Computer simulations of the dynamics of nanomembranes

Master Thesis

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November 12, 2013

A Thesis submitted to the Department of Physics at the University of Konstanz.
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Abstract

This master thesis is concerned with the dynamics of nano-membranes, which are studied by comparing theory and computer simulations. These simulations use molecular dynamics methods to calculate the individual motion of 10^3 to 10^5 atoms constituting a membrane in the sub-100nm scale in every dimension.

In the proceedings of this thesis studies done on silicon nano beams simulated by the Stillinger-Weber potential were extended to cover membranes. The studies concerned themselves mostly with the time-evolution of the membrane after excitation of mechanical oscillations. The structure, frequency and damping of these modes were studied in dependence on a wide array of parameters like size in different dimensions, temperature and strain.

The extension to membranes has several direct consequences: The dimensionality of the models increases by one and the number of atoms in the simulation increases considerably with associated costs in simulation time and memory. To reduce the first problem the massively parallel LAMMPS [1] program was used, which allows the usage of suitably parallel clusters with an efficiency of nearly 90%.

In order to understand and explain the behavior encountered, the simulations were compared with models from elasticity theory, statistical mechanics and phononics as well as the literature on experiments conducted on real nano-mechanical structures.

The general procedure of the simulation begins with exciting the mechanical main mode by applying a uniform force, which is then removed, letting the system time-evolve. This was done to investigate the process through which a macroscopic excited mode transfers its energy into the other modes to reach thermodynamic equilibrium. One of the goals was finding how this process of energy relaxation happens and how those mechanisms are dependent on other parameters of the setup. For this it was necessary to establish such a process in the simulation, extract the relevant data from it and process those data sets further.

The linear behavior in response to small forces and displacements fits with the predictions of elasticity theory. Additionally, nonlinear behavior that is inaccessible to simple elasticity theory appears and can be investigated. The quantum-mechanical effects familiar from phononic theory are obviously inaccessible to the classical simulation, but the results of the classical limit are quite well reproduced.

A specific process of relaxation could not be identified. The structures investigated exhibit a quite high quality factor and therefore very slow relaxation of the main mechanical excitation. In an effort to decrease the quality factor sufficiently to observe the full process within the simulation, the introduction of crystal faults by removing single atoms had not the effect hoped for. Nevertheless these produced additional results in regard to structural effects, which are not easily accessible by continuous models.

Zusammenfassung

Diese Masterarbeit beschäftigt sich mit der Dynamik von Nanomembranen. Diese werden untersucht indem Theorie und Computersimulationen verglichen werden. Die Simulationen benutzen Molekulardynamik-Methoden um die Bewegungsgleichungen von 10^3 bis 10^5 Atomen zu lösen. Dies entspricht Nanomembranen, die in jeder Dimension unter 100nm messen.

Im Verlauf dieser Arbeit wurden frühere Studien an Nanobrücken auf Membranen erweitert. Als Basis für Interaktionen zwischen den Atomen, die denen von Silizium entsprechen sollten, wurde das Stillinger-Weber-Potential verwendet. In diesen Studien ging es um die Zeitentwicklung der Membran nach Anregung von mechanischen Oscillationen. Untersucht wurde die Struktur, Frequenz und Dämpfung dieser Moden in Abhängigkeit verschiedenster Parameter wie Größe in unterschiedlichen Dimensionen, Temperatur und Stress.

Die Erweiterung auf Membranen hat offensichtliche Konsequenzen: Die Dimension der Modelle erhöht sich um eins und die Anzahl der Atome in der Simulation erhöht sich erheblich mit verbundenen Kosten in Simulationsdauer und Speicheraufwand. Die Simulationen wurden mit dem LAMMPS [1] Simulationsprogramm durchgeführt, welches die Nutzung von passenden parallel Rechenclustern mit Effizienz nahe 90% erlaubt.

Um das beobachtete Verhalten zu verstehen und zu erklären wurden die Simulationen mit Modellen aus der Elastizitätstheorie, der statistischen Mechanik und der Phononik sowie Literatur über Experimente an echten nanomechanischen Strukturen verglichen.

Die Simulationen beginnen mit der Anregung der mechanischen Hauptmode durch Anschalten einer gleichmäßigen Kraft. Diese Kraft wird nach einer gewissen Auslenkung abgeschaltet und die weitere Zeitentwickling des Systems simuliert mit dem Ziel die Prozesse zu untersuchen durch die eine angeregte mechanische Mode ihre Energie abgibt um ins thermische Gleichgewicht zu kommen. Eines der Ziele war herauszufinden wie dieser Relaxationsprozess von statten geht und wie diese Mechanismen von anderen Parametern abhängen.

Das Verhalten der Simulationen stimmt im linearen Regime mit den Vorhersagen auf der Elastizitätstheorie überein. Zusätzlich tauchen nicht-lineare Phänomene auf und können untersucht werden, die der einfachen Elastizitätstheorie nicht zugänglich sind.

Ein spezifischer Relaxationsprozess konnte bei den Simulationen mit dem Stillinger-Weber-Potential nicht identifiziert werden. Die Moden haben eine hohen Qualität und sind entsprechend langsam gedämpft. Im Verlauf von Bemühung des Qualitätsfaktor ausreichend zu reduzieren um den Relaxationsprozess in der Simulation direkt zu beobachten wurden Kristallfehler eingeführt. Dies hatte zwar nicht den gewünschten Effekt, aber produzierte interessante Ergebnisse um Bezug auf Struktur-Effekte, welche ebenfalls für kontinuierliche Modelle nicht leicht zugänglich sind.

Introduction and Motivation The project was started as a continuation of previous work in the group in the SFB 767 “Controlled Nanosystems” Project A06 [3]”Structrual control of nano-scale model systems”. This project deals with the dynamics of nano-mechanical systems in response to external fields and strains; this thesis is aimed to investigate computational models used to simulate such systems. Its goal is to characterize the dynamics of the model and compare it with other theoretical models and some experimental data. It is hoped that such investigations can result in the discovery of inter-dependencies that can be used to set or even control the dynamics of the system, which would allow a wider basis for the construction of nano-machinery. In particular this work should extend the work by Kristian Scholz and Daniel Mutter [11] on the dynamics of nano beams towards experiments done in SFB767-A03 “Control of vibrational modes and dissipation of nanomechanical resonators” on the vibrational modes of silicon nano-membranes and their dissipation [12, 14].

The specific target of this thesis is an extension of prior work done on nano-beams of different materials, characterizing its vibrational modes, its frequency and damping and the dependence of those parameters on controllable factors like temperature, strain and “holes”, as well as boundary conditions. This work will extend the previous investigations to silicon membranes, increasing system size and atom count, but also reducing the degrees of freedom by fixing a plane instead of only a line.

On the practical side this includes the familiarization with the LAMMPS[1] program package as well as basics and concerns of parallelization. For analysis and plotting the tools used include VMD [2] for visualization and simple primary evaluation, Matlab for Fourier transformations and comparison with some simple models and gnuplot for general plotting and fitting.

Problems that were encountered: Larger system result in more computation time can be resolved thanks to good parallelization) and more memory needs, which pose one of the main problems in evaluating simulation data. In contrast to normal experiments a molecular dynamics simulation can provide complete information about position and momentum of every single atom at every single time-step which could lead to massive amounts of data and necessitates in-progress analysis specialized for the currently investigated themes.

The practical problem of the greater resource needs for larger systems is merely a reformulation of the more profound question of how large a system needs to be so that it can be described as a system, instead of a collection of individual particles. This reduces the degrees of freedom needed to describe the system to fewer system parameters from which the individual degrees of freedom are only available as probability distributions.

The first part of the thesis will introduce the theoretical basics upon which the explanations in the following parts are based. These include a short introduction to the simplest model from continuous elasticity theory and the basics of the simulation methods used.

The second part of the thesis concerns itself with the setup and analysis of the simulations, reviewing the Stillinger-Weber potential, explaining the simulation’s setups and

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[1] Large-Scale Atomic/Molecular Massively Parallel Simulator, [9], [1]

[2] Visual Molecular Dynamics [7],[2]

providing comments about the efficiency of the parallelization.

The last part presents the results and discusses them.

Part I

Basics

This physical concern of this thesis is the mechanics of structures consisting of a few thousand to several hundred thousand atoms, which is firmly in the scope of nano materials. The typical question to ask is how such an assortment of atoms behaves, which in practicality means solving the time evolution of the system. Which time evolution equation one solves depends on what feature one wants to look at and of course how good and fast solving the problem is.

The model used in this thesis is a molecular dynamics simulation of the motion of silicon membranes. Membranes generally are defined by the fact that in one dimension the extent of an atom structure is negligible compared to the other two. This general classification applies to many of the simulated structures, although there were some edge cases where the thickness approached the radius of a circular membrane.

Molecular dynamics is a classical method for solving the coupled classical differential equations of all the atoms in the potentials of the other atoms. In general the potentials of the atoms are known only approximately. An arbitrarily exact calculation of the potential is theoretically possible ab initio, for example with Density Functional Theory, but since these calculations are quite expensive molecular dynamics uses pseudo potentials, which are approximations for the forces between the atoms/molecules. These pseudo-potentials are not quantum mechanically exact and restricted in their complexity to interactions of a small number of atoms, typically two or three, in contrast to whole cluster effects and the probability density calculations that would be required in quantum-mechanical calculations.

The model of atoms interacting through a simple independent potential is not completely correct, but for many cases suitable. The interactions between the atoms are considered to be determined through the valence electrons. The behavior of the electrons is firmly in the realm of quantum mechanics, even before one considers the de-localization of the electrons in conducting materials. The calculation of the electron structure increases the amount of particles in the model considerably, but the real problem lies in the interactions of the electrons themselves: As wave-functions the highly localized potential models are not really suited for them. This is especially obvious when one accounts for cluster effects and conduction electrons, where structures quite a distance removed and even large-scale structural configurations can have an influence on local electron density.

Through ab-initio calculations it is possible to determine an energy landscape in a typical crystal, which can be restated as a atom potential. On very common example for such calculations is provided by Density Functional Theory (DFT), which calculates the ground state of the electronic structure for a given geometry of the atoms.

This is done by more or less fixing the atom positions and using a electron density instead of a particle model. With the appropriate interactions terms of the electrons with the atoms and each other it is possible to calculate the ground state of the system, that means its electron distribution and energy. By shifting the atoms around tiny amounts and repeating the calculations it is possible to reconstruct an energy landscape in dependence of the position of the atom, which is pretty much equivalent to a potential only dependent on the spatial coordinates.

The potential used for silicon is the Stillinger-Weber potential [13]. It is a pseudo-potential that aims to recreate the diamond structure of carbon and silicon. It can be used to recreate the structure of the perfect silicon crystals and can be fitted to correspond to several other properties of silicon. Since the diamond structure is not space-filling it cannot be recreated by two-body potentials with only one type of atom, since the least energy state of these potentials obviously needs to be one of the densest packings. In the specific case of the Stillinger-Weber potential a three-body potential is used for the diamond structure.

The simulation allows full access to all position and momentum data, but this complete information does not help much in understanding the processes in models that can be understood in most human brains. In physical terms one is more interested in the thermodynamic parameters, the smallest set of variables that describes the system completely[3].

Finding such useful descriptions is the basic goal of every theoretical work. The goal of these simulations was to investigate some of the connections between atomic scale models and parameters and system scale variables. In regards to mechanics interesting system variables would be whole system modes of motion, for example thickness oscillations or "drum modes" of the whole membrane.

These could be analyzed by themselves in regards to their geometry and frequency, for example with respect to the boundary conditions and extents of the volume. Further their connection to other modes and even microscopic excitations could be investigated, for example the damping of the collective motion into the thermodynamic equilibrium of thermally distributed motion.

In the following sections there will be a short introduction to nano-mechanics, molecular dynamics simulations, elasticity theory and general simulation basics.

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[3] or rather completely in regard to the operations used on it

1 Mechanics of nano scale structures

Nano mechanics concerns itself with all the phenomena that sit in between the quantum mechanical nature of single atoms and smallish clusters at the small scale and macroscopic continuous models and pictures that we encounter on the larger scales. In regards to simulations it ranges from computationally expensive large-scale Density Functional calculations of quantum structures to approximate continuum mechanics simulations of large systems. This work sits between these two extremes, using classical molecular dynamics simulations to simulate the system as consisting of a large number of atoms, whose interactions should recreate the behavior of the real system at least in the classical limit. It is to be expected that the classical calculations remain valid for the majority of parameter choices. In these system even experimental quantum effects should only appear at very low temperatures, where the Bose-Einstein and Fermi-Dirac-distributions are markedly different from the Boltzmann-distribution. Large-scale quantum effects like the superposition or entanglement of whole clusters is already quite unlikely in experiments and will not be dealt with in this thesis.

The main questions in regard to models of real (physical) system are:

- Which behaviors and relations are intrinsic to the model applied?
- How is the behavior of the model determined by the parameters?
- Which effects are out of reach for this model?

The atomic/molecular dynamics model is quite rich in this regard. Its atomic basis allows for easy statistical mechanics calculations, which are more or less artificially superimposed on most continuous models. Furthermore those models can exhibit the full structure of the investigated materials, including crystal faults, breakage and surface effects.

Temperature as a parameter With regards to simulation the normal definition and measurement of temperature can not be as easily transferred. An equilibration with a temperature probe, a thermometer, is quite unfeasible. While introducing a thermometer showing the temperature on a comparable scale would be possible, it is not easy to do so and get reliable data. Some of the problems would be the size of the thermometer-system in comparison to the already very small system under observation, the energy transfer between the system and the thermometer as well as the equilibration time of the whole system. On the other hand this is no problem at all since in molecular dynamics one already has the complete microscopic energy data (potential and kinetic).

In simulations the definition of a temperature is often done with the average kinetic energy per degree of freedom, which is deemed correct by virtue of the equipartition theorem in thermal equilibrium. But the simulations are not in thermal equilibrium and quite often do not run long enough to reach thermal equilibrium. One of the interesting aspects, the transfer of energy in the structure and between the different degrees of freedom, would be completely smoothed away by this definition of temperature.

In equilibrium the temperature is a measure of the average energy per degree of freedom, distributed by one of the basic distribution functions (Maxwell-Boltzmann for classical, continuous system, Bose-Einstein for Bosons and Fermi-Dirac for Fermions). In practice this can be quite a bit more complicated. If continued from the system simply consisting of systems with different statistics [1] the interactions and energy transfer amongst the different subsystems can be very different. This can result in quite interesting behavior if the system is not in thermal equilibrium, for example different heat conduction in the different subsystems or a severely hindered or even locally restricted energy transfer between the subsystems.

The use of using temperature as external parameter lies in the fact, that it is the most general energy-equivalent thermodynamic value, which allows comparisons between widely different experiments and simulations and even a subdivision into smaller systems.

Comparison with experiments In most experiments it is not possible to observe the trajectory of every single atom and most of the time one would not care for this data anyway. As was already mentioned one typically searches for a minimal set of variables and parameters describing the system behavior. In the case of the mechanics of solid bodies the simplest abstraction consists of only the center-of-mass position and velocity. The dynamics of that mass point can be described by an ensemble of harmonic oscillators with frequencies f at least in the linear limit, which also corresponds with an energy. The first step into non-linearity is the addition of damping of some of these oscillators, represented by a quality factor $Q = 2\pi \frac{\text{Energy stored}}{\text{Energy Loss per Period}}$. These are the defining parameters of the oscillator model.

The quality factor establishes how much energy is lost by an oscillator with every period. It gives an estimate how well the oscillator is isolated from its environment, how “good” the oscillator is, that means how well the model of the harmonic oscillator describes the system in question. Since the quality factor divides through the governing timescale of the oscillator model (the oscillation period), it removes those dependencies from the damping constant allowing the direct comparison of oscillators that are different in size and timescale. The damping constant is often easier to fit and measure, since it is the time-constant of the exponential decay in excess energy or amplitude[2].

One way to measure these oscillators is through atomic force microscopes. These can only be used to measure the surface, but are a bit too slow for the dynamics and can strongly influence the dynamics themselves.

More elaborate constructions allow measurements without mechanical contact. This enables the measurement of free oscillations, gaining better time resolution and better control by weakly coupling the system to a electrical oscillator [10]. In exchange one loses

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[1] e.g. electrons and phonons in a solid state system

[2] Those damping constants are identical up to a constant factor.

finer spatial and atomic resolution, more precisely one measures and influences only the whole oscillating system.

2 Basics of molecular dynamics simulations

The keyword "molecular dynamics" encompasses a wide tool-set of methods that deal with one problem: The time-integration of the equation of motion of a many body system consisting of N particles (molecules) with some defined interaction. This typically means $2dN$ coupled differential equations: Here d is the number of dimensions and we solve for momentum and position degrees of freedom. This system of equations which can be solved explicitly, if the coupling is well behaved.

Sufficiently nice in this context depends on the exact circumstances, but the general assumption is a coupling only depending on the current position and momentum of all other particles. One example of this would be a simple two-body potential only dependent on the distance between the particles, like for example the electric field of charged particles. [1] The exact definition of sufficiently nice for explicit computation would be interaction by a "calculable function", which encompasses pretty much everything [2]. While the basic calculation scheme stays the same, the interaction is the determining factor for calculation time and behavior of the resulting system.

From this already follows a quite simple but powerful trick to ease the computation: If the potentials are short-ranged many of the differential equation uncouple, which can simplify the calculation and allows parallelization of the calculation on separate calculation units (cores), where only a border zone (called "halo") needs to be communicated between the cores.

The most basic molecular dynamics simulator just integrates by explicit Euler steps on all particles. While this works, it does not need to follow any of the continuous conservation laws like energy and momentum . The more sophisticated integrators are built with those conservation laws in place. In fact they quite often correspond directly to certain thermodynamic ensembles, which couples them intricately with the different possible thermostats or barostats.

In general, one tries to keep calculation at every single atom simple, aiming to let system properties emerge naturally from the interactions of many particles. This precludes in the most cases exact quantum mechanical treatment of the interaction. This would shift the single particle problem from a function evaluation to solving an eigenvalue and -vector problem, which is considerably more expensive to solve in most realistic cases. A quantum-mechanical treatment of the whole system, including system interactions,

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[1] Or the gravitational field of massive particles, but then we approach special and general relativity where time is not absolute, making the simple explicit scheme of time evolution, though not wrong per se, not such an easy and compelling picture as in the non-relativistic case.

[2] Which makes it pretty much useless as limiting and observable.

scales considerably worse.

Through variation of the different kinds of particles and their interactions nearly every behavior can be simulated by Molecular dynamics. In fact the general molecular dynamics framework has been proven to be Turing-complete. This can be seen by simulating one of the simple cellular automata Turing machines [3]in molecular dynamics. Molecular dynamics is therefore capable of computing every computable function or according to one of the strong formulations of the Church-Turing hypothesis simulating any physical system. The remaining question is how efficient this can be done or to return to the more physical questions:

- How does the interaction model influence the system behavior?
- Which interactions does one need to get certain kinds of behavior?

Simulations approach these questions more or less experimentally, checking the validity of models developed to describe atomistic behavior and comparing the behavior of the simulated system with the real system behavior. But simulations are also useful when using proven models to create configurations and experiments much more rapidly and with more accessible information than real experiments.

The typical values that are attained by system level analysis of molecular dynamics are thermodynamic quantities like energy, temperature, strain, phase transitions, entropy and so forth. Some of these are calculated in this thesis, but a further subdivision into fields of the thermodynamic values is not used for two reasons: Any further subdivision would contain so few atoms that thermodynamic values have quite large deviations from equilibrium values. Furthermore the system investigated in the simulations is not in thermodynamic equilibrium, but should be in the process of relaxing towards it.

Contrariwise and quite interesting from a theoretical view, is that the time integration is time reversible[4], but nonetheless there is damping and dissipation, therefore heat/entropy production, a process that is thermodynamically irreversible. Here one often forgets that thermodynamic values are averages, either over ensembles, or, if one follows the ergodic hypothesis, time. In its time evolution through phase space those values can be nearly arbitrarily different at every instant - conversely no system stays in one phase space point of its thermal equilibrium, but is merely found at one of those points most of the time.

Starting from any arbitrary phase space point[5], the trajectory will spend the majority of time in the equilibrium configuration in the long time limit. To be a bit more precise the probability to spend more time outside of equilibrium space falls exponentially with time. In practice this result is not as useful as one thinks it might be: The average time-constant of the exponential decay may be deduced and approximated from theoretical considerations of available phase space volume, but from this nothing can be said for any finite time trajectory and even any finite set of finite time trajectories. This is especially true for trajectories produced from similar initial configurations.

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[3] e.g. the 2-state 5-color Turing machine [15]

[4] same as the underlying equations

[5] The phase space in this case is the position-momentum phase space of the N particles $\left(\underline{x}, \underline{p}\right)^N$

According to the ergodic hypothesis the phase space trajectory will reach every permissible point in phase space eventually - eventually being the important word here, the time frame can not be limited by anything, especially not the age of the universe or any other arbitrarily large number.

3 Continuous models and elasticity theory

In the first approach we have for the position of every atom the general Newtonian equation of motion:

$$m\ddot{\underline{x}} = \dot{\underline{p}} = \underline{F}$$

The first equality stems from the non-relativistic, atomic model, where a change of the mass of an atom is prohibited. The force $\underline{F}$ can be dependent on many factors, but in this thesis we limit ourselves to particle interactions and external forces applied by a position-dependent potential. Since we are more interested in the internal workings of the system we ignore the position-dependent potential and look at the particle interactions. For this let $\underline{x}$ be the position of a test atom and $\underline{x}_i$ the fixed positions of the other atoms. The force is then a function of these positions:

$$\underline{F} = \underline{F}\left(\underline{x}, \underline{x}_i\right)$$

Let the force be mediated by a field $\underline{F} = \underline{F}\left(x\right)$ by assuming the rest of the crystal to be more or less constant. Then let us develop the force field at some position $\underline{x}_0$ by Taylor-expansion:

$$\underline{F}\left(\underline{x}\right) = \underline{F}\left(\underline{x}_0\right) + \left(\underline{x} - \underline{x}_0\right) \cdot \frac{\partial F_i}{\partial x_j}\left(x_0\right) + O\left(\left(\underline{x} - \underline{x}_0\right)^2\right)$$

If $\underline{x}_0$ is a position of rest the forces need to cancel, which eliminates the first term in the sum. This leaves the linear term with the Jacobian matrix $\frac{\partial F_i}{\partial x_j}\left(x_0\right) = \nabla\underline{F}$. In summation convention and dropping higher order terms the force is given by $\underline{F}\left(\underline{x}\right)_i = \left(\underline{x} - \underline{x}_0\right)_j \frac{\partial F_i}{\partial x_j}\left(x_0\right)$

The basic argumentation regarding the dynamics of two-dimensional membranes according to linear elasticity theory, mostly paraphrased from [5]: We look at the displacement of an atom $\underline{u} = \underline{x} - \underline{x}_0$ from its position of rest. To be more precise in the theory we look at the displacement field $\underline{u}\left(x\right)$, since linear elasticity theory is a continuous theory. The displacement is differs from the position of the atom by a constant, for which the Newtonian equation of motion should be correct:

$$\underline{F} = m\ddot{\underline{x}} \approx m\ddot{\underline{u}}$$

The argumentation like [5]:

The force on an atom in the membrane should be aimed to restore the position of rest as long as the displacement is small enough. Assuming some coupling between the atoms in the medium, if we have no displacement or a constant displacement there should be no internal force. If there is a displacement gradient and the interacting forces are assumed to be symmetric, there should be no net force on the atom.

The simplest approach to the membrane problem in the continuous case and with negligible thickness leads us to the Laplace equation for the displacement $\triangle u = 0$ with a given boundary condition, for example fixed on the boundary $\partial\Omega$: $u|_{\partial\Omega} = 0$. The formulation here is for a scalar displacement. In the simple model, where every displacement direction and its restoring force is assumed to be independent from the other ones up to linear order the extension to a vector would be:

$$\triangle \underline{u} = 0 \qquad \underline{u}|_{\partial\Omega} = 0$$

The solutions to this equation are energy-minimized surfaces, which explains why they are the stable excitations of the membrane.

According to [5] the addition of thickness changes the equation to $\triangle\triangle u = 0$ with the additional boundary condition of vanishing displacement gradient normal to the boundary $\frac{\partial u}{\partial \underline{n}}|_{\partial\Omega} = 0$. $\triangle\triangle$ consists of nine differential terms all of them of fourth order, three are the fourth order derivatives along the axis, the other six are mixed terms of second order derivatives. Under more stringent independence assumptions, this equation can also be extended to a vector displacement:

$$\triangle\triangle \underline{u} = 0 \qquad \frac{\partial \underline{u}}{\partial \underline{n}}|_{\partial\Omega} = 0$$

This constitutes the “plate equation” under pure bending conditions according to the Kirchhoff-Love plate theory. The additional Laplace operator comes from extending the continuous medium and its forces in another dimension - one could imagine a stack of membranes coupled with springs. Physically this would also include a change of a constant, but from the mathematical point of view this multiplicative factor does not matter. In this approach the additional dimensions in which a displacement can occur are ignored as well as the modes that would be coupled to these directions.

The additional boundary term is not strong enough to close the equation, but is necessary since the boundary is now a two-dimensional object with considerably stronger acting forces. For a mechanical picture, imagine fixed boundary conditions and the material growing stiffer with an increase in thickness of the material.

The application of another Laplacian would only add solutions, since every solution of $\triangle u = 0$ is also a solution to this equation. The addition of the boundary condition removes many of these solutions. It should not change too much in the underlying problem and hopefully there are solutions to the Laplacian that fits directly. The Laplace equation is still a reasonable starting point to look for solution concepts and basic modes of the dynamic system, so let us take a look at it in the general case:

$$0 = \triangle f = \partial_x^2 f + \partial_y^2 f = \frac{1}{\rho}\partial_\rho\left(\rho\partial_\rho f\right) + \frac{1}{\rho^2}\partial_\phi^2 f$$

With rectangular boundary conditions this equation would be fully separable and could be solved by multiplying the solutions to the ordinary differential equations, which would simply be sine and cosine for reasonably easy boundary conditions and Fourier series for more complicated ones.

$$f = f_1(x) f_2(y) \Rightarrow 0 = \partial_x^2 f + \partial_y^2 f = f_2 \partial_x^2 f_1 + f_1 \partial_y^2 f_2$$

$$\Rightarrow \frac{1}{f_1}\partial_x^2 f_1 = -\frac{1}{f_2}\partial_y^2 f_2 = k = const.$$

$$\Rightarrow \partial_x^2 f_1 = k f_1 \wedge \partial_y^2 f_2 = -k f_2$$

The cylindrical problem is not quite as nice. While the problem is still separable, only the angle dependent part results in an easy-to-solve, ordinary differential equation, again resulting in sine/cosine solutions.

$$f = f_1(\rho) f_2(\phi) \Rightarrow f_2 \frac{1}{\rho}\partial_\rho \left(\rho \partial_\rho f_1(\rho)\right) + \frac{1}{\rho^2} f_1 \partial_\phi^2 f_2 = 0$$

$$\Leftrightarrow \frac{\rho}{f_1}\partial_\rho \left(\rho \partial_\rho f_1(\rho)\right) = -\frac{1}{f_2}\partial_\phi^2 f_2 = const. = k$$

$$\Leftrightarrow \partial_\phi^2 f_2 = -k f_2 \wedge \rho^2 \partial_\rho^2 f_1 + \rho \partial_\rho f_1 - k f_1 = 0$$

The radius-dependent part results in a form very similar to that of the Bessel equation:

$$x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + \left(x^2 - \alpha^2\right) y = 0$$

The solutions to these equations are the eponymous Bessel functions. To be more precise, it will be Bessel functions of the first kind, since the α is a positive real number. The Bessel functions of the first kind J_α can be written as a Taylor series and are shown in 3.0.1.

These or series consisting of them constitute the basic solutions and modes of the mathematical membrane and can serve as background to characterize and evaluate the motions actually observed in the membranes encountered in practice. Of the Bessel functions of first kind only J_0 provides a non-zero value at $\rho = x = 0$, which makes it the prime candidate or the basic excitation of a membrane.

The Bessel functions do not provide a wave-length dependence quite as simple as their harmonic counterpart in 1D, where the wavelengths are simple integer fractions of a fundamental wavelength. Similarly complicated is their connection with the distribution of kinetic and potential energy in the system and conversely the frequency-energy relations in the system.

For increasing radius r the amplitude of the Bessel functions drop off with approximately $1/r$.

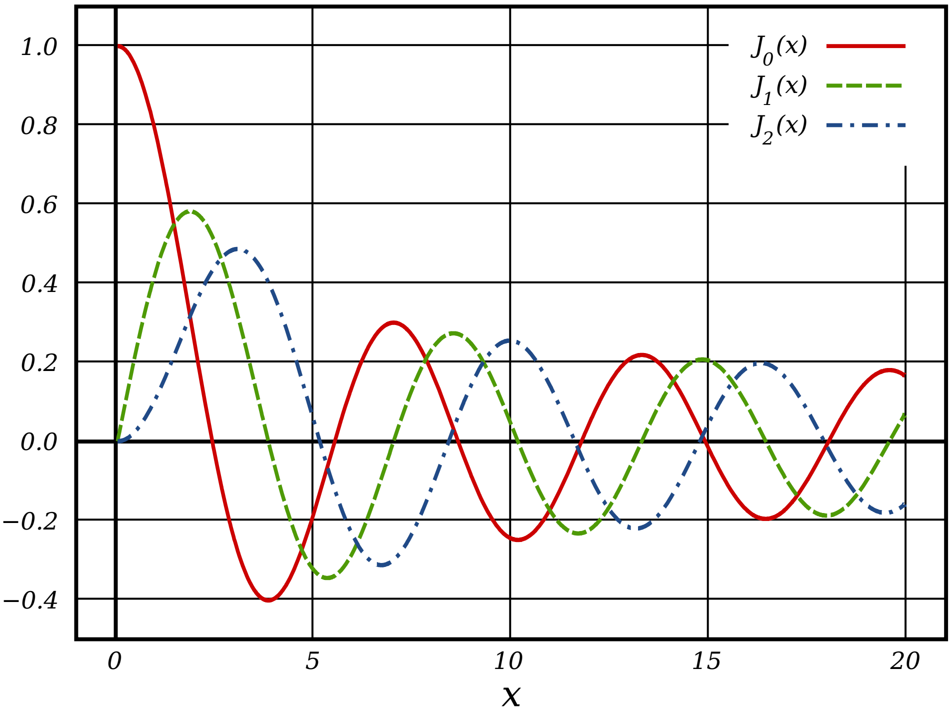

Figure 3.0.1: Bessel functions of first kind J_α. Source: [8]

4 Computational basics and data extraction

The explicit calculation of the n coupled differential equations reduces in calculation costs to basically n times the functional evaluation of the interaction. This can be parallelized quite easily since the time evolution of every atom only needs the information of the atoms within a certain interaction radius.

As an illustration: Assuming linear interactions, the time evolution could be imagined to be done by a matrix which is nearly diagonal in the sense that only the fraction of atoms in the interaction radius are referenced in the row. This allows for some parallelization of the whole matrix since you only need a fraction of the whole data to calculate the force value at any single atom. The limits of this parallelization are also obvious, since you need all this data for the calculation which needs to be communicated.

In simulations one quite often has the complimentary problem to that in experiments, instead of it being enough to get some data in a reproducible fashion, one desperately needs to reduce the amount of data to manageable levels. For this one often recreates some kind of measuring apparatus/filter in the computer. This on the other hand is quite useful for comparison with experiments themselves, since one can more or less simulate the whole experiment, instead of only the investigated system.

This allows for direct comparison with experimental data, testing the models used and verifying the correctness of the implementation.

How fast a simulation can be performed is determined by how many and what kind of calculations need to be done at each time-step. For this study we stay at a pretty abstract level and say every atom needs to be time-evolved, which is a function evaluation needing data from the neighboring atoms. This means that the calculation for the individual atoms are nearly independent, which allows parallelization across multiple serial calculating engines (CPUs or CPU cores, in continuation CU - Calculation Unit).

Since in practice keeping all data accessible for every CU proved to be not indefinitely scalable[1], the atom data is also distributed to the memory associated to the CUs, such that every CU has the data necessary for its own calculation. This includes the atoms that are time-integrated by that CU and the data of every atom that is not time-integrated by that CU, but influences the time-integration by being included in the calculation through interaction terms - these are commonly called “ghost atoms”.

After every time-step it is now only necessary to communicate any change in the ghost atoms, which reduces the amount that needs to be communicated overall and between individual pairs of CUs.

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[1] the access times were too slow for any CU not directly associated with that memory

Assuming a spatial parallelization, this would mean that every CU has a volume to calculate and only a volume of about two interaction lengths on the surface of these volumes has to be communicated with the neighboring CUs[2]. This communication is the limiting factor to the efficiency of the parallelization: As soon as communication of the new border surface takes appreciable fractions of the time of the calculation in the volume the gain of further parallelization drops. Performance gains from parallelization vanish when communication on the border and calculation take about the same time and could even turn into a loss[3].

The spatial parallelization is one of the most obvious parallelization schemes and well suited for uniform atom distributions in the simulation box, e.g. completely liquid or gas filled volumes and especially lattice systems like e.g. the Ising or Heisenberg interaction models or Lattice Boltzmann Fluid models. For the system used in this thesis - a solid state system that undergoes quite large system motions - a deviation from this is prudent. A purely spatial parallelization of the simulation box would lead to unequal distributions of atoms and the systematic motion would lead to many transfers of atoms from one CU to another.

The unequal distribution could be elevated by varying the volume belonging to one CU [4], but the solid state nature of the system allows an even better solution: Since the structure is stable with only rare single atom exchanges, one can parallelize along this structure, grouping atoms that are spatially close under the assumption that they stay more or less together over extended stretches of the time evolution, they should even be connected to the same neighboring groups.

These groups are saved with the adjacent volumes and the associated ghost atoms of the neighbors and the local volume saved in so-called neighbor lists. For a comparatively small price of extending the border regions somewhat (by about 50%) one reduces the number of atom transfers considerably.

Data extraction and analysis Although possible in practice, an extraction of the complete data from the simulation would require sending and gathering everything, increasing the communication time markedly. In addition, the amount of data can increase rapidly, for a mere 10^4 isotropic atoms, in 3 dimensions [5] with 32 bits per degree of freedom, one has $6 \cdot 10^4 \cdot 4 = 240$MB of data per time-step. Even a rather short simulation of 10^4 time-steps produces an amount of data comparable to the largest single data storage devices.

This necessitates the usage of filters and preliminary analysis in the simulation run itself.

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[2] The neighboring volumes and associated CUs are saved in so called "neighbor lists".

[3] Happens when the fraction of communication to calculation time is greater than 1, $\frac{t_{com}}{t_{cal}} > 1$.

[4] Varying the volume is quite tricky, simply increasing the volume until one has the same number of atoms in every volume can result in having to communicate with more other CUs. If one looks at a system with a defined surface the worst case example is a huge volume containing the exterior and only the surface of the system, which then needs to communicate with every CU with a volume bordering the surface.

[5] 6 degrees of freedom, 3 kinetic and 3 potential

One simple filter is only using every nth time-step. This can be very effective if the interesting dynamics happen in a time scale much larger than the integration time-step . The integration time-step is chosen primarily for reasons of numerical stability, which in molecular dynamics is connected directly to energy conservation and is mainly determined by the microscopic motion, which should be considerably faster than any whole system dynamics. This is a natural time scale separation, which can be quite helpful, but does not reduce any single data set appreciably.

Part II

Work and Setup

As starting point there was a simulation script for LAMMPS which created a silicon bridge of $6 \times 6 \times 40$ unit cells[6] of atoms at 0K, fixated the ends, applied some force to the free atoms to move the beam out of its resting position, released the force again and then just simulated the dynamics for a given time. The dynamics were then investigated by determining the frequency and damping of the vibrational mode that was excited by the force. These values were further investigated by varying parameters that seemed accessible to experimental approaches like starting temperature and unidirectional strain on the bridge[7].

At the same time parallel literature studies about nano-mechanics [6] and LAMMPS [4] were conducted.

LAMMPS uses an internal unit system specialized to the simulated material to simplify calculations and reduce the accumulation of numerical errors. The Lennard-Jones simulations use a very basic system normalized on the parameters of the Lennard-Jones potential, for this LAMMPS sets the quantities particle mass, σ, ϵ and the Boltzmann constant to one: Distances are given in multiples of σ, the zero crossing of the Lennard-Jones potential. Energies are given in multiples of ϵ, the depth of the potential well and the maximal energy a Lennard-Jones particle can acquire by falling into the potential from “infinity”. The temperature is given as a multiple of ϵ without any further factors.

For silicon metal units are used, which have the following conversions:

Quantity	Unit used
Mass	grams/mole
Distance	Angstroms (10^{-10}m)
Time	picoseconds (10^{-12}s)
Energy	Electronvolt (eV)
Temperature	Kelvin (K)
Velocity	Angstroms/picosecond ($10^2 \frac{\mathrm{m}}{\mathrm{s}}$)
Force	Electronvolt/Angstrom

These units are used implicitly for all data pertaining to silicon simulations throughout the thesis. In some cases IU was used to explicitly denote the usage of those internal units. This rule has one exception: The timestep quantity and unit is not equivalent to the internal time, since the length of a timestep can be set for each simulation separately to focus on dynamics on different time scales. For silicon energy conservation requires a timestep to be at most $1\text{timestep} = 0.001\text{IU} = 1\text{fs}$, divergences from this rule are stated explicitly.

The simulation proceeded without any larger problems.

For the cases where the starting temperature needed to be changed a Langevin thermostat was used to simulate a heat-bath around the particles giving them random boosts

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[6] The diamond structure has 8 atoms in every unit cell. A complete unit cell has 18 , 4 within, 6 on the sides and 8 in the corners. (The simulation now has around $1.2 \cdot 10^4$ atoms).

[7] Implemented by applying a constant force to the ends of the beam, extending the structure, saving the resulting configuration at certain intervals and using those configurations as the starting structure of the normal simulation scheme.

with the appropriate distribution. This was done after rescaling thermostat (Berendsen) seemed to excite some “frozen” mode further, inducing large scale system motion, instead of the distributed thermal motion one would expect of a body in thermal equilibrium.

Fixed atoms are used as boundary conditions. For the beams it is somewhat more useful to restrict the motion of the boundary atoms on the beam axis instead of fixating the atom position. This allows for relaxation of any longitudinal strains and stresses in the system. In later experiments this makes it possible to introduce such a stress and induced strain by hand. For membranes this restriction of the motion can also be done in rectangular configuration, but for a circular membrane practically every boundary atom would need its own fixed direction, making the setup quite complicated and very inflexible. Restricting only on two dimensions in the case of circular membranes is possible, but would introduce further problems in that there would be no friction to stop any center of mass motion or rotation, something that can be introduced through force imbalances on the boundaries, e.g. through slightly different cuts through the unit cells of the crystal at different points along the ring. Instead of balancing this crystal perfectly it was seen as considerably easier to just fixate the border.

The silicon beam structure used for the first trials was created by another program, which produces the structure with the minimal free energy. This includes surface reconstruction, a reordering of surface atoms with their free bonds away from the bulk configuration into a energetically “better” 2×1 symmetric dimer “paired-row” setup. This surface reconstruction is an experimentally observed feature that is quite well reproduced by the Stillinger-Weber potential. This further indicates that the Stillinger-Weber potential reproduces the structural properties of silicon.

This prefabricated structure is not directly extensible to all the simulations planned, requiring adjustment for every change in size of the simulated structure or the structure itself (e.g. for Lennard-Jones particles or introduction of crystal faults). LAMMPS allows the direct creation of atomic structures in certain lattice configurations of which diamond is one. These created structures lack the surface reconstruction, but should exhibit the same bulk behavior.

Membranes and beams consisting of atoms interacting through the Lennard-Jones potential serve as comparison, since those are the standard toy model in molecular dynamics. They serve as a bare-bones structure and a background against which one can see the differences that the additional structure of the Stillinger-Weber potential brings into the dynamics. One very welcome effect is that the vibrational modes in a Lennard-Jones structure relax very fast, which gives a measurable damping on time scales considerably shorter than those necessary for silicon.

The molecular dynamics simulations within LAMMPS scales quite well with the volume/size of the simulation, allowing for a late onset of diminishing returns of parallelization for single time-steps and providing reasonable calculation times for atom numbers from hundreds to thousands per core. These parallelizations are still far from allowing the atomistic setup to scale to experimental setups. One small nano-scale membrane had measurements of $714\mu\text{m} \times 691\mu\text{m} \times 340\text{nm}$, which would amount to about $8 \cdot 10^{15}$ atoms, for which one would need on the order of one trillion cores in parallel. This is still several orders of magnitude above the capacity of current supercomputers ($\approx 10^5 - 10^6$cores), especially since it is doubtful that this up-scaling of the problem would result in fundamentally new aspects, which could not have been gotten by simple and not so simple scaling approximations from smaller simulations.

In trying to understand the smaller simulations two problems became obvious:

Perfect silicon is quite stiff, the damping of the primary excited mode can only be conclusively determined in simulations reaching about 10 million time-steps, which would be equivalent to about 10ns. To be a bit more precise, the problem is, that the time scale of one oscillation is around 10ps, about equivalent to 10000 time-steps, separating the timescales by three orders of magnitude, with corresponding costs in calculation times - one can not increase the time-steps without losing the microscopic motion (and energy conservation) and one can not shorten the simulation time without hiding the relaxation in possible noise.

The second problem is the massive amount of data such long simulations can produce. The full data of a single simulation would amount to

$$10000\text{atoms} \times 10^{7}\text{timesteps} \times 12\frac{\text{bytes}}{\text{atom} \times \text{timestep}} \approx 10^{12}\text{bytes} = 1\text{Tb}$$

which is too much for both: normal storage and analysis without splitting. For these reasons it's necessary to reduce this data amount to something that can still resolve the motion while getting rid of much of the redundant information, basically switching from atom data to structure/solid state data. The easiest and most obvious step is dropping some of the time resolution in the output, since the highest time resolution was only necessary to guarantee energy conservation in the calculation. This alone together with some space averaging drops the memory requirements to manageable amounts. The more interesting part is of course how one can describe those systems even more concise through system level description and how and where those descriptions fail, mirroring the development of the system variables in thermodynamics and basic solutions in continuum mechanics.

The typical approach to the description of system dynamics starts off from rigid bodies, adds bending and finally ends in the continuous elasticity theory, where the bodies are described through a continuous body fulfilling stress-strain relations according to some specific constitutive equation. The stable solutions to the differential equation thus posed are used as basic descriptions of system dynamics and are called “modes” in extension of the harmonic modes in 1D strings.

Basic Procedure

1. Setup of membrane structure and boundary conditions.
2. Thermal equilibration of membrane to a chosen temperature.
3. Disturbing the equilibrium with an external force.
4. Observing the resulting dynamics (or more precise, letting the simulation run and periodically calculate some value deemed interesting).

The Lennard-Jones Potential provides a simple framework to quickly test new simulations and analysis methods, providing only small direct computation speed-up [8], but allowing a comparison to a simpler and better understood model with considerably faster dynamics. The general, basic oscillations can be seen and their form can be analyzed and compared. The isotropic Lennard-Jones potential provides a not very steep well and more easy degrees of motion , which allows for very fast damping of the collective mode. The Lennard-Jones model is not really suitable for interesting solid state crystals, since its isotropic potential does not provide any structure in excess of the densest sphere packing close to the energetic minimum.

The Lennard-Jones potential is a simple polynomial model of the pair interactions of Argon. This model is also applicable for the other noble gases and other materials (colloids) that exhibit a short-range attraction and shorter ranged repulsion without any more complicated structure. This lack of an intrinsic structure lead to a condensation into a densest packing - hexagonal or cubic, dependent on the pressure. Some of the direct effects of this are that the structure is not as stiff as the Stillinger-Weber potential, but is easily deformable and structural reorderings are quite common. Additionally the condensed structure evaporates at very low mean kinetic energy. In another description of the easy motion of its atoms in its condensed state: the phonons - the excitations of the crystal lattice - are not very well defined and their effect can be easily masked by motion of the atom. In general every system motion is not very well conserved and will be dampened within a short time.

In practice the Lennard-Jones time evolution computes about twice as fast as the same number of atoms in the Stillinger-Weber potential. While this is an obvious speed-up it is still somewhat low, since the Lennard-Jones potential is considerably easier than the Stillinger-Weber potential. The reasons for that could not be determined conclusively, but a difference in the count of nearest neighbors seems to be the most likely candidate. The silicon atoms should have four nearest neighbors in their typical tetrahedral structure, while Lennard-Jones particles can have up to twelve nearest neighbors in their densest packing. If the interaction cut-off radius is chosen accordingly, the difference in calculation time could come from this alone.

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[8] about double speed

5 The Stillinger-Weber potential

The Stillinger-Weber potential was constructed specifically to recreate diamond structures [13]. Here the atoms are bound in a tetrahedral structure with the tetrahedron angles[1] between different neighboring atoms. For this the potential requires three-body terms, in this case the angle between atoms enters directly into the calculation and with a stronger preference for the tetrahedral angles, disincentivizing rotations.

The parameters of the Stillinger-Weber potential were further optimized to conform with the elasticity tensor measured for silicon, which should yield a large-scale behavior very similar to those models, at least in the linear limit of small displacements.

The following paragraphs are pretty much a direct translation of the corresponding part of [11] with some additional comments.

With r_{ij} being the distance between particles i and j, the Stillinger-Weber potential has the general form

$$\Phi = \sum_{i<j} \phi_2 \left(r_{ij}\right) + \sum_{i<j<k} \phi_3 \left(\underline{r}_i, \underline{r}_j, \underline{r}_k\right)$$

consisting of a distance dependent two-body term ϕ_2 and a more complicated three-body term ϕ_3 dependent on the position of three atoms. The pair potential of the Stillinger-Weber potential has the form:

$$\phi_2 \left(r_{ij}\right) = \begin{cases} A(Br^{-q} - r^{-q}) \exp\left(\frac{1}{r-a}\right), & r < a \\ 0 & r \geq a \end{cases}$$

This is a polynomial potential similar to the Lennard-Jones potential with attractive and repulsive part multiplied with an exponential decay which forces the potential to zero at the cut-off radius a. The three-body potential consists of three parts, which each correspond to one permutation of the three indices. These parts depend on both of the distance vectors as well as the angle between the distance vectors $\Theta_{ijk} = \sphericalangle \left(\underline{r}_{ij}, \underline{r}_{ik}\right)$:

$$\phi_3 \left(\underline{r}_i, \underline{r}_j, \underline{r}_k\right) = h\left(r_{ij}, r_{ik}, \Theta_{jik}\right) + h\left(r_{ji}, r_{jk}, \Theta_{ijk}\right) + h\left(r_{ki}, r_{kj}, \Theta_{ikj}\right)$$

The h-terms have the form

$$h_{jik} = h\left(r_{ij}, r_{ik}, \Theta_{jik}\right) = \begin{cases} \lambda \exp\left(\frac{\gamma}{r_{ij}-a} + \frac{\gamma}{r_{ik}-a}\right) \cdot \left(\cos\Theta_{jik} + \frac{1}{3}\right)^2 & r < a \\ 0 & r \geq a \end{cases}$$

This function is zero and minimal for $\cos\Theta = -\frac{1}{3}$, which occurs for the tetrahedron angle $\Theta = 109.47°$.

---

[1] 109.47°

The typical parameter values for silicon were presented by [13] and used as provided by [11] for LAMMPS

Parameter	Value
A	7.049556277
B	0.6022245584
p	4
q	0
a	1.8
λ	21
γ	1.2

With the parameters used this potential is considerably deeper and steeper than most of the Lennard-Jones potentials in use [2] and provides the additional angle-dependent terms which favor the tetrahedral structure in the local order.

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[2] The degree of the polynomial is lower, but the constants factors are much higher for the energy and smaller for cut-off distance.

6 Practical computational concerns

In the simplest term the computational time increases linearly with the number of timesteps and with the number of atoms. The working memory requirements rise linearly with the number of atoms (this includes the additional memory cost of parallelization). The amount of data produced depends on the extraction scheme more than on the size of the problem.

The parallelization of this problem is very good. With a rather small overhead for communication, thermodynamic calculations and data, the calculation speed is proportional to the number of cores used. This stays true until the single core volumes are so small that the atoms in the surface that needs to be communicated constitute an appreciable fraction of the number of atoms per processor. Soon afterwards one reaches diminishing returns in the gains of further parallelization, making further attempts in that direction inefficient.

This can be seen in this scaling plot for 179411 atoms on the Juropa cluster tested for.

The theoretical limit of the speedup is a simple 1-1 linear relation. The optimal real speedup is linear with a constant factor smaller than 1, indicative of how much of the additional resources are needed to conduct the parallelization. This is represented in the extrapolated curve, where one simply extrapolated the increase of the first three test points. While the increase starts out linear with a parallelization factor (efficiency) of $\approx 88\%$. The speed-up decreases massively with more cores.

Run-time evaluations show that the fraction of the resources spent on the calculation of pair interactions stays constant up to 248 cores (at above 60%). But this fraction then rapidly decreases, dropping down to near 25% with 2048 cores. This most probably follow from needing to communicate a higher fractions of the atoms since the surface area that needs to be communicated increases linearly with the number of cores c, while the number of independent calculations per core decreases with $\frac{1}{c}$ (every core has a smaller fraction of the overall atoms).

To test this hypothesis the number of cores were re-normalized to "cores occupied with pair interactions" by multiplying the numbers of cores with percentage spend on calculating pair potentials. Here the linear speed up is recovered up to 488 cores. The even higher core numbers are shifted downward, indicating a constant additional cost (possibly the communication of second-next neighbors). Additionally, the slope seems to be somewhat less steep.

All in all parallelization allows the calculation of much larger system, but the question remains if this is useful and necessary, since smaller system already exhibit very good alignment with results of experiments and elasticity theory. It is quite unlikely that scaling the system ever larger will result in novel behavior worth the additional costs and not accessible by an appropriate choice of parameters for a smaller simulation. Of course

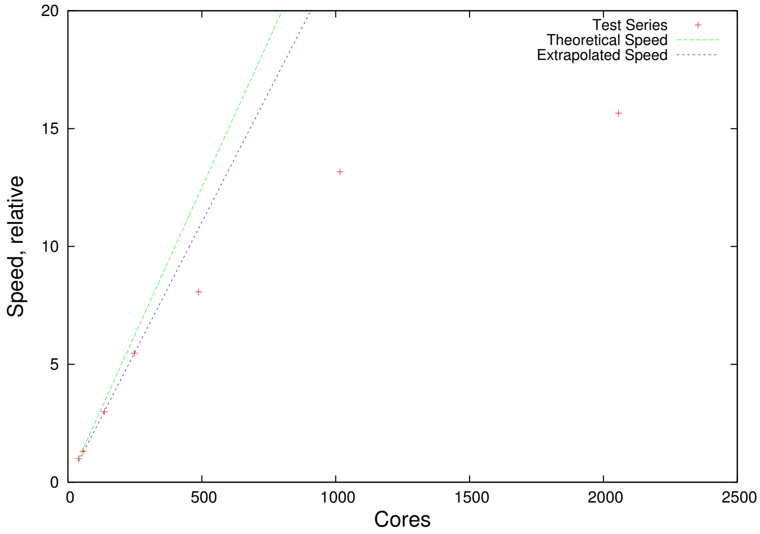

Figure 6.0.1: In this plot is depicted the increase of calculation speed with increasing number of processors/cores. The speed is gained by dividing through the execution time and normalized on the time needed on 5 nodes (40cores). The theoretical speed-up is represented by a linear curve of incline 1. The extrapolated curve is a linear fit of the first 3 points.

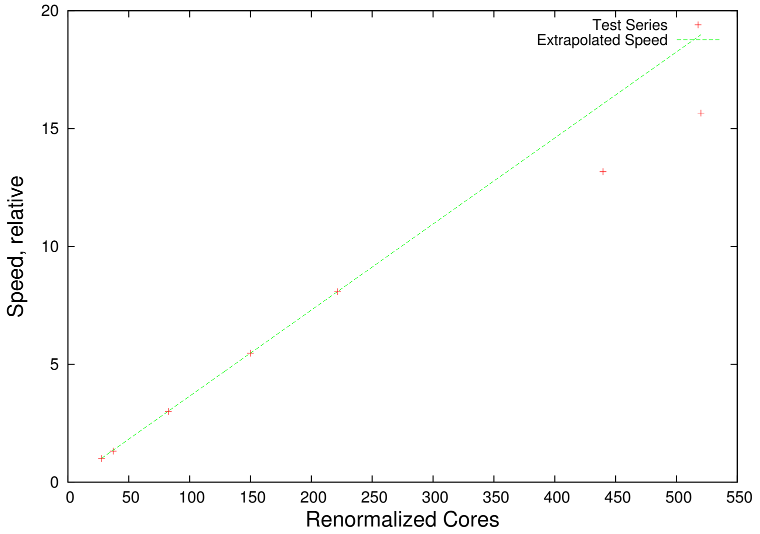

Figure 6.0.2: The same figure as 2.2.1, but the cores were re-normalized with the percentage of time spend of pair calculations.

these large scale simulations are useful to test the scaling and in providing direct comparisons to experiments, but their usefulness as replacement for actual experiments is slim. Especially since they compete here with direct finite element simulations of elasticity theory, which scale a lot better for macroscopic orders of magnitude by smoothing away the atoms. The one large advantage of molecular dynamics here is that they provide atomic and structural information, much better suited for the appearance of rare events, local restructurings and surface effects.

7 Simulation regimes and extraction methods

The basis for practically all the simulations is a round membrane with a fixed ring of atoms as boundary condition. The fixation happens by simply not time integrating those atoms. This was primarily chosen to prevent more or less random normal and angular momentum from introducing large systemic changes in the system. One could also fix only part of the circumference, but this would cause a mixture of fixed and open boundary conditions. This would be interesting, especially considering mode scattering at the boundary, but will not be investigated in this work.

The membranes are created in the diamond structure - typical measurements are a radius of eleven unit cells, with the outermost ring fixed and a thickness of about two unit cells. Many different sizes of membranes were tested. These would exhibit radii up to forty unit cells and thickness of up to ten unit cells and consisted of up to 160000 atoms.

Membranes of radius ten and thickness two were found to exhibit all of the phenomena described in this thesis combined with reasonable calculation times and memory needs - about three hours for the calculation of one nanosecond on four cores. These membranes consist of 6851 atoms of which 5675 are time evolved, the rest constitutes the fixed boundary condition. In the remainder of the thesis membranes of this size provide the standard and every membrane simulation presented uses them if not explicitly stated otherwise.

The atoms within this fixed circumference constitute the actual membrane, the dynamics of which are investigated. All atoms are setup close to their equilibrium structure: a diamond structure with a unit cell length of 0.542nm for the SW potential and cubic body centered for Lennard-Jones membranes with a unit cell length of 1 in the appropriate reduced units. Or to be more precise, they are set up as a cut-out of a larger bulk in the given structure, without regards to the energetic optimality of the surface structure. They are time-integrated in an NVE ensemble (constant number, volume and energy) which is the most common approach for solid state systems. This corresponds to an experimental setup of a (suitably) isolated system.

After the setup, several thousand time-steps are integrated to check for obvious inconsistencies. This is optionally preceded/interspersed by several thousand time-steps of integration under a thermostat, which sets the kinetic energy to a value corresponding to the desired temperature. After the thermostatting phase an additional equilibration phase of several thousand steps is performed, to distribute the energy introduced into the other degrees of freedom, particularly the potential energy.

Then the interesting part begins by exciting specific modes, which is typically done by applying a constant force to the membrane for some fixed length of time. In this thesis it is either a constant force perpendicular to the largest area of the membrane, applied to all atoms, which excites the basic drum mode. Further studies were done with counteracting “tearing” forces on the surface layer, which should excite basic thickness oscillations.

This force is then removed again and the simulation runs up to several million timesteps recreating the dynamics after such excitation. From considerations in Fourier space with a simple parabolic approximation, one would expect a damped oscillation for perfect excitation and a mixture of several damped oscillations for imperfect excitations.

The positional data of the several thousand atoms alone reaches amounts neither easily stored nor handled, therefore a complete positional snapshot is only done rarely to provide a possibility to check the simulations “by eye” with VMD (Visualization of Molecular Data [2]). Besides the thermodynamic data (temperature, kinetic, potential and total energy) the main data sets extracted are from certain pre-selected regions and groups of atoms. These sets and the values extracted are:

For the drum modes: The 15 atoms in the central 1x1x1 cube, their average height (z-axis coordinate), the direction in which the drum mode is expected to move and their average velocity in this direction. These atoms are the one displaced the furthest by the initial application of force and their position in the center makes their involvement in any systemic motions and modes very probable. In that sense they are not unlike the center-of-mass position and velocity, which would provide similar data, but is not able to also serve as a sample subset to be compared with probe sets of other simulations and at other positions in the membrane. Furthermore the same data set for cubes next to the center and halfway to the circumference were extracted to compare and to check against influence from mode-symmetries.

For the thickness oscillations: The atoms in the upper and lower surface layers constitute the groups in this case, the data collected is their average z-distance. The full surface was used instead of subgroups, because violent motions and strongly excited larger modes could change the alignment of those samples to each other. In addition, the groups existed already in order to apply the force to them.

LAMMPS provides several thermodynamic values like overall, kinetic and potential energy as well as pressure and temperature in its standard output. These should be largely unexciting, but provide an additional check and chance for further comparisons.

Frequency I tried a simple reproduction of earlier results in the case of beams: Here the relevant parameters tested were the frequency of the main mode, which can be easily extracted by Fourier transforming any positional data of the moving parts. It can also be extracted in a more complicated way by fitting a oscillation to the data, but this rarely works very well, since the optimization surface for the standard least-sum-of-squares (lsq) method itself has many sinusoidal components, making simple optimization routines only useful very close to the real value.

Fourier transforming has the further advantage of retaining much of the information, in this case all of the frequency components, which allows the identification of the higher modes and their relative amplitude. Since the Fourier transform is done in the time-frequency domain one transforms all time dependence. This can be regained by splitting the FT in sufficiently large subsets, which allows observing changes in the spectrum over time.

Damping When applicable the quality factor or damping constant[1] of the mechanical oscillator were determined by fitting an exponential decay to the amplitude of the oscillator. Two other approaches to the damping using the Fourier space were tried albeit with even less success: The width of the peak in the Fourier transform allows for a very rough guess at the damping, since it corresponds to how well the harmonic approximation fits the oscillator in question, but without knowledge or good prior guesses which mechanism changes the oscillator one is left with only qualitative statements.

Based on the model of a oscillator dampened by friction driven by an external oscillation another approach was tried: If one scans through the driving frequencies the amplitude of the oscillator should exhibit a resonance peak whose width can be mathematically connected to the friction coefficient, which would be practically equivalent to a damping coefficient. The simulation undertaken in that direction proved to be quite time-consuming and did not provide sufficient resolution. In the simplest approach[2] one of these problems could only be elevated at the expense of the other, which lead to a discontinuation of this avenue of research.

Structure Crystal faults were introduced by deleting every nth atom, where n is a number with no common denominator with the number of atoms in a unit cell to prevent the introduction of additional structural effects. n was chosen as a prime number, such that $1/n$ is close to a percentage between 0.03 and 3 percent. This was done in the hope of accelerating the relaxation and to see what would happen.

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[1] Quality factor and damping constant determine each other if the frequency is known.

[2] Just trying different frequencies.

Part III

Results

8 Beams - Geometries, frequency and quality factors

Let us start with looking at the simulations of the beams, to get a basic overview of what seems interesting: The form of the basic modes, its frequency and damping to later compare it against the data from the membrane case. These simulations served as test cases and were taken from [11] and reimplemented in LAMMPS. The results coincide in the observed cases and repeated here for future comparison. Further investigated were the differences between silicon and Lennard-Jones potential particles in these simulations.

These explanations pertain largely to the linear regimen. But molecular dynamics also allows an exploration of non-linear effects. While a too high force just rips the system from its boundary conditions, in the silicon case there is an additional in-between case where a too high force "breaks" the structure introducing a reordering that stays stable for some time - these stable structural effects are impossible in the linear models.

Concerning the direction of the oscillation, a first assumption is that silicon should here also be more rigid against shifts. It is not, more specifically, the only samples, where one sees a wandering of the oscillation direction are silicon samples. The initial explanation is wrong. Another approach: Lennard-Jones interactions are completely isotropic, while the Stillinger-Weber potential has directional bias , breaking the rotational symmetry and forcing a turning in the oscillation direction.

The effect of temperature, size and strain on the beams as found in the previous studies [11] can be found in and the temperature plots are reproduced in Figure 8.0.1 :

An increase in temperature decreases the force necessary for a certain displacement. The increase also decreases the frequency which fits with a decreased restoring force, although only from the direction and not from the numbers. Sadly the data of the force plots is so noisy that one can not determine if it follows any specific dependence.

The damping coefficient increases with temperature in a linear fashion (with some noise).

What surprises me a bit is that the data point at 0K returns a damping coefficient of 0. Quantum mechanically this is obviously wrong - since the states of relaxation exists and the transfer happens at higher temperatures these relaxations should also have a non-zero probability at low temperatures. But even classically it seems strange, the same relaxation pathways should exists and it strikes me as odd that a non-idealized model like molecular dynamics with the SW potential should exhibit an excitation of a perfect/non-dampened mode without specifically aiming for that.

The stress and strain dependence was tested by pulling at one end of the bridge with a force until a required elongation was reached, then fixating the end at the new position and proceeding with the simulation as before. The frequency increases sub-linearly

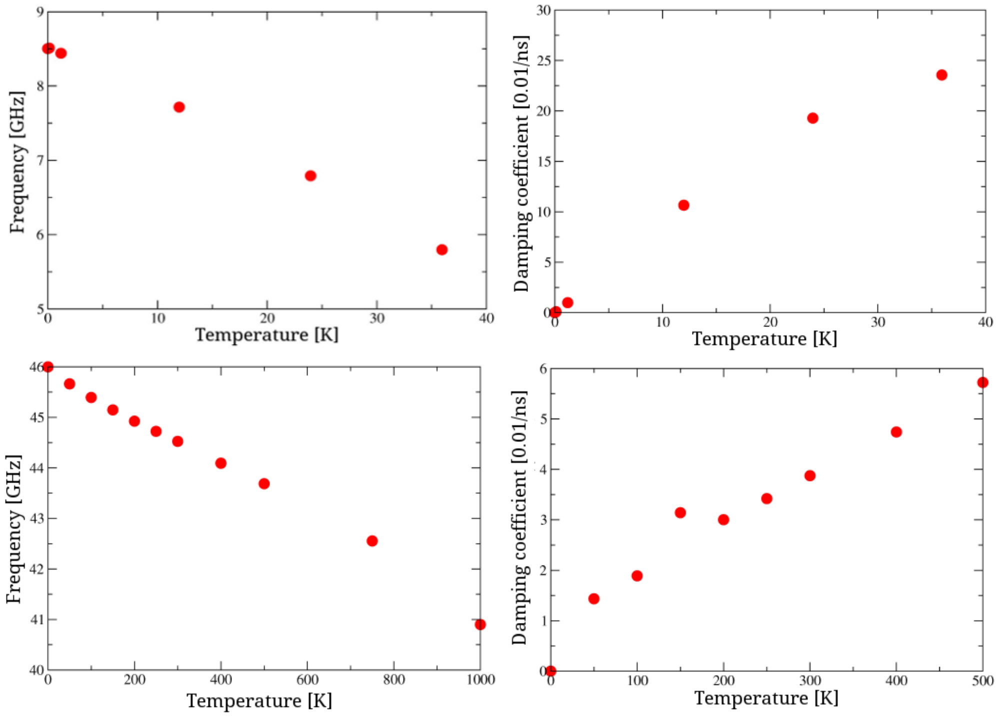

Figure 8.0.1: The dependencies of the main mechanical oscillation frequency and damping on temperature for silicon and Lennard-Jones bridges. On top the Lennard-Jones bridges, on bottom the Silicon bridges. Left the frequency, right the damping coefficient Source: [11].

with the applied elongation. The new equilibrium position could have different spring constants and the effective mass of the oscillator.

The force required to pull the bridge a certain distance as well as the frequency decreases with the size of the bridge. Contributing to the frequency decrease are the higher effective mass of the oscillator and obviously the decreasing spring constant. [11] found the frequency changes to fit well with continuum mechanics expectation, but the damping and its mechanism can not be explained that way.

9 Membranes

What changes does one expect with the switch to membranes? The basic direction of every dependence should stay the same, but the exact form of the dependence could change, e.g. an increase of the radius would increase the mass quadratically instead of linearly, yielding a different frequency from that alone. The expectation for the mode form comes from the results of elasticity theory, the lowest and largest of these modes is the most likely to be excited. Since the boundary conditions fix more area it is also likely that the form of the mode and its direction is more stable, that means less susceptible to the additional structure introduced by the Stillinger-Weber potential.

The form of the excited modes will most likely be symmetric, since breaking the radial symmetry would not just require exciting the angular mode, but also needs to reach zero displacement in the center to prevent discontinuities there. No displacement in the center is practically impossible with the kind of force that is applied (uniform over the whole area). The modes with higher frequency/shorter wavelength should also get excited, but the distribution should follow Maxwell-Boltzmann statistics.

9.1 Reaction to application of force

If the position of the membrane is somehow fixed, the application of force creates a deviation from the optimal configuration that will counterbalance this force. Under the application of uniform force on a membrane with a fixed boundary, the form is not parabolic or cosine, but is "hill"-like with a stronger displacement in the middle flowing outward, the explanation for this is similar to the argument for membrane with non-negligible thickness - there is less bending allowed - higher derivatives are zero in the membrane and less bending at the boundary. This behavior is expressed stronger in the silicon case which fits with the assumption of a more rigid structure, increasing the "effective thickness" by stronger interacting forces.

Effect of the application of different amounts of force on the initial displacement is shown in figure Figure9.1.1:

After the application of force the displacement of the membrane rises quadratically in time, fitting well with the integration of a constant force $F = ma$. This continues until the restoring forces are great enough, resulting in an oscillation around a new equilibrium position, where the internal forces counterbalance the external ones.

If one looks at the displacement after a fixed time at $t = 750$, the displacement is proportional to the force as would be expected from the simple integration $d \sim F\left(t_2^2 - t_1^2\right)$. Only the highest force deviates from this linear extrapolation, a further doubling of the force will result in tearing the membrane out of its boundary ring. Two things that are

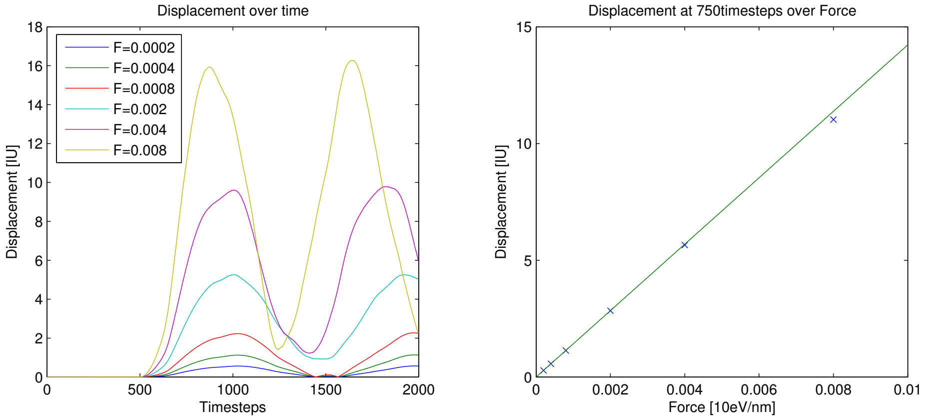

Figure 9.1.1: Effect of different force on the displacement. Displacement over time after application of a constant, uniform force (left). Displacement after a fixed time over applied force with linear fits (right).

also apparent are that higher forces lead to higher frequencies in the oscillation around the new position of rest, which fits with the expectation of larger pulling and restoring forces. Secondly the oscillation grow ever more non-ideal the stronger the force is, which is also something that is to be expected far from the small deviations.

If the force is too high one can get nonlinear relaxation at the beginning of the simulation and loses comparability to structural reordering. This structural reordering distributes energy onto other excitations, which can interact with the main mechanical mode to relax even more energy into microscopic motions.

9.2 Modulation of frequency

Fourier transformation of the displacement data in the time component returns the mechanical frequencies as peaks, which is quite a bit faster and more precise than trying to fit the data to a damped oscillation. It also allows a nearly mechanical analysis - a fact used to analyze the influence thickness, temperature and strain has on the frequency.

Let us start with geometry: The frequency rises with thickness (Figure 9.2.1). For this the increase in the spring constant needs to be higher than the increase in mass, whose increase is linear with thickness. These results are in contrast with the size studies of the beams, where the greater length reduced the spring constant by being able to distribute a certain displacement over a larger length. By increasing the thickness the restoring force actually increases - instead of making the chain longer, one cross-connects with another chain.

For easier comparison the thickness was stated relative to the radius of the membrane. Since the radius was kept constant in this simulation series, the size ratio is directly proportional to thickness. In the Fourier transformation one can directly see the shift in the frequencies. The higher order peaks are obviously a lot weaker and conversely a lot

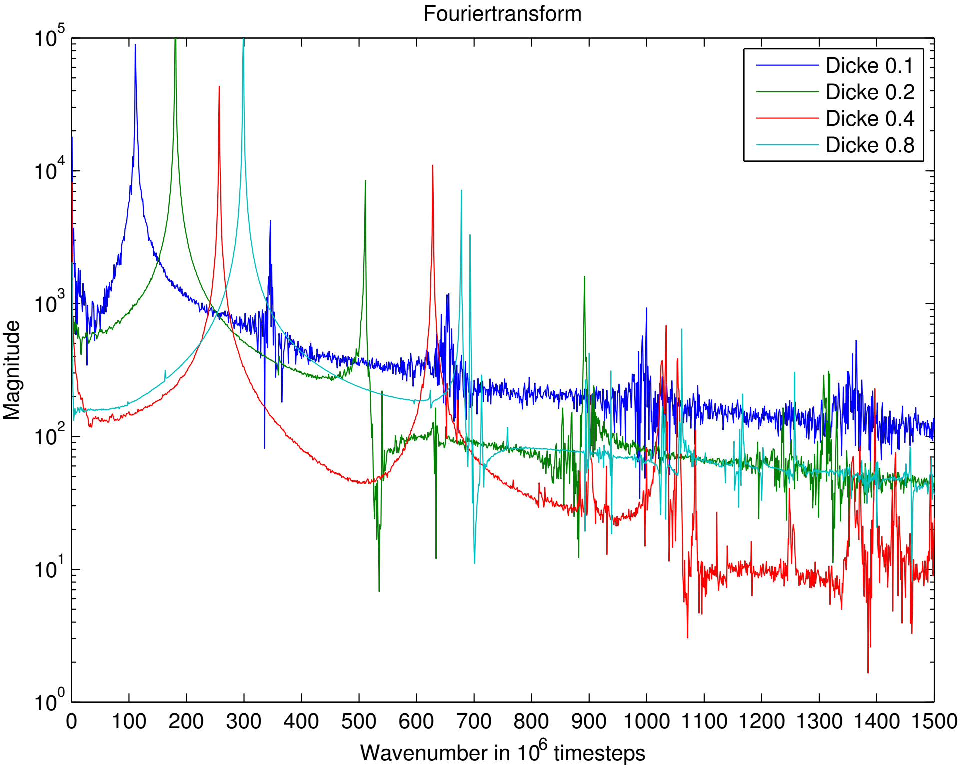

Figure 9.2.1: Frequency dependence of size ratio - Fourier transformation.

noisier.

In the double-logarithmic plot polynomial dependencies appear as straight lines. The dependence of frequency f and thickness D does not fit that model. It starts out similar to a root dependence - which would mean $f \sim \sqrt{D} \sim \sqrt{k/m} \wedge m \sim D \Rightarrow k \sim D^2$ i.e. that the spring constant increases quadratically with thickness - but then falls off in a manner than fits well to a limited exponential growth [1].

With silicon a change in temperature does not change the frequency in an appreciable amount until the temperature reaches room temperature. The maximal changes are about 5% of the way to the melting of the structure somewhere around 1200K, which is in the order of magnitude similar to the changes in the beams.

How should temperature change the frequency? Classically the energy should be distributed according to Maxwell-Boltzmann statistics, but the frequencies of the modes on which the energy is distributed should remain the same as long as certain assumptions are fulfilled. Which assumptions those are is directly connected with which influence the temperature has on the structure and mechanics of the system itself.

From a phase space picture, higher temperature allows an easier and faster exploration

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[1] or exponential decay to a fixed value

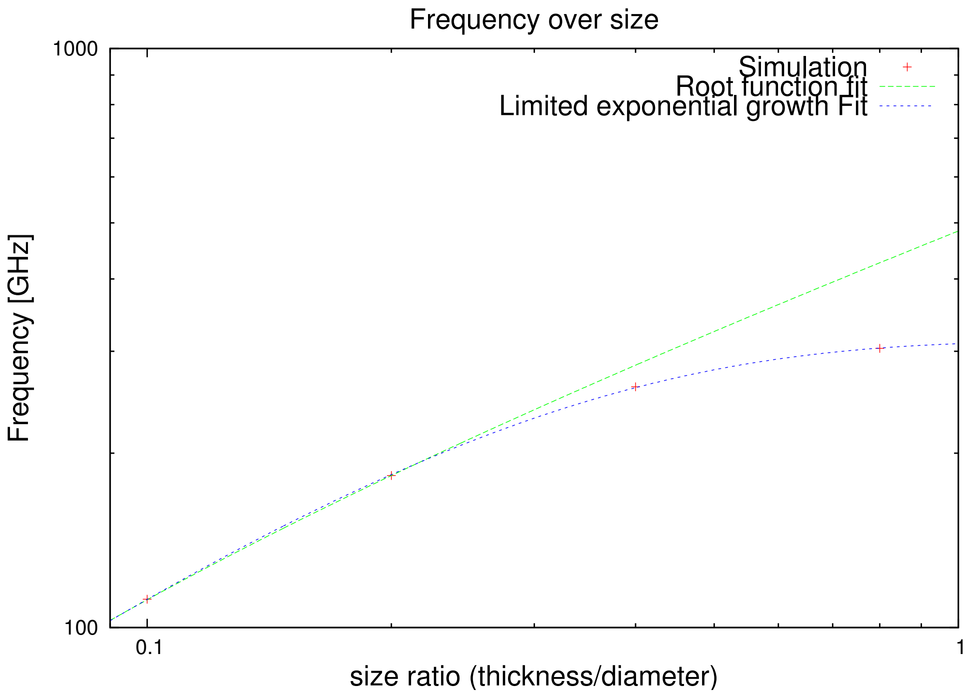

Figure 9.2.2: Frequency dependence of size ratio - plot and fit of the dependence.

of the phase space by allowing the ensemble to explore and cross over higher energy areas. At high temperatures this will result in a softening and finally melting of the structure, reducing the restoring force, the spring constant through local changes and re-orderings, which should also decrease the frequency, although not by much since the basic structure still has to remain stable in most of the material. The effect of temperature should be considerably stronger with regards to the damping coefficients.

Figure 9.2.3 shows the spectra of the motion of the membrane for different temperatures. One does not recognize that much, but one can recognize that the peaks and their frequencies stay largely until the fifth peak - but here the noise has so much influence on the width and height of the peaks that conclusions are not that useful. A zoom on the first peak is more useful for conclusions: At low temperatures the temperature change should have a very small effect on the frequency, which is what is observed (cmp Figure 9.2.4).

The introduction of stress on a circular membrane has some complications: While you can simply pull at the ends with the beam to apply stress in that direction perpendicular to the possible oscillation modes. An equivalent application of uniform stress in the membrane case would need to pull out in all directions, with possible additional interaction from the structure turning the applied forces into non-uniform stresses.

To get around that problem while still applying some stress and strain, some membranes with fixed boundaries were created with a unit cell length differing by a factor between 0.9 and 1.1, sampled in steps of 0.02. The structures thus created are subject

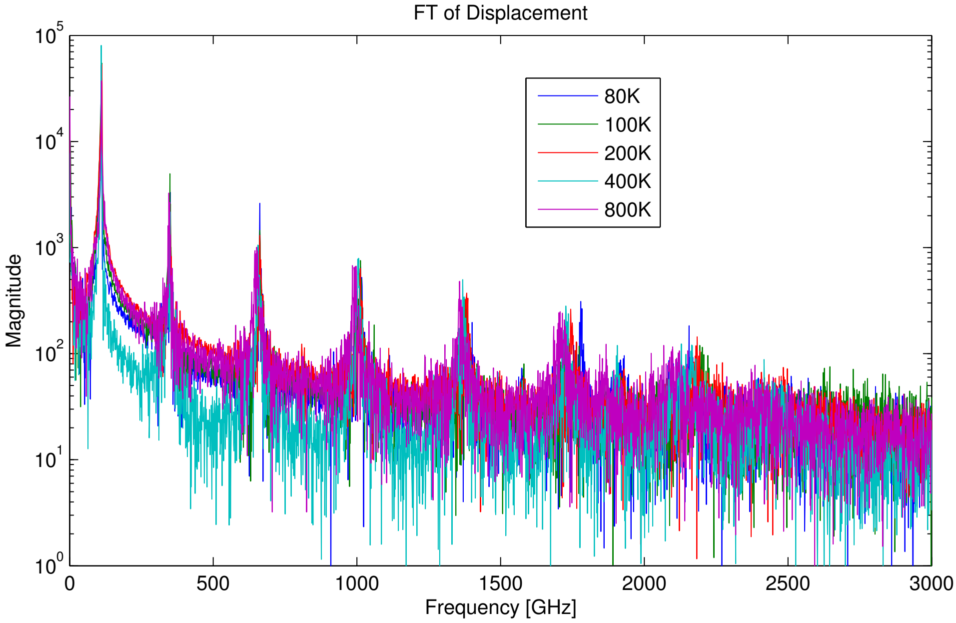

Figure 9.2.3: Fourier transform of the displacement, plotted for different temperatures. The picture shows the spectra for the frequencies until the thermal noise is too large to see anything.

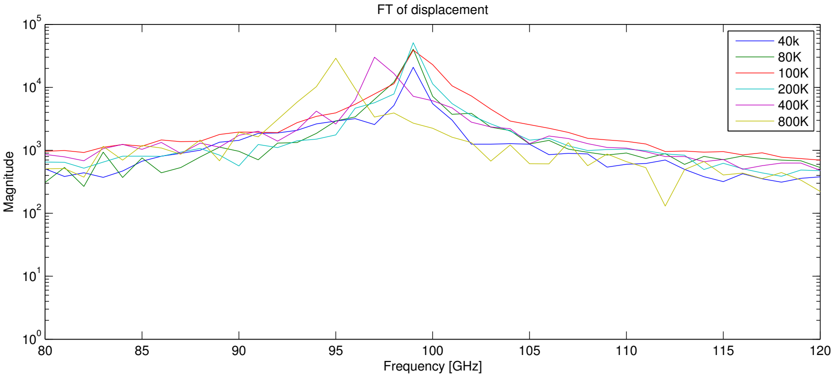

Figure 9.2.4: Fourier transform of the displacement, plotted for different temperatures. This picture is a zoom onto the first resonance frequency of figure 9.2.3.

to additional strain. The factors of 0.9 and everything over 1.04 lead to significant reordering (0.9) and even breakage in the structure (> 1.04), making them unsuitable for comparative studies.

The application of stress (factors > 1) should lead to an effective increase in the restoring force for oscillations in the perpendicular direction. The application of negative stress (pressure, factors < 1) would give the atoms an additional "push" with such oscillations, leading to a lower restoring force and conversely lower frequency.

One could imagine the stress acting on every atom the same as normally contracting forces. If the atom is somewhat displaced a projected component of the stress in the plane adds itself to the restoring forces from the structure.

The Fourier transform of the simulation testing this are found in Figure9.2.5. The predictions are fulfilled for the factors of 0.98 and 1.02. For the factor 1.04 the frequency does not change much from 1.02 while the noise increases, making the results questionable and structural effects quite likely, especially since the membrane will tear with a bit more stress. For factors below 0.98 the frequency increases again and stays somewhat constant. Here the magnitude of the Fourier transform changes rapidly, the resonance peak gets considerably smaller and lower frequencies have larger contributions. This indicates that with higher pressure very different effects take over, that are not well explained with a harmonic oscillator.

This is shown a bit clearer in Figure 9.2.6 where the frequency and the extent of the first resonance peak is plotted over the strain factor. The width of a peak in the Fourier transformation is connected to how well the harmonic oscillator fits the system. This is in turn connected how well conserved this mode is, a wider peak indicates faster relaxation. The plot restates the impressions from the Fourier transform, but also adds some estimates for the damping: It increases quite strongly with pressure on the system, indicative of some failure in the approximation with a harmonic oscillator. Under stress on the other hand, the peaks grow thinner in the first step, which speaks for a clean-up of the harmonic approximation.

9.3 Damping of the drum modes

In any non-ideal physical system with coupled degrees of freedom one expects a relaxation into the thermodynamic equilibrium. For these simulations this means, that one expects the excited collective mode to be damped into the thermodynamic equilibrium within some typical time frame.

This is a stark contrast to the continuous picture of elasticity theory and its quantization in the phonon picture. In these idealized systems it is necessary to add dissipative behavior explicitly. In elasticity theory this is done by introducing non-linear functions of strain/stress or boundary terms . In the phonon picture non-linear terms would damage the underlying picture, dissipation is introduced by scattering at pretty much anything, boundaries, crystal faults, different potentials, other phonons as well as other systems, e.g. electrons.

In molecular dynamics there should only be mechanical and structural damping - a

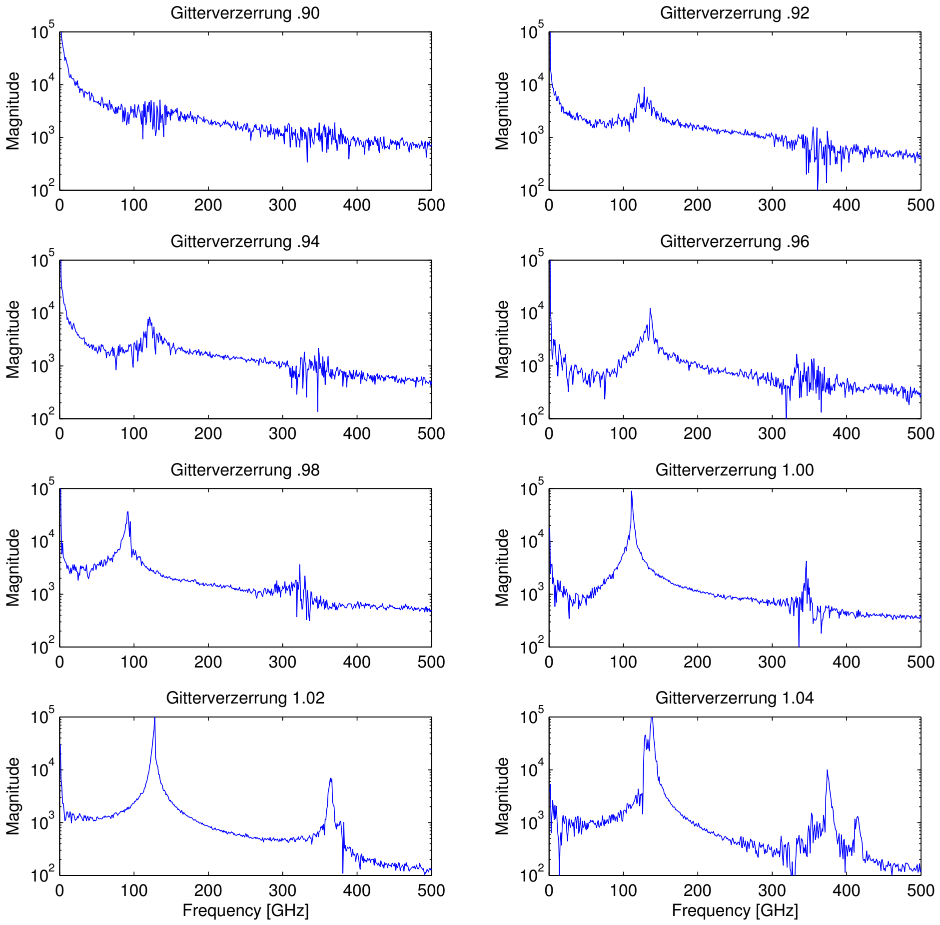

Figure 9.2.5: Fourier-Transform of the displacement under different strain conditions.

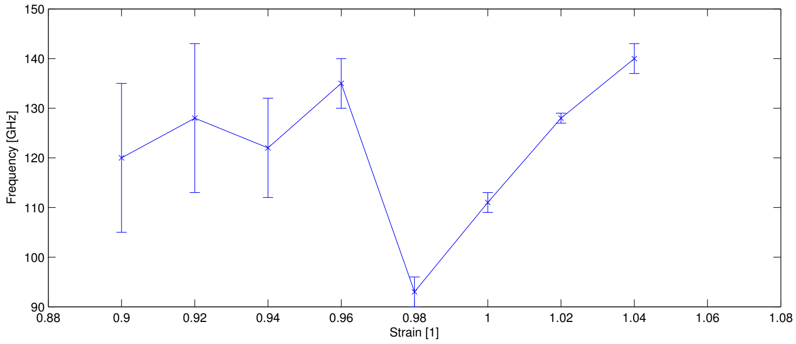

Figure 9.2.6: A plot of frequency over strain. The strain is given as an uniform elongation/compression factor. The error bars give rough estimates of the width of the peak at half maximum.

redistribution of the energy onto the possible degrees of freedom. Kinetic and potential energy of every single atom are the obvious ones. In this case especially interesting and therefore separately mentioned are energies in larger structures and modes like the oscillation modes investigated and structural reorderings - those are built up out of the energies of the single atoms, but they only appear together and are the typical object of larger-scale descriptions.

The damping increases/the quality factor decreases with width/size ratio and at least in Lennard-Jones systems it fits perfectly on a root function as seen in Figure 9.3.1.

For Stillinger-Weber the damping is too small to find a meaningful difference within 10^6 time-steps. This problem has been tackled with several methods:

The easiest approach is increasing the simulation time until the damping can be found directly. This works reasonably well with the Lennard-Jones membranes, but silicon is barely damped and especially in regard to high Quality oscillators with damping constants in the microseconds the simulations would take ages.

Another method would be to force faster damping by changing some of the parameters. This would also help in the search for how exactly the motion is damped. Temperature would be one obvious candidate but simulations showed no appreciable difference. Strain is also a candidate, but it leads to a break-down of the harmonic approximation which happens before increasing the damping strongly enough.

The final tested method was the introduction of crystal faults by deleting atoms:

9.4 Crystal faults - effects of vacancies

The introduction of Crystal faults - simple deletion of atoms in the lattice - was motivated by phonon pictures and scattering of the modes at such crystal faults. The idea is that these should increase damping. This is also supported by a phase space picture, where the removal of an atom gives more free space to the others by reducing the energy cost of movements in certain directions. This was simply tested, reapplying the method to

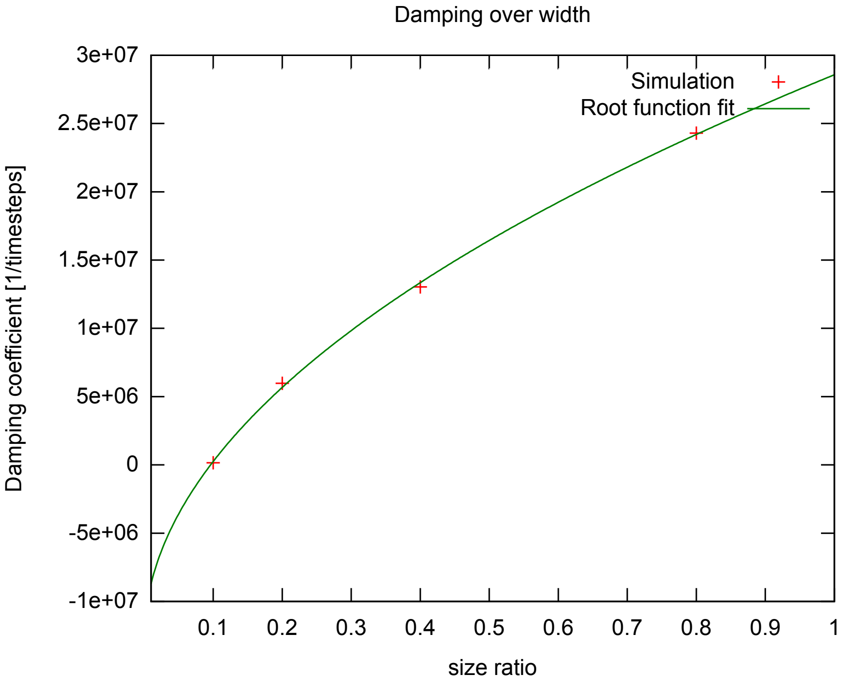

Figure 9.3.1: Lennard-Jones damping over width.

get the frequency and damping data in dependence on different concentrations of missing atoms.

The advantage of a certain concentration of more or less randomly distributed crystal faults in comparison to strictly punching holes in the structure is, that the modes itself should not change much and the introduced surface is (although larger) not connected, hopefully introducing a continuous shift of values instead of forcing a recalculation of the continuous solution by introducing new boundary conditions. The test membranes are smaller specimen with about 7000 atoms.

The Fourier transform (Figure 9.4.1) shows that the frequency is constant up to a breakdown becoming obvious at a vacancy concentration of about 1%, where the noise gets very prominent and the magnitude of the familiar peak starts to decrease. It also seems the peaks shift a bit to higher frequencies, but this could also be an effect of a fasting damping, where a large part of the energy is redistributed to higher, thermal frequencies in the time where the Fourier transform is still running. A Fourier transform on several smaller time chunks is possible, but reduces the frequency resolution considerably - on this time frame one has about 100 oscillations to work with.

On direct investigation, the first simulations looked surprising and interesting (Figure 9.4.2). For high concentrations $> 1\%$ there is a very fast relaxation of the collective mode. For the lower vacancy concentrations, the amplitude drops quite fast in a two phase process with different relaxation time constants, starting with a fast relaxation

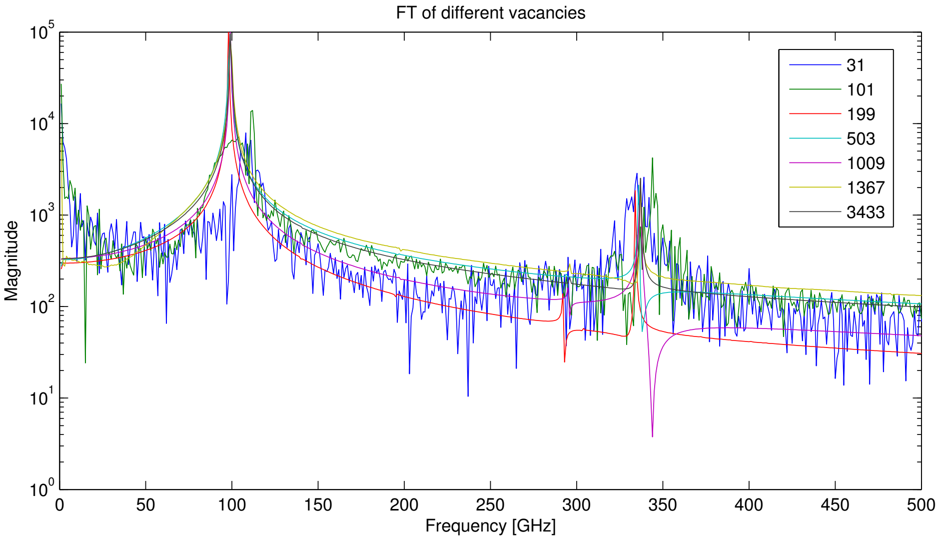

Figure 9.4.1: Fourier transform of the time-evolution of a membrane with vacancies. The numbers n of the plots mean that every nth atom is missing.

that is then slowed down considerably. The removal of some atoms should "soften" the structure, allowing structural reorderings and a bit more relaxation without changing the basic oscillation too much concerning mass and spring constant. These pronounced effects seemed suspicious - especially in the lower concentrations were only a single digit amount of atoms of the whole structure are missing. In investigating this, it became apparent that the force had not been changed accordingly with the smaller membrane size, which leads to a displacement far out of the linear regimen. At least some of the observed processes were not an effect of the introduced structural faults, but simply an effect of the non-linear displacement.

By reducing the force some of these phenomenon should be removed, hopefully to leave one relaxation time constant that would be monotonously dependent on the vacancy concentration. This was not to be as can be seen in the time evolutions in Figure 9.4.3. By going back to the linear regime not only did the non-linear process vanish for low vacancy concentration, the assumed to be linear relaxation was also slowed down very much, going back to being negligible on the time scales observed. The non-linear relaxations seem to support and strengthen the linear relaxations, which leads to the questions if that happens through structural re-orderings or simply through the introduction of more disorder in the system, which makes the crossing of more potential barriers more likely - one could draw parallels to phonon-phonon scattering, where the interactions of two phonons allows for the creation of the third one, which increases entropy.

For the high vacancy concentrations something else happens: Instead of a very fast relaxation, the two-phase process that at higher force appeared for the low vacancy concentration now seems to fit the behavior of the membrane. The structure could be weak-

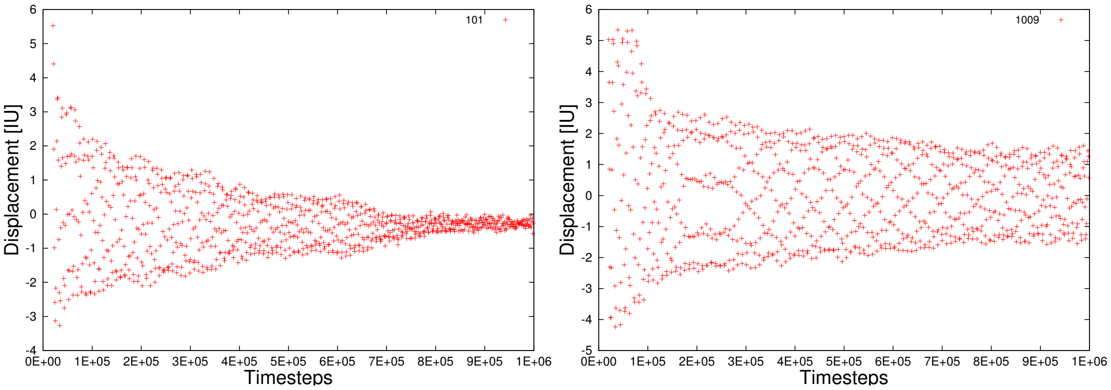

Figure 9.4.2: Time-evolution of the displacement of membranes with vacancies. (Left) One in 101 atoms missing. (Right) Every 1009th atom missing. Only one in thousand time-steps is shown - the oscillation period is about 10000 time-steps, which leads to the observed periodicities.

ened enough to let even this small force be enough to break the harmonic approximation and result in non-linear behavior.

The one obvious conclusion is that extending the membranes into nonlinear territory leads to considerably stronger damping than introducing crystal faults. This seems to indicate that scattering at crystal faults has not that strong an effect as was hoped. This also indicates that the other scattering events at the structure are not as strongly involved, for example the scattering at surfaces, which was expected to have a weaker effect alone from not being that involved in the overall motion.

In investigating the two-phase process the energy plots revealed two interesting things, examples shown in Figure 9.4.4:

First, the switch of the phases coincides with a kink in the total energy diagram. Such a change in the total energy diagrams far in excess of normal fluctuations is only possible when there are rapid changes - especially changes in configuration. Looking at the structure of the membrane in VMD revealed something at around the same time-step, which is a very likely candidate for the reason for this kink: Dimerization at the surface of the membrane, similar to the 2×1 surface reconstruction known for silicon.

The second interesting part of these plots is not quite as positive: After the surface reconstruction there remains an drift in the energy. This drift could not be correlated with surface configuration changes and should in general not happen under the integration schemes used - they should conserve the total energy of the system, fast restructurings could lead to changes, especially when the potentials are not perfectly smooth, but slow drifts are generally a sign of breakdown of the integration scheme, typically because of time steps that are too large for the dynamics governing the behavior.

In order to differentiate those effects the simulations were repeated with a 10 times bigger resolution in time, which should decrease if not remove the drifts and jumps observed and allow testing how well molecular dynamics can capture those effects while

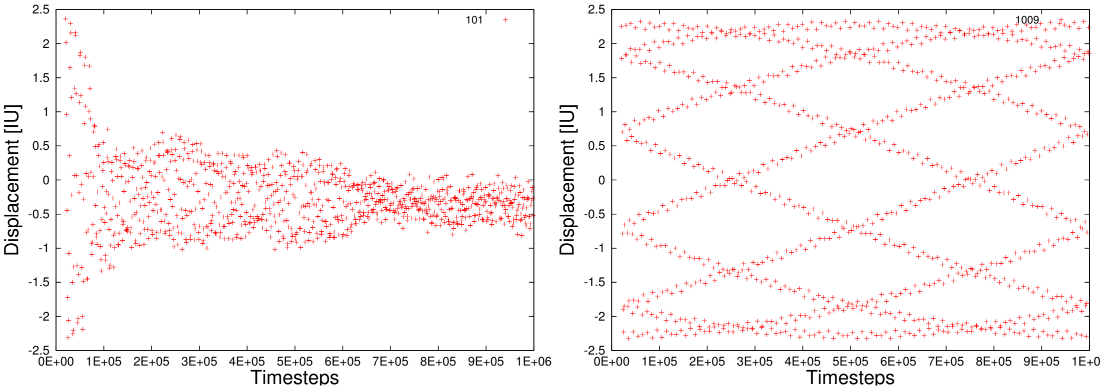

Figure 9.4.3: Time-evolution of the displacement of membranes with vacancies. (Left) One in 101 atoms missing. (Right) Every 1009th atom missing. Only one in thousand time-steps is shown - the oscillation period is about 10000 time-steps, which leads to the observed periodicities.

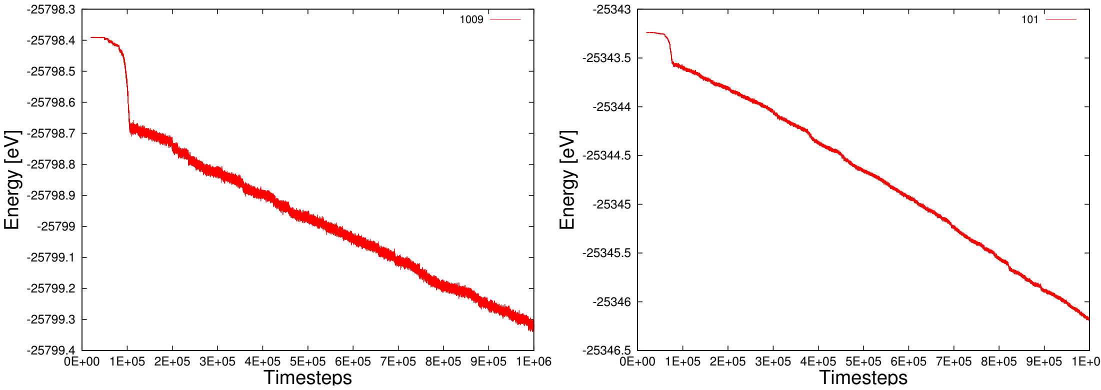

Figure 9.4.4: Energy plots of the two-phase processes of membranes with vacancies. (Left) Energy plot of (9.4.2-right), a membrane with one in 1009 atoms missing. (Right) Energy plot of ((9.4.3)-left), a membrane with one in 101 atoms missing. Both exhibit a kink occurring at the same time as the switch from one phase to the other.

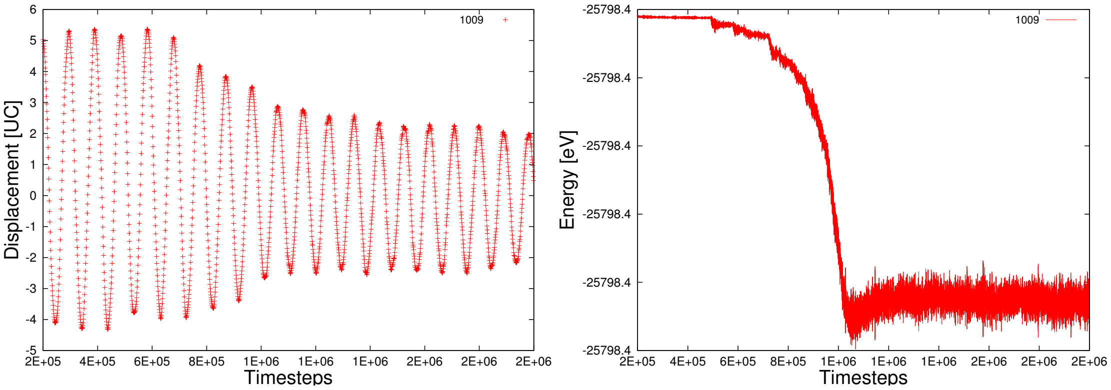

Figure 9.4.5: Higher resolution time-evolution of a membrane with one in 1009 atoms missing. One time-step here is equivalent to 0.1 in the previous plots. (Left) Displacement of the membrane. (Right) Energy plot of the membrane. The kink and the connected restructuring is approximately at the same time as before.

fulfilling energy conservation fully. The results of this test are seen in Figure 9.4.5. Here the kink is at the same time, but two successes can be seen: The drift is considerably reduced and the jump in the kink is also markedly decreased. While the structural reordering is still happening, its effect on the energy calculation is considerably lower.

A similar effect is found for the setup with 1% missing atoms Figure 9.4.6: Here there is a similar reduction of the jump at the beginning and the drift has also vanished. And what is even more interesting: The two-phase behavior is also gone or at least massively reduced, the initial non-linearity in system mode is gone within one oscillation. The system cannot overshoot the linear displacement as badly as before.

In addition to the somewhat continuous kinks of the surface reconstruction the energy plots revealed another phenomenon which could be traced back and correlated with a localized change of structure in the bulk (Figure 9.4.7). These jumps/re-orderings are of considerably smaller overall energy change than the kinks, which fits with their localization to clusters of at most a dozen atoms, in contrast to the kinks which involve many of the surface atoms. A further distinction is the speed at which this process happens, which seems instantaneous in contrast to the kinks and goes together with a quite large overshoot in energy.

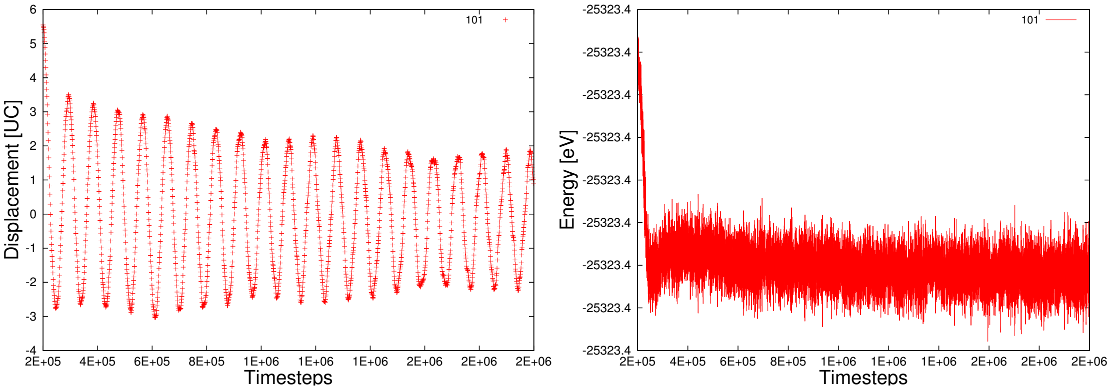

Figure 9.4.6: Higher resolution time-evolution of a membrane with one in 101 atoms missing. One time-step here is equivalent to 0.1 in the previous plots. (Left) Displacement of the membrane. (Right) Energy plot of the membrane. The kink and the connected restructuring is approximately at the same time as before.

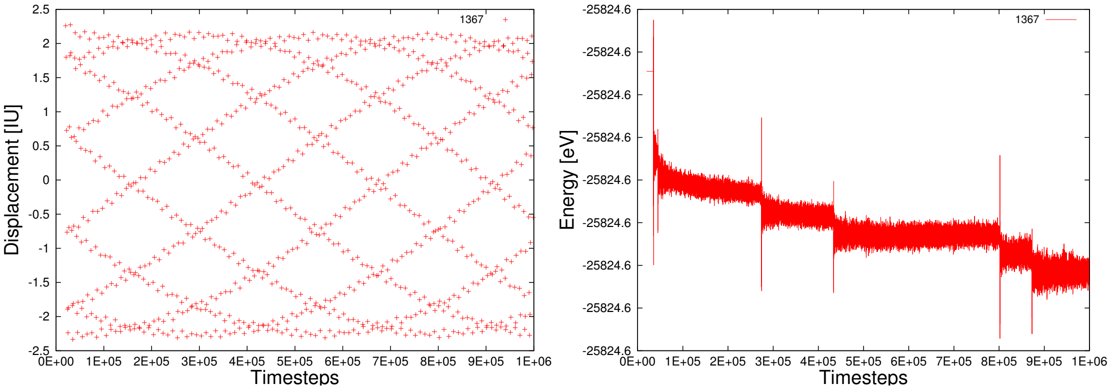

Figure 9.4.7: Time evolution of the energy of a membrane with 1 in 1367 atoms to illustrate jumps correlated with localized restructuring. (Left) Displacement of the membrane. (Right) Energy plot of the membrane. The timescale is the low resolution one (1 time-step ≈ 1ps), but force low enough to stay linear.

10 Summary and discussion

Extending the previous studies on beams to membranes provided a fruitful ground for studies. The switch to the LAMMPS program opens opportunities for scaling in size and complexity of the simulation setup. The switch from beams to membranes makes the simulations more expensive and the basic theory harder, but also reduces the degrees of freedom[1], which leads to more stability in some cases.

In regards to the predictions of linear elasticity one can get the same results as finite element calculation. The real advantage lies in the additional information and behavior one can observe in regards to structure and boundary interactions. The mechanics of the simulation quite soon reach mechanical similarity to calculations in elasticity theory, but allow for easier inclusion of specific boundary terms and structural specialties.

10.1 Scaling of molecular dynamics

The molecular dynamics simulation can be run efficiently in parallel and scaled in size proportional to the number of CPUs used. But the individual calculations costs are so high, that the size scaling cannot reach sizes possible and required by experiments, which is easily done by finite elements methods applied on elasticity theory. The finite element methods start from the system view, refining only as far down necessary to make numerical sense - in theory this could also be done with molecular dynamics methods, starting from a finite differences scheme for elasticity theory and letting the grid points be “atoms” consisting of a large number of true atoms. But this approaches the problem wrong - the strength of molecular dynamics is that it allows to determine system properties emerging from the interaction of atoms, not to fit the atomic and molecular properties to known system parameters.

The scaling issues seem relevant in directly fitting experimental observation, but for the basic properties of the molecular dynamics system an increase in size over several thousand interacting atoms is very unlikely to reveal fundamentally new properties. An increase in size increases the probability for certain rare events happening[2], but not with a higher factor than simply increasing the simulation time or - possibly - tailoring the simulation and starting conditions with this goal.

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[1] the oscillation direction of a membrane can not rotate as easily

[2] e.g. restructurings

10.2 Stillinger-Weber and Lennard-Jones potentials

The big difference between Lennard-Jones and Stillinger-Weber potential is the structure inherent in the Stillinger-Weber potential through the angle-dependent three-body part of the potential.

The Lennard-Jones potential fits considerably better with the predictions of simple, isotropic elasticity theory, as would be expected from the isotropic potential, but also does not provide additional properties in excess of the melting at higher temperatures. In regards to the non-linear effects that result in relaxation of collective modes the behavior of the Lennard-Jones potential can be explained by a phase space picture or its Fourier transform: The relaxation is quite fast, since the lack of internal structure reduces the potential barrier against energy transfer between modes in different directions and even atomic motion. Another formulation would be that the more “fluid” structure prevents a conservation of phonons.

The Stillinger-Weber potential deviates quite a bit more from those predictions, but the biggest challenge it presents is its stiffness and the resulting difference in the time scales of the different effects one would like to observe in the simulations. The factor between the time scales of relaxation of the system mode and structural re-orderings is larger than a million. The quality factor for the main mechanical mode of such the investigated systems is guaranteed to be over one-hundred and probably much higher. The stiff structure of the Stillinger-Weber potential[3] prevents a decay of small excitations in the bulk.

10.3 Structural effects

The structural phenomena observed with the Stillinger-Weber potential lead quite far away from the system descriptions, especially approaches through perfect crystals (phonons) and top-down descriptions like elasticity theory.

As a topic for discussion this is more interesting, because non-perfect crystals are more in line with realistic expectations, although the crystal fault concentration in the silicon used in experiments is quite a bit lower than the one simulated here. The structural effects also allow the “natural” construction of the surface reconstruction, which is quite an accomplishment of the potential and it is also nice to see that it is directly related to the structure.

Instead of easing the transference of energy between the different mechanical modes, the crystal faults add possibilities for energy to go into structural reordering. It would be interesting to introduce another type of atom instead of just putting holes in the structure. This would block the most massive reordering while changing the local potentials.

It is also interesting to note that atomic structural effects are one of the points, where molecular dynamics simulation methods are at a definite advantage over continuous and field methods. Those can only deal with such structural concerns in fault densities and

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[3] Comparatively deep and steep potential wells

effects of these faults densities on system properties instead of directly exploring the effects of the faults on the internal structure of the material.

10.4 Conclusion

The behavior of the simulations regarding frequencies fits well with the expectations from elasticity theory. Practically all predictions for deviations in size, temperature and stress are fulfilled - for small deviation and for the direction of change - for larger deviations it sometimes breaks down, as is only expected. But every single one of those breakdowns provides avenues for new research not already covered by elasticity theory.

In conclusion Molecular dynamics is a useful middle ground between quantum mechanical simulations and continuous models for large scale systems, providing respectively faster simulations and additional microscopic properties.

Acknowledgements

Thanks

My eternal ...well, rather reasonably timed gratitude to everyone who put up with me in the last year: The Nielaba group (Prof. Dr. Peter Nielaba, Dr. Daniel Mutter, Manuel Matt, Marcus Beck, Martin Pütz, Ulrich Siems, Birte Heinze, Kristian Scholz) and other denizens of P7 (Andreas Donges, Martin Evers, Steffen Sievering, Frank Schlickeisen)

Thanks to Kristian Scholz for all the support, material and discussions he provided while I did my thesis.

Thanks to Manuel Matt for all the technical expertise and pleasant office company.

Special thanks for reading and correcting the preliminary version(s) go to Andreas Donges, Marcus Beck and Kristian Scholz.

And my (this time for real) eternal gratitude to my family and especially my parents for feeding and raising me (and for not kicking me out, although it really should be about time now).

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