Torstein Wiiger Opsahl

# Unraveling the Nanoscale Dynamics of Ice friction

Molecular Dynamics Simulations investigating the Structural Evolution of Ice-Solid Interfaces

Master's thesis in Applied Physics and Mathematics Supervisor: Jon Andreas Støvnegn Co-supervisor: Senbo Xiao September 2023

NDUNU Norwegian University of Science and Technology Faculty of Natural Sciences Department of Physics

**Master's thesis** 



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## Sammendrag

Friksjon er et sentralt fenomen i hverdagen vår, men de fleste overser nok hvor essensielt det faktisk er. I dagliglivet omgir vi oss med både *smart* og *tradisjonell* teknologi hvor friksjonsinteraksjoner er avgjørende for kvaliteten. Med den raske teknologiske utviklingen vi ser i dag – spesielt innen regnekraft og *tenkende* maskiner – har nanoteknologi blitt sentralt for videre fremskritt.

Friksjonskrefter – som følge av interaksjoner på nanonivå – kan være dominerende. I løpet av de siste tiårene har det blitt viktig å forstå dette for å fullt ut kunne utnytte nanoteknolgi. Det er av særlig interesse å utforske komplekse fenomener, som nanoskala isfriksjon. Høykvalitets isfobiske materialer kan gjøre teknologi mer anvendelig i de nordligste, sørligste og mest høytliggende regionene i verden. For å utvikle solide isfobiske materialer, kreves en god forståelse av friksjons mekanismene som oppstår av vekselvirkningene mellom de ulike atomene i kontaktflaten.

Atomistisk modellering og molekylærdynamikk blir i dette prosjektet anvendt for å undersøke friksjon som følge av is i kontakt med polymerer. Dette prosjektet undersøker effektene av faktorer som normalkraft, hastighet og intermolekylære interaksjonspotensial på nanonivå, samt hvordan disse nøkkelfaktorene innvirker på strukturendringer som følge av friksjons interaksjonene.

Molekylærdynamikk-simuleringene viser tydelige forskjeller mellom friksjon på et makronivå og på et nanonivå. På grunn av den høye oppløsningen ved bruk av molekylærdynamikksimuleringer, ble vekselvirkningene mellom vannmolekylene og polymer kjedene avdekket i alle de modellerte systemene. Fra de ulike systemene med forskjellige friksjonsparametre, ble 4 ulike typer friksjonsinteraksjoner identifisert. Type I og Type III viste tydelig en *stick-slip* oppførsel, liknende det som er observert i eksperimenter gjennomført med atomkraftmikroskopi. Type II viste tydelig trykk og glide smelting av isoverflaten, som førte til stor friksjonskraft og vesentlige strukturelle endringer i is-mediet. Type IV viser hvordan en stor normalkraft kombinert med superhydrofobe polymerer kan føre til at vannmolekylene blir presset inn og gjennom polymeret. For alle simuleringene ble utviklingen av isens struktur, med utgangspunkt i kontaktflaten, undersøkt nøye. Dette utvikler kunnskapen vår om isfriksjon på nanonivå.

Resultatene viser at molekylærdynamikk-simuleringer er et nyttig verktøy for fremtidig forskning på hvordan kontaktflater med is utvikler seg og hvordan dette bidrar til isfriksjon. Dette kan gi nyttig innsikt i hvordan en helhetlig teori om isfriksjon kan bygges opp, fra hvert enkelt kontaktpunkt.

## Abstract

Friction is a central phenomenon in our daily lives, yet the great extent to which it is essential is often overlooked. In our daily routines, we surround ourselves with both *smart* and more *traditional* technologies, where frictional interactions play a key role in determining quality. With the rapid technological advancements today – particularly in computational power and *thinking* machines – nanotechnology has become crucial for further scientific progress. Friction forces, which result from interactions at the nano-level, can be quite dominant. In recent decades, a deep understanding of nanoscale friction phenomena has become essential to fully unlock the potential of nanotechnology. There is a particular interest in exploring complex phenomena, such as ice friction at the nanoscale. High-quality ice-phobic materials can make technology more adaptable in the world's northernmost, southernmost, and most elevated regions. To develop effective ice-phobic materials, it is imperative to understand the friction mechanisms that arise from the interactions between individual atoms at the contact surface.

In this study, atomistic modelling and molecular dynamics are employed to investigate friction resulting from ice and polymers in contact. The thesis investigates the nanoscale effects of key factors including normal force, velocity, and the intermolecular interaction potential. It further explores how these factors influence structural changes resulting from the frictional interactions.

Molecular dynamics simulations clearly differentiate between friction at macroscale and nanoscale. Owing to the superior resolution of these molecular dynamics simulations, the interactions between water molecules and polymer chains were captured in all the modelled systems. From various systems with different friction parameters, 4 distinct types of frictional interactions were identified. Type I and Type III evidently exhibited a *stick-slip* behaviour, similar to observations in experiments conducted with atomic force microscopy. Type II exhibited melting of the ice surface induced by both pressure and sliding, resulting in pronounced frictional forces and major structural changes to the ice. On the other hand, Type IV demonstrates how a significant normal force, combined with superhydrophobic polymers, can cause the water molecules to be pushed into and through the polymer. In all simulations, the evolution of the ice's structure, starting from the contact surface, was meticulously examined, offering a deeper understanding of ice friction interactions at the nanoscale.

The findings suggest that molecular dynamics simulations are a valuable tool for future research into how contact surfaces with ice evolve and how this contributes to ice friction. This could offer valuable insights into how a comprehensive theory of ice friction, grounded in each individual asperity of contact, can be constructed.

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## Acronyms

 ${\bf AFM}\,$  Atomic Force Microscopy.

CG Coarse Grained.

 ${\bf COM}\,$  Center Of Mass.

**HDPE** High-Density polyethylene.

 $\mathbf{I_h}\,$  Hexagonal Crystalline Ice.

**LAMMPS** Large-scale Atomic/Molecular Massively Parallel Simulator.

 ${\bf LJ}\,$  Lennard-Jones.

 ${\bf MD}\,$  Molecular Dynamics.

- $\mathbf{mW}$  Coarse grained water.
- **NVT** Canonical ensemble.
- ${\bf PBC}\,$  Periodic Boundary Conditions.
- **QLL** Quasi-Liquid Layer.

 $\mathbf{TraPPE-UA}$  Transferable Potentials for Phase Equilibra-United Atom model.

**UA** United Atom.

## 1 Introduction

Ice and snow, common in our colder climates, wield an impact that often extends far beyond what one might immediately recognise. These frozen elements, while perhaps seen as mere natural phenomena or weather challenges, strongly influence a wide range of daily life. From slipping while running for the bus to ice build-up on aircraft or wind turbines, ice and snow affects our lives considerably [1, 2]. Besides addressing the inconveniences resulting from ice and snow in winter daily life, such as when slipping or having to clear a windscreen, understanding how surface materials interact with ice and snow are crucial for success both in snow sports and transportation.

In competitive skiing, whether you are able to reduce the resistance between the skis and the snow/ice more effectively than your opponents can make the difference between winning an Olympic medal and finishing outside the top ten. Hausken *et al.* found that in Cross-country skiing, a 10% increase in friction force, results in a 4% increase in total time skiing time used [3]. This 4% increase would have made the difference between winning gold and finishing ninth in the men's 15 km cross-country skiing event in the 2022 Winter Olympic Games.

There are a good number of studies focusing on the interactions between ice/snow with different materials already in the literature, especially for anti-icing purposes [4–7]. However, current anti-icing materials research cannot fully explain how ice interacts with moving surfaces [1, 2]. Overwhelmingly, state-of-the-art anti-icing surfaces are mainly applied to static icing problems and not dynamic ones. The so-called passive anti-icing surfaces and ice-repellent materials have generally been developed and designed from a static perspective. This passive anti-icing methods is taken without considering the evolution of properties such as contact area, ice fractures, and regrowth, which are typically assumed to be constant at the ice/snow-solid interfaces. As we usually interact with ice in systems involving some movement, it is crucial to incorporate interface dynamics into the equation. Understanding the dynamics of ice-surface interaction, especially at the nanoscale, is important and requires further study.

In this study, we are looking at how ice and a polymer interact in motion at nanoscale, such as in friction conditions experienced during skiing. Atomistic models for capturing the fundamentals of ice friction are constructed for the purpose of simulating the resistance to movement between the interfaces. Importantly, these models are then subjected to friction test simulation with the consideration of key determinants of moving speed, surface hydrophobicity, temperatures. This work probes the key impacting parameters to ice friction, shedding light on the knowledge on nanomechanics at interfaces between ice and other materials.

1

## 1.1 Friction

Friction has been studied and utilised in throughout human history, with the making of fire by rubbing sticks together as probably the first application. The indigenous people of the northernmost part of the world started sliding on planks on snow several thousands of years ago [8], and already since then snow and ice friction have been a part of human history. Friction has been formally studied in physics since Leonardo da Vinci. Da Vinci found that the magnitude of the force of fiction is:

- 1. proportional to the load applied, and
- 2. independent of the area of contact for a given constant load.

Amonton later formulated this, which became known as Amontons' laws of friction, as da Vinci's works were not published. While Coulomb again found and formulated how the linear dependency of normal force  $(f_n)$  and resistance to movement friction  $(f_{friction})$  with linear dependence  $(\mu_0)$ .  $\mu_0$  is better known as the coefficient of friction [9]. This gives the well-known function

$$\vec{f}_{friction} = \vec{\mu}_0 \times f_n , \qquad (1)$$

independent of sliding velocity. While Equation (1) is simple, friction exhibits more complexity. For instance, post-Coulomb findings revealed that Equation (1) does not hold for really low or high velocities.

Today, in the world of micro- and nano-electronics and structures, friction is drawing increasing interest, especially at the nanoscale. Friction is demonstrated to be even more complex at these smaller scales than at the macroscopic level [10, 11]. Whenever we have movement, we must also account for wear and lubrication. At the nanoscale, interfering factors such as short-range interactions and local energy dissipation are highly significant, which could lead to failure of the friction interface structure. Therefore, understanding and investigating the various factors beyond the macroscopic coefficient of friction ( $\mu_0$ ) is critical.

## 1.2 Nanoscale friction

Our understanding of nanomaterials and -structures has significantly expanded with the development of micro- and nano-electronics. In this era of nanotechnology, particularly the field of friction had to be researched at the nanoscale, revealing new insights into friction [10, 12–14].

In the fields of nanotribology and nanomechanics, advanced Atomic Force Microscopy (AFM) is the most popular experimental methodology, thanks to the ability of AFM tips to simulate a single asperity of nanoscale contact on solid and lubricated surfaces [14–16]. AFMs have been highly successful in unveiling various tribological phenomena,

#### Friction measurement macroscale vs nanoscale



**Figure 1:** Schematic representation of friction forces at macro- and nanoscale. The static regime represents the phase where shear stress builds without motion, and the dynamic regime begins as the frictional force surpasses a threshold, resulting in movement and a lower overall friction force. The characteristic saw-tooth pattern in the nanoscale friction force profile illustrates the stick-slip behaviour common in nanoscale friction tests.

such as adhesion, friction, scratching, wear, detection of material transfer, and boundary lubrication [14].

Using AFMs to investigate friction, adhesion and wear, have greatly advanced our understanding of nanoscale friction in the last two decades. Bhushan and Kulkari used an AFM to simulate microscale friction of silicon to silicon/silicon-oxide [13]. They found conflicting results of the dependency of the normal force to what is found on a macro-scale [13]. Where they found, that under low-contact stress, the microscale coefficient of friction were orders of magnitude smaller than the macro-scale friction. However, phenomena such as *ploughing* can lead to a microscale coefficient of friction that exceeds the macro-scale under high loads, which clearly indicate that Amontons' law of friction, Equation (1), does not hold for microscale measurements [13].

Moreover, unique friction behaviours have been observed at the nano-scale, distinct from those at the macro-scale. With AFMs, it has been observed that after reaching the shearing threshold, known as the peak of static friction with static friction coefficient  $\mu_{0\text{static}}$ , a stick-slip motion is found. This motion builds to further peaks in a sinusoidal saw-tooth pattern, rather than producing a constant friction force [14]. Such phenomenon is attributed to the fact that the AFM tip consists of a few hundreds of atoms that elastically interfere with the crystalline pattern of the substrate, bending and 'jumping' across the lattice [14, 17]. These studies clearly illustrated the deviation of nanoscale friction from the traditional understanding of macroscale friction.

An example of how the output of two friction measurements could look, one macroscale against one nano-scale, is shown in Figure 1. In the figure, we see that a saw-tooth pattern of the AFM friction force measurement emerges, while the macroscale friction force

measurement is smooth. This saw-tooth pattern suggests that in difference to macroscale friction, new factors need to be considered to fully understand friction at nanoscale. With respect to this, it is of particular interest to use approaches utilising atomistic resolution, such as Molecular Dynamics (MD) simulations, to further investigate the properties of the nanoscale friction interface. Further, investigating the course of the stick-slip motion, and further decipher how the motion depends on normal force, sliding velocity, or degree of phobicity.

On macroscopic scales, friction force equations in the terms defined by, Equation (1), assumes that the interface of friction is constant. This assumption fails on atomistic scales. On the atomistic scale, different atoms and molecules, and their short-range structures, deform, break, or regenerate continuously. These phenomena are overlooked when considering macroscopic friction. In nano-mechanics, such changes in short-range structures must be accounted for, as they are the basis of the friction phenomena. The mechanics of a sliding motion in the macroscopic view, in terms of nano-mechanical events, is an ensemble average over millions of different shearing, ruptures, regenerations, and sliding interactions between the atoms and molecules.

## 1.3 Ice friction: relevance and impact



**Figure 2:** The figure displays an all-atom model of the hexagonal crystalline ice rendered by the VESTA visualization software [18]. The red spheres represent the oxygen atoms and the white spheres represent the hydrogen atoms.

Several aspects of daily life depend on understanding the friction of water in the different

phases solid, liquid, and other intermediates. Liquid-phase corrosion, deterioration, and the newest liquid water-based triboelectric nanogenerators, are popular research topics, among many others [19–21]. These topics all have multiple complex implications which arise when the liquid enters the solid state. One important issue with respect to solid water, namely ice and snow, is friction, which is the determinant for all concerned properties of relative motions of two contact surfaces. One should desirably optimise the friction in tires and shoes for high friction in contact with the ice and snow, for the sake of good driving experience and walking comfort. On the other hand, with skiing or skating one would want to reduce friction to a minimum, thus increasing the speed with the same effort.

Solid water can take many forms. For instance, it can be fully long-range crystalline hexagonal ice as in Figure 2 or it can take the form of snow with a high degree of trapped liquid water and complex geometrics. However, on a nanoscale, the crystalline structure of ice and snow usually has the hexagonal crystalline shape in the same way the atoms are arranged in Figure 2 [8].

Surface-to-surface friction is on a macroscopic level usually divided into three different types:

- 1. Dry friction: when having two solid surfaces sliding against each other, without any form of lubrication.
- 2. Hydrodynamic friction: when a lubricating layer is present between the solid surfaces thick enough to withstand the normal force of the solids, yielding the friction to be completely occurring in the lubrication layer.
- 3. Mixed friction: when a lubricating layer is present, but it is not sufficiently thick to withstand the normal force, leading to some partially solid-surface to solid-surface contact.

Ice that consists of solid water molecules does, as liquid water, hold the water molecules together in position due to the stabilised hydrogen bonding network. Hydrogen-bonds are known to be weak compared to covalent bonds [22, 23], rendering ice is less robust in comparison to metallic materials like copper, and less elastic than polymeric materials like polyethylene. This adds complexity to ice friction: if there is friction, the applied force have the high possibility of breaking the hydrogen-bonds.

For ice crystals at T > -20 °C, a QLL of between 10 to 200 Å is present [8, 24]. It is thus challenging to account for the interfacial phenomenon of ice in order to understand the different ice friction regions.

## 1.3.1 Quasi-liquid layer

A quasi-liquid water layer is known to be present on the surface of ice below melting temperature, behaving as liquid water [8, 25, 26]. Faraday predicted the existence of the

QLL over 160 years ago when bringing two cubes of ice together. He found them to quickly adhere to each other, 'at a place where liquefaction was proceeding, congelation suddenly occurred' [27]. Faraday's predictions spurred research into the causes and nature of this phenomenon. To this day, there are still disagreements on the QLL, either as a metastable liquid phase with chemical properties of liquid water or a pre-melting phase with distinct properties from ice and water. Those two hypotheses are among the ones being explored in order to find the chemical and physical aspects of the QLL. Notably, recent studies indicated that the QLLs to be kinetically formed, so no melting of the surface. Both findings of droplet kind of layers, and thin-film like kind of layers [28].



Figure 3: An all-atom model displaying hexagonal ice with a quasi-liquid layer on the surfaces, as rendered by VESTA [18]. The red spheres represent oxygen and the white spheres represent hydrogen. The quasi-liquid layer can be distinguished by the unordered surface layers highlighted inside the blue rectangle.

By looking at a block of ice, one can see how the ice molecules on the surface are missing neighbours, as depicted in Figure 3. The lack of neighbouring molecules at the edges should, by simple physics, lead to less preferable positions, hence leading to a more unstable structure with a large diffusion freedom. As such, the QLL contains mobile water molecules that are able to diffuse, instead of being arranged in a solid and crystalline lattice structure, thus featuring partially liquid properties. In Figure 3 one can see what an all-atom model of hexagonal thin-film ice looks like at around 200 K, where an unstructured water molecular layer featuring quasi-liquidity covers the crystalline hexagonal water structures underneath.

The QLLs are important to ice friction in the different temperature ranges, as the mobile surface water molecules can serve as lubricants on ice and snow. The QLL further complicate the nanoscale ice friction, as the above-mentioned three types of friction might be difficult to distinguish in nanoscale ice friction. Further, the thickness and properties of QLL also change with temperature and the wettability of the friction solid surface. As such, systematic modelling and simulations are needed for the in-depth understanding of nanoscale ice friction.

## 1.3.2 Nanoconfined water

The interactions that occur on an atomic scale between ice and a frictional medium distinguish themselves notably from those experienced with bulk ice, owing to distinct properties such as the existence of the QLL. In addition to the intrinsic properties of QLL, the contact with friction materials can further introduce other variation to the structure and dynamics of the friction interface, which make nanoscale ice friction even more complex. These properties must be accounted for when studying the interaction layers in friction.

Khan *et al.* [29] observed a sharp transition from viscous to elastic response when confining a-few-molecules-thick water layer between two sheets. The transition showed that under dynamic strain, the water molecules underwent a 'dynamic solidification'. Hence, water can behave like a solid under confinement. Qiu *et al* [30] further found that water in inhomogeneous nanoconfinement can nucleate even at temperatures such as 300 K. They found all: monolayer, bilayer, and trilayer liquid domains, to transform into ice nanoribbons in inhomogeneous nanoconfinement.

In a friction test, it is highly possible that such solidifications can occur. Given the presence of a liquid-like layer at the friction interface, the nanoscale roughness of the friction surface, and the combined effects of pressure from the normal load and sliding, these factors lead to dynamic strain and confinement of water molecules.

## 1.3.3 Ice regelation

In addition to stress-induced ice-nucleation in nanoconfined water, there is also a case where ice under pressure melts then refreezes when pressure is lifted. This phenomenon is called *ice regelation*. It has been debated and researched since the late 1800s, when, for instance, Bottomley cut through a block of ice with a wire and observed that the ice refroze above the cut during the experiment [31]. More recently, Sotthewes *et al.* [32], found a fully reversible ice-liquid water transition when applying and then alleviating pressure with an AFM on nano-confined water/ice. These findings suggest that, under significant local pressure, ice can melt at points of contact. The amount of pressure needed for a single point of contact to induce ice melting was found to be 6 GPa [32]. The impact of ice regelation, under normal conditions due to the load, on the ice friction behaviour is not yet clear.

## 1.4 Impact parameters

In this project, the focus is the nanoscale fundamentals of ice friction underlying macroscopic questions. For instance: What factors determine whether a car remains stable on icy roads? Or, what causes one ski to slide faster than another? Such nanoscale fundamentals of ice friction, on the one hand, will complement the missing piece of today's ice friction theory by macroscopic understanding, and on the other hand, shed light on the atomistic details of abnormal ice friction phenomena, such as stick-slip motion observed by AFM experiments. This project will look into some key parameters known from the macroscopic world to influence the friction and, through an atomic-length scale simulation, try to deduce some similarities or dissimilarities in the nanoscale friction:

Normal force  $f_n$  is applied to the structure during a friction test. Inducing this force from the friction media to the ice structure, it will be interesting to see whether ice regelation occurs. Both ice in bulk and confined ice have been found to melt and then refreeze as pressure is applied and released [32]. Will the amount of applied  $f_n$  be large enough to induce this phenomenon, and will it lead to more hydrodynamic friction as there may be more liquid water present?

**Velocity** v is applied in order to generate the relative sliding motion between the structures. Considering the potential presence of a QLL within the temperature ranges of the friction tests [24], confining this liquid layer between the solid ice and the friction media could lead to instances of dynamic solidification [28, 29]. Will a greater velocity lead to a higher amount of friction, as it leads to a higher dynamic strain on the ice/water molecules?

The degree of hydrophobicity is the 'attraction' of the interface materials to water, or the wettability of the friction interface. For example, a hydrophilic material will have molecules or atoms interacting with the water, attracting the water molecules into its material and making it adhere. A hydrophobic material, on the other hand, will have its molecules or atoms repelling the water molecules. The degree of phobicity may hence influence how 'sticky' the water molecules are to the friction media. If the dissociation of water molecules away from the friction media is a large proportion of the total friction, then the friction force should be largely influenced by the degree of phobicity. Otherwise, the friction force should have less contribution from the degree of phobicity of the friction media.

To obtain the fundamentals of ice friction at ranges of only a few nm, it is imperative to have modelling methods which can take into account the actual atomic structure and dynamics. MD simulations have a resolution on atomic scale. These simulations make it possible to decipher the nanomechanical aspects of friction, and also resolving the atomic structural changes at the friction interface. In this project, MD are utilised as the tool for analysing if the atomic structure of ice is changed and influenced by a sliding motion, the applied normal force, sliding velocity, and degree of phobicity.

## 1.5 Molecular Dynamics (MD) simulations

MD simulations are a computational simulation technique suitable for investigating the physical movement of atoms and molecules. MD is based on integrating the Newton's laws of motion of the atoms in a system over time. In MD, the individual atoms are considered to be point masses, where the atoms, and their interactions with each other, are described by different potentials.

It is not feasible to solve Newton's equation of motion analytically for atoms large enough to depict the real world. MD simulation algorithms make it possible to overcome challenges with the complex and large systems, allowing us to predict physical behaviour and quantities for millions of atoms for as long as the computing power allows. However, there remain some challenges to giving a real representation:

- Long MD simulations of large systems could generate cumulative errors in the numerical integrations.
- Normally, depending on the size of the simulation system, the simulations will only be a couple of hundreds of nanoseconds long.
- Quantum effects are usually neglected while being present

To circumvent these challenges, applying the correct force fields and correct approximations are of great importance. In MD simulations, the accuracy of approximations plays a key role, especially in the context of achieving the right balance between the scale of the systems being simulated, and computational cost. The challenge lies not only in being able to simulate large enough systems for long enough, but also maintaining a minimal error margin, ensuring the reliability of the results.

An optimal approximation in MD simulations, therefore, is one that offers a trade-off between the size of the system that can be simulated and the margin of error that can be tolerated. This balance is pivotal in ensuring the fidelity of the simulation to real-world phenomena while preserving computational efficiency. Notably, the choice of approximation, whether it concerns the potential model, the time step size, or the treatment of boundary conditions, should be guided by this principle of balancing system size with error tolerance.

This project focuses on the friction dynamics of a polymer substrate to ice interaction. To investigate these mechanical properties of nanoscale ice friction, it is important to have a good representation of both solid water (ice) and the polymer. In order to model the behaviour of these materials and their interactions under various conditions, it is essential to establish accurate interaction potentials and force fields. By ensuring the fidelity of these critical components in our model, we pave the way for simulations that are both reliable and insightful, allowing us to shed light on the nuanced friction dynamics at the nanoscale friction interface.

#### 1.5.1 Atomistic interaction potentials and force fields

Interaction potentials and force fields represent the energy relationships and forces acting between atoms or groups of atoms in a system. They form the cornerstone of MD simulations by providing the rules for how each molecule moves and interacts with its environment. Thus, the selection of these potentials and force fields must reflect the physical and chemical characteristics of ice and polymer to obtain a reliable representation of the real world.

Different potentials and force fields suit different molecules or atoms and comes with different computational costs. In these simulations, two types of potentials will be used: an approximation of the Transferable Potentials for Phase Equilibra-United Atom model (TraPPE-UA) [33], and the Coarse grained water (mW) water model [34]. The approximation of the TraPPE-UA potential is used to approximate the behaviour of the  $CH_2$  molecules in the polymer, while mW is used for the  $H_2O$  molecules in the ice.

#### 1.5.2 Water in MD



Figure 4: A water molecule, where the red sphere represent the oxygen atom and the grey spheres represents hydrogen atoms. The water molecule has its two H-atoms displaced in an angle of  $104.5^{\circ}$  and an O–H bond length of 95.72 pm

Water is indeed a molecule that presents intriguing challenges and opportunities in both the realms of physics and chemistry, largely due to its multifaceted and complex behaviour. From the anomalies of its liquid state to its unique structural configurations when frozen, the intricacies of water continue to spark curiosity and stimulate research.

Moreover, water plays a central role in shaping our world and society. It is not only the fundamental building block of all living organisms but also a critical component in various sectors such as agriculture, transportation, and energy production. Our ecosystems depend on the water cycle for sustenance, and human civilization has been built around the availability and management of this precious resource.

The water molecule consists of two hydrogen atoms, bonded to an oxygen atom at an angle of 104.5°, with a bond length of 0.9572 Å [35], as displayed in Figure 4. Since oxygen atoms have greater electronegativity than hydrogen atoms, the O–H bonds in water are polar. Together with the spatial ordering of the atoms, this yields an electric potential, with some regions having a higher electron density than others [35]. In MD one looks at atoms as point particles, with point charges in different potentials. While being quite simple models, it is rarely only the single molecule or atom that is of interest in MD. Rather, the area of interest in MD is primarily the dynamic behaviour of multiple and often large amounts of atoms and molecules.

Having thousands of water molecules interacting with each other, gives three times the amount of particles with an all-atom model. Therefore, translating the three-atom water molecule into a one point-particle should speed up the computations. This approach helps one avoid having to compute the mechanics of every O–H bond. When reducing from three atoms to one particle, it is critical to have the interactions with other atoms or molecules behave in the same way as the all-atom model would. Reducing the model's complexity is called *coarse-graining*. For water, one well-known and -performing model is the mW model [34].

#### 1.5.2.1 mW model

The mW model is based on having the water molecules modelled as an intermediate element in between Carbon and Silicon [34]. Molinero and Moore mimicked the behaviour of Silicon to represent the important hydrogen bonding geometry and the thermodynamic properties of water [34] in the best possible way. Water and silicon, although chemically distinct, share intriguingly similar physical properties, particularly in terms of their tetrahedral structural arrangements and amorphous phases. Water molecules form a tetrahedral structure because of the two hydrogen atoms and two lone pairs of electrons on the oxygen atom, while silicon atoms bond covalently with four other atoms to form a similar tetrahedral configuration.

Both silicon and water can be modelled as pseudoatoms with their energy described by Equation (2) in a Stillinger-Weber potential [36].

$$E = \sum_{i} \sum_{j>i} \phi_2(r_{ij}) + \sum_{i} \sum_{j\neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}),$$
(2)  
$$\phi_2(r) = A\epsilon \left[ B\left(\frac{\sigma}{r}\right)^p - \left(\frac{\sigma}{r}\right)^q \right] exp\left(\frac{\sigma}{r-a\sigma}\right),$$
  
$$\phi_3(r, s, \theta) = \lambda\epsilon \left[ \cos\theta - \cos\theta_0 \right]^2 exp\left(\frac{\gamma\sigma}{r-a\sigma} + \frac{\gamma\sigma}{s-a\sigma}\right),$$

where A = 7.049556277, B = 0.06022245584, p = 4, q = 0, and  $\gamma = 1.2$  give the form and scale for the potential. Applying the model for water, Molinero and Moore found the interaction parameters of mW: the dispersion energy  $\epsilon = 0.268381 \,\text{eV}$ , the critical distance  $\sigma = 2.3925 \,\text{\AA}$ , and the tetrahedral parameter  $\lambda = 23.15$ .

Having a Coarse Grained (CG) model can significantly reduce the computational time. For mW, Moliner and Moore found that the speed-up compared to efficient all-atom models — such as SPCE — is around 180 times faster [34]. mW is efficient for mimicking the crystalline phases, and it is proved that mW potential reproduces the melting temperatures as obtained from free energy calculations [34, 37]. This makes the model especially suitable for these simulations with ice and friction, which can lead to melting.

## 1.5.3 Friction media, and polymer in MD

In our everyday lives, common media in contact with ice, include car tires, shoe soles, coatings, skis, or boats. While shoe soles and car tires are usually designed to ensure a high degree of friction, we usually want to limit the friction of boats and skis against water, ice, or snow. They all consist of a polymer material that is in contact with the ground or water. Hence, for the friction tests, the media to be used in contact with ice is chosen to be a polymer, which can be both sticky and slippery.

For any MD simulations, we need — just as with water and ice — an effective and reliable model for the polymer. Common forms for polymers include amorphous, crystalline, and liquid forms. They can also be linear or non-linear. Polymers usually consist of long carbon chains which are intertwined or arranged in a suitable way. There are polymers that only consist of alkenes, which are the simplest, but polymers can also be doped and or modified for boosting some attributes. Even for the simplest polymers there are still Hydrogen atoms to be accounted for, and the spatial complexity are also well present in the polymers as in water.

One well-known and -tested model for CG organic compounds is the TraPPE-UA [33]. The TraPPE-UA force fields are based on intramolecular bonded interaction potentials, and non-bonded potentials for intermolecular and pseudoatoms outside the reach of the intramolecular potentials. For the intramolecular interactions, the *bonds*, *angles*, and *dihedrals* interactions [33, 38] are used. Where the United Atom (UA) alkenes have rigid bonds. Hence, the nearest neighbour intramolecular pseudoatoms are at fixed length from each other and cannot be stretched. The fact that the bonds are rigid means that it is the spatial bending and torsion, 1–3 and 1–4 interactions, that account for the short-range displacements inside the polymeric pseudoatom chains, in tandem with intermolecular and long-range intramolecular interactions described by the Lennard-Jones (LJ) potentials [33, 38].

## 2 Method

This part of the report covers the modelling of the system and the different parts of the 'experiment' and how it is conducted. Applying MD simulations provides a method of simulation that effectively characterises nanoscale ice friction. Notably, it also offers the flexibility to conduct the tests with different parameters. The model and method of study in this section have the primary goal of being good background for future work exploring the field of MD simulations focusing on the domain of nanoscale friction. To fulfil this goal, we found it important to propose a relative large-scale model, with relatively long simulations.

The purpose of the modelling is to construct a system that consists of crystalline solid water in contact with a friction media. Taking one of the most popular Norwegian winter sport, cross-country skiing, for example, skis are being built as a stiff and light construction with a High-Density polyethylene (HDPE) substrate on the bottom. In this research, thus, the polymer in question as the friction media will take form as a HDPE. In the simulations, we have aimed to keep the model sufficiently simple for the friction testing to be conducted under stable conditions, while limiting the complexity of the measurement and analysis. The length scales in the project can be looked at as simulating the true contact between one single asperity of the HDPE sole of the ski with ice.

In real-world scenarios, surfaces in contact are not perfectly smooth; they have asperities and irregularities that can create sharp edges. This is in fact the case, but inducing edge effects on the length scales of a few nm, would lead to a way larger amount of irregularities than those in nature in ranges of µm. When modelling these interactions, the presence of sharp edges might lead to the simulation of a cutting action rather than sliding, which can dominate the results and provide an unnatural depiction of the forces involved. To avoid this, the model simplifies the contact to a single asperity and omits edge effects, treating the interface as an infinite plane through the application of Periodic Boundary Conditions (PBC). This approach avoids the disproportionate impact of edge forces and offers a more representative depiction of nanoscale friction dynamics. The construction of the atomistic model, starting with the individual media and progressing with their integration, is described in Section 2.1.

## 2.1 Atomistic modelling

In the modelling phase, both structures are combined, taking into account the distinct potentials and spatial parameters associated with the ice and the polymer. After the design of both structures, they are prepared and combined to make up the full system model. The full model is then evolved through time by the MD-simulation conducting the friction experiments.

#### 2.1.1 Ice structure

Water usually arranges in a hexagonal-crystalline structure, denoted Hexagonal Crystalline Ice ( $I_h$ ), in solid phase below freezing temperature in the biosphere [8]. This hexagonal-crystalline structure was thus chosen to be the ice structure of interest in this work. In nature, perfect infinite long-range crystalline ice does not occur. However, when having such a small length scale, only a few nanometres in each direction, introducing impurities would produce numerous impurities relative to the real world ice and snow. Therefore, to reduce the complexity of the system, the ice structure was chosen not to have any impurities, thereby eliminating this extra parameter. Without having any impurities in the ice media, the simulation is resembling the contact between a single ice grain and the friction media, in a single asperity contact. The ice media is therefore starting out as a perfect crystal in the same form as the all atom model in Figure 2 did show.



Figure 5: The final structure of coarse-grained  $I_h$ , visualised by Vesta [18]. The blue spheres resemble the H<sub>2</sub>O molecules. Figure 5b shows the x-z plane, while Figure 5a shows the whole ice structure. The red axis is the x-axis, green is the y-axis, and the blue is the z-axis.

For making the ice media, the command line software genice2 [39, 40] was used to create  $10 \times 10 \times 5$  unit cells of I<sub>h</sub> with a total of 27648 H<sub>2</sub>O molecules. The ice media was loaded by the visualisation program Ovito [41], the hydrogen atoms were removed and then saved on the data format for the selected simulation software Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [42]. The mW water model [34], with the right molecular mass, was selected for this work because of its ability to capture the hydrogen bonding feature in water and ice [34]. The initial ice structure was first optimised by an energy minimisation process. For the energy minimisation, the Polak-Ribiere version of the conjugate gradient algorithm is performed by LAMMPS [42]. The energy minimisation process is performed with the following parameters:

 $etol = 1.0 \times 10^{-8}$  This means that the minimisation is stopped if the normalised change

in potential energy during an iteration is less than  $1.0 \times 10^{-8}$ .

- $ftol = 1.0 \times 10^{-8}$  This means that minimisation is stopped if the change in force is less than  $1.0 \times 10^{-8}$  force units.
- maxiter = 10000 This means that if the number of outer iterations exceeds  $1.0 \times 10^4$ , the minimisation process ends.
- maxeval = 10000 This means that if the number of total force evaluations exceeds  $1.0 \times 10^4$ , the minimisation process ends.

After the minimisation, the final process for preparing the ice media was an equilibration process for 5 ns, at experiment temperature, 270 K, with the simulation box treated with all PBC. The final block of CGed ice is displayed in Figure 5, with the blue spheres resembling the pseudoatoms.

#### 2.1.2 Polymer structure



Figure 6: The structure of coarse-grained polymer, visualised by Vesta [18]. The black spheres resemble the  $CH_2$  pseudoatoms connected with gray bonds. Figure 6a shows the whole structure consisting of 17280 pseudoatoms, while Figure 6b shows a zoomed-in version in the *xz*-plane displaying the zig-zag configuration and the bonds.

A reason for choosing a polymer for the friction test is that they are highly adaptable and possible to engineer in real life. For figuring out which kind of polymer to try to resemble, we looked into the main ski bases, which are HDPE. Based on this, a crystalline polymer based on an orthorhombic unit crystal HDPE nanofibre structure, investigated by Nejabat [43], was built as shown in Figure 6. It should be noted that the polymer structure could be highly complicated in nature. Here, the choice of crystalline polymer is used for the sake of simplicity. The investigation of the response of the internal structure of polymers is beyond the scope of this project.

As there exists no software making the data files for this polymer, Nejabat's unit-crystal, based on CG CH<sub>2</sub> groups as pseudoatoms, was made. The lattice parameters of the unit-crystal were put to a = 7.42 Å, b = 4.95 Å, and c = 2.55 Å, with a planar displacement of 0.89 Å per layer in the z-direction. The unit cell consisting of four pseudoatoms in

two molecules were then replicated  $12 \times 18 \times 20$  in x, y, z-direction, resulting in the final polymer chains visualized in Figure 6.

Usually, HDPE is composed of intertwined long polymer chains. To simulate a single asperity of contact and represent these extensive chains while maintaining manageable computational time, the polymer molecules were truncated to a length of  $40 \text{ CH}_2$  with a fixed top layer. This fixed top layer approximates *infinite* polymer chains on top, representing a dense, non-interacting structure above. Worth noting, the polymer's length is much larger than the cutoff distance for non-bonded interactions with the water molecules.

Further, the polymer structure is parameterised in a potential based on TraPPE-UA [33].



**Figure 7:** The final slabs of coarse-grained polymers after heating equilibration and quenching, visualised by Vesta [18]. The black spheres resemble the  $CH_2$  pseudoatoms connected with gray bonds. Figures 7a to 7c show the three different slabs of polymers, which are quenched after, respectively, 5 ns, 6 ns and 7 ns

For the CGed structure specifically, the energy potential has the following form:

$$E(r_1, r_2, \dots, r_N) = \sum_{ij} E_{NB}(r_i, r_j) + \sum_{ij} E_{bond}(r_i, r_j) + \sum_{ijk} E_{bend} + \sum_{ijk} E_{torsion}(r_i, r_j, r_k),$$
(3a)

$$E_{NB} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}},\tag{3b}$$

$$E_{bond} = 0$$
 (Fixed bond length), (3c)

$$E_{bend} = \frac{k_{\theta}}{2} \left(\theta - \theta_0\right)^2,\tag{3d}$$

$$E_{torsion} = c_0 c_1 [1 + \cos(\phi)] + c_2 [1 - \cos(2\phi)] + c_3 [1 + \cos(3\phi)].$$
(3e)

For our polymer chain TraPPE-UA Equation (3) has the following parameters:

q = 0 This means that the pseudoatoms have no charge.

- $\epsilon_{ij} = \sqrt{(\epsilon_{ii}\epsilon_{jj})} = \epsilon_0 = 3.964 \,\mathrm{meV}$  The dispersion energy between each CH<sub>2</sub> pseudoatom is  $3.964 \,\mathrm{meV}$ .
- $\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) = 3.95 \text{ Å}$  The critical distance between each CH<sub>2</sub>-pseudoatoms is 3.95 Å.
- $k_{\theta} = 5.386 \,\mathrm{eV \, rad^{-2}}$  The harmonic spring constant containing the angle between three consecutive psudoatoms per polymer chain gives the rate for how fixed the angles are.
- $\theta_0 = 114^{\circ}$  The equilibrium angle between three consecutive pseudoatoms per polymer chain.
- $c_0, c_1, c_2, c_3 = \{0 \text{ eV}, 30.59 \text{ eV}, -5.876 \text{ eV} \text{ and } 68.19 \text{ eV}\}$  The constants give the weighting for 1, 4 bonded interactions and yield how much energy it would need for torsional bending in space, where  $\phi = 0^\circ$  will be a complete syn-periplanar conformation and  $\phi = 180^\circ$  corresponds to anti-periplanar conformations [33].

In order to effectively sample the packing space of the polymer chains, the structure is heated for 7 ns at 750 K. The state of all atoms in the system was saved to a restart file after 5 ns, 6 ns and 7 ns, yielding a total of three different polymer structures. In the end, the three polymer structures are quenched to 300 K, leading to three different polymer structures for the friction media, as shown in Figure 7.

#### 2.1.3 Full model

To construct the final system, the ice structure and the polymer structures were joined together, placing the polymers at a distance of 2 Å relative to the z-axis, away from the



**Figure 8:** An overview of the atomistic modelling process from single molecules on the left to the full model to the right with the steps described in Sections 2.1 to 2.1.3

ice. Complete models were put in a simulation cell of about  $94 \text{ Å} \times 89 \text{ Å} \times 226 \text{ Å}$ , with the models filling the whole box in the xy-plane while having enough space in the z-direction for the atoms to not interact with their periodic image at any time during the simulations.

**Table 1:** Overview of the interaction energies,  $\epsilon$ , for H<sub>2</sub>O-CH<sub>2</sub>, with  $\epsilon_0$  as the reference interaction potential of the CH<sub>2</sub>-CH<sub>2</sub> non-bonded pseudoatoms

$\epsilon$	Value [meV]
$0.01\epsilon_0$	0.0396
$0.05\epsilon_0$	0.1982
$0.1\epsilon_0$	0.3964
$0.5\epsilon_0$	1.982
$\epsilon_0$	3.964
$2\epsilon_0$	7.928

The interaction potentials between the friction media and the ice were approximated by a non-bonded Lennard-Jones potential [44] between the different types of psudoatoms, with different values for the dispersion energy,  $\epsilon_{\rm H_2O-CH_2}$ , inspired by the work by Rønneberg [45] for modelling the wettability of the friction media. Values are shown in Table 1.

All LJ interactions were truncated at a cut-off of 14 Å. Finally, to ensure no pseudoatoms were overlapping, a structural energy minimisation was carried out on the whole structure, in the same manner as for the ice structure described in Section 2.1.1. Completing the modelling process as shown in Figure 8, the systems consist of  $17\,280\,\text{CH}_2$  and  $27\,648\,\text{H}_2\text{O}$  pseudoatoms. This results in a total of 44 928 particles interacting with each other in every system.

## 2.2 MD simulation

All the MD simulations were carried out using LAMMPS [42] (29 Sep 2021—Update 1 version) with 1 Open MP thread per MPI task by MPI on a total of 128 processors. The total simulation process contains:

- 1. An equilibration process where the models adapt to the simulation environments, and the systems stabilise.
- 2. Initiation of all forces and testing parameters.
- 3. The simulation of the friction test.
- 4. Data collection for analysis

### 2.2.1 Equilibration process

The total of 15 different systems, 3 different polymer substrates with 5 different interaction potentials, were put in a Canonical ensemble (NVT) at the temperature of 260 K, with the use of a Nosé-Hoover thermostat for controlling the simulation temperature with a coupling time constant ( $\tau_T$ ) of 100 fs [46, 47]. A simulation temperature of 260 K is chosen as I<sub>h</sub> is in a stable solid form at this temperature in nature, and it reduces the complexity of the systems not being too close to any temperature-dependent phase transition. The imaginative long polymer chains on top are approximated as described in Section 2.1.2, representing a solid wall. To achieve this representation, the top layer of the polymer is excluded from the time integration. This effectively anchors the top layer in place. The equilibration process is done with a simulation time of 10 ns, with a time step of 1 fs. During the equilibration process, the thermodynamic calculations of energy, temperature, pressure, and volume are written to a log-file for monitoring the system and verifying equilibration.

#### 2.2.2 Friction test

For the execution of a friction test within the MD simulation framework, the following key parameters were established:

- 1. Relative motion between the ice and polymer surfaces.
- 2. Application of a normal force to simulate the pressure experienced during physical contact.
- 3. Implementation of a measurement function to quantify the resulting friction force.

From a skier's perspective, one wants the force hindering the movement of your skies to be as small as possible. Hence, measuring the force from the ice to the polymer is chosen to be the force measured in the friction simulations. To achieve the relative motion of the ice and the polymer substrate, the ice was set to move while keeping the far ends of the polymers from the friction interface fixed at their initial positions.

For moving the ice to study the friction behaviours, two slabs of water molecules, vertical to the friction interface along with a parallel slab at the bottom of the ice structure, were selected and set to move at constant velocity in the x-direction. Notably, the remaining number of water molecules, not a part of the slabs, were kept as large as possible while still maintaining the effect of a constant drift-velocity for the ice structure. The varied thickness and placements of the water slabs were selected to be:

- i. 20 Å— thick xy-plane from the bottom of the ice.
- ii. 6 Å— thick yz-plane from the ice at the smallest x-edge of the simulation cell.
- iii. 6 Å— thick xz-plane from the ice at the smallest y-edge of the simulation cell.

Further, the water slabs were time-integrated along with the rest of the system in the directions perpendicular to the movement of the ice, y&z-directions. In the x-direction, the fixed water slabs were moved at a constant velocity influencing the other molecules as normal, overriding all outside forces acting on the water molecules in this direction. In the perspective of the experiment and the PBC, the movement of the box can be visualised by dividing a cuboid, with infinite reach in the xy-plane, in a grid that is moved at a constant velocity. This ensures a constant drift-velocity of the ice media relative to the polymer.

For measuring the force exerted by the relative movement of the ice onto the polymer, atoms in the polymer in the NVT ensemble are fixed in the xy-plane by massless soft springs to their initial positions after the structural energy minimisation period. The soft springs have harmonic spring constants of  $k_s = 6.95 \times 10^{-4} \,\mathrm{N \, m^{-1}} \ll \frac{\epsilon_0}{\mathrm{Distance}^2} = 6.35 \times 10^{-2} \,\mathrm{N \, m^{-1}}$ . The energy from these springs are hence a measure of the force of friction from the ice movement.

The normal load was induced in the MD-simulation through a constant, massless, and invisible force acting between the mass centres of the two media along the z-direction. Having all the three components for the friction test defined, the simulations were carried out with a time step of 1 fs for 50 ns, with the same temperature settings and thermostat as in the equilibration of the systems in Section 2.2.1.

**Table 2:** Overview of the testing parameters for the systems,  $P_N$  being the simulated normal pressure and v the relative macro-velocity of the ice in the x-direction.

Parameter	Value
$P_N \ v$	(2, 20, 40  and  200)  kPa $(0.1, 1 \text{ and } 8)  \text{m s}^{-1}$

The simulations were run with the different testing parameters given in Table 2 to probe the influence of these components on the atomic scale with different degrees of phobicity [45].

The temperature of the system, the displacement forces on the polymers, and the external forces were calculated and written to file every 100 fs. Every 0.1 ns, the atoms' positions relative to the simulation box were collected for analysis, along with the  $\{x, y, z\}$ -components of the stress tensor for each atom in the systems. The stress tensors were computed by LAMMPS [42] with the stress/atom command following previous studies by Thompson *et al.* [48].

## 3 Results

This section is dedicated to presenting and discussing the comprehensive results gathered throughout the course of the research. To maintain thematic consistency, the section is segregated into two parts. The first part discusses our model, especially looking into the equilibration process, while the second one unfolds the results derived from the friction tests.

## 3.1 Atomistic modelling process

The process of modelling and preparing the structures, as detailed in Sections 2.1 and 2.2.1, was rigorously followed in our Molecular Dynamics study. When using MD, it is paramount to ensure an exhaustive equilibration to produce consistent and trustworthy findings. To verify the efficacy of the equilibration, we analysed the thermodynamic properties obtained throughout the process of the systems monitored throughout the simulations. We also analysed the crystalline structures of the ice samples, especially those adjacent to the friction interface. But first, we look into the spatial configurations of the finished equilibrated systems, highlighting how the different polymer substrates and interactions at the friction interface affect the equilibrated systems.

## 3.1.1 Interfacial adherence: ice and polymer interaction



**Figure 9:** The figures show the results of the slab of ice not sticking to the polymer. Figure 9a shows the results for  $\epsilon = 0.01\epsilon_0$  and Figure 9b for  $\epsilon = 0.05\epsilon_0$ . This results in the ice falling through the bottom of the periodic system and ending up on top of the polymer shown in the figure.

The main purpose of the equilibration simulation is to ensure that both our friction media,
the block of ice, and the polymer substrates stabilise and adhere to each other inside our reference system. For the smallest interaction potentials where  $\epsilon = 0.01$ - and  $0.05\epsilon_0$ , the ice structure did not stick to the polymers, as shown for one polymer in Figure 9. The non-sticking ice, is found mainly owing to initial weak attraction between the polymer to ice and the thermal fluctuation of the molecular structures. Smaller initial distances between the ice and the polymer structures, down to 0.1 Å, were tried without any success.

Having the two substrates stably adhere is of utmost importance when the system is set in motion afterwards. A stable adherence between the two surfaces guarantees that the interactions between them are properly represented during the dynamic phase of the simulation. This is particularly critical when investigating the behaviour and properties of the interface, such as friction and adhesion, as these strongly depend on the quality of the interactions and the stability of the contact between the two substrates.

The absence of adhesion suggests that our chosen interaction potential may be too weak. This weak potential could prevent the formation of a stable interface between the ice and the polymer.

We made two important assumptions when creating these models. One assumption was to fix the top of the polymer substrate. This was done to simulate infinitely long and intertwined polymers that would not be influenced by the friction measurements.

Another assumption was the use of the same potential for all  $CH_2$  molecules. This is likely a good approximation for long-chain polymers. However, the end unit of the polymer is in fact a  $CH_3$ -group, since it is not connected to two  $CH_2$  molecules. In these simulations, we modelled these end groups as  $CH_2$ -groups as well, both in terms off molecular mass and using the same interaction coefficients.

These two factors could contribute to the observed lack of adhesion. The polymer substrate was restricted from moving in the z-axis, as they were fixed from the top (away from the ice). Meanwhile, the ice structure was not significantly attracted towards the end of the polymer chains. This was because they did not have a sufficiently strong interaction energy, which they would have had if the edge molecules were considered separately from the rest of the polymer chains.

Considering these limitations, the models with  $\epsilon = 0.01$  and  $0.05\epsilon_0$  were deemed unsuitable for further investigation in this study. In future studies, focusing on friction of super low interface attraction like these two, one have to try another modelling of the interface interactions. In addition, one should look into not fixing the top layer of the polymer for the equilibration, this would let the polymer easier move towards the ice as well. This will facilitate a more accurate representation of the interfacial properties and behaviours. Having the two media to stick would allow for a meaningful interpretation of the friction tests for super low interface attractions.

For the systems where the ice did sufficiently adhere to the polymer, Figure 10 provides



Figure 10: Illustration of the system evolution from pre-equilibration (after minimisation) state to post-equilibration state. Figure 10a depicts the systems post-minimisation and pre-equilibration, while Figures 10b to 10e present the systems following the equilibration process for different  $\epsilon$  values.

visual representations of these systems, both pre- and post-equilibration. In Figure 10, it is noticeable that for larger values of  $\epsilon$ , the interfacial distance between the two substrates are smaller. This spatial correlation is consistent with the expectations from the physics of LJ potentials:

A grater  $\epsilon$  signifies a stronger attraction potential, and in this experiment it is used for simulating the degree of hydrophobicity of the substrate [45].

#### 3.1.2 Thermodynamical properties

This equilibration process stabilises the system during the simulation, leading its thermodynamic attributes like temperature and energy to fluctuate around a steady equilibrium state. This strategy is key to ruling out biases or inaccuracies that might have been introduced at the time of system set-up, and could subsequently mislead the interpretation of the simulation data. The progress of thermodynamic properties, namely the system potential  $(E_T)$  and temperature (T), throughout the equilibration process is visualised in Figure 11. These visualisations provide insights into the variable phobicity degrees at the friction interface, where ice adheres to the polymer, each represented by a unique  $\epsilon$ .

The results from the thermodynamical outputs show how both the temperature and total energy reach stable oscillations around 260 K and  $-1.2 \text{ GJ mol}^{-1}$ , for  $\epsilon = 0.1 \epsilon_0$ ,  $0.5 \epsilon_0$ ,  $1 \epsilon_0$  and  $2 \epsilon_0$ . Thus, together with the system snapshots in Figure 10, the systems where the ice and polymer adhere to each other are all found stable and ready for further experiments.

For each of the interaction energy epsilon, three polymer initial structures are used for



Figure 11: The figure includes two subfigures, with the top one presenting the total energy variations during the equilibration process and the bottom one depicting the corresponding changes in temperature. The subfigures compare the evolution of the systems under the influence of four distinct interaction potentials, denoted by  $\epsilon = 0.1 \epsilon_0$ ,  $0.5 \epsilon_0$ ,  $1.0 \epsilon_0$  and  $2.0 \epsilon_0$ .

probing the different adhesion states. As examples of system properties, shown in Figure 12, show that using the different initial structures of polymers as substrates against the ice did not lead to significantly different properties and development. The system potential energy with the three different initial polymer structures stabilized at the same value, in spite of small fluctuation during the simulations. At the same time, the temperature in the three systems are also the same, thanks to the temperature coupling method used in the simulations. As the randomisation number in the simulations are the same, this indicates that the polymers are clearly different. Since they were quenched from varying times, but have the same molecular properties, this have to mean that their spatial configuration is different. Therefore, the dissimilarities between the polymers are attributed to differences in topology and/or chain orientations.

The ice model has stably adhered to the polymer substrates. This demonstrates that for  $\epsilon = 0.1 \epsilon_0$ ,  $0.5 \epsilon_0$ ,  $1 \epsilon_0$  and  $2 \epsilon_0$ , and for all three polymers, the systems are stable. Therefore, these systems are used further in the friction test.



Figure 12: The upper panel exhibits the evolution of total energy for the three distinct polymers throughout the equilibration process, while the lower panel demonstrates the corresponding temperature progression. Each case considers an interaction potential of  $\epsilon = 1.0\epsilon_0$  between the water molecules and the polymers.

### 3.1.3 Structural and Crystalline observations

Further investigation of the structures, as a result of the modelling process, is achieved by looking into the structures residing in the final systems. With an analysis of the crystalstructure of the ice, the QLL at the interface, and the stress, taking in the differences of the polymers. These insights shed light on how various polymers, with distinct spatial orientations and degree of phobicity, interact and evolve with the ice.

The first observation from the visual representations is the crystal structure of ice, as exemplified by the system snapshot in Figure 10. We find a clear evolution from Figure 10a, with only crystalline water molecules being present in the ice, to Figures 10b to 10e where there are non-crystalline water molecules clearly visible as well, for example at the interfaces. Further, the snapshots of Figures 10b to 10e also show a clear bending of the polymer chains.

By applying the CHILL+ algorithm [49], the number of amorphous (non-crystalline) water molecules are calculated through the equilibration process. Figure 13 shows that, through the equilibration process, there is a most obvious elevated amount of amorphous water molecules found for the systems with the highest LJ energy depth. Further, from the bandwidths, the fluctuations in the number of amorphous water molecules for the different



Figure 13: Graphical display of the amount of amorphous water molecules during the equilibration process. The lines show the means of the three polymers for the different  $\epsilon$ , with bandwidths in the corresponding colours. The bandwidths represent the max-min reach for the three polymers.

polymers are shown. This clearly demonstrate the impact of the different attraction energies have for different spatial configurations at the interface between the polymers and water. Especially it is to be stated out the really large differences amongst the systems having  $\epsilon = 0.1 \epsilon_0$  and 2.0  $\epsilon_0$ . In addition, the number of amorphous water molecules in the systems reached a plateau from 1 to 5 ns which further confirms that the systems are well-equilibrated.

Following the display of Figure 10, it is clear that the polymers have been compressed and had a small change in orientation, owing to the adhesion of ice. However, such conformation changes of the polymers are expected as the polymer chains are flexible. It is important to note that the change of polymer conformation did not significantly alter the covalent bond length along the polymer chains. As shown in Figure 14, the covalent bond lengths are fluctuating in a narrow range around the equilibrium value, for all  $\epsilon$ .

There are also small differences between the three polymers, as seen from the reach of the error bars of the plot. Having a change in average bond length under  $\frac{1}{100}$  of the initial 1.54 Å through the equilibration process, is a good indicator for the fact that the polymers are dense and well-equilibrated.

One of the important interface properties being expected at the friction interface is the QLL, a layer of unordered or amorphous molecules sandwiched by the crystalline ice and the polymer. In Figure 10, we can see how an unordered layer is present in all the systems after equilibration, while not being present after minimisation. It is difficult to quantify the thickness of QLL,  $d_{\text{QLL}}$ , by looking at visual representations like Figure 10. Measuring



Figure 14: Graphical display of the average bond lengths during the equilibration, where the error bars are the variance between the three polymers. The line is fitted through the means for the three polymers. The colours of the markers and lines correspond to the different  $\epsilon$ .

the QLL from a 2D orthogonal view, and defining the thickness to be a constant from the visual unordered molecules, will be highly inaccurate as there are differences over the interface in all spatial dimensions.

A new approach is used here to precisely characterise the thickness of the QLL, as shown in Figure 15. First, one starts by taking out all  $CH_2$  molecules from the model. Then the Chill+ algorithm [49] is used to identify all water molecules in crystalline form, highlighted by the red coloured spheres in Figure 15. These molecules are then removed. For the remaining molecules, a kernel density approximation is calculated to approximate the water molecule density as a function of the z-direction in the simulation box. A visual representation of the density approximation for the system is plotted alongside the snapshots furthest to the right in Figure 15. From the density approximation as a function of z, a 90% confidence interval, for the top half of the system, is found to define the thickness  $d_{QLL}$ .

The following bandwidth is used for the kernel density estimate:

$$h = \left(\frac{4\hat{\sigma}^5}{3n}\right)^{\frac{1}{5}},\tag{4}$$

In Equation (4), n is the number of molecules and  $\hat{\sigma}$  is the standard deviation of the amorphous water molecules, z-component of their spatial position.

For the three smallest  $\epsilon$  over the three different polymers, there is no significant difference in the thickness of the QLL. For the larger  $\epsilon = 2.0\epsilon_0$ , all three polymers exhibit larger



# Process for determining the QLL thickness

Figure 15: The figure show how the thickness of the QLL is determined. From left to right, the amorphous non-crystalline H<sub>2</sub>O-molecules are characterised, and a corresponding density function is approximated and shown to the right. Where the QLL thickness,  $d_{\text{QLL}}$  is determined as the 90% confidence interval shown.

**Table 3:** Calculated thickness of QLL, with corresponding standard deviation  $\hat{\sigma}$ , after the equilibration process for  $\epsilon = 0.1 \epsilon_0$ ,  $0.5 \epsilon_0$ ,  $1 \epsilon_0$  and  $2 \epsilon_0$  with the three different polymers.

	Polymer 1	Polymer 2	Polymer 3
$\epsilon$	$d_{ m QLL}\pm \sigma$	$d_{ m QLL}\pm \sigma$	$d_{ m QLL}\pm \sigma$
$0.1\epsilon_0$	$0.720\pm0.248\mathrm{nm}$	$0.796\pm0.264\mathrm{nm}$	$0.820\pm0.262\mathrm{nm}$
$0.5\epsilon_0$	$0.876\pm0.270\mathrm{nm}$	$0.733\pm0.250\mathrm{nm}$	$0.747\pm0.269\mathrm{nm}$
$\epsilon_0$	$0.733\pm0.253\mathrm{nm}$	$0.721\pm0.250\mathrm{nm}$	$0.749\pm0.259\mathrm{nm}$
$2\epsilon_0$	$0.969\pm0.305\mathrm{nm}$	$0.917\pm0.312\mathrm{nm}$	$1.329\pm0.375\mathrm{nm}$

thickness compared to other interaction potentials. This shows that a large  $\epsilon$  leads to a build-up of a thicker QLL.

In addition, when we examine the QLL thickness across the different polymers for each  $\epsilon$  value, significant variability is observed. In particular, Polymer 3 consistently displays a greater QLL thickness compared to the other two polymers, with a particularly pronounced difference at  $\epsilon = 2\epsilon_0$ . This observation underscores the inherent disparities among the polymer structures. There is clear variability in the QLL measurements between different polymer structures. This suggests that the QLL is influenced by the topology and chain orientations of the substrate, in this case the polymers, when interacting with the water molecules.

## Equilibration finishing notes

The thermodynamical properties  $E_T$  and T, did come to an equilibrium state for all  $\epsilon = 0.1 \epsilon_0$ ,  $0.5 \epsilon_0$ ,  $1 \epsilon_0$  and  $2 \epsilon_0 \epsilon_0$  at around  $-1.2 \text{ GJ mol}^{-1}$  and 260 K, for all three different polymer substrates. Further spatial examinations of the systems with  $\epsilon = 0.01 \epsilon_0$  and  $0.05 \epsilon_0$  showed that for all these systems, the ice block did not adhere to the polymer substrates. Stable adherence is critical when the system is set in motion, this to ensure that the interactions are properly represented. Thus, these systems could not be used further in the friction tests.

This study did not simulate the end-molecules of the polymer groups as free, having  $CH_3$  groups, but did simulate these as  $CH_2$  groups as well. In our simulations, this factor seems plausible for a complex and dense polymer, which naturally possesses few free  $CH_3$ -groups. Certainly, not in quantities large enough for all of them to be end-groups. Given that the  $CH_3$  groups possess a greater interaction potential, their absence consequently reduces the attraction between the polymer structure and the ice. This might also explain why systems with the weakest attraction potentials did not exhibit adherence between the water molecules and the polymer substrate.

Through the equilibration process the number of amorphous water molecules, at the interface between ice and polymers, rapidly increased and stabilised for the systems around 12 to 15 % around 1 ns. Where, a clear tendency of larger numbers of amorphous water, was found for the least hydrophobic (most hydrophilic) polymer, having  $\epsilon = 2.0\epsilon_0$ . Few to no differences were found in average bond lengths in the polymers, for the different systems with different attraction potentials. In addition, the different polymers did not lead to significant differences in average bond lengths either. Evidently, the substrates and ice structures are in an equilibrated state with small to no fluctuations in structural and thermodynamical properties, over the last part of the equilibration process.

While there were small to no changes in the polymers bond lengths, the increase in the number of amorphous water molecules, at the interface, was accounted for to be the build-up of a QLL. The QLL thickness,  $d_{QLL}$ , was significantly larger for the largest attraction potential,  $\epsilon = 2.0\epsilon_0$ , especially for the third polymer with this attraction potential. Further, there were found small but clear differences between the systems with different polymer structures, giving clear marks that the process to make different polymers were successful.

## 3.2 Friction Tests

The subsequent friction tests, carried out as detailed in Section 2.2.2, investigated the effects of various parameters on the frictional behaviours at the ice-polymer interface. This section takes into account our different systems, it looks into how the interfaces and media evolve over time. Further, different trends are identified to gain insight into the frictional behaviour of this ice-polymer system.

To unpack the results, we first present and discuss the different frictional behaviour over time for the different systems. Then we compare parameters for the different systems, aiming to reveal the atomistic details behind nano-scale ice friction. We then take a thorough look at the friction forces and examine how the structures evolve, and how that corresponds to the friction force measured.





**Figure 16:** Overview of the four different types of friction force profiles, across a full 50 ns friction test. The friction force shown in Figure 16a has the parameters  $\epsilon = 1\epsilon_0, v = 1 \text{ m s}^{-1}$ , and  $P_N = 20 \text{ kPa}$ . The friction force shown in Figure 16b has the parameters  $\epsilon = 1\epsilon_0, v = 10 \text{ m s}^{-1}$ , and  $P_N = 200 \text{ kPa}$ . The friction force shown in Figure 16c has the parameters  $\epsilon = 2\epsilon_0, v = 0.1 \text{ m s}^{-1}$ , and  $P_N = 40 \text{ kPa}$ . The last friction force profile in Figure 16d has the parameters  $\epsilon = 0.1\epsilon_0, v = 1 \text{ m s}^{-1}$ , and  $P_N = 200 \text{ kPa}$ .

The equilibrated systems include 3 polymer structures and at the same time 4 energy depths, which give rise to statistical variation for characterising different nanoscale ice friction behaviours. The equilibration process yielded small individual differences between the systems. The largest differences were found in the systems are the QLL thickness, highlighted in Table 3. The force profiles from the friction tests highlight that there are larger differences when the systems are set in motion, resulting from the difference of the QLL in the systems. As an overall result, there are found 4 different friction force profiles monitored during the friction tests in different systems. An overview comparing the four different force profiles is shown in Figure 16.

These distinct 4 types of force profiles will be introduced one by one, where patterns and behaviours resulting from the different testing parameters as well as differences between the systems will be discussed. Some initial remarks can be clearly found in the terms of maximal force measured in the different types, with Type I friction showing extraordinarily low friction force in comparison with the other friction types.



**Figure 17:** A closer look at the Type I friction test profile. Figure 17a shows the overview of the whole force profile, where the two parts, the *buildup* and the *steady state*, are distinguished. In Figure 17b the first 10 ns of the friction test are shown, while in Figure 17c we look more closely at the steady state phase and examine the friction test profile from 20 to 25 ns.

### 3.2.1.1 Type I

The Type I friction force profile is found in weak friction, with the low friction force exhibiting a distinct build-up period before entering a more steady state. This type of force profile is found for all the polymers, with attraction potentials  $\epsilon = 0.1\epsilon_0, 1.0\epsilon_0$ , for the parameters Pn = 2 kPa, 20 kPa and 40 kPa,  $v = 0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ . In Figure 17 the different periods are highlighted and shown more in-depth. The build-up



phase is of a few nanoseconds length in time, characterised by the force peaks gradually building up to steady maxima as seen in the rest of the force profiles.

**Figure 18:** Snapshots of the atomistic structure through a friction test with a Type I force profile. The snapshots are taken at 0 ns, 3 ns, 9 ns, 25.0 ns and 50.0 ns of the friction test shown in Figure 17.

Further, the profiles build up to a *steady-state* where we can see how the profile looks quite chaotic in the overview. A closer view of the chaotic behaviour found in the Type I friction force profile reveals a zig-zag pattern with recurring force peaks and drops, as depicted in Figure 17c. Through the steady state phase of friction, in the second half of the profile, the peak force fluctuates in the range of 0.4 to 0.8 nN. This peak-drop characteristic is mainly attributed to the stretching and relaxing of the polymer at the friction interface throughout the friction tests.

The ice structure adjacent to the friction interface also change during the simulation. Figures 18a to 18c show snapshots of the atomistic structure through the build-up phase of Type I. The figures show how a denser layer builds up beneath the friction interface through the first 9 ns, while in Figures 18d and 18e we see that the layer is about the same size as after 9 ns in both 25 ns and 50 ns. This finding show a correspondence between, the build-up of a denser layer of the water molecules towards the friction interface, and the build-up phase of the friction force profile. Accordingly, the amount of amorphous water molecules increase during the friction test simulations, as shown in Figure 19.

The number of amorphous water molecules stabilises at 14 to 16 % around 5 ns into the friction test, with a slight tendency to a small increase over time. Around 5 to 6 ns into the build-up phase, obvious high friction force peaks are observed, which are coinciding with the time that the number of non-crystalline water molecules stabilises. Together with the findings from the snapshots shown in Figure 18, this structural build-up of amorphous



**Figure 19:** Overview of the development of non-ih-water molecules over time. The profile is the output from the CHILL+ algorithm [49] characterising the non-ih-water molecules from the same friction test as shown in Figure 17.

water, which stabilises after about 9 ns, shows that the friction interface needs time to respond and find a new equilibrium after the system is set in motion.

#### Steady-state: Peak-drop formations

Looking further into the steady-state phase of the friction force profile, we observe also an oscillating pattern marked by repeated peak-drop cycles, shown in Figure 17c. This pattern also resembles a zig-zag formation of high friction force peaks during the friction test. The pattern could be resulting from topology of the friction interface, where close contact of ice and polymer constantly heal and break under friction force throughout the friction simulations.

It is noteworthy that the alternating steep and sudden drop in slopes before the peaks of the observed friction force profiles. For instance, at 23 to 25 ns in Figure 17c we see two cycles with really steep drops, then after some data points a instant rebound to about  $\frac{1}{2}$  to  $\frac{2}{3}$  of the previous peak force is found. These phenomena necessitate further investigations into the substrate interface.

Figure 20 provides system snapshots during the friction test, with corresponding output friction force depicted in Figure 17. Figure 20a demonstrates how the polymer chains bend at a time evolution of 23.7 ns toward the left side of the simulation box, against the direction of movement. In contrast, Figure 20b shows the polymer chains bending to the right side of the simulation box, while in Figure 20c, the polymer chains bend almost straight downward. This bending behaviour is further illustrated by the straight red lines in the z-direction in the close-ups shown in Figure 17, where it is evident that at 24.1 ns, the molecules closest to the interface have moved to just beneath the fixed top of the



**Figure 20:** The figures show snapshots of the interface between the ice and polymer around the most prominent peak of the friction measurement shown in Figure 17. Figure 20a shows before the peak, Figure 20b closest to the top of the peak, and Figure 20c at the drop. A further close-up of the above is shown in Figure 20d, with red vertical lines to use as reference points for the spatial evolution of the polymer strains.

adjacent polymer chain. Observing Figure 17c, it is apparent that 23.7 ns occurs before the most prominent peak, while 24.1 ns is close to the peak, and 24.2 ns occurs just after. As such, it can be seen that the ends of polymer chain attaching and moving with the ice, results in increasing friction force. As the friction force elevated to a certain high value, the polymer chain ends are detached from the ice, which lead to a fast drop in the monitored friction force. These cycles continue until the end of the friction test.

The peak-drop cycles in the friction force profile and the details in the adhesion and detachment of the polymer chain ends are thus in line with the known stick-slip ice friction behaviour [50, 51]. Moreover, the fact that the polymers bend *against* the direction of



Figure 21: Output of the friction calculations based on the position of the atoms. The calculations are based on the output from the same friction test as shown in Figure 17, for the output from 22.5 to 25.0 ns with similar display in Figure 17c. In this output, one can see how the calculations from the trajectory files also deviate due to many fewer data points than the output from the log files.

movement at the smaller friction force peak, and with the direction of movement at the highest force peak, together *with* the sharp drop from the tallest peaks, suggests that the smaller peaks result from the polymer chains slipping and drops.

Because the friction force is calculated based on the absolute extension of the applied harmonic pulling spring during the simulation disregard of the actual force direction, the obtained friction force is thus always positive. In our simulations, there are several thousands of  $CH_2$  groups, each contributing to the total friction force based on each groups' Center Of Masss (COMs) deviation from its initial position. Each group contributes a force which goes squared to the absolute deviation, and therefore the contributions around the initial positions are really small. Since the calculations are the total sum of each  $CH_2$  group contributions, the friction force will largely be dependent on the global deviations. The flatten area after the peaks are thus the area where the global spatial tendency of the  $CH_2$ -groups are about the initial position when locally there are deviations.

For calculations of the stress-tensors and spatial monitoring of the systems, the output trajectories (dump files) with snapshots were made at every 100 ps interval. The trajectory files do hence contain the spatial positions of the  $CH_2$  pseudoatoms, and can also be used to try to confirm the stick-slip motion. By using the simulation trajectories, the resolution of the force profile is  $\frac{1}{100}$  of that given in the log files, this difference is highlighted in Figure 21 seen by the few data points from the simulation trajectory files calculations.

The friction force calculations from the trajectories do provide different perspectives on the nanoscale stick-slip ice friction phenomenon, as the deviation used in these calculations takes the direction into account. Figure 21 shows the outcome of such a computation,

where the output calculations are shown with red markers connected by dashes and the blue output is from the friction force calculations. The calculations from the dump files show that there are stick-slip motions with possible sub-nanoscale stick- and slips similar to the ones found by Lee *et al.* [52]. Having a part with *negative* friction force necessitates a discussion on what friction is, and how one can calculate the force hindering the movement of the two structures in this experiment. This further illustrate the complexity of nanoscale friction phenomena at the friction interface, which are ignored in the traditional understanding of friction at macroscale.

Finally, the concept of friction force in this context, typically meaning opposing movement, may need to be redefined. Instead of the conventional definition, one may in this case better represent friction by the height difference between the two closest peaks, representing force induced against movement over time, hence contributing to friction.



## 3.2.1.2 Type II

**Figure 22:** Overview of the Type II friction test force profile spanning 50 ns. The force profile is divided into four main parts: two buildup periods (labelled as 'Build-up i' and 'Build-up ii'), where the force gradually increases, and two steady state periods (labelled as 'Steady-state i' and 'Steady-state ii'), where the force maintains a stable pattern of oscillations. This figure provides a comprehensive overview of the force dynamics over time.

In contrast to the Type I force profile, Type II resembles more of a classical force profile with a concrete build-up phase (static phase) and a steady-state phase (dynamical phase). Upon further investigating the Type II phase in Figure 22, we can divide it into two sections of build-up (Figures 23a and 23c) and two sections of steady-state (Figures 23b and 23d).

The friction force profile shown is from the friction test of polymer  $1, \epsilon = 1\epsilon_0, P = 200 \text{ kPa}$ 



Figure 23: Closer look into the Type II friction test profile. In Figures 23a and 23c the build-up periods of the friction tests are shown, while in Figures 23b and 23d we look closer at the steady-state phases.

and  $v = 10 \text{ m s}^{-1}$ . The force profile consists of two distinct peaks with values of 20 nN and 30 nN in the first build-up phase, while having a force level at 20 nN and 30 nN at the two steady-state phases. In the previous Type I profile, we observed the distinct *peak-drop* force measurements. However, the Type 2 force profile, does not display any similar zig-zag or peak-drop measurements. The peak-drop behaviour was found to be a product of the polymer sticking and slipping at the quasi-liquid interface. Not having found this behaviour for Type II indicates different dynamic behaviour at the interface comparing to the Type I friction.

When looking further into the first build-up phase (Figure 23a), we actually found resemblance of a static and a dynamic phase already in the first 2 ns with a peak force at 20 nN after just 0.5 ns, followed by a sudden drop to 10 nN before continuing to rise. This first rise is about linear in comparison to the two other parts with increasing friction force: 2 to 5 ns and 12 to 20 ns. Therefore, Type II describes friction force test profiles without any peak-drop patterns. Instead, it shows steady build-ups and dynamic friction areas, similar to traditional friction measurements.

If we look at the corresponding snapshots from the friction test shown in Figure 24 at 0.5 ns, 3 ns, 12 ns, 20 ns and 50 ns, we can further find how the water interacts with the bottom of the polymer surface. Despite the water molecules being densely packed at the



Figure 24: Snapshots of the atomistic structure through a friction test having a Type II force profile. The snapshots are taken at 0.5 ns, 3 ns, 12 ns, 20 ns and 50 ns of the friction test shown in Figure 23.

interface, they do not penetrate into the space between the polymer chains. The surface retains the water molecules, even under this large load and the high stress caused by the fast moving water molecules. Beneath the friction interface, we can observe how the crystalline structure crumbles and is not visible in the second steady-state period. The ice structure has transformed into a structure of denser amorphous water molecules. Thus, the different sections of the friction force profile are resulted by the evolving structures at the friction interface.



Figure 25: Overview of the development of non-ih-water molecules over time. The profile is the output from the CHILL+ algorithm [49], characterising the non-ih-water molecules from the same friction test as shown in Figure 23.

In contrast to Type I, the snapshots also show that the polymers are forced to tightly packed together. It is not possible to visually distinguish the different polymer chains from each other in the Type II snapshots (Figure 24), unlike the snapshots of Type I (Figure 20). Further, the rapid increase in number of non-crystalline oriented water molecules is shown in Figure 25. The final transformations of all crystalline water molecules occurs around 15 ns into the friction simulations, which coincides with the point where the second build-up phase of the friction profile starts to flatten (Figure 23c. This suggests that from 15 ns, there are no further structural changes at the friction interface.

Overall, the Type II force profile differs in friction interface phenomena compared to Type I, with features more closely to traditional macroscopic frictional models, consisting of explicit build-up and steady-state stages. In difference to the *peak-drop* pattern observed in the steady-state phases of Type I – a pattern resulted from the interfacial layer causing a cyclic stick-slip behaviour – Type II indicates an alternative interfacial dynamics interactions. This difference in behaviour can be attributed to the varying molecular structures at the friction interface. The progression of the friction force profile mirrors the evolution of the ice structure beneath the interface, as the water molecules infiltrate the small gaps of the polymer surface, triggered by the changes in the state of the ice structure. Visual data further reinforce these observations, revealing how the polymers compress and the ice structure transforms from a crystalline to a denser, amorphous form under high load and stress conditions.



Figure 26: Overview of the Type III friction test force profile spanning 50 ns. The figure is divided into different blocks, each displaying a build-up to a peak. This figure provides a comprehensive overview of the force dynamics over time.

## 3.2.1.3 Type III

Type III friction force profiles are found by the reoccurring build-up-drop cycles, and can be found with a stable, increasing baseline friction force. To illustrate these cycles more closely than in Figure 16c, Figure 26 provides a closer look.



Figure 27: A close look at the second build-up-drop cycle of the Type II friction profile, with associated snapshots of the friction interface in a 0.5 nm-thick slice in the middle of the system, highlighting the movement of polymer strains and trajectory between the extrema for these snapshots.

Here the different cycles are highlighted in different colours, showing six cycles for Type III friction. It is interesting to observe that the larger attraction potential leads to these larger

static build-ups before the polymers slip. For the previous Type II profile, the build-up parts were clearly correlating with the structural evolution from the friction interface and in negative z-direction through the water molecules. Comparing to other structural changes in Type I and Type II, each block cycle of this friction force profile resembles an adhesion tests, with a large increasing force profile before a substantial sudden drop.

Having a closer look at the second peak-drop cycle, Figure 27 highlights the movement of polymer chains, of a typical friction force cycle. In the figure, we highlight the displacement of the polymer beads. The orange line show each molecule's trajectories from 12.3 ns to 18.2 ns. 12.3 ns being the time of the last minimum before the friction force increases, and 18.2 ns corresponding to the maximum friction force of this cycle. In the finishing of the friction cycle after 19 ns, the polymer chains have moved all the way back to the initial positions. Thereby, highlighting the stick-slip movement of a Type III friction force cycle.



Figure 28: Snapshots of the atomistic structure throughout a friction test having a Type III force profile. The snapshots are taken at 4.5 ns, 9.0 ns, 13.5 ns, 25.0 ns, 31.2 ns and 38.2 ns of the friction test shown in Figure 26.

The build-up of friction force is found to be almost linear, which is proportional to the small velocity of  $0.1 \,\mathrm{m \, s^{-1}}$  induced relative between the two substrates. It is thus found that these peak build-ups indeed follow stick-slip motions, same as shown for the Type I force profiles. While having peak-drop patterns, the polymer terminals indeed displaced to a new position at the end of each force cycle, which significant differed from the behaviour in Type I. The displaced polymer chain terminals is a clear sign that the polymer chains were extended during the friction, showing a strong interaction between the water and the polymer in this Type of friction.

Figure 28 shows the evolution of the structures during the friction test. The ice structure keeps its shape throughout the test, while the water seems to penetrate the polymer



**Figure 29:** The bottom figures depict the number of water molecules that penetrate the polymer, with the friction force profile also plotted against the right y-axis in Figure 29c. The two snapshots represent the initial characterisation of penetrated water molecules after 0.1 ns on the left and the subsequent measurement at 47.6 ns towards the right. The water is considered to have penetrated if the molecules have a spatial position with  $\vec{z}$ -component larger than 0.6 nm.

structure, which is especially visible in Figure 28f. Further, there is visible that some polymer chains are pushed outside the polymer structure. This clearly illustrate an extremely high internal stress was accumulated in the polymer structure in this type of friction.

Looking closer into the structures at the interface, we find in fact that there is water penetrating the polymer substrate. In Figure 29a we see two snapshots of the interface from a new angle underneath the polymer at simulation time of 0.1 ns and 47.6 ns. The water molecules seem to follow into the polymer structure, where empty space was created from the polymer chains displaced to the top of the structure.

To quantify the impact of the water molecules penetrating into the polymer structure, calculated the number of water molecules in the polymer structure, above the contact interface between water and polymer. The contact interface of water and polymer was



**Figure 30:** Development of polymer strains pushing out of the polymer structure throughout the friction test. The black strains are polymer strains that remain inside the regular bounds for the polymer, while the orange are the polymer strains which are eventually pushed out of the polymer. The snapshots are taken at 0 ns, 12.6 ns, 16.6 ns, 20.3 ns, 33.0 ns and 47.9 ns.

defined for a spatial  $\vec{z}$ -value, where both polymer and water molecules are present, at 0.6 nm. We found that there is a steady increase during the friction test in the number of water molecules above the defined contact interface, as shown in Figure 29b. The number of water molecules found ranged from around 100 in the start to about 800 towards the end. Additionally, a correlation between increasing friction force and the number of water molecules penetrating the water-polymer interface was found. When plotted together, the trends in both calculations follow each other, as illustrated in Figure 29c. This indicates a correspondence between the number of water molecules inside the polymeric structure and the steady increase of the friction force cycles, found only in the Type III friction force profiles.

Further investigating the polymer structure from the snapshots of Figure 28, we find that

there are some polymer chains pushing out of the structure over time. In Figure 30 the chains which moves largely from their initial position, in comparisons to the rest of the polymer structure, are highlighted in orange. The snapshots of Figures 30a to 30f show the polymer structure at each point during the friction-test where a new polymer chain is pushed out of the polymer structure. When comparing to the friction test profile in Figure 26, we find that increasing trend in the low bound of the friction force correlates with the increasing amount of polymer chains pushed out of the structure. This leads to a probability that the actual friction force for the Type III profiles, should be taken as the friction force observed on surfaces experiencing wear and tear during friction.



**Figure 31:** A closer look at the Type IV friction test profile. Figure 31a displays the whole force profile, where the two parts, the *critical* and *non-critical*, are distinguished. Figure 31b shows the first 12 ns of the friction test, while Figure 31c displays the steady-state phase and the friction test profile from 25 to 30 ns in the non-critical domain.

### 3.2.1.4 Type IV

Type IV is found in all superhydrophobic systems ( $\epsilon = 0.1\epsilon_0$ ) for the largest loads of  $P_N =$ 

200 kPa. Figure 31 provides a closer look. The force profiles for these superhydrophobic systems are characterised by a critical and a non-critical phase, revealing important insights about friction interface phenomena at the nanoscale level. In the critical phase, evident from Figure 31b, a dramatic increase in friction force, accompanied by large force oscillations, precedes a gradual drop to virtually zero force. This phase is triggered by the forceful penetration of water molecules through the polymer, disrupting its structure.



**Figure 32:** Snapshots at 0.1 ns, 0.2 ns, 0.3 ns, 4.0 ns and 29.0 ns of the system with corresponding Type IV force profiles, shown in Figure 31. Figures 32a to 32d show snapshots from the critical phase, while Figure 32e shows a snapshot from the non-critical phase.

The Type IV friction is significantly different from all other friction types observed in this work. Specifically, the build-up of the critical pattern in the Type IV force profile is observed in Type II friction with maximum normal load. On the other hand, for Type IV friction, the polymer structure does not withstand, nor retain, the water molecules due to its superhydrophobicity. In contrast, the tests with Type III profiles did experience some penetration of water molecules, but the water molecules were retained at the bottom of the polymer structure. Having the water molecules escape the polymer leads to the non-critical phase, as displayed in Figure 31. The absence of the zig-zag formation, which is typical of the steady-state phase for Type I, is attributed to the weak interactions between the water and the polymer.

It is important to note here that the water molecules then become trapped between the upper polymer layer and the ice base due to the PBC of our test setup. Designed to simulate a macro-scale polymer interacting with snow, this setup includes a vacuum space outside of the ice block and upper polymer layer to further ensure no interactions between the top polymer and bottom ice. As the molecules that venture beyond these boundaries contradict our modelling procedure, we will exclude the corresponding force measurements of these simulations of the research.

Figure 32 shows snapshots of the spatial output where the water penetrates the whole polymer structure. This indeed demonstrates that a pronounced hydrophobic system does not inevitably translate to lower friction. Instead, it is evidenced that a highly hydrophobic surface can provoke substantial friction forces. As the water molecules infiltrate the polymer under pressure, the polymer structure is unable to disperse the pressure effectively, leading to an internal build-up. Simultaneously, the interlocked water molecules form a connection



Figure 33: Depicts the amount of water molecules that have penetrated the polymer. A water molecule is deemed to have penetrated if its spatial position has a  $\vec{z}$ -component exceeding 0.8 nm. The percentage of penetrated water is plotted on a log10 scale to highlight the variations between the critical and non-critical phases.

between the polymer and the ice surface. This tight interconnection further exacerbates the frictional forces due to the resistance provided by the entrapped water molecules within the polymer structure. Thus, what could be misconceived as a protection against friction – a hydrophobic response – might, under certain conditions, contribute to greater frictional forces as shown in Figure 31b. This challenges the conventional understanding of friction reduction at the nano-level, underscoring the complexity of friction interface phenomena and the influence of material properties and interactions.

The permeating water molecules in the polymer is the cause of high friction force in this type of friction. As quantified by the percentage of the total water molecules in the polymer, it is a nearly instant increase to 50% of the water molecules already penetrating the polymer at the early state of the friction, as shown in Figure 33. The percentage of water in the polymer then decreased, and fell to 0.5 to 1.0% in the first 10 ns of the simulation. At the end of the simulation, only 0.05% of the water molecules are left in the

polymer, corresponding to the non-critical part of the friction force.

#### 3.2.2 System comparisons: polymer structures

In Section 3.1, we found that the three different polymers gave different equilibration data on the thermodynamic properties of the systems. They were also different in QLL-thickness (Table 3). In Section 3.2.1, large differences in force profiles were found, leading from different attraction potentials,  $\epsilon$ , and simulation parameters, v and  $P_N$ , resulting in 4 characteristic types. It is important to consider whether these attributes are inherent to only one polymer structure, or if they are present for all three. Large deviation between the different polymers would mean that the attributes are largely influenced by the chain orientation and topology of the polymer structure, which will further suggest that the spatial arrangements are more important than the parameters  $\epsilon$ , Pn and v, for the resulting friction force.

This section takes a further look into the concerning properties of the different polymer structures employed. The comparisons are structured to have a look at how the 3 polymers influence the friction force simulations, in respond to different degrees of phobicity. First, we will analyse the *hydrophobic* system ( $\epsilon = \epsilon_0$ ). Then, the *superhydrophobic* ( $\epsilon = 0.1\epsilon_0$ ) and *hydrophilic* ( $\epsilon = 2\epsilon_0$ ) cases will be discussed. These cases are chosen since the two extremes show the largest differences between the polymers in the equilibration process, in terms of non-I<sub>h</sub> water content (Figure 13) and QLL-thickness (Table 3), while the *hydrophobic*, in contrast, showed few differences.

#### 3.2.2.1 Hydrophobic systems

Figure 34 compares the three different polymers and their friction measurements. Through Figures 34a to 34c we see how the different polymers lead to different friction measurements while having similar patterns. The results show indeed different friction behaviours for the three polymer structures, but the build-up phase is clearly present in all three cases before reaching the stable peak-drop friction state.

$0$ to $20 \mathrm{ns}$		10 to $15$ ns	0 to $1$ ns		
	Maximum, mean $[nN]$	Maximum, mean $[nN]$	Maximum, mean $[nN]$		
Polymer 1	0.767 , $0.145$	0.690 , $0.165$	0.184, $0.090$		
Polymer 2	0.774 , $0.172$	0.757 , $0.104$	0.311 , $0.119$		
Polymer 3	0.785 , $0.181$	0.757 , $0.216$	0.272 , $0.119$		

**Table 4:** An overview of the different maxima and means for the different polymer friction measurement shown in Figure 34.

In Table 4 the maxima and means for the different polymer friction measurements are displayed for the ranges shown in Figure 34. Across the friction tests, there are small differences in maxima and means of the friction force measured from the ice on the polymer for different polymers at  $P_N = 20 \text{ kPa}$ ,  $v = 1 \text{ m s}^{-1}$ , and  $\epsilon = \epsilon_0$ .



Figure 34: The figure shows friction tests of different polymers with parameters  $P_N = 20 \text{ kPa}, v = 1 \text{ m s}^{-1}$ , and  $\epsilon = \epsilon_0$ . Figure 34a show an overview of the first 20 ns, while Figure 34b focuses on the initial period, and Figure 34c provides a closer view of the dynamic regime.

The consistent peak-drop pattern is observed across all polymer types in the steady-state phase, as seen in Figure 34c. Moreover, the build-up period remains approximately constant at around 8 ns for all polymers and there are small differences in peak and mean force between the polymers. However, one can observe differences in phase and variations in value of the friction force across the three systems. Given these small discrepancies in peak and mean force values and their apparent non-equality, one can conclude that the polymers behave differently under the conditions  $\epsilon = 1.0\epsilon_0$ ,  $v = 1 \text{ m s}^{-1}$ , and  $P_N = 20 \text{ kPa}$ .

Despite the unique topology and chain orientation of each polymer, it is interesting to observe that these properties do not seem to significantly influence the resulting friction force. This suggests that other factors might be in play, or that the influence of topology and chain orientation might become prominent under different conditions.



Figure 35: Development of the *QLL*-thickness for the three different polymers with  $\epsilon = 1.0\epsilon_0$ ,  $v = 1 \,\mathrm{m \, s^{-1}}$ , and  $P_N = 20 \,\mathrm{kPa}$ .

While there were small differences in QLL-thickness after the equilibration process finished, the development of the QLL-thickness for the different polymers throughout the friction tests show larger differences. This can be seen in Figure 35. The QLL stabilises with the largest thickness being for Polymer 3, then Polymer 2, while Polymer 1 stabilises at the smallest thickness. These findings show that  $d_{QLL}$  is connected to the spatial orientations of the polymer structures, thus being a result of the topology at the friction interface.

### 3.2.2.2 Superhydrophobic systems

After the equilibration state, we observed the largest differences for properties like QLLthickness between the different polymers for the *superhydrophobic* and *hydrophilic* cases. When comparing the three different polymers for the systems of the superhydrophobic case, we see that there are large differences in the friction force profiles. When keeping the parameters v and  $P_N$  to be  $1 \text{ m s}^{-1}$  and 20 kPa respectively, we find that the measured force is larger in Polymer 1 than the two other. In Figure 34 we see that Polymer 1 has high force peaks, a more distinct peak-drop pattern, and peaks approaching 0.3 nN. On the other hand, for the systems with Polymers 2 and 3, the friction force peaks are more difficult to identify, and the maxima are just up to around 0.2 nN.

In this case of the superhydrophobic interaction potentials, there are clear differences between the polymers. After the equilibration process it was found, as shown in Table 3, that Polymer 1 had the smallest QLL thickness followed by Polymer 2, then Polymer 3 for the superhydrophobic case. When comparing the three superhydrophobic systems in



Figure 36: The figure shows a friction test of different polymers with parameters  $P_N = 20$  kPa, v =

 $1 \text{ m s}^{-1}$ , and  $\epsilon = 0.1\epsilon_0$ . Figure 36a provides an overview of the first 20 ns, while Figure 36b provides a closer look at the start and Figure 36c provides a closer look of the dynamic regime.

Table 5:	An	overview	of the	he different	maxima	and	means	for	the	different	polymer	friction
measurem	ent s	hown in F	`igur€	e 36.								

	0 to 20 ns Maximum, mean [nN]	10 to 15 ns Maximum, mean [nN]	0 to 1 ns Maximum, mean [nN]
Polymer 1	0.298, $0.106$	0.284 , $0.104$	0.247 , $0.100$
Polymer 2	0.232 , $0.104$	0.212 , $0.103$	0.209, $0.102$
Polymer 3	0.211 , $0.093$	0.182 , $0.093$	0.185 , $0.093$

this case, we find that Polymer 1 have the largest friction force measurements, which is shown in Table 5, both in regard to the maximum and the mean values. The result is in line with the macroscale theories where more dry friction leads to a large friction forces, while having a lubricating layer between the two solid media, reduces friction drastically.

Polymer 3

6.205, 6.073



Figure 37: The figure compares the friction tests of different polymers with parameters  $P_N = 20 \text{ kPa}, v = 0.1 \text{ m s}^{-1}$ , and  $\epsilon = 2.0\epsilon_0$ .

**3.2.2.3 Hydrophilic systems** For the hydrophilic cases when comparing the friction force, we find the same pattern of peak-drop cycles for all the polymers. Figure 37 display obviously that the system having Polymer 1 clearly have a larger friction force, when all systems having  $\epsilon = 2\epsilon_0$ ,  $P_N = 20$  kPa and  $v = 0.1 \text{ m s}^{-1}$ . This clearly indicate differences between the systems as a product of the polymers.

	yoloo bilowii ili i igale or,	0 00 10 110, 10 00 20 110, ame	20 00 20 115.
	0 to $10$ ns	10 to $20$ ns	20 to $25$ ns
	Maximum, Drop Size	Maximum, Drop Size	Maximum, Drop Size
	[nN]	[nN]	[nN]
Polymer 1	7.576, $6.667$	9.452 , $7.260$	7.971, $4.879$
Polymer 2	2.205, $2.134$	3.326 , $3.254$	4.702 , $4.631$

5.366, 5.161

4.236, 3.825

**Table 6:** Comparison of maximum peak forces and drop sizes, for the different polymers for the three first peak-cycles shown in Figure 37, 0 to 10 ns, 10 to 20 ns, and 20 to 25 ns.

The system having Polymer 1 had polymer chains pushing out of the polymer structure, which was found to increase the baseline of the calculated friction force, described in the section of friction force profile Type III. Because of this finding for Polymer 1, the comparisons of mean friction force discussed above on the Hydrophobic systems and the Superhydrophobic systems cases could be applied here. In Table 6 there is, as well, a comparison of the drop from the peaks to the following minima in addition to the maximum friction forces. We find in the same manner that we see from Figure 37 that Polymer 1 overall experience the largest friction forces both in terms of peak maxima and in drop size.

In our hydrophilic systems, Polymer 3 showed the thickest QLL after equilibration, as seen in Table 3. When we compared it with other polymer structures, the system having

Polymer 3 did not have significantly different friction force calculations in the friction tests. This suggests the QLL thickness, as a result of the equilibration process, did not play a significant role when comparing these the results of the friction tests for these systems with different polymer structures.

## 3.2.3 Load-parameter analysis

The different friction behaviours observed in the systems are originated from the system key parameters in the modelling, and simulation procedure. This section seeks to quantify the differences due to the loading parameters and their influences on the friction. The section looks into the influence of the different load parameters in terms of output friction on the nanoscale level. It also analyses the hydrophobic, superhydrophobic, and hydrophilic cases in turn.

## 3.2.3.1 Hydrophobic

By analysing the effects of varying loads on friction force within hydrophobic systems, it is evident that an increase in load corresponds to an increased friction force. The friction force profiles shown in Figure 38 highlights this trend, most notably the increase when going from 40 to 200 kPa. Holding constant values for  $v = 1 \text{ m s}^{-1}$  and  $\epsilon = 1.0\epsilon_0$ , it is observed that distinct frictional differences corresponding to the load varying. For the smaller loads, 2.0 kPa, 20 kPa and 40 kPa, we find an increase in maximum peak force as well as in peak width, as one can see in Figures 38b and 38c.

Further, it is notable that for the maximum load,  $P_N = 200$  kPa, the frictional force remains distinctly elevated compared to the profiles of the other loads, having minima around 2 nN. In contrast, the frictional forces at the lower loads approach nearly 0 nN. The divergence in profiles suggests varied dynamic interactions occurring at the interface. While the lower loads primarily display Type I friction force profiles, the highest load leads to friction force profiles similar to the steady state phase of the Type II force profile. From the snapshots shown in Figure 24, we do see an increased amount of amorphous water, which suggest similarly in this case a pressure induced melting at the interface. A pressure melting would lead to a larger number of water molecules at the interface interacting as a liquid, which seem to change the friction dynamics at the interface.

While the friction profiles at lower loads exhibit a peak-drop behaviour as depicted in Figure 21, the system subjected to a load of  $P_N = 200$  kPa displays a distinct behaviour: its frictional force minima never approach zero. This observation suggests that throughout the test, the global positions of the CH<sub>2</sub>-groups in this system did not shift to a  $\vec{x}$  value smaller than their initial positions, namely retraction of the polymer chains along the friction direction, in contrast to what was found for smaller loads in Figure 21.



Figure 38: Comparisons of friction tests with varying normal load  $P_N = 2.0$  kPa, 20.0 kPa, 40 kPa and 200 kPa,  $v = 1 \text{ m s}^{-1}$  and  $\epsilon = 1.0\epsilon_0$ 

Figure 39 display the corresponding mean and maxima plot for the ranges 0 to 1 ns, 0 to 10 ns, 20 to 30 ns, and 0 to 50 ns. It is evident that a larger load leads to a larger friction force. From Figure 39b the increase from  $P_N = 40$  kPa to  $P_N = 200$  kPa seems to result in an order of magnitude larger mean value, while in Figure 39a the increase looks linear as the increase of an order of magnitude maxima is found from  $P_N = 20$  kPa to  $P_N = 200$  kPa. Still finding these connections, there are evidently smaller changes between the first order of magnitude increase in  $P_N$  from  $P_N = 2$  kPa to  $P_N = 20$  kPa. This suggests that the increase in friction force is more complex than simply linear or quadratic, dependent of the load for the hydrophobic systems.

#### 3.2.3.2 Superhydrophobic

When further looking into the superhydrophobic case, the standout friction test is for the largest load,  $P_N = 200 \text{ kPa}$ , which have the Type IV profile. In Figure 40 we see how this



**Figure 39:** Displays the influence of varied loading parameters on the maxima and means of the friction force, at a constant velocity  $v = 1 \text{ m s}^{-1}$  and with  $\epsilon = \epsilon_0$ . The maxima and means are represented on a log10 y-axis. For the mean values within the 0 to 1 ns range, both  $P_N$  at 2 kPa and 20 kPa exhibit similar magnitudes and thus overlap. Intervals 0 to 1 ns, 0 to 10 ns, 20 to 30 ns, and 0 to 50 ns are delineated.



**Figure 40:** Comparison of friction tests with varying normal load  $P_N = 2.0$  kPa, 20.0 kPa, 40 kPa and 200 kPa,  $v = 1 \text{ m s}^{-1}$  and  $\epsilon = 0.1\epsilon_0$ 

profile behaves in comparison to the smaller loads, measuring extreme large friction forces in the first 10 ns. Consequently, comparing the output means and maxima for the largest  $P_N$  with the others does not yield significant insight, as we know that this force profile is due to the breaking of the polymer structures.

Further we examinated the other systems, with different loads, in the superhydrophobic case with  $v = 1 \text{ m s}^{-1}$ . For both  $P_N = 20 \text{ kPa}$  and 40 kPa, we found the peak-drop formations, which is shown in Figure 41. In addition, we see that having a very low load,  $P_N = 2 \text{ kPa}$ , leads to nearly no measured friction force, which probably means that there are only weak interactions between the polymer structure and the water molecules in the



Figure 41: Comparisons of friction tests with varying normal load  $P_N = 2.0$  kPa, 20.0 kPa and 40 kPa,  $v = 1 \text{ m s}^{-1}$ , and  $\epsilon = 1.0\epsilon_0$ .

superhydrophobic case for minuscule loads.

Furthermore, there is a consistent trend observed between the measured maxima and mean friction forces. Just as in the hydrophobic systems ( $\epsilon = \epsilon_0$ ), an increase in load directly corresponds to a more pronounced frictional force throughout the testing phase. When comparing the maxima and means, this is clearly shown in the Figure 42. In this case of the superhydrophobic systems, we find that increasing the load from 20 to 40 kPa results in a linear friction force response. This linear response is not found when increasing the load from 2 to 20 kPa, highlighting the complexity of friction at nanoscale.



Figure 42: Displays the impact that different loading parameters have on maxima and means for constant velocity  $v = 1 \text{ m s}^{-1}$  and  $\epsilon = 0.1\epsilon_0$ . The means and maxima are represented on a log10 y-axis. The tests with a load of  $P_N = 200 \text{ kPa}$  are removed from this comparison. Intervals 0 to 1 ns, 0 to 10 ns, 20 to 30 ns, and 0 to 50 ns are delineated.

#### 3.2.3.3 Hydrophilic



Figure 43: Comparisons of friction tests with varying normal load  $P_N = 2.0 \text{ kPa}$ , 20.0 kPa, 40 kPa and 200 kPa,  $v = 0.1 \text{ m s}^{-1}$  and  $\epsilon = 2.0\epsilon_0$ .

In the hydrophilic case, the friction force profiles are a mix of Type II and Type III. We can, for example, see for  $P_N = 200$  kPa that the force build-up rises until about 30 ns while for the remaining systems with different loads, the force measurements follow the same slow build-up trend throughout the whole friction test. For the hydrophilic systems having v = 0.1 nN, we find that, except for the largest load, they all experience about the same friction force all through the long 50 ns simulation course shown in Figure 43. In contrast to the hydrophobic and the superhydrophobic cases, peaks are not in sync between the different loads. This suggests that in this case, the friction force is more dependent on a





Figure 44: Displays the impact that different loading parameters have on maxima and means for constant velocity  $v = 0.1 \text{ m s}^{-1}$  and  $\epsilon = 2\epsilon_0$ . The means and maxima are plotted on a log10 y-axis. Intervals 0 to 1 ns, 0 to 10 ns, 20 to 30 ns, and 0 to 50 ns are delineated.

By the comparison of the maxima and means at different parts of the friction test in Figure 44, the maxima and means are almost identical for the three smallest loads, while the system with the largest load starts out giving the smallest force before ending having the largest friction force. We have thus found that, in contrast to the hydrophobic and superhydrophobic cases, the friction force is independent of the load before a threshold range for change of the friction behaviour is met, between the two largest loads,  $P_N = 40$  kPa and  $P_N = 200$  kPa.

#### 3.2.4 Velocity parameter analysis

Like the previous comparisons with regard to different loads, the impact of the velocity parameter is also useful to study. Therefore, this part looks closer into the friction force with respect to the relative velocity between the water and polymer. In the case of the hydrophilic systems, we ran into a problem with the TraPPE-UA model of the polymer. For larger velocities than  $0.1 \text{ m s}^{-1}$  all systems with  $\epsilon = 2\epsilon_0$ , and a time step of 1 fs crashed. It was not possible to rerun the simulations with a short enough time step with the given computation power. Due to the time frame of the masters, it was deemed unreasonable to restart all simulations using another CG model for the polymer. Therefore, velocity comparisons for the hydrophilic systems will not be presented in this thesis.

We have found that the length of peak-drop cycles seems to be independent of load in the friction tests where peak-drop cycles are present. When comparing the three different velocities  $0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ , we found that for the hydrophobic cases, with loads smaller than  $P_N = 200 \text{ kPa}$ , there are peak-drop cycles for all velocities. When comparing the friction force profiles over the first 20 ns, as shown in Figure 45 for  $P_N = 40 \text{ kPa}$ , we see about 1 cycle for  $v = 0.1 \text{ m s}^{-1}$  while we can clearly distinguish about 28 cycles for  $v = 1 \text{ m s}^{-1}$ . For  $v = 8 \text{ m s}^{-1}$ , we cannot count the number of cycles. For this reason, it is


Figure 45: Comparisons of friction test with varying velocity  $v = 0.1 \,\mathrm{m \, s^{-1}}$ ,  $1 \,\mathrm{m \, s^{-1}}$  and  $8 \,\mathrm{m \, s^{-1}}$ ,  $P_N = 40 \,\mathrm{kPa}$ , and  $\epsilon = \epsilon_0$ .

complicated to fully compare these friction tests based on time elapsed.

We argue that the peak-drop cycles are due to the interactions of polymer chains sticking and slipping when the water molecules move across the ends of the polymer chains. At higher velocities, the relative movement between the two media is larger, and the water molecules will thus have moved across more polymer chain ends per unit of time. If each polymer chain sticks to a water molecule for the same relative displacement – when the stick-slip behaviour is prominent in the friction tests – one could compare the friction force profiles based over the ice displacement, instead of over time. Our friction tests were cut after a number of timesteps, yielding the total displacement of the ice structures to be 5 nm, 50 nm and 400 nm, when having the velocities 0.1 mpersecond, 1 mpersecondand 8 mpersecond. Having the first 5 nm to be present for all systems with these three velocities, this displacement range is therefore of the highest interest.

A comparison plot for the first 5 nm of displacement for the velocities  $0.1 \,\mathrm{m \, s^{-1}}$ ,  $1 \,\mathrm{m \, s^{-1}}$ and  $8 \,\mathrm{m \, s^{-1}}$  is shown in Figure 46. The comparison demonstrates distinct peaks in sync between the three different friction tests, further supporting the theory of peak-drop cycles



Figure 46: Comparison of friction tests for different velocities as a function of ice displacement with  $\epsilon = \epsilon_0$  and  $P_N = 40$  kPa. The velocities are  $0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$  and the force is shown for a displacement of the first 5 nm

to be a product of the spatial movement between the water molecules and the polymer. The comparison shows strongly correlated peaks and drops. It is worth noting that Type I force profiles have a build-up phase before going into the steady-state of peak-drop cycles. When having a closer look at Figures 45a and 45c, we see that for these friction tests, the build-up phase is finished in about the first 2 to 3 ns. For the case of  $v = 8 \text{ m s}^{-1}$ , we thus find that the corresponding displacement in regard to the build-up phase is about 16 to 24 nm, which is outside the comparison range of 5 nm. Therefore, comparing the influence of velocities in these friction tests involve some difficulties, the comparisons with respect to time do not align the peak-drop cycles, and the comparisons with respect to displacement do not capture the same phases of the friction tests.

For this reason, the comparisons will focus on the maximum and the trend peak lines for the different friction tests. This will give two measures for comparisons on the same terms as maxima and means for the load comparisons. In Figure 47, the trend peak lines are highlighted over the friction force profiles for the tests with  $v = 0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and 8 m s<sup>-1</sup>,  $P_N = 40 \text{ kPa}$ , and  $\epsilon = \epsilon_0$ . In Figures 47a to 47b, the characterised peaks are marked with crosses. The red bands represent the trend limits and cover the middle 50% of the friction force peaks, resulting in a measure to compare the different friction tests.

To compare the different velocities, the two plots are showing the outcome of the trend peak calculations and the global maxima. From the friction tests with its maxima and trend peaks shown in Figure 47, the outcome is plotted in Figure 48a. The median of the maxima are plotted with error bars. The error bars highlight the width of the trend peaks, with its lower and upper limits.



**Figure 47:** Comparison of friction tests with peaks trend-band highlighted in red. The friction tests all have  $P_N = 40 \text{ kPa}$  and  $\epsilon = \epsilon_0$ , with varying velocities of  $v = 0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ .



**Figure 48:** Comparison of peak trends and maxima of friction force measurements for different velocities, with  $P_n = 40$  kPa and  $\epsilon = \epsilon_0$ . In Figure 48a the peak trends are plotted as the median value with lower and upper band values of the peak trend lines.



Figure 49: Comparison of peak trends and maxima of friction force measurements for different velocities, with  $P_n = 20$  kPa and  $\epsilon = \epsilon_0$ . In Figure 49a the peak trends are plotted as the median value with lower and upper band values of the peak trend lines.



Figure 50: Comparison of peak trends and maxima of friction force measurements for different velocities, with  $P_n = 200$  kPa and  $\epsilon = \epsilon_0$ . In Figure 50a the peak trends are plotted as the median value with lower and upper band values of the peak trend lines.



**Figure 51:** Comparison of peak trends and maxima of friction force measurements for different velocities, with  $P_n = 2 \text{ kPa}$  and  $\epsilon = \epsilon_0$ . In Figure 51a the peak trends are plotted as the median value with lower and upper band values of the peak trend lines.

For the systems having a load of 40 kPa, we find that higher velocities lead to increased friction force, which is shown in Figure 48. Figure 48a visualises the comparisons of the trend peaks friction force, and maximum friction forces are plotted in Figure 48b. The trend

peaks' lower limits increase from about 0.3 nN, at the velocities of  $0.1 \text{ m s}^{-1}$  and  $1 \text{ m s}^{-1}$ , to around 0.8 nN for  $v = 8 \text{ m s}^{-1}$ , also detailed by the bands in Figures 47a to 47c. When comparing the median peak force values and the upper limits, we find a steady increase for each increase in velocity,  $0.1 \text{ to } 1 \text{ m s}^{-1}$ , and  $1 \text{ to } 8 \text{ m s}^{-1}$ . Similarly, the maximum friction force of the friction tests also grow with higher velocities, which the plot of Figure 48b illustrates.

For the smaller load, namely 2.0 kPa and 20 kPa, the trends differ. This is highlighted in Figures 49 and 51, where negligible variations in both trend peaks and maximum peaks can be seen. For the comparisons of the systems having a load of 2 kPa, there is no evident change in friction force as a result of increasing the velocity. While for the systems having a load of 20 kPa a slightly higher trend peak and maximum friction force is found for  $v = 1 \text{ m s}^{-1}$ . This minor increase is not deemed significant because there is a considerable overlap in the trend peak limits, and the maxima do not differ largely.

In contrast, for the systems with the largest load, 200 kPa, higher velocities lead to an increase in friction force. Figure 50 clearly displays this correlation. In Figure 50a, as the velocity increases from 1 to  $10 \,\mathrm{m\,s^{-1}}$ , the trend peaks shift from about 3 to  $30 \,\mathrm{nN}$ . Similarly, the velocity rises from 1 to  $10 \,\mathrm{m\,s^{-1}}$ , resulting in a force increase from 10 to  $33 \,\mathrm{nN}$  for the maximum friction force.

### 3.2.5 Crystalline analysis

This section focuses on the crystalline structure of water in the system, and the corresponding effects on the QLL and the behaviours of the polymer. For the Type I friction force profile, we found a change in the crystal structure of the ice in the build-up period, as illustrated in Figure 18, with a denser layer beneath the friction interface. For the Type II friction force profile, the ice structure collapsed, as shown in Figure 24. Finally, for the Type III force profile, the interface maintains its structure with an accumulated denser amorphous liquid layer throughout the friction test, as shown in Figure 28. For more in-depth analysis of the crystalline structures of the water molecules in the system, this section is divided into subsections analysing the different friction force profiles. Type I is the most common type, with distinct phases of the friction force calculated. It will be the first one to be closer examined. All the crystalline analysis was carried out using the Chill+ algorithm [49].

### 3.2.5.1 Type I

It is found that the build-up phases, as outlined in Figure 17, coincide with the nucleation of a denser cubic ice structure. Figure 52 show snapshots of the water molecules highlighting the different spatial orientations, where the non-crystalline ordered water molecules are blue, the cubic ice is orange, and the hexagonal ice is teal. Through Figures 52a to 52d the whole ice structure is shown, where the build-up of a zone of non-hexagonal ice can be seen.



**Figure 52:** Close-ups of the evolution of the ice structure captured by the Chill+ algorithm [49] for a friction test with  $P_N = 20$  kPa,  $v = 1 \text{ m s}^{-1}$  and  $\epsilon = \epsilon_0$ . The molecules ordered as hexagonal ice are coloured in teal, the molecules ordered as cubic ice are orange, and the non-crystalline water molecules are blue. Figures 52a to 52d display the whole ice structure over the first 20 ns, while Figures 52e to 52i display a cross-section of the ice structure at the cubic ice nucleation zone.

Figures 52e to 52i present a closer look into the zone of the non-hexagonal build. Having a part with denser non-crystalline water molecules, and starting from the simulation time of 5.0 ns, the non-hexagonal structure gradually grows into a cubic crystalline structure which finally stabilises ath the simulation time of 8.0 ns. The growth direction of the cubic ice is found to be in the positive x-direction, the same direction as the ice moves.

Upon closer examination of the different simulation trajectories of the Type I friction force profile, the interface layer of amorphous water molecules is found to increase with increasing pressure and at the larger velocities. The size of the monitored cubic crystalline zone is also growing further down in the z-direction reaching roughly 4 to 5 unit cells in depth.

Figure 53 shows comparisons of load (2 kPa, 20 kPa, 40 kPa and 200 kPa) and velocity  $(0.1 \,\mathrm{m\,s^{-1}}, 1.0 \,\mathrm{m\,s^{-1}}$  and  $8.0 \,\mathrm{m\,s^{-1}}$ ), highlighting the different crystalline and non-crystalline structures of the ice. The figures show how the ice in the hydrophobic systems have evolved after the full 50 ns friction simulation, in view of the *yz*-plane of the simulation box. From this view is it easy to distinguish the zone where the cubic ice has nucleated from the rest. We see clear differences for the different parameters, as shown for the different loads in Figures 53b to 53d. The increase in load yields large differences in the content of cubic ice and amorphous water molecules. This increase coincides with the increased friction force found in Section 3.2.3 when increasing the load. When measuring the amorphous water



Figure 53: Comparison of ice structures after 50 ns friction tests, with different loads and velocities, captured by the Chill+ algorithm [49], and having  $\epsilon = \epsilon_0$ . The molecules ordered as hexagonal ice are coloured in teal, the molecules ordered as cubic ice are orange, and the non-crystalline water molecules are blue. The *yz*-section is shown to capture the interfacial layer of non-crystalline water molecules as well as the crystalline cubic ice nucleated in the positive x-direction perpendicular to this view.

accumulation at the friction interface, the QLL-thickness was notably larger for the load  $P_N = 200$  kPa, fluctuating around 4 nm, as shown in the comparison plot for the different loads in Figure 54a. The decrease in QLL-thickness aligns with the nucleation point of cubic ice within the structure. This suggests that the initially accumulated amorphous water molecules in fact facilitate the nucleation of cubic ice observed in these systems. Following the nucleation phase, the QLL-thickness stabilises at approximately 0.7 to 1.0 nm for these loads of 20 kPa and 40 kPa. This is at the same level as the system with a 2.0 kPa load, which maintains a thickness close to this range throughout the entire friction test.

When comparing systems at three distinct velocities, under the same load of 20 kPa, each exhibits a similar initial increase in QLL-thickness. However, for the system with the highest velocity,  $v = 8 \,\mathrm{m \, s^{-1}}$ , an additional increase in QLL-thickness was observed after the cubic ice nucleation point. For the highest velocity, the latter increase begins approximately at a simulation time of 15 ns, culminating in a QLL-thickness of more than



**Figure 54:** Comparison of  $d_{QLL}$  for friction tests with corresponding Type I friction force profile. Figure 54a compares the QLL thickness throughout the friction test for different loads with  $v = 1 \text{ m s}^{-1}$ ,  $\epsilon = \epsilon_0$ , and  $P_N = 2 \text{ kPa}$ , 20 kPa, 40 kPa and 200 kPa. Figure 54b compares the QLL thickness throughout the friction test for different velocities with  $P_N = 20 \text{ kPa}$ ,  $\epsilon = \epsilon_0$ , and  $v = 0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ .

1.5 nm. The snapshots shown in Figures 53e to 53g demonstrate that this elevated presence of amorphous water molecules contribute to a deeper nucleation zone for the cubic ice. In contrast to the large velocity systems, the systems with the smaller velocities stabilise with the QLL-thickness fluctuating around 6 to 8 nm from a simulation time of 10 ns and to the end of the simulations. When comparing the friction force of these systems, we found that the largest velocity overall was the system having the lowest trend peak friction.

However, there are no significant structural changes in the polymers at the same time. There is an important remark to make regarding the deviation of the polymer structures'



**Figure 55:** Comparison of  $d_{COM}$  for friction tests with corresponding Type I friction force profile. Figure 55a compares the *COM* deviation from the initial position for the polymer structure throughout the friction test for different loads with  $v = 1 \text{ m s}^{-1}$ ,  $\epsilon = \epsilon_0$ , and  $P_N = 2 \text{ kPa}$ , 20 kPa, 40 kPa and 200 kPa. Figure 54b compares the *COM* deviation from the initial position for the polymer structure, comparing the different velocities with  $P_N = 20 \text{ kPa}$ ,  $\epsilon = \epsilon_0$ , and  $v = 0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ .

COM, from its starting position, henceforth termed  $d_{COM}$ . This deviation, when plotted over time, aligns with the friction force profiles. When analysing the systems under varying loads, the evolution of  $d_{COM}$  over time, as illustrated in Figure 55a, closely matches the friction force comparisons in Figure 38. As for the systems looking into the changes in response of different velocities, there is negligible variation between the velocities  $0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ , with all showing fluctuations within the range of 0.02 to 0.08 nm. This can be seen in Figure 55b.

#### 3.2.5.2 Type-II

In our examination of ice structures in the Type II friction, we focused on the system with friction test parameters  $\epsilon = \epsilon_0$ ,  $v = 10 \,\mathrm{m \, s^{-1}}$ , and  $P_N = 200 \,\mathrm{kPa}$ . Here we find a significant pressure-induced build-up of amorphous water molecules. Using the Chill+ algorithm, we observe that this expanding layer of amorphous water molecules originates from the friction interface and grows in the negative z-direction, moving towards the base of the ice/water configuration, namely pressure melting of the ice structure. The pressure melting, characteristics found now in Type II, is captured in the 3D and 2D Chill+ output visualisations presented in Figures 56 and 57.

The snapshots, displayed in Figures 57a to 57e, are set to a 1:1 scale ratio. This representation not only visually emphasises the pressure melting effect, but also highlights the compression between the polymer structure and the ice, making the elevation of the interface apparent. When assessing the movement of the polymer structure, it is observed that the COM showed a 1 nm deviation from the initial position, within the first 1 ns. Subsequently, the COM remains stable, fluctuating within 1.0 to 1.2 nm after approximately



Figure 56: The figures show close-ups of the evolution of the ice structure captured by the Chill+ algorithm [49] for a friction test having  $P_N = 20 \text{ kPa}$ ,  $v = 1 \text{ m s}^{-1}$  and  $\epsilon = \epsilon_0$ . The molecules ordered as hexagonal ice are coloured in teal, while the molecules ordered as cubic ice are coloured in orange and the non-crystalline water molecules are shown in blue.



Figure 57: The figures show close-ups of a cross-section of the system, highlighting the evolution of the ice structure captured by the Chill+ algorithm [49], against the polymer structure. The friction test capture have  $P_N = 200 \text{ kPa}$ ,  $v = 10 \text{ m s}^{-1}$  and  $\epsilon = \epsilon_0$ , the polymer is displayed in black, the hexagonal ice in teal, cubic ice in orange, and the rest of the water molecules are colored blue.

20 ns, as illustrated in Figure 58. Notably, the timeframe for  $d_{COM}$  stabilisation aligns with the period required for the complete transformation of the ice structure into purely amorphous water molecules (Figure 25).



Figure 58: Evolution of  $d_{COM}$  over time, for the friction test having  $\epsilon = \epsilon_0$ ,  $v = 10 \text{ m s}^{-1}$ , and  $P_N = 200 \text{ kPa}$ .



3.2.5.3 Type-III

Figure 59: The figures show close-ups of the evolution of the ice structure captured by the Chill+ algorithm [49] for a friction test having  $P_N = 40 \text{ kPa}$ ,  $v = 0.1 \text{ m s}^{-1}$  and  $\epsilon = 2\epsilon_0$ . The molecules ordered as hexagonal ice are coloured in teal, while the molecules ordered as cubic ice are coloured in orange and the non-crystalline water molecules are shown in blue.

In the same manner as for Type I, we find a nucleation of cubic ice in Type III friction. The snapshots in Figures 59 and 60 highlight this evolution of the ice structures captured by the Chill+ algorithm. Further examination of the ice structures find that the nucleation zone of the cubic ice is just beneath the friction interface at the place where the amorphous molecules have penetrated the polymer structure a bit. The elevated part of water molecules with the nucleation zone of cubic ice beneath is visible in the snapshots of Figures 60c



Figure 60: The figures show close-ups of a cross-section of the system, highlighting the evolution of the ice structure captured by the Chill+ algorithm [49]. The friction test captured has  $P_N = 200$  kPa,  $v = 10 \text{ m s}^{-1}$  and  $\epsilon = 2\epsilon_0$ , the hexagonal ice is shown in teal, cubic ice in orange, and the rest of the water molecules are colored blue.



Figure 61: Evolution of  $d_{COM}$  over time, for the friction test having  $\epsilon = 2\epsilon_0$ ,  $v = 0.1 \,\mathrm{m \, s^{-1}}$ , and  $P_N = 40 \,\mathrm{kPa}$ .

to 60e too.

From the calculations of  $d_{COM}$ , we found that the COM of the polymer varies in the area between 0.18 to 0.34 nm during the friction test for the system having  $\epsilon = 2\epsilon_0$ ,  $v = 0.1 \text{ m s}^{-1}$ , and under the load of  $P_N = 40 \text{ kPa}$ . The stabilisation of the COM deviation is also here found to coincide with the nucleation of the cubic ice, which stabilised after 20 ns. This further underscores the connections between the stabilisation of the friction force, cubic ice nucleation, and the displacement of the polymer structures COM.

# 4 Discussion

For this study on the nanoscale ice-solid friction interface, we developed an atomistic model with a total of 44 928 molecules. The aim for this model was to replicate the real-world conditions by modelling a single asperity of contact. This nanoscale model was proposed to capture the evolution of both the ice and the solid structure caused by the friction dynamics.

Three polymers were used as the friction media. To simulate different degrees of hydrophobicity, the system was proposed with six different attraction potentials. This gave a total of 18 systems as the input to the equilibration process. Following the equilibration procedure, the attraction potentials being used in the friction tests were reduced to three,  $\epsilon = 0.1 \epsilon_0$ ,  $1 \epsilon_0$  and  $2 \epsilon_0$ .

To study the friction behaviour, a MD-simulation evolved the systems over a total of 50 ns. To impose the velocity in the system, the ice structure was divided into three slabs that were moved at a constant velocity throughout the simulations. To compare the impact of the velocity, 3 different rates were used,  $v = 0.1 \text{ m s}^{-1}$ ,  $1 \text{ m s}^{-1}$  and  $8 \text{ m s}^{-1}$ . Normal stress was applied at the friction interface, taking the both COMs of the water and the polymer as references. Four different loads,  $P_N = 2.0 \text{ kPa}$ , 20 kPa, 40 kPa and 200 kPa, were tested to research the impact of different loads.

Each  $CH_2$  group was attached to soft invisible springs. Essentially, as these groups experienced the force due to the interactions with the water molecules, they would deviate from their original positions. This deviation was opposed by the forces imposed by the springs to each  $CH_2$  group. Therefore, by measuring the springs extensions, the friction force – the force from the spring to each  $CH_2$  – was determined.

To capture more in-depth insights into the behaviours of individual molecules and the system as a whole, we recorded the trajectories of all molecules. This allowed for a detailed understanding of how each molecule moves, orders, and interacts with other molecules under the friction interactions. Additionally, the stress tensors for each water molecule were calculated. The individual measurements give insights into the strain and stresses of the systems due to the friction interactions.

## 4.1 Atomistic modelling and system building

For the MD study, it is crucial to have a successful equilibration process to make reliable findings in the friction tests. The thermodynamical outputs from this process provide insight into the degree to which this was accomplished. For all successful equilibration processes, the total system energy,  $E_T$ , was found to stabilise within 0.5 ns at about  $-1.2 \text{ GJ mol}^{-1}$ . The temperature of the system, T, stably fluctuated around 260 K within 258 to 262 K.

Throughout the equilibration period, we found at the surfaces a layer of the hexagonal ice which transformed into a layer of amorphous water molecules. This amorphous layer is found to be the QLL, with different thickness found for the attraction potentials and the different polymer structures. We did not find significant differences in  $d_{QLL}$  for the smaller attraction potentials,  $\epsilon = 0.1 \epsilon_0$ ,  $0.5 \epsilon_0$  and  $1 \epsilon_0$ , whereas the largest  $\epsilon = 2 \epsilon_0$  produced a significantly thicker QLL. Having not induced any pressure in the system, this QLL is an intrinsic property found beneath the melting point of water, consistent with the literature [8, 25–28].

After equilibration, systems with a higher attraction potential showed a reduced gap between the ice and polymer structures. These findings suggest that surface melting occurs beyond a certain interaction strength. Notably, this melting is not influenced by pressure but by the presence of another medium, affecting surface properties of ice. This suggests that the thickness of the QLL can be increased by contacting strong adhering materials, namely hydrophilic materials.

It is interesting to find that sufficiently weak interaction for ice adhesion could be screened by thermal fluctuation. Specifically, at the lower potentials of the most hydrophobic polymer structures, having  $\epsilon_{\rm H_2O-CH_2} = 0.01 \epsilon_0$  and  $0.05 \epsilon_0$ , the ice did not adhere to the polymer. To make the two structures adhere after initial failure, shorter and shorter displacements between the ice and the polymer structures were tried, but none were successful. Then in addition to small  $\epsilon$ , two primary assumptions possibly influenced this observation: the uniform treatment of all CH<sub>2</sub> molecules, and fixing the top of the polymer structure. Modelling all molecules in the polymer structure to be CH<sub>2</sub> leads to the model losing the more free CH<sub>3</sub> groups normally at the end of polymer chains. If incorporating the CH<sub>3</sub> groups at the end of the polymer chains, this would increase the interactions with the water molecules but also with the other CH<sub>2</sub> groups. The top of the polymer was fixed to limit the size of the system while keeping the polymer structure dense, similar to real-world size HDPE. On the other hand, fixing the top layer of the polymer prevents it from moving towards the ice. With smaller interaction potentials, this can make the adherence process between the media more difficult.

For further investigations into the friction behaviours of extremely hydrophobic solid media, changing the model changing these two assumptions could yield a successful equilibration process. Additionally, applying a small amount of pressure to push the structures together from the start could also be considered. This lack of adherence presents limitations with our model: having the ice structure drop through the periodic boundaries, there is of course no possibility to utilise these systems in the friction tests. Therefore, the smallest  $\epsilon$  used in the friction tests was the one at  $0.1\epsilon_0 = 0.3964 \,\mathrm{meV}$ .

The 3 polymer structures lead to minor differences in both QLL thickness and average bond lengths throughout the equilibration process. Having the same randomisation number for all equilibration simulations, this confirms that the 3 polymer structures in fact are different. This confirms that the process of making 3 polymer structures by quenching the structure from  $750\,\mathrm{K}$  after  $5\,\mathrm{ns},\,6\,\mathrm{ns}$  and  $7\,\mathrm{ns}$  heating was successful.

## 4.2 Friction interface dynamics

From the friction simulations, we were able to research the dynamic behaviour of the ice-polymer interface. This provided further insight into the nanoscale ice friction, with the implications of different loads, velocities, and interaction potentials. From the resulting friction force profiles, we classified 4 different types of friction. The four types exhibit different behaviours in the interface friction dynamics, with corresponding changes in the QLL and structural evolution.

### Type I

Type I is distinct, with a build-up period for the friction force at the start of each simulation. The friction is found to produce a *stick-slip* behaviour, where the polymer chains are dragged along with the water molecules, gradually moving from the initial position until the spring force is too large and the CH<sub>2</sub> molecules spring back. Discerning this behaviour from the other friction types, which also have a stick-slip movement present, the polymer chains do not stick to another water molecule on the way back, before having a smaller x position than initially. This we deduced by comparing the output x components for each CH<sub>2</sub> molecule over time, thereby finding a zig-zag pattern similar to the one found in research using AFM [12, 14, 16, 17]. In our study, the resolution of the trajectory files is significantly lower, being only  $\frac{1}{100}$  of the resolution of our standard friction calculations. Despite this coarse resolution, it became evident that our friction calculations, especially post-slip, might not provide an accurate depiction of the total force. This is due to the fact that in our calculations, both negative and positive deviations contribute positively to the overall force, potentially misrepresenting the real interplay of the forces in the system.

The build-up of larger and larger peak forces within the first 8 to 12 ns, depending on the system, coincides with the build-up of more amorphous water molecules. Evidently, the amorphous water building up beneath the surface was found to promote the nucleation of cubic ice beneath the surface. The cubic ice nucleated along the direction of movement, and stabilised at the same time as the force measurements finished the build-up period, reaching a the steady-state. Given that cubic ice normally occurs as a meta-stable phase, at lower temperatures than the stable hexagonal ice occurs, it would be of interest to find out more about the role played by the cubic ice in ice friction.

Both build-up periods observed in the friction force and the increase in amorphous water molecules, coupled with the nucleation of cubic ice, underscore the fact that the friction interface requires time to adapt. When these systems are brought into contact and set in motion, they need sufficient time to reach a new equilibrium. Given that the friction force simulations reached a steady-state within 10 ns, having a considerable longer 40 ns steady-state phase, it suggests that the simulation duration for systems exhibiting the Type I force profile was adequate. When comparing the impact of velocity and loads, we find clearly that a larger load leads to a larger friction force, while an increase in velocity only increases friction force when the loads are sufficiently large, at  $P_N \ge 40$  kPa. A linear dependency between a larger load and a larger friction force was not found. While there was an increase, more research and more intervals in different loads are needed to find a function for the increase in friction force as a result of increasing load.

## Type II

Type II is easily distinguished by the considerably larger friction forces, with rapidly increasingly force build-ups, more similar to the force profiles of macroscopic friction tests. For the Type II profiles, ordered peak-drop cycles were not found. Instead, steady-state parts of the force profiles were found with small fluctuations in the measured friction force. This means that the polymer chains did not, at any moment, move past the starting position in the direction of movement. Having not moved past its initial position, no stick-slip movement could occur.

For the Type II force profile to emerge, there had to be a significantly large load. In this study, Type II was only found for systems having  $P_N = 200$  kPa. This large load made the polymer structure compress significantly in comparison to the one of Type I. In addition, when looking at the snapshots in the *xz*-plane, we found the water slab that is used to induce movement in *x*-direction to be clearly visible. The slabs used to move the water molecules were frozen, thus the ice structure had clearly arranged in a denser manner as a result of the friction interactions.

Clearly, a build-up of amorphous water molecules were found, and for  $v \ge 8 \,\mathrm{m \, s^{-1}}$  the whole ice structure was transformed into amorphous water molecules. The transformation of crystalline ice to amorphous water were in all systems starting at the interface going downwards into the ice structure, which clearly indicates that the increasing QLL thickness was induced by pressure melting.

On the other hand, for  $v = 1 \,\mathrm{m \, s^{-1}}$  the whole structure was not transformed into a morphous water molecules, but merely a 4 nm thick layer. For the smallest velocities, not all crystalline ice was transformed, showing that the velocity also plays a role in the 'melting' behaviour of the ice.

When our model results in the complete melting of the ice structure, this is unlikely to reflect reality. For an accurate representation of real ice and snow structures, we should find a defined boundary between amorphous water and crystalline ice at equilibrium. Beyond this boundary, the pressure-induced melting, caused by the combination of velocity and load, should cease. To accurately determine the thickness of the QLL in relation to load and velocities for HDPE, more extensive research is needed. This research should encompass a larger ice model as well as a wider range of loads and velocities for statistical purposes.

## Type III

While Type I had clear stick-slip behaviour with a polymer chain displacement in the direction of movement and in the opposite direction, Type III is found by distinct peak-drop cycles where the initial position of the  $CH_2$  molecules are not surpassed. There is a clear difference between the Type III and Type II profiles: in the latter, the build-up stages closely correlate to an increasing number of amorphous water molecules, and after the peak force, the type II force profiles only drop marginally. It does not have clear build-up-drop cycles. In contrast, Type III exhibits interactions similar to individual adhesion tests, marked by a rising force followed by a significant drop after a visible peak force.

The Type III friction behaviour exhibits a trending baseline friction force. This trend aligns with two observations: the displacement of polymer chains from their crystalline positions and the subsequent penetration of water molecules into the vacated spaces within the polymer structures. Interestingly, Type III friction behaviour is exclusive to the hydrophilic systems. This raises the likelihood that the displacement of the polymer chains from the structure is influenced by the larger depth of the LJ potentials, emphasising the role of long-range interactions between water molecules and CH<sub>2</sub> groups.

This phenomenon of polymer chains being displaced introduces significant challenges to our model. The design of the model assumes that the volume above its fixed top simulates an impenetrable polymer structure. This assumption is thus not true in these cases. Further, comparing the different systems with different polymers is not that trivial, since the extent of polymer disruption from the crystalline structures varies among the polymers. In the systems with true stick-slip measurements, the drop size is corresponding to the force exerted by the slip length. Therefore, to draw meaningful comparisons, the force drop size is taken into account as well, when comparing Type III systems.

However, a simple comparison of the drop size proves effective only if paired with the maximum peak force and if the polymer returns close to its pre-friction test spatial position. By considering both these assumptions, we can use force comparisons to gain insight into the force exerted by displaced polymer chains (captured by the maximum peak) and the dynamics at the interface (with the drop size acting as an indicator of slip length).

For hydrophilic systems operating at velocities greater than  $0.1 \,\mathrm{m \, s^{-1}}$  with a time step of 1 fs, we found it challenging to investigate the impact of different velocities in the context of Type III force profiles.

Our friction simulations use an approximated TraPPE-UA potential, where we approximate fixed bond lengths as highly stiff springs. However, this approach was not successful for Type III profiles. Although TraPPE-UA is a widely recognised model for coarse-graining polymers, the limitations in LAMMPS – particularly the inefficiency in simulating fixed bond lengths – render this approximation problematic.

The issue lies in the extreme interactions that push polymers out of their crystalline structure. When combined with springs pulling them back to their initial positions, there

are immense forces acting on each molecule. If the magnitude of these forces is too large, the molecules can deviate significantly from their last known positions, and at the next timestep potentially be moved outside the computational boundaries set by LAMMPS. This is because LAMMPS divides the calculations between the physical computational cores, based on the molecules' spatial positions. If the molecule is not within the correct boundaries of the cores at the next timestep, the molecule is lost and the computations cease. Trying to fix this unfortunate behaviour, smaller timesteps and less rigid bonds were tried. The time step had to at least be cut by one order of magnitude per each order of magnitude increasing velocity, if the bond strength also was lowered by one order of magnitude. This would alter the model too much and need more than an order more computational cost, which were therefore not done.

Given these challenges, approximating fixed bond lengths is not viable for these simulations. For future research into Type III using LAMMPS, a different potential should be considered. Additionally, one should look into making the polymer structure larger, so the chains do not end up outside the initial structure, breaking the purpose of this model.

### Type IV

Type IV profiles were found to be experiencing extreme friction force in the start before experiencing nearly none at all. These were all found for the superhydrophobic systems with the largest load,  $P_N = 200$  kPa. The critical phase, where the friction force skyrockets, was because nearly all free water molecules penetrated into and through the polymer structure. This does in fact break the friction simulation model of this research.

Our findings suggest limited utility from exploring the effects of varied velocities for this interaction potential and load. However, they do illuminate a distinct phenomenon: under substantial loads, water molecules can infiltrate solids during friction interactions. This penetration appears to be an outcome of pressure melting combined with an overly hydrophobic composition of the solid. If both the water/ice and polymer models were expanded in the z-direction of the simulation boxes in this work, it might be possible to observe an equilibrium depth of penetrated water molecules. This cannot be seen now, as the water molecules penetrated all the way through the polymer structure. In an equilibrium state, the force required to further push water molecules into the polymer would exceed the breaking energy of the ice model in the direction of motion, resulting in renewed dynamic friction, but at a hydrated polymer interface.

### Inducing velocity

The velocity parameter was imposed in the model by fixing parts of the ice structure to move at a constant rate. This ensured that water molecules consistently moved in the x-direction during all friction simulations. For the systems that maintained a distinct frictional boundary between the two media – no water molecule penetration – the movement was not only consistent but also successfully generated frictional interactions. Significant

evidence in favour of the models' precision was its ability to reproduce stick-slip behaviours, mirroring authentic nanoscale interface dynamics found in physical experiments. Moreover, the model managed to capture structural evolution as well. There were successful transitions of hexagonal ice into an amorphous water state, which meant that the restricted walls did not cool the system too much.

### Applied load

For the friction interactions where the interface withholds – the two media does not mix – this seems to have provided a good approximation of a normal load. It was found that there are consistent interactions at the friction interface, where both stick-slip behaviours and gliding friction interactions can occur. All structural evolution of the media originates from the friction interface. The model captured both pressure and sliding induced melting. Melting induced by pressure and sliding primarily originates from the top of the ice rather than from its bottom edges. The model allows for the nucleation of cubic ice, here as a result of localised areas with elevated pressures.

Capturing these changes means that the uniformity of the applied force did not undermine localised differences in the structure. Whether these localised changes are, in fact, large enough and coincide with other research are matters for future research to explore. It is also left for future research to tweak the loading approach and quantify if there are better ways to induce this load.

### System

The systems were put together with a coarse-grain model of the  $CH_2$  and  $H_2O$  molecules. Reducing the molecules to point particles leads to a loss in the spatial configurations and entanglement of the system. For the majority of simulations, this seems unproblematic, as evidenced by the simulations where the interface remained intact. However, in the simulations where water penetrated the polymer structure, the absence of Hydrogen atoms in the model might be the cause. Not having the Hydrogen atoms themselves in the system, leaves larger distances between the molecules.

For some systems, the interactions were very small. This was, for example, the case for the superhydrophobic systems with smaller loads. In these systems, the total size of the system may have been larger than needed, as there were only changes in structures at the friction interface. This probably leads to more computationally heavy simulations than needed. In MD-simulations, computational efficiency is crucial. Excessive computational demands not only increase costs but also raise energy consumption. For the systems with resulting minimal friction interactions, these demands might be reducible, optimising both expenses and energy use.

In the context of systems containing interactions with full pressure melting – when all hexagonal ice molecules transformed into amorphous water – the size of the model might have been too small. We found increasing friction plateaus after each period of amorphous

water transformation. Having transformed all molecules in the system, this could therefore mean that there were increases in friction force not being captured as it did not capture an equilibrium between  $I_h$  and amorphous water molecules. Therefore, it is possible that the actual friction force was inaccurately represented as the whole ice structure transformed.

Future research should carefully evaluate the model sizes to accurately represent friction interactions. Striking a balance is essential to avoid oversized models, which have a significant environmental footprint, or undersized models not truly capturing all interactions. Proper model sizing ensures both computational efficiency and accurate representation of physical phenomena.

# 5 Conclusion

Extensive research into the nanoscale dynamics of ice solid friction was conducted by MD-simulations. To study the frictional behaviour, the research consisted of a modelling procedure, then an equilibration process, and then the friction simulations themselves.

The final model consisted of  $17\,280$  CH<sub>2</sub> molecules and  $44\,928$  H<sub>2</sub>O molecules, aiming to model a single asperity of contact.

The equilibration procedure was successful for all systems, with all three different polymer structures, with values of  $\epsilon$  in the set  $0.1 \epsilon_0$ ,  $0.5 \epsilon_0$ ,  $1 \epsilon_0$  and  $2 \epsilon_0$ . The thermodynamic properties of these systems, specifically  $E_T$  and T, converged to a stable equilibrium approximately at  $-1.2 \text{ GJ mol}^{-1}$  and 260 K, respectively. For the two potentials  $\epsilon = 0.01 \epsilon_0$ and  $0.05 \epsilon_0$ , the two media did not adhere. All systems experienced the build-up of a QLL, where the systems having  $\epsilon = 2.0\epsilon_0$  resulted in a significantly larger  $d_{QLL}$  than the others. The three polymer structures were successfully prepared with differences in the spatial positions and orientations of the polymer chains.

Four different friction types were found from the simulation output, all with different characteristics in comparison to macroscale friction. Type I experienced increased friction forces for increased loads, while an increase in friction force as a result of increasing velocity was only found at sufficiently large loads,  $P_N \ge 40$  kPa. Type II is only found for the largest loads of  $P_N = 200$  kPa and experience a clear increase in friction force when the velocity is increased. Type III is hydrophilic systems also experiencing a stick-slip behaviour, while not having any clear increase in friction force when increasing the load. Type IV is found for systems where the water molecules pushed through the polymer structure, breaking our model.

For both Type I and Type III, cubic ice crystallisation occurred along the direction of motion, originating from the amorphous water molecules that appeared due to the friction strain. The transformation of the structures was found to coincide with increasing friction forces, where all build-up of friction forces reached stable peaks when the ice/water structure stabilised. For increased loads, increased QLL-thickness followed, which also followed due to increased velocities to  $v \geq 8 \,\mathrm{m\,s^{-1}}$ . We thus found both pressure melting and sliding melting increasing the QLL-layers.

## Limitations and future research

One of the primary limitations in our study is the coarse-graining approach. While this strategy significantly reduces computational time, it also omits specific atomic interactions that might play a crucial role, especially in complex systems like the ice and polymer interfaces. Detailed all-atom simulations could provide further insight into these interactions, though at the cost of higher computational demands. The penetration of water molecules into the polymer structure in some simulations indicates potential issues with the realism of the models. In these cases, further investigations might benefit from incorporating hydrogen atoms. Additionally, the current study has relied on the same system sizes for all simulations. As discussed, adapting larger systems for the simulations with the largest loads and strongest interaction potentials could provide a clearer view of pressure and velocity-induced surface melting. Smaller systems could probably also be used for the cases with small interactions, optimising the computational resources needed.

Further studies could also delve deeper into understanding the exact nature and dynamics of the QLL. The thickness, behaviour, and exact role of the QLL in frictional interactions remain topics of active research, and a more in-depth exploration in this direction could shed light on whether thicker QLL gives larger friction forces or that larger friction forces lead to thicker QLL. When exploring the relationships between load, velocity, QLL, attraction potentials, and friction forces, it is clear that developing a comprehensive friction model requires a deeper understanding of how these factors interact. As we consider friction from the nanoscale to the macroscale, we must account for the potential that Type I, Type II, and Type III friction types might coexist. By examining the collective influence of these parameters, we can integrate our understanding from the nanoscale, which might enable us to further understand the physics of slipperier skis or stickier tyres.

In summary, while our study has contributed novel and valuable insight into the frictional behaviours at the ice-polymer interface – across different systems and conditions – there is considerable scope for refining the models and expanding the research to capture the full complexity of these interactions.

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# Appendix

## A LAMMPS code for making the structures

Benethe is the code for making the structures for simulation.

First is the polymers, which consists of two parts, the equilibration on a high temperature T = 750 K, and the quenching down to 300 K. Second is the ice, which consists of a minimization and equilibration of a structure made by genice [40].

### A.1 Making the polymer

```
# Initialisation
1
   units real
2
   atom_style molecular
3
   boundary
                     ррр
4
                       log.polymermin
   log
\mathbf{5}
6
   # Make polymer from two strains
7
   read_data
                      HDPE1.data
                                           #Datafile containing the two strains
8
   replicate 12 18 1
9
10
   # Fix the toplayer of the CH2molecules
11
   region stuck block INF INF INF INF 51.3625 51.3625
12
   group stuck region stuck
13
   fix 1 stuck spring/self 9999
14
15
   # Setup potential information
16
   bond_style harmonic
17
   bond_coeff 1 9999 1.54
18
   angle_style harmonic
19
   angle_coeff 1 5.386 114
20
   dihedral_style fourier
21
   dihedral coeff 1 3 0.030594 1 0.0 -0.0058762 2 -180 0.068191 3 0.0
22
   pair_style lj/cut 14
23
   pair_coeff 1 1 0.1687 3.675
24
   special_bonds lj/coul 0.0 0.0 1.0 angle yes dihedral yes
25
26
   # Equilibration at 750K
27
28
                    all create 750 10001 rot yes dist gaussian
   velocity
29
   timestep
                     1
30
```

```
31
32
   compute 1 all msd
33
34
   thermo 5000
35
   thermo_style custom step temp etotal ke pe c_1[4]
36
   fix
             2 all nvt temp 750 750 100
37
                1 all custom 20000 eq.polymer.traj id type x y z vx vy vz
   dump
38
39
40
   # Equilibration for 5 ns
41
   run 5000000
42
43
   write_restart eq.5ns.polymer.rst #Polymer 1
44
45
   #make two more systems
46
   run 1000000
47
   write_restart eq.6ns.polymer.rst #Polymer 2
48
49
   run 1000000
50
   write_restart eq.7ns.polymer.rst #Polymer 3
51
```

### A.2 Quenching the polymers

```
#########INPUT Variables ######
1
   #
2
         The different Polymers restartfiles:
   #
3
   # ${rfile}: eq.{5,6,7}ns.polymer.rst
4
   #
5
   6
7
   # Simulation for quenching the polymer down to 300K
8
   #read in file from scratch
9
   log
              log.polymer.${rfile}
10
   read_restart ${rfile} remap
11
12
   # Freeze the top
13
   region stuck block INF INF INF INF 51.3625 51.3625
14
   group stuck region stuck
15
   fix 1 stuck spring/self 9999
16
17
   # Quence the system
18
```

```
fix 2 all nvt temp 750 300 100
19
   compute 1 all msd
20
21
   # Output and calculations
22
   thermo 5000
23
   thermo_style custom step temp etotal ke pe c_1[4]
24
25
   # Run for 0.1 nano second
26
   run 1000000
27
^{28}
   # Save output to restart-file
29
   write_restart ${rfile}.300K.rst
30
31
```

#### A.3 Making the ice-block

```
#Setting the equilibration temprature
1
   variable
                    Temp string 260 #temperature variable
2
3
   units real
4
   atom_style atomic
5
   log log.eqICE
6
7
   # Input the datafiles
8
   read_data mwICE.data
9
10
11
   # Define potential
12
   pair_style
                      SW
13
   pair_coeff
                      * * parameter.mW mW
14
15
   #Run minnimization and save state
16
                    1.0e-8
   minimize
                                   1.0e-8
                                                  10000
                                                                10000
17
   write_data
                     min.mwICE.data
18
19
   # Add velocity
20
                    all create ${Temp} 123456 rot yes dist gaussian
   velocity
^{21}
22
   # Define output
23
   compute
                    1 all msd
24
   thermo
                           500
25
   thermo_style
                          custom step temp press vol etotal ke pe c_1[4]
26
```

```
27
   #set fixes
28
   fix 1 all nvt temp 260 260 100
29
30
   #Run 10 ns equilibration
31
   timestep 5
32
   run 2000000
33
34
   # Save the output
35
   write_data eq.mwICE.data
36
   write_restart eq.mwICE.rst
37
```

#### **B** LAMMPS code for the equilibration process

Benethe the code used for running the LAMMPS Equilibration process follows taking in the wholesystem put together.

```
1
   #
2
       The different Polymers
   #
3
   # ${System}: 1,2,3
4
   #
5
       The different interaction potentials
   #
6
   # ${Epsilon}: 0.01,0.05,0.1,1,2
7
   #
8
   9
10
   # Equilibration for whole system
11
   # Varibles
12
   variable epsilon_0 equal 0.091409
13
   variable epsilonPICE equal ${epsilon_0}*${Epsilon}
14
15
   # Define logfiles
16
   log ${System}/log.eq.ICEPE.${Epsilon}
17
18
   #Initialize
19
  units real
20
   atom_style molecular
^{21}
22
  boundary
                ррр
  bond_style harmonic
23
  angle_style harmonic
24
  dihedral_style fourier
25
```

```
26
   # Read in model
27
   read_data whole${System}.data
28
29
   # Define groups
30
                             # Putting all atoms of type CH2 in the
   group PE type 1
31
    \rightarrow poly-ethylene group
   group ICE type 2
                             # Putting all atoms of type H20 in the ICE-group
32
33
   # Freeze the top layer of the polymers
34
   region stuck block INF INF INF 51.3 51.4
35
   group PE_frozen region stuck
36
37
   # new interraction potential
38
   pair_style
                      hybrid lj/cut 14 sw
39
                      1 1 lj/cut ${epsilon 0} 3.675
   pair coeff
40
                      1 2 lj/cut ${epsilonPICE} 3.034
   pair_coeff
41
                      * * sw parameter.mW NULL mW
   pair_coeff
42
43
   special_bonds lj/coul 0.0 0.0 1.0 angle yes dihedral yes
44
   #minimization
45
   min_style
                    sd
46
   minimize
                    1.0e-8 1.0e-8 10000
                                              10000
47
48
   # Save the status after minimisation
49
   write_data ${System}/Aftermin.${Epsilon}.data
50
51
   # add velocity
52
   velocity all create 260 10001 rot yes dist gaussian
53
   reset_timestep 0
54
   timestep
                    1
55
56
   # Applyfixes
57
   fix 1 PE_frozen spring/self 9999
58
   fix 2 all nvt temp 260 260 100
59
60
   # Define calculations and log output
61
   thermo 1
62
   thermo 20000
63
   thermo_style
                          custom step temp press vol etotal ke pe
64
65
   # Define the Dump-output
66
```

### C LAMMPS code for the friction-test

Benethe follows the lammps code for the friction-tests

```
1
   #
             Load coefficient
\mathbf{2}
   # ${Ncoeff}: 0.1 , 1 , 2 10
3
       Velocity coefficient
   #
4
   # ${vcoeff}: 0.1, 1, 8
5
       Interaction potential coefficient
   #
6
   # ${Epsilon}: 0.1, 1, 2
   # Which polymer
8
  # ${System}: sys1, sys2, sys3
9
                                                                                          Relat
   \hookrightarrow
   \rightarrow to the polymers after 5ns,6ns,7ns at 750K
   10
11
   # Friction test for ICE pushing on polymer
12
13
   # Friction test variables
14
  variable Npress equal 20e3*${Ncoeff}
                                                                    # Simulated
15
   → pressure from normal force,20kPa x Ncoeff
                                         1/100000*${vcoeff}
  variable speed
                         equal
                                                                    # Velocity
16
   \, \hookrightarrow \, , vcoeff stands for velocity in m/s
  variable Temp
                          equal
                                        260
17
  variable epsilon_0 equal 0.091409
                                                               # Simulation
18
   \hookrightarrow temperature [K]
  variable epsilonPICE equal ${epsilon_0}*${Epsilon}
19
   variable Savepath string ${System}/${Epsilon}/${Ncoeff}.${vcoeff}.frictest
20
   \rightarrow #Path for saving files
   variable Loadpath string ../equilibration/${System}/eq.${Epsilon}.rst #
21
   \rightarrow Path for loading restart files
22
   log ${Savepath}.log
23
24
```

```
# Read in system and define potentials
25
   read restart ${Loadpath} remap
26
   pair_style
                   hybrid lj/cut 14 sw
27
   pair_coeff
                  1 1 lj/cut ${epsilon_0} 3.675
28
   pair_coeff
                   1 2 lj/cut ${epsilonPICE} 3.034
29
                   * * sw parameter.mW NULL mW
   pair_coeff
30
31
   special_bonds lj/coul 0.0 0.0 1.0 angle yes dihedral yes
32
33
   # Define groups
34
                           # Putting all atoms of type CH2 in the polymer
   group PE type 1
35
   \rightarrow group
   group ICE type 2
                           # Putting all atoms of type H20 in the ICE-group
36
37
   # Freeze top layer of the polymer
38
   region stuck block INF INF INF 51.3 51.4
39
   group PE_frozen region stuck
40
41
   # make solid ICE walls to mimick moving ICE
42
   region bsICE block INF INF INF INF $(bound(ICE,zmin)) $(bound(ICE,zmin) +
43
   → 20)
  region wsICE block $(bound(ICE,xmin)) $(bound(ICE,xmin) + 6) INF INF
44
   region psICE block INF INF $(bound(ICE,ymin)) $(bound(ICE,ymin) + 6)
45
   group bsICE region bsICE
46
   group wsICE region wsICE
47
   group psICE region psICE
48
                union bsICE wsICE psICE
   group sICE
49
   group NotSolidICE subtract ICE sICE
50
51
   # Reset timestep and set timestep for fix move not to jump at first
52
   \rightarrow timestep
   timestep 1
53
   reset_timestep 0
54
55
   # Move the solid ice
56
   fix mv sICE move linear ${speed} NULL NULL
57
   # apply normal force
58
  # Compute the force from the pressure
59
  variable Nforce equal v_Npress*lx*ly*1e-20*69.4786e12
60
  fix F n PE smd cfor ${Nforce} couple ICE NULL NULL auto 0.0
61
```

```
62
   # Apply soft springs to atoms for measuring applied force by sliding and
63
    \rightarrow pressing ICE
64
   group noFreezePE subtract PE PE_frozen
65
   fix sx noFreezePE spring/self 0.001 x
66
   fix sy noFreezePE spring/self 0.001 y
67
   # Compute the stress
68
   compute stress ICE stress/atom NULL
69
   # Put simulation parameters
70
   group NotSolid union noFreezePE NotSolidICE
71
   fix 1 NotSolid nvt temp ${Temp} ${Temp} 100
72
73
   # Simulation properties
74
   thermo 100
75
   thermo_style custom step temp f_sx f_sy
76
77
   # Define dump output for analysis including stress
78
   dump 1 all custom 100000 ${Savepath}.dump type id xsu ysu zsu c_stress[*]
79
   #Simulate over 100ns
80
   run 10000000
81
82
```

### Code for data-analysis

The data-analysis were made by using Julia. For this project:

- Calculating the friction force in nN from the log-file output.
- Calculating the thickness of the QLL from the dump-file output
- Calculating friction relative to the movement of the ice, from the dump-file output.

### Julia-code for friction force calculations

Benethe is the Julia-code returning the dataset. It takes in the log-files, which have been translated to .csv-files.It is using the Glob package for finding all log-files in each dictionary. The InMemoryDatasets package for the data-analysis. And the DLMReader for reading the csv-files into InMemoryDatasets. This is highly developed paralell running packages which were found to be usefull for this large amount of data.

The function itself can skip small files with the minsize parameter, and takes in the base  $N_{theta}$  in regards to the translation for the output load. The function then returns a

datset containing timestep in ns

```
using Glob, InMemoryDatasets, DLMReader
1
   function make_data(dirpath::String="", minsize::Int64 = 100000,
2
    ↔ N_theta::Float64 = 116.129211492645)
3
       # Finding the files
4
       files = filter!(glob("*frictest.log.csv",dirpath)) do f
5
       filesize(f) > minsize
6
       end
7
       if isempty(files)
8
            return IMD.Dataset()
9
       else
10
       total_data = IMD.Dataset()
11
12
       # Parsing the files
13
       for file in files
14
            epsilon, sys, Npar, vpar = getpars(file)
15
            println(epsilon,"\t",sys, "\t",Npar,"\t",vpar)
16
            data = filereader(file, header = true)
17
            IMD.select!(data, findall(names(data) . |> !contains("Column")))
18
            IMD.select!(data, findall(names(data) . |> !contains("f_F_n")))
19
            IMD.insertcols!(data,1, :e .=> epsilon)
20
            IMD.insertcols!(data,2, :System .=> sys)
21
            IMD.insertcols!(data,3, :Pn .=> Npar .*20) #Set the correct
22
       load_coefficient
            IMD.insertcols!(data,4, :velocity .=> vpar)
23
            append!(total_data, data)
24
       end
25
       # Modify to SI-units and do calculations for output
26
       IMD.modify!(total_data, :f_sx => ByRow(x -> x .* 0.06948)) # translate
27
      friction-force measured to SI (nano Newtons)
       IMD.insertcols!(total data,:Fn => total data.Pn .* N theta ./ 20 .*
28
      0.06948) # Translate load to normal force (nano Newtons)
       IMD.insertcols!(total_data,:u0 => ((total_data.f_sx ./
29
      total_data.Fn))) # Calculate the friction-force as a degree of load)
    \hookrightarrow
       IMD.insertcols!(total_data,:Fdelta => (total_data.f_sx .-
30
      total_data.f_sy)) # Differense between friction in y-direction and
    \hookrightarrow
      x-direction
       IMD.insertcols!(total_data,:ud => (total_data.f_sx .- total_data.f_sy)
31
       ./ total data.Fn)
    \hookrightarrow
```

```
32 IMD.modify!(total_data, :Step => ByRow(x -> x.* 1e-6) => :time) #

→ translate stepsize to time evolution in nano seconds

33 IMD.insertcols!(total_data,:displacement => total_data.time .*

→ total_data.velocity) # Translate time evolution to movement of the ice

→ in nano Newtons

34 return total_data

35 end

36 end
```

#### Julia-code for determing QLL

Benethe follows the Julia-code for determing the thickness of QLL, for input the CHILL+algorithm [49], is used by ovito [41] to classify the structures, which are run over all dump-files. The code consists of the code for reading the dump-files, and the part for calculating the kerneldensity function as well as the width of the 90% confidens intervall.

```
using Distributed, LinearAlgebra, LoopVectorization, InMemoryDatasets,
1
      DLMReader, Chain, KernelDensity
    \hookrightarrow
2
   # Optimized norm-calculation by LoopVectorization
3
   function avxnorm(A)
4
                   Sigma = zero(eltype(A))
5
                   @avx for i in eachindex(A)
6
                           Sigma += A[i] * A[i]
7
                   end
                   sqrt( Sigma )
9
           end
10
11
   # Function for reading the dump-files
12
   function dump_read( dump_path::String, type::Int8 = Int8(2))
13
            #=
14
     Analyses a dump file containing position and, stress values
15
     Takes in the path to file, and which particle type to be included
16
     Returns a dataset
17
             =#
18
            data = filereader(dump_path,
19
20
                types = [Int8, Int32, Float64, Float64, Float64, Float64, Float64,
       Float64], # Define the input types
                header = [:type, :id, :xsu, :ysu, :zsu, :stress_x, :stress_y,
21
        :stress_z], # Set the headers for the dataset
                warn = 0, delimiter = ' ' , ignorerepeated = true)
22
       # Define deilimiter and secure that all lines are taken in
```
```
IMD.filter!(data, :type, by = isequal(type), missings = false)
23
       # takes out wrong defined lines
    \hookrightarrow
            timestep = nrow(filter(data, :id, by = isequal(data.id[1]))) #
24
       Find all occurences of one molecule to define amount of timesteps
            Atoms = Int32(nrow(data)/timestep) #Find numer of atoms
25
            IMD.insertcols!(data, :Dumpnr => repeat(1:Int32(timestep), inner =
26
       Atoms)) # Define which timestep the dump is from
            IMD.insertcols!(data, :Stress => byrow( data, avxnorm, [:stress_x,
27
       :stress_y, :stress_z])) # normalizes the stress per atom
28
     # Repositions the watermolecules in regards to the boundary conditions
29
    \rightarrow (They are outputted as a n*box-size)
     if type == Int8(2)
30
     data[!,[:xsu,:ysu,:zsu]] .%= 1
31
            data[!,[:xsu,:ysu,:zsu]] .+= 1
32
            data[!,[:xsu,:ysu,:zsu]] .%= 1
33
     end
34
            return data
35
   end
36
37
   #The QLL calculation
38
   function calcQLL(data, conf = 0.90, rz = (-10, 15))
39
      #=
40
      The function takes in a dataset containing all ice-molecules with their
41
    → respective crystalline structure
      sets a confidens interval
42
      set a z-level to look into for the top-layer
43
      returns the size of the QLL, the standard deviation used, the h
44
    \hookrightarrow calculated, the kerneldensity estimate calculated and the start and
    \leftrightarrow stopp of the QLL (in regards to the z-axis)
      =#
45
       filter!(data, :structure, by = x \rightarrow x in([0,3,4,5])) #Filter out all
46
       crystalline structures
           # Chill+ output: 0:other, 1: Hexagonal ice, 2: Cubic ice, 3:
47
       Interfacial ice, 4: Gas hydrate, 5: Interfacial gas hydrate
    \hookrightarrow
       dz = IMD.filter(data, :z , by= (z-> z >=(rz[1]) && z<=(rz[2])))</pre>
48
       sigma = IMD.std(dz.z) #
49
       h = ((4 * sigma<sup>5</sup>)/(3 * nrow(dz)))*(1/5)
50
       kde_est = kde([dz.z...],bandwidth = h)
51
       cdf_est = cumsum(kde_est.density) .* step(kde_est.x)
52
       startQLL = findfirst( >=((1 - conf) /2 ), cdf_est) .* step(kde_est.x)
53
       .+ kde_est.x[1]
```

```
54 endQLL = findfirst( >(1- ((1-conf)/2)), cdf_est) .* step(kde_est.x) .+

→ kde_est.x[1]

55 return (size = abs(endQLL .- startQLL), sigma = sigma, h = h, kde =

→ kde_est , start = startQLL,stopp = endQLL)

56 end
```

## C.1 Julia-code:friction from dump-files

```
function fric_from_dump( dump_path::String)
1
        #=
2
        Function deriving an expression for the calculated friction force by
3
        each CH 2 devitaion from inital positions in the direction of
    \rightarrow
       movement(xsu)
        =#
4
        data = dump_read(dump_path , Int8(1))
5
        dumps = last(data.Dumpnr)
6
        dev = zeros(Float64, length(dumps) -1)
7
        d1 = sort(filter(data, :Dumpnr, by = ==(1)), :id)
8
        #Loop over all dumps
9
          for i in enumerate(dumps[2:end])
10
              data1 = sort(filter(data, :Dumpnr, by= ==(i[2])), :id)
11
              dev1 = IMD.sum( data1.xsu .- d1.xsu)
12
              # square the deviation, wilst also keeping the direction
13
              dev[i[1]] = dev1 .* IMD.abs(dev1)
14
          end
15
        # Return the expression f_{friction} = \frac{1}{2}kx * |x| in nano Newtons
16
              return( dev .* 6.953E-21 .* 1E16 .* 0.5)
17
   end
18
```

## D Example output from log and trajectory files

Beneath is examples of the output from the log and trajectory files produced and used in this research. The example of the log file consists of the first 200 lines highlighting how the raw log-files looks, before any data processing. For the trajectory files the first 50 lines are take to give a good insight into how these files are stuctured. The examples shown here is taken from the simulation having Polymer 1,  $\epsilon = \epsilon_0$ ,  $v = 1 \text{ m s}^{-1}$  and  $P_N = 20 \text{ kPa}$ .

## D.1 log-file output

```
1
2 # Read in system
```

```
read_restart ${Loadpath} remap
3
   read restart ../equilibration/sys1/eq.1.rst remap
4
   Reading restart file ....
5
   restart file = 29 Sep 2021, LAMMPS = 29 Sep 2021
6
   restoring atom style molecular from restart
7
   orthogonal box = (-1.8550000 -1.2375000 -126.20485) to (91.940655
8
    → 87.862500 100.00000)
   4 by 4 by 16 MPI processor grid
9
   pair style hybrid stores no restart info
10
   restoring bond style harmonic/omp from restart
11
   restoring angle style harmonic/omp from restart
12
   restoring dihedral style fourier/omp from restart
13
   44928 atoms
14
   16848 bonds
15
   16416 angles
16
   15984 dihedrals
17
   Finding 1-2 1-3 1-4 neighbors ...
18
   special bond factors lj:
                                 0
                                          0
                                                    1
19
   special bond factors coul: 0
                                          0
                                                    1
20
   2 = \max \# of 1-2 neighbors
21
   2 = \max \# of 1-3 neighbors
22
   6 = max # of special neighbors
23
   special bonds CPU = 0.012 seconds
24
   read restart CPU = 0.149 seconds
25
                    hybrid lj/cut 14 sw
   pair_style
26
   pair_coeff
                    1 1 lj/cut ${epsilon_0} 3.675
27
                    1 1 lj/cut 0.091409 3.675
   pair_coeff
28
                    1 2 lj/cut ${epsilonPICE} 3.034
   pair_coeff
29
                    1 2 lj/cut 0.091409 3.034
   pair_coeff
30
                    * * sw parameter.mW NULL mW
   pair_coeff
31
32
   special_bonds lj/coul 0.0 0.0 1.0 angle yes dihedral yes
33
   Finding 1-2 1-3 1-4 neighbors ...
34
   special bond factors lj:
                                          0
                                                    1
35
   special bond factors coul:
                                          0
                                 0
                                                    1
36
   2 = \max \# of 1-2 neighbors
37
   2 = \max \# of 1-3 neighbors
38
   32832 = # of 1-3 neighbors before angle trim
39
   32832 = # of 1-3 neighbors after angle trim
40
   6 = max # of special neighbors
41
   special bonds CPU = 0.004 seconds
42
43
```

```
# Define groups
44
  group PE type 1
                       # Putting all atoms of type CH2 in the polymer
45
   \rightarrow group
  17280 atoms in group PE
46
                        # Putting all atoms of type H20 in the ICE-group
  group ICE type 2
47
  27648 atoms in group ICE
48
49
   # Freeze top layer of the polymer
50
  region stuck block INF INF INF 51.3 51.4
51
   group PE_frozen region stuck
52
  432 atoms in group PE_frozen
53
54
   # make solid ICE walls to mimick moving ICE
55
  region bsICE block INF INF INF INF $(bound(ICE,zmin)) $(bound(ICE,zmin)) +
56
   → 20)
  region bsICE block INF INF INF INF -98.539236315713040426
57
   \rightarrow $(bound(ICE,zmin) + 20)
  region bsICE block INF INF INF INF -98.539236315713040426
   → -78.539236315713040426
  region wsICE block $(bound(ICE,xmin)) $(bound(ICE,xmin) + 6) INF INF
59
   region wsICE block -1.8539592599793837113 $(bound(ICE,xmin) + 6) INF INF
60
   region wsICE block -1.8539592599793837113 4.1460407400206165107 INF INF
61
   region wsICE block -1.8539592599793837113 4.1460407400206165107 INF INF
62
   → -98.539236315713040426 $(bound(ICE,zmax))
  region wsICE block -1.8539592599793837113 4.1460407400206165107 INF INF
63
   → -98.539236315713040426 8.8318669148792245949
  region psICE block INF INF $(bound(ICE,ymin)) $(bound(ICE,ymin) + 6)
64
   region psICE block INF INF -1.2203688086671056201 $(bound(ICE,ymin) + 6)
65
   region psICE block INF INF -1.2203688086671056201 4.7796311913328946019
66
   region psICE block INF INF -1.2203688086671056201 4.7796311913328946019
67
   → -98.539236315713040426 $(bound(ICE,zmax))
  region psICE block INF INF -1.2203688086671056201 4.7796311913328946019
68
   → -98.539236315713040426 8.8318669148792245949
  group bsICE region bsICE
69
  4608 atoms in group bsICE
70
  group wsICE region wsICE
71
```

```
1633 atoms in group wsICE
72
    group psICE region psICE
73
   2288 atoms in group psICE
74
    group sICE
                union bsICE wsICE psICE
75
   7759 atoms in group sICE
76
    group NotSolidICE subtract ICE sICE
77
    19889 atoms in group NotSolidICE
78
79
    # Reset timestep and set timestep for fix move not to jump at first
80
    \rightarrow timestep
   timestep 1
81
    reset_timestep 0
82
83
    # Move the solid ice
84
    fix mv sICE move linear ${speed} NULL NULL
85
    fix mv sICE move linear 1e-05 NULL NULL
86
    # apply normal force
87
    # Compute the force from the pressure
88
    variable Nforce equal v_Npress*lx*ly*1e-20*69.4786e12
89
    fix F_n PE smd cfor ${Nforce} couple ICE NULL NULL auto 0.0
90
    fix F_n PE smd cfor 116.129211492645 couple ICE NULL NULL auto 0.0
91
92
    # Apply soft springs to atoms for measuring applied force by sliding and
93
    \rightarrow pressing ICE
94
    group noFreezePE subtract PE PE_frozen
95
    16848 atoms in group noFreezePE
96
    fix sx noFreezePE spring/self 0.001 x
97
    fix sy noFreezePE spring/self 0.001 y
98
    # Compute the stress
99
   compute stress ICE stress/atom NULL
100
    # Put simulation parameters
101
    group NotSolid union noFreezePE NotSolidICE
102
    36737 atoms in group NotSolid
103
   fix 1 NotSolid nvt temp ${Temp} ${Temp} 100
104
    fix 1 NotSolid nvt temp 260 ${Temp} 100
105
    fix 1 NotSolid nvt temp 260 260 100
106
107
    # Simulation properties
108
    thermo 100
109
    thermo_style custom step temp f_sx f_sy f_F_n[1] f_F_n[2] f_F_n[3]
110
111
```

```
dump 1 all custom 100000 ${Savepath}.dump type id xsu ysu zsu c_stress[1]
112
    \leftrightarrow c stress[2] c stress[3]
   dump 1 all custom 100000 sys1/1/1.1.frictest.dump type id xsu ysu zsu
113
    → c_stress[1] c_stress[2] c_stress[3]
    #Simulate over 100ns
114
   run 10000000
115
   WARNING: Using a manybody potential with bonds/angles/dihedrals and
116
    → special_bond exclusions (src/pair.cpp:244)
   Unused restart file global fix info:
117
   fix style: nvt, fix ID: 2
118
   Unused restart file peratom fix info:
119
   fix style: spring/self, fix ID: 1
120
    Hybrid pair style last /omp style sw
121
   Last active /omp style is dihedral style fourier/omp
122
    Neighbor list info ...
123
    update every 1 steps, delay 10 steps, check yes
124
    max neighbors/atom: 2000, page size: 100000
125
   master list distance cutoff = 16
126
    ghost atom cutoff = 16
127
   binsize = 8, bins = 12 12 29
128
    4 neighbor lists, perpetual/occasional/extra = 4 0 0
129
    (1) pair lj/cut, perpetual, skip from (3)
130
    attributes: half, newton on, omp
131
   pair build: skip/omp
132
   stencil: none
133
134 bin: none
   (2) pair sw, perpetual, skip from (4)
135
    attributes: full, newton on, omp
136
   pair build: skip/omp
137
    stencil: none
138
   bin: none
139
   (3) neighbor class addition, perpetual, half/full from (4)
140
   attributes: half, newton on, omp
141
   pair build: halffull/newton/omp
142
   stencil: none
143
144 bin: none
   (4) neighbor class addition, perpetual
145
   attributes: full, newton on, omp
146
   pair build: full/bin/omp
147
   stencil: full/bin/3d
148
   bin: standard
149
```

150	Per 1	MPI rank memory allocatio	n (min/avg/max) = 15.49   16.87   19.38
	$\hookrightarrow$ 1	Mbytes	
151	<pre>Step Temp f_sx f_sy f_F_n[1] f_F_n[2] f_F_n[3]</pre>		
152	0 20	60.35728 0 0 0 0 -11	6.12921
153	100	244.06577 0.33368403 0	.44402893 0 0 -116.12921
154	200	245.1294 0.70323402 0.	84641115 0 0 -116.12921
155	300	245.71973 0.91011902 1	.0652257 0 0 -116.12921
156	400	247.26005 0.98882421 1	.1720528 0 0 -116.12921
157	500	244.77641 1.0286187 1.	2307264 0 0 -116.12921
158	600	243.54782 1.0614022 1.	248929 0 0 -116.12921
159	700	245.58956 1.0964787 1.	2397765 0 0 -116.12921
160	800	246.18159 1.1300254 1.	2257028 0 0 -116.12921
161	900	246.79956 1.1427564 1.	2287987 0 0 -116.12921
162	1000	246.51938 1.166134 1.	2834821 0 0 -116.12921
163	1100	245.47494 1.1854678 1	.3257675 0 0 -116.12921
164	1200	246.32674 1.1980018 1	.3498424 0 0 -116.12921
165	1300	244.72924 1.2408238 1	.356525 0 0 -116.12921
166	1400	245.08606 1.2685406 1	.3448694 0 0 -116.12921
167	1500	246.36124 1.260915 1.	3424592 0 0 -116.12921
168	1600	248.53311 1.2741769 1	.3631585 0 0 -116.12921
169	1700	247.01895 1.3130749 1	.392113 0 0 -116.12921
170	1800	246.55598 1.3269553 1	.4372744 0 0 -116.12921
171	1900	244.54845 1.3359672 1	.4789742 0 0 -116.12921
172	2000	244.3031 1.3548392 1.	524214 0 0 -116.12921
173	2100	246.47011 1.3550786 1	.5549623 0 0 -116.12921
174	2200	245.59268 1.3243044 1	.5730927 0 0 -116.12921
175	2300	246.63192 1.2985665 1	.5864487 0 0 -116.12921
176	2400	245.47182 1.2758554 1	.64228 0 0 -116.12921
177	2500	245.35839 1.2457542 1	.7041003 0 0 -116.12921
178	2600	244.69845 1.2295641 1	.7532043 0 0 -116.12921
179	2700	245.80177 1.2111386 1	.7960181 0 0 -116.12921
180	2800	245.66871 1.1913178 1	.8358385 0 0 -116.12921
181	2900	247.42902 1.1762485 1	.8919235 0 0 -116.12921
182	3000	245.58308 1.154665 1.	9465316 0 0 -116.12921
183	3100	246.85074 1.1243957 2	.0081808 0 0 -116.12921
184	3200	244.18267 1.1048907 2	.080569 0 0 -116.12921
185	3300	244.20387 1.073822 2.	1335958 0 0 -116.12921
186	3400	247.89979 1.0542142 2	.2091265 0 0 -116.12921
187	3500	245.8969 1.0583439 2.	2796706 0 0 -116.12921
188	3600	246.48552 1.0648452 2	.3492343 0 0 -116.12921
189	3700	245.63018 1.0895063 2	.4000191 0 0 -116.12921
190	3800	245.17391 1.1142848 2	.4149904 0 0 -116.12921

1913900244.690741.152772.433979400-116.129211924000245.924751.17947412.413865600-116.12921

## D.2 Trajectory file example

```
ITEM: TIMESTEP
   0
2
   ITEM: NUMBER OF ATOMS
3
   44928
4
   ITEM: BOX BOUNDS pp pp pp
5
   -1.855000000000000e+00 9.1940654609999996e+01
6
   -1.237500000000000e+00 8.786250000000011e+01
   -1.262048513000000e+02 1.00000000000000e+02
8
   ITEM: ATOMS type id xsu ysu zsu c_stress[1] c_stress[2] c_stress[3]
      18333 0.0704211 0.0581016 0.157895 313699 237569 213367
   2
10
   2
     19147
            0.0734603 0.0893263 0.15688 -248336 107250 -144695
11
            1.04741 1.09849 0.158101 -325198 -121129 -307558
   2
      19446
12
      17873
            1.06495 1.09465 0.139455 -177639 209335 -269753
   2
13
      18108
            0.0822375 0.0507594 0.147315 182547
                                                   134614 50180.4
   2
14
   2
      19057
            0.0426134 0.0470083 0.157041 -50923.8 187217 -271730
15
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