of elastomers (fully viscoelastic material) to hard surfaces is not well captured with this law. Adding contaminants like air or water is often a way to reduce the adhesion between the materials effectively. The contaminants reduce the number of interactions of the two materials, and it is easier to shear a fluid than a solid, the shear decreases.

When it comes to the wear, the adhesion induces a high level of shear, which can be sufficient to plastically deform the asperity junctions and create anisotropy. In 1959, Tabor remarked that a flow of material was created during sliding, which increased the area of contact, and it resulted in an increase of the frictional force while the normal force was not affected. This phenomenon is called "junction growth".

In 1971, Schallamach [14] performed sliding experiments between hard materials and soft rubbers where he could observe "waves of detachment propagating at high speed". Elastomers follow a cycle of de-adhesion and re-adhesion. In the re-adhesion phase, one end of the elastomer sticks to the hard surface and stay in the same position for a short time, while the other end is still moving at a constant speed. It means that some energy is stored in the material elastically. It is followed by a de-adhesion process where the energy is partially restored. The energy needed for re-adhesion is smaller than the de-adhesion energy, such as there is a net loss of energy for each cycle.

Deformation component of friction

Deformation of the materials is a component of the total friction, which is important when the adhesion is small. It can be the case when the contact is appropriately lubricated, and there is no direct contact between the two sides. Deformation either occurs because of material shear deformation close to the interface, the ploughing of the softest material or crackings. During sliding, in the beginning, the atoms are at rest, then the shear deforms the material elastically until there is a slip. After each cycle, the atoms go again to a new resting position. During this process, they vibrate and lose the energy given through heat dissipation or plastic deformation.

Polymer is usually soft viscoelastic material. Let's consider a tribological system made of a hard asperity sliding on a polymer. The elastic energy is given in front of the asperity, and a part of this energy is stored internally inside the material through potential energy. Most of this energy is restored at the rear of the asperity, and the rest of the energy is dissipated as heat. This effect is called hysteresis deformation [15]. It has a relatively small impact on the friction for metals; however, the hysteresis losses can be high for elastomers (rubbers).

At the interface, if the macroscopic pressure is "small enough", meaning that the macroscopic stress in the material is not excessively high compared to the hardness and yield strength of the material, then only the tips of the asperities are in contact. Those regions are small, and therefore the local stresses and local strains are high. High shear can often be observed in the first few nanometers close to those asperity junctions. Furthermore, the asperity of the hardest material can generate a ploughing of the softest material, where the material is pushed away from the contact. This deformation is happening in a large region underneath the contact. The distance at which the deformation is high is usually in the range of the contact radius. This ploughing or cutting of the softer material induces energy losses.

2.5 How does macroscopic friction relate to nanoscopic friction?

The phenomenological laws of Amontons and Coulomb fail to describe nanoscopic systems. Those laws work relatively well when the surfaces in contact are flat and macroscopic, and the pressure is not excessively large. A macroscale contact is a complex system, and understanding all the mechanisms leading to friction can be difficult.

One of the most important parameters used in estimating and comprehending the friction is the real contact area A_r . It is important to know this value because it dictates friction. It is equal to the sum of all junctions areas. The junctions are usually located between asperities that are in contact with one another. When a normal load is applied, the number of junctions and the surfaces of the junctions increase. The relation between the true contact area and the load depends on the material properties of the materials (yield strength, hardness, etc.). Nanoscale investigations are interesting for various reasons. A lot of the friction mechanisms can only be revealed by analysing that scale, and many MEMS/NEMS applications can benefit from nanoscale research. If we want to understand the friction mechanisms, it is important to investigate what is happening at that scale.

Simplifying the problem to a single asperity contact is a way to analyse and understand some of those mechanisms. Statistics can be used to give a prediction of the macroscopic contact. A review of the different models existing for elasticplastic contact mechanics (single asperity model) has been done by [16].

If the deformation of the asperity junctions is fully plastic, the asperities of the hardest material usually indent the softest material. If we only look at one contact asperity, we can assume that the contact area is equal to the ratio of the load F_n over the Hardness H of the material ($A_r = F_n/H$). This relation explains Amontons' law in the plastic regime because A_r is directly proportional to the load.

If the deformation of the junction asperities is fully elastic, then the contact asperity can be described by Hertz theory. The theory provides a relation between the load and the contact area. For a single asperity, A_r is proportional to $F_n^{2/3}$. It would be normal to expect flat macroscopic contact to have the same proportionality level (2/3) since the real contact area is made of a multitude of asperities. In reality, it is not the case because we know from Amontons' law that proportionality should be roughly equal to one. Based on Hertz' theory, in the 50s, Archard proposed a statistical solution where he assumed that the surfaces are fractal and the number of asperities depends on the load. He arrived at a proportionality equal to 8/9, [17] which explains relatively well Amontons' law.

The Hertz theory works relatively well for macroscopic contacts in which the amount of plastic deformation is negligible. The assumptions are that the surfaces are continuous, the contact area is small compared to the size of the objects, the bodies are perfectly elastic, and the surfaces are frictionless. Assuming the shear stress is not strongly dependent on the normal load, the contact area is:

$$A = \pi \left(\frac{RF_n}{E^*}\right)^{\frac{2}{3}},$$
 (2.9)

$$\frac{1}{E^*} = \frac{4}{3} \left[\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right]$$
(2.10)

$$R = \frac{R_1 R_2}{R_1 + R_2},\tag{2.11}$$

where F_n is the normal load, E^* is the reduced Young's modulus, and R is the reduced radius. Even if Hertz theory has been used by Archard to describe multiscale roughness contacts, the theory fails to describe accurately nanoscopic contact. Nanoscale contacts are often not fully elastic and also the adhesion of the atoms can increase significantly the contact area.

Two theoretical models that include the adhesion are the JKR model [18] that account for a short-range adhesion and the DMT model [19] that accounts for the long-range adhesion. A general model exists that reconciles those two laws [20]. At an atomistic level, friction can be understood as the sum of the forces of the various atoms interacting with one another. Using the real contact area to describe tribological systems is not a perfect solution. Fundamental parameters such as the density of atoms, the type of bonds or the motion of particles and molecules are not directly addressed in these laws [21]. In laboratory, single asperity nanoscale experiments are usually performed to investigate this scale.



Figure 2.6: An AFM tip is attached to a cantilever. The deflection of the cantilever beam is recorded via a laser and a photodetector. A motor controls the motion of the cantilever in order to have the tip scan the sample. A 3d picture of the surface is obtained (picture taken from "The Opensource Handbook of Nanoscience and Nanotechnology").

2.6 Friction Force Microscope

The nanoscale friction can be investigated in laboratory experiments, simulations or in models. In laboratory, nanoscale friction is commonly investigated with an Atomic Force Microscope (AFM) used as a Friction Force Microscope (FFM) device.

Binning, Quate and Gerber developed the first AFM device in 1985 [22]. A schematic picture of the principle is shown in Fig.2.6. This device was primarily used to perform surface analysis with high resolution. A sharp tip is attached to a cantilever.

There are two main control modes of the device that can give accurate 3d pictures of nano-surface called tapping mode and contact mode. The taping mode will not be discussed in this thesis because it does not provide direct information about the friction. The surface of interest is probed by an AFM tip where usually a constant force is applied. The normal force is controlled by moving the base of the cantilever up or down. The calibration of the FFM tip allows for the calculation of the normal and lateral forces [23]. The lateral and vertical positions of the AFM tip are controlled by a feedback loop system. When the AFM tip probes the surface, the deflection of the cantilever beam varies with the surface roughness. A laser coupled to a photodetector measure this deflection, and the position and the deflection of the AFM is recorded over time to create a 3d picture of the surface.

The normal force and the lateral force are known during sliding, which allows using this device as a tribometer. In that case, we use the term Friction Force Microscope (FFM) to speak about the method. The spring contact k corresponds to the lateral stiffness of the cantilever. It is linked to the geometrical properties of the cantilever (length and height). Depending on the application, the spring

constant is usually in the range of 0.1N/m to 100N/m. The choice of the stiffness to use in experiments is important [22] because it defines the range of the applied normal force.

2.7 Stick-Slip

In many processes involving dry friction, the friction force will experience sawtooth oscillation over time. This phenomenon was termed Stick-Slip by Bowden and Leben in 1939 [24]. In the sticking phase, the friction force increases linearly up to the force needed to overcome the static friction; it is then followed by a sharp decrease of the friction. This phenomenon can happen periodically or randomly due to thermal noise, irregularities, etc. One condition for this to happen is that the static friction must be higher than the dynamic friction. The stick-slip phenomenon can be disregarded if it does not affect what the system is supposed to do. Stickslip is often unwanted in a system because it increases friction and can create high audible noise. In rare cases, this might be wanted, for example in music when a violin bow slides on a string. The solutions to avoid this stick-slip are to use materials that have roughly the same static and dynamic COF, or to use lubricants, or to reduce the spring stiffness of the sliding body.

At an atomistic scale, stick-slip has been observed using Friction Force Microscope experiments [2]. When the nanoscopic counter body slides over the substrate, it sticks at a location on the surface that is often related to the roughness or to the energy landscape of the interface. During this sticking period, the lateral force increases gradually because of the motion of the cantilever. Then the tip rapidly slips and the lateral force is reduced. This cycle repeats over and over and thus the friction looks like a saw-tooth curve.

Prandtl-Tomlinson model

A simple mathematical model called the "Prandtl-Tomlinson model" (PT) [25–27] has been a key tool to understanding the stick-slip pattern. The PT model describes the motion of a single asperity (for example the tip of an AFM) sliding over a sinusoidal surface of period *a*. A point of mass *M* represents the tip of the AFM. This tip is attached to a support that is moving at a constant velocity *v* via a spring that has an elastic constant *K* (Fig. 2.7) and a damping parameter γ . Newton's equation of motion is:

$$M_i \ddot{x} = F - \gamma \dot{x}, \qquad (2.12)$$

where γ is the damping of the tip, and *F* is the force exerted by the gradient of the potential energy ($F = -\nabla U$). The potential is defined as:

$$U(x,t) = \frac{1}{2}U_0\cos(\frac{2\pi}{a}x) + \frac{K}{2}(x-\nu t)^2,$$
(2.13)

The sinusoidal shape mimics a regular crystalline surface structure. At a nanoscale level, the surfaces are often crystalline and periodic.



Figure 2.7: Prandtl Tomlinson model, a damped tip is attached to a support via a spring. The tip slides on a periodic surface.

where U_0 is a constant describing the amplitude of the potential corrugation, and a is the wavelength of the sinusoidal. U_0 is dependent on the load with a higher load gives higher corrugation and thus higher value of U_0 . The first term of the equation is here to represent the substrate and the second term represents the potential energy in the spring. With this model, two modes of tip motion have been identified: smooth sliding and stick-slip. The mode of motion depends on a dimensionless parameter $\beta = 4\pi \frac{U_0}{Ka^2}$. $\beta < 1$ corresponds to the smooth motion and $\beta > 1$ to the stick-slip motion. When $\beta > 4.604$ and $\gamma < \frac{4\pi}{a} \sqrt{\frac{U_0}{M}}$, multiple slips can occur, meaning that the tip can jump several neighbors before to stick again [28].

Thermal effects

A thermal effect can be added to the PT model to account for thermal noise. It is a more accurate representation of the physic of the system. Thermal noise causes random kicks that might help the mass (tip of an AFM) to jump between two potential minima. This is done by adding a thermal random force f that respect the fluctuation-dissipation theorem [29] to the equation of motion:

$$M_i \ddot{X} = F - \gamma M \dot{X} + f(t), \qquad (2.14)$$

where *F* is the force exerted by the gradient of the potential energy $(\frac{\partial U}{\partial x})$, γ is the damping constant, *T* is the temperature and f(t) is the random force. The term f(t) is simulating random collisions with a Brownian particle. It follows that the average force over time must be equal to zero $(\langle f(t) \rangle = 0)$ and the function must be delta correlated to account for the fact that the force at time *t* is uncorrelated to the force at time *t'*:

$$\langle \delta f(t) \delta f(t') \rangle = B \delta(t - t'), \qquad (2.15)$$

where *B* is a constant representing the strength of the random force. The constant *B* is equal to $2m\gamma k_B T$ with k_B being the Boltzmann constant and *T* is the temperature.

This type of equation is called Langevin equation 2.14. This is widely used in Molecular Dynamics simulations to regulate the temperature (thermostat).

The distribution of the random force is gaussian and has a standard deviation σ :

$$\sigma^2 = \frac{\sqrt{2M\gamma k_b T}}{\Delta t} \tag{2.16}$$

Each time the tip is kicked, it has a probability to jump over the potential barrier. The rate at which those jumps occurs is described by $\omega_0 \exp\left(\frac{-U_0}{k_BT}\right)$, where ω_0 is the attempt frequency. The average time at which the tip is supposed to stay in one potential (ν/a) well becomes an important parameter. The ratio of this average time over the rate of activation provides another dimensionless parameter Δ [30]. $\Delta \ll 1$ when the velocity of the tip is small or the temperature is high. If the velocity of the tip is small the tip stays a long time at the bottom of a given energy well and it has a lot of possible attempts to jump over the barrier. If the temperature is high, then the jumps occur more often. When $\Delta \ll 1$ the friction becomes low. This phenomenon is called thermal lubricity. On the contrary, if $\Delta \gg 1$, stick-slip motion is observed. When thermal lubricity is present in a system, the friction is proportional to

$$F \propto |\ln \nu|^{\frac{2}{3}},\tag{2.17}$$

where v is the sliding velocity [31].

2.8 Lubricants

A way to reduce friction is to use lubricants. Graphene lubricant has been investigated in one of our works because it has promising tribological properties. There are several types of lubricants: gases, liquid, greases or dry. Gas lubricants are usually employed for gas-lubricated bearings. The gas is usually made of Air, Nitrogen, or Helium. They can be used at high temperatures and there is no abrasion. Liquid lubricants have various compositions. They are roughly made of 90 % oil and ten per cent additives. One of the weaknesses of the liquid lubricants is that the fluid can squeeze out of the contact region and escape. Greases are thick oils that can be kept at a given location. They can be used to build a barrier against contaminants like dust, mud or water. Dry lubricants are made of solid material. Common dry lubricants are Graphite/Graphene, Molybdenum disulfide, Boron nitride, Tungsten disulfide and Polytetrafluorethylene. They can be used at high and low temperatures.

Graphene lubricant

Graphene is a two-dimensional material (Fig. 2.8) that has remarkable friction and wear properties [32]. Graphene is chemically inert and has extremely high strength over 100 GPa and Young's modulus of the order of 1 TPa [33]. Graphene on metals has been extensively studied [34–36]. Graphene reduces friction, it has anti-corrosion properties, and the wear can be drastically reduced.



Figure 2.8: picture of a graphene sheet and picture of the honeycomb structure.

2.9 Self affine surfaces

The most common way to characterise a surface is to measure its roughness. There are several roughness parameters that can be computed. Those parameters are often used for many applications in industrial design. Changing the roughness of a surface can directly influence friction (roads, shafts, etc). The roughness is a surface property that often scales dependent. More surprising, there is a lot of surfaces that can be considered to be self-affine. A surface is considered to be self-affine if by rescaling the height of the surface (height of atoms for a nanoscopic system) by a specific factor, the roughness would be the same throughout every scale.

Chapter 3

Polymers

3.1 General remarks on polymer

Polymers are large molecules made of repeating units called monomers. (Fig. 3.1). Monomers are attached via covalent bonds (electron sharing). Polymers are used in a wide variety of applications for their material properties (biomedical, aerospace, sports, food packaging, seals, etc.).

Their material properties depend on their chemical composition and structure. They also have unique properties that are not found in any other type of material. Some of them have the ability to form branches that are attached to the main chain but not to other molecules (polyethylene, PVC, Nylon 66, polymethyl methacrylate, etc), while others can fuse with adjacent chains to form a cross-linked structure (nylon, ethylene-vinyl acetate, etc.).

The length of the chains and type of atoms are nanoscopic properties that have a direct effect on material properties, including density, glass temperature, or degree of crystallinity. In return, those macroscopic material properties affect the macroscopic mechanical properties of the material (strength, ductility, toughness, etc). Mechanical properties are important because they can be used to calculate the stress and strain of the material. We usually associate polymers with high elasticity (flexibility or compliance), viscoelasticity, and toughness. These properties vary considerably depending on the polymer that is used. At room temperature, for example, rubber and polyester can stretch extensively, while epoxies are hard and tough.

A polymer material can be described at various scales. At the lowest scale



Figure 3.1: Example of a polymer chain (polyethylene) made of multiple monomers. A monomer is a group of atoms that repeats itself to form the polymer chain.

(1 nm), polymer molecules are made of long chains of similar units bonded together (monomers). At a larger scale (10 nm), we can describe the spatial configuration of the monomers within a single chain. In solid linear polymers (no branching or cross-linking), those chains fold and often form semi-crystalline structures. In the region where the parallel orientation is high, the chains can form lamellar structures (<50 nm), which can, in return, form spherical structures called spherulites (>500 nm).

Chain formations happen via a polymerisation process. There are two main types of chain growth, addition, where polymer chains react with one another, and step-growth (condensation), where a monomer reacts with a reactive site of a polymer chain.

The solidification of polymer materials occurs through a crystallisation process. Fast cooling occurs (high rate of temperature change) during a polymer melt, the chains partially align with one another, and a complex semi-crystalline structure is obtained. The material looks like a mix between a crystal and a fluid. The amorphous viscous polymer transforms into a stiffer, harder material. The atoms forming the melt do not have time to fully reorganise, and they stay frozen in their positions.

The temperature at which this transformation occurs is called the glass transition temperature, T_g . The glass transition temperature is often a parameter used to determine which polymers are better suited for certain applications. For example, rubber tyres need to have high friction when in contact with the road, which requires the tyres to accommodate the roughness of the road. Therefore, the polymers in tyres need to be soft and ductile, which happens if the polymers are above their glass transition temperature during the sliding process. Ways to increase the degree of crystallinity include decreasing the cooling rate, using shorter chains, or increasing the stiffness of the chains [37]. The stiffness of the polymer material is highly affected by temperature (Fig. 3.2). The material properties of the polymer are affected by this phase transformation. For example, it can affect the stiffness of the material. When a deformation occurs, one part of the deformation is elastic, while the other is plastic. At a microscopic level, the deformation occurs internally due to the torsion, rotation, or stretching of molecular bonds or global movement of the chains and chain scissions. When a force is applied to a polymer over a long period of time, the chains change position, and the material can creep (cold flow). The chains have a tendency to align with one another, which decreases the entropy of the system. When the force is removed, the entropy of the system increases, and the chains return to a more disordered state. This phenomenon is called 'entropic elasticity', and polymers exhibiting this behaviour are called elastomers [38].

Theory of polymers

There are important polymer properties that can be computed theoretically. The simplest model is the ideal chain model [39–41]. In this model, the monomers do


Figure 3.2: The stiffness of a polymer largely depends on the temperature. This graph illustrates this relation. The crystallinity level and the length of the chains of the polymer strongly affect the relation. If the polymer has a high level of crystallinity and long chains, the transition seen at the glass has a tendency to disappear. If the polymer chains are too short, the rubbery state is not present, and the stiffness of the polymer drops after the glass transition because the chains are disentangled.

not interact with one another. A polymer chain is modelled by a chain made of several segments that are linked by rigid bonds. The direction that a bond takes is random (random walk), and the segments can cross themselves multiple times. The end-to-end distance R_{ee} is an indication of the average stretching length of the chain. It is equal to zero if the chain is not stretched. The average square of R_{ee} is defined by:

$$\langle R_{ee}^2 \rangle = N b^2, \tag{3.1}$$

where *b* is the bond length, and *N* is the number of bonds. This size is proportional to $N^{\frac{1}{2}}$.

Another important parameter that can be computed is the radius of gyration R_g :

$$R_{g}^{2} = \frac{1}{N} \sum_{n=1}^{N} \langle (R_{n} - R_{G})^{2} \rangle, \qquad (3.2)$$

where R_G is the position of the center of mass defined as:

$$R_G = \frac{1}{N} \sum_{n=1}^{N} R_n.$$
 (3.3)

Similarly to $\langle R_{ee}^2 \rangle$, the radius of gyration gives an idea about the size of the polymer. For a large ideal chain, R_g is equal to $\frac{1}{6}Nb^2$. This model also works for branched polymers, and the value can be found experimentally via light scattering or X-ray techniques. The ideal chain model is called ideal for a reason. In reality, polymer chains do not act so nicely, and monomers take a given volume, which excludes other monomers from occupying the same spot.

3.2 Friction of polymers

Polymers are complex and have unique material properties. The adhesion of the polymer to a mating surface is due to van der Walls, ionic, or chemical bonding interactions. During sliding, the forces at the interface and the forces between the chains inside the substrate are often on the same order of magnitude. This means that the slips can either happen inside the substrate (visco-plastic deformation) or at the interface.

Temperature has a strong effect on the adhesion of polymers. An increase in temperature decreases the shear and increases the contact area, which affects friction ($f = A\tau$). Often, the shear τ and the contact area A do not vary proportionally (different change of rate) to one another, which can lead to non-linearity in the friction with respect to temperature [11, 42–44]. Above the glass transition, the friction often decreases because the shear strength of the material is reduced. Temperature affects the relaxation time of the chains and thus the viscosity of the material.

For metals, friction is often not strongly dependent on the sliding speed. However, in polymers, the sliding velocity has a major potential impact on friction. A high sliding speed increases the temperature at the interface and decreases the contact time, and it reduces the time during which individual polymer chains experience stresses. The deformation mechanisms of polymers (creep, relaxation) happen over different and potentially long time periods. These time periods are affected by temperature. For example, if the temperature increases above the glass transition temperature, the deformation rate increases, and the retardation time decreases. The relation between friction and velocity is often complex. Regarding wear, polymers are subjected to high shear deformation in the first few nanometers close to the contact. This can, in some cases, lead to the complete reorganisation of the polymer (combing). The chains disentangle during rubbing and align parallel to the direction of sliding.

It has been shown that the amount of chain ends at the surface can increase adhesion. Because of this, cross-linked polymers that have almost no chain ends experienced less friction than uncross-linked polymers [45, 46]. The reason friction increases with the amount of chain ends at the surface is that the chain ends have more mobility and can penetrate deep inside the other material (especially for polymer/polymer contact). The number of chain ends can be increased by scission of the chains simply because polymers made of shorter chains have more chain ends.

3.3 Polyvinyl alcohol polymer (PVA)

In our work, all simulations have been run using a PVA model. The reason this molecule has been chosen is that it is a polymer that was relatively simple to model. It is stable (does not react easily), and the coarse-grained potentials have already been calculated by Muller et al. [47]. PVA is odourless and non-toxic,



Figure 3.3: Example of an atactic polymer (picture taken from Wikimedia Commons, user: Benjah-bmm27).



Figure 3.4: Different polymer configuration (picture taken from Wikimedia Commons, user: Joël Gubler).

and it is used in food packaging, to strengthen textiles and paper, or as a biomedical hydrogel because it enables the construction of porous membranes [48]. It is soluble in water and has a high adhesive quality. PVA is often prepared by hydrolysis (addition of water) of polyvinyl acetate [49]. It is an atactic polymer (The substituent R in the -H2C-CH(R)- is placed randomly, see Fig. 3.3), and it has a zig-zag head-tail configuration [50] (see Fig. 3.4). When it crystallizes, it has a monoclinic (a = 7.85 Å, b = 2.55 Å, c = 5.5 Å) structure [51]. The main macroscopic properties of the PVA material are summarised in table 3.1.

Table 3.1: PVA properties at room temperature and atmospheric pressure.

Property name	value	units
Young modulus E	41	MPa
Density $ ho$	1.19	$\frac{g}{cm^3}$
Heat capacity C_p	61.5	$\frac{J}{molK}$

Chapter 4

Molecular dynamics

4.1 Explanation of the numerical method

In research, simulations of physical systems are becoming increasingly preponderant. A simulation is a numerical model that is used to mimic a real system or process. A simulation can be used for various reasons: to explore new ideas, predict performances, gain knowledge about system dynamics, understand underlying phenomenons, perform a parameter study, save time and money by removing the need for real expensive testing, etc. Almost every simulation involves some level of model simplification because it is not possible to model everything, and sometimes the system that needs to be modelled is simply too complex. Moreover, the results of a simulation are limited by the parameters that have been put into the simulation (you get what you put in).

Molecular dynamics (MD) is a numerical simulation tool that is used to simulate many-particle systems. In the 1950s, the first MD simulation was developed to describe hard-sphere materials [52, 53]. Today, MD is often used in physics to model the motion of atoms, molecules, or nanoscale systems. MD can also be used over a large range of length scales and is not limited to nanoscale systems. In MD, the positions and momenta of the particles are calculated over time. It is possible to see what individual atoms (or groups of atoms) are doing, which is much harder to do in nanoscale experiments. The motion of the particles is described by Newton's equation of motion and a set of potentials describing the interactions between the particles:

$$M\ddot{X} = -\nabla U(X_1, X_2, ..., X_n, V_1, V_2, ..., V_n)$$
(4.1)

This method often acts as a bridge between experimental and theoretical work. The other advantage of performing such simulations is the ease with which parameters can be changed (velocity, load, temperature, etc.). However, many parameters are limited in range because they require too much computing power. In this thesis, all the simulations have been run with LAMMPS [54].

This chapter explains how such simulations work.

4.2 How to run a molecular dynamics simulation?

This section provides a short summary of the physics behind MD simulations [55]. The main idea behind this simulation technique is to have a systematic way to numerically integrate the equation of motion. The equation of motion works for continuous motions, and to model it numerically, a discrete solution with small time steps needs to be implemented. Numerical integrators discretise systems, but they provide solutions that involve some level of inaccuracy. The discretisation is done by using Taylor series:

$$f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(b)}{n!} (x-b)^n$$
(4.2)

where *n* is the $n^t h$ derivative of *f* at point *a*.

$$f(x) = f(b) + \frac{f'(b)}{1!}(x-b) + \frac{f''(b)}{2!}(x-b)^2 + \cdots$$
(4.3)

Now if we apply this equation to the position f(x) = X(t), we get:

$$X_{t+1} = X(t_0) + \dot{X}(t_0)\Delta t + \frac{1}{2}\ddot{X}(t_0)\Delta t^2 + \cdots$$
(4.4)

$$X_{t-1} = X(t_0) - \dot{X}(t_0)\Delta t + \frac{1}{2}\ddot{X}(t_0)\Delta t^2 - \dots$$
(4.5)

which can be rewritten as:

$$X_{t+1} = X_t + V\Delta t + \frac{1}{2}a\Delta t^2 + \cdots$$
(4.6)

$$X_{t-1} = X_t - V\Delta t + \frac{1}{2}a\Delta t^2 - \cdots,$$
 (4.7)

where *a* is the acceleration, *V* is the speed, and t + 1 is a time index.

verlet

Adding those two equations, we get:

$$X_{t+1} + X_{t-1} = 2X_t - \nu_t \Delta t + \frac{1}{2}a_t \Delta t^2 + O(\Delta t^4).$$
(4.8)

This is the Verlet algorithm. It has significant advantages: it is time-reversible and symplectic, meaning that large time steps will not ruin the simulation. The Verlet algorithm is an integration scheme. A Hamiltonian is a mathematical formula describing the physical evolution of a system. The solutions of the Hamiltonian are on a 2dN symplectic manifold (closed smooth surface). The numerical solutions of the Hamiltonian use discrete solutions that are not precisely on the 2dN manifold, which can create long-term instability. A symplectic integrator ensures no drift of the solution over time; otherwise, there is a risk of aberrant results. However, this algorithm has some drawbacks. The position and velocity needed in the calculation are not known at the same time step.



Figure 4.1: Figure showing the different inter-atomic interactions. The interactionic interactions are described by their potentials.

Velocity Verlet

Another symplectic algorithm exists, called the Velocity Verlet algorithm, in which the position and the velocity are obtained at the same time step. The error is in the same range as the Verlet algorithm. There are three main equations for position, velocity, and force [55]. They are computed for every particle at every time step:

$$X_{t+1} = X_t + v_t \Delta t + \frac{a_t}{2} \Delta t^2$$
(4.9)

$$v_{t+1} = \frac{X_{t+1} - X_t}{\Delta t} + \frac{a_{t+1}}{2} \Delta t$$
(4.10)

$$a_{t+1} = -\frac{\nabla V(X_{t+1})}{M} \tag{4.11}$$

The position, velocity, and acceleration are known at step t, and we calculate those properties at step t + 1. We see that there is a specific order in which those quantities must be computed. The position only depends on the previous step; also, it is calculated first. Then, the force is calculated at time t + 1, which makes it possible to compute the velocity. These steps are repeated in this specific order to run the simulation.

4.3 Potentials

In this section, some of the potentials that have been used in the thesis are described. It should be noted that there are many other potentials that exist. The description of the potential energy includes an energy field that is used to calculate the magnitude and direction of the force for every atom or particle. To model the physics of a real system, we provide a set of potentials for every particle in the simulation. These potentials allow the modelled particle to mimic the behaviour of real particles. Figure 4.1 shows examples of what the potentials can model.

Bond potential

The potential of the object in question can take many forms depending on the system that needs to be modelled. If we want to simulate a bond between two particles, the most common method is to model this interaction with a harmonic

spring.

$$V = K_{ij}(r_{ij} - r_0)^2, (4.12)$$

where K_{ij} is the spring constant, r_0 is a constant defining the bond length, and r is the position of the spring.

Angle and torsion potentials

Angle and torsion potential are often described by data tables or complex functions depending on the bending and torsional angle. The energy required to twist the molecules (torsion) is often less than the energy required to bend the bonds (angle), which is usually smaller than the energy needed to stretch the bond. The torsion potential can have a significant effect on the relaxation of the polymer chains, and assigning an angle potential to a polymer chain makes it stiffer.

Non-bonded potential

The pair potential is used to model the interaction of two particles that are not chemically bonded. Two particles interacting with each other are usually comprised of a repulsive potential, a coulombic interaction, and an attractive interaction. The coulombic interaction is:

$$U_{coul} = \frac{1}{4\pi\epsilon} \frac{q_i q_j}{r_{ij}},\tag{4.13}$$

where ϵ is the permittivity of a vacuum, q_i is the quantity of charge of the particle i (in Coulombs), q_j is the quantity of charge of the particle j, and r_{ij} is the interatomic distance. The attractive interaction is:

$$U_{VdW} = -\frac{A}{r^6},$$
 (4.14)

where *A* is a constant depending of the atoms that are interacting. The power six has been validated experimentally. The repulsive interaction is:

$$U_{exclusion} = \frac{B}{r^{12}} \tag{4.15}$$

This expression is used to take into account the Pauli exclusion principle when particles are at a small distance from one another. The constant B depends on the atoms that are interacting. The power twelve is empirical, and here it represents a high repulsion for a low r-value. It is also common to see a power nine instead, usually to model softer repulsion.

In the absence of coulombic interaction, the sum of the last two potentials is called a Lennard-Jones potential. It is one of the most commonly used non-bonded potentials and is equal to:

$$V_{LJ}(r)_{ij} = 4\epsilon_{ij} [(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^6], \qquad (4.16)$$

where ϵ_{ij} is the well depth of the potential and has the unit of energy, and σ_{ij} is the distance at which the particle—particle potential energy is null. ϵ_{ij} is the strength of the interaction, while σ_{ij} is roughly equal to the diameter of the particle (if the two particles have the same radius). The resting distance of the potential is $r = r_m = 2^{\frac{1}{6}}\sigma$. The shape of this potential also has some benefits that can be seen when we calculate its gradient:

$$\frac{\vec{F}_{ij}}{M} = -4\epsilon_{ij} \left[-12 \frac{(\sigma_0)^{12}}{(r_{ij})^{13}} - (-6) \frac{(\sigma_0)^6}{(r_{ij})^7}\right] \frac{\vec{r}_{ij}}{r_{ij}}$$
(4.17)

Which is rewritten as follows:

$$\vec{F}_{ij} = \frac{48\epsilon_{ij}}{r_{ij}^2} [(\frac{\sigma_0}{r_{ij}})^{12} - \frac{1}{2} (\frac{\sigma_0}{r_{ij}})^6] \vec{r}_{ij}$$
(4.18)

This formulation is slightly faster than the previous equation because $\frac{\sigma_0}{r_{ij}}$ is repeated twice, and there is no need to calculate any expensive square root, as r_{ij} always appears with even powers. A great deal of interatomic potential between the same particles is described in the literature. This formulation is undoubtedly the most common way of describing a non-bonded interaction.

4.4 Coarse-grained potential for PVA

The main purposes of using a coarse-grained model are to be able to model large structures when compared to full atomistic simulations and to speed up simulations by eliminating the high-frequency vibration, thus being able to increase the time step. Setting the parameters of a coarse-grained model is sometimes required to perform multiscale modelling.

Multiscale modelling approaches are used by simulating systems based on information coming from models that have been conducted at a different scale. A numerical method is chosen according to the length scale that needs to be simulated. At the smallest scale (pm), density functional theory (DFT) can be used to investigate the electronic structure. Results from DFT can be used to develop interatomic potentials. Those potentials can be used in molecular dynamics simulations to run full atomistic simulations (nm). The statistics about the relative position of the atoms coming from full atomistic simulations (all atoms are modeled) can be used to create coarse-grained models in which coarse-grained particles replace groups of atoms. Continuum mechanics is used to model the highest levels (Finite Element Method, Finite Volume Method, etc.).

A coarse-grained model developed by Muller-Plathe [56–60] has been used to mimic the behaviour of a PVA material. A coarse-grained model replaces a group of atoms (2 backbones in our case) with one coarse-grained particle while assuring that the overall structural characteristic of the polymer is preserved. A set of po-



Figure 4.2: Coarse-grained model for PVA (C2H4O)x. Red atoms are oxygen, dark grey is carbon, and clear grey is hydrogen. One green circle represents one coarse-grained particle that replaces the group of atoms C2H4O.

tentials describes the interactions between the coarse-grained particles (Eq. 4.20).

$$V_{\text{total}} = V_{\text{bonded}} + V_{\text{non bonded}} \tag{4.19}$$

$$V_{\text{total}} = (V_{\text{bond}} + V_{\text{angular}} + V_{\text{torsion}}) + (V_{\text{van der Waals}} + V_{\text{electro-static}})$$
(4.20)

In the PVA coarse-grained model that we used, assigning suitable bond, pair, and angular potentials is sufficient for modelling the molecules (Fig. 4.2). The electrostatic forces are not needed because the PVA is a neutral polymer, and it appears that there is no torsion potential needed because the real torsion of the molecule is taken into account by the coarse-grained bending potential. What Muller Plathe did to build the model was to preserve some structural properties. Interesting properties that need to be preserved are the intra- and interchain distribution functions. A Radial Distribution Function (RDF) describes the average density taken from a reference particle or group of particles over a given radial distance. A full atomistic simulation of a polymer chain is placed in water while the temperature and pressure are controlled. A set of RDFs is computed that gives information about the structure of the polymer. The RDFs functions become the target functions that need to be preserved when replacing the particles with the coarse-grained particle. For polyvinyl alcohol (PVA) materials, the terms of the potentials are adjusted in the order of their relative strength :

$$V_{\text{bond}} \rightarrow V_{\text{angular}} \rightarrow V_{\text{van der Waals}}.$$
 (4.21)

The distribution of two successive backbones has a Gaussian shape, and this function is Boltzmann inverted to get the spring potential.

$$V_{\text{bond}(l)} = k_b T \ln(P(l)), \qquad (4.22)$$

where k_b is the Boltzman constant, T is the temperature, and P is the distribution. The same approach is used for the angle potential:

$$V_{\text{bond}(\alpha)} = k_b T \ln(\frac{P(\alpha)}{\sin(\alpha)}).$$
(4.23)

The non-bonded interaction is modelled via a Lennard-Jones 9-6 potential.

$$V_r = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^6\right) \tag{4.24}$$

There is a power nine instead of twelve, which is the most common parameter used for Lennard-Jones potentials. This makes the repulsive part of the potential a bit softer.

4.5 Thermostats

We used Nosé Hover (global) and Langevin (local) thermostats to regulate the temperature in our simulation. It is important to use a thermostat when performing a sliding simulation because energy is brought continuously to the system, increasing the temperature indefinitely.

Langevin

The Langevin equation is described in Section 2.7.

Nosé-Hoover

For the Nosé-Hoover thermostat, a term is added to the equation of motion:

$$M_i \ddot{X}_i = F_i - \zeta(t) M_i \dot{X}_i \tag{4.25}$$

This accelerates or slows down the acceleration of the particle until the right temperature is reached. ζ defines how fast the change of momentum $M_i v_i$ is occurring.

$$\frac{d\zeta(t)}{dt} = \frac{1}{Q} \left[\sum_{i=1}^{N} M_i \frac{\dot{X}_i^2}{2} - \frac{3N+1}{2} k_b T \right], \tag{4.26}$$

where *Q* is a parameter expressing the thermal inertia, and T is the target temperature. When the right temperature is reached, there is no need to add the frictional term ζ to Eq. 4.25, whereas when there is a large difference between the target temperature and the temperature of the system, the value of ζ needs to be high. Eq. 4.26 expresses this change by subtracting the target kinetic energy $\frac{3N+1}{2}k_{bT}$ (equipartition function) from the kinetic energy $M_i \frac{v_i^2}{2}$ of the system.

4.6 Some Molecular Dynamics applications

Polymers

MD simulations have been widely used to investigate the crystallisation of polymers [61–64]. The results of these simulations have shown the importance of the stiffness of the polymer on the crystallisation level[62, 65, 66].

The coarse-grained model developed by Muller-Plathe [56] can be used to increase the simulation time and dimensions of the system (Sec. 4.4). This model has been used to show the effect of the chain length on crystallisation [57].

Nanofriction

It is a common practice to combine FFM experiments with MD simulations [67]. It can also be used as a predictive tool, where the effects of various parameters on tribological systems can be observed numerically.

As we described in Sec. 2.6, in an AFM experiment, a nanoscale tip is attached to a cantilever that is pulled. A review from 2013 describes the important parameters that are used and what can be expected from such a simulation [68]. The stiffness provided by the tip and the cantilever needs to be introduced artificially in the model. The tip is attached to a support (virtual atom) via harmonic springs. The support is pulled at a constant speed in the x direction. The normal load (z direction) can be applied thanks to a harmonic spring attached to the tip or directly by applying the load to every particle on the tip. The harmonic spring can lead to unwanted artificial oscillations in the system. Directly applying the load to the atoms of the tip solves this issue. The spring in the y direction can be the same as the one used to pull the tip. This spring often has little to no effect on the friction, so it can be discarded. Thermostats are needed in the simulation to remove the excess energy due to the pulling of the tip. The thermostat needs to be placed as far as possible from the contact because it could make the result unreliable since it directly affects the dynamics of the particles in an unrealistic way.

Two examples of studies involving molecular simulation are briefly described next to illustrate the results obtained via this numerical method. Li et al. ran a molecular dynamics simulation of graphene [69]. They showed that, contrary to traditional materials, the true contact area was not the driving force for the friction at the nanoscale. They described a 'contact quality', which increases the friction. The contact quality depends on how well synchronised the atoms of the two materials in contact are. In the beginning, the atoms of the two surfaces are not aligned with one another. After some sliding, they start to align, which increases the contact quality. Pre-wrinkling of a graphene sheet can increase this contact quality.

Hinkle et al. [70] wanted to understand how roughness originated. One of the possible contributors to the emergence of roughness was assumed to be the deformation of the bulk material. They compressed different metals (gold) or alloys and found that the self-affine roughness phenomenon was linked to the deformation. However, no such work has been done with a polymer.

Chapter 5

Summary of the articles

The work has been described in three articles. In those articles, MD simulation was the primary tool used to investigate and explore various ideas. MD provides a substantial amount of information on the dynamics of a system. Since there has been little MD work on solid polymer friction [71–74], there is room for discoveries using this method.

5.1 Nanoscale Simulations of Wear and Viscoelasticity of a Semi-Crystalline Polymer (article 1)

The research described in the first article was performed to investigate the mechanisms of polymer friction at a nanoscale level. The main idea was to investigate the frictional behaviour of a polymer PVA, a material for which the coarse-grained potentials have been well defined in the literature (Fig. 5.1). The mechanisms in that material should also be relevant for other materials and help to explain their material behaviours. In this investigation, we sought to determine the effect of temperature on the frictional forces and wear of a polymer material. We created solid polymers via MD simulation. Polymer chains were randomly laid into a box and relaxed at a high temperature. Quenching was applied at two different cooling rates on four different polymer chain lengths having 10, 30, 50, and 100 coarse-grained particles per chain, respectively. The crystallinity level of the samples was obtained by analysing the regularity of the bond angles. In this publication, we show the sliding simulation performed on a sample composed of 50 coarse-grained particles per chain at one crystallinity level. The glass transition T_{σ} of this sample was calculated to be around 350 K). This realistic semi-crystalline sample was used as a substrate, and a virtual AFM tip indented this substrate. When the indentation was complete, the tip was attached to a moving support via a spring. The friction was computed as well as a number of structural (alignment, density) and dynamic properties (displacements) to determine what happening during sliding at different temperatures (between 55 K and 385 K) and normal loads (between 0.185 nN and 0.741 nN).



Figure 5.1: Picture of an AFM tip, which is sliding over a solid PVA substrate. The tip is attached to a moving support via a spring. The coarse-grained particles that are in the same polymer chain have the same colour.

As expected, we observed that, for a given temperature, the friction increased with the normal load. Interpolating the friction, we observed that the friction did not vanish at zero loads. The evolution of friction with temperature is more complex to comprehend. The minimum friction was around 160 K.

In all the simulations, the polymer chains aligned in the sliding direction close to the contact and high-density regions formed below the AFM tip. For temperatures below the glass transition, the analyses of the particle displacement showed backward motion at the rear of the tip associated with the restoration of elastic energy. When the temperature was higher than the glass transition, the polymer chain flowed deep inside the substrate, and the backward motion disappeared. Temperature had a considerable effect on the motion of the particles around the tip.

5.2 Nanoscale friction and wear of polymer-coated with graphene (article 2)

The second article investigated the addition of a graphene layer on top of the polymer substrate (Fig. 5.2). Graphene has been studied intensively with metals, which are usually harder materials than polymers. By comparing a nanoscopic tribological system of polymer with and without graphene, it is possible to deduce how this layer helps to simultaneously protect and reduce the friction of the system. A silicon rigid tip indented the substrate, and the penetration depth was recorded. We compared the penetration depth over time for the case where the tip was only indented and the case where the tip was indented and rubbed over the surface (in the x-direction). The penetration depth increased significantly more over time when there was sliding. During sliding, the graphene constrained the



Figure 5.2: An AFM tip slides over a graphene sheet that has been placed on top of a solid PVA substrate.

polymer chain and therefore limited the wear of the substrate. The displacements of the chains were roughly an order of magnitude lower when a graphene sheet was present. The uncrumpled graphene was the most efficient at reducing friction and wear because the penetration depth of the tip was lower.

5.3 Emergence of surface roughness in a polymer undercompression (article 3)

In the previous article, we saw that nanoscopic roughness may have a strong impact on friction. Surfaces around us are rough and self-affine (see Sec. 2.9). It is interesting to understand which mechanisms are responsible for the emergence of roughness. This article describes roughness at different length scales. A bi-compression test at a nanoscopic scale was performed on a polymer (Fig. 5.3). This bi-compression induced a large anisotropy, where the chains tended to align vertically. We observed a transition from fully elastic to plastic behaviour. At the beginning of the compression, the material was mostly elastic; when the level of compression increased, the amount of plastic deformation increased, and the material behaviour became elasto-plastic. During compression, we observed that there were small structural changes in the polymer. When the compression was finished, the dimension of the simulation box remained constant, and the material was relaxed over 7.5ns. This relaxation indicates that the surface continued to evolve slightly when the compression stopped.



Figure 5.3: Bi-compression is performed on a PVA substrate, and the surface is changing. The evolution of the surface roughness is investigated.

Chapter 6

Discussion and Conclusion

In this doctoral thesis, nanoscale polymer friction was investigated via MD simulations. This is an important topic because polymers are present almost everywhere. Friction is a complex phenomenon, more so when studying nanoscale friction. Humans are accustomed to dealing with and understanding everyday macroscale friction. Still, nanoscale friction may not be as intuitive—the relative simplicity of the macroscopic phenomenological laws of friction masks the complexity of its underlying mechanisms. Macroscopic friction arises from a multitude of nanoscopic contacts where atoms interact with each other. Studying tribology at a nanoscale level provides insight on the physics of contact friction.

MD is an important numerical tool that allows us to investigate, visualise, and analyse these different interactions and thus to obtain a more fundamental understanding of our surroundings. The position, the motion of the particles, the interatomic forces, etc. can be investigated with this method. There are only a few MD simulations that have involved sliding polymers, and therefore much remains unexplored and is not yet understood. We chose to model a PVA material in all our simulations because it was relatively simple to model. The idea is that most of the mechanisms present for that polymer are expected to be present in many other polymer applications.

The models used in the thesis have limitations. First, such simulations are time consuming, and considerable computer resources are needed, meaning that only short time simulations or small systems can be modelled. The limited amount of data that can be produced in a simulation often makes the analysis challenging. Furthermore, these simulations are simplistic. The interatomic interactions, thermostats, use of periodic boundary conditions, and other parameters might represent an idealised and oversimplified view of the system. Real systems are often more complicated. Typically, there are contaminants, polymer branching, chemical interactions, or other variables that are not considered in the model. Finally, the range of simulated parameters tends to be small and restricted (contact shape velocity, etc.).

However, this method allowed us to understand how the polymer deforms, which is one of the keys to understanding the mechanisms of polymer friction.

All simulations share the same initiation steps. In the beginning, randomly placed chains are put in a periodic box. One of the periodic boundaries is broken to create a surface. A set of potentials is given to the particles that are inside the chains to mimic the behaviour of PVA. Then, the system needs to be equilibrated for some time, and a realistic melt polymer is obtained. Finally, the melt polymer is cooled down to obtain a solid semi-crystalline material. In our case, the structural and material properties of the solid sample depended on the length of the chains, the damping parameter of the thermostat, the size of the system, and the cooling rate. To increase our understanding of the subject, we studied the viscoelastic response of the PVA polymer for different tribological systems.

The first article focussed on a polymer-polymer sliding system. In this article, we performed an exploration in which we tried to understand the material behaviour (friction and wear) of a virtual FFM test. Laboratory FFM experiments on polymers have shown that chain reorientation occurs during sliding [75–77]. In such tests, however, understanding how the chains reorient and the level of that reorientation is challenging. The results of our simulations may be used to explain some mechanisms of polymer friction and thus better explain the FFM results of polymers. This project allowed us to become familiar with the PVA model but also to explore different ideas and parameters and to develop methods to analyse the data. In the results, the motion of the particles in the substrate is rather complex. There is a backward motion of the polymer particles at the rear of the tip at low temperatures. High temperature leads to high wear, i.e., plastic deformation, and to a large zone of chain reorientation. Right under the tip of the FFM, in the first few nanometres, there are regions of high density where the chains align in the sliding direction. In this article, the contact interaction was rather simple. The contact surfaces of real materials are often complex due to the presence of contaminants or lubricants. Modelling the presence of contaminants is complicated because the potential interactions between the surface and contaminants are generally unknown. Hence, in the second article we chose to investigate the effect of graphene used as a lubricant.

A common problem in polymer–polymer sliding is that the level of friction and wear can be relatively high, which is often unwanted. One way to solve this issue is to add lubricants. Graphene is often used in polymer applications as a lubricant [78] or to create self-lubricated materials [79]. We thus sought to determine if a layer of graphene could protect and reduce friction when placed on top of a polymer substrate. There are almost no studies on such a system at a nanoscale level. In these simulations, the graphene layer behaved like a soft membrane and spread the deformation over large distances. The graphene layer was undamaged, efficiently reducing friction and protecting the polymer. In contrast with the polymer-polymer sliding system, the graphene layer restrained the polymer chains underneath. As in many other applications, there was a strong influence of surface roughness on friction. If the roughness was small (flat graphene), we observed little penetration depth of the FFM tip. Consequently, the number of particles in contact was relatively small. When the roughness was higher (crumpled graphene), the number of particles in contact increased, which contributed to an increase in the frictional forces. Due to the impact roughness, it is important to better define it and its origin. Accordingly, the next article focussed on quantifying nanoscopic roughness.

Our third article attempted to understand how the roughness of a polymer material emerges and develops. We did not investigate the effect of roughness on the polymer-polymer sliding simulations. However, we would still expect, as in the graphene polymer system, that the roughness would impact friction and wear. In our polymer-polymer sliding simulations, the sample's roughness was due to the crystallisation process. However, the roughness of the surface in real polymer systems is not solely a result of the crystallisation process but is also impacted by the material history. The way in which material roughness emerges and develops is still the subject of debate today. One suspected mechanism for the formation of surface roughness is compression of the material [70]. We performed a bi-compression process on a solid polymer slab. As a result, we observed a gradual increase in roughness. Like many surfaces, the surface of our sample was self-affine, which means that the roughness displayed in similar ways at different length scales. The Hurst exponent of the surface roughness is a parameter that has been used to quantify the self-affinity of a sample. This parameter continued to increase smoothly during the bi-compression process. The evolution of this parameter was found to be significantly different from the results of similar simulations on metals performed by Hinkle et al. [70]. We attribute this difference in behaviour to the viscoelastic properties of the polymer and a gradual increase of anisotropy during bi-compression.

A general conclusion of this work on polymer systems is described next. The main goal of this work was to increase our understanding of polymer friction. The knowledge gained here could be used to promote the development of new materials. As polymer systems are often complex, it is interesting to use MD simulations. Although contacts are potentially made of billions and billions of particles, the numerical analyses of small systems (less than a million particles) helped us understand some of the underlying mechanisms of polymer systems. The After crystallisation, polymers form semi-crystalline structures with both crystalline and amorphous domains, and those domains may change when a force is applied to the material. This was the case in our sliding and bi-compression simulations. The glassy behaviour of polymers induces dynamics phenomena happening over long time scales. Polymers are viscoelastic materials; the deformation seen in those materials is partly elastic and partly plastic. It is relatively hard to know precisely the relative amount of the plastic and elastic contribution but usually, large deformation is a sign of plastic deformation. There is residual elastic strain even when the plastic deformation is large. MD simulations make it possible to obtain information about a system's dynamics, deformations, and the change of structure happening at the surface and inside the substrate.

More research is needed to strengthen our understanding of polymer friction and to promote the development of new materials. Better knowledge could be used to improve material properties and to generate better tribological applications.

We hope that this work will be used to promote the testing of nanoscale polymer systems in the laboratory. The results of those tests could be, for example, used to experimentally validate some of the results of this work. Notably, the tribological effect of the stretching of the graphene when placed on top of a polymer or the emergence of roughness in polymer materials could be studied. It would be extremely interesting to see how much of the system complexity is captured in the type of simulations that have been used. Attempting to simulate the material properties of a real sample is certainly challenging. The chain length, level of crystallinity, roughness of the material, and many other variables should be modelled. While not impossible to achieve, it would require meticulous experimental and numerical work.

The change in the distribution of chain lengths should be investigated more in depth because it is one of the main material parameters that affects material and tribological properties of polymers. In real systems, all the chains do not have the same length. Assigning a Gaussian distribution to the chain length should give a better description of real systems. Moreover, it might be interesting to create polymer samples with two different chain lengths. For example, we could model a material made of a lot of short chains and a few long chains. During sliding, the friction and wear on such a material may be low, although that would have to be confirmed numerically and experimentally. Materials made of small chains tend to have a high level of crystallinity. The small chains might create a crystallise region at the surface. Meanwhile, longer chains may be useful to maintain the cohesion of the substrate because long chains occupy large spatial regions, and it is relatively hard to break the covalent bond of the chain.

More information can be obtained from the analysis of our simulations. For example, it would be interesting to see the correlation between the local temperature and the level of deformation and damage in the material. We could examine that by computing the local temperature below the FFM tip.

There are many parameters that are worth more in-depth research in order to fill the gap in the current science knowledge. Providing an exhaustive list with detailed information about the effects of those parameters is a daunting task, so only a list is provided here. We can cite, for example, the type of polymer or lubricant, the level of crystallinity, the level of branching, the chain length, the glass transition temperature, the orientation of the polymers, the Young modulus, the stiffness of the spring, the sliding velocity, the temperature, the load, the size of the system, the strength of the adhesion, and the presence of contaminants. The length of this list should illustrate the complexity in such systems. MD offers many routes for investigation, and it is challenging to choose which paths are most relevant because many parameters can influence the results. However, the complexity of the field does not eclipse its useful applications and the scientific imperative to answer such important questions.

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Paper I

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ORIGINAL PAPER



Nanoscale Simulations of Wear and Viscoelasticity of a Semi-Crystalline Polymer

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Abstract

We investigate the underlying tribological mechanisms and running-in process of a semi-crystalline polymer using moleculardynamics simulations. We subject a slab of simulated polyvinyl alcohol to a sliding contact asperity resembling a friction force microscope tip. We study the viscoelastic response of the polymer to the sliding and show both plastic and elastic contributions to the deformation, with their relative strength dependent on the temperature. As expected, the elastic deformation penetrates deeper into the surface than the plastic deformation. Directly under the tip, the polymer has a tendency to co-axially align and form a layered structure. Over time, the plastic deformation on and near the surface builds up, the friction decreases, and the polymers in the top layer align with each other in the sliding direction (conditioning).

Keywords Tribology · Molecular dynamic · Polymers

1 Introduction

Many of the objects surrounding us are made of polymers. The friction that we experience while walking on our shoes with rubber soles or the wear of the soles are macroscopic properties. This scale has been studied widely for obvious practical reasons and there are many non-trivial effects in friction and wear specific to polymers, such as non-linearities and non-trivial temperature dependence. The origin of many of those macroscopic effects can be found at smaller scale, especially the molecular scale. Studying the contact at this nanoscale can thus provide better understanding of the underlying tribological mechanisms leading to friction and wear on the macro-scale.

The past few decades have seen rapid nanoscale developments of experimental techniques such as friction force microscopy (FFM). This technique gives accurate measurement of surface properties and frictional behavior of a single asperity, and enables to some extent speculation about what

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is happening below the contact, see [1]. FFM experiments on polymers have already shown that molecular chain reorientation, due to displacement or rotation of a chain segment or a side group (relaxation), occurs during sliding [8, 10, 17]. This restructuring has an influence on the friction. Not surprisingly, in polymers the biggest changes in tribological properties in experiments occur at the same temperature where the polymer's bulk mechanical properties also change drastically, the glass transition temperature T_g .

Currently, theoretical understanding of the frictional behavior of polymers is still lacking. As a result, the development of novel low friction solid polymer materials can only be achieved through expensive testing. Nevertheless, tools for theoretically investigating this problem at the nanoscale exist: molecular-dynamics (MD) simulations. Massive MD simulations of this problem are however extremely challenging, due to the high level of complexity of both the material and friction phenomena. There is a large elastic response, but also plastic deformation and permanent damage. Polymers form semi-crystalline structures, with both crystalline and amorphous domains that may change during sliding. The simplest limit of this semi-crystalline structuring is the ideal, but unrealistic, single crystal, and this has been investigated numerically by Heo et al. [7]. It has also been shown that the structure of the polymers changes near the tip as a result of the high stresses during indentation and sliding [16].

The aim of the present study is to improve our understanding of polymer friction and wear, especially in relation to the structure in semi-crystalline polymers. We perform MD simulations that are designed to model an FFM experiment on polyvinyl alcohol (PVA), a commonly used prototype polymeric material. This approach allows us to investigate in detail what happens to the individual chains and monomers, something that is not possible in heavily coarsegrained finite element simulations or real experiments.

2 Simulation Setup

We simulate an FFM experiment by rubbing a model atomic force microscope (AFM) tip against a polymer surface. The molecular-dynamics software LAMMPS [14] is used to calculate particle motions via a coarse-grained model, see [11, 18]. In this study, we used the coarse-grained model for PVA (CG-PVA) developed by Meyer and Muller-Plathe [12].

Each simulation contains 200,000 coarse-grained monomers for the substrate and around 25,000 particles for the tip. The radius of the tip is 4.68 nm. The atoms of the tip are arranged in a fcc configuration with a lattice spacing of 2.08 nm. They are kept that way during the entire simulations. The tip is a rigid body. The lowest atoms (last row) are removed in order to create a flat contact surface. The melt relaxation, cooling, indentation and sliding take roughly 15000 CPU-hours for a simulation of 8 ns with a time-step of 8×10^{-16} s.

2.1 Coarse-Grained Model

The coarse-grained model replaces a group of atoms by one coarse-grained particle while assuring that the overall structural characteristic of the polymer is preserved. In the coarse-grained model we use, this is done by assigning suitable bond, pair and angular potentials, Fig. 1.



Fig. 1 Coarse-grained model for PVA $(C_2H_4O)_x$. Red atoms are oxygen, dark gray are carbon, and clear gray are hydrogen. One green circle represents one coarse-grained particle which replaces the group of atoms C_2H_4O

The interactions between monomers consist of bonded and non-bonded contributions. Below, we express all quantities in terms of Lennard–Jones units, with $\epsilon_0 = 7.6 \times 10^{-21} \text{ J}, \tau_0 = 1.6 \times 10^{-12} \text{ s}, \sigma_0 = 0.52 \text{ nm}.$

Our simulation box is 42 nm in the sliding direction. During our simulation, the tip passes over the same point around 5–10 times (Fig. 2).

The bonded interactions are between monomers in a chain, and the potential energy is a sum of stretching and bending contributions. The stretching of a bond is described by a harmonic potential $V_{\text{bond}} = K(r - r_0)^2$ where K characterizes the stiffness of a spring $(K = 1352\epsilon_0/\sigma_0)$, and $r_0 = 0.5\sigma_0$ is the equilibrium bond length. To account for possible bond-breaking, this interaction is replaced by a Morse potential during the sliding simulations, $V_{\text{bond}} = D[1 - e^{-\alpha(r-r_0)}]^2$, where $D = 95\epsilon_0$ determines the depth of the potential well (the bond energy), $\alpha = 3.77/\sigma_0$ is a stiffness parameter and $r_0 = 0.5\sigma_0$ is the equilibrium bond distance. These values were chosen to preserve the equilibrium bond length and the second derivative in the minimum. The bending potential is approximated by an angular potential which is provided in table format. Because each monomer contains several carbon atoms, it accounts also for the torsion stiffness.

The non-bonded interaction is given by a Lennard–Jones 9–6 potential $V_{\text{pair}}(r) = 4\epsilon[(\frac{\sigma}{r})^9 - (\frac{\sigma}{r})^6)]$, where $\epsilon = 0.38\epsilon_0$ is the depth potential, $\sigma = 0.89\sigma_0$ is the distance at which the potential vanishes, and *r* is the distance between the monomers.

2.2 Melt Relaxation and Cooling

In order to obtain a realistic surface for our simulations, we start from a polymer melt and cool it down. Our simulation box is periodic in x and y, but confined by impenetrable hard walls in the z direction.

We generate physical initial conditions for the melt using the DPD-push-off method [15] which is designed to efficiently obtain equilibrated polymer melts. In this approach, we start from non-physical random overlapping initial conditions and a non-physical soft hybrid interaction potential. This potential consists of a 12–6 Lennard–Jones potential for the non-bonded interactions and a spring potential for the bonded interactions. After this system is equilibrated for



Fig. 2 FFM tip in 2d and 3d view

0.25 ns using the DPD-push-off protocol, the non-physical soft hybrid potential is replaced by the realistic coarsegrained PVA potential described above. The system is no longer in equilibrium for the PVA potential, so it is equilibrated again for another 0.25 ns. At this point, the melt is still unphysically hot, around 5000 K. The melt is coupled to a Nosé–Hoover thermostat at 520 K, slightly above the glass transition temperature, and time scale of 1 in LJ units. The system is then equilibrated for 4 ns at which point we have a physical and properly equilibrated melt at 520 K. We confirm this by checking that the radius of gyration is stable.

Next, the temperature is gradually decreased to 220 K with a cooling rate of 75 K/ns. We vary the cooling rate to obtain different structural properties.

2.3 Crystallinity

The crystallinity level is calculated at various stages during the simulation. The method to calculate the crystallinity is called Individual Chain Crystallinity, see [19]. We define this quantity as the ratio between the number of aligned bonds and the total number of bonds in our coarse-grained force field. For every bond we calculate the bond vector \mathbf{b}_i and a directional vector made of the average of the ten neighboring bonds, \mathbf{d}_i . If the normalized scalar product of those two quantities is higher than 0.95 (18.2°), the bond is considered as aligned, i.e., a bond is deemed straight if

$$\cos(\theta) = \frac{\mathbf{b}_i \cdot \mathbf{d}_i}{\|\mathbf{b}_i\| \|\mathbf{d}_i\|} > 0.95.$$
(1)

2.4 Sliding

Once we have obtained a simulation of a physical polymer surface, we perform indentation and sliding simulations using a simulated AFM tip. The tip is represented by a hemispherical rigid body consisting of a rigid fcc arrangement of the same PVA monomers, see Fig. 3. The interaction between tip particles and the monomers is given by the same non-bonded pair potential as the monomer–monomer interaction. A constant load is applied to the tip in the *z* direction. The center of mass of the tip is tethered to a support using a harmonic springs in the *x* and *y* directions with spring constant $17.8 \epsilon_0/\sigma_0^2$. During sliding, the support moves at a constant velocity in the *x* direction of 15 m/s. The force $F_{\text{lat}}(t)$ needed to keep the support moving at constant velocity corresponds to the lateral force in an FFM experiment, and its average gives the friction.

To prevent the substrate from moving with the tip, the centers of mass of the chains in the lower quarter of the substrate are tethered to their original positions using springs with spring constant ϵ_0/σ_0^2 . A Langevin thermostat with



Fig. 3 A snapshot of the simulation bow before the sliding process. The tip is the semi-sphere red body, the particles being in the same chain are of the same color. The xyz dimensions of the substrate are 42, 29 and 11 nm

decay time 1000 τ_0 is also applied to these chains and set to the appropriate temperature for each simulation.

2.5 Collecting Statistics

In order to collect enough statistics to understand what is happening around the tip during sliding, we investigate averaged quantities in a frame that move with the tip so that the tip is always at the origin. The simulation box is divided into a grid that moves with the tip. For any given time and for each individual bin, the properties of the atoms present within the bin are recorded and averaged. We note that as the tip moves, the atoms enter and leave the co-moving bins. In the cases where we investigate the displacement over finite times, we assign the entire displacement to the atom's initial bin.

The density is calculated by counting the average number of particles in the bin. To obtain a mapping of the orientation of the chain in the sliding direction, we compute the dot product between the bond vectors, \mathbf{b}_i , and the unit vector $\hat{\mathbf{x}}$.

3 Results and Discussion

We first discuss the equilibrium substrate. Examples of the substrates we obtain using the method described above are shown in Fig. 4, where one can see different structures depending on the chain length. The surface breaks the symmetry, and therefore the surface structure is not necessarily the same as the bulk. The shortest chains (m = 10) form a layer of polymers perpendicular to the surface. For longer chains the substrate becomes more homogeneous with an increase of the amount of folded segments and entanglement of the chains.



Fig.4 Substrate built with different chain lengths, m, which represents the number of coarse-grained particles per chain. The particles belonging to the same chain are of the same color

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Fig. 5 The crystallinity level as a function of temperature during a cooling simulation with cooling rate of 75 K/ns. The glass transition temperature is estimated from the point of maximum slope, i.e., when the rate of change of the crystallinity is the highest. The final crystallinity level of the substrate was around 0.4. It represents the mass fraction of crystalline phase

Because of limitations in computation time, we restrict the study of the sliding to one chain length, m = 50. This chain length produces a surface that is representative of surfaces consisting of longer chains. The amount of end monomers at the surface is low, and the chains are long enough to fold back on themselves. We show the crystallinity as a function of the system temperature for a constant cooling rate of 75 K/ns in Fig. 5. In general, the glass transition temperature and melting temperature of a sample of this size are subject to finite-size effects. Nevertheless, we have estimated the glass transition temperature for our system from the temperature with maximum rate of change of the crystallinity and found it to be approximately 350.4 K, as can be seen from Fig. 5. We have estimated the melting temperature by melting a crystalline sample, and found it to be around 407 K.

3.1 Indentation

Still at 220 K, we place the tip over the slab of polymer and apply a specific load force to it. The tip is then pushed into the surface with some violence, and we wait for it to come to full rest, which takes 0.4 ns. After this, we switch the thermostat to the target temperature and equilibrate the system for 1.6 ns. We do not observe any significant further creep during this equilibration period that could be relevant for our sliding simulations.
3.2 Frictional Forces

We show the lateral force as a function of time in Fig. 6a for different loads at T = 220 K. The frictional force decreases with time during the running-in period. The force fluctuates and has a repeating pattern due to repetitive crossing of the simulation cell. It takes around 2.1 ns to cross this cell. The system has not fully reached the steady state as the friction is still going down slowly.



Fig. 6 a Lateral force as a function of time. b Friction as a function of the load. The noise in the lateral force was smoothed by using a moving average with small interval of 1.6 ps. At this velocity (15 m/s), the simulation box is completely traversed in approximately 2.8 ns. The vertical lines represent the time when the virtual atom which is attached to the spring goes back to his initial position. The friction is calculated from the lateral force by averaging over the last two passes of the simulation. Extrapolation to zero shows a non-zero friction at vanishing load, which indicates that there is a substantial contribution from adhesion

The average frictional force is calculated over the entire time interval and the results are shown in Fig. 6b. The friction shows a nearly linear dependence on the load. If we extrapolate the data to zero load, the frictional force will be around 0.53 nN, which is due to adhesion.

In order to understand the effect of the viscoelasticity of the polymer, we investigate the dependence of the friction on temperature. We show the lateral force as a function of time in Fig. 7a for different temperatures at the same load of 0.38 nN. The lateral forces are initially very similar for the different temperatures. This is due to the fact that we have used very well controlled and similar initial states. Such initial similarities would not be



Fig.7 a Moving average of the frictional force vs time for different temperatures. At regular intervals, the total lateral forces between the tip and the substrate are measured. The data were then smoothed by a moving average with small interval of 1.6 ps in order to reduce the noise. b Average frictional force over the last two passes vs. temperature

achievable in experiments. As soon as the sliding begins, the systems at different temperatures start to diverge due to different mechanical properties of the polymer as well as thermal activation. The lateral force decreases with time for most temperatures, but increases slightly with time at the highest temperatures. This increase is related to more and more molecules adhering to the tip and thus needing to be dragged over the surface. Since this is occurs above the glass transition temperature, it is part of a purely viscous response. The mechanism by which the friction decreases with time below the glass transition temperature is more interesting and complicated, and we will discuss and investigate it in more detail below.

The average frictional force as a function of temperature is shown in Fig. 7b. The friction shows a non-linear dependence on the temperature with a minimum around 200 K. This is known to be the result of a competition between the local shear stress which decreases with the temperature and the contact area which increases with temperature [4].

3.3 Structure

Figure 8 shows a snapshot of the substrate after multiple passes at temperature 220 K. From this figure, we see that there are significant changes in the structure on the surface. In order to understand what is happening during the runningin period, we investigate the structure in more detail.

Figure 9 shows the average density in cross sections of the surface directly under the middle of the tip for three different temperatures. We note that the gentle density gradient in the first few nanometers of the surfaces is due to the fact that the surface is not atomically flat, but has some nm-scale roughness. There are a small number of alternating high- and low-density lines around the tip, as can be seen from the



Fig.8 A snapshot of the simulation cell after 15 passes of the tip at T = 220 K, seen from above. The tip is the round red body and it is moving to the right. The particles being in the same chain are the same color. The polymer chains in the wear track have become aligned with the sliding direction



Fig.9 The density in the y_z plane directly under the tip at different temperatures. The dashed line indicates the tip surface. $\rho_0 = 22 \text{ monomers/nm}^3$ is the bulk density (the sliding is in the *x* direction)



Fig. 10 The average density under the flat region of the tip as a function of the depth directly under the tip, normalized by the bulk density. The vertical line represents the lowest surface of the tip. It is the sum of the height of the tip lowest atom plus the value r_0 of the Lennard–Jones potential

horizontal red lines in the figure. In Fig. 10, we quantify this further and show the density in the region under the flat part of the tip as a function of the depth under the tip. There is a fast decay in the fluctuation with respect to the height. The first maximum is around 3 times the bulk density and the first minimum is half of the bulk density. Temperature somewhat reduces the effect, as is to be expected, but is still quite pronounces, even above the glass transition. This formation of a layered structure is not unexpected; it is commonly found in strongly confined materials under high pressure.

Finally, the snapshot in Fig. 8 shows specifically that the chains in the center are aligned in the sliding direction in the wear track. Most of the adjacent chains to this wear track show partial alignment with respect to the sliding direction. The chains further away from the wear track show little to no sign of this. Such behavior has been observed experimentally for rubbers [3, 6, 13].

We investigate this more systematically by considering the orientation of the bonds in the chains. Figure 11 shows the average component of the bond in the sliding direction for different temperatures. In the first few nanometers from the surface, there is a strong preferential orientation of the chains in the sliding direction (combing effect). The thickness of this reorientation layer increases with the temperature (Fig. 12).

3.4 Dynamic

The viscoelastic flow of the material surrounding the tip is an important characteristic of the contact [9]. We therefore investigate the average displacement around the tip,



Fig. 11 Average of the normalized scalar product between the bonds vector and the x direction at different temperatures. The circular dotted line indicates the surface of the tip

including the elastic restoration and permanent plastic deformation; the former is removed from the system by the thermostat.



b) $T = 220 K, \Delta t = 2.8 ns$





Fig. 12 Top views (z cross sections) displaying average displacement in the x direction (sliding direction) right below the tip. The average displacements are calculated after a time interval Δt of 2.8 ns corresponding to one pass of the tip. The plastic deformation can be identified from the fact that it is still present after a full pass of the tip through the simulation cell, returning to its original position

Figures 13a, c, e and 14a, c, e show the vector displacements calculated after a time interval Δt of 0.08 ns and 0.4 ns, respectively. We first consider the temperatures below the glass transition, 50 K and 220 K. In front of the tip, the material near the surface moves downward and in the direction of the sliding. Directly below the tip, it moves upward and slightly in the direction opposite to the sliding. The atoms near the surface at the rear of the tip move slightly downwards and also in the direction opposite to the sliding. This change of direction before and after the tip indicates that elastic energy is stored in the deformation and returned. In addition, some energy is dissipated as heat and in plastic deformation. The latter can be seen from the displacements after the longer time interval in Fig. 14. At temperature 385 K, above the glass transition, there is predominantly a viscous response, and no elastic restoration. In this case, the substrate mainly moves towards the sliding direction.

Figures 13b, d, f and 14b, d, f show cross sections in the yz plane of the vector displacements calculated after time intervals Δt of 0.08 ns and 0.4 ns. There are symmetrical displacements in the y and z directions. We also note that there are quite large fluctuations visible in Fig. 14. It is nevertheless possible to discern significant displacement near the tip.

Figure 15 shows the displacement in the x direction (sliding direction). There is a small zone surrounding the tip where the displacements are large, at least an order of magnitude higher, in the first few nanometers than in the bulk material. They also do not recover, indicating that this is plastic deformation, as can been seen from the top view displacement map after one pass of the tip, see Fig. 12. The thickness of the layer with plastic deformation increases with the temperature. This observation is in agreement with Briscoe hypothesis [5] of a thin top layer of polymer being submitted to higher shear stresses close to the surface. It is also consistent with alignment of the polymers on the surface in the sliding direction. The right side of the dashed line represents the front of the tip. As can be seen from Fig. 15, there are atoms counted at positions overlapping with the final position of the tip. This is due to the fact that we are investigating finite time intervals and we assign the entire displacement to the atoms initial bins.

In the displacements, we see no indication that the layers visible in Fig. 10 under the tip shear significantly with respect to one another. There is likely due to the fact that there are covalent bonds between the high-density planes where the polymer chains fold around from one to the next. The layer with high plastic displacement is roughly the same thickness as the area with more structure under the tip. Even though the precise rearrangements are different, this similarity in size is to be expected, because the monomers in this region are subjected to forces that are strong enough to cause significant structural rearrangements.

At T = 55 K and 220 K, the chains have a strong cohesion and are strongly attached to the substrate. Only the very surface of the substrate sees high deformation. At the rear of the tip, the substrate detaches from the tip. Part of the energy is restored where the substrate is moving backwards. One can notice the presence of transition zones going from negative to positive displacement. We suppose that this effect can be



Fig. 13 x and y cross sections displaying average displacement vector fields. The AFM tip move towards the x positive direction. The average displacements are calculated after a time interval Δt of 0.08 ns.

The dashed line and the green line represent, respectively, the initial and final position of the FFM tip



Fig. 14 X and Y cross sections displaying the average displacement vector field. The average displacements are calculated after a time interval Δt of 0.4 ns. The dashed line and the green line represent, respectively, the initial and final position of the FFM tip



Fig. 15 y cross section of the average displacement in the x direction (sliding direction) shown for three different temperatures and two different time intervals Δt . The dashed line and the green line represent,

explained by the production of fast propagation of Schallamach waves during sliding, see [2].

At T = 385 K, the chains are not sufficiently attached to the substrate and are free to move with the tip. This free movement implies a reduction of the shear stress and an increase of the surface area (higher penetration).

4 Conclusion

We have performed molecular-dynamics simulations of an AFM tip sliding on a polymer substrate of PVA chains. We have investigated structural changes occurring in the surface on the atomic scale, as well as the viscoelastic response. We have investigated the system at several temperatures below and around the glass transition and relate the response to the proximity of the glass transition.

We compute the friction as well as a number of structural and dynamic properties. For low temperatures, the friction

respectively, the initial and final position of the FFM tip. We assign the entire displacement to the initial bin of the atom

decreases with temperature, as the shear strength decreases. For higher temperatures, but still below the glass transition, the friction increases again as the contact area increases due to larger plastic deformation. At low temperatures, we see that the polymer is mostly elastic, and we see this in a large recovery and backwards motion of the material in the substrate behind the tip. At higher temperatures, close the glass transition, there is a much larger viscous component. In all cases, the polymers near the surface reorient and align permanently with the sliding direction. While our simulations are for a specific polymer, the qualitative behavior is likely to be general and present in other polymers. Using MD simulations has allowed us to provide a detailed picture of the molecular behavior of sliding polymers. Nevertheless, much remains to be investigated, as there are many additional complications in many realistic polymers that can affect the structure and friction, such as stronger interchain interactions, cross-linking, or the presence of water and other contaminants.

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Nano-scale friction and wear of polymer coated with graphene

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7 Abstract

Background: Friction and wear of polymers at the nano scale is a challenging problem due to the 8 complex viscoelastic properties and structure. Using molecular-dynamics simulations, we investi-9 gate how a graphene sheet on top of a semicrystalline polymer (PVA) affects the friction and wear. 10 Results: Our setup is meant to resemble an AFM experiment with a silicon tip. We have used two 11 different graphene sheets: an unstrained, flat sheet, and one that has been crumpled before being 12 deposited on the polymer. 13 Conclusion: The graphene protects the top layer of the polymer from wear and reduces the fric-14 tion. The unstrained flat graphene is stiffer, and we find that it constrains the polymer chains and 15

¹⁶ reduces the indentation depth.

17 Keywords

¹⁸ polymer; friction; graphene; molecular dynamics

¹⁹ Introduction

²⁰ Graphene is a two dimensional material that has remarkable properties, both electronic [1,2] and

²¹ mechanical [3,4]. Even before anything was known about graphene, the mechanical properties

²² were already being utilised in engineering applications. Graphite powder, essentially thick flakes

of graphene, has been used as a lubricant additive for over a century to reduce wear and friction 23 during sliding [5-7]. Nevertheless, we still don't understand all the different mechanisms at play 24 in such systems. During the last few decades, with the development of the Atomic Force Micro-25 scope [8] and increases in computing power, it has become possible to investigate more deeply and 26 develop understanding of the mechanisms that play a role in the friction of graphene (see, for ex-27 ample [9-21]). The effect of graphene coatings, and their ability to protect against wear, depends 28 on the substrate underneath. Nevertheless, so far, they have been studied almost exclusively on 29 metals [22,23]. Polymers coated with graphene have barely been studied on the nanoscale, due to 30 the added complexity of the polymer, the tribology of which even without any coatings is still not 31 well-understood [24,25]. In experiments, the tribology of polymer composite materials contain-32 ing graphene has been studied with the goal of constructing a self-lubricating material [26]. Sara-33 vanan et al. [27] have measured the friction and wear of polymer materials such as PE (polyethy-34 lene), PC (polycarbonate), POM (polycymethylene), PMMA (polymethyl methacrylate), PEEK 35 (polyetheretherketone) and PTFE (Polytetrafluoroethylene [28]). The polymers balls have been 36 rubbed on a steel surface covered with layers of graphene oxide and PEI (polyethylenimine). They 37 show that a transfer film of graphene on the polymer leads to lower friction. While to our knowl-38 edge there have been no numerical studies of friction on graphene coated polymers, the graphene 39 polymer interface has been studied. Rissanou et al. [29,30] show that graphene has a strong ef-40 fect on the structure and dynamics of the polymer chains near the interface. In this work, we aim 41 to develop our understanding of the frictional behaviour of polymer coated with graphene by us-42 ing molecular dynamics simulations of a single sliding asperity at the nanoscale. We show that 43 graphene protects the polymer substrate from wear and identify the mechanism of this protection. 44 We show that crumpling of the graphene has an impact on the friction. In section we first describe 45 the simulation setup. Then we move on to discussing our simulations of depositing, indenting, and 46 sliding on the graphene in section . Finally, we draw some conclusions in section . 47

2

48 Simulation setup

- 49 We simulate a slab of polyvinyl alcohol (PVA) coated with a single layer of graphene and a coun-
- 50 terbody representing an AFM tip consisting of silicon. The simulations were peformed using
- LAMMPS [31]. We use the same setup for the polymer as our previous work [25], which we sum-
- 52 marise below.

53 Interaction potentials



Figure 1: Coarse grained model for polyvenyl alcohol (PVA), $C_2H_4O_{x}$. Red atoms are oxygens, dark gray are carbon, and clear gray are hydrogen. One green circle represents one coarse grained particle which replaces the group of atoms C_2H_4O

- 54 The PVA is described using a united-atom force field developed by Müller-Plathe et al. [32]. Each
- polymer particle represents a monomer of one structural unit (C_2H_4O) (see Fig. 1). The nonbonded
- interaction is given by a Lennard-Jones 96 potential $V_{\text{pair}}(r) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r}\right)^9 \left(\frac{\sigma_0}{r}\right)^6 \right]$ where $\epsilon_0 = \frac{1}{2} \left[\left(\frac{\sigma_0}{r}\right)^9 \left(\frac{\sigma_0}{r}\right)^6 \right]$
- 57 0.0179 eV, $\sigma_0 = 4.628$ Å, and r is the distance between the interacting monomers. The bonded
- interactions are described by a harmonic potential $V_{\text{bond}} = K(r r_0)^2$ where $K = 2.37 \text{ eV}/\text{\AA}^2$ is the
- stiffness and $r_0 = 2.6$ Å is the equilibrium bond length. The bending potential is approximated by
- ⁶⁰ an angular potential described in a table format.
- For graphene, we use the potential developed by O'Connor et al [33] (AIREBO-M potential). It is
- ⁶² an empirical many-body potential that is directly implemented in LAMMPS.

$$V = \sum_{i} \sum_{j \neq i} E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} E_{kijl}^{\text{TORSION}}$$
(1)

The interaction between the PVA and graphene is modelled using a Lennard-Jones 12-6 potential and Lorentz-Berlot mixing rule. $\sigma_1 = (\sigma_i + \sigma_j)/2 = 4.025$ Å, $\epsilon_1 = \sqrt{\epsilon_i \epsilon_j} = 0.015066$ eV.



Figure 2: Snapshot of the simulation after the deposition of the graphene on the polymer and before indentation and sliding for \mathbf{a}) the flat graphene and \mathbf{b}) the crumpled graphene.

⁶⁶ We model the interaction between the silicon tip and graphene using a Lennard-Jones 12-6 with the

same parameters used by Li et al.[34]. $V_{\text{pair}}(r) = 4\epsilon_2 \left[\left(\frac{\sigma_2}{r}\right)^{12} - \left(\frac{\sigma_2}{r}\right)^6 \right]$ where $\epsilon = 0.092$ eV is the

depth potential, and $\sigma_2 = 3$ Å is the distance at which the potential is equal to zero.

⁶⁹ In our system, the tip and polymer are never in direct contact. They are always separated by

⁷⁰ graphene. We therefore do not need to model their interactions, but to be sure that no extremely

⁷¹ unphysical events can occur, we have used the same potential as for the polymer-polymer interac-⁷² tion.

The masses of the particles were chosen to be equal to 12.01 g/mol for the carbon atom of graphene, 44.17 g/mol for the monomers in the PVA and, 2.8 g/mol for the particles of the FFM tip. This leads to a fairly small total tip mass. While this is not entirely physical, such a low mass will help speed up the dynamics and damping of the tip and save computation time without compromising the results[34]. We simulate the system with a time step of 1 fs.

78 Substrate cooling and characterization

⁷⁹ We start from a box with periodic boundary conditions in the *x* and *y* direction (sizes 428 Å and ⁸⁰ 285 Å), filled up with PVA molecules placed randomly and constrained by hard walls in the *z* di-⁸¹ rection. The average density inside the polymer bulk is around 22 monomers/nm³. The chains have ⁸² a length of 50 monomers. Because there are overlaps, we initially give them no interaction. To re-⁸³ move overlapping gently, we first applied a nonphysical soft hybrid interaction potential, for 0.25 ns to remove particle overlapping, and then slowly ramp up the potential over a period of 0.25 ns to

185 the coarse-grained potential described in the previous section. The hybrid interaction potential con-

sists of a 12–6 Lennard–Jones potential for the non-bonded interactions and a spring potential for

87 the bonded interactions.

Once we have reached a melt with the correct interaction, we equilibrate it for 0.25 ns in the NVE ensemble. The temperature of the melt at this point is extremely high. To obtain a realistic semicrystallized substrate structure, we cool down the sample using a Nosé-Hoover thermostat with a linearly decreasing temperature, starting at 5000 K down to 220 K with a cooling rate of 75 K/ns. After this, the temperature is kept constant at 220 K for 4 ns. At this point, we remove the walls and the *z* direction as they are no longer needed.

Graphene deposition

After the solidification of the semi-crystalline substrate, a layer of graphene is deposited on top.

⁹⁶ We use two different graphene sheets in our simulations. The first one is a single flat sheet of

graphene that has the size of the box (Fig. 2a). The second one is also a single sheet, but the

graphene has been crumpled by being compressed along x and y directions by 10%, which leads

⁹⁹ to wrinkles on the surface (Fig. 2b).

In both cases, we deposited the graphene on the surface of the polymer substrate by placing the graphene at around 90 Å from the surface and then applying a force to each of the graphene atoms equal to 0.00005 eV/Å (8.0×10^{-14} N) for a period of 75 ps, after which it sits on the surface and has stopped moving. The total normal force applied is around 4 nN (3.3 MPa). Then the force is removed and the graphene stays on the surface due to the adhesion.

¹⁰⁵ Indentation and sliding procedure

In order to avoid sliding of the entire graphene sheet over the polymer substrate, we fix the position
 of some of the graphene atoms during the indentation and the sliding process. The two regions



Figure 3: Top view of the simulation. The positions of the fixed graphene atoms are shown. The AFM tip is fixed to a support (virtual atom) via a spring, This support is moving at a constant speed in the sliding direction.

where the graphene atoms are fixed are located in strips along the *x* direction, which is the sliding direction, as far away as possible from the trajectory of the tip (Fig. 3).

¹¹⁰ The FFM tip is rigid and consists of atoms arranged in an fcc lattice with a period of 5.43 Å, which

is the crystal structure of silicon. A semisphere is cut out from this material. The tip is placed

above the surface. A constant normal force is applied to the tip so that it moves towards and indents

the surface. After 1 ns, the tip has reached a stable depth. The tip is then attached to the support

¹¹⁴ with a harmonic spring along the sliding direction. The spring constant is equal to 30 N/m. The

¹¹⁵ support is moving at a constant horizontal velocity of 2 m/s. We run the sliding simulation for a

distance of 100 Å, which takes roughly 6000 CPUcore hours.

Method of analysis

The box is divided into a grid that moves with the tip. During sliding, we bin the individual polymer particles depending on their position in the reference frame of the tip. This enables us to create heat maps of average properties around the tip, such as the density or the average displacements of the particles.

We calculate the surface roughness of the top polymer atoms. We first divide the box into bins of size σ_0 in both x and y. Each bin is assigned the height of the atom with the highest z position. We ¹²⁴ finally compute the surface roughness as the root mean square height of a given area,

$$S_q = \sqrt{\frac{1}{A} \sum \sum Z^2(x, y) \Delta x \Delta y} , \qquad (2)$$

where A is the surface area and Z is the height of the particles on the surface.

Results and Discussion

128 Graphene deposition

125

After the deposition of graphene, we investigate its effect on the surface. The deposited graphene alters the structure and shape of the surface. This can be seen in Fig. 4, where we show the density as a function of the position in a cross-section of the substrate for the cases with and without a graphene layer.

We characterise the shape of the polymer surface by the roughness. We computed the roughness of
the bare surface, as well as surfaces covered in flat and crumpled graphene just after the deposition.
Before the deposition of graphene, the roughness of the polymer surface is equal to 0.543 Å. After
the deposition of the flat graphene, the roughness decreases to 0.186 Å. After deposition of the
crumpled graphene, the roughness changes to 0.581 Å. The flat graphene flattens the surface, while
the crumpled graphene accommodates to it.

In addition to the shape, the structure of the polymer near the surface is affected by the graphene.
In the case of the flat graphene, the particles of the polymer align in layers parallel to the surface,
as can be seen in Fig. 4b. In Figure b), the red flat region corresponds to a depth at which there is
a high density of polymers. A similar effect has been observed for other polymers as well [29,30].
For the crumpled graphene, the structure of the polymer is not as strongly affected by the deposition (Fig. 4c), though there is some sign of it.

145 Indentation

After the graphene is deposited, we add the AFM tip to our simulation and indent it into the surface. Figure 5 shows the indentation depth as a function of time for a normal load of 6.4 nN on the flat graphene. Different loads have been applied in the range 1-100 nN. The depth was determined as the distance between the lowest atom of the tip and the average height of the graphene sheet before indentation minus the tip-graphene interaction equilibrium distance σ_2 . We have performed this type of analysis for two different radii, 50 and 100 Å. The sliding starts directly after the indentation process.

We have run a long indentation simulation with a load of 6.4nN to determine the penetration depth after a long period of time (see Fig. 5). We only observe a slight increase in the depth between 1 ns and 4 ns of around 1 Å. Thus, we consider the tip indented fully after 1ns.

The indentation depth depends strongly on the load, as expected (Fig. 6). At low normal force, the tip with a higher radius penetrates deeper due to adhesion, which contributes significantly to the effective load force by pulling the tip into the surface. At higher loads, the smaller tip penetrates further, as it is subjected to larger external pressure. In the case of the crumpled graphene, we see a larger indentation depth compare to the flat graphene (Fig. 8). The tip has more freedom to sink inside the material when the graphene is crumpled (membrane buckling) than in a case of flat graphene (stiff membrane).

Figure 7 shows the cross-section of the density under the tip at the end of the indentation process. We can see regular lines of high density right below the graphene which indicate a local reorganisation of the polymer chains. The graphene, especially the flat sheet, is also curved away from the tip a little, which plays a role in reducing the local pressure comparing to the case with no graphene.

8

168 Frictional forces

Once the tip is sufficiently indented into the surface (after 1 ns), we start the sliding. Figure 10 shows the lateral force as a function of the displacement of the support in the case of the flat graphene.

To better highlight the influence of the tip radius, we average the frictional forces between the support displacement 50 and 100 Å. We plot those results as a function of the normal load for two diffreent tip sizes (radius of 50 and 100 Å) in Fig. 11. We observe a regular stick-slip motion. The distance between sticks corresponds to one lattice period of the graphene.

We observe in Fig. 10 that for the highest loads the frictional force increases during sliding. This
may be due to local frictional heating leading to a change in mechanical properties of the polymer
below the tip.

¹⁷⁹ In the case of the crumpled graphene (Fig. 12), the frictional curve is subject to more fluctuations.

The calculation of the average frictional force taken between support displacements 50 and 100 Å 180

¹⁸¹ (Fig. 14) shows the strong impact of the flexibility of the graphene. Again, the higher indentation ¹⁸² depth of the tip leads to a stronger frictional force (2 to 3.5 times).

We compare this to sliding without graphene. In a simulation with no graphene, a normal load of 51 nN, and a tip radius of 100 Å, we found that the tip moves deeply inside the substrate and the average friction is above 90nN, almost an order of magnitude higher than with graphene. This clearly shows that the graphene layer darstically reduces the friction.

To observe the effect of sliding on the wear of the polymer material, we compare three simulations: 187 one without graphene, one with flat graphene, and one with crumpled graphene. All have a nor-188 mal load of 1 nN and a tip radius of 50 Å (Fig. 13). To improve the averaging by increasing the 189 total sliding distance, we increase the sliding speed by a factor 10 to 20 m/s. The displacement 190 vectors are recorded after 0.6 ns, meaning that the support has moved 120 Å. This is indicated by 191 the dashed and solid lines. Without graphene, the vector displacements close to the surface are 192 high and in the sliding direction, this indicates that strong residual deformation remains at the sur-193 face because of the shearing of the chains. We observe that the displacements of the polymer are 194

¹⁹⁵ roughly an order of magnitude less when graphene is present. This indicates that graphene effi¹⁹⁶ ciently prevents damage of the substrate. The displacements are the smallest in the case of the flat
¹⁹⁷ graphene sample, where the graphene is not just protecting the polymer from the tip, but also con¹⁹⁸ straining the chains.

The graphene we have used, both flat and crumpled, is constrained to remain at a specific length 199 because of the periodic boundary conditions of the simulation box. This means that any elastic 200 stretching of the graphene sheet is limited to a fairly small area. In reality, most of the graphene 201 sheets are larger than the length of our simulation box and depending on how they attach to the sur-202 face, they may thus have more length to stretch elastically. Our crumpled graphene, by having a 203 longer equilibrium length than the box, is more representative of completely unconstrained, loose, 204 graphene sheets. However, graphene that is bound to the polymer surface, through adhesion or co-205 valent chemical bonds, would behave more like the flat graphene in our simulations, and provide 206 additional protection. 207

208 Conclusion

We simulate friction force microscope experiments with molecular dynamics. A rigid counter-209 body simulating the tip of the FFM is rubbed against a substrate made of a semicrystalline polymer 210 (PVA) with a graphene sheet on top. Doing such simulations enables us to understand some of the 211 mechanisms at play in such systems. Two different graphene sheets have been investigated: a flat 212 graphene that has the same size as the simulation box and a crumpled graphene sheet that has been 213 bi-axially compressed by 10%. Before and after the sheet is deposited on the substrate, we com-214 puted the roughness. We can observe that the crumpled graphene accommodates to the roughness 215 of the polymer, while the flat graphene reduces the roughness. We also observe a rearrangement 216 of the chain near the surface into a layered structure, indicating that the chains tend to align paral-217 lel to the surface. During sliding, the tip sink slowly into the material. This sinking affects the real 218 surface area and has a noticeable effect on the friction when the normal load is high. The displace-219 ments of the chains are roughly an order of magnitude less when a graphene sheet is present com-220

pared to the case with no graphene. Since this is where the most severe wear occurs the graphene therefore reduces wear. We can see that the graphene is curved away from the tip, this is especially true for the flat graphene. This helps to spread out the pressure, and reduce the local pressure in the polymer. The flat graphene is the most efficient at reducing the friction and wear of the system by this mechanism, as it is harder to penetrate.

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a Density before deposition of the graphene sheet.

b Density after deposition of the flat graphene sheet.

c Density after deposition of the crumpled graphene sheet.



Figure 4: Density of the substrate through the full length of the simulation box (polymer only), \mathbf{a}) before deposition of the graphene, \mathbf{b}) after deposition of the flat graphene, and \mathbf{c}) after deposition of the crumpled graphene. The graphene affects the roughness and structure of the substrate.



Figure 5: The penetration depth versus time for a long indentation and for the sliding process, for a tip with radius 50 Å and load 6.4 nN (4 eV/Å), on the flat graphene. The dashed line represents the time at which we measure the indentation depth and compare this value with other simulations. The sliding process is starting after the dashed line. Without sliding the tip does not indent much further, but with sliding it does.



Figure 6: Indentation depth as a function of the normal load for the flat graphene specimen with a tip radius r = 50 Å and 100 Å.



a Density of the polymer for the flat graphene, r=50 Å, F_n =3.2 nN.

b Density of the polymer for the flat graphene, r=100 Å, F_n =12.8 nN.

c Density of the polymer for the crumpled graphene, r=50 Å, $F_n=3.2$ nN.



Figure 7: Density maps of the polymer for **a**) the flat graphene with r=50 Å and F_n =3.2 nN, **b**) the flat graphene with r=100 Å and F_n =12.8 nN, and **c**) the crumpled graphene with r=50 Å and F_n =3.2 nN. The cuts are taken right below the middle of the tip on a small thickness (14 Å). The tip indents further on the crumpled graphene.



Figure 8: Indentation depth of the flat graphene and crumpled graphene for different normal loads and a tip radius of r = 50 Å.



Figure 9: Snapshots of the simulation during sliding for a tip radius of 50 Å and a load of 102 nN (64 eV/Å) for **a**) the flat graphene, and **b**) the crumpled graphene.



Figure 10: Frictional force versus the position of the support on the flat graphene specimen for **a**) a tip radius r = 50 Å, and **b**) a tip radius r = 100 Å.



Figure 11: Average frictional force measured between support displacement 50 and 100 Å of the support displacement versus load applied for a tip radius of 50 and 100 Å on the flat graphene specimen. For comparison, in a simulation with no graphene, a normal load of 51 nN, and a tip radius of 100 Å, we find an average friction above 90nN.



Figure 12: Frictional force versus the position of the support for a tip of radius r = 50 Å, on the crumpled graphene specimen.



Figure 13: Average displacement of the atoms bellow the tip during sliding for \mathbf{a} the case without graphene, \mathbf{b} the flat graphene, and \mathbf{c} the crumpled graphene.



Figure 14: Average frictional force measured between 50 and 100 Å of the support displacement versus load applied for a tip radius r=50 Å on the crumpled and flat graphene.

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Paper III





Article Molecular-Dynamics Simulations of the Emergence of Surface Roughness in a Polymer under Compression

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Abstract: Roughness of surfaces is both surprisingly ubiquitous on all length scales and extremely relevant practically. The appearance of multi-scale roughness has been linked to avalanches and plastic deformation in metals. However, other, more-complex materials have mechanisms of plasticity that are significantly different from those of metals. We investigated the emergence of roughness in a polymer under compression. We performed molecular-dynamics simulations of a slab of solid polyvinyl alcohol that was compressed bi-axially, and we characterised the evolution of the surface roughness. We found significantly different behaviour than what was previously observed in similar simulations of metals. We investigated the differences and argue that the visco-elasticity of the material plays a crucial role.

Keywords: polymer; roughness; molecular dynamics



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1. Introduction

Roughness of surfaces plays an important role in many practical settings, such as friction and adhesion (see, for example, [1]). It appears on all length scales, from geological roughness of mountain ranges, to the microscale roughness of polished surfaces, down to atomic scales. It has been shown that many surfaces display roughness in similar ways on different length scales and are close to self-affine [2–5], meaning that there is a scale invariance of the roughness, and the roughness profile looks similar. This applies to many different materials, rocks, glasses, metals, etc. Roughness of surfaces is a random, statistical property that appears naturally, with no or very minimal intentional interference.

While the self-affinity is extremely universal, we do not yet have a general understanding of why it appears. The development of roughness of a material surface involves a range of complex physical phenomena such as dislocation dynamics and crack formation (see, for example, [6,7]). In metals, for example, the surface evolution at a microscopic scale is mainly linked to the emergence of dislocations [8]. The heterogeneity of the deformation in the material across different length scales is a common mechanism cited to explain the origin of the roughness and the self-affine surface properties [7,9–12]. In order to investigate this phenomenon, Hinkle et al. [9] performed molecular-dynamics simulations of the compression of metals and showed that self-affine roughness appeared spontaneously.

Roughness appears in many other materials besides metals, including in much more complex materials. Zhang et al. showed that self-affine roughness appears in oxide glasses obtained from the cooling down of melts but that fractured surfaces are different [7]. Even more complex materials, such as polymers, are likely to have even more complex mechanisms that play a role and that involve new length scales that enter into the structure and dynamics [13]. Moreover, the self-affinity of roughness plays a crucial role in the friction of polymers [14,15].

In this work, we investigated the emergence of surface roughness in polymer surfaces. We performed molecular-dynamics simulations of solid polyvinyl alcohol (PVA). We analysed the roughness and found qualitative differences between the polymer and metals. We investigated these differences in detail and linked them to the structure and dynamics of the polymer.

2. Materials and Methods

2.1. Simulation Setup

We used a non-crosslinked polymer, polyvinyl alcohol (PVA), to create a solid polymer substrate. The approach is similar to that in our previous work [16]. The PVA was described using a coarse-grained force field developed by Müller–Plathe et al. [17]. Each polymer particle represents one structural unit of C₂H₄O (see Figure 1). The interaction between monomers consists of bonded and non-bonded contributions. The non-bonded interaction is given by a Lennard–Jones 96 potential $V_{\text{pair}}(r) = 4\epsilon_0[(\frac{\sigma_p}{r})^9 - (\frac{\sigma_p}{r})^6]$ where $\epsilon_0 = 0.0179\text{eV}$ is the depth of the potential, $\sigma_0 = 4.628\text{Å}$ the distance at which the potential vanishes, and r is the distance between the monomers. The stretching of a bond is described by a harmonic potential $V_{\text{bond}} = K(r - r_0)^2$ where $K = 2.37eV/\text{Å}^2$ characterizes the stiffness of a spring, and $r_0 = 2.6\text{Å}$ is the equilibrium bond length. The bending potential was approximated by an angular potential, which is provided in table format. The system was integrated using the Velocity Verlet algorithm, and the time step was set to 0.8 fs. The simulations were performed using LAMMPS [18].



Figure 1. Coarse-grained model for polyvinyl alcohol (PVA) $(C_2H_4O)_x$. Red atoms are oxygen; dark gray are carbon; and light gray are hydrogen. One green circle represents one coarse-grained particle that replaces the group of atoms C_2H_4O . Each monomer contains two carbons from the backbone. The model has harmonic stretching and bending provided in tabular form.

A solid polymer sample was created by quenching a polymer melt. The melt was set up using the same approach as described in [16]. We simulated 10 million particles in chains of 50. Our box had a length in x and y of 83 nm and was much larger in the z direction. Before solidification, two repulsive walls at a distance of 200 nm apart and perpendicular to the z direction were used to contain the melt.

The temperature of the melt was controlled using a Nosé–Hoover thermostat with a damping parameter equal to 0.16 ps. Initially, the melt was equilibrated at a temperature of 2000 K for 5 ns. Then, the temperature was reduced gradually to 270 K with a cooling rate equal to 216 K/ns. This produced a slab of solid semi-crystalline material, as is shown in the snapshot in Figure 2. The walls in the *z* direction could then be safely removed.

Once we had created the solid slab of polymer, for our investigations of the emerging roughness, we compressed the material equi-biaxially with a strain $\epsilon = \Delta L/L_0$ of up to 40% and a strain rate of 0.09375/ns. This was achieved by rescaling the system in the *x* and *y* but not *z* directions. During this compression the temperature was kept constant at 270 K using the same Nosé–Hoover thermostat.


Figure 2. Polymer substrate after the cooling process and before compression. The colours represent different chains of the polymer. The simulation box had periodic boundary conditions in the x and y direction, with, initially, a length of 83 nm. It was extended in the z direction. Initially, the height of the slab was about 95 nm. Once we obtained this sample, we compressed it in the x and y directions, and it expanded in z, while becoming rougher.

2.2. Calculation of the Self-Affinity of the Roughness under Magnification

As we compressed our simulated polymer block, we analysed the evolution of the roughness of the surface. We followed the approach of Hinkle et al. [9] and calculated a Hurst exponent [19] for the roughness profile, to characterise its self-affinity.

We defined the height of a section of the surface down to the resolution of 1 LJ unit σ_0 . We divided the box in the *x* and *y* directions into bins of this size. The height in each bin was taken as the position of the highest monomer in each bin. The surface roughness S_q was then calculated as the variance of the height, i.e., $S_q = \sqrt{\left[\frac{1}{N_{\text{bins}}}\sum_{i=1}^{N_{\text{bins}}}(Z_i - \bar{Z})^2\right]}$, where the sum runs over all N_{bins} bins involved in the section of the average over all bins in the section.

We investigated the self-affinity by considering the surface under different magnification ζ and splitting the surface into $\zeta \times \zeta$ smaller sections. The roughness was calculated for every section, and this value was averaged over all sections.

We then considered the dependence of the average roughness on the magnification. If the surface is self-affine, this is a power-law. The exponent of this power-law, the Hurst exponent, gives the scaling of the self-affinity. We estimated the Hurst exponent of this dependence via a least square linear fit taken between a magnification of 2 and 60. Higher magnifications above 60 are not meaningful, as the size of each section becomes comparable to σ_0 .

2.3. Calculation of the Nodal Displacements

To investigate the visco-elasticity during compression, we characterised the displacement of monomers relative to their neighbours and used it to determine the plasticity. We measured the changes in the distance between neighbouring particles. Particles that are at a distance less than $2\sigma_0$ were considered neighbours. After a change in strain of 0.0375, the distances between a particle and its neighbours changed. A probability distribution function (PDF) was computed to elucidate how the changes in the distance evolve during the compression. If the distance between two neighbouring particles increases by more than a specific threshold amount, then we assumed they will no longer return directly to each other's vicinity when the strain is reversed. We used a value of $1.5\sigma_0$ as the threshold that defines when a pair is considered to have a reversible elastic or an irreversible deformation. When the variation of distance of a pair of particles is above that limit, then this pair is counted as having an irreversible (plastic) deformation. The ratio of the plastic pairs over the total number of pairs provides the level of plasticity. We restricted ourselves here to direct elastic deformation with monomers returning to their original positions when the strain was reduced. In principle, also entropic contributions to the elasticity are possible. However, in glasses, which are not in equilibrium, this is poorly defined.

We note that we did not distinguish further based on how the irreversible deformation depends on the deformation rate, i.e., if it is viscous or not. In glassy materials like polymers, there is usually some kind of rate dependence that can be quite complex.

3. Results

During compression, our sample becomes visibly rougher, as expected. This can be seen in Figure 3, which shows snapshots of the surface at different values of the strain. Without strain, there was a small initial roughness. To quantify the self-affinity of the evolving roughness profile, we calculated the surface roughness at different magnifications. This is shown in Figure 4 for several different strain values. The slope of the curves gives the Hurst exponent of the roughness. The surface had an initial non-vanishing roughness and self-affinity. While initially the melt was confined by flat walls, it shrunk as it cooled, and the walls were far away from the final surfaces. The cooling down of the melt already produced self-affine roughness on the surface. Similar behaviour has also been observed in atomic-scale simulations of other glassy materials [7].



Figure 3. Snapshots of the surface during the biaxial compression, for (**a**) no strain, (**b**) $\epsilon = 0.154$, and (**c**) $\epsilon = 0.304$. Fig. (**d**) is the colour scale. The colour represents the height of the surface particles compared to the highest one. The same colour scale was used of $12\sigma_0$ between red and blue. As the sample is compressed, the surface area becomes smaller and the roughness increases.



Figure 4. Log-log plot of the roughness versus magnification for different strains. The Hurst exponent is the exponent of the power-law dependence. High compression leads to higher roughness as well as an increase in the Hurst exponent. Details on how the roughness was calculated and how the magnification was defined can be found in Section 2.2.



Figure 5. The Hurst exponent of the surface roughness of the compressed polymer sample as a function of the strain. The Hurst exponent continued to increase with increasing strain, rather than levelling off to a constant value, as it has been shown to do in metallic materials [9]. The dashed lines are here to underline the values of the Hurst exponent at different strains.

In Figure 5, we show how the Hurst exponent develops with the strain. It clearly increases gradually but does not reach a plateau. This is qualitatively different from what has been found for metallic materials [9], where the Hurst exponent levels off around strain 0.1 and converges to a value around 0.4. This qualitatively different behaviour must be related to the qualitatively different dynamical and structural properties of the polymer. This could lead to time-dependent structure changes, combined with the critical slowdown of equilibration due to glassiness, which would not appear in metallic systems. In order to investigate this further, we analysed the structure of the polymer in our simulations. This will allow us to draw conclusions about polymers in general, beyond what happens in just PVA.

We first characterised the structure using the radial distribution function (RDF), which is shown in Figure 6. The large peak around 1.0 corresponds to the bonds inside the polymer chain and was not changed significantly during compression, as we did not allow for bond breaking. At shorter distances, around 0.9, there was a shoulder that resulted from non-bonded monomers approaching each other quite closely. This increased in height with increasing strain. Correspondingly, the density decreased at the slightly longer distances in the range of $1.1\sigma_0 - 1.4\sigma_0$. Further out, there was an increase. However, the peaks remained in place and were qualitatively similar. These changes in the RDF are indicative of distortion in the material but not any dramatic structural changes.



Figure 6. Radial distribution function of the monomers for three different values of the strain, as a measure of the internal structure in the material. There were quantitative differences in the height of the peaks for the different strains, but there were no qualitative structural changes.

As our compression was anisotropic, it is possible that anisotropic structural changes may appear that would not be picked up in the RDF. We therefore investigated anisotropy by considering the mean component of the monomer–monomer bonds in the z direction. This is shown in Figure 7.

We can see that close to the surface, from the beginning, the chains tend to be aligned parallel to the surface, as expected. Before compression, in the bulk, the average *z* component was around 0.47, which is close to the value expected from purely random directions, $\frac{1}{2}$. The small difference was likely due to the finite size of our sample and the long-range effects of the boundaries. The average *z* component of the bonds increased during the compression, indicating that there is a vertical reorientation of the chains. These results clearly indicate that the polymer, once compressed, is no longer isotropic.



Figure 7. Average normalized component of the bond in the *z* direction as a function of the *z* position in the slab relative to the highest particle, for three different strains. As the sample is deformed the bonds become more anisotropic, aligning with the direction that is stretching.

Now that we have established that there is distortion of the structure in the polymer, we consider the dynamics in more detail. Deformation of materials can generally be described as a combination of elastic (reversible) and plastic (irreversible). In polymers, elastic deformation can be quite large, unlike in metals, where, for large deformations, plasticity dominates. We investigated this in our system through the nodal displacement (see Section 2.3), which describes how many monomers have left their original environment of neighbouring particles.

Figure 8 shows the distribution of nodal displacements for different strains. We can see that the nodal displacements increased during the compression and especially that bigger displacements become much more likely for larger strains. An important point to notice in this plot is that the tails of the distributions are exponential for all strains shown. This means that on the length scale of our simulations, there is no power-law distribution

of rearrangements. This further indicates that different mechanisms are at play in our system on different scales, rather than a single mechanism that acts on all length scales, which would produce scale-free behaviour in the form of a power-law. We suspect that on small scales, rearrangements of single monomers are dominant, while the length of the polymers and size of the crystal grains become important on larger scales.



Figure 8. The probability distribution function of the relative displacements of monomers for several different values of the strain. The vertical line represents the limit displacement at which a pair of monomers are considered to have been plastically displaced.

One obvious distinction between displacement mechanisms that occur in this system, but not to the same degree in metallic systems, is the combination of significant elastic and plastic deformation. We can quantify the contributions from the different mechanisms through the magnitude of the nodal displacements. Elastic deformation would distort the neighbourhood but not remove monomers from their neighbourhoods. High nodal displacements are therefore related to plasticity, while low nodal displacements indicate that the distortion is elastic. We considered a node plastically displaced if the nodal displacement exceeds $1.5\sigma_0$ over a change in total strain of 0.0375, i.e., enough to have left the energy minima in the non-bonded potential of their neighbours.

Figure 9 shows the fraction of neighbour pairs that have been displaced plastically, as a function of the strain. At the beginning of the compression, there was almost no irreversible plastic deformation, i.e., all deformation was elastic. Then, there was a transition where plastic deformation started to appear around 0.08 strain. At large strains, more than 70% of the monomers are part of plastic deformation. Plastic flow has taken over.



Figure 9. Relative plasticity, i.e., the fraction of monomer pairs that displayed plastic local changes. We defined plasticity in terms of the change in distance between monomers. The change in distance was recorded between two states with a 0.0375 difference in strain. A pair of monomers was considered to have moved plastically if the change in the distance between them is more than $1.5\sigma_0$.

To investigate if the nature of the plasticity changed significantly during the compression, we considered the shape of the distribution of nodal displacements. We rescaled the nodal displacement and distribution shown in Figure 8 by a scale factor α that is linear in the strain. We obtained this linear function by considering the nodal displacements corresponding to the maximum in the PDF and fitting a linear function, which gives $14.667 \times \epsilon + 0.33$. The result is shown in Figure 10. For the most common displacements, the curves fall neatly on top of each other. However, the curve for the small strain is different from the others, as expected from the fact that at small strains, elastic deformation dominates, while at larger strains, both elastic and plastic deformation occur.



Figure 10. Rescaled PDF vs rescaled nodal distance presented in a semi-log plot. The scaling parameter was linear in the strain and obtained from a linear fit (see inset) of the ratio of the nodal displacements corresponding to the maximum in the PDF, $14.667 \times \epsilon + 0.33$. For large strains, the tail of the distribution was exponential, indicating that the mechanism involved acts on a limited length scale.

Finally, we considered the time scale of the dynamics of rearrangements and changes inside the material and how they affect the roughness. While we cannot probe significantly different strain rates due to limitations in available computing power, we can explore the time scales by allowing a strained substrate to relax without further compression and observing changes in the roughness over time. We stopped the compression at a strain of 0.372. We then ran the simulation with a constant box size for 7.5 ns. A comparison of the roughness before and after is shown in Figure 11. We could observe a decrease in the surface roughness at high magnification and an increase at low magnification. This suggests that there are dynamic processes still going on at the surface or inside the bulk of the material on all length scales. Since there was nothing special about the strain of 0.372, we expected that similar behaviour would appear if we stopped the compression earlier or later.



Figure 11. Roughness versus magnification when the compression was stopped at a strain of $\epsilon = 0.372$. The blue curve corresponds to the moment when the compression was stopped, while the orange curve was after 7.5 ns of relaxation. There are changes in the roughness at both high and low magnification.

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4. Discussion

It is clear from our results that the polymer in our simulations does not produce self-affine roughness in the same way that metallic materials do. Unlike in the case of metals, under compression, the Hurst exponents of our polymer surfaces did not converge to a constant value. This means that the nature of the roughness continued to change.

In order to understand the reasons for this behaviour and to be able to draw general conclusions, we investigated this difference in more detail through a number of indicators of structure. As the material is compressed, we observed changes in structural properties, such as the radial distribution function and the average alignment of bonds. These structural properties continued to change and did not reach a plateau. This indicates that the material itself continues to change, and therefore it is not surprising that mechanical properties such as the distribution of rearrangements also continue to change during further compression, which in turn can affect the formation of the surface roughness.

A crucial difference between metals and polymers that plays a role here is the viscoelasticity. The elastic deformation of the polymer in our simulations was significant compared to the total strain, which means that even at high strain, when plastic strain dominates completely in metals, there is residual elastic strain in our polymer. This combination of elastic and plastic strain shifts during the compression, giving a straindependence to the mechanical properties.

We also considered the rearrangements in the structure that occurred during the compression. In general, a power-law distribution of rearrangements would be expected to be linked to avalanches in rearrangements [20–22], as well as self-affine roughness profiles [9]. We therefore investigated the displacement of monomers from their environment. While we would not expect long-range power-law behaviour here, due to the finite size of our simulation box, we did not observe any power-law at all (see Figure 10). This may be related to the fact that the displacements are in fact within the length of the polymer, and any power-law rearrangements would have to include the entire chain.

Finally, we consider the dynamics. Our polymer was glassy, which means that dynamics may occur on very long time scales. In the simulation where we stopped compressing, the material continued to change, reducing the roughness on small length scales while also increasing it on longer length scales. It may be that small-scale surface flow is occurring, which smooths out the surface. Meanwhile, large, long-time glassy rearrangements in the bulk material could be producing higher roughness on larger scales. Hinkle et al. [9] observed a temperature dependence of the emerging Hurst exponent in their simulations of metallic glasses, which also suggests dynamic (thermal) relaxation effects.

It would be extremely desirable to compare our results to experiments on materials surfaces during compression. However, to our knowledge, such experiments are not yet being performed anywhere. We hope that our simulation results, and those of Hinkle et al., will stimulate experimental investigations of the emergence of roughness on atomic scales.

From all of the above, it is clear that some of the remaining questions about this system could be resolved if we could significantly increase the size of our simulation box. We are however limited in the length scales that we can achieve, due to limitations in computational power. The simulations we presented in this work contained 10 million coarse-grained particles, and the full compression takes around 0.2 million CPUcore hours to run. An order of magnitude larger range of length scales would require a larger simulation box, with three orders of magnitude more particles, which would become prohibitively computationally expensive. Similarly, repeating these simulations for a number of other polymers would be computationally very expensive as well, especially since many polymers have electrostatic interactions, which by their long-range nature slow down simulations considerably.

5. Conclusions

We investigated the emergence of roughness and its scale invariance in polymers using molecular-dynamics simulations, by compressing a large slab of material. We found qualitative differences when compared to metals. The Hurst exponent, which quantifies the self-affinity, continues to change with increasing strain. We attributed this to the viscoelastic properties of the polymer combined with structural changes in the material, such as anisotropy resulting from anisotropic stresses. We further investigated the structural changes and dynamics during compression. We found, in addition, that there are long time scales involved in the dynamics, and the roughness continued to evolve when the compression was stopped.

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