Molecular Dynamics with C++

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Contents

Chapter 1

Introduction

Context: We start by introducing the concept of the potential energy and the interatomic force. Those are the central ingredients to the molecular dynamics simulation method.

1.1 Structure of matter at the atomic scale

All matter is build out of quark and leptons, or perhaps even smaller particles, but for the sake of modeling the real material world the atom is the fundamental unit. Atoms can be described by nuclei and electrons or through "coarse-grained" models that ignore the fact that there are electrons. Both types of models are useful for describing materials, and the latter ones will be extensively used in this class.

Atoms in solids can arrange in different configurations that are called crystals when there is long-ranged order or glasses when there is not. (All solid matter typically has short-ranged order that is determined by the chemical bonds between atoms.) Atoms in solids are immobile and self-diffusion is limited. Conversely, liquids and gases are disordered (like glasses) but have mobile constituent atoms. Macroscopic object typically contain a lot of atoms – on the order of Avogadro's constant $N_A \approx 6 \times 10^{23}$. The atomic-scale simulation techniques discussed in this class can at the time of this writing (2020) treat on order of $\sim 10^6$ atoms, $10^8 - 10^9$ if you use the biggest computers available to us. Of course, this boundary is pushed towards larger systems as computer technology evolves.

We can nowadays even observe matter at atomic scales and "see" individual atoms. The collaborative research center 103 has produced an extremely

instructive video on the structure of specific type of alloys, dubbed "superal-loy", that is used in e.g. turbine blades. Enjoy the ride from the blade to the atom. This class is about modeling matter at the smallest scales that you see in this video.

1.2   Interatomic forces and the potential energy

Atoms interact via forces. As Feynman put it in his famous lectures on physics, the fundamental truth about man's understanding of the physical world is "that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another". Indeed this is the essence of the molecular dynamics simulation method.

As the simplest example why atoms attract each other, let us consider the example of simple salt, e.g. Na-Cl that we all have sitting in our kitchen. Na-Cl in its solid form is an ionic crystal. Na atoms have approximately a charge of $q_{\mathrm{Na}} = +1|e|$, where e is the electron charge, and Cl atoms have a charge of approximately $q_{\mathrm{Na}} = -1|e|$. The Coulomb interaction between these atoms is a fundamental force of nature. Basic physical principles tell us, that the interaction energy between a Na and a Cl atom is given by

$$V_{\mathrm{Coulomb}}(r; q_{\mathrm{Na}}, q_{\mathrm{Cl}}) = \frac{1}{4\pi\varepsilon_0}\frac{q_{\mathrm{Na}}q_{\mathrm{Cl}}}{r}. \tag{1.1}$$

We also know that this energy is pair-wise additive, allowing us to write down the Coulomb interaction energy for Na-Cl consisting of N atoms,

$$E_{\mathrm{Coulomb}}(\{\vec{r_i}\}) = \sum_{i=1}^{N}\sum_{j=i+1}^{N} V_{\mathrm{Coulomb}}(r_{ij}; q_i, q_j) = \frac{1}{4\pi\varepsilon_0}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{q_i q_j}{r_{ij}} \tag{1.2}$$

where q_i is the charge on atom i and $r_{ij} = |\vec{r_i} - \vec{r_j}|$ the distance between atom i and j. Note that we have introduced — in passing — a central quantity of the molecular dynamics method, the atomic positions $\vec{r_i}$ and Eq. (1.2) indicates that the interaction energy depends on the positions of all atoms.

The Coulomb interaction has a singularity at $r \to 0$. The attractive force between opposite charges becomes infinitely large. The salt crystal does not collapse because atoms are, as Feynman puts it, "repelling upon being squeezed into one another". While the attraction between our Na and Cl atoms are described by a fundamental force of nature, it is more difficult to

understand the origin of this repulsion. Hand-wavingly, it goes back to the fact that electrons are Fermions and electrons from the electron shells of Na and Cl therefore cannot exist at the same point in space (and the same spin state). This is the Pauli exclusion principle and the resulting repulsive force is called Pauli repulsion.

Different models for the Pauli repulsion exist. While the Coulomb interaction is a fundamental force of nature, these models are approximations to the true quantum physics that is the origin of the repulsive form. Two common forms are exponential repulsion,

$$E_{\text{rep,exp}}(\{\vec{r}_i\}) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} A e^{-r/\rho},$$ (1.3)

or an algebraic repulsion of the form

$$E_{\text{rep,12}}(\{\vec{r}_i\}) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} A r^{-12}.$$ (1.4)

Note that A and ρ are *parameters*, that need to be somehow determined. This can be done with the help of either experimental data or *first-principles* calculations, that treat the electrons explicitly. These parameters depend on the atom types under consideration and in contrast to the parameter that show up in the Coulomb interaction (the permittivity ε_0), they are not universal.

For our Na-Cl model, we combine Coulomb interaction with an exponential repulsion, to give the total energy

$$E_{\text{pot}}(\{\vec{r}_i\}) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(A_{ij} e^{-r_{ij}/\rho_{ij}} + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \right).$$ (1.5)

This energy is called the *potential energy* and is the central property of an atomic-scale model. With Eq. (1.5), we have also encountered our first atomic-scale model for a real material. Potentials that can be decomposed as Eq. (1.5) into pair-wise terms are called *pair potentials*. They are often written as

$$E_{\text{pot}}(\{\vec{r}_i\}) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} V(r_{ij}),$$ (1.6)

with

$$V(r_{ij}) = A_{ij} e^{-r_{ij}/\rho_{ij}} + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$ (1.7)

for the above potential. The quantity $V(r_{ij})$ is called the pair interaction energy.

Likely the most famous pair-potential is the Lennard-Jones potential. Its pair interaction energy is given by

$$V(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]. \tag{1.8}$$

The repulsive term $\propto r^{-12}$ is one of the models for Pauli repulsion discussed above. The attractive term $\propto r^{-6}$ arises from *London dispersion interactions*. Dispersion forces exist between all atoms, even uncharged molecules or noble gases. They are widely employed for the nonbonded portion of valence force-fields. Simple Lennard-Jones systems are often used to study generic phenomena found in real materials, e.g. for example the glass transition or plasticity of amorphous materials. There are limitations of pair potentials and more sophisticated potential energy models have been developed over the past decades. We will discuss a few of those in Chapter 3.

> **Note:** A repulsive term of the form r^{-12} is more attractive from a simulation point of view since it is faster to compute than an exponential. This has helped popularize the Lennard-Jones potential in the early days of molecular dynamics simulations.

The significance of the potential energy is that we can derive forces from it,

$$\vec{f}_k = -\frac{\partial}{\partial \vec{r}_k} E_{\text{pot}}(\{\vec{r}_i\}). \tag{1.9}$$

These forces are the essential ingredient to *molecular dynamics*, as they determine the motion of the atoms.

The potential energy itself describes what is called the *potential energy landscape*. The potential energy landscape depends on $3N$ degrees of freedom (as compared to the landscape we experience while walking, which depends on 2 degrees of freedom); it is therefore an object that is complex to visualize. Simplifying aspects of it is the core of *molecular statics*. For example, it is typically important to at least identify the ground-state of a system; this is the most stable configuration of a material and has the lowest possible potential energy. There is usually some crystal that is lower in energy than the energy of a glass with the same stoichiometry. Yet, in many real-world engineering applications the materials are not in their crystalline ground-state, the most common material we encounter with this property may be window

glass. In molecular statics we therefore seek to enumerate those *local minima* of the potential energy landscape and energy barriers between them.

Since the dynamics of a molecular system is determined by the forces, we only need to specify the potential energy up to a constant which disappears in the derivative Eq. (1.9). We can therefore measure the potential energy with respect to any reference configuration. This reference configuration is often the atomized state of the material, where all of the constituent atoms sit individually in vacuum and are not interacting with each other. If this reference situation is assigned the energy 0, then the potential energy is generally negative, because if it was positive the system would spontaneously atomize. (Remember, any physical system evolves to a state of lower energy.)

Chapter 2

Molecular dynamics

Context: Molecular *dynamics* follows the motion of individual atoms through a solution of Newton's equations of motion. We need integration algorithms to be able to solve this set of coupled differential equations on a computer.

2.1 Equations of motion

2.1.1 Newton's equations of motion

We have now (almost) all the ingredients to carry out a molecular dynamics simulation. From our or potential energy expression $E_{\mathrm{pot}}(\{\vec{r}_i\})$ discussed in the previous chapter, we obtain the force

$$\vec{f}_i = \partial E_{\mathrm{pot}}/\partial \vec{r}_i \tag{2.1}$$

on each of the N atoms. Once we know the forces, we can obtain the accelerations $\vec{a}_i$ through Newton's third law,

$$\vec{f}_i = m_i \vec{a}_i. \tag{2.2}$$

We are therefore assuming that atom i can be described as a point of mass m_i! The mass can be obtained from the periodic table of elements. Note that the mass listed in the periodic table is usually the average over all isotopes weighted by their occurrence on earth, and this mass is used for most practical purposes. For some application, in particular to understand the different behavior of Hydrogen and Deuterium, it can be necessary to actually model the individual isotopes by using their respective mass.

We further have $\vec{a}_i = \dot{\vec{v}}_i$, where $\vec{v}_i$ is the velocity of atom i, and $\vec{v}_i = \dot{\vec{r}}_i$. The dot superscript indicates derivative with respect to time. The set of linear differential equations to solve is therefore

$$\dot{v}_i(t) = \vec{f}_i(t)/m_i \ \text{ and } \ \dot{\vec{r}}_i(t) = \vec{v}_i(t) \tag{2.3}$$

with the initial (boundary) conditions $\vec{r}_i(0) = \vec{r}_0$ and $\vec{v}_i(0) = \vec{v}_0$. Note that the boundary condition is an integral part of the differential Eq. (2.3). The state of the system is therefore fully and uniquely determined by the positions $\vec{r}_i$ and the velocities $\vec{v}_i$ of all atoms. This set of positions $\vec{r}_i$ and momenta $\vec{p}_i = \vec{v}_i/m_i$ defines a point in *phase-space* $\vec{\Gamma} = \{\vec{r}_i, \vec{p}_i\}$. The evolution of position and velocities given by Eq. (2.3) can therefore be thought of as a single point moving in the $6N$ dimensional phase-space. The concept of a phase-space will become important in the next chapter when we talk about statistical mechanics.

Code example: For a molecular dynamics code, it is useful to have a data structure that represents the state of the simulation and stores at least positions and velocities. This data structure could also store element names (or atomic numbers), masses and forces. An example that uses Eigen arrays as the basic array container is shown below.

```
1  using Positions_t = Eigen::Array3Xd;
2  using Velocities_t = Eigen::Array3Xd;
3  using Forces_t = Eigen::Array3Xd;
4
5  class Atoms {
6  public:
7      Positions_t positions;
8      Velocities_t velocities;
9      Forces_t forces;
10
11     Atoms(Positions_t &p) :
12             positions{p}, velocities{3, p.cols()}, forces
       {3, p.cols()} {
13         velocities.setZero();
14         forces.setZero();
15     }
16
17     size_t nb_atoms() const {
18         return positions.cols();
19     }
20 };
```

As a general rule, the data structure should be designed in a way that data that is processed consecutively is also stored in memory in a continuous

manner. This ensures cache coherenece. For example, we could be tempted to create a class `Atom` that contains the positions, velocities, etc. of a single atom and than use an array (e.g. `std::vector<Atom> atoms`) of that class as the basic data structure. However, positions are then no longer consecutive in memory. A function (e.g. computing forces) does not need the velocities would still load them into the cache, as the cache line size for all modern CPUs is 64 bytes. For high-performance numerical code, it is therefore *always* preferable to use structures of arrays rather than arrays of structure.

2.1.2 Kinetic energy and energy conservation

In addition to the potential energy $E_{\text{pot}}(\{\vec{r}_i\})$, the dynamical state of a system is characterized by its kinetic energy,

$$E_{\text{kin}}(\{\vec{p}_i\}) = \sum_i \frac{1}{2} \frac{p_i^2}{m_i}. \tag{2.4}$$

Note: The *temperature* is simply a measure of the kinetic energy of the system, $\frac{3}{2} N k_B T = E_{\text{kin}}$ where N is the number of atoms. In other words, E_{kin} measures the variance of the velocity distribution, which is Gaussian. We will learn more about this when discussing the basics of statistical mechanics.

The total energy

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) = E_{\text{kin}}(\{\vec{p}_i\}) + E_{\text{pot}}(\{\vec{r}_i\}) \tag{2.5}$$

is a conserved quantity during the motion of the atoms. This can be seen by showing that the derivative of the total energy with respect to time vanishes,

$$\dot{H} = \dot{E}_{\text{kin}} + \dot{E}_{\text{pot}} = \sum_i \frac{\vec{p}_i \dot{\vec{p}}_i}{m_i} + \sum_i \frac{\partial E_{\text{pot}}}{\partial \vec{r}_i} \dot{\vec{r}}_i = \sum_i \vec{v}_i \vec{f}_i - \sum_i \vec{v}_i \vec{f}_i = 0. \tag{2.6}$$

H is also called the *Hamiltonian* of the system.

Note: Measuring the total energy (or any other conserved quantity!) and checking whether it is constant in a molecular dynamics simulation is a way of testing if the time step Δt used in the numerical integration is small enough. We will discuss numerical integration in detail below.

A generalization of Newton's equations of motion are *Hamilton's equations of motion*,

$$\dot{\vec{r}}_i = \frac{\partial H}{\partial \vec{p}_i} \tag{2.7}$$

$$\dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{r}_i}, \tag{2.8}$$

and it is straightforward to show that these equations reduce to Newton's equations of motions for the Hamiltonian given by Eq. (2.5). Hamilton's equation of motion remain valid when positions $\vec{r}_i$ and momenta $\vec{p}_i$ are replaced by generalized coordinates that consider constraints, such as for example the angle of a (rigid) pendulum. These equations will become important when we discuss statistical mechanics and temperature control in molecular dynamics simulations using *thermostats*, where a generalized degree of freedom is the internal state of the heat bath that controls the temperature. A full derivation of Hamilton's equations of motion is given in Chap. A.

2.2   Integration algorithms

The main ingredient in any molecular dynamics simulation, regardless of the underlying model, is the numerical solution of Eqs. (2.3). A plethora of algorithms have been developed over the years, but for most practical purposes the Velocity-Verlet algorithm is used nowadays. For instructive purposes we will start out with a simple integration method, the Euler integration, before discussing Velocity-Verlet.

2.2.1   Euler integration

In order to follow the trajectories of all atoms we need to integrate the above differential equation. On a computer, a continuous differential equation needs to be replaced by a discrete equation. Equations (2.3) are continuous in time and hence need to be discretized. (Note that our system is already discrete spatially since we are dealing with mass points, but each of these points corresponds to a physical object so this is not the result of a discretization procedure.) The simplest integration is the Euler algorithm in which forces and velocities are assumed to be constant over time intervals Δt.

To see this, we write the above differential equation as

$$d\vec{v}_i = \frac{\vec{f}_i(t)}{m_i} \ \text{ and } d\vec{r}_i(t) = \vec{v}_i(t)\, dt \tag{2.9}$$

i.e., we move the differential dt of $\dot{\vec{v}}_i = d\vec{v}/dt$ to the right hand side of the equation. We can now straightforwardly integrate the equation from time t to time $t + \Delta t$ while assuming that $\vec{f}_i$ and $\vec{v}_i$ remain constant. This yields

$$\vec{v}_i(t + \Delta t) - \vec{v}_i(t) = \frac{\vec{f}_i(t)}{m_i}\Delta t \qquad (2.10)$$

$$\vec{r}_i(t + \Delta t) - \vec{r}_i(t) = \vec{v}_i(t)\Delta t \qquad (2.11)$$

which is obviously only a good approximation for small Δt! This algorithm is called Euler integration.

Same equation can be derived by Taylor-expanding $\vec{r}_i(t + \Delta t)$ up to first order in Δt. The algorithm is hence $O(\Delta t^2)$. The Euler algorithm is not reversible, i.e. starting from time $t + \Delta t$ and integrating backwards one ends up with a different result at time t. Applying the Euler algorithm with timestep $-\Delta t$ gives

$$\vec{v}_i(t) - \vec{v}_i(t + \Delta t) = -\frac{\vec{f}_i(t + \Delta t)}{m_i}\Delta t \qquad (2.12)$$

$$\vec{r}_i(t) - \vec{r}_i(t + \Delta t) = -\vec{v}_i(t + \Delta t)\Delta t \qquad (2.13)$$

These equations cannot be re-arranged to give Eqs. (2.10) and (2.11). Euler integration is generally not a good algorithm and requires very small time steps.

2.2.2   Leap-frog integration

Leap-frog stores position at times t_i and velocities at times $t_i + \Delta t/2$ and can be derived from a argument similar to the one given above. Specifically, we combine the results of a Taylor expansion $\pm\Delta t/2$, yielding

$$\vec{v}_i(t + \Delta t/2) - \vec{v}_i(t - \Delta t/2) = \frac{\vec{f}_i(t)}{m_i}\Delta t \qquad (2.14)$$

$$\vec{r}_i(t + \Delta t) - \vec{r}_i(t) = \vec{v}_i(t + \Delta t/2)\Delta t. \qquad (2.15)$$

Note that Eq. (2.14) is similar to Eq. (2.10), except the force is evaluated at the mid-point. The resulting algorithm is reversible. Applying the Leap-frog algorithm with timestep $-\Delta t$ gives

$$\vec{v}_i(t - \Delta t/2) - \vec{v}_i(t + \Delta t/2) = -\frac{\vec{f}_i(t)}{m_i}\Delta t \qquad (2.16)$$

$$\vec{r}_i(t) - \vec{r}_i(t + \Delta t) = -\vec{v}_i(t + \Delta t/2)\Delta t \qquad (2.17)$$

Bring the terms on the left hand side to the right and vice-versa, and you arrive at the original equations for forward integration. Leap-frog is therefore *reversible*.

2.2.3 Verlet integration

Let us now Taylor expand $\vec{r}_i(t \pm \Delta t)$ up to third order in $\pm \Delta t$,

$$\vec{r}_i(t \pm \Delta t) = \vec{r}_i(t) \pm \vec{v}_i(t)\Delta t + \frac{1}{2m_i}\vec{f}_i(t)\Delta t^2 \pm \frac{1}{6}\dddot{\vec{r}}_i(t)\Delta t^3 + O(\Delta t^4). \quad (2.18)$$

Note that only the odd exponents see the sign of $\pm \Delta t$. The sum of this equation for expansion in $+\Delta t$ and $-\Delta t$ gives the positions update,

$$\vec{r}_i(t + \Delta t) + \vec{r}_i(t - \Delta t) = 2\vec{r}_i(t) + \frac{1}{m_i}\vec{f}_i(t)\Delta t^2 + O(\Delta t^4). \quad (2.19)$$

Eq. (2.19) is called the Verlet algorithm. Instead of requiring the positions $\{\vec{r}_i(t)\}$ and velocities $\{\vec{v}_i(t)\}$ it requires the positions of the current $\{\vec{r}_i(t)\}$ and past $\{\vec{r}_i(t - \Delta t)\}$ times for the integration.

The difference between the expansion for $+\Delta t$ and $-\Delta t$ yields the velocities,

$$\vec{r}_i(t + \Delta t) - \vec{r}_i(t - \Delta t) = 2\vec{v}_i(t)\Delta t + O(\Delta t^3). \quad (2.20)$$

Note that in order to compute the velocities at time t in the regular Verlet algorithm, we need to know the positions at time $t + \Delta t$. Verlet and Leap-Frog are identical algorithms, since Leap-Frog stores the velocities at the intermediate time $t + \Delta t/2$. It is usually useful to be able to know both, positions and velocities, at time t. This problem is solved by the Velocity-Verlet algorithm, described in the following section.

2.2.4 Velocity-Verlet integration

Let us now also Taylor expand $\vec{r}_i(t)$ up to third order in Δt at $\vec{r}_i(t + \Delta t)$, i.e. we integrate backwards in time from $t + \Delta t$ to t. This gives

$$\vec{r}_i(t) = \vec{r}_i(t + \Delta t) - \vec{v}_i(t + \Delta t)\Delta t + \frac{1}{2m_i}\vec{f}_i(t + \Delta t)\Delta t^2 - \frac{1}{6}\dddot{\vec{r}}_i(t)\Delta t^3 + O(\Delta t^3)$$

$$(2.21)$$

Equation (2.18) is the positions update of the Velocity-Verlet algorithm. The sum of Eq. (2.18) and Eq. (2.21) gives the velocity update in the Velocity-Verlet algorithm:

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2m_i}\vec{f}_i(t)\Delta t^2 \quad (2.22)$$

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{1}{2m_i}\left(\vec{f}_i(t) + \vec{f}_i(t + \Delta t)\right)\Delta t, \quad (2.23)$$

Note that this algorithm is often split in the form of a predictor-corrector scheme since this saves computation time and the necessity to keep past forces around. The predictor step is

$$\vec{v}_i(t + \Delta t/2) = \vec{v}_i(t) + \frac{1}{2m_i}\vec{f}_i(t)\Delta t \qquad (2.24)$$

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t + \Delta t/2)\Delta t \qquad (2.25)$$

where $\vec{v}_i(t + \Delta t/2)$ is the predicted velocity. After this we compute new forces, $\vec{f}_i(t + \Delta t)$. We then correct the velocities via

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t + \Delta t/2) + \frac{1}{2m_i}\vec{f}_i(t + \Delta t)\Delta t \qquad (2.26)$$

The Velocity-Verlet algorithm is the integration algorithm used in most molecular dynamics codes. It has the additional properties that is it *symplectic*, which means it conserves phase-space volume. We will come back to what this mean when talking about statistical mechanics.

Code example: We can implement the velocity-verlet algorithm in a few lines of C++ code using vectorized `Eigen` operations. The prediction step

```
1 void verlet_step1 (Atoms &atoms, double timestep, double
    mass) {
2    atoms.velocities += 0.5 * atoms.forces * timestep /
    mass;
3    atoms.positions += atoms.velocities * timestep;
4 }
```

implements Eq. (2.24). We then compute new forces and correct the velocities via

```
1 void verlet_step2 (Atoms &atoms, double timestep, double
    mass) {
2    atoms.velocities += 0.5 * atoms.forces * timestep /
    mass;
3 }
```

Note: The timestep in MD simulations has to be on the order of femtoseconds, in order to resolve the fastest atomic vibrations. For example, in simulations with metals and Embedded Atom Method (EAM) potentials, $\Delta t = 1$ fs is typically a safe choice. How can we check that the timestep is sensible? One possibility is to simply propage a configuration in time

using the Velocity-Verlet algorithm. This is sometimes called the micro-canonical or NVE ensemble. (NVE because number of atoms, volume and energy is constant.) We then record the evolution of the total (kinetic plus potential) energy, which should be constant. The discrete time integration scheme will introduce numerical errors. If Δt is too large, there will be noticeable drift of the total energy. The figures below show the results of such a simulation. A system of 108000 Au atoms was simulated for 100 ps with various values of Δt. The y-axis shows the difference between the current and initial values of the total energy. The data was smoothened to suppress high-frequency fluctuations in the figure. For this system, even 5 fs would still be an acceptable time step.
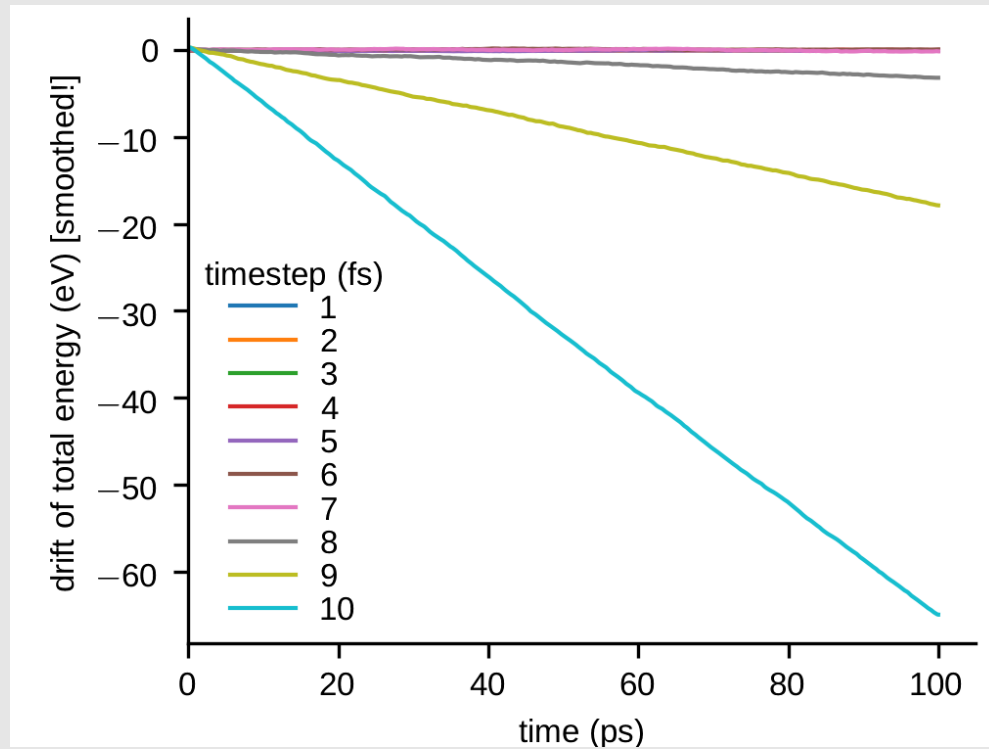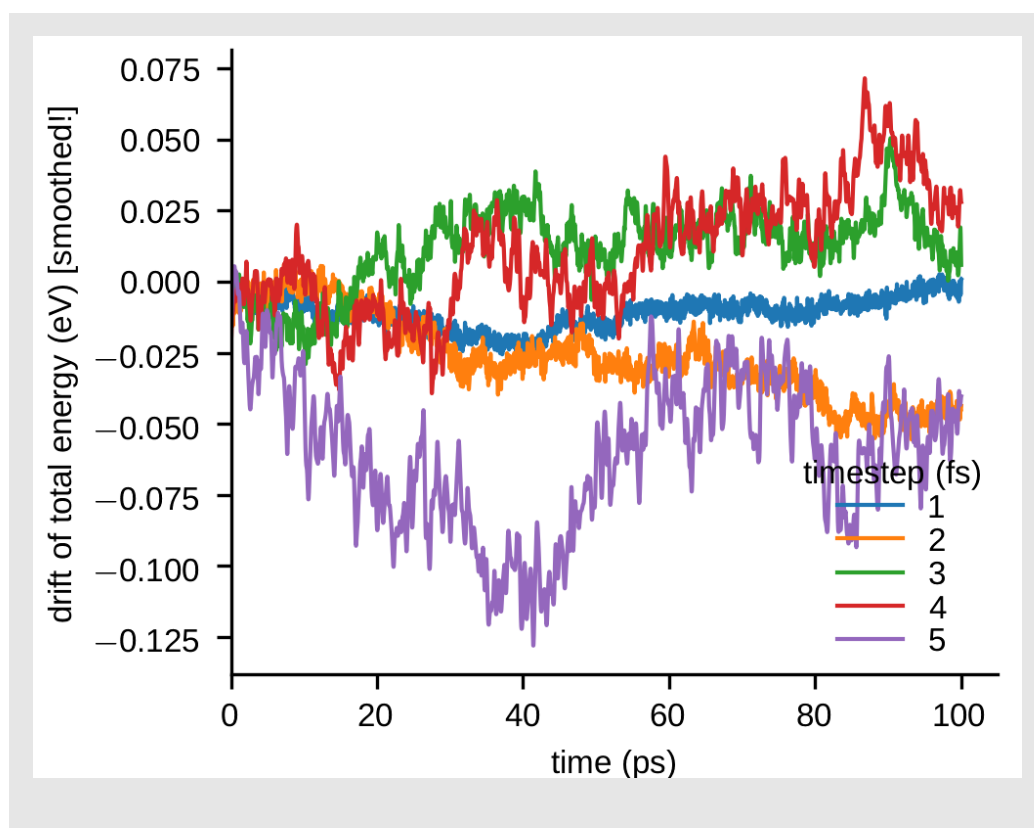
Chapter 3

Pair potentials

Context: Interatomic forces or interatomic potentials determine the material that we want to study. There is a plethora of interatomic potentials of varying accuracy, transferability and computational cost available in the literature. We here discuss simple pair potentials and point out algorithmic considerations.

3.1 Introduction

The expression for $E_{\mathrm{pot}}\left(\{\vec{r}_i\}\right)$ is the *model for the material* that we use in our molecular dynamics calculations. It determines whether we model water, proteins, metals, or any other physical object. Models are typically characterized by their *accuracy*, their *transferability* and the *computational cost* involved. (Computational cost also includes the *computational complexity*.) At constant computational cost, there is always a tradeoff between accuracy and transferability. Accuracy and transferability can typically only be improved at the expense of additional computational cost.

- *Accuracy:* How close to we get to the true, measured value. For example, the absolute error of vacancy formation energy $E_{\mathrm{vac}} - E_{\mathrm{vac}}^{\mathrm{exp}}$ with respect to experiment can be 1 eV, 0.1 eV (typical), 0.01 eV (computationally expensive!). The vacancy formation energy is the energy required to remove a single atom from a solid. The resulting "hole" in the solid is called a vacancy.

- *Transferability:* Let's assume we get the vacancy formation energy right to within 0.1 eV of the experimental value. Does the interstitial formation energy, i.e. the energy to insert an additional atoms between

lattice sites, give the same value? If so, then the potential is transferable between these two situations. *Most interatomic potentials are not generally transferable,* and they need to be tested when used in new situations, e.g. when the potential has been used to study crystals but you want to use it now to study a glass.

- *Computational cost:* The number of floating point operations determine how expensive it is to compute an energy or a force. (Nowadays, actual energy requirement for doing the calculation would be a better measure.) This is related to computational complexity, that says how the computational cost (i.e. the number of operations requires to compute the result) scales with the number of atoms. We want $O(N)$ complexity, but many methods scale worse. Quantum methods (tight-binding, density-functional theory) are usually $O(N^3)$ or worse.

3.2 Pair potentials

We have already encountered the simplest (and oldest) form of an interaction potentials, the pair potential. The total energy for a system interacting in *pairs* can be written quite generally as

$$E_{\text{pot}}\left(\{\vec{r}_i\}\right) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} V\left(r_{ij}\right) = \sum_{i<j} V(r_{ij}) \qquad (3.1)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between atom i and atom j. $V(r_{ij})$ is the pair interaction energy or just the pair potential and we assume that the interaction is pair-wise additive. The sum on the right ($\sum_{i<j}$) runs over all pairs while sum on the left double counts each pair and therefore needs the factor $1/2$. We have already seen a combination of the electrostatic potential and Pauli repulsion as an example of a pair-potential earlier.

Forces are computed by taking the negative gradient of this expression. The force on atom k is given by

$$\vec{f}_k = -\frac{\partial E_{\text{pot}}}{\partial \vec{r}_k} = -\frac{1}{2}\sum_{ij}\frac{\partial V}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial \vec{r}_k} = -\frac{1}{2}\sum_{ij}\frac{\partial V}{\partial r_{ij}}\hat{r}_{ij}\left(\delta_{ik} - \delta_{jk}\right) = \sum_{i}\frac{\partial V}{\partial r_{ik}}\hat{r}_{ik},$$
$$(3.2)$$

where $\hat{r}_{ik} = \vec{r}_{ik}/r_{ik}$ is the unit vector pointing from atom k to atom i. Note that these forces are symmetric, i.e. the term $\partial V/\partial r_{ik}\hat{r}_{ik}$ shows up in the expression not only for the force on atom k, but also (with an opposite sign) for the force on atom k. This a consequence of momentum conservation. (The sum over all forces needs to vanish.) In an implementation one can therefore

loop over all *pairs* between atoms, compute this pair term and add it to the array entries holding the forces for both atoms.

3.2.1 Dispersion forces

An important contribution to interatomic and intermolecular interactions is the London dispersion force. This interaction is attractive, and acts between all atoms even noble gases. Its origin lies in fluctuations of the atomic dipole moment. (This is a quantum mechanical effect, but the simplest model would be an electron orbiting a nucleus with a rotating dipole moment.) This fluctuating dipole *induces* a dipole in a second atom and these interact. The interaction decays as r^{-6} at short distances. London dispersion forces are one of the forces that are often subsumed under the term van-der-Waals interaction.

3.2.2 Lennard-Jones potential

The Lennard-Jones potential combines dispersion forces with an empirical r^{-12} model for Pauli repulsion. It is typically used for the interaction of noble atoms or molecules, i.e. systems that have closed electronic shells and therefore do not form covalent bonds. The interaction described by the Lennard-Jones potential are often called nonbonded interactions, because the typical interaction energy is on the order of $k_B T$ (with room temperature for T). Thermal fluctuation can thereby break this bond, hence the term nonbonded.

One typical form to writing the Lennard-Jones potential is

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{3.3}$$

where ε is an energy and σ a length. The potential has a minimum as $r = 2^{1/6}\sigma$ and is repulsive for shorter distances and attractive for larger distances. For a noble gas (e.g. Argon), $\varepsilon \sim 0.01$ eV and $\sigma \sim 3$ Å.

3.3 Short-ranged potentials

Implementing Eq. (3.1) naively leads to a complexity of $O\left(N^2\right)$ because the sum contains N^2 terms. The trick is to cut the interaction range, i.e. set energies and forces to zero for distances larger than a certain cut-off distance r_c. This is possible because the asymptotic behavior $V(r) \to 0$ as $r \to \infty$.

Potentials for which this asymptotic decay is fast enough can be cut-off and are called short-ranged. Note that we have already encountered a case in Chap. 1 for which this is not possible, the Coulomb interaction that has the form $V(r) \propto 1/r$.

A simple way to see why this is not possible for the Coulomb interaction is to lump the charge-neutral infinite solid into charge-neutral dipoles. The effective interaction between dipoles then falls of as $V^{\text{eff}}(r) \propto 1/r^3$. The contribution to the energy from all dipoles at distance r is $V(r) r^2 \propto 1/r$. The full energy is obtained by integrating this function over r, but the integral does not converge! This illustrates the problem. The discrete sum is convergent, but only conditionally so, i.e. the outcome depends on the order of summation. We therefore can only cut interactions that decay as r^{-4} or faster.

The potential energy with a cutoff looks as follows:

$$E_{\text{pot}}\left(\{\vec{r}_i\}\right) = \frac{1}{2} \sum_{i=1}^{N} \sum_{\{j | r_{ij} < r_c\}} V\left(r_{ij}\right) \tag{3.4}$$

The difference to Eq. (3.1) is that the second sum runs only over *neighbors* of i, i.e. those atoms j whose distance $r_{ij} < r_c$ where r_c is the cutoff radius. This sum has $N\bar{n}$ elements where $\bar{n}$ is a constant, is the average number of neighbors within the cutoff radius r_c. The complexity of an algorithm that implements the above sum is hence $O(N)$.

A simple pair potential is often shifted at the cutoff to make the energy continuous (since $V(r_c) \neq 0$). The potential energy expression is then $E_{\text{pot}} = \sum_{i<j} \left(V\left(r_{ij}\right) - V\left(r_c\right)\right)$. Note that only by shifting the potential, forces and potential energy become consistent. Since only the forces affect the dynamics, the potential energy must be continuous and the integral of the forces, otherwise the Hamiltonian H is not a conserved quantity. The shifted potential fulfills these requirements, the unshifted one does not.

3.4   Neighbor list search

The sum Eq. (3.4) runs over all neighbors. One important algorithmic step with complexity $O(N)$ in molecular dynamics codes is to build a *neighbor list*, i.e. find all pairs *i-j* with $r_{ij} < r_c$. This is usually done using a *domain decomposition* (see Fig. 3.1) that divides the simulation domain in cells of a certain size and sorts all atoms into one of these cells. The neighbor list can then be constructed by looking for neighbors in neighboring cells only. If the cell size b is larger than the cutoff radius, $b > r_c$, then we only need to look exactly the neighboring cells.
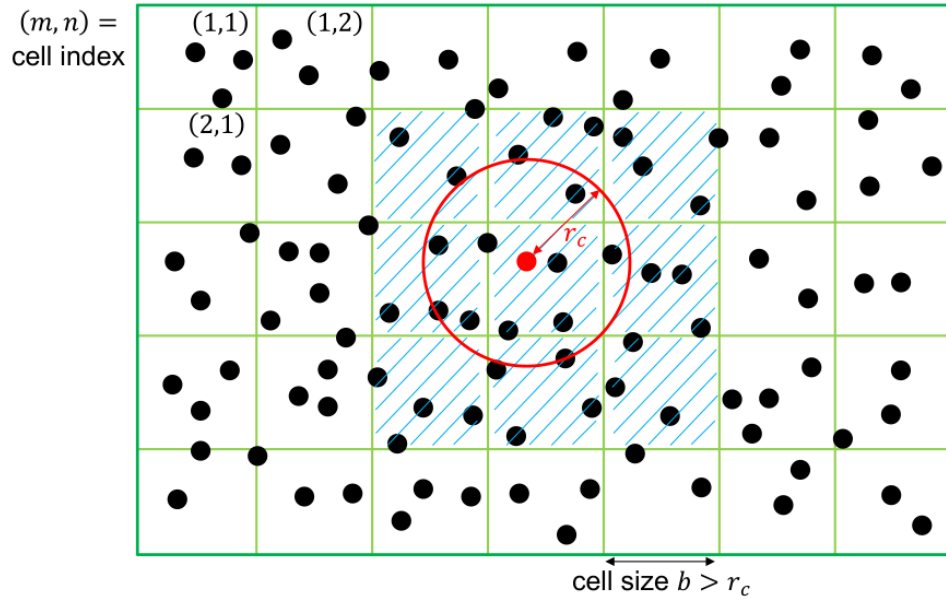
Figure 3.1: Illustration of the typical data structure used for an $O(N)$ neighbor search in a molecular dynamics simulation. For searching the neighbors within a cutoff r_c of the red atom, we only need to consider the candidate atoms that are in the cell adjacent to the red atom.

We will here illustrate a typical neighbor search using the two-dimensional example shown in Fig. 3.1. Let us assume that each atom has a unique index $i \in [1, N]$, where N is total number of atoms. (Attention, in C++ and other languages indices typically start at 0 and run to $N-1$.) A typically algorithm first builds individual lists $\{B_{k,mn}\}$ that contain the indices off all atoms in cell (m, n), i.e. $k \in N_{nm}$ where N_{nm} is the number of atoms in this cell. The cell can simply be determined by dividing the position of the atom by the cell size b, i.e. atom i resides in cell $m_i = \lfloor x_i/b \rfloor$ and $n_i = \lfloor y_i/b \rfloor$ where $\lfloor \cdot \rfloor$ indicates the closest smaller integer. The lists $\{B_{k,mn}\}$ are most conveniently stored in a single contiguous array; for purposes of accessing individual cells a second array is required that stores the index of the first entry of cell (m, n). Note that this second array is equal to the number of cells and can become prohibitively large when the system contains a lot of vacuum.

The neighbor search then proceeds as follows: For atom i, compute the cell (m_i, n_i) in which this atom resides and then loop over all atoms in this cell and in cells $(m_i \pm 1, n_i)$, $(m_i, n_i \pm 1)$ and $(m_i \pm 1, n_i \pm 1)$. In two dimensions, this yields a loop over 9 cells, in three-dimensions there the loop runs over 27. If the distance between these two atoms is smaller than the cutoff r_c, we add it to the neighbor list. Note that if the cell size b is smaller than r_c we need include more cells in the search.

Chapter 4

Temperature control

Context: Most molecular dynamics calculations are carried out in *thermal equilibrium*. Equilibrium is typically maintained by coupling the molecular calculation to a virtual *heat bath*, with which it exchanges energy but no particles. This chapter discusses properties of thermal equilibrium and introduces simple algorithms for heat-bath coupling.

4.1 Introduction

In order to talk about temperature control, we need to discuss the properties of thermal equilibrium. This is the realm of *statistical mechanics* or *statistical thermodynamics* that is discussed in more detail in Chapter 11 and Appendix B. A key outcome is that the velocity components are distributed according to a Boltzmann distribution. The velocity magnitude is then distributed according to a Maxwell-Boltzmann distribution.

A thermostat implicitly models the coupling to a heat bath much larger than the atomistic system under investigation. Because it is much larger, its temperature will not change when energy flows from and to the heat bath. The atomistic system becomes canonical and its statistics follows the *canonical ensemble*. An ensemble here describes which parameters are constrained, and the canonical ensemble is often also called the *NVT-ensemble*, because particle number N, volume V and temperature T are constrained (fixed). An ideal thermostat guarantees relaxation of the distribution of atomic degrees of freedom to the *canonical distribution function* (see Chapter 11).

We will here start with a mechanistic treatment of thermostats and underpin it with more rigorous theory in Chapter 11. The present chapter teaches the basic concepts required for an implementation of simple thermostatting

schemes. Thermostats can be roughly categorized into constraint methods (velocity rescaling and Berendsen), stochastic methods (Andersen, Langevin and dissipative particle dynamics) and extended system methods (Nosé-Hoover). Constraint and extended system methods are deterministic, i.e. they follow the same path when starting from the same initial state. In this chapter we will only discuss the simple constraint methods. We will come back to more advanced methods for temperature control later in these notes.

4.2 Simple themostatting schemes

4.2.1 Velocity rescaling

The crudest (and simplest) form of fixing the temperature in a molecular dynamics simulation to a value of T_0 is by velocity rescaling. Since the instantaneous temperature is

$$\frac{3}{2}k_B T = \sum_i \frac{1}{2} m v_i^2, \tag{4.1}$$

we obtain a temperature of T_0 if we rescale all velocities by

$$\vec{v}_i \to \lambda \vec{v}_i \quad \text{with} \quad \lambda = \sqrt{\frac{T_0}{T}} \tag{4.2}$$

after every time step. This is a very intrusive way of setting the temperature and should not be used in any practical situations, but it is a good illustration of how a simple constraint method works.

4.2.2 Berendsen thermostat

The Berendsen et al. (1984) thermostat uses a damping or acceleration term to control the temperature. The governing equations of motion of the Berendsen thermostat are

$$m\dot{\vec{v}}_i = \vec{f}_i + \frac{m}{2\tau}\left(\frac{T_0}{T} - 1\right)\vec{v}_i \tag{4.3}$$

where τ is a relaxation time constant. The factor in front of the velocity is a damping coefficient. The coefficient vanishes for $T = T_0$, Eq. (4.3) then reduces to Newton's equation of motion. However, it has a positive sign (=speeds up particles) for $T < T_0$ and has negative sign (=slows down particles) for $T > T_0$. From Eq. (4.3) we can easily derive a differential

equation for the evolution of the temperature:

$$3k_B \frac{dT}{dt} = \sum_i m\vec{v}_i \cdot \dot{\vec{v}}_i \tag{4.4}$$

$$= \sum_i \left[\vec{v}_i \cdot \vec{f}_i + \frac{1}{2\tau} \left(\frac{T_0}{T} - 1 \right) mv_i^2 \right] \tag{4.5}$$

$$= -\frac{dE_{\text{pot}}}{dt} + \frac{3k_B(T_0 - T)}{\tau} \tag{4.6}$$

This can be written as

$$\frac{dT}{dt} = -\frac{T - T_0}{\tau} + S \tag{4.7}$$

where $S = -\frac{1}{3k_B} \frac{dE_{\text{pot}}}{dt}$ is the change of *potential* energy and constitutes an additional temperature (energy) source.

For $S = 0$, this equation is solved by

$$T(t) = T_0 + (T_1 - T_0)e^{-t/\tau} \tag{4.8}$$

The temperature relaxes exponentially from the intial value T_1 towards T_0. We directly see that τ in Eq. (4.3) is indeed the relaxation time constant.

Note that Eq. (4.8) suggests an implementation of the Berendsen thermostat in terms of velocity rescaling. During at single time step $\Delta t \ll \tau$, the temperature changes from T to $T_0 + (T - T_0)e^{-\Delta t/\tau}$. We can implement this as velocity rescaling, Eq. (4.2), with

$$\lambda = \sqrt{\frac{T_0}{T} + \left(1 - \frac{T_0}{T} \right) e^{-\frac{\Delta t}{\tau}}} \approx \sqrt{1 + \left(\frac{T_0}{T} - 1 \right) \frac{\Delta t}{\tau}} \tag{4.9}$$

where T is the current (measure) temperature and T_0 is the target temperature.

A Berendsen thermostat therefore constitutes a gentle way of rescaling velocities. The relaxation time τ determines the strength of the coupling between thermal bath and atomistic system. The velocity rescaling limit $\lambda \to \sqrt{T_0/T}$ is obtained as $\tau \to 0$. Thermostats should be tuned as weak as possible and as strong as necessary to disturb the system the least while still allowing it to reach the target temperature within the simulation time. There is the additional requirement $\tau \gg \Delta t$ (where Δt is the time step), otherwise equation Eq. (4.7) will not be sampled properly numerically. The velocity rescaling thermostat discussed above is bad because it is very strong, but also because it violates $\tau \gg \Delta t$.

4.3 Equilibrating a molecular simulation

A "happy" molecular dynamics simulation will nicely run at constant temperature. Simulations are only this happy once they are *equilibrated* and this equilibration implies that the positions $\{\vec{r}_i\}$ are such that the system resides somewhere near a (potentially local) minimum in the potential energy landscape. When we set up a new simulation, we have to guess a set of $\{\vec{r}_i\}$ that are often far away from this minimum. (For crystalline solids this guess is simple, since we typically know the crystal structure that we are interested in. For liquids, the guess is more difficult since the overall structure is disordered.) Since the forces $\{\vec{f}_i\}$ point towards the minimum, the system will evolve in this direction and the potential energy E_{pot} will decrease over time, $dE_{\text{pot}}/dt < 0$. Equation (4.7) tells us, that this leads to an increase in temperature since $S > 0$.

A common problem is that this temperature can be large enough to vaporize the system, i.e. the temperature increases above the vaporization point. The first step in any molecular dynamics simulation is hence to *equilibrate* the system while avoiding a temperature rise above the point of vaporization (or melting if you are setting up a solid). This can be achieved by running a calculation with a Berendsen thermostat and a strong coupling (i.e. a small τ). Once the system has equilibrated, the value of τ can be adjusted to a more reasonable relaxation time that does not disturb the calculation too much. Good values for τ are between 1 ps and 10 ps.

Note that if we *continuously* pump energy into our system, for example because we deform it externally, then Eq. (4.7) acquires a non-zero source term, $S > 0$. Assuming S is constant over time, the final temperature is shifted to $T_0{}' = T_0 + S\tau$. This temperature offset gets smaller with increasing coupling strength $1/\tau$.

Chapter 5

Embedded-atom method potentials

> **Context:** We here introduce a more complex interatomic potential that is suitable for modeling metals, the embedded atom method potential. It belongs to the class of *many-body* interatomic potentials and can be used to model mechanical or thermodynamic properties of metals.

5.1 Introduction

Metals are often cubic crystals with anisotropic mechanical properties. Crystals with cubic symmetry have three independent elastic constants, C_{11}, C_{12} and C_{44} that roughly describe the resistance to volume change, dilational shear and simple shear. The original driving force behind the development of the embedded atom method (EAM) was to overcome the zero Cauchy pressure $P_C = (C_{11} - C_{44})/2$ for solids obtained for pair potentials: Pair potentials always satisfy the *Cauchy relation* $C_{11} = C_{44}$, hence there are only two independent elastic constants for cubic solids. [Compare: For an *isotropic* solid there are also two independent elastic constants, but this condition is different, bulk modulus $K = (C_{11} + 2C_{12})/3$ and shear modulus $G = C_{44} = (C_{11} - C_{12})/2$.] The Cauchy relation can be relaxed by adding an energy term that depends on the volume per atom $v = V/N$ (Vitek, 1996)

$$E(\{\vec{r}_i\}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} V(r_{ij}) + NU(V/N) \qquad (5.1)$$

The *volume dependent term* contributes only to deformation modes that do not conserve the volume, i.e. C_{11} or C_{12}. This hence breaks the Cauchy

25

relationship $C_{12} = C_{44}$ and gives a non-zero Cauchy-pressure $P_C = (C_{12} - C_{44})/2$

While a potential of the type given by Eq. (5.1) can be adjusted to give the correct elastic constant (and can therefore be accurate), *it cannot be used for e.g. free surfaces* (and is therefore not transferable). This has historically driven the development of more advanced methods for modeling solids such as the EAM described here. Note that EAM potentials are not confined to the realm of solids but can also be used for studying properties of melt, or the transition between solid and melt.

5.2   Functional form

The EAM is based on the assumption that the energy of an impurity in a host crystal lattice is a functional of the overall electron density $\rho(\vec{r})$ (that leads to an attraction), plus some form of repulsion (i.e. due to Pauli exclusion). This can be written as $E_{\mathrm{pot}} = \mathcal{F}\left[\rho(\vec{r})\right] + \phi$, where $\mathcal{F}$ is called the embedding functional that tells us the relationship between energy and electron density and ϕ some repulsive interaction.

We view each individual atom in the system as an impurity in the host consisting of all other atoms (Daw and Baskes, 1983). $\mathcal{F}$ is then approximated by a *function* that depends on the *local* electron density ρ_i at atom i:

$$E_{\mathrm{pot}}(\{\vec{r}_i\}) = \sum_i \mathcal{F}(\rho_i) + \frac{1}{2} \sum_{i,j} \phi(r_{ij}) \qquad (5.2)$$

Note the first sum is over atoms, not pairs, and the second term is a simple pair interaction. The missing ingredient is now the local electron density ρ_i, which we approximate from the local density of the nuclei. This assumes that each atom in the vicinity of atom i contributes a certain number of electrons to the position of atom i.

The embedding function $\mathcal{F}(\rho)$ is negative and (typically) decreases monotonously with increasing density. The more closely a structure is packed the lower the energy. The repulsive term that is physically due to electrostatic and Pauli repulsion then stabilizes the structure. This is balance between attractive and repulsive contribution a common feature of most interatomic potentials, and we have already seen it for the Lennard-Jones potential.

The local density of the atomic system is easily computed from

$$\rho_i = \sum_j f(r_{ij}) \qquad (5.3)$$

If $f(r)$ is a step function that drops to zero at a distance r_c then ρ_i becomes the coordination number, i.e. the number of atoms within a sphere of radius r_c. By normalizing the step function with the volume of the sphere, it becomes clear that ρ_i is some measure of the average atomic density within a distance r_c from atom i. However, a step function is not differentiable. All distance dependent functions are therefore smoothly connected to zero at a distance r_c (the cutoff). This makes the whole functional form differentiable at least once!

Examples of early EAMs are Gupta (1981), Finnis and Sinclair (1984) and Cleri and Rosato (1993). They all employ the specific functional forms

$$\mathcal{F}(\rho) = -A\sqrt{\rho} \tag{5.4}$$

$$f(r_{ij}) = e^{-2q(r_{ij} - r_0)} \tag{5.5}$$

$$V(r_{ij}) = B e^{-p(r_{ij} - r_0)} \tag{5.6}$$

where A, B, q, p and R_0 are parameters. For example, Cleri and Rosato (1993) give parameters for the elements Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Al, Pb, Ti, Zr, Co, Cd, Zn and Mg. Note that the cutoff radius r_c in most potentials based on the embedded-atom approach reaches out to second nearest neighbors or further, e.g. to fifth nearest neighbor for fcc metals in the Cleri and Rosato (1993) potential. These potentials do not describe fundamental forces of nature but they must be parametrized for a specific material. The parametrization also includes choice of cutoff radius r_c.

5.3 Parameterization

There exist different strategies to actually determine the parameters of a potential. Cleri and Rosato (1993), as an example, have five parameters and they fit the potential directly to *experimental values* of the cohesive energy, lattice constant and the three cubic elastic constants.

Some authors adjust the either embedding function or repulsive pair potential to reproduce the *universal equation of state* (see Ferrante et al. (1983); Rose et al. (1984)). For example, Foiles et al. (1986) obtain $f(r_{ij})$ from the electron density of free atom calculations, and assume the pair repulsion is entirely electrostatic, $V(r_{ij}) = Z_i(r_{ij}) Z_j(r_{ij})/r_{ij}$ (with atomic charges Z_i actually depending on the distance between atoms, $Z(r_{ij}) = Z_0(1 + \beta R^\nu) \exp(-\alpha r_{ij})$ where Z_0, β, ν and α are parameters). The embedding function $F(\rho)$ is then adjusted to reproduce the universal equation of state. Note that Foiles et al. (1986) have more parameters in their model than Cleri and Rosato (1993)!

A more modern approach is *force matching* due to Ercolessi and Adams (1994). Force matching potentials are fit to a set of calculations carried out

with a more accurate and more transferable but also more expensive method (e.g. a quantum chemical method) at finite temperature. This generates a molecular dynamics trajectory that has configurations with nonzero forces on each atom. (Fitting to equilibrium properties such as Cleri-Rosato means fitting to structures where all forces are zero.) The potential parameters are then fit to reproduce these forces. This method has the advantage that, in principle, an unlimited set of fitting target can be generated easily and the potential can be fit to a large number of parameters. An example of a force-matched EAM is Grochola et al. (2005). It has no fixed functional form, but splines are used to represent the three functions $\mathcal{F}(\rho)$, $f(r)$ and $V(r_i j)$. Figure 5.1 shows these functions for the Grochola et al. (2005) potential.

> **Note:** While early EAM potentials had a purely attractive embedding contribution $\mathcal{F}(\rho)$ and a purely repulsive pair contribution $\phi(r)$, this condition is relaxed in more complex potential. As can be seen from Fig. 5.1, Grochola et al. (2005)'s potential includes a repulsive contribution from the embedding term.

> **Note:** Note that these two approaches, fitting to experimental ground-state data and force-matching, are quite different from a philosophical point of view. It has been argued by Sukhomlinov and Müser (2016), that the potential should contains as few parameters as possible (Occam's razor!) to achieve best transferability. Potential with many parameters are often accurate for the fitting data set but not accurate outside and hence not transferable. This problem is typically referred to as overfitting.

5.4 Forces

From the total energy expression we can straightforwardly derive forces, $\vec{f}_k = -\partial E/\partial \vec{r}_k$, leading to

$$\vec{f}_k = -\sum_i \frac{\partial \mathcal{F}(\rho_i)}{\partial \rho_i}\frac{\partial \rho_i}{\partial \vec{r}_k} - \frac{1}{2}\sum_{i,j}\frac{\partial V}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial \vec{r}_{ij}} \tag{5.7}$$

$$= -\sum_i \frac{\partial \mathcal{F}(\rho_i)}{\partial \rho_i}\sum_j \frac{\partial f}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial \vec{r}_k} - \frac{1}{2}\sum_{i,j}\frac{\partial V}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial \vec{r}_k} \tag{5.8}$$
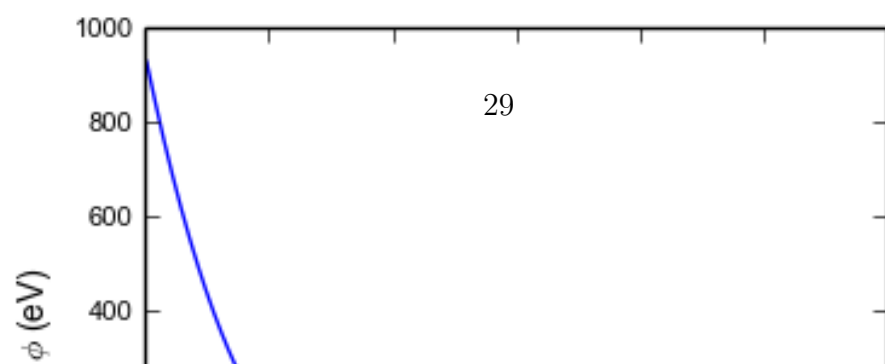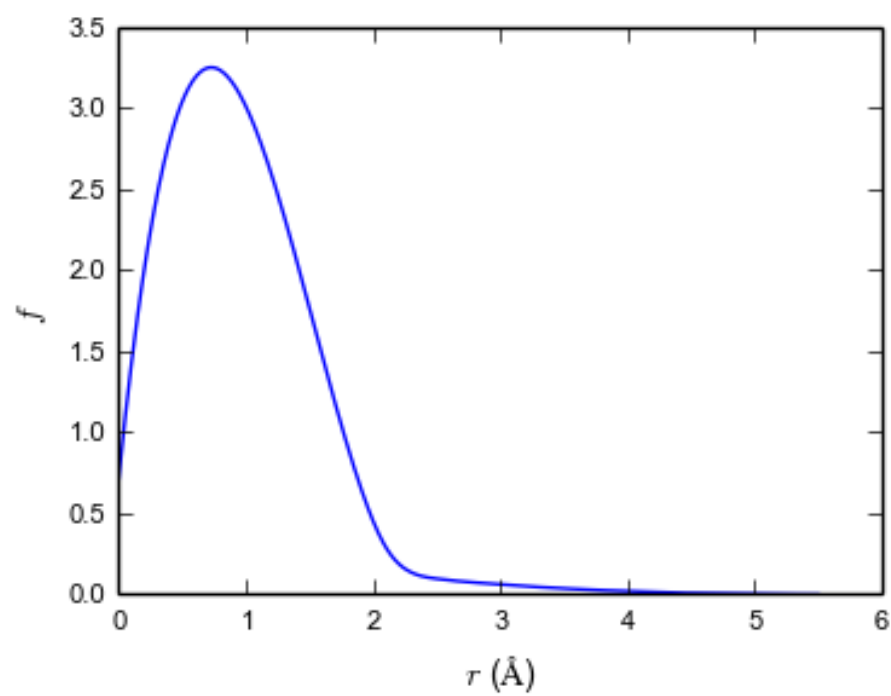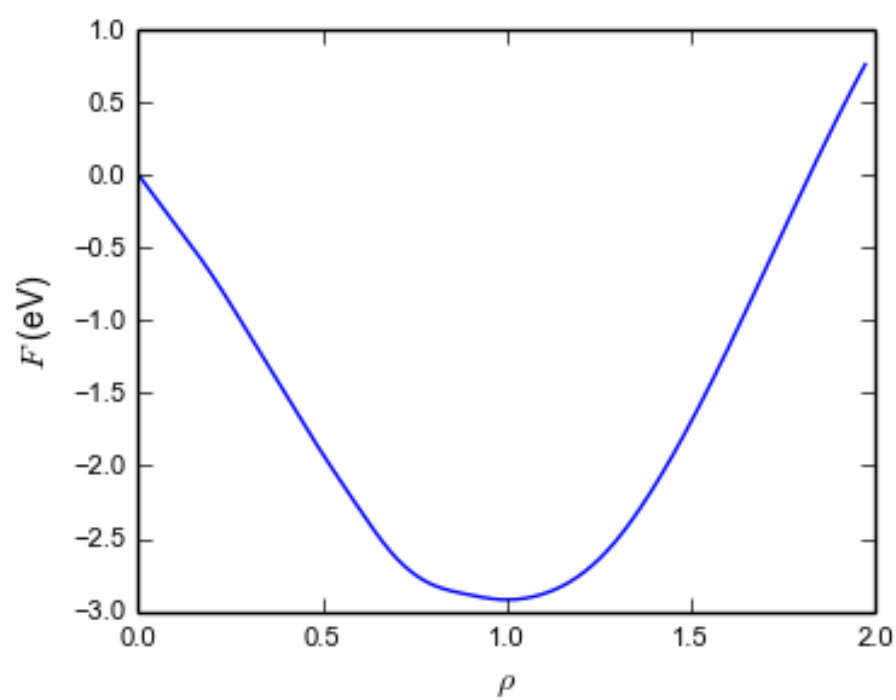
Note that $\partial r_{ij}/\partial \vec{r}_k = (\delta_{ik} - \delta_{jk})\,\hat{r}_{ij}$. Hence

$$\vec{f_k} = -\sum_i \frac{\partial \mathcal{F}(\rho_i)}{\partial \rho_i}\sum_j \frac{\partial f}{\partial r_{ij}}(\delta_{ik} - \delta_{jk})\,\hat{r}_{ij} - \frac{1}{2}\sum_{i,j}\frac{\partial V}{\partial r_{ij}}(\delta_{ik} - \delta_{jk})\,\hat{r}_{ij} \qquad (5.9)$$

$$= -\sum_i \left(\frac{\partial \mathcal{F}(\rho_k)}{\partial \rho_k}\frac{\partial f}{\partial r_{ki}}\hat{r}_{ki} - \frac{\partial \mathcal{F}(\rho_i)}{\partial \rho_i}\frac{\partial f}{\partial r_{ik}}\hat{r}_{ik} \right) - \frac{1}{2}\sum_i \left(\frac{\partial V}{\partial r_{ki}}\hat{r}_{ki} - \frac{\partial V}{\partial r_{ik}}\hat{r}_{ik} \right)$$
$$(5.10)$$

Using $\hat{r}_{ik} = -\hat{r}_{ki}$ gives

$$\vec{f_k} = \sum_i \left(\frac{\partial \mathcal{F}(\rho_k)}{\partial \rho_k} + \frac{\partial \mathcal{F}(\rho_i)}{\partial \rho_i} \right)\frac{\partial f}{\partial r_{ik}}\hat{r}_{ik} + \sum_i \frac{\partial V}{\partial r_{ik}}\hat{r}_{ik} \qquad (5.11)$$

Energies and forces are typically implemented analytically in a molecular dynamics code. Derivation (and correct implementation) of the force can be tedious for complicated potential expressions!

Chapter 6

Parallel computers and the Message Passing Interface

Context: This chapter sets the stage for discussing parallelization of the molecular dynamics simulation method introduced in the previous chapters. We first need to talk about parallel hardware architectures and how to program for them. The specific programming model that we will employ is known under the term *Single Program Multiple Data*. The Message Passing Interface (MPI) is a library that facilitates programming for massively parallel machines under this programming model.

6.1 Parallel hardware architectures

Parallel hardware has become ubiquitous over the past decade. Most central processing units (CPUs) in computers, phones or other hardware have multiple cores that can execute instructions in parallel. Massively parallel computing systems combine multiple CPUs into nodes that share a common memory. These nodes are then combined into the full compute system through a network interconnect.

Parallel architecture are often hierachical and have parallelization at different levels. Notable is vectorization at the core-level, share memory parallelization for multicore architectures and distributed memory parallelization for large computing systems that communicate via an interconnect (a network connection).

6.2 Scaling consideration

Software that runs on parallel computers needs to scale. Scaling describes how the time to returning the result changes as the number of available compute units (cores) changes. The simplest model for scaling assumes that our code can be divided into a fraction f_s that needs to be executed on a single core while a fraction f_p scales perfectly, i.e. its execute time is $\propto 1/p$ where p is the number of available processes or cores. (Note that $f_s + f_p = 1$ since they are fractions.) This leads to Amdahl's law that describes the speedup S as a function of p:

$$S = pf_p + f_s p \tag{6.1}$$

6.3 Programming model

The Message Passing Interface (MPI) is an application programming interface (API) for distributed memory parallelization. (A code parallelized with MPI also works on shared memory machines!) The programming model underlying MPI is called single program multiple data (SPMD): The identical program is executed multiple times but operates on different datums.

6.3.1 Example: Monte-Carlo estimate of the number π

As the simplest example of a parallelization, we consider a Monte-Carlo estimate of the number π.

Chapter 7

Domain decomposition

Context: Parallelization in molecular dynamics typically occurs through *domain decomposition.* The simulation domain is divided into subdomains, each of which runs within an MPI process. This distributes the workload among different compute units. Communications occurs only at the interface of the subdomain, either to exchange atoms between subdomains or to communicate *ghost atoms* that are required for the computation of correct forces in short-range interatomic potentials.

7.1 Simulation domain

Our atomic system has so far lived in an infinite space consisting of vaccum. We have made no reference to a simulation domain and the code developed up to Milestone 07 makes not reference to such a domain. We now introduce domain decomposition and for this need a simulation domain, i.e. a region of space Ω in which our atoms can reside. This domain can be periodic, which we will discuss in more detail in the next chapter.

We will assume that the simulation has its origin at $(0, 0, 0)$ and is spanned by three linearly independent vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$. Any atomic position can then be expressed as

$$\vec{r}_i = s_{i,1}\vec{a}_1 + s_{i,2}\vec{a}_2 + s_3\vec{a}_{i,3} \tag{7.1}$$

with $s_\alpha \in [0, 1)$. s_α must remain in this interval since we do not allow atoms outside of the simulation domain. The vector $\vec{s}_i$ is the scaled position of the atom i. Using the *domain matrix* $\underline{A} = (\vec{a}_1, \vec{a}_2, \vec{a}_3)$, we can express this more compactly as $\vec{r}_i = \underline{A} \cdot \vec{s}_i$. Conversely, we obtain the scaled positions from $\vec{s}_i = \underline{A}^{-1} \cdot \vec{r}_i$.

In what follows, we assume rectilinear domains, i.e. $\vec{a}_1 = (L_x, 0, 0)$, $\vec{a}_2 = (0, L_y, 0)$ and $\vec{a}_3 = (0, 0, L_z)$ where L_x, L_y and L_z are the linear dimensions of the domain. The methods that are described in the following are straightforwardly extended to arbitrary (tilted) domains.

7.2 Decomposition into Cartesian domains

We decompose the full system into $N_x \times N_y \times N_z$ subdomains. For a rectilinear domain, this means teach subdomain has linear dimensions of L_x/N_x, L_y/N_y and L_z/N_z. Each subdomain propagates its own atoms. When atoms leave the subdomain, they are transferred to the respective neighboring domain. We call this process *atom exchange*.

Domain decomposition algorithms for MD simulations have started to appear in the literature around 1990. Some of the earliest references to this type of algorithm are Brugè and Fornili (1990); Liem et al. (1991); Chynoweth et al. (1991); Pinches et al. (1991); Brown et al. (1993); Plimpton (1995).

7.3 Ghost atoms

The atoms within each subdomain are not sufficient to compute the forces upon these atoms. In order to compute forces for atoms near the domain boundary, we need to transfer atoms that sit outside of the subdomain from the neighboring subdomains. These atoms are called ghost atoms. All atoms up to a distance r_G from the subdomain boundary are transferred. For a Lennard-Jones potential, $r_G = r_c$ but for the EAM potential discussed here $r_G = 2r_c$. This is because a force in the EAM potential is affected by an atom that sits twice the cutoff radius r_c away.

7.4 Communication pattern

The basic communication pattern involves two `MPI_Sendrecv` commands per Cartesian direction. The atoms that are send (either exchanged or as ghost atoms) must be serialized into a send buffer. Given that serialization has occured into the buffers `send_left` and `send_right`, the communication pattern looks as follows:

```
1 MPI_Sendrecv(&send_left, left_, &recv_right, right_, comm_)};
2 MPI_Sendrecv(&send_right, right_, &recv_left, left_, comm_)};
```

Here `comm_` contains the MPI communicator and `left_` and `right_` the MPI ranks of the processes that host the subdomain to the left and the

right, respectively, of the current subdomain. The buffers `recv_left` and `recv_right` hold the serialized atomic information received from the left and right, respectively. This information needs to be deserialized into the respective atom data type.

Chapter 8

Periodicity and pressure

Context: Now that we have introduced the notion of the simulation domain, we can introduce *periodicity*. In a periodic domain, atoms on the right interact with atoms on the left. Periodic domains are commonly used to represent bulk solid or fluid materials and eliminate the effect of interfaces or surfaces. They are sometimes referred to as *periodic volume elements (RVEs)*. The state of the RVE depends on its volume (or the full domain matrix) and we can introduce the conjugate variable, the pressure (or stress tensor).

8.1 Periodicity

All energy expressions here are written as $E_{\text{pot}}(\{\vec{r}_i\})$. If there is no periodic interaction across the domain boundaries, the energies depends on positions only. For periodic interactions, they depend explicity on the domain vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ or the corresponding matrix $\underline{A}$: $E_{\text{pot}} = E_{\text{pot}}(\underline{A}; \{\vec{s}_i\})$, where we have expressed the positions in the respective scaled coordinates.

Periodicity is implicitly contained in the way the potential is written. E.g. for a pair potential,

$$E_{\text{pot}}(\{\vec{r}_i\}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \phi(r_{ij}) = \sum_{i<j} \phi(r_{ij}), \qquad (8.1)$$

the energy depends only on relative positions $\vec{r}_{ij}$. This distance vector contains the information of the simulation domain implicitly. All potential energy expression must be a function of relative positions, never of absolute positions, since this would violate momentum conservation (Newton's second law). Note

that in terms of the matrix $\underline{A}$ and the scaled positions, the potential energy becomes

$$E_{\text{pot}}(\underline{A}; \{\vec{s}_i\}) = \sum_{i<j} \phi(|\underline{A} \cdot \vec{s}_{ij}|), \qquad (8.2)$$

where $\vec{s}_{ij} = \vec{s}_i - \vec{s}_j$ is the scaled distance between the atoms i and j.

8.2 Ghost atoms

There are different ways to realize periodic domains in MD simulation codes. A common way is to incorporate periodicity into the neighbor list, which is then build to include neighbors across domain boundaries with the correct distance vector $\vec{r}_{ij}$. The potential energy of the system is then given by Eq. (8.2).

An alternative is to construct a supercell of the domain, i.e. replicate the domain such that the repeating periodic image is explicitly present. In practice, this is equivalent to creating a region of ghost atoms around the domain and this is naturally incorporated into the portion of the code handling the domain decomposition (that was described in the previous chapter). In this case, the potential energy is given by

$$E_{\text{pot}}(\{\vec{r}_i\}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N+N_{\text{G}}} \phi(r_{ij}), \qquad (8.3)$$

where it is important to realize that the sum over i runs over all atoms in the domain, while the sum over j runs over the N domain atoms as well as the N_{G} ghost atoms with index $j \in [N + 1, N_{\text{G}}]$. This strategy is for example found in the widely used MD code LAMMPS.

8.3 Pressure and stress

For a periodic domain (an RVE) we can ask what the pressure of the system is. From a thermodynamic perspective, the (potential energy contribution to the) pressure is given by

$$P = -\frac{\partial E_{\text{pot}}}{\partial V}, \qquad (8.4)$$

where $V = \det \underline{A}$ is the volume of the domain. This expression is only valid at zero temperature; at finite temperature we need to use the free energy rather than the potential energy and this yields an additional kinetic contribution to the pressure.

When working with solids, we are often interested in the full stress tensor $\underline{\sigma}$ of the system. Let us assume our RVE undergoes a deformation. This means the domain matrix is taken from $\underline{A}$ to $\underline{A}' = \underline{F} \cdot \underline{A}$ where $\underline{F}$ is called the *deformation gradient*. The Cauchy stress is then given by

$$\underline{\sigma} = \frac{1}{V} \left. \frac{\partial E_{\text{pot}}(\underline{A}'; \{\vec{s}_i\})}{\partial \underline{F}} \right|_{\underline{F}=\underline{1}} , \tag{8.5}$$

where the derivative with respect to the deformation gradient $\underline{F}$ is taken component-wise.

Evaluating the stress for Eq. (8.2) yields

$$\underline{\sigma} = \frac{1}{V} \sum_{i<j} \left. \frac{\partial \phi(|\underline{F} \cdot \vec{r}_{ij}|)}{\partial \underline{F}} \right|_{\underline{F}=\underline{1}} = \frac{1}{V} \sum_{i<j} \frac{\partial \phi}{\partial r_{ij}} \vec{r}_{ij} \otimes \vec{r}_{ij} \tag{8.6}$$

where $\otimes$ is the outer product, $[\vec{a} \otimes \vec{b}]_{ij} = a_i b_j$. Equation Eq. (8.6) can be directly used to compute the stress of a pair-potential in molecular dynamics, and similar expression can derived for other potentials such as the EAM.

8.4   Stress and ghost atoms

In the presence of ghost atoms, there is a simpler way to compute the stress in the simulation cell. While an expression like Eq. (8.6) needs to be derived for every functional form of a potential, this strategy is independent of the functional form of the potential.

The idea is to use the forces on the ghost atoms that enclose the simulation domain to compute the stress. The relevant expression can be derived from the conservation of the moment of inertia. (The moment of inertia is only conserved for a *nonperiodic* system - which is why this method is only applicable to supercells!) Taking the derivative of the moment of inertia $I = \sum_i m_i r_i^2$ yields

$$\frac{1}{2} \frac{dI}{dt} = \sum_i m_i \vec{v}_i \cdot \vec{r}_i \tag{8.7}$$

The second derivative then becomes

$$\frac{1}{2} \frac{d^2 I}{dt^2} = \sum_i (\vec{f}_i \cdot \vec{r}_i + m_i v_i^2) = 2E_{\text{kin}} + \sum_i \vec{f}_i \cdot \vec{r}_i \equiv 0 \tag{8.8}$$

which has to be zero (because I is a constant of motion). This expression is called the virial theorem.

Since our simulation domain is enclosed by ghost atoms, the forces $\vec{f}_i$ have a contribution from these ghosts (the container walls). Hence $\vec{f}_i = \vec{f}_i^{\text{domain}} + \vec{f}_i^{\text{G}}$. From Eq. (8.8) we get $\sum_i \vec{f}_i^{\text{G}} \cdot \vec{r}_i = -2E_{\text{kin}} - \sum_i \vec{f}_i^{\text{domain}} \cdot \vec{r}_i$.

Now $\vec{f}_i^{\text{G}}$ can be related to the external pressure. By virtue of Newton's third law (for every action there is an equal and opposite reaction), the forces $\vec{f}_i^{\text{G}}$ (with $i \in [1, N]$) need to be exactly balanced by the forces $\vec{f}_i$ (with $i \in [N + 1, N_{\text{G}}]$) on the *ghost atoms themselves*.

Let's assume that the particles that feel a wall force are located infinitely close to the wall itself (hard-wall assumption). If we now have a container with its *origin at one corner of the box*, then $\sum_i \vec{f}_i^{\text{ext}} \cdot \vec{z}_i = L_z \sum_i \vec{f}_i^{\text{ext}} = L_z(-PL_xL_y)$ because $\vec{z}_i$ is located at the wall, etc., or taking x-, y- and z-components, $\sum_i \vec{f}_i^{\text{ext}} \cdot \vec{r}_i = -3PL_xL_yL_z$. This means

$$PV = \frac{2}{3}E_{\text{kin}} + \frac{1}{3}\sum_i \vec{f}_i^{\text{int}} \cdot \vec{r}_i = NkT + \frac{1}{3}\sum_i \vec{f}_i^{\text{int}} \cdot \vec{r}_i = NkT + W \qquad (8.9)$$

Eq. (8.9) is called the virial theorem. This expression is valid for non-periodic systems only! The quantity W is called the virial.

Chapter 9

Pressure control

9.1 Berendsen

The Berendsen barostat [2] works like the Berendsen thermostat. Instead of slowly rescaling the velocities, the barostat rescales the (periodic) simulation cell. The cell is rescaled such that the pressure obeys the equation

$$\frac{dP}{dt} = \frac{P_0 - P}{\tau_p} \tag{9.1}$$

where P is the system pressure obtained from the virial expression (including the kinetic contribution). The Berendsen barostat updates positions $\vec{r}_i$ and cell volume $\dot{V}$ according to

$$\dot{\vec{r}}_i = \vec{v}_i + \alpha \vec{r}_i \quad \text{and} \quad \dot{V} = 3\alpha V \tag{9.2}$$

where α is a volumetric strain rate. We know that $dP/dV = -K/V$ where K is the bulk modulus. (Indeed, this is just the definition of the bulk modulus.) Hence

$$\frac{dP}{dt} = -\frac{K}{V}\frac{dV}{dt} = -3K\alpha = \frac{P_0 - P}{\tau_p} \tag{9.3}$$

and we have $\alpha = (P - P_0)/3K\tau_p$. This can be implemented by rescaling all lengths by the factor

$$\mu = \left[1 - \frac{\Delta t}{K\tau_p}(P_0 - P) \right]^{1/3} \approx 1 - \frac{\Delta t}{3K\tau_p}(P_0 - P) \tag{9.4}$$

Note that we need to know the bulk modulus to be able to set a specific time constant τ_p! No additional material parameter was required for the thermostats above.

Practical note: The default bulk modulus in LAMMPS is orders of magnitude lower than typical moduli for solids. If you used a Berendsen barostat in LAMMPS, make sure to adjust the bulk modulus.

9.2   Andersen

The Andersen barostat [7] is an extended system method similar to the Nosé-Hoover thermostat discussed above. The Hamiltonian for the Andersen barostat is typically expressed in terms of the scaled coordinates $\vec{\rho}_i = \vec{r}_i/V^{1/3}$ and momenta $\vec{\pi}_i = \vec{p}_i/V^{1/3}$, where V is the volume of the system. It can be shown that the Hamiltonian becomes

$$H_s(\{\vec{\pi}_i\}, \{\vec{\rho}_i\}, p_V, V) = V^{-2/3} \sum_i \frac{\pi_i^2}{2m} + E_{pot}\left(\left\{V^{1/3}\vec{\rho}_i\right\}\right) + \frac{p_V^2}{2Q} + PV \quad (9.5)$$

with the fictious mass Q for the volume degree of freedom and pressure P. We can again write down the Hamiltonian equations of motion. Like in the Nosé-Hoover thermostat, the extended system Hamiltonian H_s is conserved.

9.3   Parrinello-Rahman

The Parrinello-Rahman barostat [11] is the extension of the Andersen method for arbitrary cell deformation.

Chapter 10

Valence force fields

Valence force fields are interatomic potential energy expressions mainly developed in the chemistry community to model structure of liquids and mixtures of organic compounds, including biochemical problems such as protein folding. The force-fields come in many flavors and usually with their specific acronym. The most widely used (and oldest) valence force fields are AMBER (Assisted Model Building and Energy Refinement, 1981) [2], CHARMM (Chemistry at HARvard Molecular Mechanics, 1983) [3] and GROMOS (GROningen MOlecular Simulationm, 1987) force-fields. CHARMM comes from the group of Martin Karplus group who received the 2013 nobel price in chemistry. There are also simulation codes with the same names that implement these force fields.

The potential energy of a valence force-field is written as a sum of individual contributions:

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{electrostatic}} + E_{\text{van der Waals}} + E_X \quad (10.1)$$

Atoms typically have fixed charges in this type of model, but variations that employ variable charges or atomic polarizabilities also exist. We have already seen what $E_{\text{van der Waals}}$ and $E_{\text{electrostatic}}$ look like. The contribution E_X is just a placeholder for additional energy contributions, such as a special treatment of Hydrogen bonds. While the first five terms in Eq. (10.1) are common to all valence force fields, E_X can differ significantly.

Bond, angle and dihedral contributions (see Fig. 10.1) are often written down in a harmonic approximation, i.e. bond are represented as springs, angular interaction as torsional spring and dihedral (angle rotation) as a trigonometric function (because they need to be periodic under a 360° degree rotation).
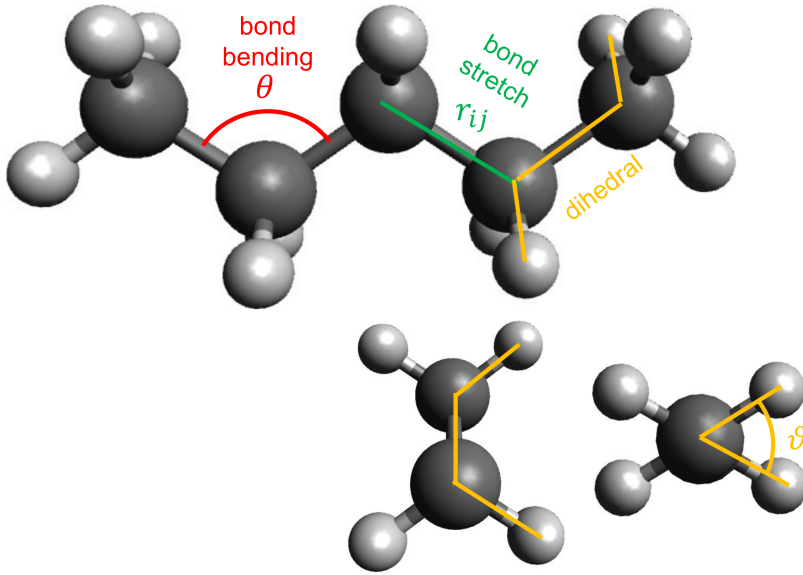
Figure 10.1: Illustration of bond bending, bond stretching and dihedral deformation of a molecule.

The specific energy expressions are:

$$E_{\text{bond}} = \sum_{i<j} K_r (r_{ij} - r_{\text{eq}})^2 \tag{10.2}$$

$$E_{\text{angle}} = \sum_{i<j} K_\theta (\theta - \theta_{eq})^2 \tag{10.3}$$

$$E_{\text{dihedral}} = \sum_{\text{dihedrals}} \frac{1}{2} K \left[1 + \cos\left(n\vartheta - \gamma\right) \right] \tag{10.4}$$

K_r, r_{eq}, K_θ, θ_{eq}, K, n, γ are parameters that depend on the chemical species on the *type of bond*. Some force fields approximate covalent bonds as rigid, i.e. $K_r \to \infty$.

Note that valence force field do not allow for (covalent) bond dissociation and hence chemical reactions. Since bonds are pre-defined, the *topology* of bonding is an additional input to the simulation. Valence force fields were not initially designed for solids (but parameterizations, in particular for surfaces, exist).

43

Chapter 11

Equilibrium statistical mechanics

11.1 The microcanonical ensemble

A complex molecular system with many degrees of freedom is chaotic. It samples the full phase space (if it is ergodic) or a portion of it in which the system lives (if it not ergodic) in time. The *phase space* here is the abstract concept that combines all positions $\{\vec{r}_i\}$ and momenta $\{\vec{p}_i\}$ of the molecular system. A point in phase space, also called a microstate, of a system with N atoms is characterized by a point in $6N$-dimensional space. (The coordinates of this point are exactly all positions and momenta.) Hamilton's equation of motion describe how this point moves through phase space in time.

Rather than asking about the time evolution, we can ask about the probability of finding the system in a certain point in phase-space. If the system is isolated (i.e. cannot exchange energy or particles with surrounding), we have to assume that every point in phase-space is equally likely. This is a consequence of our ignorance about the system and is called the postulate of *equal a-priori probabilities.*

Let us first discuss such an isolated system. As the system evolves in time, we know that it can only evolve on the manifold in phase space that corresponds to a certain total energy E, simply because E is a conserved quantity. Formally, this manifold is defined by all points $\{\vec{r}_i\}, \{\vec{p}_i\}$ that satisfy the equation

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) \equiv E \tag{11.1}$$

The postulate of equal a-priori probabilities now says, that our system is equally likely in all points $\{\vec{r}_i\}, \{\vec{p}_i\}$ for which Eq. (11.1) holds. All other points are prohibited because they belong to a different total energy and our

system cannot evolve there. The phase space that is accessible at energy E has a total volume of

$$\Omega(E) = \int_{H(\{\vec{r}_i\},\{\vec{p}_i\})=E} d^{3N}r_i d^{3N}p_i. \tag{11.2}$$

All accessible points form an *ensemble* of points. This constant energy ensemble is called the *microcanonical* ensemble.

11.2 The canonical ensemble

Let us know split our (microcanonical) system into a small system with energy E_A and a large heat-bath with energy E_B. The total energy is still $E = E_A + E_B$. If there is only energy exchange, then we can write $\Omega(E) = \Omega_A(E_A)\Omega_A(E_B)$ since the total Hamiltonian (of system and heat bath) is just the sum of the two individual Hamiltonians. Note that Ω is not an extrinsic property: It is not proportional to the number of particles N, but taking the logarithm of Ω is extrinsic. We *define* the extrinsic property

$$S(E) = k_B \ln \Omega(E) = k_B \ln \Omega_A(E_A) + k_B \ln \Omega_A(E_B) = S_A(E_A) + S_B(E_B), \tag{11.3}$$

where k_B is the Boltzmann constant. The property S is called the *entropy*.

We now note that the *probability* $f(E_A)$ of finding subsystem A in with energy E_A must then be proportional to $\Omega_B(E-E_A)/\Omega(E)$, i.e. the probability of finding system B with energy $E - E_A$. From Eq. (11.3) we can write this in terms of the entropy

$$f(E_A) \propto \Omega_B(E - E_A) = \exp\left[\frac{S_B(E - E_A)}{k_B}\right]$$
$$\approx \exp\left[\frac{1}{k_B}\left(S_B(E) - \frac{\partial S_B}{\partial E}E_A\right)\right] \tag{11.4}$$

where $\approx$ holds for $E_A \ll E$. (We have Taylor-expanded the entropy and discarded all quadratic and higher-order terms.)

From thermodynamics (see Appendix B) we know that

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{11.5}$$

where T is the *temperature* of the system. The temperature is the conjugate to the entropy. This yields

$$f(E_A) = \frac{1}{Z(T)}\exp\left(-\frac{E_A}{k_B T}\right) \tag{11.6}$$

where $T \equiv T_B$ is the temperature of the bath and $Z(T)$ a suitable normalization (called the *partition sum*) that turns $f(E_A)$ into a probability density. Equation (11.6) is called the *canonical distribution function* and the exponential term is called a *Boltzmann factor*. The corresponding ensemble is called the *canonical* or *NVT* ensemble. This distribution tells us the probability of finding a system with energy E_A, given it is coupled to a heat bath with temperature T.

As a first example of the use of Eq. (11.6), let us show that velocities are distributed according to a Gaussian. For the Hamiltonian $H(\{\vec{r}_i\}, \{\vec{p}_i\}) = \sum_i \left(\frac{\vec{p}_i^2}{2m_i} + E_{\text{pot}}(\{\vec{r}_i\}) \right)$ we obtain

$$f(\{\vec{r}_i\}, \{\vec{p}_i\}) = Z^{-1} \exp\left[-\frac{1}{kT} \sum_i \left(\frac{\vec{p}_i^2}{2m_i} + E_{\text{pot}}(\{\vec{r}_i\}) \right) \right] \qquad (11.7)$$

with

$$Z(T) = \int d^3 r_1 \cdots d^3 r_n d^3 p_1 \cdots d^3 p_N \, \exp\left[-\frac{1}{kT} \left(\frac{\vec{p}_i^2}{2m_i} + E_{\text{pot}}(\{\vec{r}_i\}) \right) \right]. \tag{11.8}$$

$f(\{\vec{r}_i\}, \{\vec{p}_i\})$ is the joint probability distribution of finding our system at the phase-space point $\{\vec{r}_i\}, \{\vec{p}_i\}$. We are now only interested in the probability of finding atom 1 with a certain momentum $\vec{p}_1$. This is the marginal distribution $f_m(\vec{p}_1)$ of the random variable $\vec{p}_1$. It is given by integrating out all degrees of freedom except p_1,

$$f_m(\vec{p}_1) = \int d^3 r_1 \cdots d^3 r_n d^3 p_2 \cdots d^3 p_N \, f(\{\vec{r}_i\}, \{\vec{p}_i\}). \qquad (11.9)$$

Since the exponential of the Boltzmann factor factorizes, the integral becomes a product of independent integrals over each momentum degree of freedom plus an integral over all positional degrees of freedom. Those integrals are simply constants, leading to

$$f_m(\vec{p}_1) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{1}{k_B T} \frac{\vec{p}_i^2}{2m_i} \right) \qquad (11.10)$$

with a suitable normalization factor that ensures that $\int d^3 p_1 f(\vec{p}_1) = 1$. This is the famous Boltzmann distribution.

We can also use the canonical distribution values to compute *ensemble averages*. Given an *observable*, a function $O(\{\vec{r}_i\}, \{\vec{p}_i\})$ that depends only on

the phase-space coordinate, the ensemble average is given as the weighted average

$$\langle O \rangle = \int d^3 r_1 \cdots d^3 r_n d^3 p_1 \cdots d^3 p_N \, f(\{\vec{r}_i\}, \{\vec{p}_i\}) O(\{\vec{r}_i\}, \{\vec{p}_i\}) \qquad (11.11)$$

For example, the expectation values of the temperature $\langle k_B T \rangle$ and its fluctuations $\langle (k_B T)^2 \rangle - \langle k_B T \rangle^2$ from a canonical ensemble average,

$$\langle k_B T \rangle = \int_{-\infty}^{\infty} dp_1 \frac{p_1^2}{2m} \frac{1}{\sqrt{2\pi m k_B T}} \exp\left(-\frac{p_1^2}{2m k_B T}\right) = k_B T \qquad (11.12)$$

$$\langle (k_B T)^2 \rangle = \int_{-\infty}^{\infty} dp_1 \frac{p_1^4}{4m^2} \frac{1}{\sqrt{2\pi m k_B T}} \exp\left(-\frac{p_1^2}{2m k_B T}\right) = (k_B T)^2, \quad (11.13)$$

yield $\langle (k_B T)^2 \rangle - \langle k_B T \rangle^2 = 0$. The temperature does not fluctuate in the canonical ensemble!

However the total energy does. We can estimate the energy fluctuations from the ensemble averages $\langle H \rangle$ and $\langle H^2 \rangle$,

$$\langle H \rangle = \frac{1}{Z} \int \prod_{\alpha \in B} dr_\alpha dp_\alpha H(\{r_\alpha\}, \{p_\alpha\}) \exp\left(-\beta H(\{r_\alpha\}, \{p_\alpha\})\right) \qquad (11.14)$$

where we have abbreviated $\beta = 1/k_B T$. We can now use a mathematical trick to get $\langle H \rangle$. Since $H \exp(-\beta H) = -\frac{\partial}{\partial \beta} \exp(-\beta H)$, we have

$$\langle H \rangle = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z = -\frac{\partial}{\partial \beta} \ln Z \qquad (11.15)$$

and

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \frac{1}{Z^2} \left(\frac{\partial}{\partial \beta} Z\right)^2 = \langle H \rangle^2 - \langle H^2 \rangle \neq 0 \qquad (11.16)$$

Hence energy fluctuates in the canonical ensemble. (Remember, it was constant in the microcanonical or NVE ensemble.)

Chapter 12

Properties of liquids

During a molecular dynamics simulation it is useful to observe some measurable, integral quantities of the system. This will be a brief overview of two of the most important quantities, namely temperature and pressure. More details will be discussed in the next chapter on statistical mechanics.

12.1   Radial distribution function and structure factor

The radial distribution function (or pair correlation function) is a measure for the structure of the solid (or liquid)

$$g(r) = \frac{V}{N^2} \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \tag{12.1}$$

where $\rho = N/V$ is the number density of the material (N is the number of atoms and V its volume). $g(r)$ gives the probability of finding two particles a distance r apart. Note that $g(r) \to 1$ for $r \to \infty$, i.e. the probably of finding a particle an infinite distance apart becomes one.

When computing $g(r)$ from a computer simulation, the δ-function is smeared out, typically in equally spaced bins. The above definition Eq. (12.1) is exactly valid for just a system of infinite size. Note that the usual definition involves an ensemble average rather than a particle average (the sum over i). We will discuss this in the next chapter.

For a pair potential, this can be used to e.g. compute the potential energy $\int d^3r = 4\pi \int dr r^2$ and double counting correction)

$$E_{\text{pot}} = 2\pi N\rho \int_0^\infty dr \, r^2 V(r) g(r) \tag{12.2}$$

The pair distribution function is related to another important quantity, the structure factor $S(k)$. This is the power spectrum of the density of the system and hence related to the spatial Fourier transform of the number density fluctuations, $\rho(\vec{r}) = \sum_i \delta(\vec{r}-\vec{r}_i)$, $\rho(\vec{k}) = \int d^3r \exp(-i\vec{k}\cdot\vec{r})) = \sum_i \exp(-i\vec{k}\cdot\vec{r}_i)$, by

$$S(\vec{k}) = N^{-1}\rho(\vec{k})\rho(-\vec{k}) \tag{12.3}$$

$$= N^{-1}\int d^3r \exp(-i\vec{k}\vec{r}) \int d^3r\,'\rho(\vec{r\,'})\rho(\vec{r}+\vec{r\,'}) \tag{12.4}$$

$$= N^{-1}\int d^3r \exp(-i\vec{k}\vec{r}) \sum_{ij} d^3r\,'\delta(\vec{r\,'}-\vec{r}_j)\delta(\vec{r}+\vec{r\,'}-\vec{r}_i) \tag{12.5}$$

$$= N^{-1}\int d^3r \exp(-i\vec{k}\vec{r}) \sum_{ij} \delta(\vec{r}-\vec{r}_{ij}) \tag{12.6}$$

$$= 1 + \frac{1}{N}\int d^3r \exp(-i\vec{k}\cdot\vec{r}) \sum_i \sum_{j\neq i} \delta(\vec{r}-\vec{r}_{ij}) \tag{12.7}$$

$$= 1 + \frac{1}{N}\int d^3r \exp(-i\vec{k}\cdot\vec{r})g_2(\vec{r}) \tag{12.8}$$

where $g_2(\vec{r}) = \frac{V}{N^2}\sum_i\sum_{j\neq i}\delta(\vec{r}-\vec{r}_{ij})$ contains directional information. Note that $g(r) = (4\pi)^{-1}\int d\Omega\, g_2(|\vec{r}|)$, i.e. the radial average over $g(\vec{r})$. We can also compute the radial average over the structure factor

$$S(k) = 1 + 4\pi\rho\int dr\, r^2 \int d\theta\, \exp(-ikr\cos\theta)g(r) \tag{12.9}$$

$$= 1 + 4\pi\rho\int dr\, r\frac{\sin(kr)}{k}g(r) \tag{12.10}$$

The structure factor is usually quoted in the context of liquids, but it is also important for solids since it can be measured directly in e.g. X-ray diffraction (XRD) experiments on powders. We need the Bragg condition to relate the scattering angle θ to the wavevector, $2d\sin\theta = n\lambda = 2\pi n/k$.

12.2 Diffusion

Diffusion on macroscopic scales is described by Fick's law, i.e. the flux $\vec{j}$ of a species is related to the concentration gradient ∇c

$$\vec{j}(\vec{r},t) = -D\nabla c(\vec{r},t) \tag{12.11}$$

and the constant of proportionality is the diffusion constant. We also need the continuity equation because the total number of diffusing particles $\int d^3r\, c = 1$ must be conserved,

$$\frac{\partial c}{\partial t} + \nabla \cdot \vec{j} = \frac{\partial c}{\partial t} - D\nabla^2 c = 0 \tag{12.12}$$

Now let's consider the time dependence of the second moment of the concentration profile $\langle r^2(t)\rangle = \int d^3r\, c(r,t)r^2$. We get

$$\frac{\partial \langle r^2(t)\rangle}{\partial t} = D \int d^3r\, \nabla^2(c(r,t)r^2) \tag{12.13}$$

$$= D \int d^3r\, \nabla \cdot (r^2 \nabla c) - D \int d^3r\, \nabla r^2 \cdot \nabla c \tag{12.14}$$

$$= D \int d^2r\, \hat{n} \cdot (r^2 \nabla c) - 2D \int d^3r\, \vec{r} \cdot \nabla c \tag{12.15}$$

$$= -2D \int d^3r\, (\nabla \cdot \vec{r} c) + 2D \int d^3r\, (\nabla \cdot \vec{r}) c \tag{12.16}$$

$$= 2dD \int d^3r\, c \tag{12.17}$$

$$= 2dD \tag{12.18}$$

where d is the dimensionality of the system ($\nabla \cdot \vec{r} = d$).

The concentration profile is related to the density of the species, $c(\vec{r}) = 1/N \sum_i \delta(\vec{r} - \vec{r}_i)$ where N is the total number of atoms. We can therefore express all averages as

$$\langle f(\vec{r}_i)\rangle = \int d^3r\, \frac{1}{N} \sum_i \delta(\vec{r} - \vec{r}_i)\, f(\vec{r}_i) = \frac{1}{N} f(\vec{r}_i) \tag{12.19}$$

i.e. a sum over all diffusing atoms. Hence we arrive at the microscopic expression for the diffusion constant

$$2dDt = \frac{1}{N} \sum_i r_i^2(t) \tag{12.20}$$

Appendix A

Dynamical systems

A.1   Hamilton's equations of motion

Newton's equations of motion are limited to describing the motion of independent point masses in Cartesian coordinates. A more general dynamical postulate is Hamilton's principle. It can be used to derive equations of motions for arbitrary dynamical variables (e.g. the angle of a pendulum, or in the context of molecular dynamics the internal degrees of freedom of a heat bath; this is useful when discussing constant-temperature molecular dynamics). Hamilton's principle is the *postulate* that the action S, an integral quantity of the whole dynamics, has to be stationary. Newton's equations of motion are contained in this postulate, as will be shown below.

The action S for a system moving between time t_1 and t_2 is given by

$$S = \int_{t_1}^{t_2} dt \ L\left(\{q_i\}, \{\dot{q}_i\}, t\right) \tag{A.1}$$

where $L = E_{\text{kin}} - E_{\text{pot}}$ is called the *Lagrangian*.[1] Hamilton's principle now states that the system will move along (generalized) coordinates $\{q_i(t)\}$ such that the action S is stationary. This means the action does not vary for infinitesimal deviations from this path, it is a maximum or minimum.

To determine this stationary path let us assume we have some path $\{q_i(t)\}$ and infinitesimal variations $\{\varepsilon_i(t)\}$ around that path. The change of the

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[1]We are being sloppy here and it what follows. E_{kin} that enters the Lagrangian is actually the kinetic *co*energy (and not the kinetic *energy*). The coenergy transforms to the kinetic energy in the Hamiltonian. We can be sloppy because there is no distinction between the energy and coenergy for non-relativistic systems.

action functional would then be

$$\delta S = \int_{t_1}^{t_2} dt \ \left[L\left(\{q_i + \varepsilon_i\}, \{\dot{q}_i + \dot{\varepsilon}_i\}, t\right) - L\left(\{q_i\}, \{\dot{q}_i\}, t\right) \right]$$
$$= \int_{t_1}^{t_2} dt \ \sum_i \left[\varepsilon_i \frac{\partial L}{\partial q_i} + \dot{\varepsilon}_i \frac{\partial L}{\partial \dot{q}_i} \right].$$

(A.2)

Integration by parts yields

$$\delta S = \sum_i \left[\varepsilon_i \frac{\partial L}{\partial q_i} \right]_{t_1}^{t_2} + \int_{t_1}^{t_2} dt \ \sum_i \varepsilon_i \left[\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \right].$$

(A.3)

The first part of Eq. (A.3) vanishes because $\varepsilon_i(t_1) = 0$ and $\varepsilon_i(t_2) = 0$ (by definition; those are the start and endpoints of our path). Stationarity requires $\delta S = 0$ for any ε_i. This leads to

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0,$$

(A.4)

the *Lagrange equation of motion*.

Let us reiterate that stationarity of the action is a *postulate*. By the above derivation, we showed that it is equivalent to the Lagrange equation of motion. The equation of motion can be physically observed; the action itself cannot be observed. An alternative derivation of the Lagrange equation of motion from Newton's equations of motion employs d'Alemberts principle. This derivation is given in Section A.2.

Note: We will now need to compute the Legendre transform of the Lagrangian. The Legendre transform of a function $F(x)$ is defined as

$$F^*(y) = \min_x \left[xy - F(x) \right].$$

(A.5)

In what follows, we will assume that $F(x)$ is differentiable. Then $y(x) = \frac{dF}{dx}$ and with this definition for $y(x)$ and its inverse $x(y)$ we have

$$F^*(y) = x(y)y - F\left(x(y)\right).$$

(A.6)

It is instructive to write the total differential of Eq. (A.6),

$$dF^* = xdy + ydx - dF = xdy + \frac{dF}{dx}dx - dF = x(y)dy.$$

(A.7)

Noting that the total differential of the original function F is

$$dF = \frac{dF}{dx}dx = y(x)dx \qquad (A.8)$$

we immediately see that we have changed the independent variable from x to y when going from F to F^*. The same statement can be expressed as

$$F(x) = \int \mathrm{d}F = \int y(x)\,\mathrm{d}x \qquad (A.9)$$

$$F^*(y) = \int \mathrm{d}F^* = \int x(y)\,\mathrm{d}y \qquad (A.10)$$

A common way of expressing the relationships above is

$$\frac{\mathrm{d}F^*}{\mathrm{d}y} = \left(\frac{\mathrm{d}F}{\mathrm{d}x}\right)^{-1}(y). \qquad (A.11)$$

The derivatives of the Legendre transformation pairs are their respective inverses.

Starting from the Lagrangian L, we define an additional state function, the Hamiltonian

$$H\left(\{q_i\}, \{p_i\}, t\right) = \min_{\{\dot{q}_i\}}\left[\sum_i \dot{q}_i p_i - L\left(\{q_i\}, \{\dot{q}_i\}, t\right)\right], \qquad (A.12)$$

from the Legendre transformation of $\dot{q}_i$ to p_i. The minimization in Eq. (A.12) implies that the momenta p_i are given by

$$p_i = \frac{\partial L}{\partial \dot{q}_i}. \qquad (A.13)$$

Equation (A.13) constitutes the definition of what are called *generalized momenta*. We insert this expression into Lagrange's equation, Eq. (A.4), to get

$$\dot{p}_i = \frac{\partial L}{\partial q_i}. \qquad (A.14)$$

Furthermore, Eq. (A.12) becomes

$$H\left(\{q_i\}, \{p_i\}, t\right) = \sum_i \dot{q}_i p_i - L\left(\{q_i\}, \{\dot{q}_i\}, t\right), \qquad (A.15)$$

53

and using $L\left(\{q_i\}, \{\dot{q}_i\}, t\right) = E_{\text{kin}}\left(\{\dot{q}_i\}\right) - E_{\text{pot}}(\{q_i\}, t)$ we find $p_i = \frac{\partial E_{\text{kin}}}{\partial \dot{q}_i}$.
Since $E_{\text{kin}}\left(\{p_i\}\right)$ is the Legendre transformation of $E_{\text{kin}}\left(\{\dot{q}_i\}\right)$,

$$H\left(\{q_i\}, \{p_i\}, t\right) = E_{\text{kin}}\left(\{p_i\}\right) + E_{\text{pot}}\left(\{q_i\}, t\right). \tag{A.16}$$

Using Eq. (2.33), the total differential of H is given by

$$dH = \sum_i \dot{q}_i dp_i + \sum_i p_i d\dot{q}_i - \sum_i \frac{\partial L}{\partial q_i} dq_i - \sum_i \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i - \frac{\partial L}{\partial t} dt \tag{A.17}$$

With the definition of the generalized momenta, Eq. (2.31), and their time derivatives, Eq. (2.32), this becomes

$$dH = \sum_i \dot{q}_i dp_i - \sum_i \dot{p}_i dq_i - \frac{\partial L}{\partial t} dt. \tag{A.18}$$

We can furthermore straightforwardly express the total differential of $H\left(\{q_i\}, \{p_i\}, t\right)$ by

$$dH = \sum_i \frac{\partial H}{\partial p_i} dp_i + \sum_i \frac{\partial H}{\partial q_i} dq_i + \frac{\partial H}{\partial t} dt. \tag{A.19}$$

Comparison of Eqs. (2.36) and (2.37) yields

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \tag{A.20}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{A.21}$$

$$-\frac{\partial L}{\partial t} = \frac{\partial H}{\partial t} \tag{A.22}$$

Equations (A.20) to (A.22) are called *Hamilton's equations of motion.*

For our molecular systems (without thermostats), the Hamiltonian H is just the total energy E_{tot} of the system and not explicitly time-dependent. The last Eq. (A.22) then vanishes and H becomes a conserved quantity. Hamilton's equations of motion are two coupled differential equations of first order. They describe the motion of the system in the phase space spanned by the generalized coordinates, $\vec{\Gamma} = \{q_i\}, \{p_i\}$. In contrast, Lagrange's equation of motion is a single differential equation of second order.

A.2 D'Alembert's principle

A.2.1 Constraints and generalized coordinates

An alternative derivation of the Lagrange equations of motion is by explicitly considering constraints. Constraints are sometimes used to approximate some

or all interactions in a molecular dynamics calculation. Consider for example a hydrocarbon molecule whose fastest vibrational motion typically occurs at C-H and C-C bonds. One often approximates C-H and C-C bonds as being rigid, i.e. fixing their length. This allows to choose larger time steps for the integration algorithm.

As another example, consider an extended solid body. While the atoms within this body interact via some interaction law, for extended macroscopic objects this motion manifests itself in the elastic deformation of a solid body. It is often desirable to ignore the fact that bodies can deform elastically and model them as rigid bodies. Effectively, all atoms inside this body are then constrained at a certain distance from each other.

We distinguish two types of constraints. *Holonomic* constraints can be expressed in the form

$$\phi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \ t\right) = 0. \tag{A.23}$$

For example, fixing the distance between particle i and particle j to c_{ij} can be expressed as $\left(\vec{r}_i - \vec{r}_j\right)^2 - c_{ij}^2 = 0$.

If k holonomic constraints are present, this decreases the total number of degrees of freedom of our N-particle system from $3N$ to $3N - k$. In other words, we can use the k expressions of type Eq. (2.1) to eliminate the dependency on k of the initial Cartesian degrees of freedom. This elimination can also be expressed by the introduction of $3N - k$ independent variables $q_1, q_2, \ldots, q_{3N-k}$ called *generalized coordinates*. We can always express the Cartesian degrees of freedom as a function of these generalized coordinates, i.e.

$$\vec{r}_1 = \vec{r}_1\left(q_1, q_2, \ldots, q_{3N-k}, t\right) \tag{A.24}$$

As a simple example, consider a pendulum where a bead is moving at the end of a stick of length a in a two-dimensional plane. The motion the bead can be expressed by two Cartesian coordinates, $x\left(t\right)$ and $y\left(t\right)$ with the additional constraints $x^2 + y^2 = a^2$. However, we already know that the only coordinate that changes during the motion of the bead is its angle $\theta\left(t\right)$, which the becomes the generalized coordinate. The Cartesian coordinates are then straightforwardly expressed as $x\left(t\right) = a\cos\theta\left(t\right)$ and $y\left(t\right) = a\sin\theta\left(t\right)$.

Constraints that cannot be expressed in the way described above are called *nonholonomic*. An example would be the wall of a cylinder that cannot be passed by particles inside. This constrained could be expressed as $r_i^2 - a^2 \leq 0$, where a is the radius of the cylinder. Another example is a cylinder of radius a rolling on a surface. If the center of the cylinder is a position $\vec{r}$, then the distance to the surface cannot become larger than its radius a.

For nonholonomic constraints, we cannot remove a degree of freedom from the description of the problem. Therefore, no general formal solution, such as

the introduction of generalized coordinates for holonomic constraints, exists for the imposition of nonholonomic constraints.

A.2.2   D'Alembert's principle

The existence of a constraint implies that there is a *constraint force* that acts implicitly to fulfill that constraint. We decompose the force on particle i into applied force, $\vec{F}_i^a$, and constraint force, $\vec{f}_i$,

$$\vec{F}_i = \vec{F}_i^a + \vec{f}_i. \tag{A.25}$$

We now consider *virtual displacements* $\delta\vec{r}_i$ of our particles. Virtual displacements are displacements carried out at some instant in time t under the conditions valid at that instant; i.e. we ignore the fact that during a time interval dt forces and constraints can change.

The virtual work is carried out by the virtual displacements is given by

$$\delta\mathcal{W}^s = \sum_i \vec{F}_i \cdot \delta\vec{r}_i = \sum_i \vec{F}_i^a \cdot \delta\vec{r}_i + \sum_i \vec{f}_i \cdot \delta\vec{r}_i. \tag{A.26}$$

Note that in (static) equilibrium $\vec{F}_i = 0$ and hence the virtual work vanishes, $\delta\mathcal{W}^s = 0$.

We now consider systems for which *the net virtual work of the forces of constraint, $\sum_i \vec{f}_i \cdot \delta\vec{r}_i$, is zero.* This means the virtual displacements are perpendicular to the constraint forces. For equilibrium we then have,

$$\delta\mathcal{W}^s = \sum_i \vec{F}_i^a \cdot \delta\vec{r}_i = 0 \tag{A.27}$$

Equation (A.27) is called the principle of virtual work, but it only describes equilibrium for static systems.

The corresponding principle for dynamical systems goes back to James Bernoulli and was further developed by Jean le Rond D'Alembert. Newton's equation of motion can be written as

$$\vec{F}_i - \dot{\vec{p}}_i = 0. \tag{A.28}$$

The condition for dynamic equilibrium can then be case into the virtual work formulation,

$$\delta\mathcal{W}^d = \sum_i \left(\vec{F}_i - \dot{\vec{p}}_i \right) \cdot \delta\vec{r}_i = 0, \tag{A.29}$$

or when again considering only virtual displacements perpendicular to the constraint forces,

$$\delta \mathcal{W}^d = \sum_i \left(\vec{F}_i^a - \dot{\vec{p}}_i \right) \cdot \delta \vec{r}_i = 0. \tag{A.30}$$

Equation (A.30) is often referred to as *D'Alemberts principle*. In what follows, we will drop the superscript a for brevity.

We now introduce generalized coordinates. Virtual displacements in the Cartesian coordinates can then be expressed as

$$\delta \vec{r}_i = \frac{\partial \vec{r}_i}{\partial q_i} \delta q_i, \tag{A.31}$$

and hence the virtual work becomes

$$\delta \mathcal{W}^s = \sum_i \vec{F}_i \cdot \delta \vec{r}_i = \sum_{ij} \vec{F}_i \cdot \frac{\partial \vec{r}_i}{\partial q_j} \delta q_j = \sum_j Q_j \delta q_j = 0. \tag{A.32}$$

The Q_j's are called *generalized forces.*

The second contribution to D'Alembert's principles, Eq. (2.8), is given by

$$\delta \mathcal{W}^s - \delta \mathcal{W}^d = \sum_i \dot{\vec{p}}_i \cdot \delta \vec{r}_i = \sum_i m_i \ddot{\vec{r}}_i \cdot \delta \vec{r}_i = \sum_{ij} m_i \ddot{\vec{r}}_i \cdot \frac{\partial \vec{r}_i}{\partial q_j} \delta q_j, \tag{A.33}$$

which can be expressed as

$$\delta \mathcal{W}^s - \delta \mathcal{W}^d = \sum_{ij} m_i \left[\frac{d}{dt} \left(\dot{\vec{r}}_i \cdot \frac{\partial \vec{r}_i}{\partial q_j} \right) - \dot{\vec{r}}_i \cdot \frac{d}{dt} \left(\frac{\partial \vec{r}_i}{\partial q_j} \right) \right] \delta q_j. \tag{A.34}$$

Note that

$$\dot{\vec{r}}_i \equiv \frac{d\vec{r}_i}{dt} = \sum_j \frac{\partial \vec{r}_i}{\partial q_j} \dot{q}_j + \frac{\partial \vec{r}_i}{\partial t} \tag{A.35}$$

and hence

$$\frac{\partial \dot{\vec{r}}_i}{\partial \dot{q}_j} = \frac{\partial \vec{r}_i}{\partial q_j}. \tag{A.36}$$

We can therefore rewrite Eq. (2.12) as

$$\sum_{ij} m_i \left[\frac{d}{dt} \left(\vec{v}_i \cdot \frac{\partial \vec{v}_i}{\partial \dot{q}_j} \right) - \vec{v}_i \cdot \frac{\partial \vec{v}_i}{\partial q_j} \right] \delta q_j = \sum_{ij} \left\{ \frac{d}{dt} \left[\frac{\partial}{\partial \dot{q}_j} \left(\frac{1}{2} m v_i^2 \right) \right] + \frac{\partial}{\partial q_j} \left(\frac{1}{2} m v_i^2 \right) \right\} \delta q_j. \tag{A.37}$$

Since $T^* = \frac{1}{2}mv_i^2$, D'Alembert's principle becomes

$$\delta\mathcal{W}^d = \sum_j \left\{ \left[\frac{d}{dt}\left(\frac{\partial T^*}{\partial \dot{q}_j} \right) - \frac{\partial T^*}{\partial q_j} \right] - Q_j \right\} \delta q_j = 0 \qquad (A.38)$$

Note that Eq. (2.13) must hold for *all possible virtual displacements*. The individual δq_j are not necessarily independent of each other for general constraints. For holonomic constraints, however, we can find coordinates q_j that automatically fulfill the constrained, the *generalized coordinates*. If this is the case, then we can vary each δq_j independently and the constraints are still fulfilled; Eq. (2.15) must hence be fulfilled independently for each of the summands.

If all constraints are implicitly contained in the set of generalized coordinates, then

$$\left[\frac{d}{dt}\left(\frac{\partial T^*}{\partial \dot{q}_j} \right) - \frac{\partial T^*}{\partial q_j} \right] - Q_j = 0. \qquad (A.39)$$

Note that if the forces can be derived from a potential, $\vec{F}_i = -\frac{\partial V}{\partial \vec{r}_i}$, then

$$Q_j = \sum_i \vec{F}_i \cdot \frac{\partial \vec{r}_i}{\partial q_j} = -\sum_i \frac{\partial V}{\partial \vec{r}_i} \cdot \frac{\partial \vec{r}_i}{\partial q_j} = -\frac{\partial V}{\partial q_j} \qquad (A.40)$$

and Eq. (2.16) can be written as

$$\left[\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} \right] = 0 \qquad (A.41)$$

with $L = T^* - V$. The function L is called the *Lagrangian* and Eq. (2.18) is called the *Euler-Lagrange equation* or just the *Lagrange equation*.

Just like the kinetic energy and the potential energy, the Lagrangian is a *state function*. The generalized coordinates q_i do not need to have units of length and generalized forces Q_i do not need to have units of force, but the work $Q_i\delta q_i$ must have units of energy (work). The utility of the Euler-Lagrange equation is that we get the equations of motion for the generalized coordinates without the need to transform into these coordinates via something like Eq. (2.13). It is important to realize that this is only valid if the potential U is independent of velocity. A notable difference are electromagnetic forces, see Goldstein chapter 1-5. Because Eq. (2.14) contains terms $\vec{v}_i \cdot d\vec{v}_i$ we get the kinetic coenergy T^* rather than the kinetic energy T.

Goldstein does not make this distinction but Williams does. Non-conservative forces simply remain as generalized forces in the Euler-Lagrange equation, $\left[\frac{d}{dr} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} \right] = Q_j^{\mathrm{nc}}$ where Q_j^{nc} is the non-conservative contribution to the generalized force.

Appendix B

Phase space, statistics and thermodynamics

Statistical mechanics describes a physical system given we know little about its microscopic details. At a first glance, this appears the converse of what we do in molecular dynamics. In molecular dynamics calculations, we have to specify an initial condition, the positions $\vec{r}_i$ and momenta $\vec{p}_i$ (this chapter will use momenta $\vec{p}_i = m_i \vec{v}_i$ instead of velocities $\vec{v}_i$). These initial conditions define the state of the system *exactly*, which means we know everything there is to know about our molecular system. Note that a single state, as specified by $\{\vec{r}_i, \vec{p}_i\}$ is also called a microstate in the context of statistical mechanics. All microscopic degrees of freedom are specified for a microstate.

In most practical situations, we usually don't have information to this level of detail, and in most cases the results don't depend on the details of the microstate. In MD calculations, we have to initially guess what a good *representative* microstate could be. This means while we do know exactly what our microstate is, we don't really know how representative this would be for the real, physical situation that we want to describe with our calculation. Note that the momenta (velocities) are usually picked randomly because we really don't know these quantities. However, we do know their statistical distribution. Obtaining this distribution is one of the objectives of statistical mechanics and is discussed in detail below.

Another goal of statistical mechanics is to compute the functional dependence of macroscopic properties, for example the dependence of pressure on volume, $P(V)$, or the lattice constant of a crystal as a function of temperature, $a(T)$. Macroscopic properties are expressed as averages over *all* microstates, weighted by the probability with which they occur. The goal is therefore to reduce the number of degrees of freedom from $N_A \sim 10^{24}$ to a few. This is sometime referred to as coarse-graining.

Note that we have computed $P(V)$ for a solid in the previous chapter. This was possible because the calculation was carried out at a temperature of zero. Then, there is no thermal motion and for a single crystal we know the positions (and velocities, they are zeor) of all atoms exactly. Hence there is only a single microstate and we can carry out the calculation by just considering this state without averaging. In most cases, however, we need to compute averages. We will start our discussion of statistical mechanics with details on how averages are carried out.

B.1   Phase space and phase space averages

The positions $\vec{r}_i$ and momenta $\vec{p}_i$ of all atoms define a microstate. This microstate is typically characterized by a $6N$ (in 3D) dimensional vector $\vec{\Gamma}$ that defines a point in *phase space*. Imagine we now have an observable $O(\vec{\Gamma})$. The observable gives a certain property as a function of the point in phase space, i.e. as a function of the positions and momenta of all atoms. We have already encountered three such "observables", the potential energy E_{pot}, the kinetic energy E_{kin} and the total energy $H = E_{\text{kin}} + E_{\text{pot}}$. Other examples are the lattice constant a of a crystal, for example as obtained from scattering experiments or from averaging over the individual bond-lengths of our crystal. Note that the potential energy and lattice constant depend on just position and the kinetic energy on just velocities, so each is constant in large portions of the full phase space.

A phase space average is now obtained from a simple integral over all possible configurations, weighted with the probability of their occurrence, $\rho(\vec{\Gamma})$. The function $\rho(\vec{\Gamma})$ is called the *phase space density*. Since it is a probability density, it needs to be normalized, $\int d^{6N}\Gamma \rho(\vec{\Gamma}) = 1$. Averages $\langle \cdot \rangle$ are obtained by

$$\langle O \rangle = \int d^{6N}\Gamma \rho(\vec{\Gamma})O(\vec{\Gamma})$$
$$= \int d^3p_1 d^3r_1...d^3p_N d^3r_N \, \rho(\{\vec{r}_i\},\{\vec{p}_i\})O(\{\vec{r}_i\},\{\vec{p}_i\}) \qquad \text{(B.1)}$$

and are called *ensemble averages*. From the knowledge of the full phase space density, we can also compute the variance of fluctuations of this quantity around the average,

$$\langle \Delta O^2 \rangle = \langle O^2 \rangle - \langle O \rangle^2 \qquad \text{(B.2)}$$

which are a measure for the uncertainty of the quantity. The trick is now to choose the phase space density $\rho(\vec{\Gamma})$ properly.

B.2   Few microstates

For illustrative purposes, we will start by discussing the phase-space density for just a few microstates. We can express just a single microstate – let us call it A with positions $\vec{r}_i^A(t)$ and momenta $\vec{p}_i^A(t)$ – in this density:

$$\rho(\{\vec{r}_i\}; \{\vec{p}_i\}; t) = \prod_i \delta(\vec{r}_i - \vec{r}_i^A(t))\delta(\vec{p}_i - \vec{p}_i^A(t)) \qquad (B.3)$$

Since $\int dx\, \delta(x - x_0)f(x) = f(x_0)$, or rather $\int dx\, \delta(x - x_0) = 1$ we have $\int d^{6N}\Gamma \rho(\vec{\Gamma}) = 1$, i.e. the phase space density is a *density*. Of course, this constructed example does not really express any probability since we have just one microstate. Note that this phase space "density" depends on time t explicitly since the microstate evolves according to Hamilton's equations of motion!

As the simplest example of how probabilities emerge in the phase space density, let us consider the (probabilistic) combination of two microstates. Let us call the second state B, then

$$
\begin{aligned}
\rho(\{\vec{r}_i\}; \{\vec{p}_i\}; t) = & w_A \prod_i \delta(\vec{r}_i - \vec{r}_i^A(t))\delta(\vec{p}_i - \vec{p}_i^A(t)) \\
& + w_B \prod_i \delta(\vec{r}_i - \vec{r}_i^B(t))\delta(\vec{p}_i - \vec{p}_i^B(t)),
\end{aligned}
\qquad (B.4)
$$

where w_A and w_B are the statistical weights of each of these states. For example, if $w_A = w_B = 1/2$ then both states will occur with the same probability. Note that $w_A + w_B = 1$ to ensure normalization of ρ. Note that ρ still depends explicitly on time t.

Rather than using two states, we are in most practical situations interested in an infinite number of states. We are also typically interested in equilibrium. By definition, equilibrium is a steady state and hence the time dependence disappears. Therefore, for all cases discussed in the following ρ will be independent of t.

B.3   The microcanonical ensemble, equal a-priori probabilities and entropy

Equation (B.4) is the simplest example of an *ensemble* of microstates, in this case the two states A and B that we explicitly specified. Rather than explicitly expressing the microstates through their positions and momenta, we can also ask what the ensemble of state is that belongs to a certain (macroscopic)

observable. This ensemble consists of all states that are compatible with this observable. The simplest one is the ensemble of microstates belonging to a certain value of the total energy (or Hamiltonian) H, which is a conserved quantity of the microscopic motion. This ensemble is called the *microcanonical* or sometimes the *NVE* (for constant particle number N, constant volume V and constant energy E) ensemble.

This microcanonical ensemble is a statistical average over all states with the same total energy E, i.e. $\rho = \rho(\vec{\Gamma}; E)$ is a function of the energy E. We know that all microstates $\vec{\Gamma}$ that have total energy E must fulfill $H(\vec{\Gamma}) = E$. How do we now assign probabilities to each of these microstates that fulfill $H(\vec{\Gamma}) = E$? Since we do not know anything about the specific state, we must assume that all occur with identical probabilities. This is the fundamental postulate of the microcanonical ensemble, the postulate of equal *a-priori* probabilities. We assume that all possible states are equally likely, because we don't have any information about them, except for the their total energy E. The phase-space density is the given by

$$\rho^{\text{eq}}(\vec{\Gamma}; E) = \begin{cases} 1/\Omega(E), & \text{if } H(\vec{\Gamma}) = E \\ 0, & \text{else} \end{cases}, \qquad (B.5)$$

where $\Omega(E)$ is called the phase space volume. The (constant) factor $1/\Omega(E)$ is necessary such that the density is normalized. Not that the phase space volume just counts the number of available states,

$$\Omega(E) = \int_{H(\vec{\Gamma})=E} d^{6N}\Gamma \qquad (B.6)$$

Note that the superscript *eq* in ρ^{eq} indicates that we are in equilibrium, i.e. there is no time dependence left.

Equation (B.5) can be written alternatively as

$$\rho^{\text{eq}}(\vec{\Gamma}; E) = \frac{1}{\Omega(E)}\delta\left(H(\Gamma) - E\right), \qquad (B.7)$$

where now the δ-function selects the surface of constant total energy E. The superscript *eq* will be dropped in what follows, unless we want to make explicitly clear the distinction between equilibrium and nonequilibrium situations.

B.3.1 Entropy

A central concept in statistical mechanics is the entropy of a system. The general (nonequilibrium) entropy quantifies the number of microstates for a

given phase-space density. It is *defined* as

$$S^{\mathrm{noneq}}[\rho] = -k_B \int d^{6N}\Gamma\,\rho\ln(\rho), \qquad (\text{B.8})$$

where k_B is the Boltzmann constant. Note that the factor k_B has the role to turn temperatures from units of energy into units of K; this will be discussed below. There is no fundamental physical reason to have k_B in Eq. (B.8). Equation (B.8) is called the Shannon entropy in information theoretical contexts. Its construction is *designed* to have the following properties:

- The entropy is maximal for equal probabilities. We therefore find the equilibrium of a system by maximizing it. The principle of equal *a priori* probabilities is build into the entropy! This can be most easily seen by using a discrete phase space density, i.e. a set of probabilities ρ_α for a discrete state α. The nonequilibrium entropy is then given by

$$S^{\mathrm{noneq}} = \sum_\alpha \rho_\alpha \ln(\rho_\alpha) \qquad (\text{B.9})$$

  which we now maximize. It is important to realize that the probabilities need to be normalized, $\sum_\alpha \alpha = 1$, and we hence need to maximize the entropy under this normalization constraint. This can be achieved by introducing a Lagrange multiplier λ and maximizing

$$S^{\mathrm{noneq}} = \sum_\alpha \rho_\alpha \ln(\rho_\alpha) + \lambda\left(\sum_\alpha \alpha - 1\right). \qquad (\text{B.10})$$

  This leads to the condition $\ln(\rho_\alpha) + 1 + \lambda = 0$ and hence $\rho_\alpha = \mathrm{const}$. A similar derivation applies for the continuous case.

- The entropy is not affected by the number of states with zero probability. All states with zero probably disappear from the integral/sum.

- The entropy is extensive, i.e. proportional to the size of the system. Consider two separate isolated systems A and B that can exchange neither energy nor particles and have individual entropies S_A and S_B. Then the total entropy should be $S = S_A + S_B$. We can describe each within their of phase space $\vec{\Gamma}_A$ and $\vec{\Gamma}_B$. This means we can define two independent phase space densities $\rho_A(\vec{\Gamma}_A)$ and $\rho_B(\vec{\Gamma}_B)$. The combined system lives in the combined space $\vec{\Gamma} = (\vec{\Gamma}_A, \vec{\Gamma}_B)$ and since they are

independent, we can just multiply the probability densities to give $\rho(\Gamma) = \rho_A(\vec{\Gamma}_A)\,\rho_B(\vec{\Gamma}_B)$. The combined entropy is the given by

$$
\begin{aligned}
S &= -k \int d^{6N_A+6N_B}\Gamma \rho_A \rho_B \ln(\rho_A \rho_B) \\
&= -k \int d^{6N_A}\Gamma_A d^{6N_B}\Gamma_B \rho_A \rho_B (\ln \rho_A + \ln \rho_B) \\
&= -k \int d^{6N_B}\Gamma_B \rho_B \int d^{6N_A}\Gamma_A \rho_A \ln \rho_A - k \int d^{6N_A}\Gamma_A \rho_A \int d^{6N_B}\Gamma_B \rho_B \ln \rho_B \\
&= -k \int d^{6N_A}\Gamma_A \rho_A \ln \rho_A - k \int d^{6N_B}\Gamma_B \rho_B \ln \rho_B \\
&= S_A + S_B
\end{aligned}
$$

(B.11)

The equilibrium entropy for the microcanonical ensemble is

$$
S^{\mathrm{eq}}(E) = -k_B \int d^{6N}\Gamma \rho^{\mathrm{eq}} \ln(\rho^{\mathrm{eq}}) = k_B \ln \Omega(E) \tag{B.12}
$$

These are equal probabilities! Equilibrium maximizes the entropy.

Note that in the microcanonical ensemble the macrostate is characterized by the total energy E. In general, we can use any type of constraint, representing our *knowledge* about the system, as a macrostate. The entropy then depends on the observer.

B.3.2   The ideal gas

The ideal gas is the simplest meaningful system that we can treat with these statistical methods. It also turns out to be one of the few systems that can be solved analytically. The Hamiltonian (total energy) of the ideal gas is

$$
H(\{\vec{r}_i\}; \{\vec{p}_i\}) = \sum_i \frac{\vec{p}_i^2}{2m} \tag{B.13}
$$

i.e. there is just kinetic energy. For the sake of simplicity, the positional degrees of freedom $\vec{r}_i$ will be ignored in the following.

Let's start by considering a few particles (or rather a few degrees of freedom) of identical mass m. The statistics of the system will become useful for many degrees of freedom, but some concepts can be easily discussed in few dimensions. The phase space density for two degrees of freedom is

$$
\rho_2^{\mathrm{eq}}(p_1, p_2; E) = \pi^{-1}\delta(p_1^2 + p_2^2 - 2mE) \tag{B.14}
$$

i.e. a circle. It is straightforward to see that this phase-space density is indeed normalized,

$$\int dp_1 dp_2 \rho_2^{\text{eq}}(p_1, p_2; E) = \pi^{-1} \int dp_1 dp_2 \delta(p_1^2 + p_2^2 - 2mE) \tag{B.15}$$

$$= 2 \int_0^\infty dp\, p\delta(p^2 - 2mE) \tag{B.16}$$

$$= \int_0^\infty dp\, (-\delta(p + \sqrt{2mE}) + \delta(p - \sqrt{2mE})) \tag{B.17}$$

$$= 1 \tag{B.18}$$

where we have used the δ-function identity $2x\delta(x^2 - a^2) = -\delta(x+a) + \delta(x-a)$.

Having the combined probability density of both particles is usually not very useful. A useful quantity is the probability of finding particle 1 in momentum p_1, irrespective of the state of particle two. This is a marginal probability density which we will denote by $f_2(p_1; E)$ and it is obtained by integrating over all possible realizations of particle p_2. It is given by

$$f_2(p_1; E) = \int dp_2\, \rho_2^{\text{eq}}(p_1, p_2; E)$$

$$= \int_{-\infty}^\infty dp_2\, \pi^{-1}\delta(p_1^2 + p_2^2 - 2mE)$$

$$= \frac{1}{2\pi} \int_{-\infty}^\infty dp_2\, \frac{1}{\sqrt{2mE - p_1^2}} \left[\delta\left(p_2 + \sqrt{2mE - p_1^2} \right) + \delta\left(p_2 - \sqrt{2mE - p_1^2} \right) \right]$$

$$= \begin{cases} 0 & \text{if } |p_1| > \sqrt{2mE} \\ \pi^{-1}(2mE - p_1^2)^{-\frac{1}{2}} & \text{otherwise} \end{cases}$$

$$\tag{B.19}$$

where we have used $\delta(x^2 - a^2) = \frac{1}{2|a|}[\delta(x+a) + \delta(x-a)]$. Note that $f_2(p_1; E)$ is normalized properly

$$\int dp_1\, f_2(p_1) = \frac{1}{\pi} \int_{-\sqrt{2mE}}^{\sqrt{2mE}} dp_1\, \frac{1}{\sqrt{2E - p_1^2}} = \frac{1}{\pi} \int_{-1}^1 dx\, \frac{1}{\sqrt{1 - x^2}} = 1. \tag{B.20}$$

This construction is not particularly useful for two degrees of freedom, but it is for many degrees of freedom. The equilibrium phase space density for an ideal gas of n degrees of freedom (usually $n = 3N$ where N is the number of particles) is

$$\rho_n^{\text{eq}}(\{p_i\}; E) = \frac{1}{\Omega(E)} \delta\left(\sum_i p_i^2 - 2mE \right) \tag{B.21}$$

66

with

$$\Omega(E) = \frac{\pi^{n/2}}{\Gamma(n/2)}(2mE)^{n/2-1} \qquad (B.22)$$

being the total volume of the phase space. (Here $\Gamma(x)$ is the Gamma function.) This is the surface area of a sphere of radius $\sqrt{2mE}$ in n dimensions and the full expression is derived in Appendix B.7!

If we now integrate out all degrees of freedom $p_2...p_N$ except for p_1, we get the marginal distribution function

$$f_n(p_1; E) = \int dp_2 \ldots dp_n \, \rho_n^{\text{eq}}(\{p_i\}; E) = \frac{\Gamma\left(\frac{n}{2}\right)/\Gamma\left(\frac{n}{2} - \frac{1}{2}\right)}{\sqrt{2\pi mE}} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{n}{2} - \frac{3}{2}}$$
$$(B.23)$$

For n = 2 this gives Eq. (B.19) and the full derivation of Eq. (B.23) is given in Appendix B.8. For illustration purposes, let us look at the expressions for $n = 3$, and $n = 4$. We find

$$f_3(p_1; E) = \frac{1}{\sqrt{8mE}}\theta(p_1^2 - 2mE) \qquad (B.24)$$

and

$$f_4(p_1; E) = \frac{2}{\pi}\frac{1}{\sqrt{2mE}}\sqrt{1 - \frac{p_1^2}{2mE}}. \qquad (B.25)$$

It is straightforward to show (see Appendix B.9, that in the thermodynamic limit $N \to \infty$ (for a three dimensional space with $n = 3N$), Eq. (B.23) becomes

$$f(p_1; E) = \frac{1}{\sqrt{2\pi m(2E/3(N-1))}}\exp\left(-\frac{p_1^2}{2m}\frac{3(N-1)}{2E}\right) \qquad (B.26)$$

Now $E/(N-1)$ is the kinetic energy per particle, i.e. $2E/3(N-1) = k_B T$. This is the probability distribution for each particle:

$$f(p_1; T) = \frac{1}{\sqrt{2\pi mk_B T}}\exp\left(-\frac{p_1^2}{2mk_B T}\right) \qquad (B.27)$$

The function $f_3(p_1; E)$ simply constant over an interval of p_1. f_4 then peaks at $p_1 = 0$, i.e. finding a particle with zero velocity has a maximum likelihood. The function the approaches a Gaussian in the thermodynamic limit $n \to \infty$. The progression of the marginal distribution with n is shown in Fig. B.1.

Note that the entropy for the marginal distribution function is given by

$$S(E) = -k \int dp_1 \, f(p_1; E) \ln\left(f(p_1; E)\right) \qquad (B.28)$$
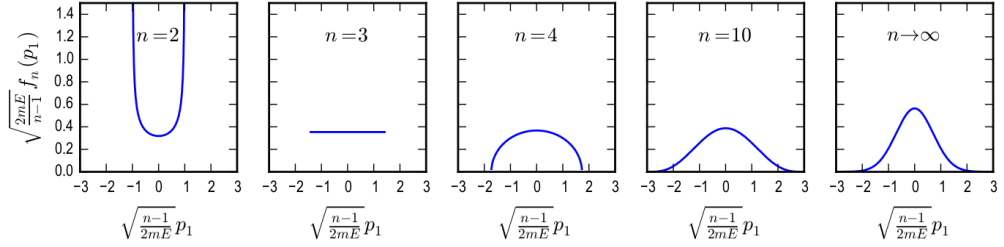
67

Figure B.1: Marginal distribution function for the momentum of a single particle in the ideal gas model for different degrees of freedom.

The estimate Eq. (B.22) is not fully correct. First, it is missing the phase space volume of the positional degrees of free $\vec{r}_i$, but this integral is trivial to carry out and yield just V^N (where V is the volume).

The correct expression also needs to account for indistinguishability of the particles and includes a factor $h^{3N}N!$ ($N!$ is the number of possibilities N particles can be permuted and h is the Planck constant). This factor is called the Gibbs factor and has its origin in quantum statistical mechanics. It can be thought of as describing the quantization of the phase space volume. The correct number of states for the ideal gas is then

$$\Omega(E) = V^N \frac{\sqrt{2\pi mE/h^2}^{3N}}{N!(3N/2)!} \qquad (B.29)$$

B.4   The canonical ensemble

B.4.1   Temperature, pressure, chemical potential

Assume two isolated subsystems with energy E_A and E_B (total energy $E = E_A + E_B$), volume V_A and V_B (total volume $V = V_A + V_B$) and particle numbers N_A and N_B (total particle number $N = N_A + N_B$). All of these quantities are *extensive* quantities, i.e. they scale with system size.

These systems occupy a phase space of volume $\Omega_A(E_A, V_A, N_A)$ etc. and have entropies $S_A(E_A, V_A, N_A)$. Now we let these systems exchange energy ΔE, volume ΔV and particles ΔN, we equilibrate them. Note that we loose information when allowing these exchanges. Rather than knowing the Since we don't know the configuration of the joint system, let's find the entropy by maximizing it (remember, this is the equilibrium condition):

$$S_{AB}^{\text{eq}}(E, V, N) = \max_{E_A, V_A, N_A} S_A^{\text{eq}}(E_A, V_A, N_A) + S_B^{\text{eq}}(E - E_A, V - V_A, N - N_A)$$
$$(B.30)$$

We find three equations that determine the equilibrium between the two systems,

$$\frac{1}{T_A} = \frac{1}{T_B} \ \text{with} \ \frac{1}{T} = \frac{\partial S}{\partial E}, \frac{P_A}{T_A} = \frac{P_B}{T_B} \ \text{with} \ \frac{P}{T} = \frac{\partial S}{\partial V}$$

$$\text{and} \ \frac{\mu_A}{T_A} = \frac{\mu_B}{T_B} \ \text{with} \ \frac{\mu_A}{T_A} = \frac{\mu_A}{T_A} \quad \text{(B.31)}$$

where we have identified temperature T, pressure p and chemical potential μ.

Taking the entropy for the ideal gas above, we find for the temperature of the ideal gas

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k\frac{\partial}{\partial E} \ln \Omega(E) = k\frac{3N}{2E} \quad \text{(B.32)}$$

i.e. $kT = 2E/3N$.

B.4.2   The heat bath

Imagine a system A in contact with a much larger system B, i.e. $N_A \ll N_B$ and $E_A \ll E_B$. Similarly to the ideal gas example above, we can integrate out all degrees of freedom of system B. Indeed since B is just a heat bath, we can simply assume that it is a heat bath that is an ideal gas. It is then straightforward to show, that the marginal distribution function then becomes

$$f(\{r_\alpha\}, \{p_\alpha\}; T) = \mathcal{P}_\mathcal{A}\rho^{eq} = Z(T)^{-1} \exp\left(-\frac{H(\{r_\alpha\}, \{p_\alpha\})}{kT}\right) \quad \text{(B.33)}$$

with $kT = \frac{2}{3}\frac{E_B}{N_B}$ and the projection operator

$$\mathcal{P}_A \cdot = \frac{1}{N_A!} \int \prod_{\alpha \in B} dr_\alpha dp_\alpha \quad \text{(B.34)}$$

The normalization factor $Z(T)$ is called the *partition sum* and has a similar significance as the phase space volume $\Omega(E)$,

$$Z = \int \prod_{\alpha \in B} dr_\alpha dp_\alpha \exp\left(-\frac{H(\{r_\alpha\}, \{p_\alpha\})}{kT}\right) \quad \text{(B.35)}$$

An alternative (and simpler) derivation of the canonical distribution function goes as follows. We know that in the microcanonical ensemble, the probability $f(E_A)$ of finding subsystem A in with energy E_A must be proportional to

$\Omega_B(E - E_A)/\Omega(E)$, i.e. the probability of finding system B with energy $E - E_A$. From Eq. (B.12) we can write this in terms of the entropy

$$f(E_A) \propto \Omega_B(E - E_A) = \exp\left[\frac{S_B(E - E_A)}{k}\right]$$
$$\approx \exp\left[\frac{1}{k}\left(S_B(E) - \frac{\partial S_B}{\partial E}E_A\right)\right] \qquad \text{(B.36)}$$

where $\approx$ holds for $E_A \ll E$. From Eq. (B.31) we can identify the derivative of the entropy as the temperature and get,

$$f(E_A) = Z(T)^{-1}\exp\left(-\frac{E_A}{kT}\right) \qquad \text{(B.37)}$$

The canonical ensemble makes it straightforward to see, that velocities should always follow a Gaussian distribution. If we use the classical Hamiltonian $H(\{\vec{r}_i\}, \{\vec{p}_i\}) = \sum_i \frac{\vec{p}_i^2}{2m_i} + E_{pot}(\{\vec{r}_i\})$, then

$$f(\vec{p}_1) = Z^{-1}\exp\left(-\frac{1}{kT}\frac{\vec{p}_i^2}{2m_i}\right)\int d^3r_1\cdots d^3r_n d^3p_2\cdots d^3p_N$$
$$\exp\left[-\frac{1}{kT}\left(\sum_{i=1}^{N}\frac{\vec{p}_i^2}{2m_i} + E_{pot}(\{\vec{r}_i\})\right)\right] \qquad \text{(B.38)}$$

but the integral is just a constant.

We can estimate the expectation value of the temperature $\langle k_B T \rangle$ and its fluctuations $\langle (k_B T)^2 \rangle - \langle k_B T \rangle^2$ from a canonical ensemble average.

$$\langle k_B T \rangle = \int_{-\infty}^{\infty} dp_1 \frac{p_1^2}{2m}\frac{1}{\sqrt{2\pi m k_B T}}\exp\left(-\frac{p_1^2}{2mk_b T}\right) = k_B T \qquad \text{(B.39)}$$

$$\langle (k_B T)^2 \rangle = \int_{-\infty}^{\infty} dp_1 \frac{p_1^4}{4m^2}\frac{1}{\sqrt{2\pi m k_B T}}\exp\left(-\frac{p_1^2}{2mk_b T}\right) = (k_B T)^2 \qquad \text{(B.40)}$$

$$\text{(B.41)}$$

Hence $\langle (k_B T)^2 \rangle - \langle k_B T \rangle^2 = 0$. The temperature does not fluctuate in the canonical ensemble!

However the total energy does. We can estimate the energy fluctuations from the ensemble averages $\langle H \rangle$ and $\langle H^2 \rangle$,

$$\langle H \rangle = \frac{1}{Z}\int \prod_{\alpha \in B} dr_\alpha dp_\alpha H(\{r_\alpha\}, \{p_\alpha\})\exp\left(-\beta H(\{r_\alpha\}, \{p_\alpha\})\right) \qquad \text{(B.42)}$$

where we have abbreviated $\beta = 1/k_B T$. We can now use a mathematical trick to get $\langle H \rangle$. Since $H \exp(-\beta H) = -\frac{\partial}{\partial \beta} \exp(-\beta H)$, we have

$$\langle H \rangle = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z = -\frac{\partial}{\partial \beta} \ln Z \tag{B.43}$$

and

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \frac{1}{Z^2} \left(\frac{\partial}{\partial \beta} Z \right)^2 = \langle H \rangle^2 - \langle H^2 \rangle \neq 0 \tag{B.44}$$

Hence energy fluctuates in the canonical ensemble.

B.5 The grand-canonical ensemble

The grand canonical ensemble allows exchange of particles in addition to exchange of energy. A possible derivation follow along the line of the one given above for the canonical ensemble, but allows for changes in number of particles

$$f(E_A, N_A) = \frac{1}{\mathcal{Z}} \exp\left(-\frac{E_A - \mu N_A}{k T_B} \right) \tag{B.45}$$

Here $\mathcal{Z}$ is called the grand-canonical partition function and μ is the chemical potential from Eq. (B.12).

B.6 Ergodicity

Ergodicity: " The trajectory of almost every point in phase space passes arbitrarily close to every other point on the surface of constant energy." [1] Note that two trajectories in phase space cannot cross, unless it is a periodic orbit.

This implies: Time averages equal microcanonical ensemble averages

$$\bar{O} = \langle O \rangle \tag{B.46}$$

where

$$\bar{O} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt \, O\left(\vec{\Gamma}(t) \right) \tag{B.47}$$

This means we can compute ensemble averages from molecular dynamics trajectories, given our system is ergodic.

The statement $\bar{O} = \langle O \rangle$ implies that we can get the distribution function $f(\vec{\Gamma})$ that qualifies the ensemble from a dynamical run by computing the

distribution during the time evolution, i.e. by treating each instant in time as its own independent realization of the system. We can therefore use a molecular dynamics run to compute $f(\vec{\Gamma})$. For example, the distribution of momenta $f(p_1)$ is straightforwardly obtained even from single snapshots. Since all particles are indistinguishable, we can just use the momenta of all particles $\vec{p}_i$ as the random variables to construct $f(p_1)$.

B.7 Normalization of the n-dimensional phase-space density

The normalization for n dimensions involves n-dimensional integrals. We have

$$\rho^{eq}(\{p_i\}; E) = \frac{1}{\Omega(E)} \int d^n p \, \delta \left(\sum_i p_i^2 - 2mE \right),$$ (B.48)

and, because of the normalization of the $\int d^n \, \rho^{eq}(\{p_i\}; E) \equiv 1$,

$$\begin{aligned}
\Omega(E) &= \int d^n p \, \delta \left(\sum_i \frac{p_i^2}{2m} - E \right) \\
&= S_n \int_0^\infty dp \, p^{n-1} \delta(p^2 - 2mE) \\
&= S_n \int_0^\infty dp \frac{p^{n-1}}{2\sqrt{2mE}} \left(\delta(p + \sqrt{2mE}) - \delta(p - \sqrt{2mE}) \right) \\
&= \frac{1}{2} S_n \sqrt{2mE}^{n-2}
\end{aligned}$$ (B.49)

$\Omega(E)$ is the volume of phase space occupied by the ideal gas at constant energy E.

The prefactor S_n is the surface area of the unit sphere. We can find its value by a simple trick that involves integrals over Gaussians. Consider the following n-dimensional integral of a rotationally symmetric function, which we can carry out directly (because the n-dimensional Gaussian factorizes and the indefinite integral over a Gaussian can be carried out easily):

$$\int d^n x \, \exp \left(-\frac{1}{2} \sum_{i=1}^n x_i^2 \right) = \left[\int_{-\infty}^\infty dx \, \exp \left(-\frac{1}{2} x^2 \right) \right]^n = (2\pi)^{\frac{n}{2}}$$ (B.50)

But using $r = \sum x_i^2$ we can express this integral also as

$$\int d^n x \, \exp\left(-\frac{1}{2}\sum_{i=1}^{n} x_i^2\right) = S_n \int_0^\infty dr \, r^{n-1} \exp\left(-\frac{1}{2}r^2\right) = S_n A(n) \quad \text{(B.51)}$$

with $A(n) = \int_0^\infty dr \, r^n \exp(-r^2/2)$. The substitution $t = r^2/2$ gives

$$A(n) = 2^{n/2-1} \int_0^\infty dt \, t^{n/2-1} \exp(-t) \equiv 2^{n/2-1}\Gamma(n/2)$$

where $\Gamma(x)$ is the Gamma function. Note that $\Gamma(n) = (n-1)!$ for integer n. Hence we can equate Eq. (B.50) and (B.51) to get $2^{n/2-1}\Gamma(n/2)S_n = (2\pi)^{n/2}$, or

$$S_n = \frac{2\pi^{n/2}}{\Gamma(n/2)} \quad \text{(B.52)}$$

Note that this gives $S_2 = 2\pi$ (circle) and $S_3 = 4\pi$ (sphere).

We therefore find the final expression for the phase-space volume

$$\Omega(E) = \frac{\pi^{n/2}}{\Gamma(n/2)}(2mE)^{n/2-1} \quad \text{(B.53)}$$

73

B.8 Integrating out $n - 1$ degrees of freedom

We follow the above procedure, but integrate out $n - 1$ degrees of freedom. This gives the marginal distribution for finding particle 1 with momentum p_1,

$$
\begin{aligned}
f_n(p_1; E) &= \int dp_2 \cdots dp_n \rho^{eq}(\{p_i\}; E) \\
&= \frac{1}{\Omega(E)} \int d^{n-1}p\, \delta\left(\sum_i p_i^2 - 2mE\right) \\
&= \frac{S_{n-1}}{\Omega(E)} \int dp\, p^{n-2}\delta(p_1^2 + p^2 - 2mE) \\
&= \frac{S_{n-1}}{\Omega(E)} \int_0^\infty dp\, \frac{p^{n-2}}{2\sqrt{2mE - p_1^2}} \left[\delta\left(p + \sqrt{2mE - p_1^2}\right) + \delta\left(p - \sqrt{2mE - p_1^2}\right)\right] \\
&= \frac{1}{2}\frac{S_{n-1}}{\Omega(E)} \sqrt{2mE - p_1^2}^{\,n-3} \\
&= \frac{S_{n-1}}{S_n} \frac{\sqrt{2mE - p_1^2}^{\,n-3}}{\sqrt{2mE}^{\,n-2}} \\
&= \frac{1}{\sqrt{2\pi mE}} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n}{2} - \frac{1}{2}\right)} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{n}{2} - \frac{3}{2}}
\end{aligned}
$$

(B.54)

B.9 The thermodynamic limit: Integrating out $3N \to \infty$ degrees of freedom

We have until now only considered n degrees of freedom. For N particles moving in three dimensions, $n = 3N$. The limit of large particle numbers, $N \to \infty$, is called the thermodynamic limit. The marginal distribution function for N particles is

$$
f_{3N}(p_1; E) = \frac{\Gamma\left(\frac{3N}{2}\right)/\Gamma\left(\frac{3N}{2} - \frac{1}{2}\right)}{\sqrt{2\pi mE}} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3}{2}(N-1)}
\tag{B.55}
$$

WE now use the identity $\lim_{n\to\infty}(1 + x/n)^n = e^x$ and $\Gamma\left(\frac{n}{2}\right)/\Gamma\left(\frac{n}{2} - \frac{1}{2}\right) \approx \sqrt{(n-3)/2}$ for large n to obtain (in the thermodynamic limit)

$$
f(p_1; E) = \sqrt{\frac{3(N-1)}{4\pi mE}}\, e^{-\frac{p_1^2}{2m}\frac{3(n-1)}{2E}}
\tag{B.56}
$$

Note that the total energy E is an extensive quantity, $E \to \infty$ as $N \to \infty$. However, the only quantity that shows up in the Eq. (B.56) is $E/(N-1)$. With the temperature $3k_B T/2 = E/(N-1)$, hence

$$f(p_1; T) = \frac{1}{\sqrt{4\pi m k_B T}} e^{-\frac{p_1^2}{2mk_B T}} \qquad (\text{B.57})$$

Note that $3k_B T/2 = E/(N-1)$ rather than $3k_B T/2 = E/N$ because the movement of the center of mass of all particles does not contribute to the temperature.

Appendix C

Advanced temperature control

C.1   Extended system methods

C.1.1   Nosé-Hoover

The Nosé-Hoover thermostat (Nosé, 1984b,a; Hoover, 1985) introduces an additional degree of freedom that models the heat bath. The degree of freedom extends the explicit particle system. It is therefore called an *extended system method*. Energy can flow from the additional degree of freedom to the particles and vice versa. The degree of freedom, s, can be regarded as an additional virtual particle living in one-dimensional space. It has the associated momentum π_s.

Before postulating the Nosé-Hoover Hamiltonian (and then showing its properties) we introduce rescaled momenta, $\vec{\pi}_i = s\vec{p}_i$ where $\vec{p}_i$ are the standard Cartesian momenta. It becomes clear that s is a scaling factor that rescales the momenta and can be used to speed the system up or slow it down, in a fashion comparable to what was discussed in the context of the Berendsen thermostat above. The coupling between particle and bath degrees of freedom therefore happens in the momentum term.

The Hamiltonian for the total Nosé-Hoover system is

$$H_s(\{\vec{\pi}_i\}, \{\vec{r}_i\}, p_s, s) = \sum_i \frac{\pi_i^2}{2ms^2} + E_{\text{pot}}(\{\vec{r}_i\}) + \frac{\pi_s^2}{2Q} + (3N+1)k_B T_0 \ln s \quad \text{(C.1)}$$

where Q is the effective mass of the bath degree of freedom and $3N$ the number of degrees of freedom of the particle system. Note again that π_i is not the physical momentum of a particle.

The equations of motion can be derived directly from the Hamiltonian.

Remember Hamilton's equations of motion,

$$\dot{\vec{\pi}}_i = -\frac{\partial H_s}{\partial \vec{r}_i}; \quad \dot{\vec{r}}_i = \frac{\partial H_s}{\partial \vec{\pi}_i}; \quad \dot{\pi}_s = -\frac{\partial H_s}{\partial s}; \quad \dot{s} = \frac{\partial H_s}{\partial \pi_s} \qquad \text{(C.2)}$$

When applied to the Nosé-Hoover Hamiltonian, Eq. (C.1), they yield

$$\dot{\vec{\pi}}_i = \vec{f}_i \quad \text{and} \quad \dot{\vec{r}}_i = \vec{\pi}_i/ms^2 = \vec{p}_i/ms \qquad \text{(C.3)}$$

$$\dot{\pi}_s = \sum_i \pi_i^2/ms^3 - (3N+1)k_B T_0/s \quad \text{and} \quad \dot{s} = \pi_s/Q \qquad \text{(C.4)}$$

Note that Eq. (C.4) implicitly contains a measurement of the temperature. We can express it as

$$\dot{\pi}_s = \frac{2}{s}\left[\sum_i \frac{p_i^2}{2m} - \frac{(3N+1)}{2}k_B T_0\right] = \frac{2}{s}\left[\frac{3N}{2}k_B T - \frac{(3N+1)}{2}k_B T_0\right],$$
$$\text{(C.5)}$$

i.e. the momentum of the heat-bath degree of freedom stops changing when the current temperature T is close to the target temperature T_0.

We now show *rigorously* why the Nosé-Hoover equations of motion actually controls the temperature. The microcanonical phase-space density for total energy E_s (of the combination of the system of interest and the heat-bath) is

$$\rho_s(\{\vec{\pi}_i\}, \{\vec{r}_i\}, \pi_s, s; E_s) \propto \delta(H_s(\{\vec{\pi}_i\}, \{\vec{r}_i\}, \pi_s, s) - E_s) \qquad \text{(C.6)}$$

In the following derivation, all constants are absorbed into the $\propto$ (proportional to) sign. They can always be reintroduced by requiring that the distribution functions need to be normalized to unity. We first change variables from $\vec{\pi}_i$ to the canonical momenta $\vec{p}_i = \vec{\pi}_i/s$. This change of variables needs to conserve probabilities, i.e.

$$\rho_s(\{\vec{\pi}_i\}, \{\vec{r}_i\}, \pi_s, s; E_s)d^{3N}\pi_i d^{3N}r_i d\pi_s ds$$
$$= \rho_s'(\{\vec{p}_i\}, \{\vec{r}_i\}, \pi_s, s; E_s)s^{3N}p_i d^{3N}r_i d\pi_s ds \quad \text{(C.7)}$$

with the primed phase-space density

$$\rho_s'(\{\vec{p}_i\}, \{\vec{r}_i\}, \pi_s, s; E_s) \propto \delta(H_s'(\{\vec{p}_i\}, \{\vec{r}_i\}, \pi_s, s) - E_s) \qquad \text{(C.8)}$$

and

$$H_s'(\{\vec{p}_i\}, \{\vec{r}_i\}, \pi_s, s) = H(\{\vec{p}_i\}, \{\vec{r}_i\}) + \frac{\pi_s^2}{2Q} + (3N+1)k_B T_0 \ln s \qquad \text{(C.9)}$$

with

$$H(\{\vec{p}_i\}, \{\vec{r}_i\}) = \sum_i \frac{p_i^2}{2m} + E_{\text{pot}}(\{\vec{r}_i\}) \tag{C.10}$$

Note that the H_s' is the sum of four functions that depend on just a single set of degrees of freedom, $\{\vec{p}_i\}, \{\vec{r}_i\}, \pi_s$ or s, each. These individual contributions to H_s' therefore no longer couple in the primed variables. Note that the Hamiltonian $H(\{\vec{p}_i\}, \{\vec{r}_i\})$ is the Hamiltonian of the thermostatted system.

We now integrate out the heat bath degrees of freedom π_s and s to obtain the marginal distribution function

$$f(\{\vec{p}_i\}, \{\vec{r}_i\}) \propto d\pi_s ds \; s^{3N} \rho_s'(\{\vec{p}_i\}, \{\vec{r}_i\}, \pi_s, s; E_s). \tag{C.11}$$

We now need the δ-function identity $\delta[g(s)] = \delta(s - s_0)/g'(s_0)$ where s_0 is the root of $g(s)$, i.e. $g(s_0) = 0$, to substitute the δ-function in ρ_s'. We have $g(s) = H_s'(s) - E_s$,

$$s_0 = \exp\left[-\frac{1}{(3N+1)k_B T_0}\left(H(\{\vec{p}_i\}, \{\vec{r}_i\}) + \frac{\pi_s^2}{2Q} - E_s\right)\right] \tag{C.12}$$

and

$$g'(s_0) = \frac{(3N+1)k_B T_0}{s_0} \tag{C.13}$$

Hence

$$f(\{\vec{p}_i\}, \{\vec{r}_i\}) \propto \int d\pi_s ds \; s^{3N} s_0 \delta(s - s_0) = \int d\pi_s \; s_0^{3N+1} \tag{C.14}$$

Note that integration of π_s just yields a constant prefactor. We therefore have

$$f(\{\vec{p}_i\}, \{\vec{r}_i\}) \propto \exp\left(-\frac{H(\{\vec{p}_i\}, \{\vec{r}_i\})}{k_B T_0}\right) \tag{C.15}$$

which is the canonical distribution function for temperature T_0 from the previous chapter.

The *ensemble* average of the Nosé-Hoover equations of motion therefore samples the proper canonical distribution. In order to sample this distribution in molecular dynamics simulations, time averages needs to equal ensemble averages. There is numerical evidence that this is not the case for the Nosé-Hooever equations of motion, i.e. this thermostat is not ergodic for some systems (Tuckerman and Martyna, 2000).

C.2 Stochastic methods

C.2.1 Andersen

The Andersen thermostat [7] makes use of the fact that we know the equilibrium velocity distribution of our particles from statistical mechanics. The thermostat then replaces the velocity of a single (or a few) particles by a random velocity chosen from the Maxwell-Boltzmann distribution. Andersen also suggested choosing the distance of those thermalization events independent of each other, i.e. to wait a random time δ with probability distribution $p(\delta t) = \exp(-\delta t/\tau)/\tau$ before thermalizing. (This is the Poisson distribution, which means the thermalization events are uncorrelated.) A combination of waiting time and number of atoms that are thermalized can be chosen to implement a certain relaxation rate. The Andersen thermostat is a *stochastic method*.

C.2.2 Langevin

The Langevin thermostat is related to Berendsen's method in that there is a damping and acceleration term for each particle. The Langevin thermostat is based on the Langevin equation of motion (Langevin, 1908) that predates Berendsen's method. Indeed, Berendsen used the Langevin equation of motion to motivate his approach.

The historic origin of the Langevin equation is an observation of the motion of small particles suspended in water by botanist Robert Brown in 1827. Brown observed the motion was completely independent of the kind of suspended particle, ruling out manifestations of life. This new phenomenon was termed *Brownian motion* and initially theoretically described by Einstein (1905). Einstein regarded the distribution of the suspended particles and derived a diffusion equation for the distribution function. Effectively, he found the *Fokker-Planck equation* for the problem of Brownian motion giving the evolution of the phase-space density.

Some time later, a different model for the same phenomenon was presented by Langevin (1908). He claimed to have found a simpler solution, describing the movement of the particles themselves instead of the evolution of the probability distribution. The respective equations of motion are since then termed *Langevin equations*. The model used by Langevin assumes that the particles' velocities are being dissipated by friction with the fluid. Additionally, they are pushed around by random hits from molecules. In his equations, this is expressed by a viscous drag (dissipation) and a white noise (pushing

around) term,

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \tag{C.16}$$

$$\dot{\vec{p}}_i = \vec{f}_i - \frac{\vec{p}_i}{\tau} + \sigma_i \vec{\xi}_i \tag{C.17}$$

with r_i being the position and p_i the momentum component, τ the relaxation time constant, σ_i the noise amplitude and ξ_i white noise. White noise is a random process, i.e. $\xi_i(t)$ is the realization of a continuous time *random* process. *White noise* means that the individual variates have zero mean and are uncorrelated. If we compute ensemble averages $\langle \cdot \rangle$, i.e. averages over multiple realization of a random variate, then $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = \delta(t - t')\delta_{ij}$. We will discuss these properties and their implications in more detail below.

From a mathematical point of view, Langevin's and Einstein's model are identical. Langevin's equation *samples* one path through the probability distribution derived by Einstein. Both models can be easily transformed into each other by means of stochastic calculus as will be seen in the following.

Note that extra care needs to be taken when discretizing the Langevin equation of motion. To see this, let us ask the question what the integral over a random variable is. Suppose we want to solve

$$\dot{y} = \sigma \xi(t), \tag{C.18}$$

then clearly

$$y(t) = \sigma \int_0^t dt\, \xi(t) \tag{C.19}$$

and $y(t)$ is also a random variable that is on average zero, $\langle y(t) \rangle = 0$. In order to understand the underlying distribution of that random variable, we compute its variance,

$$\langle y^2(t) \rangle = \sigma^2 \int_0^t dt' \int_0^t dt'' \langle \xi(t')\xi(t'') \rangle = \sigma^2 \int_0^t dt' \int_0^t dt'' \, \delta(t' - t'') = \sigma^2 t. \tag{C.20}$$

The variance grows with t which means the standard deviation (width) of the distribution scales with $t^{1/2}$. Note that to reconstruct the full distribution function, we could compute all higher cumulants. We would see that all higher cumulants vanish, meaning that the underlying distribution is the normal distribution. (See for example Gardiner (2004) for a more detailed discussion of this type of cumulant expansion.)

We now integrate the Langevin equation, Eq. (C.17), over a finite time step Δt. The above argument showed that the integral over the noise term

ξ_i gives: $\int_0^{\Delta t} dt\, \xi_i = \chi \sqrt{\Delta t}$ where χ is a random number drawn from a normal distribution with unit variance. In practice, Langevin dynamics can be implemented on top of the Velocity-Verlet algorithm by using the force

$$\vec{f}_i = -\frac{\partial E_{\text{pot}}}{\partial \vec{r}_i} - \frac{\vec{p}_i}{\tau} + \frac{\sigma_i \vec{\chi}_i}{\sqrt{\Delta t}} \tag{C.21}$$

where $\vec{\chi}_i$ are random numbers drawn from normal distributions with unit variance. Note that the force in Eq. (C.21) depends explicitly on the time step! From Eq. (C.21) is also becomes clear, that σ_i has weird units of force $\times \sqrt{\text{time}}$.

Note that in the absence of forces $\vec{f}_i = 0$ and fluctuations $\vec{\xi}_i = 0$ the above equation reads $\dot{\vec{p}}_i = -\vec{p}_i/\tau$ and has the familiar solution

$$\vec{p}_i(t) = \vec{p}_i(0)e^{-t/\tau}, \tag{C.22}$$

i.e. the momenta decay exponentially to zero and the temperature would approach zero. We need these random forces to maintain a certain finite temperature!

Stochastic differential equations

A common form to write down differential equations which include noise terms are *stochastic differential equations* (SDE). The differential equation is written in terms of the infinitesimal increments. For the Langevin equation (C.17) this becomes

$$d\vec{r}_i = \frac{\vec{p}_i}{m_i} dt \tag{C.23}$$

$$d\vec{p}_i = \vec{f}_i dt - \frac{\vec{p}_i}{\tau} dt + \sigma_i d\vec{W}_i \tag{C.24}$$

where $dW_i = \xi_i dt$ is called the Wiener increment (Gardiner, 2004). The Wiener process is the simple diffusional process described above whose evolution is given by just a white noise term. The resulting distribution is Gaussian, the Wiener increment itself represents the infinitesimal integral over a white noise variable.

We will now briefly discuss some properties of stochastic differential equations. The solution of a stochastic differential equation given by

$$dx(t) = a(x(t), t)dt + b(x(t), t)dW(t) \tag{C.25}$$

is formally defined as the integral

$$x(t) = \int_{t_0}^{t} dt'\, a(x(t'), t') + \int_{t_0}^{t} dW(t')b(x(t'), t') \tag{C.26}$$

where $\int dW(t')$ has to be defined more precisely. It turns out that there is unfortunately more than one way to define this integral with the two most common choices being known as the Itô and Stratonovich integral.

The stochastic integral over a function $f(t)$ is defined as a Riemann integral, which means dividing the integration interval into n subintervals. For each subinterval the integration is approximated by the product of the value of the function at an intermediate point and the width of the subinterval, giving the partial sum S_n. When taking the limit $n \to \infty$ one finds the definition of the stochastic integral. The partial sum is given by the expression

$$S_n = \sum_{i=0}^{n-1} f(s_i)(W(t_{i+1}) - W(t_i)) \qquad (C.27)$$

with $W(t)$ being the outcome of a Wiener process. The choice of intermediate point s_i is important because the outcome of the integration *can depend on the choice of intermediate points*, a fact that is known as the Itô-Stratonovich dilemma. Thus, one has to define the *interpretation* of a stochastic integral when talking about stochastic calculus. Using $s_i = t_i$ gives the *Itô* interpretation which will be used throughout these notes.

The above mentioned Stratonovich interpretation is only defined for a function of two variables, namely $f = f(x(t), t)$. In this interpretation one uses the mean of left and the right sum in the definition of the partial sum, namely

$$S_n^S = \sum_{i=0}^{n-1} f\left(\frac{1}{2}(x(t_{i+1}) + x(t_i))\right)(W(t_{i+1}) - W(t_i)). \qquad (C.28)$$

This definition of the stochastic integral and the Itô definition can be transformed into each other. Suppose $x(t)$ is given by the Itô integral (C.26), then the equivalence between the Stratonovich and the Itô integral is

$$S \int_{t_0}^{t} \beta(x(t'), t')dW(t') = \int_{t_0}^{t} \beta(x(t'), t')dW(t') + \frac{1}{2} \int_{t_0}^{t} b(x(t'), t')\frac{\partial}{\partial x}\beta(x(t'), t')dt'$$

$$(C.29)$$

where $S \int$ denotes Stratonovich integration and α and β are the parameters of the Stratonovich stochastic differential equation corresponding to a and b in the Itô stochastic differential equation. With the choice

$$\alpha(x, t) = a(x, t) - \frac{1}{2}b(x, t)\frac{\partial}{\partial x}\beta(x, t) \qquad (C.30)$$

$$\beta(x, t) = b(x, t) \qquad (C.31)$$

one can transform an Itô stochastic differential equation into a Stratonovich one.

In modeling physical problems, one usually writes down the corresponding differential equation directly. When dealing with stochastic differential equations one has to additionally provide an interpretation rule, unless the derivative $\partial_x \beta(x,t)$ vanishes. In this case which is also called non-multiplicative noise, the Itô and the Stratonovich interpretation give the same result. Fortunately, in Brownian dynamics, dissipative particle dynamics and dissipative particle dynamics with energy conservation, the noise is always non-multiplicative so we can safely go ahead and use the Itô interpretation, which turns out to be also the simpler of the two. Español and Öttinger (1993) have presented additional arguments that the Itô interpretation is the natural one for the interpretation of Langevin-type equations as discussed below.

Fokker-Planck equation

For the sake of simplifying the notation of the derivation that follows we express the phase-space position as $\{r_\alpha\}, \{p_\alpha\}$ rather than in their vectorial form $\{\vec{r}_i\}, \{\vec{p}_i\}$ in this section. The index α and other Greek letters are indices that combine particle and component indices of the positions and momenta. Thus, r_α has $3N$ components where N is the number of particles in the system. We switch between i and α where it simplifies the notation.

The time evolution equation for the phase-space density $\rho(\{r_\alpha\}, \{p_\alpha\})$ for the Langevin equation of motion, the so-called Fokker-Planck equation, can be derived using stochastic calculus. The basic rule in stochastic calculus is the correlation of the Wiener increments: $dW_\alpha dW_\beta = \delta_{\alpha\beta} dt$ already introduced above (Gardiner, 2004). Thus, a Wiener increment can be seen as an infinitesimal of order $dt^{1/2}$.

We now calculate the total differential of an arbitrary function $A(\{r_\alpha\}, \{p_\alpha\})$ (often called an *observable* or a *phase variable*) up to second order,

$$dA = \sum_\alpha \left(\frac{\partial A}{\partial r_\alpha} dr_\alpha + \frac{\partial A}{\partial p_\alpha} dp_\alpha \right) + \sum_{\alpha,\beta} \frac{1}{2} \frac{\partial^2 A}{\partial p_\alpha \partial p_\beta} dp_\alpha dp_\beta. \qquad (C.32)$$

Note that Eq. (C.32) is nothing else than the Taylor series expansion of A up to first order in r_α and up to second order in p_α. We will later discard all terms of order dt^2, but need to keep terms of second order in p_α in the above expansion because of the Wiener increments, as detailed below.

Using the equation of motion, Eq. (C.24), this becomes

$$
\begin{aligned}
dA = \sum_\alpha & \left(\frac{p_\alpha}{m_\alpha} \frac{\partial}{\partial r_\alpha} + f_\alpha \frac{\partial}{\partial p_\alpha} - \frac{p_\alpha}{\tau} \frac{\partial}{\partial p_\alpha} \right) A \, dt \\
& + \sum_\alpha \sigma_\alpha \frac{\partial A}{\partial p_\alpha} dW_\alpha \\
& + \frac{1}{2} \sum_{\alpha,\beta} \left(f_\alpha f_\beta + \frac{p_\alpha p_\beta}{\tau} - \frac{2 f_\alpha p_\beta}{\tau} \right) \frac{\partial^2 A}{\partial p_\alpha \partial p_\beta} (dt)^2 \qquad \text{(C.33)} \\
& + \frac{1}{2} \sum_{\alpha,\beta} \sigma_\alpha \left(f_\beta - \frac{p_\beta}{\tau} \right) \frac{\partial^2 A}{\partial p_\alpha \partial p_\beta} dW_\alpha dt. \\
& + \frac{1}{2} \sum_{\alpha,\beta} \sigma_\alpha^2 \frac{\partial^2 A}{\partial p_\alpha \partial p_\beta} dW_\alpha dW_\beta.
\end{aligned}
$$

Now we want to examine *ensemble averages* of the function A, i.e. averages over all realizations of the random process W_α. We have $\langle dW_\alpha \rangle = 0$ but $\langle dW_\alpha dW_\beta \rangle = \delta_{\alpha\beta} dt$. This gives

$$
\langle dA \rangle = \left\langle \sum_\alpha \left(\frac{p_\alpha}{m_\alpha} \frac{\partial}{\partial r_\alpha} + f_\alpha \frac{\partial}{\partial p_\alpha} - \frac{p_\alpha}{\tau} \frac{\partial}{\partial p_\alpha} + \frac{\sigma_\alpha^2}{2} \frac{\partial^2}{\partial p_\alpha^2} \right) A \right\rangle dt. \qquad \text{(C.34)}
$$

An ensemble average can also be expressed as the weighted average using the phase-space density ρ as a weight, because the phase-space density gives the probability density for finding the system in a certain point in phase space $\{r_\alpha\}, \{p_\alpha\}$. The ensemble average of an observable A can be written as

$$
\langle A(t) \rangle = \int d^{3N} r \, d^{3N} p \, \rho(\{r_\alpha\}, \{p_\alpha\}, t) A(\{r_\alpha\}, \{p_\alpha\}). \qquad \text{(C.35)}
$$

First, note that

$$
\left\langle \frac{dA}{dt} \right\rangle = \frac{d}{dt} \langle A \rangle = \frac{d}{dt} \int d^{3N} r \, d^{3N} p \, \rho A = \int d^{3N} r \, d^{3N} p \, \frac{\partial \rho}{\partial t} A. \qquad \text{(C.36)}
$$

Let us now explicitly express the first term in the sum of Eq. (C.34). We have

$$
\left\langle \frac{p_\alpha}{m_\alpha} \frac{\partial}{\partial r_\alpha} \right\rangle = \int d^{3N} r \, d^{3N} p \, \frac{p_\alpha}{m_\alpha} \rho \frac{\partial A}{\partial r_\alpha} = \int d^{3N} r \, d^{3N} p \, \frac{p_\alpha}{m_\alpha} \left[\frac{\partial}{\partial r_\alpha} (\rho A) - \frac{\partial \rho}{\partial r_\alpha} A \right]
$$
$$
\text{(C.37)}
$$

where the first term on the right hand side can be turned into a surface integral that needs to vanish because ρ has to vanish for $r_\alpha \to \infty$ (and $p_\alpha \to \infty$). We

have therefore shifted the derivative $\partial/\partial r_\alpha$ from A to ρ while acquiring a minus sign,

$$\left\langle \frac{p_\alpha}{m_\alpha} \frac{\partial}{\partial r_\alpha} \right\rangle = -\int d^{3N}r \, d^{3N}p \, \frac{p_\alpha}{m_\alpha} \frac{\partial \rho}{\partial r_\alpha} A. \tag{C.38}$$

We can carry out the same procedure for the other terms in Eq. (C.34). This yields

$$\left\langle \frac{dA}{dt} \right\rangle = \int d^{3N}r \, d^{3N}p \, \frac{\partial \rho}{\partial t} A$$

$$= \int d^{3N}r \, d^{3N}p \left(-\frac{p_\alpha}{m_\alpha} \frac{\partial}{\partial r_\alpha} - f_\alpha \frac{\partial}{\partial p_\alpha} + \frac{p_\alpha}{\tau} \frac{\partial}{\partial p_\alpha} + \frac{\sigma_\alpha^2}{2} \frac{\partial^2}{\partial p_\alpha^2} \right) A, \tag{C.39}$$

which is independent of the specific form of A. It must therefore hold for *any* function A, hence the following partial differential equation for the time evolution of the phase-space density,

$$\frac{\partial}{\partial t}\rho = \sum_\alpha \left(-\frac{p_\alpha}{m_\alpha} \frac{\partial}{\partial r_\alpha} - f_\alpha \frac{\partial}{\partial p_\alpha} + \frac{p_\alpha}{\tau} \frac{\partial}{\partial p_\alpha} + \frac{\sigma_\alpha^2}{2} \frac{\partial^2}{\partial p_\alpha^2} \right) \rho \equiv \mathcal{L}\rho, \tag{C.40}$$

must hold. Note that $\mathcal{L}$ is the *Fokker-Plank operator*. It corresponds to the *Liouvillean* in Hamiltonian mechanics (Evans and Morriss, 2004).

Now that the time evolution of ρ is known, we focus on the equilibrium situation. Thermal equilibrium is the steady-state solution of the Fokker-Plank equation, *i.e.* $\partial_t \rho^{\mathrm{eq}} = 0 = \mathcal{L}\rho^{\mathrm{eq}}$. On the other hand, we know the equilibrium distribution from statistical mechanics (see chapter 11). For classical particles in the canonical ensemble this should be the Boltzmann distribution

$$\rho^{\mathrm{eq}}(\{r_\alpha\}, \{p_\alpha\}; T) = \frac{1}{Z} \exp\left[-\frac{1}{k_B T} \left(\sum_\alpha \frac{p_\alpha^2}{2m_\alpha} + E_{\mathrm{pot}}(\{r_\alpha\}) \right) \right] \tag{C.41}$$

whose time derivative is (trivially) zero. Remember that k_B is the Boltzmann constant, T the temperature and Z the partition function.

We now evaluate $\mathcal{L}\rho^{\mathrm{eq}} = 0$. The individual derivatives in Eq. (C.40) become:

$$\frac{\partial}{\partial r_\alpha}\rho^{\mathrm{eq}} = -\frac{1}{k_B T} \frac{\partial E_{\mathrm{pot}}}{\partial r_\alpha} \rho^{\mathrm{eq}} = \frac{1}{k_B T} f_\alpha \rho^{\mathrm{eq}} \tag{C.42}$$

$$\frac{\partial}{\partial p_\alpha}\rho^{\mathrm{eq}} = -\frac{1}{k_B T} \frac{p_\alpha}{m_\alpha} \rho^{\mathrm{eq}} \tag{C.43}$$

The equilibrium condition therefore becomes

$$\mathcal{L}\rho^{\mathrm{eq}} = \sum_\alpha \left[-\frac{1}{k_B T}\frac{p_\alpha}{m_\alpha}f_\alpha + \frac{1}{k_B T}f_\alpha\frac{p_\alpha}{m_\alpha} + \left(\frac{p_\alpha}{\tau} - \frac{1}{k_B T}\frac{\sigma_\alpha^2}{2}\frac{p_\alpha}{m_\alpha}\right)\frac{\partial}{\partial p_\alpha} \right]\rho^{\mathrm{eq}}.$$

(C.44)

The first two terms on the right hand side cancel each other. The last term only cancels if

$$\sigma_\alpha^2 = \frac{2m_\alpha k_B T}{\tau},$$

(C.45)

which is called the *fluctuation-dissipation theorem*. It is a condition which assures the system relaxes to the correct equilibrium state. If the system is not at equilibrium the constant τ is a measure for the rate at which the system approaches equilibrium.

Unfortunately, the Langevin equations of motion do model only *diffusive* behavior because they do not conserve momentum. Momentum conservation is necessary for hydrodynamics because this ensures that a velocity field can be sustained. In Brownian motion, every velocity field will eventually vanish if unperturbed because particles exchange momentum with an infinitely large momentum bath. In hydrodynamics "fluid particles" exchange momentum with neighboring fluid particles.

C.3 Dissipative particle dynamics

In 1992, Hoogerbrugge and Koelman presented a new model Hoogerbrugge and Koelman (1992) called dissipative particle dynamics (DPD) introducing *hydrodynamic* behavior by letting the friction and noise work on pairs of particles, thus conserving the total momentum. In 1995, DPD was set on a solid theoretical basis by Español and Warren Español and Warren (1995) who derived the corresponding Fokker-Planck equation and required DPD to sample a certain Gibbs canonical ensemble. In the following the main results of these authors and other, subsequent developments are summarized.

C.3.1 Stochastic differential equations

In order to obtain *hydrodynamic* behavior the forces acting on each particle have to conserve momentum. The forces responsible for dissipation and for the noise in DPD will depend on the relative velocity and the distance of

particles only. The equations of motion become

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \tag{C.46}$$

$$\dot{\vec{p}}_i = \sum_{j \neq i} \left(\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R \right) \tag{C.47}$$

with $\vec{F}_{ij}^C$ being the conservative force acting between particle i and particle j and $\vec{F}_{ij}^D$ and $\vec{F}_{ij}^R$ being the dissipative and the random force, respectively. We set the latter ones to be

$$\vec{F}_{ij}^D = -\gamma w_D(r_{ij})(\vec{e}_{ij} \cdot \vec{v}_{ij})\vec{e}_{ij} \tag{C.48}$$

$$\vec{F}_{ij}^R = \sigma w_R(r_{ij})\vec{e}_{ij}\xi_{ij}^p \tag{C.49}$$

with $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$. The functions $w_D(r)$ and $w_R(r)$ are the weighting function for the dissipative and random contribution to the forces, respectively. These weighting functions assure the forces becomes negligible at a certain particle separation, the cut-off radius r_c. The term ξ_{ij}^p is Gaussian white noise with the stochastic property of being uncorrelated for every pair i-j. Namely it has to satisfy the properties $\xi_{ij}^p = \xi_{ji}^p$ and

$$\langle \xi_{ij}^p(t) \rangle = 0 \tag{C.50}$$

$$\langle \xi_{ij}^p(t)\xi_{i'j'}^p(t') \rangle = (\delta_{ii'}\delta_{jj'} + \delta_{ij'}\delta_{i'j})\delta(t - t'). \tag{C.51}$$

This ensures momentum conservation for the noise term. The parameters γ and σ are the dissipation constant and the noise amplitude, respectively.

In the form of stochastic differential equations the DPD equations of motion are

$$d\vec{r}_i = \frac{\vec{p}_i}{m_i}dt \tag{C.52}$$

$$d\vec{p}_i = \sum_{j \neq i} \left[\vec{F}_{ij}^C - \gamma w_D(r_{ij})(\vec{e}_{ij} \cdot \vec{v}_{ij})\vec{e}_{ij} \right] dt + \sum_{j \neq i} \sigma w_R(r_{ij})\vec{e}_{ij}dW_{ij}^p \tag{C.53}$$

with $dW_{ij}^p = \xi_{ij}^p dt$ being the Wiener increment (Gardiner, 2004).

Note that when going from the original definition of Brownian dynamics to dissipative particle dynamics the interpretation of a particle changes. Brownian dynamics tries to describe the motion of suspended particles that do exist. When using Brownian dynamics as a tool for simulating diffusive processes or when using dissipative particle dynamics this notion changes. The "particles" are regarded as *lumped* or *coarse-grained* fluid particles containing a large number of actual molecules. Thus, these methods can be regarded as a coarse graining tool, giving the motion of tracer particles within the flow field.

C.3.2 Fokker-Planck equation

Using stochastic calculus one can easily obtain the Fokker-Planck equation for DPD which describes the motion of the probability density $\rho(\{\vec{r}_i\}, \{\vec{p}_i\}, t)$ in the $6n$-dimensional phase-space. The Fokker-Planck equation for DPD is (see appendix C.4.1)

$$\frac{\partial}{\partial t} \rho = \mathcal{L}_C \rho + \mathcal{L}_D \rho + \mathcal{L}_R \rho. \tag{C.54}$$

The operator $\mathcal{L}_C$ is the well-know classical Liouville operator describing the motion in phase space of an ensemble of particles subject to only conservative forces, whereas the operators $\mathcal{L}_D$ and $\mathcal{L}_R$ describe the effect of the dissipative and random forces, respectively:

$$\mathcal{L}_C = -\left[\sum_i \frac{\vec{p}_i}{m_i} \cdot \frac{\partial}{\partial \vec{r}_i} + \sum_{i,j \neq i} \vec{F}_{ij}^C \cdot \frac{\partial}{\partial \vec{p}_i}\right] \tag{C.55}$$

$$\mathcal{L}_D = \sum_{i,j \neq i} \gamma w_D(r_{ij})(\vec{e}_{ij} \cdot \vec{v}_{ij}) \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i}\right) \tag{C.56}$$

$$\mathcal{L}_R = \sum_{i,j \neq i} \frac{1}{2} \sigma^2 w_R^2(r_{ij}) \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i}\right) \left(\vec{e}_{ij} \cdot \left[\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j}\right]\right) \tag{C.57}$$

The steady-state solution $\partial_t \rho = 0$ of the Fokker-Planck equation gives the equilibrium distribution. From statistical mechanics we know that the equilibrium distribution should be given by the Gibbs canonical ensemble for the Hamiltonian system (Huang, 1987),

$$\rho^{\text{eq}} = \frac{1}{\mathcal{Z}} \exp\left[-\beta \left(\sum_i \frac{\vec{p}_i^2}{2m_i} + V(\vec{r})\right)\right] \tag{C.58}$$

with $\beta = 1/k_B T$, $\mathcal{Z}$ being the partition function and $V(\vec{r})$ being the potential that gives rise to the conservative forces $\vec{F}^C$. The equilibrium solution satisfies $\partial_t \rho^{\text{eq}} = 0$ immediately giving $(\mathcal{L}_C + \mathcal{L}_D + \mathcal{L}_R)\rho^{\text{eq}} = 0$ as the requirement for detailed balance. This can only be achieved if a condition is imposed on the weighting function w_R and w_D as well as the model parameters γ and σ (see appendix C.4.2), the fluctuation-dissipation theorem for DPD,

$$w_R^2(r) = w_D(r) \tag{C.59}$$
$$\sigma^2 = 2k_B T \gamma. \tag{C.60}$$

If these conditions are met the system subject to the equations of motion Eq. (C.46) and Eq. (C.47) relaxes to the equilibrium distribution ρ^{eq} given by Eq. (C.58). The dissipative and random forces act as a thermostat. The speed at which relaxation takes place is determined by the dissipation constant γ.

C.4   Dissipative particle dynamics

C.4.1   The Fokker-Planck equation

First, let us restate the stochastic differential equation for dissipative particle dynamics Español and Warren (1995):

$$
\begin{aligned}
d\vec{r}_i &= \frac{\vec{p}_i}{m_i} dt && \text{(C.61)}\\
d\vec{p}_i &= \sum_{j\neq i}\left[\vec{F}_{ij}^C - \gamma w_D(r_{ij})(\vec{e}_{ij}\cdot\vec{v}_{ij})\vec{e}_{ij}\right] dt + \sum_{j\neq i}\sigma w_R(r_{ij})\vec{e}_{ij}dW_{ij}^p && \text{(C.62)}
\end{aligned}
$$

Regarding an arbitrary function $f = f(\vec{r},\vec{p})$, the expectation value of its time derivative $\langle \dot{f}\rangle$ can be found by computing a Taylor expansion of f to second order:

$$
df = \sum_i \frac{\partial f}{\partial \vec{r}_i}d\vec{r}_i + \sum_i \frac{\partial f}{\partial \vec{p}_i}d\vec{p}_i + \sum_{i,j}\frac{1}{2}\frac{\partial^2 f}{\partial p_i^\alpha \partial p_j^\beta}dp_i^\alpha dp_j^\beta \tag{C.63}
$$

Note that terms like $dr_i^\alpha dr_j^\beta$ or $dr_i^\alpha dp_j^\beta$ do not contribute because they only contain infinitesimals of dt to second order. The term $dp_i^\alpha dp_j^\beta$ has to be inspected more closely as it contains expressions of the kind $dW_{ij}^p dW_{i'j'}^p$ which do not equate to zero but are of the order dt:

$$
\begin{aligned}
dp_i^\alpha dp_j^\beta &= dt\sum_{k\neq i}\sum_{l\neq j}\sigma^2 w_R(r_{ik})w_R(r_{jl})e_{ik}^\alpha e_{jl}^\beta(\delta_{ij}\delta_{kl}+\delta_{il}\delta_{jk})\\
&= dt\begin{cases}\displaystyle\sum_{k\neq i}\sigma^2 w_R^2(r_{ik})e_{ik}^\alpha e_{ik}^\beta & \text{if } i=j\\[2mm] \sigma^2 w_R^2(r_{ij})e_{ij}^\alpha e_{ji}^\beta & \text{if } i\neq j\end{cases}
\end{aligned}
\tag{C.64}
$$

Thus the expectation value $\langle \dot{f} \rangle = \int d^3 r d^3 p \, \rho \dot{f}$ becomes with $\mathcal{A} = \frac{\partial f}{\partial \vec{r}_i} \cdot \dot{\vec{r}}_i + \frac{\partial f}{\partial \vec{p}_i} \cdot \dot{\vec{p}}_i$ being the contribution from the conservative and the dissipative forces:

$$
\langle \dot{f} \rangle = \int d^3 r d^3 p \, \rho \left(\mathcal{A} + \sum_{i,j} \frac{1}{2} \frac{\partial^2 f}{\partial p_i^\alpha \partial p_j^\beta} \begin{cases} \sum_{k \neq i} \sigma^2 w_R^2(r_{ik}) e_{ik}^\alpha e_{ik}^\beta & \text{if } i = j \\ \sigma^2 w_R^2(r_{ij}) e_{ij}^\alpha e_{ji}^\beta & \text{if } i \neq j \end{cases} \right)
$$

$$
= \int d^3 r d^3 p \, \rho \left(\mathcal{A} + \sum_{i,j \neq i} \frac{1}{2} \sigma^2 w_R^2(r_{ij}) e_{ij}^\alpha e_{ij}^\beta \left[\frac{\partial^2 f}{\partial p_i^\alpha \partial p_i^\beta} - \frac{\partial^2 f}{\partial p_i^\alpha \partial p_j^\beta} \right] \right) \tag{C.65}
$$

Taking into account that ρ has to vanish for $r \to \infty$ and $p \to \infty$ and integrating by parts yields

$$
\langle \dot{f} \rangle = \int d^3 r d^3 p \left\{ -f \sum_i \frac{\partial}{\partial \vec{r}_i} \cdot \dot{\vec{r}}_i - f \sum_i \frac{\partial}{\partial \vec{p}_i} \cdot \dot{\vec{p}}_i \right.
$$

$$
\left. - \sum_{i,j \neq i} \frac{1}{2} \sigma^2 w_R^2(r_{ij}) e_{ij}^\beta \left[\frac{\partial f}{\partial p_i^\beta} - \frac{\partial f}{\partial p_j^\beta} \right] \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \right) \right\} \rho. \tag{C.66}
$$

Integrating by parts for the second time gives

$$
\langle \dot{f} \rangle = \int d^3 r d^3 p \, f \left\{ -\sum_i \frac{\partial}{\partial \vec{r}_i} \cdot \dot{\vec{r}}_i - \sum_i \frac{\partial}{\partial \vec{p}_i} \cdot \dot{\vec{p}}_i \right.
$$

$$
\left. + \sum_{i,j \neq i} \frac{1}{2} \sigma^2 w_R^2(r_{ij}) \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \right) \left(\vec{e}_{ij} \cdot \left[\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right] \right) \right\} \rho \tag{C.67}
$$

and expressing $\dot{\vec{r}}_i$ and $\dot{\vec{p}}_i$ by (C.61) and (C.62), respectively, gives the final expression for the Fokker-Planck equation for DPD,

$$
\frac{\partial}{\partial t} \rho = \mathcal{L}_C \rho + \mathcal{L}_D \rho + \mathcal{L}_R \rho \tag{C.68}
$$

where use was made of the property (C.50). The operator $\mathcal{L}_C$ is the well-known Liouville operator of a classical system interacting through the conservative forces F_{ij}^C. The new operators $\mathcal{L}_D$ and $\mathcal{L}_R$ describe the effect of the dissipative

and random forces, respectively. They have the form

$$
\mathcal{L}_C \;=\; -\left[\sum_i \frac{\vec{p}_i}{m_i} \cdot \frac{\partial}{\partial \vec{r}_i} + \sum_{i,j \neq i} \vec{F}_{ij}^C \cdot \frac{\partial}{\partial \vec{p}_i} \right] \tag{C.69}
$$

$$
\mathcal{L}_D \;=\; \sum_{i,j \neq i} \gamma w_D(r_{ij}) \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \right) (\vec{e}_{ij} \cdot \vec{v}_{ij}) \tag{C.70}
$$

$$
\mathcal{L}_R \;=\; \sum_{i,j \neq i} \frac{1}{2} \sigma^2 w_R^2(r_{ij}) \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \right) \left(\vec{e}_{ij} \cdot \left[\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right] \right) \tag{C.71}
$$

C.4.2   The fluctuation-dissipation theorem

The Fokker-Planck equation gives the dynamics with which the system relaxes to the steady-state solution where $\partial_t \rho = 0$ holds. We consider the case where the system relaxes to a thermodynamic equilibrium distribution, the Gibbs canonical ensemble

$$
\rho^{\mathrm{eq}}(\{\vec{r}_i\}, \{\vec{p}_i\}) = \frac{1}{\mathcal{Z}} \exp\left\{ -\beta \left(\sum_i \frac{\vec{p}_i^2}{2m_i} + V(\vec{r}) \right) \right\} \tag{C.72}
$$

with $\beta = 1/k_B T$. It is already known from statistical mechanics that $\mathcal{L}_C \rho^{\mathrm{eq}} = 0$ because ρ^{eq} is the equilibrium distribution for a Hamiltonian system with Liouville operator $\mathcal{L}_C$. Noting that the operator $\mathcal{L}_R$ acting on ρ^{eq} pulls the velocity difference $\vec{v}_{ij}$ into the equation we find

$$
\mathcal{L}_R \rho^{\mathrm{eq}} = -\beta \sum_{i,j \neq i} \frac{1}{2} \sigma^2 w_R^2(r_{ij}) \left(\vec{e}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \right) \left(\vec{e}_{ij} \cdot \left[\frac{\vec{p}_i}{m_i} - \frac{\vec{p}_j}{m_j} \right] \right) \rho^{\mathrm{eq}} \tag{C.73}
$$

and can compare the coefficients immediately to $\mathcal{L}_D \rho^{\mathrm{eq}}$. This gives

$$
\gamma w_D(r) = \frac{1}{2kT} \sigma^2 w_R^2(r) \tag{C.74}
$$

which immediately leads to

$$
w_R(r) \;=\; w_D^{\frac{1}{2}}(r) \tag{C.75}
$$

$$
\sigma \;=\; (2kT\gamma)^{\frac{1}{2}} \tag{C.76}
$$

for the weighting functions and the model parameters. Only under these conditions the system will relax to the equilibrium distribution ρ^{eq}. This is the fluctuation-dissipation theorem for dissipative particle dynamics.

Appendix D

Advanced pressure control

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