

2022S 260007-1 Advanced Computational Physics

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based on lecture notes by
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Part I

Monte Carlo Simulations

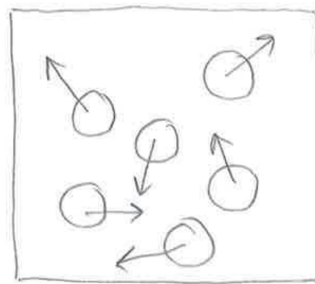
Chapter 1

Statistical Mechanics and Simulation

1.1 Introduction

Consider the problem of computing the pressure p of a system of N hard disks (in $d=2$) or spheres (in $d=3$) in a volume V at temperature T .

This problem of determining the equation of state can be solved analytically for the ideal gas, but not for hard disks or spheres. In 1953 a method for solving this problem with Monte Carlo (MC) simulations was suggested [Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth, Augusta H. Teller and Edward Teller, *Equation of State Calculations by Fast Computing Machines*, J. Chem. Phys. **21**, 1087 (1953)]. This was the birth of MC simulations in statistical mechanics.



The idea of using simulations in statistical mechanics was a real breakthrough. Since the times of Gibbs and Boltzmann, the general formalism to compute thermodynamic properties from knowledge of intermolecular interactions was known, but there was no way to compute the high-dimensional integrals appearing in this formalism analytically. Simulations provided an efficient way to evaluate these integrals. Today we can simulate very complex systems on the computer.

Simulations can provide “numerically exact” results. Using simulations, we can

- test assumptions and predictions of simplified theories.
- study realistic models under conditions not realizable in experiment.

Similar to experiments, simulations produce sets of data, but do not automatically yield physical insights. Further *analysis* is usually required. Also, simulations do not produce “new physics”. However, they can give insight into the complex collective behavior of systems consisting of many simple components (building blocks). In this sense, simulations *can* produce “new phenomena”. In this course we discuss different particle-based simulation techniques:

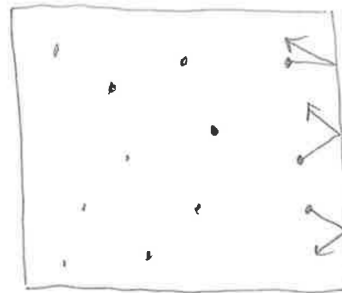
- *atomistic* simulations
- *mesoscopic* particles (colloids)

We shall mainly focus on Monte Carlo (MC) and molecular dynamics (MD). Before we talk about these methods in more detail, let us review some basic concepts of thermodynamics and statistical mechanics.

1.2 Statistical-Mechanical Averages

In general, we consider many particle systems (N-particle systems) consisting of identical building blocks (atoms, molecules, colloids, spins,...). The *goal of statistical mechanics* is to predict the properties of such a system based on knowledge of intermolecular interactions. Time and length scales of a macroscopic experiment are, however, much larger than molecular dimensions. For example,

- pressure exerted on a container wall by a gas or liquid in the container is the result of many collisions of atoms with the wall.
- pressure measured in a macroscopic experiment is the result of both a temporal and a spatial average.



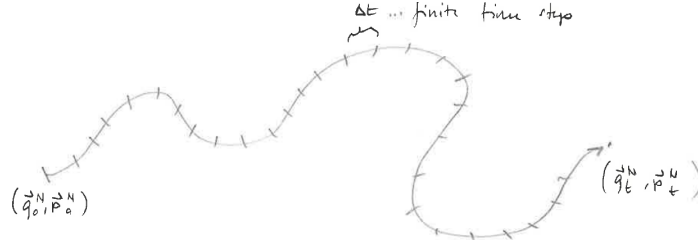
In principle, for a classical point particle system, such a microstate consists of a snapshot of all coordinates and momenta

$$\mathbf{r}^N \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_N\}, \quad \mathbf{p}^N \equiv \{\mathbf{p}_1, \dots, \mathbf{p}_N\}$$

Its knowledge completely determines the state of the system and provides initial conditions for the solution of the equations of motion at times t extending arbitrarily far into the future (or past). However, in practice one can never control all degrees of freedom but only an *ensemble* of all microstates that are compatible with the macroscopic states of the system as described through a small number of parameters (V, N, T, p , magnetic field $H \dots$).

In an MD simulation (discussed in detail in the next chapter) we integrate the equations of motion and determine the time evolution in the phase space

spanned by all coordinates and momenta. The simulation yields a *trajectory*, a series of snapshots of the system:



Each snapshot is a complete microstate of the system. The central assumption is that during a measurement the system visits all the microstates compatible with these macroscopic parameters. The measured quantities are therefore *averages* of the respective observable over all microstates.

To determine the statistical-mechanical expectation values of an observable, one averages over the snapshots of this “movie”. In equilibrium (and for quantities that depend only on one time i.e. not on two or more times separately), the sequence in which the snapshots occur in the movie is not important; it is sufficient to know the *probabilities* with which the microstates occur, but not their particular order in time. Once we know this probability distribution, which defines the *ensemble* compatible with the prescribed macroscopic parameters, we can carry out the averaging over the distribution rather than over a trajectory, which is therefore called an *ensemble average*.

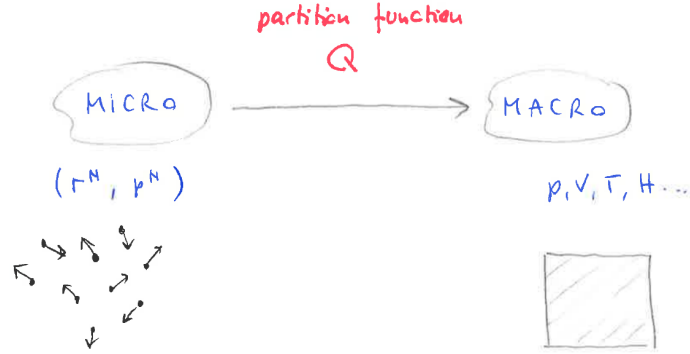
In a MC simulation, one also generates samples of microstates according to the probability distribution of the ensemble that one wants to study.

Before we discuss MC and MD simulations in detail, we need to review a few central notions of statistical mechanics and thermodynamics.

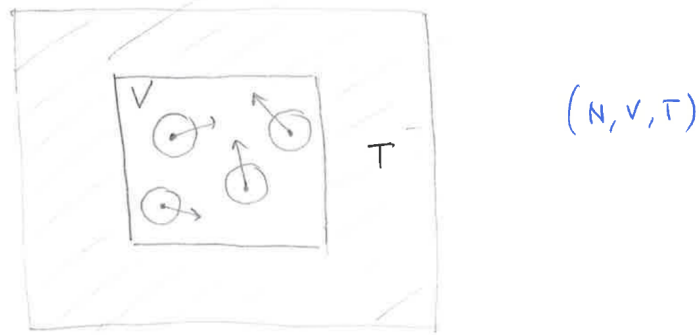
1.3 Classical Canonical Ensemble

1.3.1 Partition Function

The central quantity that connects the microscopic and the macroscopic world is the canonical partition function Q_{NVT} :



For simplicity we consider a system of N identical point particles, i.e. particles which have no internal degrees of freedom. The microstates of the system are therefore completely defined by the collection $(\mathbf{r}^N, \mathbf{p}^N)$ of all positions and momenta of the particles ($\mathbf{p}_i = m\mathbf{v}_i$). This system is enclosed in a fixed volume V and is in contact with a heat bath at fixed temperature T . This defines the *canonical ensemble* (*NVT-ensemble*)



The *classical canonical partition function* is

$$Q_{NVT} = \frac{1}{N!(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)} \quad (1.1)$$

where

- the integral is taken over the entire phase space.
- the factor $1/N!$ resolves the notorious “Gibbs paradox” by correcting the overcounting due to the fact that all permutations of identical particles over the microstates result in the same physical microstate.

- $h^3 = (2\pi\hbar)^3$ is a measure of the “cell size” in phase space and makes Q_{NVT} dimensionless.
- $\beta = 1/k_B T$ denotes the reciprocal/inverse temperature.
- k_B is the Boltzmann constant.
- $H(\mathbf{r}^N, \mathbf{p}^N)$ is the classical Hamilton function which gives the total energy of the classical microstate $(\mathbf{r}^N, \mathbf{p}^N)$.
- the so-called *Boltzmann factor* $e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}$ is proportional to the probability of observing this microstate in the canonical ensemble.

We now assume that $H(\mathbf{r}^N, \mathbf{p}^N)$ is given by

$$H(\mathbf{r}^N, \mathbf{p}^N) = \underbrace{\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}}_{\text{kinetic energy}} + \underbrace{U(\mathbf{r}^N)}_{\text{potential energy}} \quad (1.2)$$

Therefore, since the kinetic energy depends only on the momenta, while the potential energy depends only on the positions, the above partition function factorizes into a product of two separate integrals, one over configuration space and one over momentum space:

$$Q_{NVT} = \frac{1}{N!(2\pi\hbar)^{3N}} \left\{ \int d\mathbf{p}^N e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} \right\} \left\{ \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \right\} \quad (1.3)$$

The momentum space integral can be factorized further into a product of Gaussian integrals

$$\int d\mathbf{p}^N e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} = \left(\int_{-\infty}^{\infty} dp e^{-\frac{1}{2} \frac{p^2}{m/\beta}} \right)^{3N} = (2\pi m/\beta)^{3N/2} \quad (1.4)$$

Therefore

$$\begin{aligned} Q_{NVT} &= \frac{1}{N!} \frac{(2\pi m/\beta)^{3N/2}}{(2\pi\hbar)^{3N}} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \\ &= \frac{1}{N!} \left(\frac{m/\beta}{2\pi\hbar^2} \right)^{3N/2} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \end{aligned} \quad (1.5)$$

i.e.

$$Q_{NVT} = \frac{1}{N!} \frac{1}{\Lambda^{3N}} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \quad (1.6)$$

where Λ is the so-called *thermal de Broglie wave length* defined by

$$\Lambda^2 = \frac{2\pi\hbar^2\beta}{m} \quad (1.7)$$

and $Z \equiv \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$ is called the *configuration integral*.

Excess formulation

For the example of an *ideal gas*, where by definition $U(\mathbf{r}^N) \equiv 0$, the above configuration integral is given by

$$\int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} = \int_{V^N} d\mathbf{r}^N 1 = V^N \quad (1.8)$$

such that the canonical partition function of the ideal gas is given by

$$Q_{NVT}^{(id)} = \frac{V^N}{N!\Lambda^{3N}} \quad (1.9)$$

Using this result, we can rewrite the partition function

$$Q_{NVT} = \frac{1}{N!} \frac{V^N}{\Lambda^{3N}} \frac{1}{V^N} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \quad (1.10)$$

as a product

$$Q_{NVT} = Q_{NVT}^{(id)} \cdot Q_{NVT}^{(ex)} \quad (1.11)$$

of an *ideal part* $Q_{NVT}^{(id)}$ and an *excess part*

$$Q_{NVT}^{(ex)} = \frac{1}{V^N} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \quad (1.12)$$

which contains all the non-trivial effects due to the interactions between the particles.

1.3.2 Relation with thermodynamics

Thermodynamics is a macroscopic, phenomenological theory which does not consider the microscopic structure of matter. Where thermodynamics and statistical mechanics deal with the same phenomena, the two theories need to be related to each other. This connection is given by the *partition function* and the related *thermodynamic potential* of the respective ensemble.

Thermodynamic potentials are *state functions*:

- they depend only on the parameters defining a macroscopic state.
- they do not depend on the particular way in which this state is reached; thermodynamic potentials are defined only for *equilibrium states*.

In the canonical ensemble, the relevant thermodynamic potential is the *Helmholtz free energy* $F(N, V, T)$ related to the canonical partition function Q_{NVT} by

$$F(N, V, T) = -k_B T \ln Q_{NVT} \quad (1.13)$$

$F(N, V, T)$ cannot be measured directly, but its derivatives can, and they have a clear physical meaning:

- *entropy*: $S = -\frac{\partial F}{\partial T}$
- *pressure*: $p = -\frac{\partial F}{\partial V}$
- *chemical potential*: $\mu = \frac{\partial F}{\partial N}$

In thermodynamics, the free energy is usually introduced as

$$F = E - TS \quad (1.14)$$

where E is the *internal energy*. To gain more insight into the nature of E , let us compute the partial derivative $\frac{\partial(\beta F)}{\partial \beta}$ both thermodynamically and statistical-mechanically

- thermodynamical calculation: Since $\frac{\partial T}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{1}{k_B \beta} = -\frac{1}{k_B \beta^2}$, we have

$$\begin{aligned} \frac{\partial(\beta F)}{\partial \beta} &= F + \beta \frac{\partial F}{\partial \beta} = F + \beta \frac{\partial F}{\partial T} \frac{\partial T}{\partial \beta} = F - \beta \frac{\partial F}{\partial T} \frac{1}{k_B \beta^2} \\ &= F - T \underbrace{\frac{\partial F}{\partial T}}_{-S} \stackrel{(1.14)}{=} E - TS + TS \end{aligned} \quad (1.15)$$

i.e.

$$\frac{\partial(\beta F)}{\partial\beta} = E \quad (1.16)$$

- statistical-mechanical calculation: starting from $F = -k_B T \ln Q_{NVT}$, we get

$$\begin{aligned} \frac{\partial(\beta F)}{\partial\beta} &= -\frac{\partial \ln Q_{NVT}}{\partial\beta} = -\frac{1}{Q_{NVT}} \frac{\partial Q_{NVT}}{\partial\beta} \\ &= -\frac{1}{Q_{NVT}} \frac{\partial}{\partial\beta} \left[\frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)} \right] \\ &= -\frac{1}{Q_{NVT}} \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)} [-H(\mathbf{r}^N, \mathbf{p}^N)] \\ &= \frac{\frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)} H(\mathbf{r}^N, \mathbf{p}^N)}{\frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}} \end{aligned} \quad (1.17)$$

i.e.

$$\frac{\partial(\beta F)}{\partial\beta} = \langle H \rangle \quad (1.18)$$

In summary, we conclude that the thermodynamic inner energy is equal to the statistical-mechanical expectation value of the Hamilton function in the canonical ensemble:

$$E = \langle H \rangle \quad (1.19)$$

1.3.3 Averages and fluctuations

The *probability density function* of the canonical ensemble is

$$f(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \frac{e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}}{Q_{NVT}} \quad (1.20)$$

Here, the canonical partition function Q_{NVT} plays the role of a normalization factor that makes sure that

$$\int d\mathbf{r}^N d\mathbf{p}^N f(\mathbf{r}^N, \mathbf{p}^N) = 1 \quad (1.21)$$

The *canonical average* (or *expectation value*) of an observable (i.e. a phase space function) $A(\mathbf{r}^N, \mathbf{p}^N)$ is defined as

$$\langle A(\mathbf{r}^N, \mathbf{p}^N) \rangle = \int d\mathbf{r}^N d\mathbf{p}^N f(\mathbf{r}^N, \mathbf{p}^N) A(\mathbf{r}^N, \mathbf{p}^N) \quad (1.22)$$

Examples.

- If $A = A(\mathbf{p}^N)$ depends only on the momenta, we can often carry out the integration analytically. The reason is that the probability density of the momenta is simply a Gaussian. For instance, one can easily obtain the *equipartition theorem*

$$\begin{aligned} \frac{\langle \mathbf{p}_i^2 \rangle}{2m} &= \frac{\int d^3p \frac{\mathbf{p}^2}{2m} e^{-\beta \frac{\mathbf{p}^2}{2m}}}{\int d^3p e^{-\beta \frac{\mathbf{p}^2}{2m}}} = -\frac{\partial}{\partial \beta} \ln \int d^3p e^{-\beta \frac{\mathbf{p}^2}{2m}} = -\frac{\partial}{\partial \beta} \ln (2\pi m / \beta)^{3/2} \\ &= \frac{3}{2} \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2\beta} = \frac{3}{2} k_B T \end{aligned} \quad (1.23)$$

or

$$\frac{\langle (p_i^x)^2 \rangle}{2m} = \frac{\langle (p_i^y)^2 \rangle}{2m} = \frac{\langle (p_i^z)^2 \rangle}{2m} = \frac{k_B T}{2} \quad (1.24)$$

A more interesting case occurs when $A = A(\mathbf{r}^N)$ depends only on the particle positions:

$$\begin{aligned} \langle A(\mathbf{r}^N) \rangle &= \int d\mathbf{r}^N d\mathbf{p}^N f(\mathbf{r}^N, \mathbf{p}^N) A(\mathbf{r}^N) \\ &= \frac{1}{Q_{NVT}} \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \underbrace{\int d\mathbf{p}^N e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}}}_{Q_{NVT}^{(id)}/V^N} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} \\ &\stackrel{(1.11)}{=} \frac{\cancel{Q_{NVT}^{(id)}}}{\cancel{Q_{NVT}^{(id)}} Q_{NVT}^{(ex)} V^N} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} \end{aligned} \quad (1.25)$$

If we (re-)define the *configuration integral*

$$Z := Q_{NVT}^{(ex)} V^N \stackrel{(1.12)}{=} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \quad (1.26)$$

we obtain

$$\langle A(\mathbf{r}^N) \rangle = \frac{1}{Z} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} \quad (1.27)$$

Integrals (1.26), (1.27) are highly non-trivial and difficult (usually impossible) to compute by analytical means. This is why we need MC simulations!

The idea is to replace the expectation value (1.27) with an average over a large sample of configurations generated with the *Metropolis procedure*. Its big advantage is that the *probability density does not need to be normalized*, because in the acceptance step we only need the ratio of probabilities in which any constant factor cancels. In other words, the sample can be produced using the unnormalized probability density $e^{-\beta U(\mathbf{r}^N)}$ while the normalization factor Z can remain undetermined

- Usually, Z is unknown and very difficult to calculate. Knowledge of Z corresponds to knowing the true free energy of the system, but for the moment this is not needed.

In many cases it is interesting to know not just the average of an observable. Also its *fluctuations* (variances and covariances) carry important physical information. Let us calculate $\frac{\partial^2(\beta F)}{\partial \beta^2}$ both thermodynamically as well as statistical-mechanically:

- statistical-mechanical calculation: starting from $\beta F = -\ln Q_{NVT}$, we get

$$\begin{aligned} \frac{\partial^2(\beta F)}{\partial \beta^2} &= -\frac{\partial^2 \ln Q_{NVT}}{\partial \beta^2} = -\frac{\partial}{\partial \beta} \left(\frac{1}{Q_{NVT}} \frac{\partial Q_{NVT}}{\partial \beta} \right) \\ &= \frac{1}{Q_{NVT}^2} \left(\frac{\partial Q_{NVT}}{\partial \beta} \right)^2 - \frac{1}{Q_{NVT}} \frac{\partial^2 Q_{NVT}}{\partial \beta^2} \end{aligned} \quad (1.28)$$

We have

$$\frac{\partial Q_{NVT}}{\partial \beta} = -\frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H} H = -Q_{NVT} \langle H \rangle \quad (1.29)$$

$$\frac{\partial^2 Q_{NVT}}{\partial \beta^2} = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H} H^2 = Q_{NVT} \langle H^2 \rangle \quad (1.30)$$

Therefore

$$\frac{\partial^2(\beta F)}{\partial \beta^2} = \langle H \rangle^2 - \langle H^2 \rangle = -\langle \Delta H^2 \rangle = -\langle (H - \langle H \rangle)^2 \rangle \quad (1.31)$$

where

$$\Delta H \equiv H - \langle H \rangle \quad (1.32)$$

denotes the deviation of H from its thermal average (i.e. thermal *energy fluctuations*).

- thermodynamical calculation: Recalling $\frac{\partial T}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{1}{k_B \beta} = -\frac{1}{k_B \beta^2}$, we have

$$\begin{aligned} \frac{\partial^2(\beta F)}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \left(\frac{\partial(\beta F)}{\partial \beta} \right) \stackrel{(1.15)}{=} \frac{\partial}{\partial \beta} (F + TS) = \frac{\partial}{\partial T} (F + TS) \frac{\partial T}{\partial \beta} \\ &= \left(\cancel{\frac{\partial F}{\partial T}} + S + T \frac{\partial S}{\partial T} \right) \left(-\frac{1}{k_B \beta^2} \right) \end{aligned} \quad (1.33)$$

i.e.

$$\frac{\partial^2(\beta F)}{\partial \beta^2} = T \frac{\partial S}{\partial T} (-k_B T^2) \quad (1.34)$$

Recall that in thermodynamics, the heat capacity at constant volume is defined as the heat δQ needed to change the temperature by δT , i.e.

$$C_V = \frac{\delta Q}{\delta T} \quad (1.35)$$

and since the (reversible) entropy change is defined as $dS = \frac{\delta Q}{T}$, one arrives at

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (1.36)$$

Hence

$$\frac{\partial^2(\beta F)}{\partial \beta^2} = -C_V k_B T^2 \quad (1.37)$$

Combining the two results, we find

$$C_V = \frac{1}{k_B T^2} [\langle H^2 \rangle - \langle H \rangle^2] \quad (1.38)$$

i.e. the specific heat is proportional to the fluctuations of the energy. This relation can be used to compute C_V in MC or MD simulations.

- The left hand side of this relation corresponds to the reaction of the system to a change in an external control variable (here β), while the right hand side measures the fluctuations of the freely evolving system. Eq. (1.38) is an example of a *fluctuation-response relation*.

Note that using $S = -\frac{\partial F}{\partial T}$, we can also write C_V as the second derivative

$$C_V = -T \frac{\partial^2 F}{\partial T^2} \quad (1.39)$$

Second derivatives of thermodynamics are generally related to *fluctuations*. Analogous expressions can be derived for the isochoral compressibility, the thermal expansion coefficient and others.

- Of course, these relations depend on the underlying ensemble; for instance, in the micro-canonical NVE ensemble $\langle \Delta H \rangle = 0$ and the above relation is not applicable.

1.3.4 Equation of state

The *equation of state* is the relation

$$p = p(\rho, T) \quad (1.40)$$

between pressure p , density ρ and temperature T of a system. Here ρ is the *number density*

$$\rho = \frac{N}{V} \quad (1.41)$$

- We could just as well consider $p(N, T)$ at fixed V or $p(V, T)$ at fixed N .

We would like to express $p(\rho, T)$ as a canonical average. To accomplish that, we use the microscopic/macroscopic strategy applied before. We know that $p = -\frac{\partial F}{\partial V}$ and thus

$$\beta p = -\beta \frac{\partial F}{\partial V} = -\frac{\partial(\beta F)}{\partial V} = \frac{\partial \ln Q_{NVT}}{\partial V} = \frac{\partial \ln Q_{NVT}^{(id)}}{\partial V} + \frac{\partial \ln Q_{NVT}^{(ex)}}{\partial V} \quad (1.42)$$

The first term is the ideal gas term corresponding to the ideal gas equation of state

$$p^{id} = \rho k_B T \quad \Rightarrow \quad \beta p^{(id)} = \rho \quad (1.43)$$

Therefore we are left with

$$\beta p = \rho + \frac{1}{Q_{NVT}^{(ex)}} \frac{\partial Q_{NVT}^{(ex)}}{\partial V} \quad (1.44)$$

where the last term contains all the non-trivial contributions to the pressure. We realize that

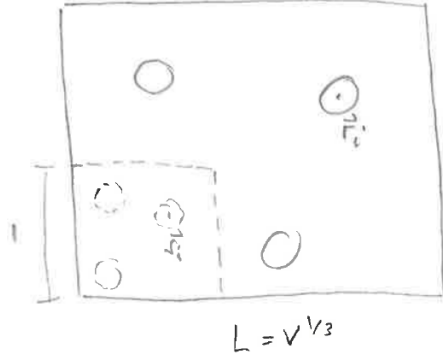
$$Q_{NVT}^{(ex)} = \frac{1}{V^N} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \quad (1.45)$$

depends on V both explicitly (through $1/V^N$) and implicitly (through the integration limits). To be able to carry out the differentiation w.r.t. the volume,

we introduce *scaled coordinates* that allow to shrink and expand the volume conveniently. Let us write the coordinates as

$$\mathbf{r}_i = V^{1/3} \mathbf{s}_i, \quad i = 1, \dots, N \quad (1.46)$$

In this way, we rescale our coordinates to lie inside a box \hat{V} of unit volume. For a cubic box



Transforming from \mathbf{r}_i to \mathbf{s}_i , we have to take into account the Jacobian

$$\left| \frac{\partial(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\partial(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_N)} \right| = (V^{1/3})^{3N} = V^N \quad (1.47)$$

we rewrite the integral as

$$Q_{NVT}^{(ex)} = \frac{1}{V^N} \int_{\hat{V}} d\mathbf{s}^N V^N e^{-\beta U((V^{1/3}\mathbf{s})^N)} \quad (1.48)$$

where $(V^{1/3}\mathbf{s})^N$ is a shorthand for $(V^{1/3}\mathbf{s}_1, \dots, V^{1/3}\mathbf{s}_N)$. This integral runs over the unit volume \hat{V} . So, with scaled coordinates, the integration volume does not depend on V , and we can carry out the derivative with respect to V :

$$\frac{\partial Q_{NVT}^{(ex)}}{\partial V} = \int_{\hat{V}} d\mathbf{s}^N e^{-\beta U((V^{1/3}\mathbf{s})^N)} \left(-\beta \frac{\partial U(V^{1/3}\mathbf{s}_1, \dots, V^{1/3}\mathbf{s}_N)}{\partial V} \right) \quad (1.49)$$

We compute

$$\begin{aligned} -\frac{\partial U(V^{1/3}\mathbf{s}_1, \dots, V^{1/3}\mathbf{s}_N)}{\partial V} &= -\sum_{i=1}^N \frac{\partial U(V^{1/3}\mathbf{s}_1, \dots, V^{1/3}\mathbf{s}_N)}{\partial(V^{1/3}\mathbf{s}_i)} \frac{\partial V^{1/3}\mathbf{s}_i}{\partial V} \\ &= \sum_{i=1}^N \mathbf{F}_i((V^{1/3}\mathbf{s})^N) \frac{1}{3} V^{-2/3} \mathbf{s}_i \end{aligned} \quad (1.50)$$

where

$$\mathbf{F}_i((V^{1/3}\mathbf{s})^N) = -\frac{\partial U(V^{1/3}\mathbf{s}_1, \dots, V^{1/3}\mathbf{s}_N)}{\partial(V^{1/3}\mathbf{s}_i)} \quad (1.51)$$

is the force on particle i . So

$$\begin{aligned}
 \frac{\partial Q_{NVT}^{(ex)}}{\partial V} &= \beta \int_{\hat{V}} d\mathbf{s}^N e^{-\beta U((V^{1/3}\mathbf{s})^N)} \sum_{i=1}^N \mathbf{F}_i((V^{1/3}\mathbf{s})^N) \frac{1}{3} V^{-2/3} \mathbf{s}_i \\
 &= \beta \int_V \frac{d\mathbf{r}^N}{V^N} e^{-\beta U(\mathbf{r}^N)} \sum_{i=1}^N \mathbf{F}_i(\mathbf{r}^N) \frac{1}{3} V^{-2/3} \frac{\mathbf{r}_i}{V^{1/3}} \\
 &= -\frac{\beta}{3V} \frac{1}{V^N} \int_V d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \left(-\sum_{i=1}^N \mathbf{F}_i(\mathbf{r}^N) \mathbf{r}_i \right) \quad (1.52)
 \end{aligned}$$

In terms of the *virial*

$$W(\mathbf{r}^N) = -\sum_{i=1}^N \mathbf{F}_i(\mathbf{r}^N) \mathbf{r}_i \quad (1.53)$$

we have shown that

$$\frac{1}{Q_{NVT}^{(ex)}} \frac{\partial Q_{NVT}^{(ex)}}{\partial V} = -\frac{\beta}{3V} \langle W \rangle \quad (1.54)$$

and the equation of state turns into

$$p = \rho k_B T - \frac{1}{3V} \langle W \rangle \quad (1.55)$$

- At first sight, the definition (1.53) of the virial seems to be problematic, since it appears to depend on the choice of origin $\mathbf{0}$ for the particle coordinates \mathbf{r}_i . However, suppose that we shift our coordinate system to a new origin $\mathbf{0}'$ by a constant vector \mathbf{R} . With respect to this shifted coordinate system $\mathbf{r}'_i = \mathbf{r}_i - \mathbf{R}$, and the virial is

$$W(\mathbf{r}'^N) \stackrel{(1.53)}{=} -\sum_{i=1}^N \mathbf{F}'_i(\mathbf{r}'^N) \mathbf{r}'_i = W(\mathbf{r}^N) + \mathbf{R} \sum_{i=1}^N \mathbf{F}'_i(\mathbf{r}'^N) \quad (1.56)$$

Since there are only internal forces, the sum $\sum_{i=1}^N \mathbf{F}'_i(\mathbf{r}'^N) \equiv \mathbf{0}$ over all forces should vanish by Newton's third law, such that $W(\mathbf{r}'^N) \equiv W(\mathbf{r}^N)$.

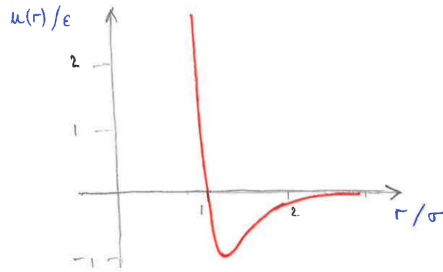
After all, in the absence of an external field the pressure should depend only on relative coordinates, i.e. on the differences $\mathbf{r}_i - \mathbf{r}_j$. So we would like to rewrite the virial in a way that manifestly exhibits this dependence on relative coordinates. This task is particularly easy if the particles interact only through a *pairwise additive potential* that depends only on the relative distance

$$U(\mathbf{r}^N) = \sum_{i < j} u(r_{ij}) = \frac{1}{2} \sum_{i \neq j} u(r_{ij}), \quad r_{ij} = |\mathbf{r}_{ij}| \quad (1.57)$$

In general, such a decomposition is not possible for a real material, but for some systems it may be a valid approximation.

A simple and frequently used pair potential to describe the noble gases like He, Ne, Ar, ... is the *Lennard-Jones (LJ) potential*

$$u_{LJ}(r) := 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1.58)$$



The parameters ϵ and σ depend on the substance one considers:

- Parameter σ can be viewed as a measure of the diameter of the (spherically assumed) particles.
- The LJ potential has a minimum at $r = 2^{1/6}\sigma$.
- Parameter ϵ , which equals the depth of the well at this minimum, describes the *strength* of the potential.
- For $r > 2^{1/6}\sigma$, the LJ potential is *attractive*. The r^{-6} form of this attractive part is motivated by the quantum-mechanical analysis of the fluctuation-induced dipole interaction (the so-called *dispersion* or *Van der Waals* forces.)
- For $r < 2^{1/6}\sigma$, it is *repulsive*. The r^{-12} form, which should account for the Pauli exclusion principle of electrons is chosen purely for computational convenience.

In the case of a pairwise additive potential, the total force $\mathbf{F}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r}^N)$ becomes

$$\mathbf{F}_i = -\frac{1}{2} \sum_{\substack{j,l \\ j \neq l}} \nabla_{\mathbf{r}_i} u(r_{jl}) \quad (1.59)$$

Since we differentiate w.r.t. \mathbf{r}_i , only terms for which either j or l equals i are different from zero. Therefore, the above double sum reduces to two single sums

$$\mathbf{F}_i = -\frac{1}{2} \left\{ \sum_{\substack{l \\ l \neq i}} \nabla_{\mathbf{r}_i} u(r_{il}) + \sum_{\substack{j \\ j \neq i}} \nabla_{\mathbf{r}_i} u(r_{ji}) \right\} \quad (1.60)$$

and since

$$\begin{aligned} \nabla_{\mathbf{r}_i} u(r_{il}) &= u'(r_{il}) \nabla_{\mathbf{r}_i} r_{il} = u'(r_{il}) \nabla_{\mathbf{r}_i} \sqrt{(\mathbf{r}_l - \mathbf{r}_i)^2} = u'(r_{il}) \frac{2(\mathbf{r}_l - \mathbf{r}_i)(-1)}{2\sqrt{(\mathbf{r}_l - \mathbf{r}_i)^2}} \\ &= -u'(r_{il}) \frac{\mathbf{r}_{il}}{r_{il}} \end{aligned} \quad (1.61)$$

and similarly

$$\nabla_{\mathbf{r}_i} u(r_{ji}) = u'(r_{ji}) \frac{\mathbf{r}_{ji}}{r_{ji}} = -u'(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (1.62)$$

Thus, the total force on particle i

$$\mathbf{F}_i = -\frac{1}{2} \left\{ -\sum_{\substack{l \\ l \neq i}} u'(r_{il}) \frac{\mathbf{r}_{il}}{r_{il}} - \sum_{\substack{j \\ j \neq i}} u'(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}} \right\} = \sum_{\substack{j \\ j \neq i}} u'(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (1.63)$$

can be written as a sum of *pair forces*

$$\mathbf{F}_i = \sum_{\substack{j \\ j \neq i}} \mathbf{f}_{ij} \quad (1.64)$$

where

$$\mathbf{f}_{ij} = u'(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (1.65)$$

is the *force exerted by particle j on particle i* . This formula explicitly shows that $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$, illustrating Newton's principle of "actio=reactio", i.e. pair forces are of equal magnitude but opposite directions.

Using these results, we obtain the alternative representation

$$\begin{aligned} W(\mathbf{r}^N) &= -\sum_i \mathbf{r}_i \cdot \mathbf{F}_i = -\sum_i \mathbf{r}_i \cdot \sum_{\substack{j \\ j \neq i}} \mathbf{f}_{ij} = -\sum_{i \neq j} \mathbf{r}_i \cdot \mathbf{f}_{ij} \\ &\stackrel{(i \leftrightarrow j)}{=} -\sum_{i \neq j} \mathbf{r}_j \cdot \underbrace{\mathbf{f}_{ji}}_{-\mathbf{f}_{ij}} = \sum_{i \neq j} \mathbf{r}_j \cdot \mathbf{f}_{ij} \end{aligned} \quad (1.66)$$

of the virial. Symmetrizing, we arrive at

$$\begin{aligned} W(\mathbf{r}^N) &= \frac{1}{2} [W(\mathbf{r}^N) + W(\mathbf{r}^N)] = \frac{1}{2} \left[-\sum_{i \neq j} \mathbf{r}_i \cdot \mathbf{f}_{ij} + \sum_{i \neq j} \mathbf{r}_j \cdot \mathbf{f}_{ij} \right] \\ &= \frac{1}{2} \sum_{i \neq j} \underbrace{(\mathbf{r}_j - \mathbf{r}_i)}_{\mathbf{r}_{ij}} \cdot \mathbf{f}_{ij} \end{aligned} \quad (1.67)$$

and since the scalar product $\mathbf{r}_{ij} \mathbf{f}_{ij} = \mathbf{r}_{ji} \mathbf{f}_{ji}$ is symmetric in the indices i, j , we can write the virial as a sum over ordered pairs of particles (like we did for the energy) that, as promised, manifestly only depends on relative coordinates:

$$W(\mathbf{r}^N) = \frac{1}{2} \sum_{i \neq j} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} = \sum_{i < j} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \quad (1.68)$$

In fact, for spherically symmetric particles the pair forces \mathbf{f}_{ij} are parallel to \mathbf{r}_{ij} (see the derivation Eq. (1.63)), such that this simplifies further to

$$W(\mathbf{r}^N) = \sum_{i < j} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} = \sum_{i < j} \mathbf{r}_{ij} \cdot u'(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}} = \sum_{i < j} u'(r_{ij}) \frac{r_{ij}^2}{r_{ij}} \quad (1.69)$$

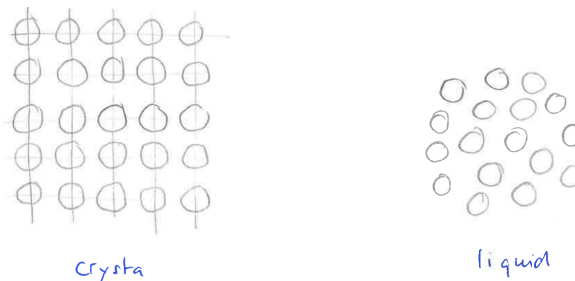
i.e.

$$W(\mathbf{r}^N) = \sum_{i < j} r_{ij} u'(r_{ij}) \quad (1.70)$$

which depends only on scalar quantities.

1.3.5 Pair distribution function

Consider a *gas* or a *liquid* (the term *fluid* includes both of them). In contrast to a crystalline solid, where atoms are arranged on a lattice with long-ranged order, atoms in a fluid lack long-range order:



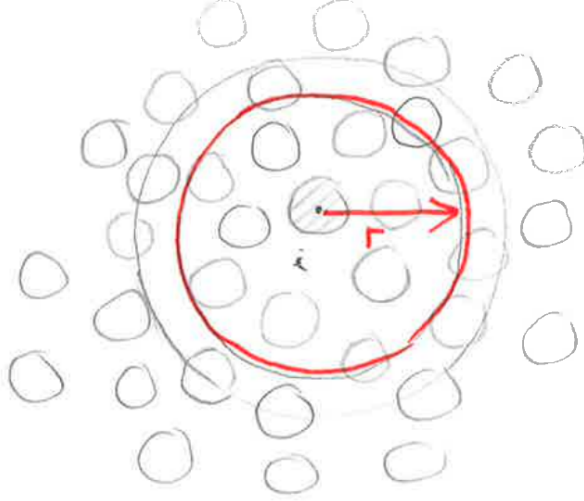
Nevertheless, a liquid is not completely disordered, simply because a place occupied by a particle cannot be taken by another particle. This leads to a certain short-ranged structural order in a liquid, which can be quantitatively described with the *pair distribution function* $g(r)$ (also called *radial distribution function* or *pair correlation function*).

$g(r)$ is important for a number of reasons:

- It characterizes local structures around an atom. It can be measured via the structure factor $S(\mathbf{k})$ which can be determined via x-ray and neutron scattering.
- Thermodynamic properties of systems with additive pair potentials are completely determined by $g(r)$.
- There are theoretical approaches that allow an approximate analytical calculation of $g(r)$.

Definition of $g(r)$ for a system of atoms.

- Consider a system of N atoms and pick particle i as *reference particle*.



- Count how many particles there are in a sphere of radius r around particle i . In terms of the Heaviside step function $\theta_H(x)$, the average number of such particles can be written as

$$n(r) = \left\langle \sum_{\substack{j \\ j \neq i}} \theta_H(r - r_{ij}) \right\rangle \quad (1.71)$$

- Taking the derivative of $n(r)$ with respect to r gives

$$\frac{dn(r)}{dr} = \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle \quad (1.72)$$

where $\delta(x)$ is the Dirac delta distribution. The average number of particles in a thin shell of thickness dr is then given by

$$\frac{dn(r)}{dr} dr \approx \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle dr \quad (1.73)$$

- In a completely disordered system with a homogeneous density ρ of particles (an ideal gas), the corresponding number of particles in such a shell would be given by

$$\frac{dn(r)}{dr} dr \approx \rho \cdot 4\pi r^2 dr \quad (1.74)$$

The pair correlation function describes the *relative deviation of the number of particles at distance r compared to this completely homogeneous*

distribution:

$$g(r) = \frac{1}{4\pi r^2 \rho} \left\langle \sum_{\substack{j \\ j \neq i}} \delta(r - r_{ij}) \right\rangle \quad (1.75)$$

– Thus, for the ideal gas $g(r) = 1$.

- Since all particles are equivalent, we can average over the N different choices of reference particle i , such that we arrive at

$$g(r) = \frac{1}{4\pi r^2 \rho N} \left\langle \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle = \frac{1}{2\pi r^2 \rho N} \left\langle \sum_{i < j} \delta(r - r_{ij}) \right\rangle \quad (1.76)$$

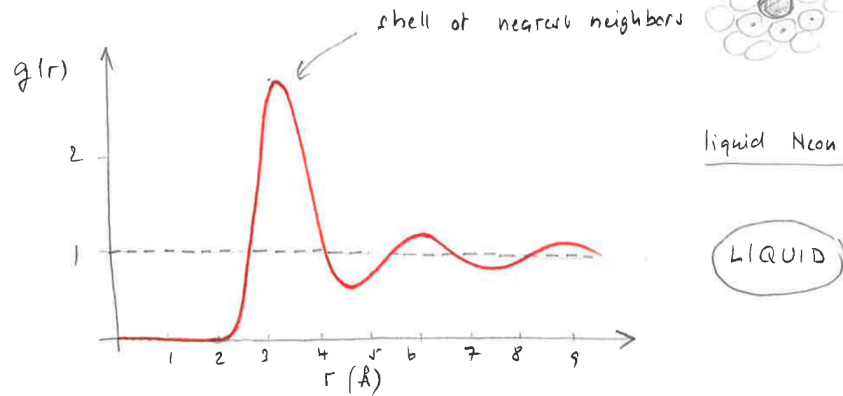
Integration over r from zero to infinity yields

$$4\pi\rho \int_0^\infty dr r^2 g(r) = N - 1 \quad (1.77)$$

which is just the number of all particles minus the reference particle. If we instead integrate only up to a certain finite radius r , we obtain the number of particles in the sphere with radius r minus the reference particle:

$$n(r) = 4\pi\rho \int_0^r dr' r'^2 g(r') \quad (1.78)$$

Typical form



We can regard $g(r)$ as a measure of the *local density* at distance r from the reference particle:

- If $g(r) < 1$ it is lower than ρ . In particular, $g(r) \equiv 0$ for small r , because the presence of the reference particle at the origin excludes all other particles from being there.
- If $g(r) > 1$ the local density is higher than the macroscopic density $\rho = \frac{N}{V}$.
- Particles in the *first shell* (or *first coordination shell*) around the reference particle all have approximately the same distance from it, so there is a maximum. These particles are the *nearest neighbors* of the reference particle.
- For growing r , $g(r)$ decreases again below 1 because of similar exclusion effects (particles cannot be in the space already occupied by those in the first shell). The maximum corresponding to the second shell is lower because as r increases the order gets successively smeared out.
- Depending on the thermodynamic state there may be more maxima and minima. As a rule, these are more distinct at high ρ and low T .
- For $r \rightarrow \infty$, correlations should die out completely such that we expect $g(r) \rightarrow 1$ in this limit. This, however, is strictly true only in the *grand-canonical ensemble*, where N can fluctuate. In the canonical ensemble, we instead obtain

$$\lim_{r \rightarrow \infty} g(r) = 1 + O(1/N) \quad (1.79)$$

which only approaches 1 in the thermodynamic limit.

So far, we have assumed that particles are arranged isotropically, i.e. that there are no preferred directions. Accordingly, $g(r)$ depends only on the distance r but not on the direction \mathbf{r} . One can, however, also define a direction-dependent pair correlation function

$$g(\mathbf{r}) := \frac{1}{\rho N} \left\langle \sum_{\substack{j \\ j \neq i}} \delta^3(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle \quad (1.80)$$

In a slightly more formal way, the pair correlation function can be introduced via the *two-particle density*

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \frac{1}{Z} \int d\mathbf{r}_3 \dots d\mathbf{r}_N e^{-\beta U(\mathbf{r}^N)} \quad (1.81)$$

- Note that $N(N-1) = \frac{N!}{(N-2)!}$

This is (essentially) the *marginal distribution* where only the positions of particles 1 and 2 are of interest and all other degrees of freedom have been integrated out. If the system is not subject to an external potential, the two-particle density depends only on the difference $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$, and so

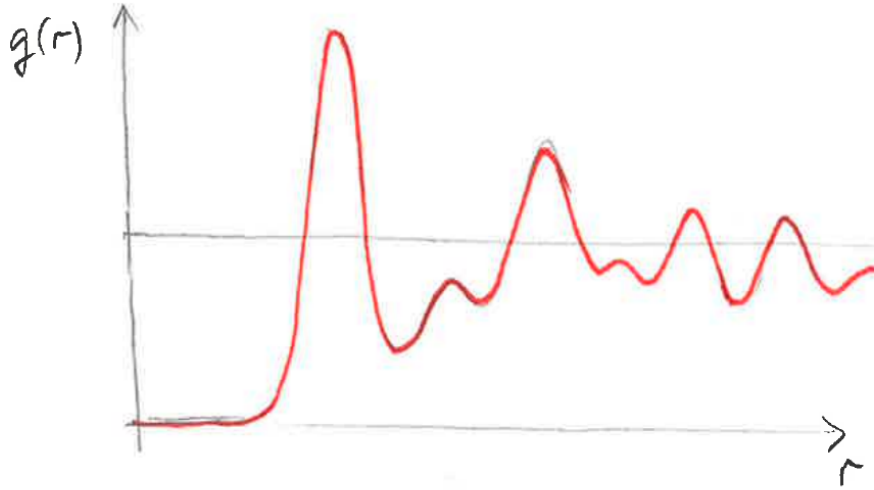
$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(\mathbf{r}_{12}) \quad (1.82)$$

The pair correlation function is then defined as

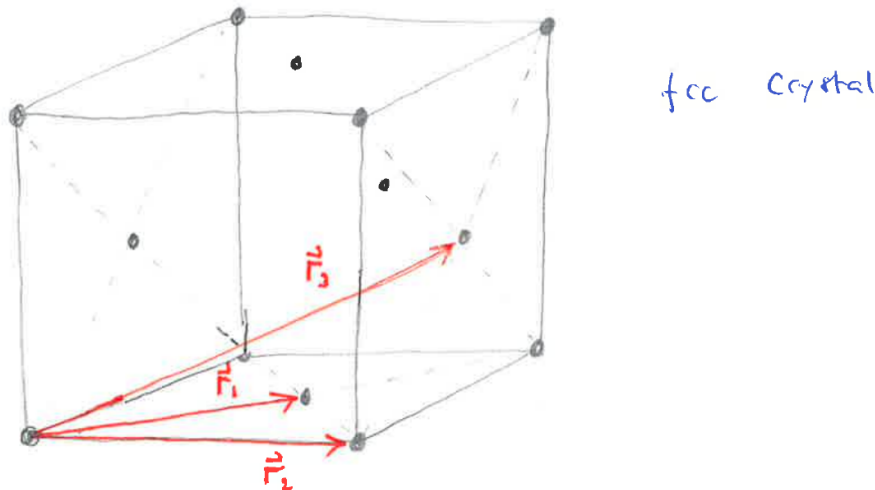
$$g(r_{12}) = \frac{1}{\rho^2} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (1.83)$$

In fact, in analogy to the two-particle density, there exists a whole hierarchy of n -particle densities $\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$, which are also obtained by marginalizing with respect to particle positions.

For a *solid*, $g = g(r)$ depends on magnitude *and* direction of the distance vector \mathbf{r} . Nevertheless, one often considers the pair correlation function obtained by averaging over all directions. Such a $g(r)$ for a crystal might look like this:



For a crystal, $g(r)$ exhibits more peaks than for a liquid, and they are more pronounced. The positions of these peaks depend, of course, on the particular structure of the crystal.



In an fcc crystal, for example, the typical distances of particles corresponding to the first three peaks in $g(r)$ have ratios

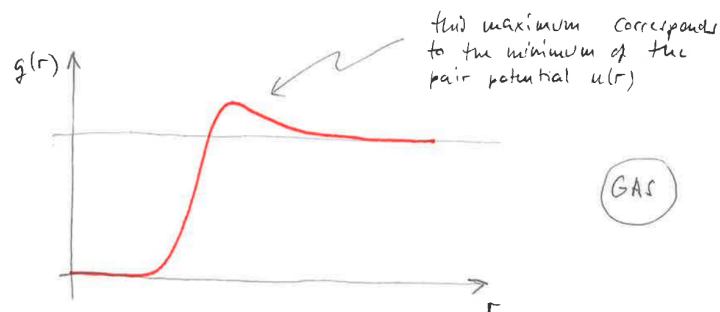
$$r_1 : r_2 : r_3 = 1 : \sqrt{2} : \sqrt{3} \quad (1.84)$$

The finite width of the peaks is due to the thermal fluctuations of the particles around the sites of the perfect lattice.

At low density, i.e. for a dilute gas, the pair correlation function allows for a simple approximation. In fact, to first order in the density, $g(r)$ is given simply by the Boltzmann factor of the pair potential:

$$g(r) \approx e^{-\beta u(r)} \quad (1.85)$$

- This result follows from Eq. (1.81) under the assumption that when two particles interact, the others are far away. A derivation can be found in J.P. Hansen and I.R. McDonald, "Theory of simple liquids", Academic Press.



For high temperature and low density, $g(r)$ thus becomes a step function.

1.3.6 Virial equation of state

$g(r)$ contains a lot of thermodynamic information about a given system. For instance, based on the knowledge of $g(r)$, one can compute the expectation of any observable

$$A(\mathbf{r}^N) = \sum_{i < j} a(r_{ij}) = \frac{1}{2} \sum_{i \neq j} a(r_{ij}) \quad (1.86)$$

that can be written as a sum of pair contributions $a(r_{ij})$, *irrespective of whether the interactions are pairwise additive or not!* To see this, we rewrite the expectation of $A(\mathbf{r}^N)$ by inserting 1 in the form of an integral over a delta function

$$\begin{aligned} \langle A(\mathbf{r}^N) \rangle &= \left\langle \frac{1}{2} \sum_{i \neq j} a(r_{ij}) \right\rangle = \left\langle \frac{1}{2} \sum_{i \neq j} \int_0^\infty dr a(r_{ij}) \delta(r - r_{ij}) \right\rangle \\ &= \frac{1}{2} \int_0^\infty dr a(r) \left\langle \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle \end{aligned} \quad (1.87)$$

Recalling the definition

$$g(r) \stackrel{(1.76)}{=} \frac{1}{4\pi r^2 \rho N} \left\langle \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle \quad (1.88)$$

we obtain

$$\langle A(\mathbf{r}^N) \rangle = \int_0^\infty dr a(r) 2\pi r^2 \rho N g(r) \quad (1.89)$$

If A is an *extensive* variable, the average of A per particle is given by

$$\frac{\langle A(\mathbf{r}^N) \rangle}{N} = 2\pi \rho \int_0^\infty dr a(r) r^2 g(r) \quad (1.90)$$

Example: pairwise additive interactions. If the interactions are pairwise additive, i.e. if

$$U(\mathbf{r}^N) = \sum_{i < j} u(r_{ij}) \quad (1.91)$$

and thus the virial is

$$W = \sum_{i < j} w(r_{ij}), \quad w(r) = r u'(r) \quad (1.92)$$

then the average potential energy and virial per particle are given by

$$\frac{\langle U \rangle}{N} = 2\pi\rho \int_0^\infty dr r^2 g(r) u(r) \quad (1.93)$$

$$\frac{\langle W \rangle}{N} = 2\pi\rho \int_0^\infty dr r^2 g(r) [ru'(r)] \quad (1.94)$$

For pairwise additive potentials, the general form of the equation of state can therefore be rewritten explicitly as

$$p \stackrel{(1.55)}{=} \rho k_B T - \frac{1}{3V} \langle W \rangle = \rho k_B T - \frac{2\pi\rho N}{3V} \int_0^\infty dr r^2 g(r) [ru'(r)] \quad (1.95)$$

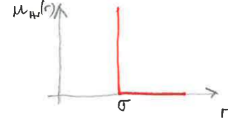
i.e. as the *virial equation of state*

$$p = \rho k_B T - \frac{2\pi\rho^2}{3} \int_0^\infty dr r^2 g(r) [ru'(r)] \quad (1.96)$$

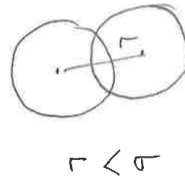
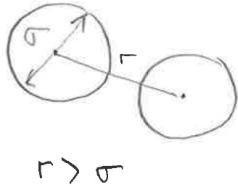
1.3.7 Hard spheres equation of state

For hard spheres (HSs), the pair potential is given by

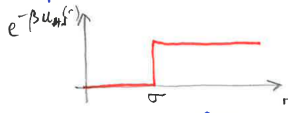
$$u_\sigma(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases} \quad (1.97)$$



σ is the diameter of the spheres. This particular form of the pair interaction potential simply means that in the N -particle system any particle configuration is forbidden that contains two or more *overlapping* particles, while all other configurations are assigned the same energy.



Since the potential $u_\sigma(r)$ is discontinuous at $r = \sigma$, we cannot directly apply the virial equation of state. Note, however, that the Boltzmann factor of the HS potential is just the Heaviside unit step function shifted to $r = \sigma$:

$$e^{-\beta u_\sigma(r)} = \begin{cases} 0, & r < \sigma \\ 1, & r > \sigma \end{cases} = \theta_H(r - \sigma) \quad (1.98)$$


Thus we have (in the distribution sense)

$$\delta(r - \sigma) = \frac{d}{dr} \theta_H(r - \sigma) = \frac{d}{dr} [e^{-\beta u_\sigma(r)}] = -\beta u'_\sigma(r) e^{-\beta u_\sigma(r)} \quad (1.99)$$

Therefore, we can express

$$u'_\sigma(r) = -k_B T e^{\beta u_\sigma(r)} \delta(r - \sigma) \quad (1.100)$$

Plugging this expression in the virial equation of state (1.96), we obtain

$$\begin{aligned} \frac{p}{k_B T \rho} &\stackrel{(1.96)}{=} 1 - \frac{2\pi\rho}{3k_B T} \int_0^\infty dr r^2 g_\sigma(r) [r u'_\sigma(r)] \\ &\stackrel{(1.100)}{=} 1 + \frac{2\pi\rho}{3} \int_0^\infty dr r^3 g_\sigma(r) e^{\beta u_\sigma(r)} \delta(r - \sigma) \end{aligned} \quad (1.101)$$

We introduce the so-called *cavity function* $y_\sigma(r)$ for the hard sphere system. For a general pair potential $u(r)$, the corresponding cavity function $y(r)$ is defined by

$$y(r) := g(r) e^{\beta u(r)} \quad (1.102)$$

In terms of $y_\sigma(r)$, Eqn. (1.101) becomes

$$\frac{p}{k_B T \rho} = 1 + \frac{2\pi\rho}{3} \int_0^\infty dr r^3 y_\sigma(r) \delta(r - \sigma) \quad (1.103)$$

The important point to recognize is now that even if the correlation function or the potential $u(r)$ happen to be discontinuous, the cavity function $y(r)$ still *is continuous*.

- *Proof.* In fact, recall the formal definition of $g(r_{12})$ via Eqs. (1.81) and (1.83)

$$g(r_{12}) = \rho^{-2} \frac{N!}{(N-2)!} \frac{1}{Z} \int d\mathbf{r}_3 \dots d\mathbf{r}_N e^{-\beta \sum_{i < j} u(r_{ij})} \quad (1.104)$$

Since the integration does not run over \mathbf{r}_1 and \mathbf{r}_2 , the factor $e^{-\beta u(r_{12})}$ can be pulled out of the integral:

$$g(r_{12}) = \frac{N!}{(N-2)!} \frac{e^{-\beta u(r_{12})}}{Z} \rho^{-2} \int d\mathbf{r}_3 \dots d\mathbf{r}_N e^{-\beta \sum_{i < j} u(r_{ij})} \quad (1.105)$$

Here $\sum'_{i < j}$ indicates a sum without the term $(i = 1, j = 2)$. This formula shows that any discontinuity in $g(r_{12})$ must originate from a discontinuity of $e^{-\beta u(r_{12})}$. In the cavity function

$$y(r_{12}) = g(r_{12})e^{\beta u(r_{12})} = \frac{N!}{(N-2)!} \frac{\rho^{-2}}{Z} \int d\mathbf{r}_3 \dots d\mathbf{r}_N e^{-\beta \sum'_{i < j} u(r_{ij})} \quad (1.106)$$

precisely this factor has, however, been absorbed. ✓

We may therefore evaluate the delta function in (1.103), which yields

$$\frac{p_\sigma}{\rho k_B T} = 1 + \frac{2\pi\rho\sigma^3}{3} y_\sigma(\sigma) \quad (1.107)$$

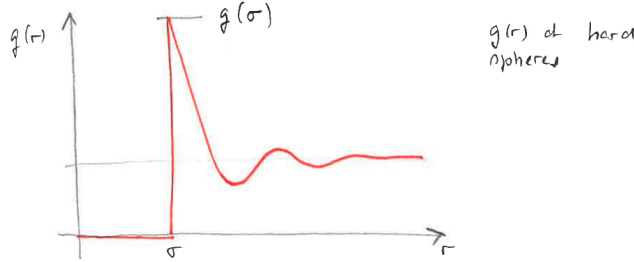
For the hard sphere potential, however, we obviously have

$$y_\sigma(r) = g_\sigma(r) \quad \forall r > \sigma \quad (1.108)$$

Thus, we conclude that due to continuity

$$y_\sigma(\sigma) = \lim_{r \rightarrow \sigma} y_\sigma(r) = \lim_{r \searrow \sigma} g_\sigma(r) \equiv g_\sigma(\sigma^+) \quad (1.109)$$

The $g_\sigma(\sigma^+)$ value on the right hand side is known as the *pair correlation function at contact*.



We therefore finally are in the position to evaluate the delta function in (1.103), which yields the hard sphere equation of state

$$\frac{p_\sigma}{\rho k_B T} = 1 + \frac{2\pi\sigma^3\rho}{3} g_\sigma(\sigma^+) \quad (1.110)$$

Since the volume of one hard sphere of diameter σ is $\frac{4\pi}{3} \left(\frac{\sigma}{2}\right)^3 = \frac{\pi}{6}\sigma^3$, the *volume fraction* ϕ_σ of these spheres at number density ρ is

$$\phi_\sigma = \frac{\pi}{6}\sigma^3\rho \quad (1.111)$$

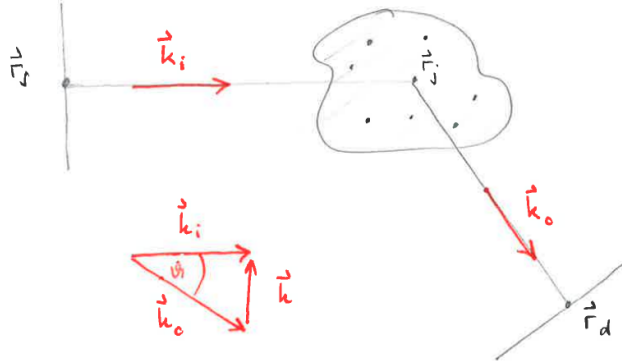
The *hard sphere equation of state* then takes the form

$$\frac{p_\sigma}{\rho k_B T} = 1 + 4\phi_\sigma g_\sigma(\sigma^+) \quad (1.112)$$

This expression is also known as the *contact formula*.

1.3.8 The structure factor

The pair correlation function $g(r)$ can be obtained from x-ray or neutron scattering experiments. In such experiments, a *monochromatic* wave hits a sample with N scattering centers located at positions \mathbf{r}_j . Each of these scattering centers leads to a *spherical wave* propagating outward and interfering constructively or destructively with the spherical waves coming from the other scattering centers.



We assume that both

- the position \mathbf{r}_s of the source
- the position \mathbf{r}_d of the detector

are located sufficiently far away from the sample, such that the incoming waves hitting the sample as well as the outgoing wave reaching the detector can be approximated as plane waves. Denoting the incoming and outgoing wave vector by \mathbf{k}_i and \mathbf{k}_o , respectively, we have

$$k_i = |\mathbf{k}_i| = \frac{2\pi}{\lambda} = \begin{cases} p/\hbar, & \text{for neutrons} \\ \omega/c, & \text{for x-rays} \end{cases} \quad (1.113)$$

The amplitude A of the radiation reaching the detector

$$\begin{aligned}
 A &\propto \sum_{j=1}^N e^{i\mathbf{k}_i \overbrace{(\mathbf{r}_j - \mathbf{r}_s)}^{\text{incoming optical path length}}} \times e^{i\mathbf{k}_o \overbrace{(\mathbf{r}_d - \mathbf{r}_j)}^{\text{outgoing optical path length}}} \\
 &= e^{-i\mathbf{k}_i \mathbf{r}_s} e^{i\mathbf{k}_o \mathbf{r}_d} \sum_{j=1}^N e^{i(\mathbf{k}_i - \mathbf{k}_o) \mathbf{r}_j}
 \end{aligned} \tag{1.114}$$

only depends on the relative phases of the contributions coming from the scattering centers. For *elastic scattering* defined by

$$k_i = k_o = \frac{2\pi}{\lambda} \tag{1.115}$$

having the same wave length λ , the wave vectors \mathbf{k}_i , \mathbf{k}_o and the *scattering vector*

$$\mathbf{k} = \mathbf{k}_i - \mathbf{k}_o \tag{1.116}$$

form an isosceles triangle, and the *scattering angle* θ is related to $k = |\mathbf{k}|$ by

$$k^2 = (\mathbf{k}_i - \mathbf{k}_o)^2 = k_i^2 - 2\mathbf{k}_i \mathbf{k}_o + k_o^2 = \left(\frac{2\pi}{\lambda}\right)^2 \underbrace{2(1 - \cos \theta)}_{2 \sin^2 \frac{\theta}{2}} \tag{1.117}$$

i.e. the *Bragg law*

$$k = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \tag{1.118}$$

The *intensity* of the radiation arriving at the detector is proportional to the square of the amplitude

$$I(\mathbf{k}) \propto \left| \sum_{j=1}^N e^{i\mathbf{k} \mathbf{r}_j} \right|^2 = \sum_{j,l=1}^N e^{i\mathbf{k} \mathbf{r}_j} e^{-i\mathbf{k} \mathbf{r}_l} = \sum_{j,l=1}^N e^{-i\mathbf{k} \mathbf{r}_{jl}} \tag{1.119}$$

where $\mathbf{r}_{jl} = \mathbf{r}_l - \mathbf{r}_j$ is the vector going from particle j to particle l .

For a statistical-mechanical many-particle system we now have to average this appropriately over all the positions of the scattering centers. The *instantaneous particle number density* of the fluid under consideration is a sum

$$\rho(\mathbf{r}) = \sum_{j=1}^N \delta^3(\mathbf{r} - \mathbf{r}_j) \tag{1.120}$$

of δ -functions at the particle positions. The Fourier transform of this particle number density is

$$\rho_{\mathbf{k}} = \int d\mathbf{r} e^{-i\mathbf{k} \mathbf{r}} \rho(\mathbf{r}) = \sum_{j=1}^N \int d\mathbf{r} e^{-i\mathbf{k} \mathbf{r}} \delta^3(\mathbf{r} - \mathbf{r}_j) = \sum_{j=1}^N e^{-i\mathbf{k} \mathbf{r}_j} \tag{1.121}$$

The *structure factor* is defined as the statistical average of the squared modulus of $\rho_{\mathbf{k}}$ per particle, i.e.

$$S(\mathbf{k}) \equiv \frac{1}{N} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle = \frac{1}{N} \left\langle \sum_{j,l=1}^N e^{-i\mathbf{k}\mathbf{r}_j} e^{i\mathbf{k}\mathbf{r}_l} \right\rangle = \frac{1}{N} \left\langle \sum_{j,l=1}^N e^{-i\mathbf{k}\mathbf{r}_{lj}} \right\rangle \quad (1.122)$$

or

$$S(\mathbf{k}) = 1 + \frac{1}{N} \left\langle \sum_{\substack{j,l=1 \\ j \neq l}}^N e^{-i\mathbf{k}\mathbf{r}_{lj}} \right\rangle \quad (1.123)$$

Up to the prefactor (and the average), this expression is identical to Eq. (1.119) for the intensity $I(\mathbf{k})$, i.e.

$$S(\mathbf{k}) \propto I(\mathbf{k}) \quad (1.124)$$

Since $S(\mathbf{k})$ is a statistical average of a sum of pair contributions, we can express it in terms of $g(r)$. In fact, recalling that

$$g(\mathbf{r}) \stackrel{(1.80)}{=} \frac{1}{\rho N} \left\langle \sum_{\substack{j=1 \\ j \neq i}}^N \delta^3(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle \quad (1.125)$$

we derive

$$\begin{aligned} \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} g(\mathbf{r}) &= \frac{1}{\rho N} \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} \left\langle \sum_{\substack{j=1 \\ j \neq i}}^N \delta^3(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle \\ &= \frac{1}{\rho N} \left\langle \sum_{\substack{j=1 \\ j \neq i}}^N e^{-i\mathbf{k}\mathbf{r}_{lj}} \right\rangle \end{aligned} \quad (1.126)$$

Comparing Eqs. (1.123) and (1.126), we conclude that

$$S(\mathbf{k}) \equiv 1 + \rho \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} g(\mathbf{r}) \quad (1.127)$$

The structure factor is therefore essentially the Fourier transform of the pair correlation function. However, the above expression contains a singularity, because for $r \rightarrow \infty$ we know that $g(r) \rightarrow 1$, for which there is a contribution

$$\int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} 1 = (2\pi)^3 \delta^3(\mathbf{k}) \quad (1.128)$$

to the Fourier transform that corresponds to forward ($\mathbf{k} = \mathbf{0}$) scattering and needs to be isolated. We therefore define a *reduced structure factor*

$$\widehat{S}(\mathbf{k}) := S(\mathbf{k}) - (2\pi)^3 \delta^3(\mathbf{k}) = 1 + \rho \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} [g(\mathbf{r}) - 1] \quad (1.129)$$

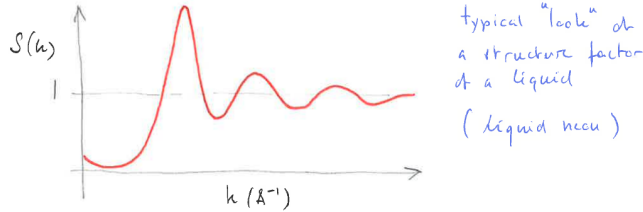
Inverting this formula, we obtain

$$g(\mathbf{r}) = 1 + \frac{1}{(2\pi)^3 \rho} \int d\mathbf{k} e^{i\mathbf{k}\mathbf{r}} [\widehat{S}(\mathbf{k}) - 1] \quad (1.130)$$

For an *isotropic* fluid, $g(\mathbf{r})$ and $\widehat{S}(\mathbf{k})$ depend only on the magnitude of their arguments. Transformation to spherical coordinates and integration over the angular variable yields

$$\widehat{S}(k) = 1 + 4\pi\rho \int_0^\infty dr r^2 \frac{\sin kr}{kr} [g(r) - 1] \quad (1.131a)$$

$$g(r) = 1 + \frac{1}{2\pi^2\rho} \int_0^\infty dk k^2 \frac{\sin kr}{kr} [\widehat{S}(k) - 1] \quad (1.131b)$$



- In the limit $\mathbf{k} \rightarrow \mathbf{0}$ one can show that the *compressibility relation*

$$\lim_{\mathbf{k} \rightarrow \mathbf{0}} \widehat{S}(\mathbf{k}) = \widehat{S}(\mathbf{0}) = \rho k_B T \kappa_T \quad (1.132)$$

holds, which relates the long-wavelength limit $\widehat{S}(\mathbf{0})$ to the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (1.133)$$

For the ideal gas, we have

$$pV = Nk_B T \Rightarrow \kappa_T^{id} = -\frac{p}{Nk_B T} \frac{\partial}{\partial p} \bigg|_T \frac{Nk_B T}{p} = \frac{1}{\rho k_B T} \quad (1.134)$$

such that the above compressibility relation can actually be written as

$$\widehat{S}(\mathbf{0}) = \kappa_T / \kappa_T^{id} \quad (1.135)$$

1.4 Cutoffs

In computer simulations, a large part of the computer time is usually spent calculating forces and energies. For short-ranged interactions, one can reduce the computational effort by neglecting contributions to the potential energy due to pairs of particles that are farther apart than a certain *cutoff radius* r_c . Of course, this can be done only if the total potential energy is dominated by interactions with neighboring particles closer than r_c (this is just what the term “short-ranged” means).

Truncated potentials

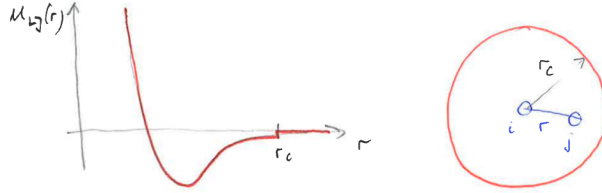
For the LJ potential

$$u_{LJ}(r) \stackrel{(1.58)}{=} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1.136)$$

the simplest way to implement a cutoff is to simply *truncate* the interaction, setting

$$u_{trunc}(r) = \begin{cases} u_{LJ}(r), & r < r_c \\ 0, & r \geq r_c \end{cases} \quad (1.137)$$

This corresponds to simply neglecting energies and forces beyond a distance r_c .



The potential energy then becomes

$$U(\mathbf{r}^N) = \frac{1}{2} \sum_{\substack{i \neq j \\ r_{ij} < r_c}} u(r_{ij}) \quad (1.138)$$

How much computer time can we save by this strategy?

- Without cutoff, we have to consider all $\frac{N(N-1)}{2}$ pairs of particles to compute the energy, which means that $O(N^2)$ pair energy terms need to be evaluated.
- With cutoff r_c , each particle sees (on average) $\frac{4\pi r_c^3}{3} \rho$ other particles, so if we increase the system size, which is proportional to N , while keeping $r_c = \text{const}$, the total number of pair energies to evaluate scales like

$$\frac{1}{2} \cdot N \cdot \frac{4\pi r_c^3}{3} \rho \sim O(N) \quad (1.139)$$

In molecular simulations, the goal often is to achieve such a linear scaling with system size. Otherwise, the simulation of large systems would be impossible.

Of course, truncating a potential that is not strictly zero beyond r_c , one certainly introduces an error. One can make this error arbitrarily small by making r_c large, but that, of course, increases the computational load of the simulation. A smarter alternative is to try to estimate the so-called *tail corrections*, by which the results obtained for small r_c differ from those that would result from using the untruncated potential.

Let us consider the expectation value of the total potential energy per particle. Assuming that r_c is sufficiently large, such that $g(r) \approx 1$ for $r > r_c$, we split

$$\begin{aligned} \frac{\langle U \rangle}{N} &= 2\pi\rho \int_0^\infty dr r^2 g(r) u(r) \\ &\approx \underbrace{2\pi\rho \int_0^{r_c} dr r^2 g(r) u(r)}_{(1)} + \underbrace{2\pi\rho \int_{r_c}^\infty dr r^2 u(r)}_{(2)} \end{aligned} \quad (1.140)$$

- the first contribution

$$(1) = \frac{1}{N} \left\langle \sum_{\substack{i < j \\ r_{ij} < r_c}} u(r_{ij}) \right\rangle \quad (1.141)$$

may be determined by simulating the system with the truncated potential.

- the second contribution

$$(2) = 2\pi\rho \int_{r_c}^\infty dr r^2 u(r) \quad (1.142)$$

resembles the *tail correction* as the total interaction energy per particle beyond r_c . For the example of the LJ potential, it can be computed analytically with the result

$$(2) = \frac{8}{3}\pi\rho\epsilon\sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c} \right)^9 - \left(\frac{\sigma}{r_c} \right)^3 \right] \quad (1.143)$$

– *Proof.*

$$\begin{aligned} 2\pi\rho \int_{r_c}^\infty dr r^2 u_{LJ}(r) &= 2\pi\rho \int_{r_c}^\infty dr r^2 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \\ &= 8\pi\epsilon\sigma^3\rho \int_{r_c}^\infty d\left(\frac{r}{\sigma} \right) \left(\frac{r}{\sigma} \right)^2 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \\ &= 8\pi\epsilon\sigma^3\rho \int_{r_c/\sigma}^\infty dx \left(x^{-10} - x^{-4} \right) \\ &= 8\pi\epsilon\sigma^3 \left[\frac{1}{9} \left(\frac{r_c}{\sigma} \right)^{-9} - \frac{1}{3} \left(\frac{r_c}{\sigma} \right)^{-3} \right] \\ &= \frac{8}{3}\pi\rho\epsilon\sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c} \right)^9 - \left(\frac{\sigma}{r_c} \right)^3 \right] \end{aligned} \quad (1.144)$$

A similar tail correction can be applied to the virial by splitting

$$\frac{\langle W \rangle}{N} \approx \frac{1}{N} \left\langle \sum_{\substack{i < j \\ r_{ij} < r_c}} r_{ij} u'(r_{ij}) \right\rangle + 2\pi\rho \int_{r_c}^{\infty} dr r^2 [r u'(r)] \quad (1.145)$$

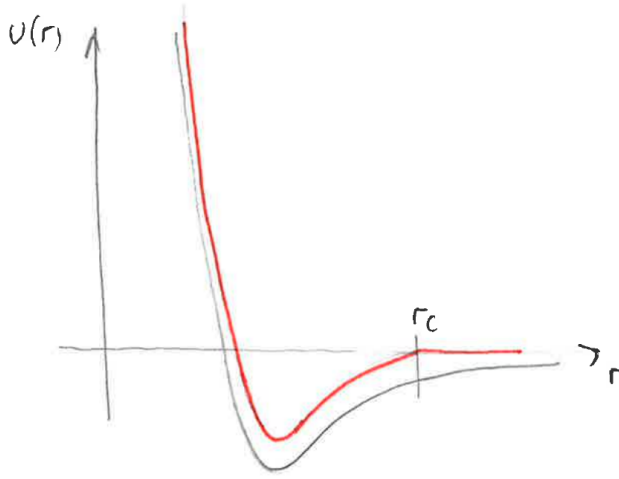
and again assuming that $g(r) \sim 1$ for $r > r_c$.

Truncated and shifted potentials

Another possibility to implement a cutoff is to *truncate and shift* the potential:

$$u_{tr-sh}(r) \equiv \begin{cases} u(r) - u(r_c), & r < r_c \\ 0, & r \geq r_c \end{cases} \quad (1.146)$$

This approach is often used in MD, as it avoids a discontinuity in the energy (and a singularity in the forces). Some authors modify the potential further to also avoid a discontinuity in the forces. Again, the error introduced by the cutoff and shifting can be take care of by appropriate tail corrections.



- **Warning.** If the above tail correction integrals are to converge, the potential $u(r)$ must decay stronger than r^{-3} , which excludes e.g. Coulomb and dipolar potentials.

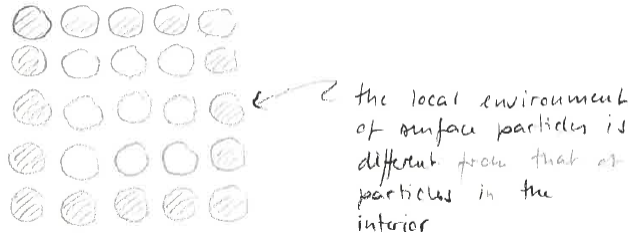
1.5 Boundary Conditions

Often the goal of MC or MD simulations is to determine the properties of a macroscopic sample. However, macroscopic samples have sizes that exceed those that are accessible to simulations on a computer by many orders of magnitude. While macroscopic systems have particle numbers that are of the order of Avogadro's number $N_A = 6.02 \cdot 10^{23}$, systems simulated on a computer usually consist of a few hundred to a few thousand particles simply because larger

systems are computationally more expensive to simulate. Now, in small systems, the choice of boundary conditions may have a strong effect, because in a small system a large fraction of particles are located near the surface.

- Imagine, for instance, a simple cubic crystal of $10 \times 10 \times 10 = 1000$ particles, almost half of them are located on its surface!
 - Indeed, $8 \times 8 \times 8 = 512$ are located beneath its surface, leaving $1000 - 512 = 488$ particles on its surface, which corresponds to 48.8%.
- Even for a crystal of 10^6 particles, 5.8808% of the particles are surface particles.

Surface particles, whose fraction scales like $N^{-1/3}$ with the total particle number N , experience a different local environment, and thus have a different influence on the physical properties of the system than so-called *bulk particles* that are located well in the interior of the system



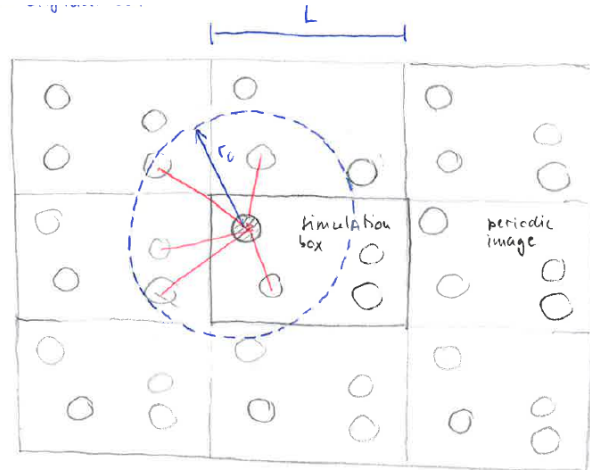
To better reproduce the properties of a bulk system in the thermodynamic limit, molecular simulations are typically carried out with *periodic boundary conditions* (PBC). With such boundary conditions, there are no surfaces such that finite size effects should be less pronounced than for systems enclosed in a container. With PBC, one imagines that the volume containing the particles is the primitive cell of an infinite lattice of identical cells. Efficiently, one *replicates the system periodically* in all directions. Each of the replicated cells is an exact copy of the original one. Each particle then interacts with all other particles in this infinite arrangement, i.e. it interacts with all other particles in its own cell, but also with all their *periodic images* (including its own periodic image!).

For pairwise additive interactions, the total energy with PBC is given by

$$U(\mathbf{r}^N) = \frac{1}{2} \sum_{i,j,\mathbf{n}}' u(|\mathbf{r}_{ij} + \mathbf{n}L|) \quad (1.147)$$

- This *infinite sum* runs over all particle pairs i, j and over all cells.
- L is the side length of the simulation box (for simplicity assumed cubic).
- The vector $\mathbf{n} = (n_x, n_y, n_z) \in \mathbb{Z}^3$ consists of three integers that specify the particular periodic image.

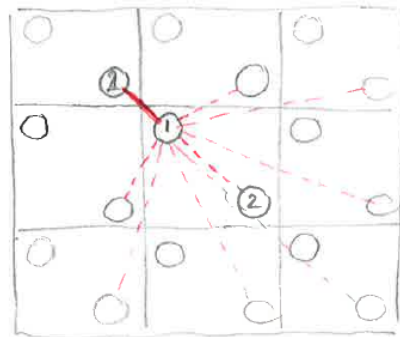
- In particular, $\mathbf{n} = \mathbf{0}$ corresponds to the original simulation box. The prime \sum' implies that for $\mathbf{n} = \mathbf{0}$ the terms $i = j$ are excluded from the sum to avoid self-interactions.



As it stands, the infinite sum (1.147) is not particularly practical for simulations, as calculating the total energy would require an infinite number of operations. For systems with short-ranged interactions, however, only a finite number of particles in the vicinity of a given particle need to be considered as indicated in the above figure by the cutoff-sphere.

While PBC are a practical way to mimic a macroscopic bulk system, it should be noted that *finite size effects* may still affect the result. For instance, if long wavelength fluctuations with a wavelength λ larger than the linear box size L are important, large finite size effects are to be expected. This may, for instance, happen in the vicinity of a continuous phase transition, where critical fluctuations become dominant.

With PBC, sometimes pair interactions are truncated using the so-called *minimum image convention*. This convention stipulates that one can always use the *nearest periodic image* in the calculation of pair interactions.



In the calculation of the interaction between particles 1 and 2, one uses the periodic image of 2 that is closest to 1 (solid line)

Chapter 2

Canonical Monte Carlo Simulations

In this section we discuss the main ingredients of a MC simulation for a classical many-particle system in the canonical ensemble. Before we do that, we will briefly review the theoretical basis for the Metropolis algorithm.

2.1 The Metropolis Algorithm

As discussed in the previous chapter, our goal often is to compute averages of a phase space observable $A(\mathbf{r}^N)$. For this task, we have seen that it suffices to average over configuration space, i.e.

$$\langle A \rangle = \frac{\int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} A(\mathbf{r}^N)}{\int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}} \quad (2.1)$$

If we can generate a *sample* of M configuration space points \mathbf{r}_i^N , $i = 1, \dots, M$ according to the probability density

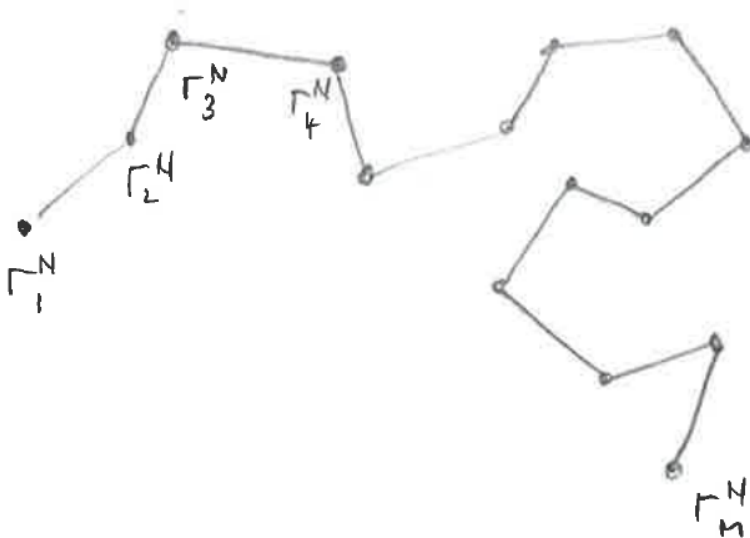
$$f(\mathbf{r}^N) = \frac{e^{-\beta U(\mathbf{r}^N)}}{\int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}} \quad (2.2)$$

then we can approximate the above canonical average $\langle A \rangle$ by the average over the sample

$$\langle A \rangle \approx \frac{1}{M} \sum_{i=1}^M A(\mathbf{r}_i^N), \quad \mathbf{r}_i^N \text{ distributed according to (2.2)} \quad (2.3)$$

The difficulty, of course, lies in generating such a sample with the correct distribution. This is a particular challenge, since in general the normalization factor $\int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$ in (2.2) is unknown. A solution of this problem was provided

by the Metropolis algorithm suggested in 1953 by Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth, Augusta H. Teller and Edward Teller [J. Chem. Phys. **21**, 1087 (1953)]. The basic idea of this very powerful method is to generate a *Markov chain* of configurations $\{\mathbf{r}_i\}$ by taking a given configuration, generating a new configuration and accepting or rejecting it. Repeating these basic steps generates a sequence of configurations which, provided the generation and acceptance/rejection of configurations is done in the correct way, samples the desired distribution $f(\mathbf{r}^N)$. Since the generation and acceptance/rejection steps involve a stochastic step based on random numbers, this algorithm is a “Monte Carlo” method.



Such a sequence is a *Markov chain*, because new configurations are produced randomly with a probability that depends only on the current state and not on the prior history of the system (this is the *Markov property*).

To make the basic idea of Metropolis MC more precise, consider a sequence of configurations

$$\{\mathbf{r}_1^N, \mathbf{r}_2^N, \mathbf{r}_3^N, \dots, \mathbf{r}_M^N\} \quad (2.4)$$

generated according to a stochastic procedure (i.e., involving random numbers) to be specified later. Such a sequence is called a *Markov chain* if the conditional probability that the configuration at time n is \mathbf{r}_n^N depends only on \mathbf{r}_{n-1}^N but not on prior configurations:

$$p(\mathbf{r}_n^N | \mathbf{r}_{n-1}^N, \mathbf{r}_{n-2}^N, \dots, \mathbf{r}_2^N, \mathbf{r}_1^N) \stackrel{!}{=} p(\mathbf{r}_n^N | \mathbf{r}_{n-1}^N) \quad (2.5)$$

- Note that the “time” we are talking about here is not the physical time but rather a kind of “MC-time” that just specifies the position in the sequence.

The conditional probability $p(\mathbf{r}^{N'}|\mathbf{r}^N)$ is also called the *transition probability*, and is denoted by

$$p(\mathbf{r}^N \rightarrow \mathbf{r}^{N'}) = p(\mathbf{r}^{N'}|\mathbf{r}^N) \quad (2.6)$$

The particular form of transition probability $p(\mathbf{r}^N \rightarrow \mathbf{r}^{N'})$ depends on how exactly $\mathbf{r}^{N'}$ is generated from \mathbf{r}^N .

Before discussing the form of $p(\mathbf{r}^N \rightarrow \mathbf{r}^{N'})$ in a Metropolis MC simulation, let's consider the general properties the transition probability needs to have such that the sample produced by the procedure follows the desired distribution.

- To simplify our discussion and save some writing effort, let $x \equiv \mathbf{r}^N$ denote the entire configuration of the system, and $p(x \rightarrow y)$ for the transition probabilities $x \rightarrow y$.

Let us consider a large collection of configurations x which are distributed according to some distribution $f^{(n)}(x)$, and imagine that for each of these states x you attempt to carry out transitions $x \rightarrow y$ to all states y (including the possibility of a trivial transition $x \rightarrow x$ itself), success governed by the transition probability $p(x \rightarrow y)$. The resulting new distribution of steps will then be given by

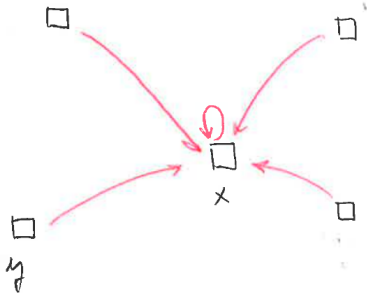
$$f^{(n+1)}(x) = \sum_y f^{(n)}(y)p(y \rightarrow x) \quad (2.7)$$

Since we would like the procedure to sample the equilibrium distribution $f(x)$, we require that $f^{(n)}(x)$ converges towards $f(x)$ for $n \rightarrow \infty$, i.e.

$$\lim_{n \rightarrow \infty} f^{(n)}(x) \equiv f(x) \quad (2.8)$$

A *necessary* condition for that to happen is that $f(x)$ is *stationary* with respect to the “dynamics” mediated by $p(x \rightarrow y)$. In other words, applying $p(y \rightarrow x)$ to a large set of configurations distributed according to $f(y)$ should not change this distribution but leave it *invariant*, such that the following *stationarity condition* for the transition probabilities $p(y \rightarrow x)$ should hold:

$$f(x) = \sum_y f(y)p(y \rightarrow x) \quad \text{for all states } x \quad (2.9)$$



the probability to find the system in x at time $n+1$ is the sum (integral) to find the system in y at time n times the transition probability from y to x .

2.1.1 Global balance

To understand the meaning of stationarity condition (2.9), let us slightly rewrite it. Recognizing that since the transition probabilities are normalized as

$$\sum_y p(x \rightarrow y) = 1 \quad (2.10)$$

we multiply the left-hand side of Eq. (2.9) by 1, such that

$$f(x) \sum_y p(x \rightarrow y) = \sum_y f(y) p(y \rightarrow x) \quad (2.11)$$

and pull $f(x)$ into the sum on the left hand side. Then we get

$$\sum_y p(x \rightarrow y) f(x) = \sum_y f(y) p(y \rightarrow x) \quad \text{for all states } x \quad (2.12)$$

- The left hand side describes the decrease in probability of the state x due to transitions away from x to any one of the other states y .
- The right hand side describes the increase in probability of the state x due to transitions to x from any one of the other states y .

The above stationarity condition means that *in equilibrium for all states x the loss in probability described by the left hand side must be exactly compensated by the increase in probability described by the right hand side*. Therefore, Eq. (2.12) is also called the *condition of global balance* or *condition of full balance*.

2.1.2 Detailed balance

The stationarity condition (2.9) for $p(x \rightarrow y)$ can be guaranteed to hold by imposing a much stronger condition than the global balance condition (2.12): one may require that in equilibrium transitions from x to y are exactly compensated by transitions from y to x , *separately* for each state x and y . In other words, we impose the *condition of detailed balance* or *condition of microscopic balance*

$$f(x) p(x \rightarrow y) = f(y) p(y \rightarrow x) \quad \text{for all states } x, y \quad (2.13)$$

Obviously, if detailed balance holds, the global balance is automatically satisfied. Note, however, that the converse is not necessarily true. In practical implementations of MC simulations, one usually requires detailed rather than global balance. The simple reason is that for a given algorithm detailed balance is usually much easier to demonstrate than global balance.

- *For the curious:* This is not to say that there are no correct MC algorithms that satisfy global balance while violating detailed balance. Examples include
 - * the class of *sequential update algorithms* in which particles are moved or spins are flipped according to a prescribed sequential order instead of picking them at random (see e.g. [R. Ren & G. Orkoulas, J. Chem. Phys. **124**, 064109 (2006)])
 - * Event-chain Monte Carlo algorithms originally devised for hard-spheres [E.P. Bernard, W. Krauth, and D.B. Wilson, Phys. Rev. E **80**, 056704 (2009)] and subsequently generalized to arbitrary pair potentials

2.1.3 Metropolis MC

Let us now consider what detailed balance means for the particular form of the transition probability $p(x \rightarrow y)$ corresponding to a basic *Metropolis MC* step. As mentioned before, a step of a Metropolis MC procedure consists of two parts:

1. First, a new configuration y is *generated* from a given (old) configuration. This *trial move* usually contains an element of randomness (for instance, a particle is displaced by a random amount in a random direction), and so a *generation probability*

$$p_{gen}(x \rightarrow y) \quad (2.14)$$

as the probability density for generating the trial move from x to y .

2. In the second stage of the MC step, the new configuration is either *accepted* or *rejected*. The trial move (i.e. the new configuration y) is accepted with probability

$$p_{acc}(x \rightarrow y) \quad (2.15)$$

$p_{acc}(x \rightarrow y)$ is the probability for accepting y , which was generated from x :

- If y is accepted, it becomes the new configuration of the system.
- If y is rejected, the system stays in x , i.e. the old state is *counted again* for the calculation of averages of the quantities of interest.

Since the generation and acceptance probabilities are statistically independent, the total transition probability $p(x \rightarrow y)$ for a transition from $x \rightarrow y$ is simply the *product* of the generation and acceptance probability:

$$p(x \rightarrow y) = p_{gen}(x \rightarrow y)p_{acc}(x \rightarrow y) \quad (2.16)$$

In other words, $p(x \rightarrow y)$ is the product of the probability to *attempt* a move $x \rightarrow y$ and the probability to accept it.

Since we would like the algorithm to sample the equilibrium distribution $f(x)$, we require this MC transition probability $p(x \rightarrow y)$ to satisfy detailed balance:

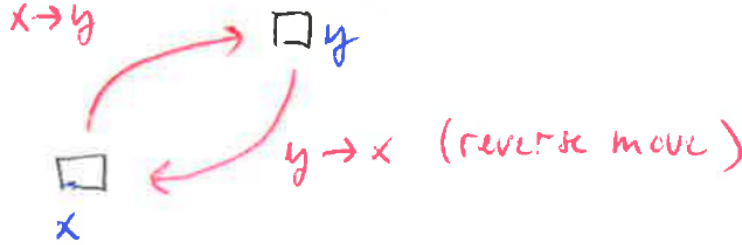
$$f(x)p_{gen}(x \rightarrow y)p_{acc}(x \rightarrow y) = f(y)p_{gen}(y \rightarrow x)p_{acc}(y \rightarrow x) \quad (2.17)$$

For a given fixed form of the generation probability $p_{gen}(x \rightarrow y)$ this equation can be trivially rewritten as a condition for the acceptance probability of the move $x \rightarrow y$ and the *reverse* move $y \rightarrow x$:

$$\frac{p_{acc}(x \rightarrow y)}{p_{acc}(y \rightarrow x)} = \frac{f(y)p_{gen}(y \rightarrow x)}{f(x)p_{gen}(x \rightarrow y)} \quad (2.18)$$

Often, *symmetric* generation probabilities are used, i.e. the probability of generating y from x and the probability of generating x from y are the same, i.e.

$$p_{gen}(x \rightarrow y) = p_{gen}(y \rightarrow x) \quad (\text{symmetric generation}) \quad (2.19)$$

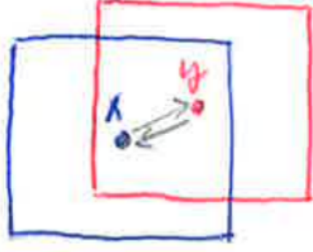


In this case, condition (2.18) simplifies to

$$\frac{p_{acc}(x \rightarrow y)}{p_{acc}(y \rightarrow x)} = \frac{f(y)}{f(x)} \quad (\text{symmetric generation}) \quad (2.20)$$

Note that there are many useful MC algorithms in which the generation probabilities are not symmetric, and we will get to know some of them later in the course.

- As an example of a symmetric move, consider the random displacement of a particle to a new position uniformly distributed in a small region around the old position.



If $f(x)$ is the canonical distribution, i.e. $f(x) = \frac{e^{-\beta H(x)}}{Z}$, condition (2.20) becomes

$$\frac{p_{acc}(x \rightarrow y)}{p_{acc}(y \rightarrow x)} = \frac{e^{-\beta H(y)}}{e^{-\beta H(x)}} = e^{-\beta \Delta H} \quad (\text{symmetric generation}) \quad (2.21)$$

where

$$\Delta H = H(y) - H(x) \quad (2.22)$$

is the energy difference between the old and new configuration. Note that, as promised, in this expression *the normalization factor Z does not appear!* This is important because it means that MC can be applied without knowing the normalization factor Z of the canonical distribution function!

- If Z (and thus the canonical free energy) were known, there would be no need to carry out MC simulations in the first place.

Also note that for putting (2.21) to work, only energy **changes** ΔH need to be calculated, which is e.g. for short range interactions computationally *much* cheaper than calculating the total energy itself.

2.1.4 Metropolis rule

Any acceptance probability satisfying the detailed balance condition in the symmetric form (2.20) can be used in a MC simulation, and many forms of $p_{acc}(x \rightarrow y)$ have been proposed.

- Note that $p_{acc}(x \rightarrow y)$ also needs to be a number between 0 and 1.

A particularly simple and efficient acceptance probability was suggested by Metropolis et al. in 1953. For the choice of Metropolis

$$p_{acc}(x \rightarrow y) = \begin{cases} \frac{f(y)}{f(x)}, & \text{if } f(y) < f(x) \\ 1, & \text{if } f(y) \geq f(x) \end{cases} \quad (\text{symmetric generation}) \quad (2.23)$$

the trial move is accepted with certainty if the new configuration has a larger statistical weight than the old one, while it is only accepted with probability $f(y)/f(x)$ if its weight is smaller.

- To show that this choice indeed satisfies detailed balance, we separately consider the following two cases:

– $f(y) < f(x)$: Then

$$\frac{p_{acc}(x \rightarrow y)}{p_{acc}(y \rightarrow x)} = \frac{\frac{f(y)}{f(x)}}{1} = \frac{f(y)}{f(x)} \quad \checkmark \quad (2.24)$$

– $f(y) \geq f(x)$: Then

$$\frac{p_{acc}(x \rightarrow y)}{p_{acc}(y \rightarrow x)} = \frac{1}{\frac{f(x)}{f(y)}} = \frac{f(y)}{f(x)} \quad \checkmark \quad (2.25)$$

- An alternative to the Metropolis rule is the so-called *symmetric rule*

$$p_{acc}(x \rightarrow y) = \frac{f(y)}{f(x) + f(y)} \quad (2.26)$$

which is used frequently for simulating spin systems.

The Metropolis acceptance rule can be expressed in a compact way as

$$p_{acc}(x \rightarrow y) = \min \left[1, \frac{f(y)}{f(x)} \right] \quad (\text{symmetric generation}) \quad (2.27)$$

For the canonical ensemble

$$p_{acc}(x \rightarrow y) = \min [1, e^{-\beta \Delta H}] , \quad \Delta H = H(y) - H(x) \quad (\text{symm. gen.}) \quad (2.28)$$

In other words,

- moves downhill in energy are always accepted.
- moves in which the energy increases are accepted with probability $e^{-\beta \Delta H}$.

According to the Metropolis acceptance rule, a trial move $x \rightarrow y$ with $f(y) < f(x)$ needs to be accepted with probability $f(y)/f(x)$, which is a number between 0 and 1. One can implement this *rejection/acceptance decision* by drawing a random number ξ from a uniform distribution in the interval $[0, 1]$. If

$$\xi \leq \frac{f(y)}{f(x)} \quad (2.29)$$

then the trial move is accepted and is rejected otherwise.

2.1.5 Rejected moves

In applying the Metropolis MC scheme it is essential that if a trial move is rejected, the old configuration is counted again. Let us look at this issue in some more detail.

So far we had argued that the transition probability of Metropolis MC is given by

$$p(x \rightarrow y) = p_{gen}(x \rightarrow y)p_{acc}(x \rightarrow y) \quad (2.30)$$

However, this transition probability is *not normalized*:

$$\sum_y p(x \rightarrow y) = \sum_y p_{gen}(x \rightarrow y)p_{acc}(x \rightarrow y) \leq 1 \quad (2.31)$$

The reason is that the generation probability $p_{gen}(x \rightarrow y)$ itself *is* normalized, i.e. $\sum_y p_{gen}(x \rightarrow y) = 1$, but in the above sum, it is multiplied by $p_{acc}(x \rightarrow y)$, a number smaller than or equal to 1. Therefore, the above sum is also smaller than or equal to 1. In fact, the transition probability $p(x \rightarrow y)$ fails to be normalized precisely because *it misses all rejected moves*! In order to be useful, a transition probability *must* be normalized, because something rather than nothing should always happen and we need a prescription of what to do. *So what's wrong here?*

We can fix this problem by explicitly including the rejected moves into the transition probability by counting the old configurations again if the trial move is rejected. To do that we first define the *total acceptance probability*

$$P_{acc}(x) := \sum_y p_{gen}(x \rightarrow y)p_{acc}(x \rightarrow y) \quad (2.32)$$

for trial moves starting from configuration x , from which we read off the *total rejection probability* $P_{rej}(x)$ for trial moves starting from x :

$$P_{rej}(x) := 1 - P_{acc}(x) \quad (2.33)$$

In the full transition probability, we need to also include this probability of rejected moves! Therefore, we really should define

$$p(x \rightarrow y) \equiv \underbrace{p_{gen}(x \rightarrow y)p_{acc}(x \rightarrow y)}_{\text{accept}} + \underbrace{P_{rej}(x)\delta_{x,y}}_{\text{reject}} \quad (2.34)$$

where $\delta_{x,y}$ is the Kronecker delta. The last term on the right hand side says that with probability $P_{rej}(x)$ the system stays at x . This transition probability,

which reflects the prescription that after a rejection the old configuration is counted again, *is* normalized:

$$\begin{aligned} \sum_y p(x \rightarrow y) &\equiv \underbrace{\sum_y p_{gen}(x \rightarrow y) p_{acc}(x \rightarrow y)}_{\stackrel{(2.32)}{=} P_{acc}(x)} + P_{rej}(x) \underbrace{\sum_y \delta_{x,y}}_{=1} \\ &= P_{acc}(x) + P_{rej}(x) = 1 \quad \checkmark \end{aligned} \quad (2.35)$$

We can also explicitly check that the correct transition probability as defined in Eq. (2.34) obeys the condition of detailed balance:

- For $y \neq x$, Eq. (2.34) reduces to

$$p(x \rightarrow y) = p_{gen}(x \rightarrow y) p_{acc}(x \rightarrow y) \quad (2.36)$$

for which we have already verified that, using the Metropolis rule, this transition probability satisfies detailed balance (in fact, it was just constructed such that it does).✓

- For $y = x$, Eq. (2.34) reduces to

$$p(x \rightarrow x) = p_{gen}(x \rightarrow x) p_{acc}(x \rightarrow x) + P_{rej}(x) \cdot 1 \quad (2.37)$$

which trivially satisfies detailed balance:

$$f(x)[p_{gen}(x \rightarrow x) + P_{rej}(x)] = f(x)[p_{gen}(x \rightarrow x) + P_{rej}(x)] \quad \checkmark \quad (2.38)$$

In detail, according to the Metropolis rule

$$p_{acc}(x \rightarrow x) = \min[1, f(x)/f(x)] = 1 \quad (2.39)$$

and therefore

$$p(x \rightarrow x) = p_{gen}(x \rightarrow x) + P_{rej}(x) \quad (2.40)$$

As encoded in Eq. (2.40), there are thus two possibilities for the system to stay at x :

- either the identical state x is generated in the generation state (and then, of course, accepted), which is the trivial case.
- or the system stays in the state x because a trial step to some other state y had been generated but was rejected.

In summary, we have shown that - upon including rejected moves by recounting the old configuration after a rejection - the transition probability (2.34) corresponding to the Metropolis procedure (2.28)

- satisfies detailed balance.

- is correctly normalized to 1.

Also, we concluded that if a trial move is rejected, the old configuration must be counted again. If this is not done, the simulation samples the *wrong* ensemble.

- It is instructive to try out how the results of a MC simulation change, if instead of recounting the old configuration again, a new trial move is attempted over and over until another configuration is found that is accepted. That such a strategy gives erroneous results is very obvious taking the example of a two-state system with just two states x_0, x_1 at energy levels $E_0 < E_1$, for which the simulation would just jump between these energies back and forth, leading to an energy average $\langle E \rangle = (E_0 + E_1)/2$, *regardless of which temperature T is imposed!* This is clearly wrong.

2.2 Ergodicity

Another condition that an MC simulation should obey is that it should be *ergodic*: any physically admissible configuration of the system should be reachable from any other configuration in a *finite* number of steps.

Ergodicity can be proven for some simple MC schemes, but these are not necessarily the most efficient ones. On the other hand, there are more efficient algorithms which have either not been proven to be ergodic or, even worse, have been shown to be explicitly *non-ergodic*. The solution to this dilemma is to mix a more efficient but possibly non-ergodic MC scheme with a less efficient but ergodic one. The resulting MC scheme will then, of course, as a whole be ergodic.

2.3 A basic MC simulation code

Now that we know the theoretical foundation of Metropolis MC (or, more generally, of Markov chain MC), let's have a look on how an MC simulation of a simple N -particle system is implemented in practice.

The general structure of a generic MC program is as follows.

- Note that we will discuss the individual steps in greater detail in subsequent sections.

To simplify the discussion, we imagine that we are simulating a system of N identical classical particles with energy $U(\mathbf{r}^N)$.

```

program monte carlo
{
  read in parameters;
  initialize system (or read in initial positions from file);
  perform  $N_{steps}$  Monte Carlo steps:
  {
    compute energy  $E_{old} = U(\mathbf{r}^N)$  of current configuration  $\mathbf{r}^N$ ;
    pick random vector  $\Delta$ ;
    pick random particle  $\mathbf{r}_{picked}$ ;
    displace  $\mathbf{r}'_{picked} := \mathbf{r}_{picked} + \Delta$ ;
    compute energy  $E_{new} = U(\mathbf{r}^{N'})$  of trial configuration  $\mathbf{r}^{N'}$ ;
  }
}

```

```

    accept trial configuration  $\mathbf{r}^{N'}$  with probability
       $p_{acc} = \min[1, \exp\{-\beta[E_{new} - E_{old}]]\}$ ;
    update averages;
  }
  compute and output averages;
}
```

2.3.1 For the curious: So why does it work?

So why does Markov MC work? Let us give a brief sketch of proof which, while being mathematically far from thorough, should provide a hint on why the MC recipe outlined above actually samples the target equilibrium distribution after discarding a initial equilibration period.

We shall consider the (for most practical purposes over-simplified) case of a finite state space with N states labeled $n = 1, \dots, N$ with transition probabilities $p_{nm} \equiv p(m \rightarrow n)$, such that a given probability distribution $p_n(t)$ evolves with time according to the master equation

$$\frac{df_n(t)}{dt} = \sum_m \left[\underbrace{p_{nm}f_m(t)}_{\text{gain}} - \underbrace{p_{mn}f_n(t)}_{\text{loss}} \right] \quad (2.41)$$

We are, of course, looking for a *stationary solution* $\frac{d\mathbf{f}^s(t)}{dt} = 0$ of this equation, which should then correspond to the sought-after equilibrium distribution. Again, such a stationary solution will only exist if global balance $0 \equiv \sum_m \left[p_{nm}^s f_m(t) - p_{mn}^s f_n(t) \right]$ holds.

Let us now introduce a more compact notation for the above master equation. We introduce the matrix \mathbf{P} of so-called *rate constants* defined by

$$P_{nm} \equiv \begin{cases} p_{nm}, & n \neq m \\ -\sum_{k \neq n} p_{kn}, & n = m \end{cases} \quad (2.42)$$

Then our master equation can be rewritten in the compact form

$$\frac{d\mathbf{f}(t)}{dt} = \mathbf{P} \cdot \mathbf{f}(t) \quad (2.43)$$

Moreover, a stationary distribution \mathbf{f}^s then must satisfy the relation $\mathbf{P} \cdot \mathbf{f}^s = \mathbf{0}$, i.e. it must be an *eigenvector of \mathbf{P} for eigenvalue $\lambda = 0$* .

Now note that \mathbf{P} is, of course, a real matrix, but generally *not* a symmetric one. Therefore, it has right and left eigenvectors ψ_α and ϕ_β , respectively, such that

$$\mathbf{P}\psi_\alpha = \lambda_\alpha\psi_\alpha, \quad \phi_\beta\mathbf{P} = \mu_\beta\phi_\beta \quad (2.44)$$

are different but their spectrum $\{\lambda_\alpha\} = \{\mu_\beta\}$ agrees.

- Of course, ϕ_α is formally a row vector, while ψ_α is a column vector. What is meant is that the relations

$$\mathbf{P}\psi_\alpha = \lambda_\alpha \psi_\alpha, \quad \mathbf{P}^t \phi_\beta^t = \mu_\beta \phi_\beta^t \quad (2.45)$$

hold.

In addition, orthogonality $\phi_\beta \cdot \psi_\alpha = \sum_i \phi_{\beta i} \psi_{\alpha i} \propto \delta_{\alpha\beta}$ of left and right eigenvectors to different eigenvalues $\lambda_\alpha \neq \lambda_\beta$ holds.

Let us expand $\mathbf{f}(t) = \sum_\alpha c_\alpha(t) \psi_\alpha$ in the left eigenbasis $\{\psi_\alpha\}$ of \mathbf{P} . If we insert this expansion into the master equation, then $\sum_\alpha \dot{c}_\alpha(t) \psi_\alpha \equiv \sum_\alpha c_\alpha(t) \underbrace{\mathbf{P} \cdot \psi_\alpha}_{\lambda_\alpha}$.

Using orthogonality (and ignoring the possibility of degenerate eigenvalues), it follows that $\dot{c}_\alpha(t) = \lambda_\alpha c_\alpha(t)$ for all α . These equations are solved as $c_\alpha(t) = c_\alpha(0)e^{t\lambda_\alpha}$, such that the time evolution of $bm\mathbf{f}(t)$ is given by

$$bm\mathbf{f}(t) = \sum_\alpha e^{\lambda_\alpha t} c_\alpha(0) \psi_\alpha \quad (2.46)$$

Observe now that from the definition of P_{ij} we see that the relation $\sum_i P_{ij} = 0$ holds for all j . We may interpret this relation by saying the the row vector $\phi_0 \equiv (1, 1, \dots, 1)$ is a *left* eigenvector $\phi_0 \cdot \mathbf{P} = 0$ for eigenvalue 0. Thus, there also exists *at least* one *right* eigenvector ψ_0 with $\mathbf{P} \cdot \psi_0 = 0$, and one shows that $\psi_0 \geq 0 \forall i$.

The central ingredient for understanding the convergence properties of the above time evolution of $\mathbf{f}(t)$ is now that one can also show that all eigenvalues λ_α are either real or come in complex conjugate pairs. In addition, all eigenvalues have *non-positive real parts* $\Re \lambda_\alpha \leq 0$. Therefore, we can write

$$\mathbf{f}(t) = c_0 \psi_0 + \sum_{\alpha \neq 0} \underbrace{e^{\Re \lambda_\alpha t}}_{(t \rightarrow \infty)_0} e^{i \Im \lambda_\alpha t} c_\alpha(0) \psi_\alpha \xrightarrow{(t \rightarrow \infty)} c_0 \psi_0 \quad (2.47)$$

It follows that all components other than ψ_0 decay exponentially. In addition, one can also show that all components $\psi_{0i} \geq 0$ are non-negative, such that it qualifies for a probability distribution upon normalizing by chppsing the factor $c_0 \equiv 1 / \sum_{i=1}^N \psi_{0i}$.

In summary, while not be 100% mathematically bullet-proof, the above reasoning should make it clear why indeed *any initial distribution \mathbf{f} will converge towards the stationary distribution $\mathbf{f}^s \equiv c_0 \psi_0$ with normalization $c_0 \equiv 1 / \sum_{i=1}^N \psi_{0i}$ provided the transition probabilities of out Markov chain have been properly set up as explained in the previous sections.*