To Problem 1: Purpose

1. Getting you started with Python (defining constants, functions, loops, if statements, plotting, numpy, scipy), and Jupyter notebooks
2. Understand idea of Direct Monte Carlo method!

Please note

- **Deadline**: 9th Feb 2026 at 5pm. Submit ipynb on Gradescope, assessments. Filename: surname-problem1.ipynb

General comments

- Put Handout to Problem 2 on Minerva

Provisional timetable:

Semester Week	Overall Week	Date/Time	Location	Session Format	Content
1	14	Monday 26th January 12pm-1pm	RSLT 11	Lecture	Introduction to Monte Carlo Methods, Direct Monte Carlo
		Thursday 29th January 1pm-3pm	SCAPE (GR.06)	Workshop	
2	15	Monday 2nd February 12pm-1pm	RSLT 11	Lecture	Calculating statistical averages in the classical limit, Metropolis Monte Carlo
		Thursday 5th February 1pm-3pm	Esther Simpson (1.09)	Workshop	
3	16	Monday 9th February 12pm-1pm	RSLT 11	Lecture	Intermission: Molecular Dynamics vs Monte Carlo
		Thursday 12th February 12pm-2pm	Fourman O&P (8.49)	Workshop	
4	17	Monday 16th February 12pm-1pm	RSLT 11	Lecture	Generalised Monte Carlo: Disease Propagation and the Ising Model of Atomic Spin
		Thursday 19th February 1pm-3pm	SCAPE (GR.06)	Workshop	
5	18	Monday 23rd February 12pm-1pm	RSLT 11	Lecture	Drop-in session
		Thursday 26th February 1pm-3pm	SCAPE (GR.06)	Workshop	
6	19	Monday 2nd March 12pm-1pm	RSLT 11	Lecture	Simulating a Dynamic Molecular System
		Thursday 5th March 1pm-3pm	SCAPE (GR.06)	Workshop	Exploring the Brownian and Langevin Gas - Energies and Diffusion

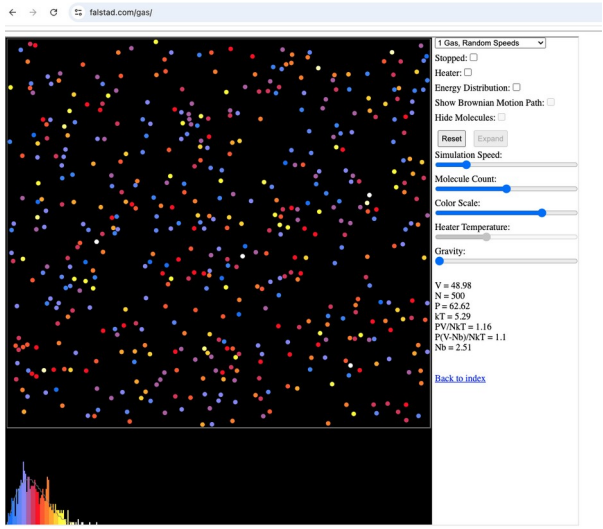
Direct calculation of statistical averages in the classical limit

Internal energy: (N,V,T)

$$U = \langle E \rangle = \sum_i E_i p_i = \ldots = kT^2 \left(\frac{\partial \ln Q_N}{\partial T} \right)_V$$

$$p_i = \frac{e^{-E_i/kT}}{Q_N} \qquad Q_N = \sum_j e^{-E_j/kT}$$

Canonical partition function



In general for any observable *X*:

$$\langle X \rangle = \sum_i x_i p_i = \ldots$$

$$x_i = \int_{\text{All space}} \phi_i^* \hat{x} \phi_i$$

expectation value of QM operator $\hat{x}$ in state ϕ_i

Tasks of calculating statistical averages:

1. Solve time-independent Schrödinger equation for many body system to obtain ϕ_i
2. Calculate expectation value (observable)
3. Calculate average

Impossible task for many body system!!!

Illustration: How to derive expression for the calculation of ensemble average in the classical limit

A clever person solves a problem. A wise person avoids it.

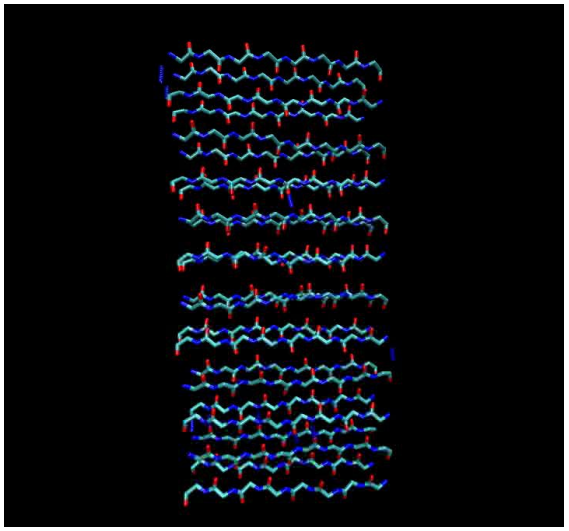
Albert Einstein

Calculating statistical averages in the classical limit

Main result:

$$\langle X \rangle = \frac{\int_{\Gamma} X(\vec{p}^N, \vec{r}^N) e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N}{Q_N}$$

$$Q_N = \int_{\Gamma} e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N$$



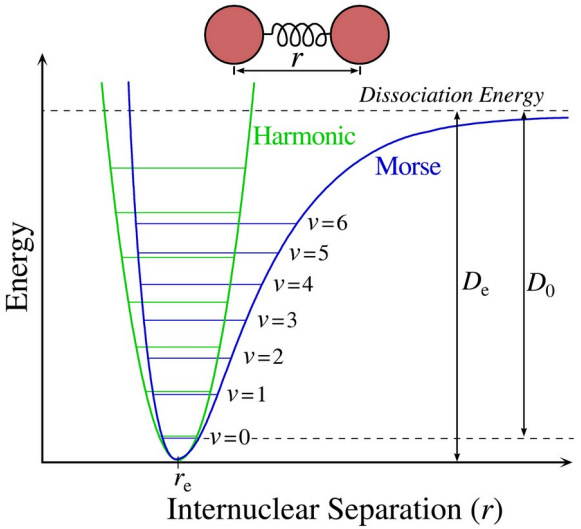
Remark: The importance of Q_N is that all thermodynamic quantities can be derived from it!!!! (Lecture 1)

$$U = kT^2 \left(\frac{\partial \ln Q_N}{\partial T} \right)_V$$

$$A = -kT \ln Q_N$$

$$S = k \ln Q_N + kT \left(\frac{\partial \ln Q_N}{\partial T} \right)_V$$

Classical limit: One dimensional harmonic oscillator

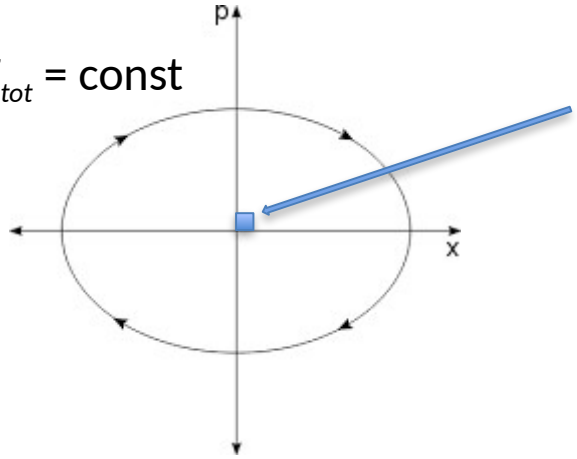


$$V(x) = \frac{k_f}{2}(x - x_0)^2$$

$$E_{tot} = E_{kin} + E_{pot} = \frac{p_x^2}{2m} + \frac{k_f}{2}(x - x_0)^2$$

$\Gamma : (p_x, x)$ "Phase space"

E_{tot} = const



Graininess:

$$\Delta x \Delta p_x \geq h$$

Oscillation of 1d harmonic oscillator is described by ellipsoid in phase space

Canonical ensemble (N, V,T)

$$\langle E \rangle = \sum_i E_i p_i = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \approx \frac{h^2 \int_\Gamma E\, e^{-E/kT}\, dp_x dx}{h^2 \int_\Gamma e^{-E/kT}\, dp_x dx} \; ¿ \; \frac{\int_\Gamma E\, e^{-E/kT}\, dp_x dx}{\int_\Gamma e^{-E/kT}\, dp_x dx}$$

$$p_i = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

classical limit

Classical limit:

$$E_i \mapsto E(x, p_x)$$

$$\sum_i \mapsto \frac{1}{h^2} \underbrace{\int_\Gamma dp_x\, dx}_{\text{area within ellipsoid}}$$

graininess

(total number of energy levels within ellipsoid)

Calculate average energy of 1d harmonic oscillator in classical limit

$$\langle E \rangle = \frac{\int_\Gamma E\, e^{-E/kT}\, dp_x dx}{\int_\Gamma e^{-E/kT}\, dp_x dx}$$

$$E_{tot} = E_{kin} + E_{pot} = \frac{p_x^2}{2m} + \frac{k_f}{2}(x - x_0)^2$$

$$\langle E_{tot} \rangle = \langle E_{kin} + E_{pot} \rangle = \langle E_{kin} \rangle + \langle E_{pot} \rangle$$

$$\langle E_{kin} \rangle = \frac{\int_\Gamma \frac{p_x^2}{2m} e^{-\left(\frac{p_x^2}{2m} + \frac{k_f}{2}x^2\right)/kT}\, dp_x dx}{\int_\Gamma e^{-\left(\frac{p_x^2}{2m} + \frac{k_f}{2}x^2\right)/kT}\, dp_x dx} = \frac{\int \frac{p_x^2}{2m} e^{-\left(\frac{p_x^2}{2m}\right)/kT}\, dp_x \int e^{-\left(\frac{k_f}{2}x^2\right)/kT}\, dx}{\int e^{-\left(\frac{p_x^2}{2m}\right)/kT}\, dp_x \int e^{-\left(\frac{k_f}{2}x^2\right)/kT}\, dx} = \frac{1}{2}kT$$

$$\langle E_{pot} \rangle = \ldots = \frac{1}{2}kT$$

In agreement with equipartition theorem !!!

$$\langle E \rangle = kT$$

Reminder: Equipartition theorem (classical mechanics)

Each quadratic term that appears in the total energy of a system Contributes ½kT to the internal energy.

$$E_{tot} = E_{kin} + E_{pot} = \frac{p_x^2}{2m} + \frac{k_f}{2}(x - x_0)^2 \qquad \Rightarrow U = \langle E \rangle = kT$$

Classical limit in 3 dimensions

$$E_i \mapsto E(\vec{p}^N, \vec{r}^N)$$

$$\sum_i \mapsto \frac{1}{N! h^{3N}} \underbrace{\int_\Gamma d\vec{p}^N \, d\vec{r}^N}_{\text{area within 3N dimensional ellipsoid}}$$

h^{3N}: graininess 3N dimensional phase space
$N!$: Particles are indistinguishable (overcounting)

$$\langle E \rangle = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \cong \frac{\int_\Gamma E(\vec{p}^N, \vec{r}^N) e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N}{\int_\Gamma e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N}$$

$$= \frac{\int_\Gamma E(\vec{p}^N, \vec{r}^N) e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N}{Q_N}$$

where

$$Q_N = \int_\Gamma e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N$$

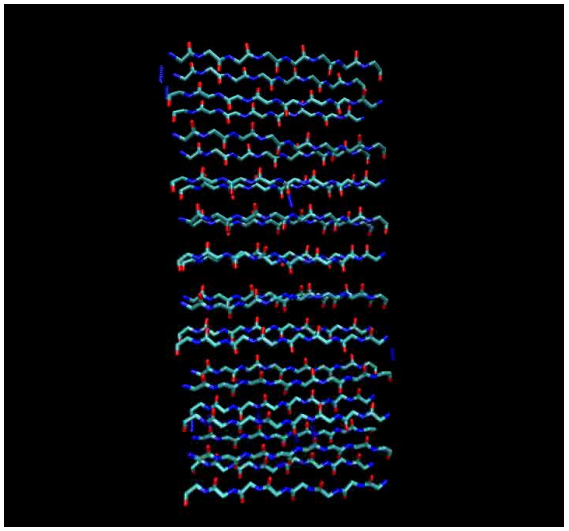
Canonical partition function

Calculating statistical averages in the classical limit

Main result:

$$\langle X \rangle = \frac{\int_{\Gamma} X(\vec{p}^N, \vec{r}^N) e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N}{Q_N}$$

$$Q_N = \int_{\Gamma} e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N$$



Remark: The importance of Q_N is that all thermodynamic quantities can be derived from it!!!! (Lecture 1)

$$U = kT^2 \left(\frac{\partial \ln Q_N}{\partial T} \right)_V$$

$$A = -kT \ln Q_N$$

$$S = k \ln Q_N + kT \left(\frac{\partial \ln Q_N}{\partial T} \right)_V$$

Remark to problem 1: Real gases

$$Q_N = \int_{\Gamma} e^{-E(\vec{p}^N \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N$$

$$E(\vec{p}^N, \vec{r}^N) = \frac{\vec{p}^{2N}}{2m} + U(\vec{r}^N)$$

$$\Rightarrow Q_N = \frac{Z_N}{\Lambda^{3N}} \qquad \text{where} \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k T}}$$

Thermal de Broglie wavelength

$$Z_N = \frac{1}{N!} \int e^{-U(\vec{r}^N)/kT} \, d\vec{r}^N$$

Configuration integral (see e.g. Atkins 9th edition, chapter 16.5, page 605)

Problem 1:

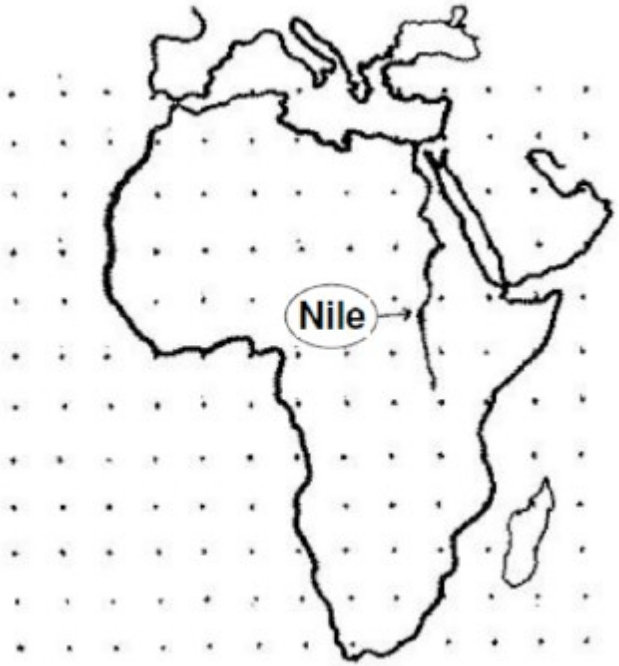
Substitution of $Q_N = \frac{Z_N}{\Lambda^{3N}}$ into $p = kT \left(\frac{\partial \ln Q_N}{\partial V} \right)_T$ and comparison to

$$\frac{pV}{nRT} = 1 + B_2 \left(\frac{n}{V} \right) + \ldots$$

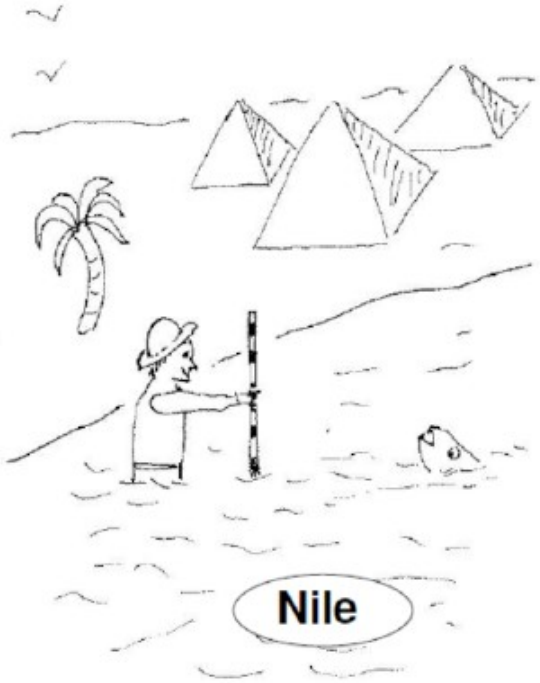
allows determination of B's, such as B_2 used in problem 1!!!

Metropolis Algorithm (Main idea)

Task: Measuring the depths of the Nile



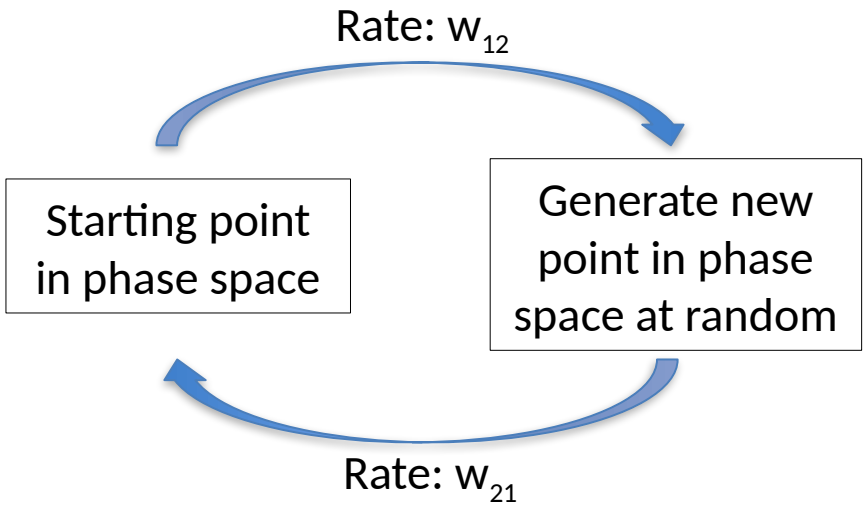
Direct Monte Carlo method



Metropolis Monte Carlo method

Importance sampling

Generate a random walk in phase space (position, momentum) based on the Boltzmann distribution



To ensures that points are sampled according to Boltzmann distribution it is sufficient to impose DETAILED BALANCE:

$$\frac{w_{12}}{w_{21}} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-\Delta E/kT} \quad \text{where} \quad \Delta E = E_2 - E_1$$

Note:

- Detailed balance also ensures that any one point in phase space can be reached

In practice:

Metropolis algorithm accepts new point in phase space based on the ratio of the probabilities of moving between old and new point:

Starting point in phase space with energy $E_1(\Gamma_1)$ → New point in phase space with energy $E_2(\Gamma_2)$ → …

If $E_2 < E_1$, accept new point

If $E_2 > E_1$: Generate a random number between 0 and 1

$$\text{if } e^{-(E_2-E_1)/kT} > \text{random number, accept new point}$$

$$\text{if } e^{-(E_2-E_1)/kT} < \text{random number, reject new point}$$

Statistical average:

$$\langle X \rangle = \frac{\int_{\Gamma} X(\vec{p}^N, \vec{r}^N) e^{-E(\vec{p}^N, \vec{r}^N)/kT} \, d\vec{p}^N \, d\vec{r}^N}{Q_N} \approx \frac{\sum_{i=1}^{M} X_i(\vec{p}_i^N, \vec{r}_i^N)}{M}$$

where M is the number of phase points generated, and r_i the value measured.

Look at problem 2 given in HandoutToProblem2

Fluctuations

Standard deviation:

$$\sigma = \sqrt{\frac{1}{M}\sum_{i=1}^{M}\left(X_i - \langle X\rangle\right)^2} = \sqrt{\langle X^2\rangle - \langle X\rangle^2}$$

For example: Energy

$$\sigma_E = \sqrt{\langle E^2\rangle - \langle E\rangle^2} \qquad \text{with} \qquad C_V = \frac{1}{kT^2}\sqrt{\langle E^2\rangle - \langle E\rangle^2}$$

$$\sigma_E = \sqrt{kT^2 C_V}$$