

# Computational biophysics

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## Part I

# Computational Biophysics - Lattanzi

## 0.1 Questions Tuckerman

### 1. Chapter 1

- what is a phase space?
- write lagrangian
- what is the euler lagrange equation
- what is a lagandre transformation? what is an hamiltonian in that sense?
- explain H. equations of motion
- write derivative of H with respect to time
- what does the constant energy surface mean?
- How do you compute the work needed for the passage between a state to another?
- How does symmetries, implied by the Hamilton's conservation, are written? Poisson brackets
- What happens if a quantity included in a Poisson bracket is conserved over time? The poisson bracket becomes 0
- What happens if you translate all the coordinates of a system by a value  $a$ ? You generate the translation group, which is made of all the configurations that maintain the Hamiltonian
- What conservation law is associated to that invariance? Noether's theorem
- What does it mean that the Hamiltonian is incompressible? There will be no source of sinks or sources for the flow. This type of condition can be expressed as it is done in hydrodynamics. Given that a vector in the phase space is

$$x = (q_1, q_{3N} \dots p_1, p_{3N})$$

you can take the derivative which has the form

$$\eta(x) = \left( \frac{\partial H}{\partial p_1} \dots \frac{\partial H}{\partial p_{3N}}, \frac{\partial H}{\partial q_1} \dots \frac{\partial H}{\partial q_{3N}} \right)$$

The incompressibility condition means that

$$\Delta_x \dot{x}(x) = 0$$

- What is the symplectic property? Quantities like the Hamilton's equations can be written as follows:

$$\dot{x} = M \frac{\partial H}{\partial x},$$

where M is like

$$M = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix}$$

The symplectic property is written as follows:

$$M = J^T M J$$

where J indicates the Jacobian matrix values.

- What is a Fourier expansion? 1.8
- What are normal modes in a polymer? Each normal mode corresponds to a specific pattern of motion in which all parts of the system move sinusoidally with the same frequency. These modes are "normal" in the sense that they are independent of each other and form a complete set of orthogonal functions.
- What is an action integral? what does it mean if it is stationary? what it is possible to say about that path?
- what are holonomic and non holonomic constraints?
- what happens to the n of degrees of freedom?
- What are Lagrange multipliers? 1.10
- How could be the constraints expressed?
- what equations should be satisfied in a way that the constraints are followed in time?
- How can you write the hamilton's equations to follow all the conditions?
- Is the hamiltonian conserved when a series of time-independent holonomic constraints are applied?
- How are constraints inserted in a simulation? as forces
- How does the Velocity Verlet change? A new force term is added
- How are the Lagrange multipliers found in this case? You take the taylor expansion to the first derivative of the constraint formulaton given after a certain time  $\Delta t$ , then you apply one of the methods listed below
- Describe and list some of the methods used to produce the  $\tilde{\lambda}_k$  Lagrange multipliers
- What are non-Hamiltonian systems?
- What happens if the compressibility is negative to the phase space?
- 

## 2. Chapter 2

- Why it is impossible to classically solve the dynamics of a biological system? Sheer size and Loschmidt's paradox
- How are quantities computed in statistical mechanics?
- What is an ensemble?
- What is a thermodynamic system?
- What is a thermodynamic equilibrium?
- What are the fundamental thermodynamic parameters?
- What is an equation of state? for an ideal gas?
- What is a thermodynamic transformation
- What is a state function? "state function is any function  $f(n, P, V, T)$  whose change under any thermodynamic transformation depends only on the initial and final states of the transformation and not on the particular thermodynamic path taken" (Tuckerman, 2015)
- Write the work that you need to change the number of particles or the value of the volume

- What is the chemical potential?
- How do you write the heat needed to have a certain change in temperature?
- list the 3 thermodynamic laws
- talk about the first
- talk about the second
- talk about the third
- What is an ensemble? How do you calculate averages in an ensemble?
- What does the Liouville theorem say?
- Explain what is the ensemble distribution function
- In what conditions does it stay stationary?
- How can you write the calculation of a quantity if the dependence of the ensemble distribution function from time is 0?
- what is a partition function? how do you write it?

### 3. Chapter 3

- what is a microcanonical ensemble?
- how do you write the equation for entropy?
- what are the formula to obtain its components?
- what is the Boltzmann equation?
- what is a partition function? how do you write it?
- how does the correction work?
- how do you compute averages by using the partition function?
- what is the classical Virial theorem? proof
- describe thermal equilibrium finding the partition function and the entropy function. What happens at the end?
- write single free particle in ideal gas
- describe Gibbs paradox qualitatively, but write the classical entropy equation and the Sackur-Tetrode entropy equation
- How are positions set for a molecular dynamics simulation?
- How are velocities set?
- How is potential defined for a system? What is the name of a famous force field?

### 4. Chapter 4

- what are the fundamental properties of a canonical ensemble?
- what type of ensemble can be obtained from a canonical one?
- How can you obtain the Helmholtz free energy?
- how do you obtain the other not conserved macroquantities from the Helmholtz free energy?
- how do you obtain the canonical phase space distribution?

- Once you derived the canonical phase space distribution, how do you derive the canonical partition function?
- write the Boltzmann law
- write the formula for heat capacity
- Because of the fact that in a canonical ensemble there is not a conservation of energy, how can you quantify this difference? When is the canonical ensemble very similar to a microcanonical one?
- What type of observation you have to take into account to sample from a canonical ensemble? the fact that the temperature is conserved
- what type of thermostats we saw? describe all of them
- talk about the theorem (fluctuation and dissipation theorem) that is exploited in Langevin thermostats
- What are extended phase thermostats?
- what happens in a non-Hamiltonian system to the compressibility? What type of conservation you obtain involving the phase space?
- How can you generalize the Liouville equation? what type of microcanonical partition function do you obtain at the equilibrium, given that you recognize all the constraints of your system?
- What happens if you use this equation with the Nosé Hoover Hamiltonian? what kind of correction is needed?
- Explain principle behind Nosé-Hoover chains and write them. Do you obtain the correct canonical partition function by calculating the microcanonical partition function for that complex Hamiltonian?

## 5. Chapter 5

- How do you obtain the isenthalpic-isobaric ensemble?
- How do you obtain the isothermal-isenthalpic ensemble
- what are the energies associated?
- How do you obtain the two distribution functions?
- How does the isothermal-isobaric partition function relate to the canonical one?
- How does the Gibbs free energy relate to the isothermal-isobaric partition function?
- What is the Maxwell square?
- Tell about the Pressure virial theorem?
- Tell about the Work Virial theorem? What type of "degree of freedom" is added due to the variation in volume?
- Which method exploits the Work virial theorem to perform molecular dynamics simulations of the isobaric system?
- What is the Hamiltonian that is conserved by the Andersen's barostat? When it becomes the enthalpy of the system?
- Can you transform the Andersen's method in something that allows you to simulate isothermal-isobaric ensembles?

- talk about the MTK algorithm
- What kind of thermostat can be added to this barostat? how many Nosé-Hoover chains are produced for this scope?
- What is the langevin piston principle?
- Is the Langevin piston used in common simulations?

### 6. Chapter 6

- what is the euler's theorem? rewrite all the formulation for the energies of the various ensembles
- what is a grand canonical ensemble?
- what is the energy of a grand canonical ensemble?
- How do you compute the main quantities for a grand canonical simulation?
- explain how do you obtain the partition function and the phase space distribution function for the grand canonical ensemble
- What is the result for ideal gas?
- What is the value of the relative fluctuation  $\frac{\nabla N}{N}$ . When is the grand canonical ensemble similar to a canonical ensemble? when is the difference between these two ensembles negligible?

### 7. Chapter 7: Markov chains

- what is the starting principle? what can you obtain with a random process?
- what does the central limit theorem say?
- How do you sample a distribution by using random numbers?
- What happens if your variables if there are multiple components, which are independent from each other?
- what is the principle behind the importance sampling approach?
- what is the optimal value of  $h(x)$
- what allows you to do the  $M(RT)^2$ ?
- how do you write the detailed balance condition?
- how do you write the acceptance probability of an event  $x$  given  $y$ ?
- When do you accept moves that have a  $r$  value lower than 1?
- what happens to the probability associated to the coordinate in the phase space  $x$  with infinite number of trials?
- What is a good choice for the trial probability? what happens if the trial prob is symmetric to the Acceptance probability?
- how do you sample a canonical ensemble? how do you solve the problem that, if you move too much particles, you have a very intractably high difference in potential energy?
- How do you perform the sampling by moving a single particle at a time?
- what are the differences between MD and Monte Carlo?
- how do you sample a isothermal isobaric ensemble



- how do you sample a grand canonical ensemble?
- what is the purpose of hybrid monte carlo?
- How do you do hybrid Monte Carlo
- what type of attention you have to pay with the momenta?
- What is the replica exchange Monte Carlo process?
- How do you perform it?
- What is the purpose of the transition path integral?
- What kind of ensemble you can generate out of the possible paths going from a point A to a point B??
- What is a problem associated with the transition path integral? You have to know the path and you have to generate an initial configuration
- How can you solve the previous problem in the context of proteins?

# Chapter 1

## Canonical ensemble

### 1.1 Introduction

In the canonical ensemble energy can fluctuate and is not conserved, temperature is conserved. The system is put into contact with an heat reservoir, which it will exchange energy with the system maintaining constant the temperature.

### 1.2 Thermodynamics derivatives

In the canonical ensemble the thermodynamics parameters that are fixed are the number of particles, the volume and temperature. Everything will be expressed in term of these parameters. Entropy, the state function for the microcanonical ensemble, will not be useful, because it do not depend on the fixed variables. From the microcanonical ensemble and thermodynamics:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N,E} \quad -\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{V,E}$$

These thermodynamics derivatives can always be re conducted to the first law of thermodynamics, which in differential form is:

$$dE = TdS - PdV + \mu dN$$

Expressing  $S$  as a differential form the three previous derivatives are found. The temperature will be the derivative of the energy with respect to entropy:

$$T = \left( \frac{\partial E}{\partial S} \right)_{N,V} \quad -P = \left( \frac{\partial E}{\partial V} \right)_{N,S} \quad \mu = \left( \frac{\partial E}{\partial N} \right)_{V,S}$$

Pressure can be obtained as the derivative of the energy with respect to the volume, this works keeping fixed the number of particles and entropy. Keeping entropy fixed is complex on the experimental side. The chemical potential is the derivative of the energy with respect to the number of particles keeping fixed entropy and volume. The objective is to express everything in terms of number of particles, volume and temperature. Because temperature is the derivative of the energy with the respect of entropy, the energy should be expressed as a function of its derivative with respect to entropy.

### 1.2.1 Legendre transform of E

To do so energy is Legendre transformed. Recalling the formula for a Legendre transform:

$$\tilde{f}(s) = f(x(s)) - sx(s) \quad s = f'(x)$$

Applying this to energy:

$$\tilde{E}\left(N, V, \frac{\partial E}{\partial S}\right) = E\left(N, V, S\left(N, V, \frac{\partial E}{\partial S}\right)\right) - \left(\frac{\partial E}{\partial S}\right)_{N,V} S\left(N, V, \frac{\partial E}{\partial S}\right)$$

The Legendre transformed is called  $A$ , which will have the form:

$$A(N, V, T) = E(N, V, T) - TS(N, V, T)$$

### 1.2.2 The Helmholtz free energy

The function  $A$  is the Helmholtz free energy, the Legendre transform of Energy when it is expressed as a function of number of particles, volume and temperature. This is the state function of the canonical ensemble:

$$A(N, V, T) = E(N, V, T) - TS(N, V, T)$$

Computing the differential of  $A$ , its infinitesimal variation:

$$dA = dE - TdS - SdT = \underbrace{TdS - PdV + \mu dN - TdS - SdT}_{\text{first law of thermodynamics}}$$

So that:

$$dA = -SdT - PdV + \mu dN$$

Writing the thermodynamics derivatives with respect to this formula:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \quad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$$

So now the thermodynamics of the systems can be computed.

### 1.2.3 Thermal contact

To link the macroscopic quantities to the microscopic ones the distribution function has to be found. Looking at the canonical ensemble there is a thermal reservoir that surrounding the system, so much that the energy will remain constant. It can be assumed that the energy of system one is so small that  $E_2$  is much more than  $E_1$ . Assume that the system is in the microcanonical ensemble and that the two system exchange energies. The universe can be described with the microcanonical ensemble.

$$E = E_1 + E_2 \quad E_2 \gg E_1$$

$$N = N_1 + N_2 \quad N_2 \gg N_1$$

$$E = E_1 + E_2 \quad E_2 \gg E_1$$

$$\mathcal{H}(c) = \mathcal{H}(x_1) + \mathcal{H}(x_2)$$

The microcanonical partition function of the universe is:

$$\Omega(N, V, E) = M_N \int dx \delta(\mathcal{H}(x) - E) = M_N \int dx_1 dx_2 (\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)$$

The objective is to compute the distribution function for system 1. The energy can assume all values between 0 and total energy  $E$ , all with some probability. The objective is to find the function that represent the probability of system 1 to have energy  $E$ . To do that the distribution function of the system (the Dirac delta function) is used and all variables corresponding to system 2 needs to be integrated out.

### 1.2.3.1 Phase space distribution

Doing this the phase space distribution for system 1 is obtained, so the objective. So assume phase space distribution function  $f$  of the microcanonical ensemble, so the distribution function of the universe is considered and all the terms corresponding to system 2 are integrated out. It is better to consider the logarithm of  $f$ :

$$f(x_1) = \int dx_2 \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E) \quad \ln f(x_1) = \ln \int dx_2 \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)$$

Considering that  $E_1$  is very small when compared to  $E_2$ , so  $\mathcal{H}_1 \ll \mathcal{H}_2$ , so a Taylor expansion from  $\mathcal{H}_1(x_1) = 0$  can be performed, approximating the logarithm to the first order:

$$\ln f(x_1) \approx \ln \int dx_2 \delta(\mathcal{H}_2(x_2) - E) + \frac{\partial}{\partial \mathcal{H}_1(x_1)} \ln \int dx_2 \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E) |_{\mathcal{H}_1(x_1)=0} \mathcal{H}_1(x_1)$$

Considering the fact that the sum of the two Hamiltonian is equal to the energy the dependence of the delta function is linear with respect to the Hamiltonian and the Energy.

$$\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E = 0 \Rightarrow \frac{\partial}{\partial \mathcal{H}_1(x_1)} \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E) = -\frac{\partial}{\partial E} \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)$$

So the derivative with respect to  $\mathcal{H}$  can be substituted with  $-$  the derivative with respect to  $E$ :

$$\ln f(x_1) \approx \ln \int dx_2 \delta(\mathcal{H}_2(x_2) - E) - \frac{\partial}{\partial E} \ln \int dx_2 \delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E) |_{\mathcal{H}_1(x_1)=0} \mathcal{H}_1(x_1)$$

Considering  $\mathcal{H}_1(x_1) = 0$ :

$$\ln f(x_1) \approx \ln \int dx_2 \delta(\mathcal{H}_2(x_2) - E) - \frac{\partial}{\partial E} \ln \int dx_2 \delta(\mathcal{H}_2(x_2) - E) \mathcal{H}_1(x_1)$$

The first integral is  $\Omega$  depending on  $N_2$ ,  $V_2$  and  $E$ , so the formula for the microcanonical ensemble:

$$\int dx_2 \delta(\mathcal{H}_2(x_2) - E) \propto \Omega_2(N_2, V_2, E)$$

Or the number of micro states corresponding to those state variables not considering a normalization constant. Remembering that  $\Omega_2$  is related to the entropy and remembering that  $k$  is the Boltzmann constant:

$$\begin{aligned} \ln f(x_1) &\approx \ln \Omega_2(N_2, V_2, E) - \mathcal{H}_1(x_1) \frac{\partial}{\partial E} \ln \Omega_2(N_2, V_2, E) \\ &\approx \frac{S_2(N_2, V_2, E)}{k} - \frac{\mathcal{H}_1(x_1)}{k} \frac{\partial S_2(N_2, V_2, E)}{\partial E} \end{aligned}$$

Considering that the derivative of entropy with respect to energy is  $\frac{1}{T}$  and taking the exponential:

$$\ln f(x_1) \approx \frac{S_2(N_2, V_2, E)}{k} - \frac{\mathcal{H}_1(x_1)}{kT} \Rightarrow f(x_1) \propto e^{-\frac{\mathcal{H}_1(x_1)}{kT}}$$

So there is a given probability at which system 1 will assume a value  $\mathcal{H}_1(x_1)$ . Omitting subscript 1:

$$f(x) \propto e^{-\beta \mathcal{H}(x)} \quad \beta = \frac{1}{kT}$$

This is the probability distribution function for the canonical ensemble, where  $\beta$  is the Boltzmann factor. Normalizing the probability distribution:

$$\int dx f(x) = 1 \Rightarrow f(x) = \frac{e^{-\beta \mathcal{H}(x)}}{N! h^{3N} Q(N, V, T)}$$

Where  $Q$  is the partition function:

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int dx e^{-\beta \mathcal{H}(x)}$$

### 1.3 From micro to macro

Notice that:

$$A = E - TS = E + T \left( \frac{\partial A}{\partial T} \right)_{N, V} = E - \beta \left( \frac{\partial A}{\partial \beta} \right)_{N, V}$$

However, energy varies in the canonical ensemble and the Hamiltonian assume values from the Boltzmann distribution, so to find a measurable value of the energy an average over the ensemble has to be found, so energy is the average value of the Hamiltonian over the canonical ensemble:

$$E = \langle \mathcal{H} \rangle = \frac{1}{N! h^{3N}} \frac{\int dx \mathcal{H}(x) e^{-\beta \mathcal{H}(x)}}{\int dx e^{-\beta \mathcal{H}(x)}} = - \frac{1}{Q(N, V, \beta)} \frac{\partial Q(N, V, \beta)}{\partial \beta} = - \frac{\partial \ln Q(N, V, \beta)}{\partial \beta}$$

Hence the function of  $A$  and its solution are:

$$A + \frac{\partial \ln Q}{\partial \beta} + \beta \frac{\partial A}{\partial \beta} = 0 \Rightarrow \ln Q(N, V, \beta) = -\beta A(N, V, \beta)$$

So the relationship between the Helmholtz free energy and the partition function is:

$$A(N, V, T) = -kT \ln Q(N, V, T)$$

Now when dealing with the canonical ensemble the partition function has to be found and once that is computed the Helmholtz free energy can be computed.

### 1.3.1 Energy and temperature

The energy can be obtained by performing an average in the canonical ensemble:

$$E = \langle \mathcal{H}(x) \rangle = \frac{C_N \int dx \mathcal{H}(x) e^{-\beta \mathcal{H}(x)}}{C_N \int dx e^{-\beta \mathcal{H}(x)}} = \frac{1}{Q} \frac{\partial Q}{\partial \beta} \quad C_N = \frac{1}{N! h^{3N}}$$

Where  $\mathcal{H}(x)$  is the energy estimator. Taking the average of the Hamiltonian the energy is obtained. Also an estimator of temperature can be obtained, and this will be related to the kinetic energy by applying the equipartition theorem:

$$\left\langle \sum_i \frac{\vec{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} NkT \Rightarrow T = \frac{2}{3Nk} \left\langle \sum_i \frac{\vec{p}_i^2}{2m_i} \right\rangle = \frac{1}{3Nk} \left\langle \sum_i \frac{\vec{p}_i^2}{m_i} \right\rangle = \langle \mathcal{T}(x) \rangle$$

So  $\mathcal{T}(x)$  is the temperature estimator, so that temperature is the average of the estimator:

$$\mathcal{T}(x) = \frac{1}{3Nk} \sum_i \frac{\vec{p}_i^2}{m_i} \quad T = \langle \mathcal{T}(x) \rangle = \frac{C_N \int dx \mathcal{T}(x) e^{-\beta \mathcal{H}(x)}}{C_N \int dx e^{-\beta \mathcal{H}(x)}}$$

#### 1.3.1.1 Energy fluctuations

Energy will be fluctuating, so computing the energy fluctuations, which are defined as:

$$\Delta E = \sqrt{\langle (\mathcal{H}(x) - \langle \mathcal{H}(x) \rangle)^2 \rangle} \quad \langle (\mathcal{H}(x) - \langle \mathcal{H}(x) \rangle)^2 \rangle = \langle \mathcal{H}^2(x) \rangle - \langle \mathcal{H}(x) \rangle^2$$

Now, computing:

$$\langle \mathcal{H}^2(x) \rangle = \frac{C_N \int dx \mathcal{H}^2(x) e^{-\beta \mathcal{H}(x)}}{C_N \int dx e^{-\beta \mathcal{H}(x)}} = \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} \quad \langle \mathcal{H}(x) \rangle^2 = \left[ \frac{C_N \int dx \mathcal{H}(x) e^{-\beta \mathcal{H}(x)}}{C_N \int dx e^{-\beta \mathcal{H}(x)}} \right]^2 = \left[ \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right]^2$$

Computing the second derivative of the logarithm of  $Q$  with respect to  $\beta$ :

$$\frac{\partial^2 \ln Q}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left[ \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right] = -\frac{1}{Q^2} \left[ \frac{\partial Q}{\partial \beta} \right]^2 + \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} = \langle \mathcal{H}^2(x) \rangle - \langle \mathcal{H}(x) \rangle^2 = \Delta E^2$$

So the fluctuation squared and considering that  $\frac{\partial \ln Q}{\partial \beta} = -E$ :

$$\Delta E^2 = \frac{\partial^2 \ln Q}{\partial \beta^2} = -\frac{\partial E}{\partial \beta} = -\left( \frac{\partial E}{\partial T} \right) \frac{\partial T}{\partial \beta} = kT^2 \frac{\partial E}{\partial T} = kT^2 C_V$$

Where  $C_V$  is the specific heat of the system. Comparing the fluctuation of the energy with the energy to see if they are negligible or big. Considering that  $C_V$  and  $E$  increase linearly with the number of particles:

$$\frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{E} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

So if  $N$  is small the factor is not negligible, and becomes more negligible as it increases. So when working with a thermodynamics system the fluctuation with respect to energy are negligible. So in the thermodynamics limit the energy fluctuations in the canonical ensemble are negligible. The difference between the microcanonical and canonical ensemble is that the energy is fixed only in the first, but in the second the fluctuation of the energy is negligible, so that from a practical point of view all the results from the two ensembles are equivalent.

### 1.3.2 Pressure estimator

Considering pressure:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = kT \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{kT}{Q} \left(\frac{\partial Q}{\partial V}\right)_{N,T}$$

The objective is to look on the dependence of the partition function on volume and not considering normalization constant:

$$\frac{1}{Q} \left(\frac{\partial Q}{\partial V}\right)_{N,T} = \frac{1}{\int d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N e^{-\beta \mathcal{H}(\vec{r}, \vec{p})}} \frac{\partial}{\partial V} \int d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N e^{-\beta \mathcal{H}(\vec{r}, \vec{p})}$$

Considering the Hamiltonian it will have the kinetic and potential energy part. The kinetic part will always be the same and do not depend on the volume and it will be integrated out, this is called configuration partition function, so the integral can be written only over the coordinates and only the potential energy.

$$\frac{1}{Q} \left(\frac{\partial Q}{\partial V}\right)_{N,T} = \frac{1}{\int d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N e^{-\beta U(\vec{r})}} \frac{\partial}{\partial V} \int d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N e^{-\beta U(\vec{r})} = \frac{1}{Z} \frac{\partial Z}{\partial V}$$

Where  $Z$  is the configuration partition function:

$$P = \frac{kT}{Z} \frac{\partial Z}{\partial V} \quad Z(N, V, T) = \int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta U(\vec{r})}$$

Now considering  $Z$  it is an integral over all the coordinates and  $U$  is the force fields. The problem is that the integral depends on volume through its limits, in order to do that all the possible dependencies on the integral on the volume. The best thing to do is to consider dimensionless coordinates. Changing coordinates and considering a cubic box, the coordinates are scaled into  $\vec{s}_i$ , where  $L$  is the side of the cube and considering there are  $3N$  coordinates:

$$\vec{s}_i = \frac{1}{L} \vec{r}_i = V^{-\frac{1}{3}} \vec{r}_i \Rightarrow d\vec{r}_1 = V^{\frac{1}{3}} d\vec{s}_i \quad Z(N, V, T) = \int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta U(\vec{r})} = V^N \int d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U(V^{\frac{1}{3}} \vec{s})}$$

In this way the dependence on volume has been highlighted and the derivative of  $Z$  with respect to volume can be taken:

$$\begin{aligned}
 \frac{\partial Z(N, V, T)}{\partial V} &= \frac{N}{V} V^N \int d\vec{s}_1 \cdots d\vec{s}_N e^{-\beta U(V^{\frac{1}{3}} \vec{s})} + V^N \int d\vec{s}_1 \cdots d\vec{s}_N e^{-\beta U(V^{\frac{1}{3}} \vec{s})} \sum_{i=1}^N \left( -\beta \frac{\partial U}{\partial V^{\frac{1}{3}} \vec{s}_i} \right) \left( \frac{1}{3} V^{-\frac{2}{3}} \vec{s}_i \right) = \\
 &= \frac{N}{V} Z - \frac{\beta}{3V} \int d\vec{r}_1 \cdots d\vec{r}_N e^{-\beta U(\vec{r})} \sum_{i=1}^N \frac{\partial U}{\partial \vec{r}_i} = \\
 &= \frac{N}{V} Z + \frac{\beta}{3V} \int d\vec{r}_1 \cdots d\vec{r}_N e^{-\beta U(\vec{r})} \sum_{i=1}^N \vec{F}_i \cdot \vec{r}_i
 \end{aligned}$$

Reconsidering now the formula for pressure and considering  $kT\beta = 1$ :

$$P = \frac{kT}{Z} \frac{\partial Z}{\partial V} = \frac{NkT}{V} + \frac{1}{3VZ} \int d\vec{r}_1 \cdots d\vec{r}_N e^{-\beta U(\vec{r})} \sum_{i=1}^N \vec{F}_i \cdot \vec{r}_i = \frac{NkT}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^N \vec{F}_i \cdot \vec{r}_i \right\rangle$$

This formula makes sense as when considering ideal gas there are no internal forces, so they are all equal to 0, obtaining the ideal gas law. So the second part contains the correction that considers these internal forces. Considering that temperature can be expressed as an average:

$$T = \frac{1}{3Nk} \left\langle \sum_i \frac{\vec{p}_i^2}{m_i} \right\rangle \Rightarrow P = \frac{1}{3V} \left\langle \sum_i \frac{\vec{p}_i^2}{m_i} \right\rangle + \frac{1}{3V} \left\langle \sum_{i=1}^N \vec{F}_i \cdot \vec{r}_i \right\rangle$$

Now, recollecting everything into one single formula:

$$P = \frac{1}{3V} \left\langle \sum_i \left[ \frac{\vec{p}_i^2}{m_i} + \vec{F}_i \cdot \vec{r}_i \right] \right\rangle = \langle \mathcal{P}(\vec{r}, \vec{p}) \rangle$$

So the pressure estimator is:

$$\mathcal{P}(\vec{r}, \vec{p}) = \frac{1}{3V} \sum_i \left[ \frac{\vec{p}_i^2}{m_i} + \vec{F}_i \cdot \vec{r}_i \right]$$

## 1.4 Entropy in a canonical system with respect to microcanonical one

The formula for the entropy in the canonical system is written as follows:

$$S = -k_B \langle \ln P_r \rangle = -k_B \int P_r \ln P_r d\omega$$

Notice that, if the energies are all equal, then also the probabilities are the same and can be written as follows

$$S = -k_B \sum_{r=1}^{\Omega} \frac{1}{\Omega} \ln \left( \frac{1}{\Omega} \right) = k \ln \Omega$$

Which is exactly the form for the entropy in the microcanonical system.



You can find a very telling formula with the following passages:

$$\begin{aligned}
S &= -k_B \int P_r \ln P_r d\omega \\
&= -k_B \int P_r (-\beta H - \ln Z) d\omega \\
&= k_B (\beta \langle H \rangle + \ln Z) \\
S &= \frac{1}{T} U + k_B \ln Z
\end{aligned}$$

You can then play with the  $\ln Z$

$$\begin{aligned}
\frac{\partial}{\partial \beta} (\ln Z) &= \frac{1}{Z} \frac{\partial Z}{\partial \beta} \\
&= \frac{1}{Z} \int \frac{\partial}{\partial \beta} (\exp(-\beta H)) d\omega \\
&= 1/Z \int -H \exp(-\beta H) d\omega \\
&= -\langle H \rangle = -U
\end{aligned}$$

Therefore  $U = -\frac{\partial}{\partial \beta} (\ln Z)$  and

$$S = k_B T \frac{\partial}{\partial T} \ln Z + k_B \ln Z = k_B \frac{\partial}{\partial T} (T \ln Z)$$

From here, you can observe that

$$A = -k_B T \ln Z$$

### 1.4.1 Canonical systems

**particles with a radius and interacting between themselves and with the wall**

L (Lagrangian)

$$L = \sum_i \frac{1}{2} m \dot{\vec{r}}_i^2 - \left( \sum_{i < j} u(r_{ij}) + \left[ \sum_{i\alpha} u_{wall}(z_{i\alpha}) + u_{wall}(L - z_{i\alpha}) \right] \right)$$

## 1.5 Cartesian to polar coordinates momentum

Certainly! Let's derive the differential volume element in momentum space,  $d^3p$ , using spherical coordinates step by step.

Step 1: Cartesian to Spherical Coordinates In Cartesian coordinates, the momentum vector  $\vec{p}$  is given by components  $p_x$ ,  $p_y$ , and  $p_z$ . In spherical coordinates, this same vector is represented by  $p$ ,  $\theta$ , and  $\phi$ , where: -  $p$  is the magnitude of the momentum vector. -  $\theta$  is the polar angle, measured from the  $z$ -axis. -  $\phi$  is the azimuthal angle, measured in the  $xy$ -plane from the  $x$ -axis.

The relationships between Cartesian and spherical coordinates are: -  $p_x = p \sin \theta \cos \phi$  -  $p_y = p \sin \theta \sin \phi$  -  $p_z = p \cos \theta$

Step 2: Differential Volume Element in Cartesian Coordinates In Cartesian coordinates, the differential volume element is:

$$d^3p = dp_x dp_y dp_z$$

Step 3: Transforming the Differential Volume Element We need to transform  $dp_x dp_y dp_z$  into spherical coordinates  $p, \theta, \phi$ . This transformation requires the Jacobian determinant of the transformation from  $(p_x, p_y, p_z)$  to  $(p, \theta, \phi)$ .

The Jacobian matrix  $J$  for the transformation is:

$$J = \begin{pmatrix} \frac{\partial p_x}{\partial p} & \frac{\partial p_x}{\partial \theta} & \frac{\partial p_x}{\partial \phi} \\ \frac{\partial p_y}{\partial p} & \frac{\partial p_y}{\partial \theta} & \frac{\partial p_y}{\partial \phi} \\ \frac{\partial p_z}{\partial p} & \frac{\partial p_z}{\partial \theta} & \frac{\partial p_z}{\partial \phi} \end{pmatrix}$$

Calculating the partial derivatives:

$$\frac{\partial p_x}{\partial p} = \sin \theta \cos \phi$$

$$\frac{\partial p_x}{\partial \theta} = p \cos \theta \cos \phi$$

$$\frac{\partial p_x}{\partial \phi} = -p \sin \theta \sin \phi$$

$$\frac{\partial p_y}{\partial p} = \sin \theta \sin \phi$$

$$\frac{\partial p_y}{\partial \theta} = p \cos \theta \sin \phi$$

$$\frac{\partial p_y}{\partial \phi} = p \sin \theta \cos \phi$$

$$\frac{\partial p_z}{\partial p} = \cos \theta$$

$$\frac{\partial p_z}{\partial \theta} = -p \sin \theta$$

$$\frac{\partial p_z}{\partial \phi} = 0$$

Thus, the Jacobian matrix  $J$  is:

$$J = \begin{pmatrix} \sin \theta \cos \phi & p \cos \theta \cos \phi & -p \sin \theta \sin \phi \\ \sin \theta \sin \phi & p \cos \theta \sin \phi & p \sin \theta \cos \phi \\ \cos \theta & -p \sin \theta & 0 \end{pmatrix}$$

Step 4: Determinant of the Jacobian Matrix The volume element  $d^3p$  in spherical coordinates is given by the absolute value of the determinant of  $J$ :

$$|\det(J)| dp d\theta d\phi$$

Calculating the determinant of  $J$ :

$$\begin{aligned}
\frac{\partial(x, y, z)}{\partial(p, \theta, \phi)} &= \begin{vmatrix} \sin \theta \cos \phi & p \cos \theta \cos \phi & -p \sin \theta \sin \phi \\ \sin \theta \sin \phi & p \cos \theta \sin \phi & p \sin \theta \cos \phi \\ \cos \theta & -p \sin \theta & 0 \end{vmatrix} \\
&= \sin \theta \cos \phi (p \cos \theta \sin \phi \cdot 0 - p \sin \theta \cos \phi \cdot (-p \sin \theta)) \\
&\quad - p \cos \theta \cos \phi (\sin \theta \sin \phi \cdot 0 - p \sin \theta \cos \phi \cdot \cos \theta) \\
&\quad - p \sin \theta \sin \phi (\sin \theta \sin \phi \cdot (-p \sin \theta) - p \cos \theta \sin \phi \cdot \cos \theta) \\
&= \sin \theta \cos \phi (p^2 \sin^2 \theta \cos \phi) \\
&\quad - p \cos \theta \cos \phi (-p \sin \theta \cos \theta \cos \phi) \\
&\quad - p \sin \theta \sin \phi (-p \sin^2 \theta \sin \phi - p \cos^2 \theta \sin \phi) \\
&= p^2 \sin^3 \theta \cos^2 \phi + p^2 \cos^2 \theta \sin \theta \cos^2 \phi + p^2 \sin \theta (\sin^2 \theta + \cos^2 \theta) \sin^2 \phi \\
&= p^2 \sin \theta (\sin^2 \theta \cos^2 \phi + \cos^2 \theta \cos^2 \phi + \sin^2 \phi) \\
&= p^2 \sin \theta (\cos^2 \phi (\sin^2 \theta + \cos^2 \theta) + \sin^2 \phi) \\
&= p^2 \sin \theta (\cos^2 \phi + \sin^2 \phi) \\
&= p^2 \sin \theta \cdot 1 \\
&= p^2 \sin \theta.
\end{aligned}$$

Thus, the volume element in spherical coordinates is:

$$d^3p = p^2 \sin \theta dp d\theta d\phi$$

Given this result, you can also derive the volume of a spherical shell using spherical coordinates. To find the volume of a thin spherical shell of radius  $p$  and thickness  $dp$ :

- **Integration Over Angles:** Integrate over all angles  $\theta$  and  $\phi$ :

$$\text{Volume of shell} = \int_0^{2\pi} \int_0^\pi p^2 \sin \theta dp d\theta d\phi$$

Here,  $dp$  is the thickness of the shell and is fixed in the shell volume computation.

- **Evaluate the Angular Integrals:**

$$\begin{aligned}
\int_0^{2\pi} d\phi &= 2\pi \\
\int_0^\pi \sin \theta d\theta &= -\cos \theta \Big|_0^\pi = 2
\end{aligned}$$

- **Combine the Results:**

$$\text{Volume of shell} = p^2 \left( \int_0^\pi \sin \theta d\theta \right) \left( \int_0^{2\pi} d\phi \right) dp$$

$$\text{Volume of shell} = p^2 \cdot 2 \cdot 2\pi \cdot dp$$

$$\text{Volume of shell} = 4\pi p^2 dp$$

So, indeed, using spherical coordinates and integrating over all angles confirms that the volume of a thin spherical shell of radius  $p$  and thickness  $dp$  is  $4\pi p^2 dp$ , aligning with the result obtained from the volume difference method.

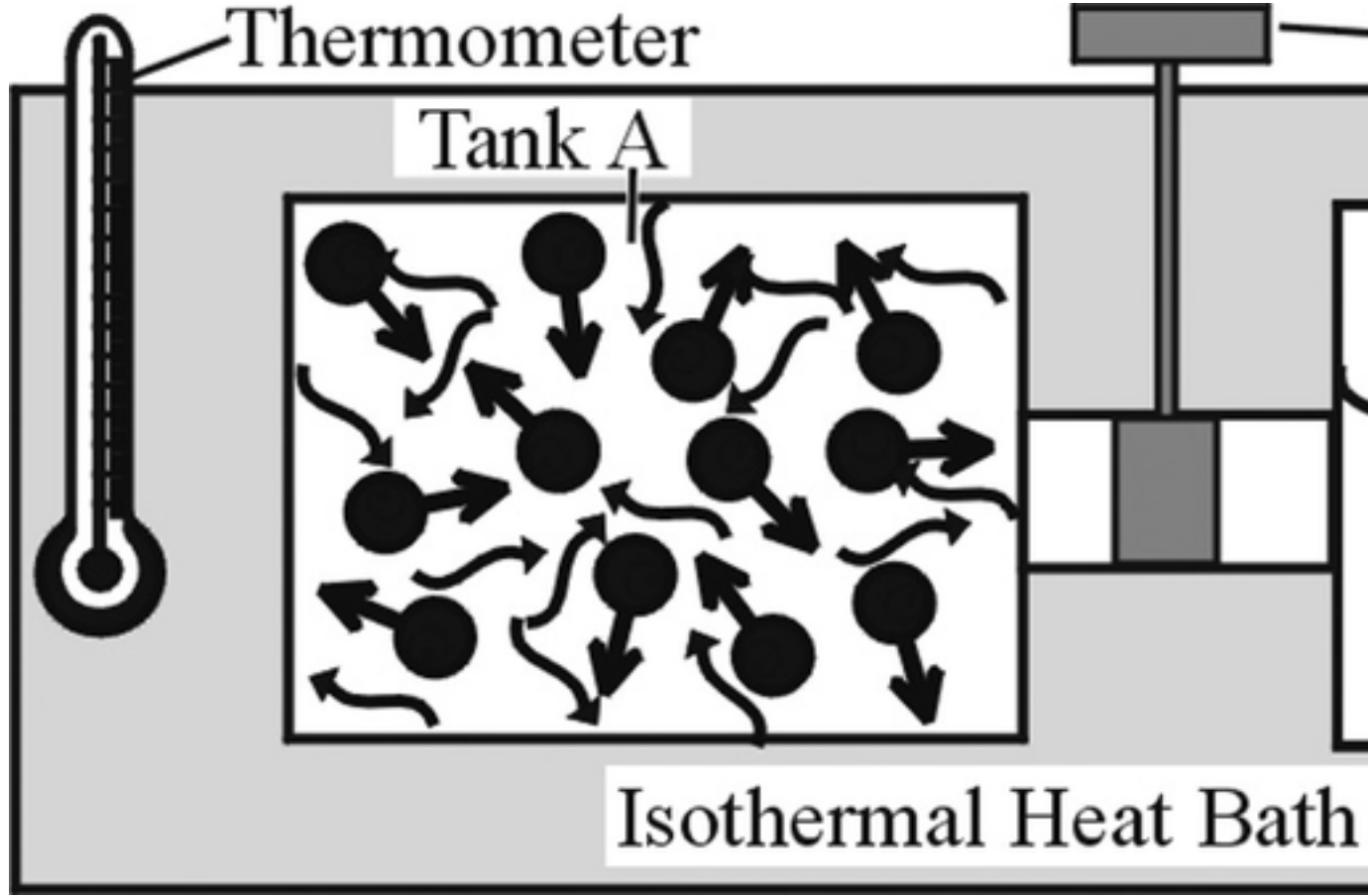


Figure 1.1: Joule experiment

## 1.6 The Joule and Joule-Thomson Experiments

Given that the change of energy in an adiabatic system can be written as

$$\begin{aligned} dU &= \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \\ &= \left( \frac{\partial U}{\partial V} \right)_T dV + C_V dT \end{aligned}$$

Considering that

$$dU = dQ + dW = C_P dT - P dV$$

Than we have that

$$\begin{aligned}C_P dT - P dV &= \left( \frac{\partial U}{\partial V} \right)_T dV + C_V dT \\C_P - P \left( \frac{dV}{dT} \right)_P &= \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + C_V \\C_P - C_V &= \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P\end{aligned}$$

It is possible to demonstrate that

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

Therefore

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \tag{1.1}$$

## Part II

# Multi-Scale methods in soft matter physics - Potestio

## 1.7 Questions related to the course of Multiscale Methods for Soft matter Physics

All in notes if not specified

Legend:

- tuckerman: Tuckerman book
- not notes
- demonstrate: make the demonstration
- LJ: Lennard-Jones potential

Lessons questions

- Lesson 1
  1. What is soft matter?
  2. Is active moving matter soft material?
  3. What is the definition of soft matter?: Soft matter or soft condensed matter is a subfield of condensed matter comprising a variety of physical systems that are deformed or structurally altered by thermal or mechanical stress of the magnitude of thermal fluctuations.
  4. What does it mean to define soft matter as mesoscopic? what are the consequences?
  5. How should be defined the bigger compounds? what happens to time and space scale when those are utilized?
  6. Will have the force to be specific?
  7. What is the approximation that allow to simplify quantum mechanical problems with classical mechanics?
  8. How are thermal systems driven?
  9. What is the Helmholtz free energy? Which system is described? How is it obtained? (Tuckerman): The Helmholtz free energy, often denoted by  $A$ , is a thermodynamic potential that describes the amount of energy available to do useful work in a system at constant temperature and volume. It is obtained with the formula  $F = U - TS$ , where  $U$  is the potential energy,  $T$  is the temperature and  $S$  is the entropy.
  10. What is the critical point? (See tuckerman) What happens?
  11. What is the Ising model? How can you describe with it the critical point?
  12. What is necessary to make Multiscale methods relevant? (hierarchy) The use of a mapping function
  13. What procedure allows the coarse-graining?
- Lesson 2
  1. Where are defined experimental observations? In a Universe
  2. What is the Newton principle of determinacy
  3. What elements are defined in your experimental space?
  4. What is Galilean invariance? In which conditions it is maintained?
  5. What is a model? and what allows to build? A definition of a system
  6. Is invariance maintained in case of isolated systems? and in the case of systems with several bodies?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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7. When are forces conservative? In physics, a force is considered conservative if the work done by the force on an object is independent of the path taken by the object. In other words, the total mechanical energy of the system (kinetic energy plus potential energy) remains constant as the object moves within the force field.
  8. What is the action integral? What does it tell? What does satisfy a path called stationary? (demonstrate) (tuckerman)
  9. What does the action integral concept suggest? (tuckerman)
  10. Write Euler lagrange equation
  11. What is the formula of the Lagrangian?
  12. What is the Legendre transformation (tuckerman)
  13. What is the Hamiltonian? how is it obtained? (tuckerman)
  14. Which are the Hamilton equations?
  15. What happens to the Hamiltonian when the Lagrangian is conserved?
  16. What is an ensemble? In classical statistical mechanics, the ensemble is a probability distribution over phase points (as opposed to a single phase point in ordinary mechanics), usually represented as a distribution in a phase space with canonical coordinate axes.
  17. How is the value of a macroscopic observable normally obtained? (through a time average ...)
  18. To what a time average can be converted? what is a phase space average?
  19. When is a stochastic process called ergodic? relating to or denoting systems or processes with the property that, given sufficient time, they include or impinge on all points in a given space and can be represented statistically by a reasonably large selection of points
  20. How do we obtain a microcanonical ensemble?  $N, V, E$
  21. What are Poisson brackets? When is a quantity conserved? (tuckerman)
  22. What does the Liouville theorem say? It says that as the systems contained in a tiny region of phase space evolve according to classical mechanics, the volume they occupy remains constant.
  23. When is the average of a quantity constant in time?
  24. How can you write the average of that quantity in a microcanonical ensemble?
  25. What is a partition function? what type of coefficient it has? (case of microcanonical ensemble)
  26. Formula for entropy in the microcanonical ensemble
- Lesson 3
    1. Describe the canonical partition function, what is the related coefficient?
    2. What is a Boltzmann weight? it is the probability of a certain configuration, the lower is the energy associated to the configuration, the higher is the Boltzmann weight and viceversa
    3. What type of ansatz you assume to simplify your work? What is the adiabatic approximation
    4. Describe the Born-Oppenheimer approximation
    5. What is meant by separability when talking about the potential energy? and additivity?
    6. What is a multi-body potential? What type of truncation you can perform?
    7. What are the differences between VdW and Coulomb interactions?
    8. What is the difference between bonded and non-bonded interactions?
  - Lesson 4: calculation of interactions
    1. How can be non bounded interactions truncated?



## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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2. What is a periodic boundary condition? A periodic boundary is an important technique in a molecular dynamics simulation. It is a clever trick to make a simulation that consists of only a few hundred atoms behave as if it was infinite in size.
  3. Why should you use periodic boundary conditions
  4. How do you write the energy due to cut-off short distance interactions, what's the tail correction?
  5. In which case you can't absolutely ignore the epsilon tail energy?
  6. What is the typical length for the cut-off distance?
  7. what is the difference between LJ and VdW?
  8. How do you compute the Coulombic and LJ interactions?
  9. How are interactions classified as short and long?
  10. Write formula for short potential and long range potential (consider PBC)
  11. What is the minimum image convention?
  12. What is the Verlet list algorithm
  13. How do you avoid bumps in short potential? You add a correction switching function to be multiplied to the short range potentials.
  14. How do you calculate long range potential?
  15. What is an integrator? How does it use time?
  16. Write Euler integrator
  17. What is the problem with the Euler integrator?
  18. What is the Euler-Cromer integrator?
  19. What is the mathematical difference between the two previous integrators?
  20. What is the meaning of symplectic?
  21. What is a unitary matrix what is the case for the Euler-Cromer integrator?
- Lesson 5
    1. How do you express the average of a quantity in equilibrium? Introduce the Liouville operator
    2. How can you decompose the Liouville operator? What changes do the parts produce?
    3. What problem do you face by doing that separation? what expansion comes into play? The trotter expansion
    4. Write the Velocity Verlet algorithm, do the evolutions remind you of something?
    5. What is conserved by applying the Velocity Verlet algo?
    6. How is different the shadow H with respect to the real Hamiltonian?
    7. How would you call then the Velocity Verlet algo?
    8. \_\_\_\_\_
    9. How can you transform a time evolution? and in which condition?
    10. How do time dependent correlation functions behave in time? Write the formula
    11. How would you find in general a quantity A? But what's the problem with the integration process?
    12. What's the idea behind stochastic integration? You take the values associated to a series of random inputs. Afterwards you take the average
    13. How do you write an integration performed by using a uniform distribution?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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14. What's the limit of stochastic sampling? What is the Bulk problem? (topic included also in the next lecture)
- Lesson 6: Markov chains
    1. What happens when you sample with more and more dimensions?
    2. How can you improve the sampling process?
    3. What is the objective of Markov chains?
    4. On which configuration Markov chain structures depend upon?
    5. What the transition probability matrix? how transitions are formalized?
    6. What is the definition of ergodic (ergodicity expresses the idea that a point of a moving system, either a dynamical system or a stochastic process, will eventually visit all parts of the space that the system moves in, in a uniform and random sense. This implies that the average behavior of the system can be deduced from the trajectory of a "typical" point. Equivalently, a sufficiently large collection of random samples from a process can represent the average statistical properties of the entire process.)
    7. What is therefore the density function obtained with a time going to infinity consequently, given that the ergodic hypothesis is true
    8. What does the Frobenius theorem say? In the
    9. What is the behavior of the eigenvectors of a transition matrix over time? What is the detailed balance?
    10. How are computed the elements in the transition matrix?
    11. Write general formulation of the Metropolis
    12. Write the Metropolis algorithm using the Boltzmann equation for the distribution
    13. What can you calculate at the end
    14. What if a transition is rejected?
    15. What is a sweep? When is an operation of order  $n$ ? (make use of the example with the spins)
    16. When do you prefer to use Markov chains? instead of Molecular Dynamics?
    17. What is the difference between Markov chains and Molecular Dynamics?
  - Lesson 7: Brownian motion
    1. What is the Brownian motion? What does it represents?
    2. In which relation are the short atomistic time scales, the relaxation times of the colloids and the diffusion time?
    3. What steps would you like to follow to proceed with the coarse graining?
    4. what is the markov property? and how do you use it in this context?
    5. What is the Smoluchovski equation?
    6. How do you write the infinitesimal change of  $f$  in time? What equation does it reminds?
    7. What is the time derivative of  $f$ ? (Fokker Plank equation )
    8. How are newtonian systems positions related to the time of simulation
    9. How Diffusion dynamics is different? What is the general solution?
    10. Make an example of solving equation of dynamics for diffusion
  - Lesson 8A: the Fluctuation-Dissipation theorem

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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1. What case we considered up to now? Why it is not possible to use the Hamiltonian formulation in biological systems?
  2. Is a normal system (like a biological solution) Hamiltonian? No, because of the friction energy that is dissipated
  3. what is gamma in the Force of friction  $\vec{F}_{\text{friction}} = -\gamma\vec{v}$ : the  $\gamma$  factor is equal to  $\gamma = 6\pi\nu a$ , where  $a$  is the diameter of the bead, and  $\nu$  is the viscosity of the medium.
  4. Describe the forces in that system, average? correlation?
  5. What is  $\tau$ ?
  6. Find the diffusion formula?
  7. What is the Langevin equation? The Langevin equation is a stochastic differential equation that describes the motion of a particle undergoing Brownian motion in a fluid or a similar random environment.
  8. What is the equipartition theorem?
  9. How do you find the amplitude of correlation  $g$ ?
  10. What does the Fluctuation-Dissipation theorem say? What are the important points? What thermostat uses it? (langevin)  $\rightarrow$  It correlates the random forces and the capacity of diffusion.
  11. What is a Langevin thermostat? A Langevin thermostat is a mathematical and computational tool used in molecular dynamics simulations to mimic the effects of a thermal reservoir on a simulated system. It is commonly employed to maintain a desired temperature in the simulation by introducing a stochastic (random) force that mimics the collisions of the particles with the surrounding solvent or thermal bath.
- Lesson 8B: The radial distribution function
    1. What is a partition function
    2. Write in two different forms the one for the canonical ensemble
    3. How can you simplify the calculation of the average of a quantity  $\langle A \rangle$ ?
    4. How do you obtain the correlation function?
    5. How do you obtain the partition function?
    6. How is the radial function for a non-interacting system (ideal gas)?
    7. How is the radial function taking into consideration just a single particle
    8. How is the radial function taking into consideration just two particles, what assumptions do you make?
    9. How are the partition function and the density function related?
    10. What is the radial distribution function final formula?
    11. How is the graph of that distribution? why are there bumps?
    12. What type of reduction did you obtain by introducing the radial distribution function?
    13. How can you calculate energy, pressure on the base of that?
  - Lesson 9: Free Energy calculation
    1. which is the partition function of the canonical ensemble
    2. How is it calculated in case of ideal gas?
    3. write the Helmholtz free energy formula
    4. With what type of integral you can rewrite the difference formula. How can you write it if you assume that just the potential can change in value?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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5. Write consequently the Kirkwood Thermodynamical Integration theorem
  6. What does the Kirkwood Thermodynamical Integration theorem allows you to do? To calculate differences in free energies
  7. Obtain  $P_0(v)$ , which is the probability associated to a certain value of energy, which shape does it have?
  8. Supposing the Gaussian shape, what's the inequality that you obtain?? What is the gibbs Bogoliubov inequality?
  9. What does the calculation of the free energy difference allows you to do
  10. How can you simplify the calculation? make the example regarding the solvated ion
  11. What is a reaction coordinate
  12. Make the example taking the distance as collective coordinate
- Lesson 10: Renormalisation group
    1. what is a renormalization group in biophysics and why it is called a group? In biophysics, as in other fields of physics, the renormalization group (RG) is a theoretical framework used to understand the behavior of complex systems across different scales. The term "group" in renormalization group refers to a mathematical structure, specifically a group of transformations. The renormalization group provides a systematic way to analyze how physical properties change as we zoom in or out, or as we move through different energy or length scales.
    2. what happens to a liquid with high Temperatures? and with low temperatures? What happens to the partition function?
    3. How is entropy while varying the temperature?
    4. What is phase transition?
    5. What is the order of a phase transition? What happens at the critical point
    6. How is correlation changing outside the CP and in the CP?
    7. When is a system self-similar? what does it mean? To how many parameters depend the correlation length?
    8. How would you write the hamiltonian of the Ising model by making use of the renormalisation group? And the partition function?
    9. What is the meaning of defocusing? How can defocusing be done?
    10. What is a projection operator?
    11. How are the partition function and the free energy after defocusing?
    12. What happens when you defocus your system in terms of entropy? And what free energy do you obtain?
    13. What happens to a correlation function at each step if not on a critical point? what if on a critical point?
  - Lesson 11: The process of coarse graining and the multibody potential
    1. What is the aim of Coarse Graining?
    2. How are interactions called in Coarse Graining?
    3. What is a reference?
    4. What are the possible modelling approaches?
    5. How is the partition factor for the all atom model? and for the CG model?
    6. What free energy formula can you obtain from the CG partition function?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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7. How is the degeneracy factor?
  8. How can you write the mapping process? How mapping has to be? (specific)
  9. How is the CG process?
  10. Is mapping invertible?
  11. What is the consistency condition?
  12. Obtain the potential energy that you get coarse-graining the system
  13. what is the multibody potential of mean force?
  14. When is your CG system ok? talking about the measured potential energy
  15. What is transferability? In the context of coarse-graining in molecular simulations or modeling, "transferability" refers to the ability of a coarse-grained model or representation to accurately capture and reproduce relevant properties of the system being studied. Transferability implies that the parameters and interactions used in the coarse-grained model, which are often derived from a more detailed or atomistic representation, are applicable and meaningful across different conditions or environments. This happens when the coarse grained potential is similar to the multibody potential of mean force?
  16. How do you allow the consistency condition for the momenta?
- Lesson 12: How is it possible to equate our potential to the multibody potential?
    1. How can we force  $U(R)$  to satisfy that condition?
    2. What is relative entropy?
    3. How do you compute the distance between two distributions? What is the most important probability?
    4. How do you compute  $P_r(r|U)$ ? What is the degeneracy factor?
    5. What type of values can the  $w$  have?
    6. What is the value of the partition function?
    7. What is the mapping entropy from the relative entropy?
    8. How do you average the atomic probabilities? what does this allow you to do with the mapping entropy?
    9. How do you write a Kullback-Leibler distance that is indicative of the coarse graining quality ?
    10. When and how does the mapping entropy change? By changing the mapping, in fact, the relative entropy can be considered as a distance of two probability distributions that depend on mapping.
    11. What do you obtain by mapping in terms of relative entropy? a distance
    12. What formula of relative entropy do you obtain that should be minimized? (Gibbs-Bogoliubov inequality)
    13. What is the condition that is satisfied when you are at the minimum of the relative entropy? See the signed element
    14. What is also conserved in case in which the relative entropy is at the minimum? The radial distribution functions computed for the coarse grained and the all atom system.
    15. Make the straightforward conclusion.
  - Lesson 13
    1. What is the Boltzmann inversion process?
    2. Write the process to obtain the potential energy through Boltzmann inversion
    3. What is a more general way to write the Boltzmann inversion?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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4. What happens if we have more than a single collective coordinate? explain the two possible cases
  5. What is the double counting problem?
  6. What is the iterative solution?
  7. Write the case where you consider as the collective coordinate the distance between the particles
  8. What problems you have to face in cases with a number of interacting particles? If you consider the distance as the collective coordinate, what are you minimizing and what not?
- Lesson 14: Inverse Monte Carlo
    1. What is the problem that you have with Boltzmann Inversion?
    2. How do you solve the limitation?
    3. What is Inverse Monte Carlo?
    4. What do you have to compute by using inverse Monte Carlo? (susceptibility matrix)
    5. What does the susceptibility matrix tell you?
    6. How do you calculate the infinitesimal change in potential energy after
    7. How does Monte Carlo converge?
    8. obtain from relative entropy the susceptibility matrix
    9. What softer do you generally use to parametrize the CG potential?
    10. Is the cut-off important in Boltzmann inversion?
    11. Is parametrization always correct or is it specific?
  - Lesson 15: Force Matching
    1. What is force matching?
    2. What is the MB force field and how can you write it?
    3. How do you compare force fields?
    4. How can you also write the comparison of the atomic force field and the coarse grained force field (in terms of the multibody force field)?
    5. What do you deduce from that relation?
    6. How can you find an  $F$  (coarse grained f.f.) which is as close as possible to  $f$  (atomistic f.f.) (concept)? ( $\chi^2$  method)
    7. What is the meaning of  $\chi^2$  applied to this problem? (until plane explanation)
    8. How do you find the minimum in the difference  $\vec{f} - \vec{F}$
    9. What happens when all your interactions are all independent?
    10. How does  $\chi^2$  differentiate himself from relative entropy?
    11. Why Force Matching does not produce very good radial distribution functions?
  - Lesson 16: Protein models
    1. what does the Anfinsen experiment tell us?
    2. what is the protein folding funnell?
    3. why to use CG?
    4. what type of approaches are available?
    5. what models are available?
    6. what is a lattice model?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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7. which types protein models exist?
  8. what is a martini model?
  9. what is a go model?
  10. what is inferred by saying that proteins are conformationally selected by ligands?
  11. How is the vibrational nature of proteins involved?
  12. what is a elastic network model?
  13. What are modes?
  14. how can you evaluate slow modes in ENMs?
  15. what are quasi-rigid domain description models?
- Lesson 17:
    1. what is a polymer?
    2. what are the types of a polymer?
    3. what quantities you should consider?
    4. what is the contour length
    5. what is hte end to end distance? what is on average if symmetric polymer
    6. what is the radius of gyration?
    7. what are the models generally used for polymer modelling?
    8. what are freely jointed chains?
    9. what is a kreatky-porog model? how do you write the bending potential? How do you write the correlation between the bonds orientations?
    10. what is the persistance length? and the kuhn length?
    11. what are self-avoiding chains? How does the potential change? and the end to end distance? how can you describe the average difference in volume?
    12. what is the kremer-grest model?
    13. how can you evaluate the stiffness of a polymer?
    14. main characteristics of DNA
    15. what is oxDNA
    16. what are the resolutions types used on the base of the length wanted
    17. what is a crumpled globule model?
  - Lesson 18
    1. what is a topological problem in soft matter?
    2. what are for example topologies in biology?
    3. what is a knot mathematically?
    4. how do you define a knot?
    5. what are Reidemaster moves?
    6. how do you distinguish knots? By the number of overlaps/crossings which is at the minimum.
    7. properties of a knot
    8. which are the most common types of knots? torus knots twist knots
    9. can you define knots in open chains?

## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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10. what is the concept of minimally interfering closure? with what process do you find it?
  11. what is a knotoid? how can it help you?
  12. what are in-protein links?
  13. what is a Gauss number in this context?
  14. to what is proportional the folding rate? to what is negatively correlated? – proportional to Gauss number, negatively correlated to topological complexity.
  15. what is knot dynamics? what type of chain model is normally used in this context?
  16. what is the transmission coefficient?
  17. where do the knots tend to position themselves? why not on the stationary nodes? In which positions do they move?
  18. how can you intend the position of a knot on a length? what type of ... you expect on the stationary points?
  19. what is interesting about knots in proteins? why you don't expect them?
  20. what characteristics are necessary for self-folding? what type of measures do you adopt as a consequence?
  21. what is an elastic folder model? what is its main role?
  22. what is the process through which you evaluate the folding rate through the elastic folder model
  23. What type of measure do you adopt to evaluate the folding process?
  24. what is the RMSD?
- Lesson 19 - multi-resolution and dual resolution models
    1. which are the top-down and the bottom-up models?
    2. what is the purpose of adaptive resolution simulations?
    3. what is a switching function? How it is used for the score
    4. how do you write the force of a system described by a multi-resolution model?
    5. what is the purpose of quasi-grand canonical (AdResS) simulations? what is changing and in what condition?
    6. what are the problems related to AdResS?
    7. what is the hamiltonian version of AdResS? what kind of force you obtain?
    8. what is the problem that you observe by looking to the force formula? In which way do the particles behave on the interface between AA and CG?
    9. what kind of correction you have to give to compensate the drift force (precedent point)?
    10. what kind of system do you have after the first correction?
    11. how can you obtain a system that has instead equal density? make a scheme at the end
    12. Is it possible to have a system with same density and pressure?
    13. what type of advantage you have by using a multi-resolution scheme in the water-gas model?
    14. how do you measure normally the chemical potential? how can you use the multi-resolution scheme to improve it?
    15. what is the fast calculation of solvation energy process?
    16. what can you also investigate with the multi-resolution models? of proteins
    17. what is a dual resolution? what are the main problems?
    18. how you solve them?



## 1.7. QUESTIONS RELATED TO THE COURSE OF MULTISCALE METHODS FOR SOFT MATTER PHYSICS

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19. what is the problem that you encounter in the previous point?
  20. what can you solve with both the methods?
- Lesson 20: Fluids
    1. what does the navier stokes law says? why you can't use it in MD
    2. what is a celular automata?
    3. what is multiparticle collision dynamics? what is the reasoning behind stochastic rotation dynamics?
    4. what is the strategy (the passages) behind stochastic rotation dynamics?
    5. is it possible to use multiparticle collision dynamics with different types of particles
    6. how can you study hydrodynamics?
    7. what is Dissipative particle dynamics?
  - Lesson 21: Neural Networks
    1. General: neurons, activation functions, ultiple layers
    2. How do you train a neural network? What is hte MSE?
    3. Write correlation boltzmann weight and bayesian theorem
    4. What is an affine transformation? it gives you the linear results without non-linear transformation
  - Lesson 22: Machine learning usage
    1. What assumption has to be done to allow the computation of energies through neural networks? How has the input to be transformed also?
    2. What is the structure of the NN?
    3. Can you characterize local structures with neural networks? make water example
    4. Tell how it is possible to sample CG structures

# Part III

## Additions

## 1.8 Fourier Series

The aim of a Fourier expansion is to represent a given function as a sum of sinusoidal functions (sines and cosines) or complex exponentials. This expansion is particularly useful because it allows us to analyze and understand complex functions in terms of simpler sinusoidal components. A very good explanation can be found at

The formula for a function defined by other periodic subfunctions is written as follows:

$$f(t) = \sum_{n=-N}^N c_n e^{2\pi i n t} \quad (1.2)$$

each exponential can be considered as a sort of rotating vector, as stated in the video. The  $c_n$  factor is indicative of the amplitude of that circle, while instead the term in the exponential would indicate the angle of start of the rotation. This term represents the complex exponential function with frequency  $2\pi n$  multiplied by time  $t$ . It's a periodic function with a frequency determined by the integer  $n$ . The complex exponential function captures the phase information of the corresponding frequency component. The function indicates a periodicity/frequency that is indicated by  $|n|$ , which is the considered modulating factor. If it's hard for you to understand that the term in the exponential is a periodic function, remember that

$$e^{ix} = \cos(x) + i\sin(x)$$

Considering that you have a constant term in the summation, which is  $c_0 e^{i0t}$ , if you compute the integral as follows (given that you are considering a distance of 1, so the integral divided by one is the average)

$$c_0 = \int_0^1 f(t) dt$$

You obtain the value of the coefficient. By taking the whole integral of  $f(t)$

$$\int_0^1 f(t) dt = \int_0^1 (c_{-N} e^{-2\pi i N t} + \dots + c_N e^{2\pi i N t}) dt$$

This corresponds to the sum of the averages of each part. However, the only vector not moving is the one with  $c_0$ , while the others have all an average of 0. In this way, you obtain the formula needed to compute the value of  $c_0$ :

$$\int_0^1 f(t) dt = c_0 \quad (1.3)$$

In a clever way, you can multiply all the terms by an exponential of choice to make constant another rotation. Consequently, you can retrieve the general formula:

$$c_n = \int_0^1 f(t) e^{-2\pi i n t} dt \quad (1.4)$$

## 1.9 Laplace transformation

From video video.

Given that a Fourier transformation can be written as

$$X(\omega) = \int x(t) e^{-i\omega t} dt$$

Notice that when the frequency distribution hits the y axis, the position corresponds to the value of the integral for the function  $x(t)$

## 1.10. LAGRANGE MULTIPLIERS

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While  $\omega$  is a real number, the value  $X(\omega)$  has a real and an imaginary component, from which we can calculate the magnitude. You can calculate  $\omega(1), \omega(2) \dots$  and see that you obtain the magnitude plot (axis  $x$  with  $\omega$ ).

Therefore, from a fourier transformation of a function with an exponential and a periodic componen (e.g.  $e^{-t} \sin t$ ), you obtain a magnitude graphs of the frequencies.

The Laplace transformation can be written as

$$\begin{aligned} X(s) &= \int_0^{\infty} x(t)e^{-st} dt \\ &= \int_0^{\infty} x(t)e^{-(\alpha+i\omega)t} dt \\ &= \int_0^{\infty} x(t)e^{-\alpha t} e^{-i\omega t} dt \end{aligned}$$

Therefore, the Laplace transformation of  $x(t)$  is the fourier transformation of  $x(t)e^{-\alpha t}$ .

In the case of Laplace transformation, input with imaginary and real part. However, when  $s = 0$  than

## 1.10 Lagrange multipliers

Given that you have a closed curve that you have to optimize, and a constraint to respect, the point of maximum is that where the two curves touch. In that point, the gradient of the two functions ( $f(x, y)$  and  $g(x, y)$ ) has the same direction.

With one constraint. Let  $f$  and  $g$  be functions of two variables with continuous partial derivatives at every point of some open set containing the smooth curve  $g(x, y) = 0$ . Suppose that  $f$ , when restricted to points on the curve  $g(x, y) = 0$ , has a local extremum at the point  $(x_0, y_0)$  and that  $\vec{\nabla}g(x_0, y_0) \neq 0$ . Then there is a number  $\lambda$  called a Lagrange multiplier, for which

$$\vec{\nabla}f(x_0, y_0) = \lambda \vec{\nabla}g(x_0, y_0)$$

(Remember that a gradient is a vector realized in the following way:)

$$\vec{\nabla}g = \frac{\partial g}{\partial x} \hat{i} + \frac{\partial g}{\partial y} \hat{j} + \frac{\partial g}{\partial z} \hat{k} \quad (1.5)$$

In general, you should follow the following passages:

1. Determine the objective function  $f(x, y)$  and the constraint function  $g(x, y)$ . Does the optimization problem involve maximizing or minimizing the objective function?
2. Solve the equation  $\vec{\nabla}f(x_0, y_0) = \lambda \vec{\nabla}g(x_0, y_0)$  given that  $g(x_0, y_0) = 0$
3. Solve for  $x_0$  and  $y_0$ .
4. The smallest values minimize  $f$ , while instead the bigger values maximize it.

When you have two constraints, what happens is that you have the following

$$\begin{aligned} \vec{\nabla}f(x_0, y_0, z_0) &= \lambda_1 \vec{\nabla}g(x_0, y_0, z_0) + \lambda_2 \vec{\nabla}h(x_0, y_0, z_0) \\ g(x_0, y_0, z_0) &= 0 \\ h(x_0, y_0, z_0) &= 0 \end{aligned}$$

## 1.11 Methods to solve integrals

### 1.11.1 Gauss Integral

$$\int_{-\inf}^{+\inf} a e^{-bx^2+cx+d} dx = a \sqrt{\frac{\pi}{b}} \exp\left(\frac{c^2}{4b} + d\right) \quad (1.6)$$

Method to evaluate Gauss integrals with the Polar coordinates:

$$\begin{aligned} J &= \int_0^\infty e^{-x^2} dx = \int_0^\infty e^{-y^2} dy \\ J^2 &= \left( \int_0^\infty e^{-x^2} dx \right) \left( \int_0^\infty e^{-y^2} dy \right) \\ &= \int_0^\infty \left( \int_0^\infty e^{-(x^2+y^2)} dx \right) dy \\ &= \int_0^{2\pi} \left( \int_0^\infty e^{-r^2} r dr \right) d\theta \\ &= \int_0^{2\pi} \left[ -\frac{1}{2} e^{-r^2} \right]_0^\infty d\theta \\ &= \int_0^{2\pi} \frac{1}{2} d\theta \end{aligned} \quad \rightarrow J = \sqrt[2]{\pi}$$

### 1.11.2 Gamma function

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt$$

It is also valid that

$$\Gamma(x) = (x-1)!$$

and

$$\Gamma(n) = (n-1)\Gamma(n-1)$$

Another method is represented by the Laplace transform, which is described in chapter 1.10

## 1.12 Laplace transform

It can be used to convert differential equations into algebraic equations. It is written as

$$L\{f(t)\} = F(s) \quad (1.7)$$

with

$$F(s) = \int_0^\infty e^{-st} f(t) dt \quad (1.8)$$

Therefore, it produces a new function out of the first one given in input.

It has the following properties:

- **Linearity:**  $L\{af(t) + bg(t)\} = aL\{f(t)\} + bL\{g(t)\}$

- **Existence:** Given that  $f(t)$  is of "exponential order" if  $|f(t)| \leq Me^{ct}$  for large  $t$ , some  $M$  and  $c$ . Therefore  $\lim_{t \rightarrow \infty} \frac{f(t)}{e^{ct}} = 0$ . The existence theorem says that if  $f(t)$  is continuous and exponential order with constant  $c$ , then

$$F(s) = \mathcal{L}\{f(t)\}$$

is defined for all  $s > c$ . In practice, the  $F(s)$  value converges

- **Inverses:** It is possible to obtain  $f(t)$  such that  $F(s) = \mathcal{L}\{f(t)\}$ . And it exists a unique answer. Therefore, it is possible to perform

$$f(t) = \mathcal{L}^{-1}\{F(s)\}$$

- **Translation property:** If  $\mathcal{L}\{f(t)\} = F(s)$ , then  $\mathcal{L}\{e^{at}f(t)\} = F(s - a)$ . Indeed,

$$\begin{aligned}\mathcal{L}\{e^{at}f(t)\} &= \int_0^\infty e^{-st} \cdot e^{at}f(t) dt \\ &= \int_0^\infty e^{-(s-a)t}f(t) dt \\ &= F(s - a)\end{aligned}$$

e.g.

$$\begin{aligned}\mathcal{L}\{t^n\} &= F(s) = \int_0^\infty e^{-st}t^n dt \\ &= \int_0^\infty e^{-u} \left(\frac{u}{s}\right)^n \frac{du}{s} \\ &= \left(\int_0^\infty e^{-u}u^n du\right) \frac{1}{s^{n+1}} \\ &= \frac{1}{s^{n+1}}\Gamma(n+1) = \frac{n!}{s^{n+1}}\end{aligned}$$

**e.g.:** Given the partition function  $Q_N(V, T) = \int g(\epsilon)e^{-\beta\epsilon}d\epsilon$ , You notice that  $Q_N(V, T) = \int g(\epsilon)e^{-\beta\epsilon}d\epsilon = \mathcal{L}\{f(\epsilon)\}$ . Therefore

$$\mathcal{L}\{f(\epsilon)\} = \frac{8\pi V}{h^3} \frac{1}{\beta^3 c^3} = \int g(\epsilon)e^{-\beta\epsilon}d\epsilon$$

You can observe that the value of  $s$  is  $\beta$ , therefore

$$F(s) \propto \frac{1}{\beta^3}$$

This form is similar to the known form

$$F(s) = \frac{n!}{s^{n+1}} \quad s > 0$$

which is obtained when  $f(t) = t^n$ .

$$\begin{aligned}F(\beta) &\propto \frac{1}{\beta^3} \\ &= \frac{2!}{\beta^{2+1}} \cdot \frac{1}{2} \\ &= \frac{1}{2} \cdot \frac{2}{\beta^{2+1}}\end{aligned}$$

### 1.13. CYCLIC IDENTITY FOR PARTIAL DERIVATIVES

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Therefore,  $n=2$  and  $g(\epsilon) (f(t))$  is

$$g(\epsilon) = \left( \frac{4\pi V}{h^3 \beta^3 c^3} \right) \epsilon^2$$

#### 1.12.0.1 Laplace transform of derivatives and integrals

Suppose that  $f(t)$  is continuous, piece-wise smooth, and of exponential order.

$$\begin{aligned} L\{f'(t)\} &= \int_0^\infty e^{-st} f'(t) dt \\ &= (e^{-st} f(t))_0^\infty - \int_0^\infty (-s) e^{-st} f(t) dt \\ &= -f(0) + sF(s) = -f(0) + sL\{f(t)\} \end{aligned}$$

Similarly

$$\begin{aligned} L\{f''(t)\} &= L\{g'(t)\} \\ &= -g(0) + sL\{g(t)\} \\ &= -f'(0) + sL\{f'(t)\} \\ &= -f'(0) + s[-f(0) + sL\{f(t)\}] \\ &= s^2 L\{f(t)\} - sf'(0) - f'(0) \end{aligned}$$

### 1.13 Cyclic identity for partial derivatives

Given a function  $z(x, y)$ , we can state that

$$\begin{aligned} dz &= \left( \frac{\partial z}{\partial x} \right)_x dx + \left( \frac{\partial z}{\partial y} \right)_y dy \\ \left( \frac{\partial z}{\partial y} \right)_z &= \left( \frac{\partial z}{\partial x} \right)_x \left( \frac{dx}{dy} \right)_z + \left( \frac{\partial z}{\partial y} \right)_y \left( \frac{dy}{dy} \right)_y \\ 0 &= \left( \frac{\partial z}{\partial x} \right)_x \left( \frac{dx}{dy} \right)_z + \left( \frac{\partial z}{\partial y} \right)_y \\ - \left( \frac{\partial z}{\partial y} \right)_y &= \left( \frac{\partial z}{\partial x} \right)_x \left( \frac{dx}{dy} \right)_z \\ \left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x &= -1 \end{aligned}$$

You can observe a sort of rotation of the variable

**example::** evaluate  $\left( \frac{\partial P}{\partial T} \right)_V$

You can try to evaluate it from

$$\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial V}{\partial P} \right)_T = -1$$

Which is also equal to

$$\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{1}{V\alpha} \right) (-Vk)$$

### 1.13. CYCLIC IDENTITY FOR PARTIAL DERIVATIVES

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Where  $\alpha$  is the isobaric compressibility and  $k$  is the isothermal compressibility such that

$$-V\alpha = \frac{\partial V}{\partial P}_T \quad V\alpha = \frac{\partial V}{\partial T}_P$$