Statistical Mechanics
for
Molecular Dynamics

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Why Statistical Mechanics?

- Solving the trajectories of N atoms is of no use if we cannot extract experimentally meaningful properties. We need things like temperature (T), presure (P), energy (E) etc. i.e. **Macroscopic properties**.

- Macroscopic properties are generally **averages** of some kind so statistical methods are natural tools.

- Individual events in a trajectory **may not** be significant (however interesting). We need statistical methods to determine their relevance.

- How can we relate molecular properties to system properties?

- Most of what's interesting assumes equilibrated (or steady state) systems. How can we tell we are in equilibrium?

- Statistical Mechanics has all the answers!

Notes: Boltzmann and Gibbs Averages

There are two distinct ways of calculating averages in statistical mechanics. The oldest method is due to **Boltzmann** and is an average of the system properties over time. The second is the **Gibbs** method, which is an average over multiple replicas of the system, which are independent but are thermodynamically identical – meaning they are all the same size and at the same temperature, pressure *etc.*

It is fair to say that the Gibbs method is the more powerful, but the two methods, applied correctly, should yield the same results.

Boltzmann Averaging
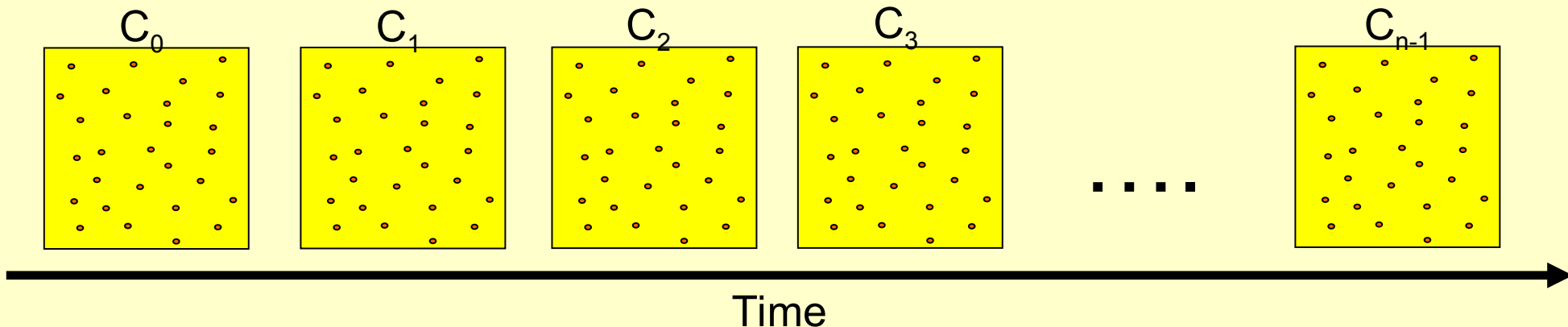
Sampled configurations **must be** causally connected via equations of motion but **we assume** that if they are separated by a sufficiently large time interval they will be **statistically independent.**

Boltzmann Averaging

The average properties of a system are obtained by observing the system at a given state point **for a long time** T_∞ and averaging an observed property (say) A **over the time** T_∞ :
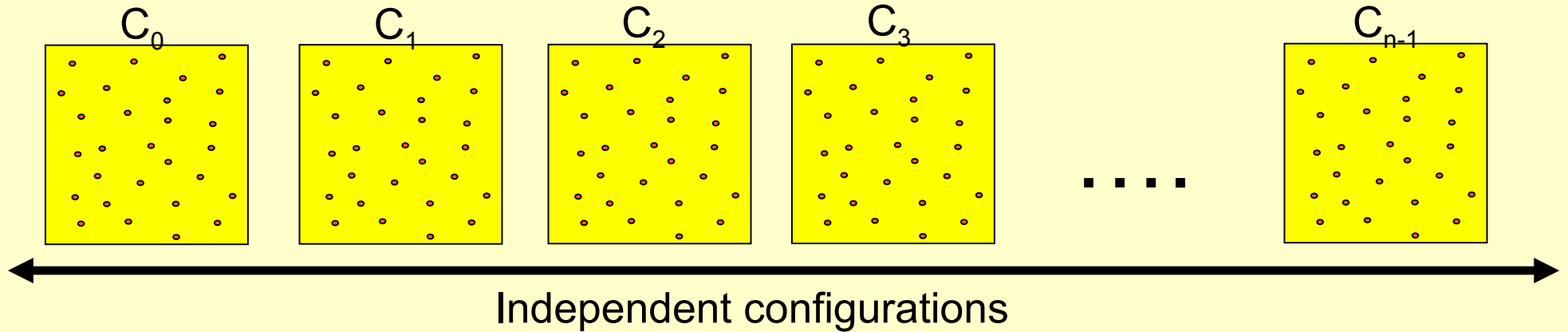
$$\bar{A} = \frac{1}{T_\infty} \int_0^{T_\infty} A(t)\, dt \approx \frac{\Delta t}{T_\infty} \sum_{n=1}^{N_{T_\infty}} A_n \quad with: \quad \Delta t = \frac{T_\infty}{N_{T_\infty}}$$

(N_{T_∞} is the number of system configurations used in the average.)

Note that this implies the instantaneous value of *A(t)* fluctuates about the mean value. The mean square fluctuation is defined as:

$$\overline{\delta A^2} = \frac{1}{T_\infty} \int_0^{T_\infty} (A(t) - \bar{A})^2\, dt \approx \frac{\Delta t}{T_\infty} \sum_{n=1}^{N_{T_\infty}} (A_n - \bar{A})^2.$$

Gibbs Averaging

C_0 C_1 C_2 C_3 C_{n-1}

Independent configurations

Configurations **cannot be** causally connected because they are independent, so must also be **statistically independent.**

Gibbs Averaging

We observe many replicas of the system, all nominally at the same state point, and average the instantaneous values of the observed variable (i.e. an **Ensemble Average**) :

$$\langle A \rangle = \frac{1}{N_\infty} \sum_{n=1}^{N_\infty} A_n.$$

Fluctuation is necessarily a property of the Gibbs sampling also:

$$\langle \delta A^2 \rangle = \langle (A(t) - \langle A \rangle)^2 \rangle = \frac{1}{N_\infty} \sum_{n=1}^{N_\infty} (A_n - \langle A \rangle)^2.$$

The Ergodic Hypothesis

- The averages obtained by Boltzmann and Gibbs averaging will be the same on condition that:
  - Enough samples are taken i.e. T_∞ and N_∞ are large.
  - Successive samples are statistically independent i.e. there is *no correlation* between the samples.
- This is easy to establish in Gibbs' method since samples are chosen arbitrarily.
- In the Boltzmann method samples must be taken sufficiently far apart in time. MD trajectories must be sampled at intervals longer than the relaxation time.
- The 'Blocking Method' can be used to ensure statistically independent sampling (see later).

Simple Properties of Averages

Average:

$$\langle A \rangle = \frac{1}{N} \sum_{n=1}^{N} A_n$$

A is some system property, such as temperature, pressure, energy etc.
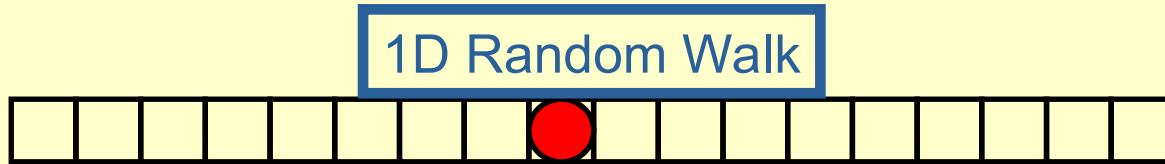
Average of fluctuation:

$$\langle A - \langle A \rangle \rangle = \frac{1}{N} \sum_{n=1}^{N} (A_n - \langle A \rangle) = \langle A \rangle - \langle A \rangle = 0$$

Mean square of fluctuation:

$$\langle (A - \langle A \rangle)^2 \rangle = \frac{1}{N} \sum_{n=1}^{N} (A_n^2 - 2 A_n \langle A \rangle + \langle A \rangle^2),$$

$$= \langle A^2 \rangle - 2 \langle A \rangle^2 - \langle A \rangle^2,$$

$$= \langle A^2 \rangle - \langle A \rangle^2.$$

All these are constants of equilibrium systems

Example 1: Mean Squared Displacement

1D Random Walk
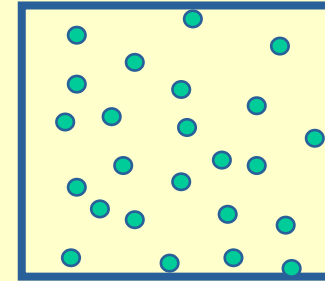
$$x_n = \sum_{i=1}^{n} h_i, \text{ where } h_i = \pm d.$$

$$\langle x_n \rangle = \left\langle \sum_{i=1}^{n} h_i \right\rangle = \sum_{i=1}^{n} \langle h_i \rangle = 0.$$ The ensemble average.

$$\langle x_n^2 \rangle = \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} h_i h_j \right\rangle = \sum_{i=1}^{n} \langle h_i^2 \rangle + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \langle h_i h_j \rangle = n d^2.$$

(Since $\langle h_i h_j \rangle = 0$ if $i \neq j$.)

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Example 2: The Clausius Virial Theorem

$$\frac{d}{dt}\left\langle \sum_i^N m_i \vec{r}_i \cdot \dot{\vec{r}}_i \right\rangle = \left\langle \sum_i^N m_i \dot{\vec{r}}_i \cdot \dot{\vec{r}}_i \right\rangle + \left\langle \sum_i^N m_i \vec{r}_i \cdot \ddot{\vec{r}}_i \right\rangle$$

$$= 2\langle KE \rangle + \left\langle \sum_i^N \vec{r}_i \cdot \vec{f}_i \right\rangle$$

$$= 2\langle KE \rangle + \left\langle \sum_i^N \vec{r}_i \cdot \vec{f}_i^{\,Internal} \right\rangle + \left\langle \sum_i^N \vec{r}_i \cdot \vec{f}_i^{\,External} \right\rangle$$

$$= 2\langle KE \rangle - \langle \Phi \rangle + \left(L_x P A_{yz} + L_y P A_{zx} + L_z P A_{xy} \right)$$

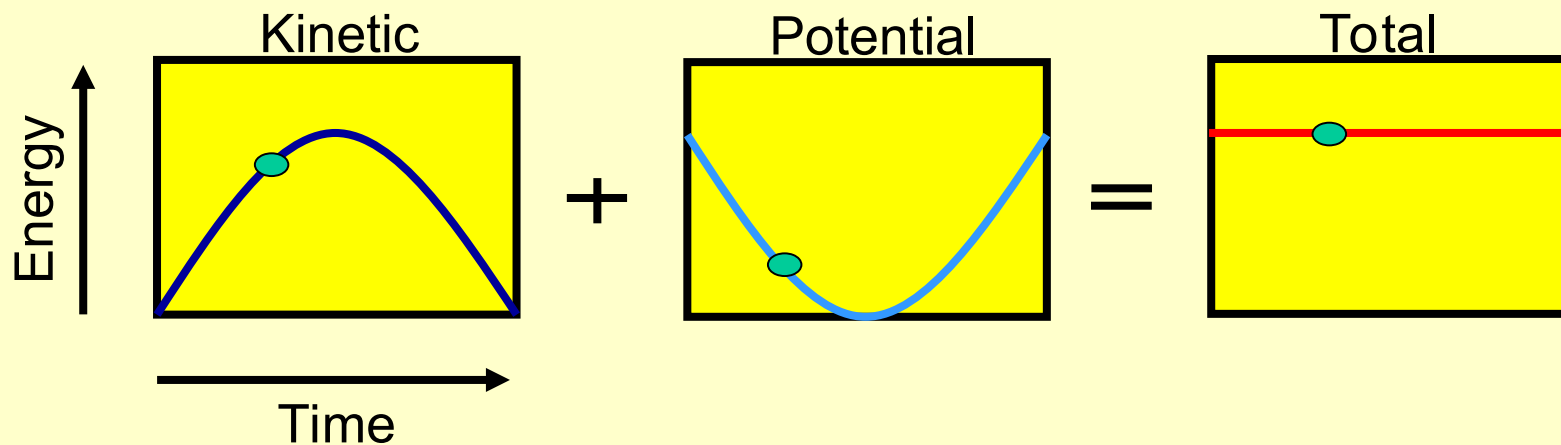$$= 2\langle KE \rangle - \langle \Phi \rangle - 3PV.$$

External force equals the pressure.

But $\left\langle \sum_i^N m_i \vec{r}_i \cdot \dot{\vec{r}}_i \right\rangle = 0$, (no correlation between position and velocity).

So LHS=0 and: $\quad P = \left(2\langle KE \rangle = \langle \Phi \rangle \right) / 3V.$

Fluctuations

- Why do system properties fluctuate?
- Energy is constantly being exchanged between different components.
- Example: Harmonic oscillator (one oscillation).

- Almost all thermodynamic variables fluctuate!

Correlation

- Two sampled variables are correlated if a given value of one of them implies the value of the other
- The variables can be of the same or different types and be sampled at different points in time and space.
- Random (stochastic) variables are by definition uncorrelated.
- If two variables are correlated, then by definition they are not statistically independent, which implies a possible causal link.
- Correlation usually decays with time (or distance), except for ideal systems. The rate of decay is determined by the *correlation time* (or distance) τ.
- Correlation (e.g. dynamics) and randomness (e.g. dissipation) can both be present at the same time.

Calculating Correlation

Integral form: ($A(t)$, $B(t)$ exist over $[0 \leq t \leq T_\infty]$):

$$C(t) = \frac{1}{T_\infty - t} \int_0^{T_\infty - t} (A(u+t) - \bar{A})(B(u) - \bar{B}) \, du .$$

Discrete form: A_i, B_i exist for $[0 \leq i \leq N_\infty]$):

$$C_n = \frac{1}{(N_\infty - n - 1)} \sum_{i=0}^{N_\infty - n - 1} (A_{n+i} - \langle A \rangle)(B_i - \langle B \rangle).$$

Note: C is often normalised so that:

$$C(t)^{max} = C_n^{max} = 1$$

Variable t can be time or distance

Note $C(t)$ and C_n are defined via fluctuations.

Why Correlate the Fluctuations?

$$C_n = \frac{1}{(N_\infty - n - 1)} \sum_{i=0}^{N_\infty - n - 1} (A_{n+i} - \langle A \rangle)(B_i - \langle B \rangle)$$

$$= \frac{1}{(N_\infty - n - 1)} \sum_{i=0}^{N_\infty - n - 1} (A_{n+i} B_i - \langle A \rangle B_i - A_{n+i} \langle B \rangle + \langle A \rangle \langle B \rangle)$$

$$= \frac{1}{(N_\infty - n - 1)} \sum_{i=0}^{N_\infty - n - 1} (A_{n+i} B_i) - \langle A \rangle \langle B \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle$$

$$= \frac{1}{(N_\infty - n - 1)} \sum_{i=0}^{N_\infty - n - 1} (A_{n+i} B_i) - \langle A \rangle \langle B \rangle$$

$$\therefore C_n = C'_n + \langle A \rangle \langle B \rangle.$$

So C_n and C'_n differ only by a constant, $\langle A \rangle \langle B \rangle$, which contains no time dependent information. The time dependence of the correlation thus lies entirely in the fluctuations. C_n decays to zero at long time showing the loss of correlation with time.

Example: Velocity Autocorrelation
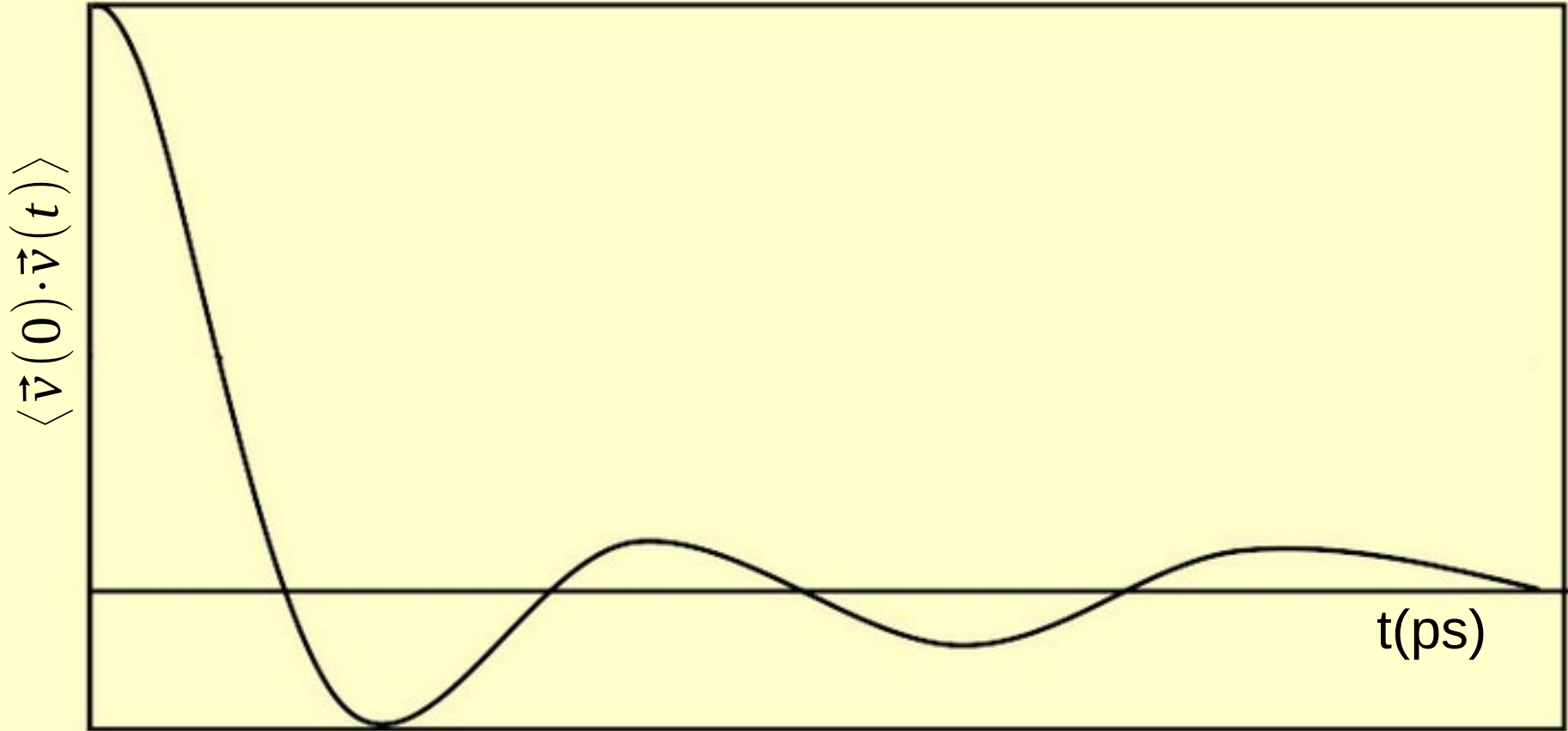
Correlation and Randomness (i)

This is exemplified by the relation between the MSD and the VACF:

Displacement:

$$\vec{r}(t) = \int_0^t \vec{v}(u)\, du$$

Square displacement:

$$\therefore r^2(t) = \int_0^t \int_0^t \vec{v}(u')\cdot\vec{v}(u)\, du'\, du, \quad \text{Let: } u' = u + s$$

Change of variable

$$r^2(t) = \int_0^t \int_{-u}^{t-u} \vec{v}(u+s)\cdot\vec{v}(u)\, ds\, du,$$

Independence of time origin

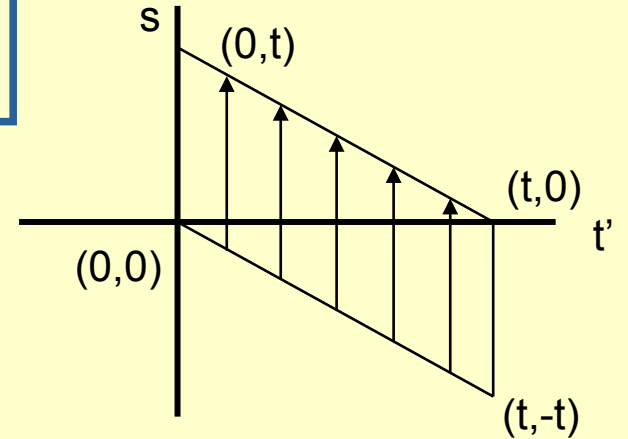$$\langle r^2(t) \rangle = \int_0^t \int_{-u}^{t-u} \langle \vec{v}(s)\cdot\vec{v}(0)\rangle\, ds\, du,$$

Correlation and Randomness (ii)

$$\langle r^2(t)\rangle = 2\int_0^t \int_s^t \langle \vec{v}(s)\cdot\vec{v}(0)\rangle \, ds \, du,$$

$$\langle r^2(t)\rangle = 2\int_0^t (t-s)\langle \vec{v}(s)\cdot\vec{v}(0)\rangle \, ds,$$

$$\langle r^2(t)\rangle = 2t\int_0^t \langle \vec{v}(s)\cdot\vec{v}(0)\rangle \, ds - 2\int_0^t s\langle \vec{v}(s)\cdot\vec{v}(0)\rangle \, ds.$$

Switch order of integration

Until $\langle \vec{v}(s)\cdot\vec{v}(0)\rangle \to 0$ as t increases, $\langle r^2\rangle$ cannot be linear. Only then do both the integrals above settle on a constant value and we can write:

$$\langle r^2(t)\rangle = C_1 t + C_0,$$

where C_1 is the well known diffusion coefficient.

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Example: The Radial Distribution Function

- The RDF is an example of a pair correlation function.
- It is 3D but ignores angular dependence (spherical averaging).
- Describes the average structure of a liquid or solid in terms of the displacements of atoms from each other. i.e. a function of $r_{ij} = |\underline{r}_i - \underline{r}_j|$.
- It is experimentally measurable via its relation to the structure factor $S(k)$, which is related to scattering.
- Can be used to estimate thermodynamics quantities: energy, pressure etc.

RDF Formulae

- Radial Distribution Function (pair correlation):

$$g(r) = \frac{\langle n(r) \rangle}{\rho 4 \pi r^2 \Delta r} = \frac{V}{N^2} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta(r - r_{ij}) \right\rangle.$$
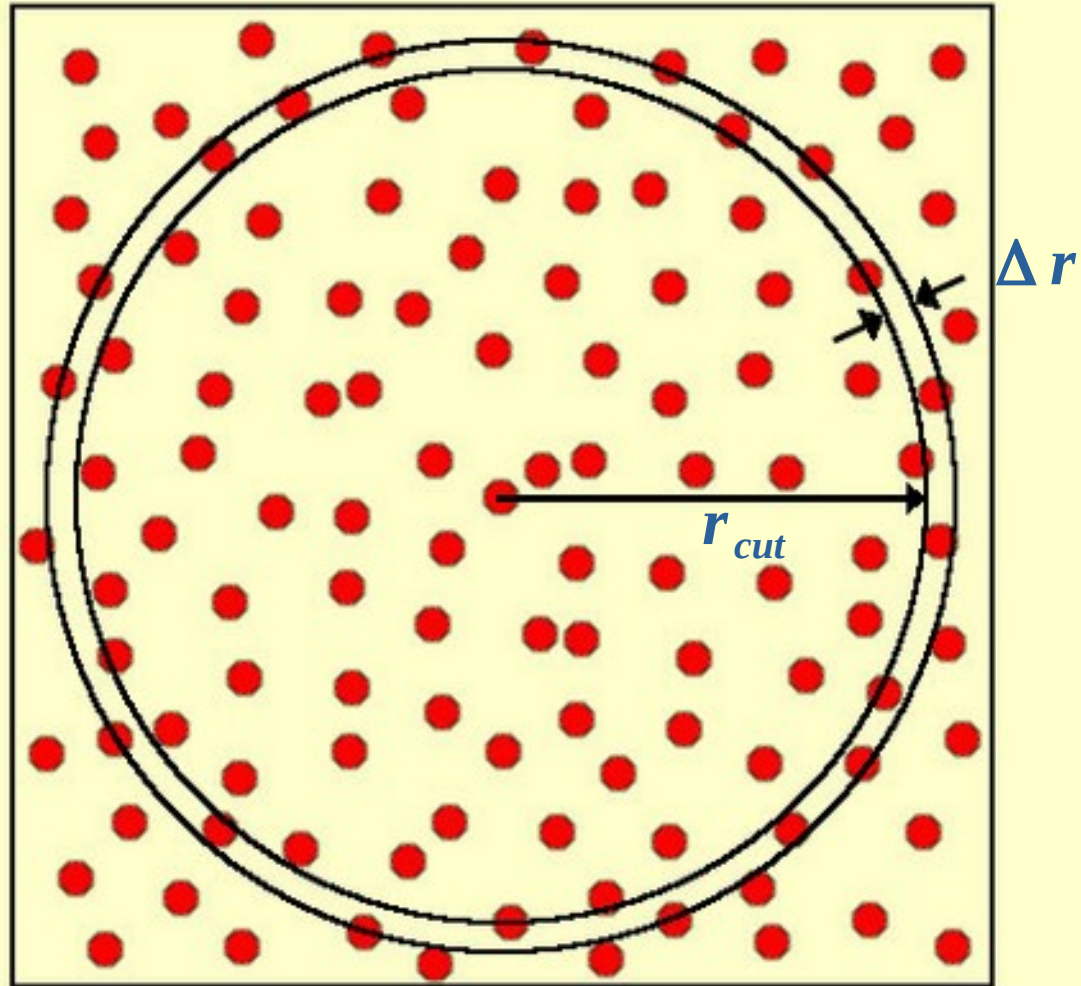
- Structure factor:

$$S(k) = 1 + 4 \pi \rho \int_0^\infty \frac{\sin(kr)}{kr} g(r) r^2 \, dr.$$

$S(k)$ is available from x-ray diffraction.

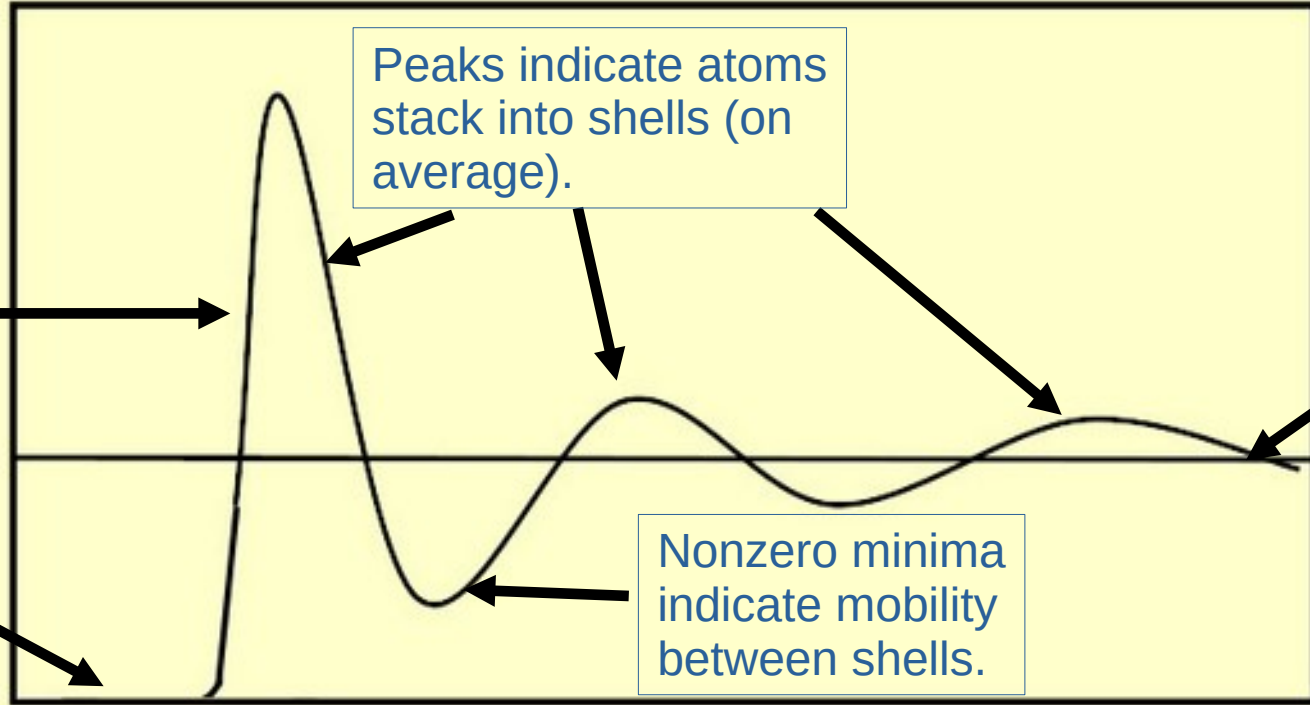# Calculating the RDF

Calculate over the full range of r ($r = n \, \Delta r$) up to r_{cut}

Accumulate data using every atom as the centre in turn.

Continue to accumulate data for new configurations sampled at intervals

Δr

r_{cut}

Typical RDF (Liquid)

Peaks indicate atoms stack into shells (on average).

Peaks broaden as T rises.

In general $g(r)$ tends to the value 1 at long range (uniform density).

At short range atoms cannot fully overlap so $g(r) \sim 0$.

Nonzero minima indicate mobility between shells.

The RDF and Thermodynamic Properties

If $u(r)$ is the pair interaction energy then:

$$U_{conf} = 2\pi\rho_0 \int_0^{r_{cut}} u(r)g(r)r^2\,dr.$$

This integral stops at r_{cut} and requires the long range correction:

$$U_{corr} = 2\pi\rho_0 \int_{r_{cut}}^{\infty} u(r)g(r)r^2\,dr,$$

$$\approx 2\pi\rho_0 \int_{r_{cut}}^{\infty} u(r)r^2\,dr, \quad (g(r)\sim 1 \text{ if } r > r_{cut}).$$

Properties of Correlation Functions (i)

General form (where u,v are time variables):

$$C_{AB}(u,v)=\langle \delta A(u)\,\delta B(v)\rangle=\langle (A(u)-\langle A\rangle)(B(v)-\langle B\rangle)\rangle$$

Stationary property (independence of time origin):

$$C_{AB}(u,v)=\langle \delta A(u-w)\,\delta B(v-w)\rangle=\langle \delta A(u-v)\,\delta B(0)\rangle,$$

$$\equiv\langle \delta A(t)\,\delta B(0)\rangle=C_{AB}(t).$$

Time symmetry:

$$C_{AA}(t)=\langle \delta A(t)\,\delta A(0)\rangle=\langle \delta A(-t)\,\delta A(0)\rangle=C_{AA}(-t).$$

Properties of Correlation Functions (ii)

Time derivatives:

$$\dot{C}_{AB}(t) = \frac{d}{du}\langle \delta A(t+u)\,\delta B(u)\rangle,$$

$$= \langle \delta \dot{A}(t+u)\,\delta B(u)\rangle + \langle \delta A(t+u)\,\delta \dot{B}(u)\rangle = 0.$$

$$\therefore \quad \langle \delta \dot{A}(t)\,\delta B(u)\rangle = -\langle \delta A(t)\,\delta \dot{B}(0)\rangle \quad \text{And}\, \langle \delta \dot{A}(t)\,\delta A(u)\rangle = 0.$$

Fourier Transforms:

Given: $\widetilde{A}(f), \widetilde{B}(f), \widetilde{C}_{AB}(f)$ where $\widetilde{F}(f) = \int_{-\infty}^{\infty} F(t)\exp(-2\pi i f)\,dt$,

then $\quad \widetilde{C}_{AB}(f) = \widetilde{A}^*(f), \widetilde{B}(f).$

Central Limit Theorem

This applies when we have

- M sets of data (samples) taken from a population.
- Each data set consists of N measurements
- The average of each set is: $\bar{A}_N = \dfrac{1}{N} \sum\limits_{i=1}^{N} A_i$
- Then the **Central Limit Theorem** says:
- The mean of the M averages is the mean of the population;
- The error in the population mean is $\sqrt{N}$ times the error of the mean of the averages;
- The distribution of averages tends to Gaussian, no matter what the distribution of the population.

CLT and Gaussian Distribution

$P(R_n)$

0   R_n 1
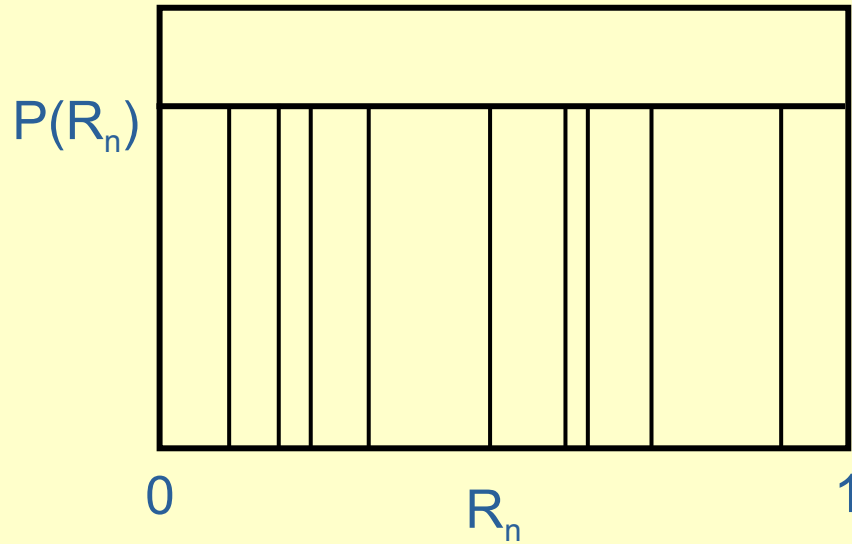
$$\bar{A}_N = \frac{1}{N} \sum_{i=1}^{N} R_i$$

$$\bar{A}_N \approx \text{ Gaussian random Number for } N > 12.$$

$P(R_N) = $ Uniformly sampled number over interval [0,1]

Statistical Errors in Simulations

The error in an average computed by simulation is the expected deviation from the true ensemble average.

- – Simulation average:

$$\bar{A} = \frac{1}{N} \sum_{i=1}^{N} A_i .$$

- – Ensemble average:

$$\langle \bar{A} \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle A_i \rangle .$$

- – Variance:

$$\sigma^2 = \langle \bar{A}^2 \rangle - \langle \bar{A} \rangle^2 .$$

- – Standard Error of the Mean:

$$\delta A = \pm \frac{\sigma}{\sqrt{N}}$$

Caution!

Fluctuations and Standard Error

$$\langle \bar{A} \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} A_i \right\rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} (\delta A_i + \langle \bar{A} \rangle) \right\rangle,$$

$$\langle \bar{A}^2 \rangle = \left\langle \left(\frac{1}{N} \sum_{i=1}^{N} A_i \right)^2 \right\rangle = \left\langle \left(\frac{1}{N} \sum_{i=1}^{N} (\delta A_i + \langle \bar{A} \rangle) \right)^2 \right\rangle,$$

$$= \left\langle \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left(\delta A_i \delta A_j + \delta A_i \langle \bar{A} \rangle + \delta A_j \langle \bar{A} \rangle + \langle \bar{A} \rangle^2 \right) \right\rangle$$

$$= \frac{1}{N^2} \sum_{i=1}^{N} \langle \delta A_i^2 \rangle + \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \langle \delta A_i \delta A_j \rangle + \langle \bar{A} \rangle^2,$$

$$\therefore \langle \bar{A}^2 \rangle = \frac{1}{N} \langle \delta \bar{A}^2 \rangle + \langle \bar{A} \rangle^2,$$

$$\therefore \frac{1}{N} \langle \delta \bar{A}^2 \rangle = \langle \bar{A}^2 \rangle - \langle \bar{A} \rangle^2 = \sigma^2, \quad \text{i.e.} \quad \sigma = \sqrt{\langle \delta \bar{A}^2 \rangle / N}.$$

Fluctuation w.r.t. ensemble mean:
$$\delta A_i = A_i - \langle \bar{A} \rangle$$

Both average to zero:
$$\langle \delta A_i \rangle = 0.$$

$$\delta A_i, \delta A_j$$
are uncorrelated.
$$\therefore \langle \delta A_i \delta A_j \rangle = 0$$

Standard error.

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Example: MSD Error Bars (i)

Recall: $x_n = \sum_{i=1}^{n} h_i$, where $h_i = \pm d$. (In one dimension.)

$$\langle x_n^2 \rangle = \left\langle \left(\sum_{i=1}^{n} h_i \right)^2 \right\rangle = \left\langle \left(\sum_{i=1}^{n} \sum_{j=1}^{n} h_i h_j \right)^2 \right\rangle \Rightarrow n d^2$$

$$\sigma_n^2 = \langle (x_n^2)^2 \rangle - \langle x_n^2 \rangle^2 = \langle x_n^4 \rangle - \langle x_n^2 \rangle^2$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} \langle h_i h_j h_k h_l \rangle - (n d^2)^2$$

Now $\langle h_i h_j h_k h_l \rangle = 0$ if $i \neq j \neq k \neq l$ etc. and $\langle h_i h_j h_k h_l \rangle = d^4$ if (i=j & k=l), (i=k & j=l), (i=l & j=k).

$\Rightarrow$ 30

Example: MSD Error Bars (ii)

From which it can be shown that:

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n}\sum_{l=1}^{n}\left\langle h_i h_j h_k h_l \right\rangle \approx 3\,n^2 d^4.$$

$$\therefore \sigma_n^2 \approx 2\,n^2 d^4, \text{ or } \sigma_n \approx \sqrt{2}\,nd^2, \text{ or } \sigma_n \approx \sqrt{2}\left\langle x_n^2 \right\rangle.$$

This is large! However, most systems have many diffusing particles. So if there are N particles, the analysis yields
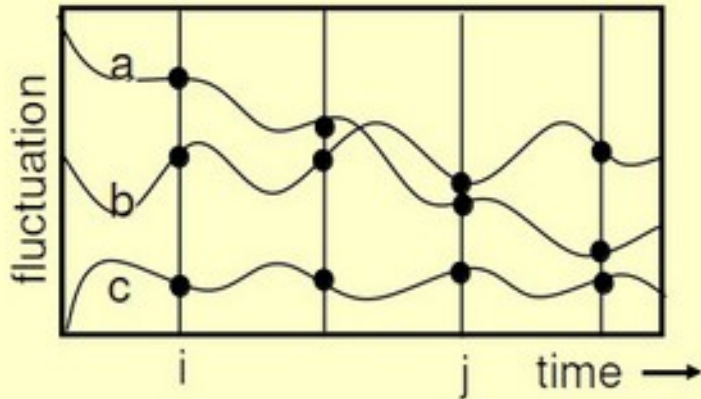
$$\sigma_n \approx \sqrt{\frac{2}{N}\left\langle x_n^2 \right\rangle},$$

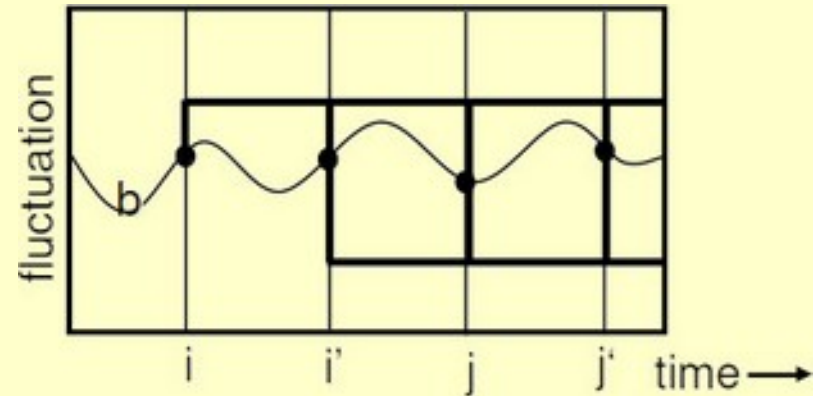as expected from the central limit theorem.

Standard Error in MD

Problem: In molecular dynamics we must calculate ensemble averages (denoted as $\langle A \rangle$) as averages over time, but the data points $\{A_i\}$ may be correlated.
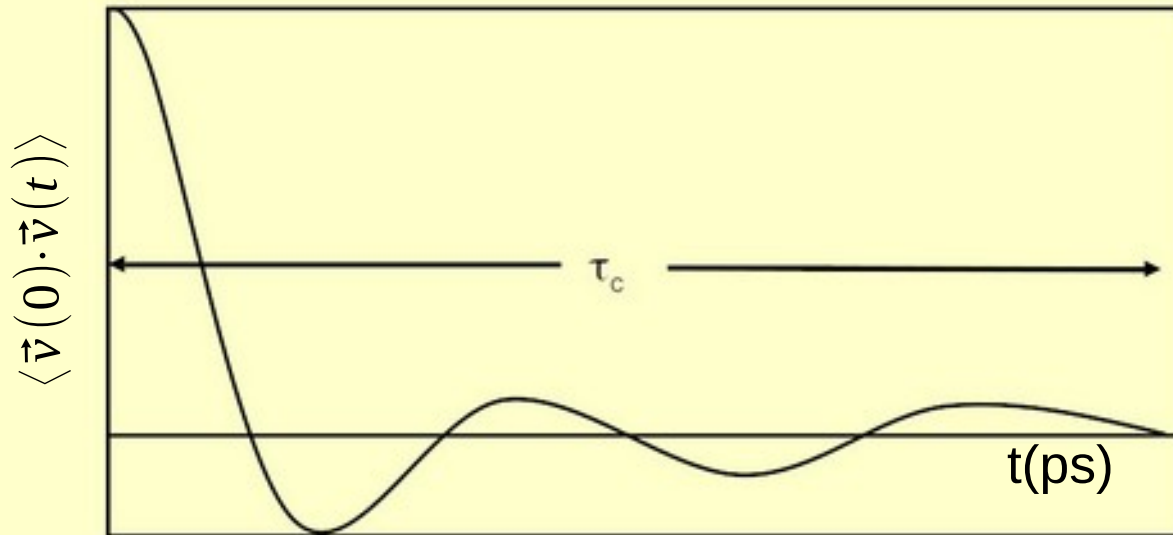
Correlation time τ_c

Tells us the correct separation to use between origins. Can be estimated from correlation functions:

$$\tau_c = \frac{1}{\langle A \rangle^2} \int_0^\infty \left(\langle A(t) A(0) \rangle - \langle A \rangle^2 \right) dt$$


Also indicates when the related MSD plot becomes linear (i.e. becomes a random walk).

Blocking Method

- Blocking transform: $A_i' = \dfrac{1}{2}\left(A_{2i-1} + A_{2i}\right).$

- We can show that $\langle \bar{A}' \rangle = \langle \bar{A} \rangle$ and $\sigma'^2 = \sigma^2$ if data uncorrelated.

- But note that $\Delta t' = 2\Delta t$ (the time interval between data points doubles).

- So successive blocking transforms eventually wash out the correlation time and the estimated σ^2 will converge on the real value. (In general σ^2 increases.)
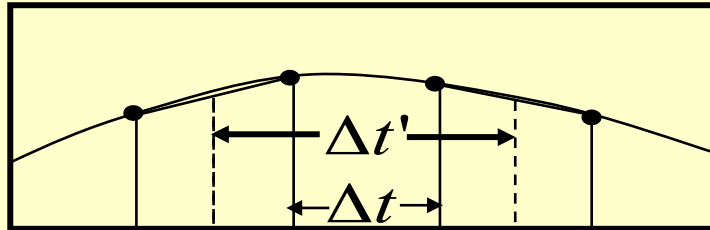
Blocking Procedure

1. For original set $\{A_i\}$ calculate $\bar{A}$ and σ^2.

2. Perform blocking transform $\{A_i\} \Rightarrow \{A'_i\}$.

3. Calculate σ'^2.

4. Repeat steps 2-3 until $N=2$.

5. Plot σ'^2 versus transform number T_n.
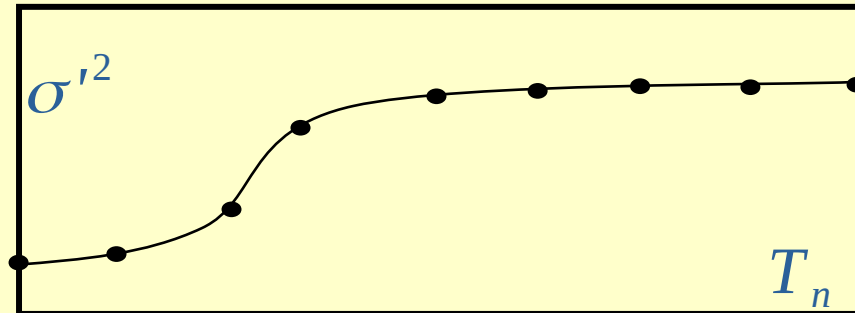
Blocking: Comments

N' decreases by a factor of 2 with each block transform, so the error in σ'^2 increases rapidly. So a smooth convergence is unlikely.

It may not converge at all is there is insufficient data. In which case the maximum value of σ'^2 is used as the best value available.

The same analysis can be used on correlation functions, MSDs etc. since each point on the plot is itself an average.

Ref: H. Flyvbjerg and H. Petersen, J. Chem. Phys. 91 (1989) 461.

Distribution Functions
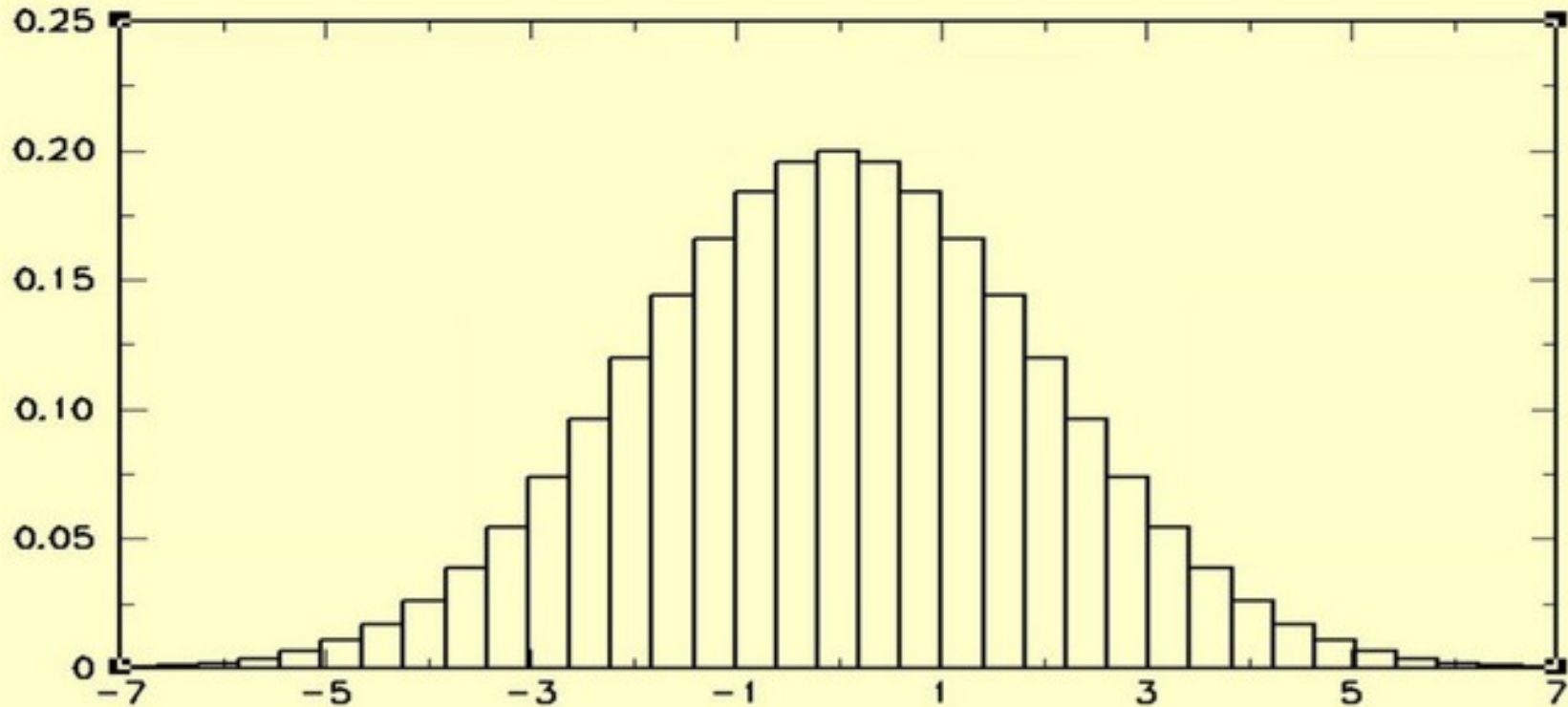
The Gaussian Distribution

Discrete and Continuous Calculations

Discrete normalisation:

$$\sum_{i=-n}^{n} f_i = N$$

Functional normalisation:

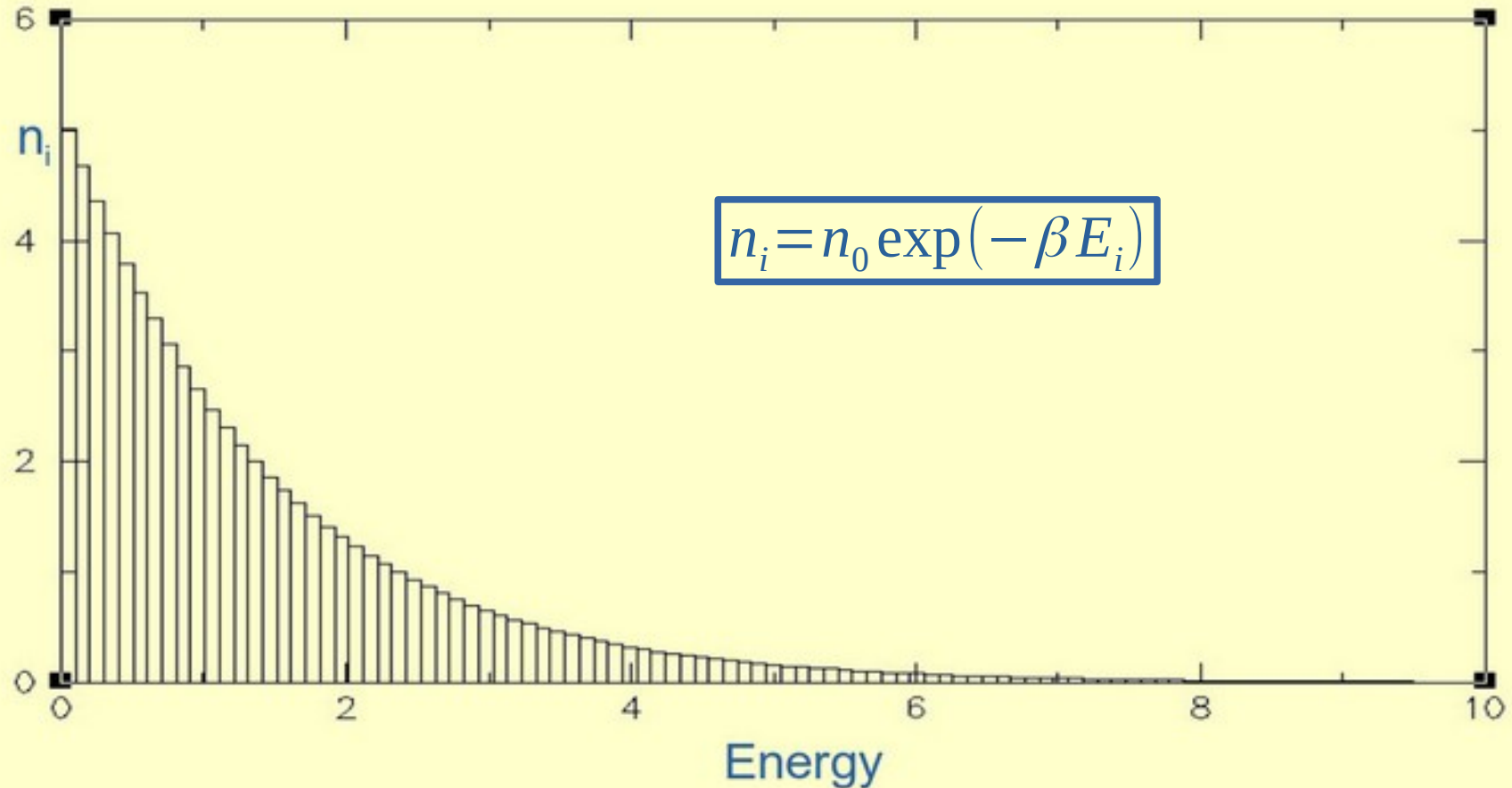$$\int_{-\infty}^{\infty} f(x)\,dx = N$$

Discrete average:

$$\langle A \rangle = \frac{1}{N} \sum_{i=-n}^{n} f_i A_i$$

Functional average:

$$\langle A \rangle = \frac{1}{N} \int_{i=-\infty}^{\infty} f(x) A(x)\,dx$$

The Boltzmann Distribution Function

$$n_i = n_0 \exp\left(-\beta E_i\right)$$

Energy

Why the Boltzmann Distribution?

- Energy among molecules is like money among people: some have a lot, but most have very little.

- Recipe:
  - Start with 1,000,000 'particles/people'
  - Give each particle/person 1 unit of energy/euro
  - Pick a pair of particles/people at random
  - The first particle/person gives one unit of energy/euro to the second (if it has any to give!).
  - Repeat *ad infinitum*.
  - How is the energy/money distributed after *infinite* time?

Result (i)

Looks exponential - but is it?
Try log N vs E plot.

Result (ii)

log(N)

Energy   infinite
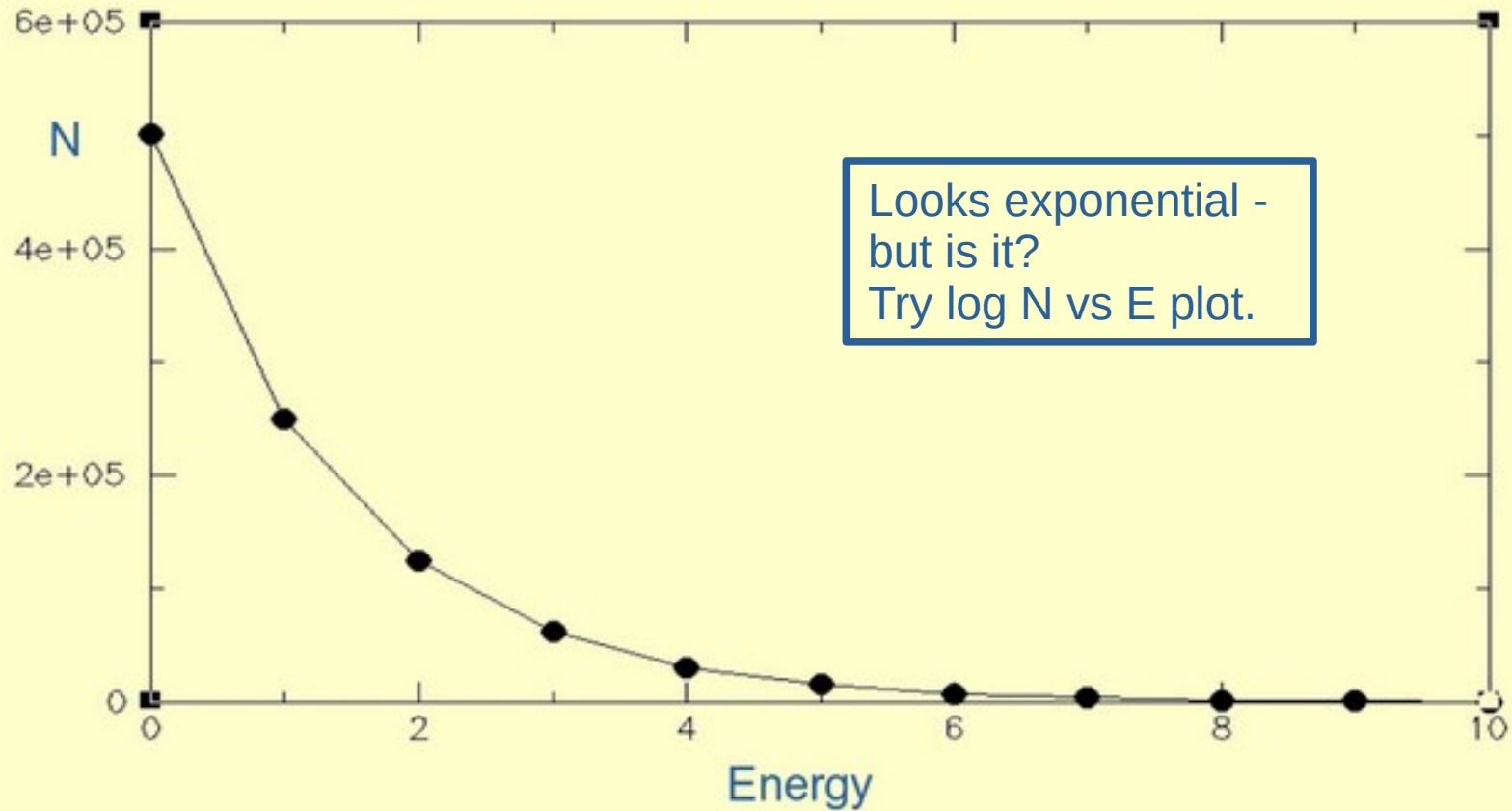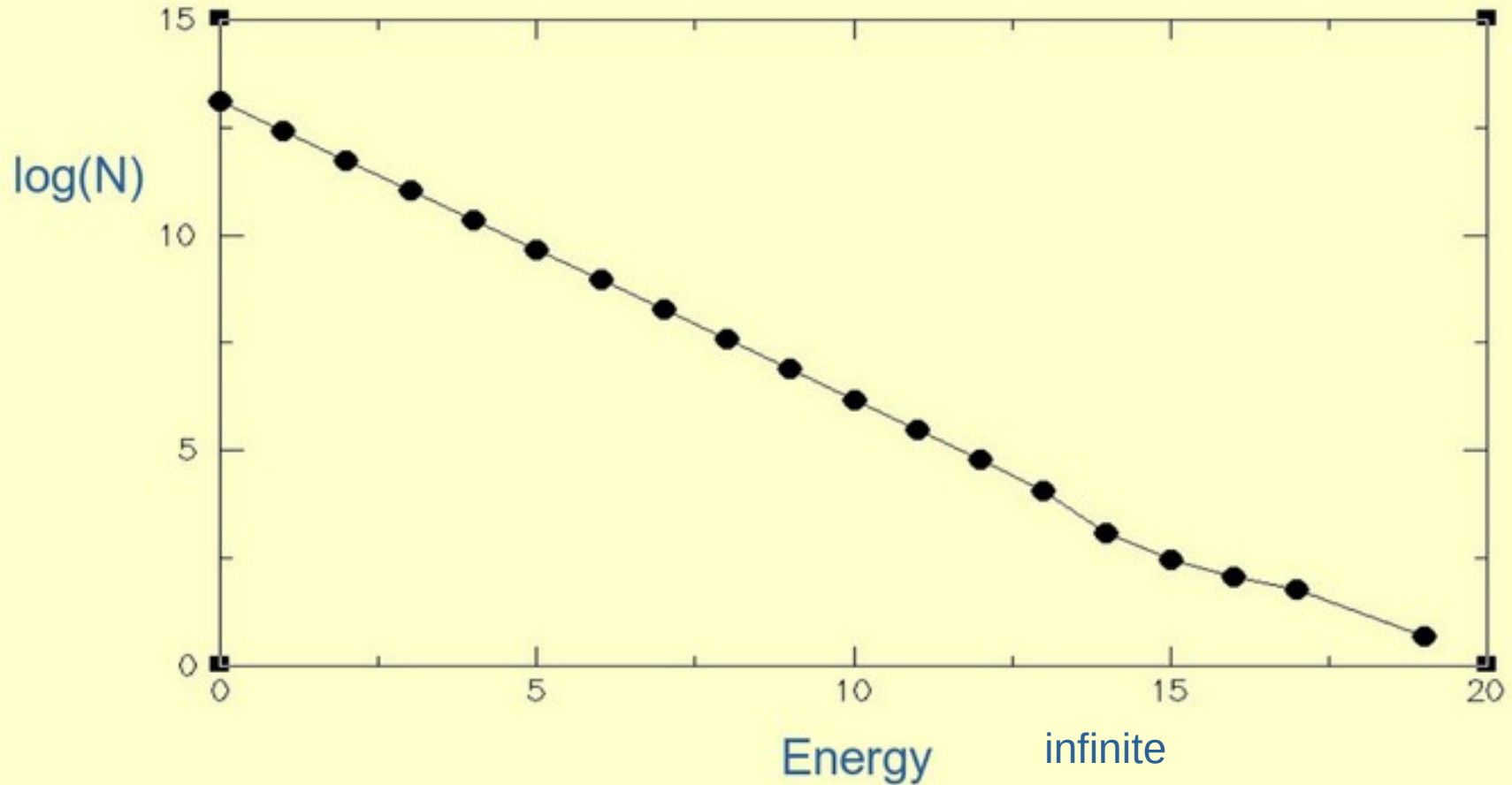
"Proof" of Boltzmann Result (i)

Energy level i populated by n_i molecules.

N molecules and N quanta in total.

So probability of level i losing one quantum is:

$P_i^- = n_i / N$, (where $(n_i \ll N)$ and ignoring second order processes).

Probability of level ($i+1$) losing one quantum is:

$P_{i+1}^- = n_{i+1} / N$, (ignoring second order processes).

Probability of level ($i-1$) gaining one quantum is:

$P_{i+1}^+ = n_{i-1} / (N-1)$, (ignoring second order processes).

"Proof" of Boltzmann Result (ii)

At equilibrium: $P_i^- = P_{i+1}^- + P_{i-1}^+$ so:

$$\frac{n_i}{N} = \frac{n_{i+1}}{N} + \frac{n_{i-1}}{N-1},$$

$$\therefore \delta n_i = (n_{i+1} - n_i) = -\frac{N}{N-1} n_{i-1}.$$

Since $N \approx N-1$ and $n_i \approx n_{i-1}$ we can write: $\delta n_i \approx -n_i$.

It follows that:

$$\frac{\delta n}{\delta \epsilon} = -\alpha n, \text{ and so } n = n_0 \exp(-\alpha \epsilon),$$

is the expected exponential result.

Newtonian Mechanics

Newton's mechanics is best suited to particles moving in three dimensional space, subject to inter-particle forces.

Standard equation of motion:

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

Conservative systems

with:

$$\vec{a}_i = \frac{d^2 \vec{r}_i}{dt^2}.$$

Easiest implementation: Cartesian coordinates

For simple atomic systems:

$$\vec{f}_i = \sum_{j \neq i}^{N} \vec{f}_{ij} = \sum_{j \neq i}^{N} \left\{ \vec{i} \frac{\partial}{\partial x_j} + \vec{j} \frac{\partial}{\partial y_j} + \vec{k} \frac{\partial}{\partial z_j} \right\} u(r_{ij})$$

Example: Motion Under Gravity

$$\vec{r}=(x,y), \qquad \vec{f}=(0,-mg),$$
$$\vec{r}_0=(x_0,0), \qquad \vec{v}_0=(v_0\cos\alpha, v_0\sin\alpha), \quad \boxed{\text{(initial conditions).}}$$

Now, $m\ddot{x}=0$, so $\dot{x}=v_0\cos\alpha$. $\therefore x=x_0+t\,v_0\cos\alpha$, $\boxed{\text{(x \& y separable).}}$

Also, $m\ddot{y}=-mg$, so $\dot{y}=v_0\sin\alpha-gt$, $\therefore y=t\,v_0\cos\alpha-\dfrac{1}{2}gt^2$,

Plotting x vs. y:
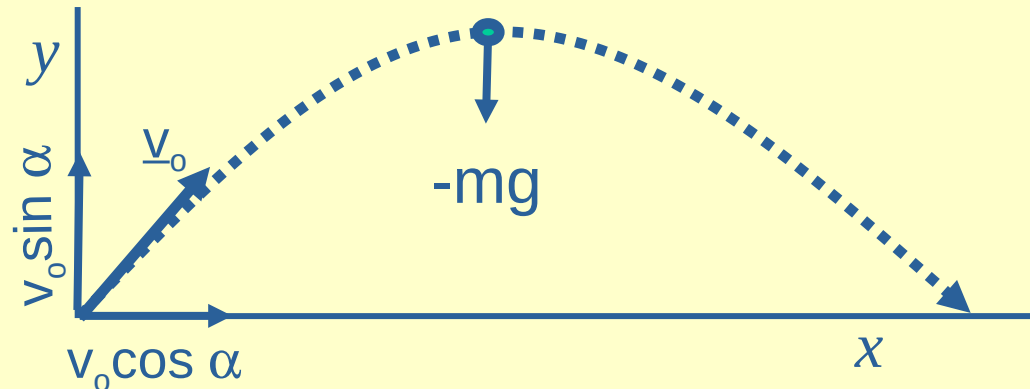
Lagrangian Mechanics (i)

Define: $\Phi = \Phi\left(q_1, q_1, q_2, \ldots, q_i, \ldots, q_{3N}\right)$

q_i = generalised coordinates.

e.g. $\Phi = \sum_{i=1}^{N-1} \sum_{j>i}^{N} u(r_{ij})$,

Conservative systems.

and $K = K\left(q_1, \ldots, q_{3N}, \dot{q}_1, \ldots, \dot{q}_{3N}\right)$

e.g. $K = \dfrac{1}{2} \sum_{i=1}^{N} m_i v_i^2.$

Define Lagrangian as: $L = K - \Phi$. Then the equation of motion is:

Lagrange's equation of motion
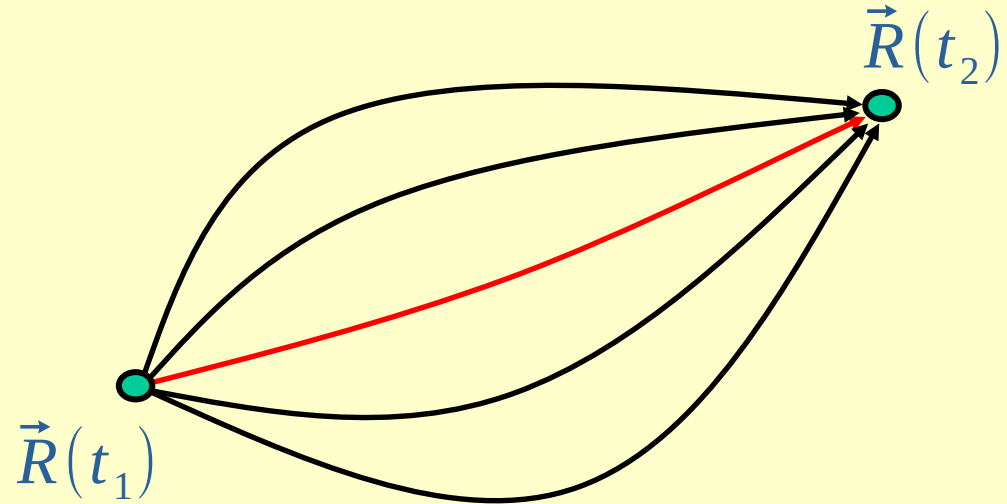
$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = \frac{\partial L}{\partial q}.$$

Equation has the same form for all coordinates

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Lagrangian Mechanics (ii)

Hamilton's principle:
Actual path taken is one
where integral of $L=K-\Phi$
is *extremal*

$$\vec{R}(t_2)$$

$$\vec{R}(t_1)$$

$$\delta s = \delta \int_{t_1}^{t_2} L\left(\{q_i\},\{\dot{q}_i\}\right) dt = 0.$$

Example: Diatomic Molecule (i)

m (x₂,y₂)

θ

d

(X,Y)

(x₁,y₁)

m
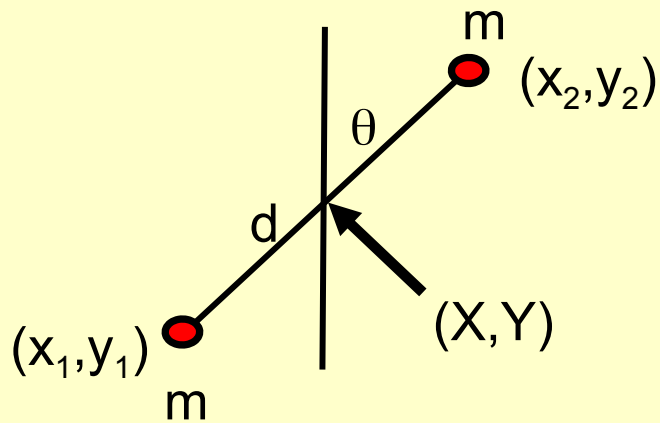
Homonuclear diatomic in 2D free space

$$X=\frac{1}{2}(x_1+x_2), \qquad Y=\frac{1}{2}(y_1+y_2),$$

$$d^2=(x_1-x_2)^2+(y_1-y_2)^2,$$

$$\tan\theta=(x_1-x_2)/(y_1-y_2). \qquad \Rightarrow$$

$$K=m\dot{X}^2+m\dot{Y}^2+\frac{1}{4}md^2\dot{\theta}^2+\frac{1}{4}m\dot{d}^2,$$

$$\Phi=\Phi(d), \qquad L=K-\Phi. \qquad \Rightarrow$$

$$\frac{1}{2}m\ddot{d}=\frac{1}{2}md\dot{\theta}^2-\Phi'(d),$$

Modified vibration equation

$$d\ddot{\theta}+2\dot{d}\dot{\theta}=0,$$

Conserved angular momentum

$$\ddot{X}=0, \qquad \ddot{Y}=0.$$

Conserved linear momentum

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Hamiltonian Mechanics (i)

If $K = K(q_1, \ldots, q_{3N}, \dot{q}_1, \ldots, \dot{q}_{3N})$,

$\Phi = \Phi(q_1, q_1, q_2, \ldots, q_i, \ldots, q_{3N})$

$\boxed{\text{Conservative system}}$

and $L = K - \Phi$, is the Lagrangian, then we define

$$\pi_i = \frac{\partial L}{\partial \dot{q}_i},$$

as the particle momentum *conjugate* to q_i.

Then the classical Hamiltonian is defined as:

$$H = \sum_{i=1}^{3N} \pi_i \dot{q}_i - L.$$

Hamiltonian Mechanics (ii)

Now, it can be shown that for a conservative system:

$$H = 2K - L = K + \Phi,$$
$$\therefore H = E$$

Conservative system

and the equations of motion are:

$$\dot{\pi}_i = -\frac{\partial H}{\partial q_i} \quad \& \quad \dot{q}_i = \frac{\partial H}{\partial \pi_i}.$$

Note $\left(\pi_i, q_i\right)$ are *conjugate variables*.

Example: Diatomic Molecule (ii)

Using same coordinates as before we have:

$$K = m\dot{X}^2 + m\dot{Y}^2 + \frac{1}{4}md^2\dot{\theta}^2 + \frac{1}{4}m\dot{d}^2,$$

$$\Phi = \Phi(d), \qquad L = K - \Phi.$$

$$\pi_d = \frac{1}{2}m\dot{d}, \qquad \pi_\theta = \frac{1}{2}md^2\dot{\theta},$$

$$\pi_X = 2m\dot{X}, \qquad \pi_Y = 2m\dot{Y},$$

$$\frac{1}{2}m\ddot{d} = \frac{1}{2}md\dot{\theta}^2 - \Phi'(d),$$

Modified vibration equation

$$d\ddot{\theta} + 2\dot{d}\dot{\theta} = 0,$$

Conserved angular momentum

$$\ddot{X} = 0, \qquad \ddot{Y} = 0.$$

Conserved linear momentum

m
(x₂,y₂)

θ

d

(X,Y)

(x₁,y₁)

m

Homonuclear diatomic in 2D free space

Same equations as before!
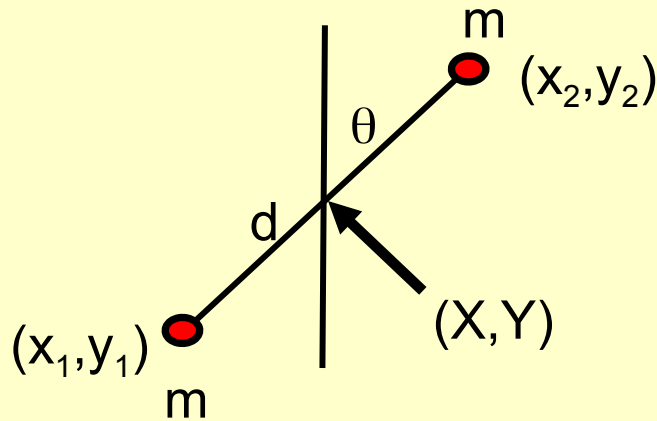
Phase Space

The configuration of a system is defined by the set of Cartesian coordinates $\{x_1,,\dots,x_{3N}\}$ and momenta $\{p_1,,\dots,p_{3N}\}$, which can be represented as a vector in a *6N* dimensional space known as *Phase Space*:

$$\vec{\Gamma}^N\left(x_1,\dots,x_{3N},p_1,\dots,p_{3N}\right).$$

This vector defines a single point in phase space. Every configuration of the system is represented by one point. A set of many different configurations is a cloud of points. A configuration evolving in time traces out a line or trajectory in phase space.

Probability Density

Notation:

$$f_N(\vec{\Gamma}^N;t) \equiv f_N(\vec{r}^n,\vec{p}^n;t) \equiv f_N(x_1,\ldots,x_{3N},p_1,\ldots,p_{3N};t).$$

Normalisation:

$$\int f_N(\vec{\Gamma}^N;t)d\vec{\Gamma}^N \equiv f_N(\vec{r}^n,\vec{p}^n;t)d\vec{r}^N d\vec{p}^N \equiv$$

$$\int \ldots \int f_N(x_1,\ldots,x_{3N},p_1,\ldots,p_{3N};t)dx_1\ldots dx_{3N}dp_1\ldots dp_{3N} = N_{ens}.$$

Probability:

$$\frac{f_N(\vec{\Gamma}^N;t)d\vec{\Gamma}^N}{N_{ens}} \equiv \frac{f_N(x_1,\ldots,x_{3N},p_1,\ldots,p_{3N};t)dx_1\ldots dx_{3N}dp_1\ldots dp_{3N}}{\int \ldots \int f_N(x_1,\ldots,x_{3N},p_1,\ldots,p_{3N};t)dx_1\ldots dx_{3N}dp_1\ldots dp_{3N}}.$$

The Single Particle Distribution Function

The *n* particle distribution:

$$f_n(\vec{r}^{\,n},\vec{p}^{\,n})=\frac{N!}{(N-n)!}\int\int f_N(\vec{r}^{\,N},\vec{p}^{\,N})\,d\vec{r}^{\,(N-n)}\,d\vec{p}^{\,(N-n)}.$$

The one particle distribution:

$$f_1(\vec{r}^{\,1},\vec{p}^{\,1})=N\int\int f_N(\vec{r}^{\,N},\vec{p}^{\,N})\,d\vec{r}^{\,(N-1)}\,d\vec{p}^{\,(N-1)}.$$

The Canonical Ensemble (NVT)

Many simulations are performed in the *Canonical Ensemble*, for which the distribution function is:

$$f_N(\vec{\Gamma}^N) = \frac{h^{-3N}}{N!} \frac{\exp\left(-\beta H_N(\vec{\Gamma}^N)\right)}{Q_N(V,T)}, \qquad \text{with } \beta = \frac{1}{k_B T}.$$

Where $H_N(\vec{\Gamma}^N)$ is the N-particle Hamiltonian and

$$Q_N(V,T) = \frac{h^{-3N}}{N!} \int \exp\left(-\beta H_N(\vec{\Gamma}^N)\right) d\vec{\Gamma}^N.$$

Is the *partition function* or *sum-over-states*.

Ensemble Averages

The probability that the system is at $\vec{\Gamma}^N$ in the volume $d\vec{\Gamma}^N = d\vec{r}^N d\vec{p}^N$ is

$$P(\vec{\Gamma}^N)d\vec{\Gamma}^N = \frac{h^{-3N}}{N!}\frac{\exp\left(-\beta H_N()\vec{\Gamma}^N\right)}{Q_N(V,T)}d\vec{\Gamma}^N.$$

The average of a measurable property $X(\vec{\Gamma}^N)$ is therefore:

$$\langle X\rangle_{NVT} = \frac{h^{-3N}}{N!}\frac{\int \exp\left(-\beta H_N()\vec{\Gamma}^N\right)d\vec{\Gamma}^N}{Q_N(V,T)}.$$

The Configuration Integral

If the Hamiltonian is separable we may write:

$$Q_N(V,T) = \frac{h^{-3N}}{N!} \int_{-\infty}^{\infty} \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m_i}\right) d\vec{p}^N \int_{-\infty}^{\infty} \exp\left(-\beta \Phi(\vec{r}^N)\right) d\vec{r}^N.$$

Since $\displaystyle\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\pi/a}$, then $Q_N(V,T) = \left(\dfrac{\Lambda^{-3N}}{N!}\right) Z_N(V,T)$, where

$$\Lambda = \sqrt{\beta h^2 / 2\pi m}$$

is the deBroglie thermal wavelength and

$$Z_N(V,T) = \int_{-\infty}^{\infty} \exp\left(-\beta \Phi(\vec{r}^N)\right) d\vec{r}^N$$

is the *Configuration Integral*. Note that for an Ideal Gas: $\Phi(\vec{r}^N) = 0$, so

$$Z_N(V,T) = V^N \quad \text{(for Ideal Gas)}.$$

Free Energy

The Helmholz Free Energy (or the thermodynamic potential of the Canonical Ensemble) is defined as:

$$A = -\beta^{-1} \log Q_N(V,T), \text{ where } A = U - TS.$$

For a separable Hamiltonian

$$A = -\beta^{-1} \log\left(\frac{\Lambda^{-3N} V^N}{N!}\right) - \beta^{-1} \log\left(\frac{Z_N(V,T)}{N^N}\right), \text{ or}$$

$$A = A_{id} + A_{ex}, \quad \text{where}$$

$$A_{id} = -\beta^{-1} \log\left(\frac{\Lambda^{-3N} V^N}{N!}\right) \text{ and } A_{ex} = -\beta^{-1} \log\left(\frac{Z_N(V,T)}{N^N}\right).$$

Other Thermodynamic Relations

Pressure:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

Entropy:

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

Internal Energy:

$$U = \left(\frac{\partial(\beta A)}{\partial \beta}\right)_V$$

Specific Heat:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Microcanonical Ensemble (NVE)

Distribution function:

$$f_N(\vec{\Gamma}^N) = \frac{h^{-3N}}{N!} \frac{\delta(H_N(\vec{\Gamma}^N) - E)}{Q_N(V, E)}$$

Partition function:

$$Q_N(V, E) = \frac{h^{-3N}}{N!} \int \delta(H_N(\vec{\Gamma}^N) - E) \, d\vec{\Gamma}^N.$$

Thermodynamic potential (negative entropy):

$$-TS = -\beta^{-1} \log Q_N(V, E).$$

Ensemble of basic Molecular Dynamics simulations (almost!)

Isothermal-Isobaric Ensemble (NPT)

Distribution function:

$$f_N(\vec{\Gamma}^N, V) = \frac{h^{-3N}}{V_0 N!} \frac{\exp\left(-\beta\left(H_N(\vec{\Gamma}^N) + PV\right)\right)}{Q_N(P, T)}$$

Partition function:

$$Q_N(P, T) = \frac{h^{-3N}}{V_0 N!} \int dV \int \exp\left(-\beta\left(H_N(\vec{\Gamma}^N) + PV\right)\right) d\vec{\Gamma}^N$$

Thermodynamic potential (Gibbs free energy):

$$G = -\beta^{-1} \log Q_N(P, T), \quad \text{where} \quad G = A + PV.$$

Grand Canonical Ensemble (μVT)

Distribution function:

$$f(\vec{\Gamma}^N; N) = \frac{h^{-3N}}{N!} \frac{\exp(\beta N \mu) \exp(-\beta H_N(\vec{\Gamma}^N))}{Q(\mu, V, T)}$$

Partition function:

$$Q(\mu, V, T) = \sum_{N=0}^{\infty} \frac{h^{-3N}}{N!} \exp(\beta N \mu) \int \exp(-\beta H_N(\vec{\Gamma}^N)) d\vec{\Gamma}^N$$

Thermodynamic potential (Grand potential Ω):

$$\Omega = -\beta^{-1} \log Q(\mu, V, T), \text{ where } A - N\mu = -PV.$$

Converting Between Ensembles

Partition Function: Thermodynamic Potential:

$$Q_N(V,E) = \frac{h^{-3N}}{N!} \int \delta(H_N(\vec{\Gamma}^N) - E) d\vec{\Gamma}^N, \qquad\qquad -TS,$$

$$Q_N(V,T) = \int Q_N(V,E) \exp\left(-\beta H_N(\vec{\Gamma}^N)\right) d\vec{\Gamma}^N, \qquad A = E - TS,$$

$$Q_N(P,T) = \frac{1}{V_0} \int Q_N(V,T) \exp\left(-\beta PV\right) dV, \qquad\qquad G = A + PV,$$

$$Q(\mu,V,T) = \sum_{N=0}^{\infty} \frac{h^{-3N}}{N!} \exp(\beta N \mu) Q_N(V,T), \qquad -PV = A + N\mu,$$

$$Q_{new} = \int Q_F \exp\left(-\beta f F\right) dF, \qquad\qquad \Psi_{new} = \Psi_F + fF.$$

Where f is an *intensive* variable and F is an *extensive* variable.

TOTT* 1 : Differentiate Q_N by β

For the NVT ensemble:

$$\frac{\partial \log Q_N}{\partial \beta} = \frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} = -\frac{1}{Q_N} \int \int H_N \exp\left(-\beta H_N\right) d\vec{r}^N d\vec{p}^N .$$

So: $U \equiv \langle H_N \rangle = -\dfrac{\partial \log Q_N}{\partial \beta}$. But also it can be shown that:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial \langle H_N \rangle}{\partial T}\right)_V = k_B \beta^2 \left(\langle H_N^2 \rangle - \langle H_N \rangle^2\right).$$

So C_v is related to the fluctuations in U.

* TOTT=Trick of the Trade

TOTT 2: Thermodynamic Perturbation (i)

Let $H = H_0 + \lambda H_1$ with $H_0 \gg H_1$ and $0 \leq \lambda \leq 1$, then:

$$\langle B \rangle_\lambda = Q_N^{-1} \int B \exp\left(-\beta\left(H_0 + \lambda H_1\right)\right) d\vec{\Gamma}^N ,$$

$$\therefore \frac{\partial \langle B \rangle_\lambda}{\partial \lambda} = -\beta Q_N^{-1} \int B H_1 \exp\left(-\beta\left(H_0 + \lambda H_1\right)\right) d\vec{\Gamma}^N$$

$$+ \langle B \rangle_\lambda \beta Q_N^{-1} \int H_1 \exp\left(-\beta\left(H_0 + \lambda H_1\right)\right) d\vec{\Gamma}^N ,$$

$$= -\beta \langle B H_1 \rangle_\lambda + \beta \langle B \rangle_\lambda \langle H_1 \rangle_\lambda$$

$$\therefore \frac{\partial^2 \langle B \rangle_\lambda}{\partial \lambda^2} = \beta^2 \langle B H_1^2 \rangle_\lambda - 2\beta^2 \langle B H_1 \rangle_\lambda \langle H_1 \rangle_\lambda$$

$$+ 2\beta^2 \langle B \rangle_\lambda \langle H_1 \rangle_\lambda^2 - \beta^2 \langle B \rangle_\lambda \langle H_1^2 \rangle_\lambda .$$

TOTT 2: Thermodynamic Perturbation (ii)

Taylor's Expansion:

$$\langle B \rangle_\lambda = \langle B \rangle_\lambda \big|_{\lambda=0} + \lambda \frac{\partial \langle B \rangle_\lambda}{\partial \lambda}\bigg|_{\lambda=0} + \frac{\lambda^2}{2} \frac{\partial^2 \langle B \rangle_\lambda}{\partial \lambda^2}\bigg|_{\lambda=0} + O(\lambda^3).$$

$$\therefore \langle B \rangle_\lambda \approx \langle B \rangle_0 - \lambda \beta \big\{ \langle B H_1 \rangle_0 - \langle B \rangle_0 \langle H_1 \rangle_0 \big\} +$$

$$\frac{\lambda^2}{2} \beta^2 \left\{ \begin{array}{l} \langle B H_1^2 \rangle_0 - 2 \langle B H_1 \rangle_0 \langle H_1 \rangle_0 + \\ 2 \langle B \rangle_0 \langle H_1 \rangle_0^2 - \langle B \rangle_0 \langle H_1^2 \rangle_0 \end{array} \right\} \quad \text{(set } \lambda = 1.\text{)}$$

TOTT 3: Bias Potential

$$\langle B \rangle_0 = \frac{\int \int B(\vec{\Gamma}^N) \exp\left(-\beta H(\vec{\Gamma}^N)\right) d\vec{\Gamma}^N}{\int \int \exp\left(-\beta H(\vec{\Gamma}^N)\right) d\vec{\Gamma}^N},$$

$$\langle B \rangle_0 = \frac{\int \int B(\vec{\Gamma}^N) \exp\left(-\beta\left\{H(\vec{\Gamma}^N) + \Phi_b(\vec{R}^N) - \Phi_b(\vec{R}^N)\right\}\right) d\vec{\Gamma}^N}{\int \int \exp\left(-\beta\left\{H(\vec{\Gamma}^N) + \Phi_b(\vec{R}^N) - \Phi_b(\vec{R}^N)\right\}\right) d\vec{\Gamma}^N},$$

$$\langle B \rangle_0 = \frac{\int \int B(\vec{\Gamma}^N) \exp\left(-\beta\left\{H(\vec{\Gamma}^N) + \Phi_b(\vec{R}^N)\right\}\right) \exp\left(\beta\Phi_b(\vec{R}^N)\right) d\vec{\Gamma}^N}{\int \int \exp\left(-\beta\left\{H(\vec{\Gamma}^N) + \Phi_b(\vec{R}^N)\right\}\right) \exp\left(\beta\Phi_b(\vec{R}^N)\right) d\vec{\Gamma}^N},$$

$$\langle B \rangle_0 = \frac{\left\langle B(\vec{\Gamma}^N) \exp\left(\beta\Phi_b(\vec{R}^N)\right) \right\rangle_b}{\left\langle \exp\left(\beta\Phi_b(\vec{R}^N)\right) \right\rangle_b}.$$

Bias potential:
$\Phi_b(\vec{R}^N)$.

Applications:
Umbrella sampling,
Hyperdynamics.

TOTT 4: Mixed Hamiltonian

Let: $H = (1-\lambda)H_1 + \lambda H_2$, with $(0 \le \lambda \le 1)$.

Differentiate $A = -\beta^{-1}\log Q_N$ with respect to λ,

so: $\quad \dfrac{\partial A}{\partial \lambda} = \dfrac{1}{Q_N}\int (H_2 - H_1)\exp(-\beta H)\,d\vec{\Gamma}^N = \langle \Delta H_{12}\rangle_\lambda$.

It follows that $\quad \Delta A_{12} = \displaystyle\int_{\lambda=0}^{\lambda=1} \langle H_{12}\rangle_\lambda \, d\lambda$.

Application: Free energy calculations

TOTT 5: Calculating Pressure

Given $P = -\left(\dfrac{\partial A}{\partial V}\right)_T$ and $A = -\beta^{-1} \log Q_N(V, T)$,

it follows that $P = \left\langle \left(\dfrac{\partial}{\partial V} H_N(\vec{r}^N, \vec{p}^N)\right)_T \right\rangle$.

Define the scaling relations: $\vec{r}_i = V^{1/3} \vec{s}_i,\ \ \vec{p}_i = V^{-1/3} \vec{\pi}_i,\ \ \vec{\pi}_i = V^{2/3} m_i \dot{\vec{s}}_i$,

where $\{\vec{r}_i, \vec{p}_i\},\ \ \{\vec{s}_i, \vec{\pi}_i\}$, are *conjugate pairs* of variables.
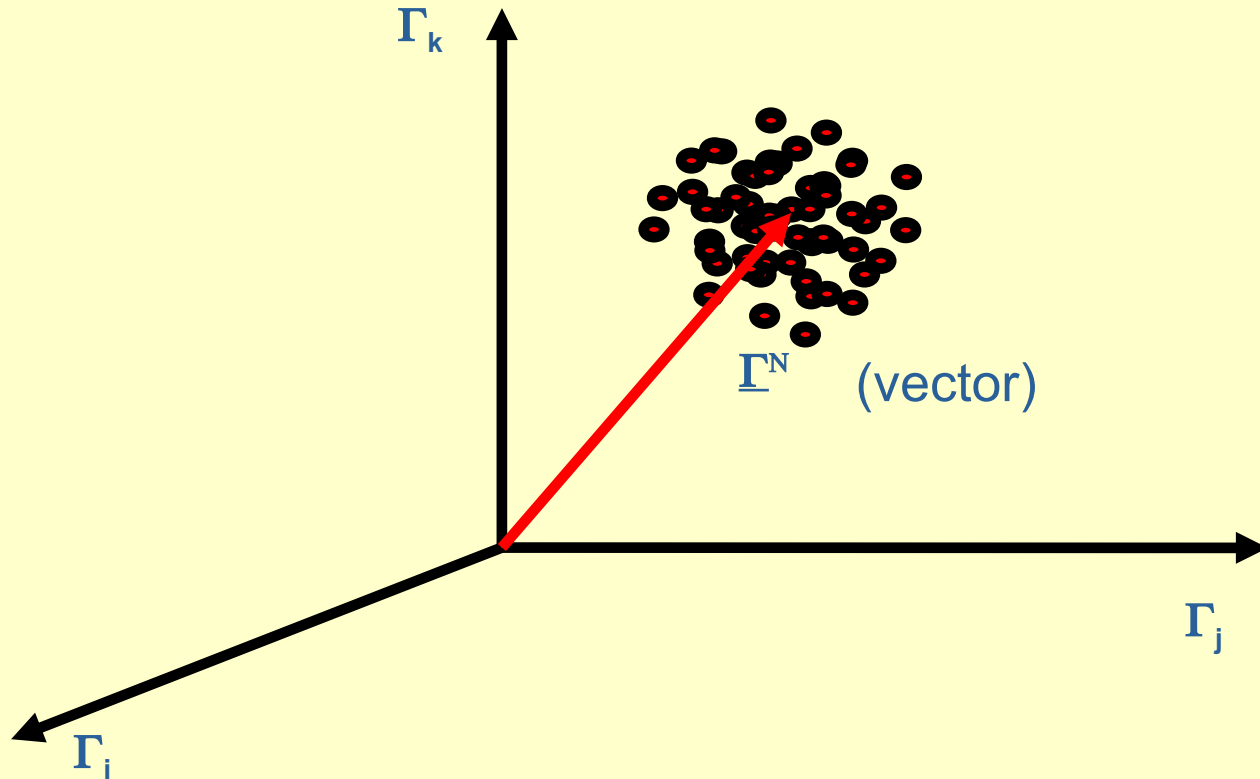
We can show that: $P = \left\langle \left(\dfrac{\partial}{\partial V} H_N(V^{1/3} \vec{s}^N, V^{-1/3} \vec{\pi}^N)\right)_T \right\rangle$.

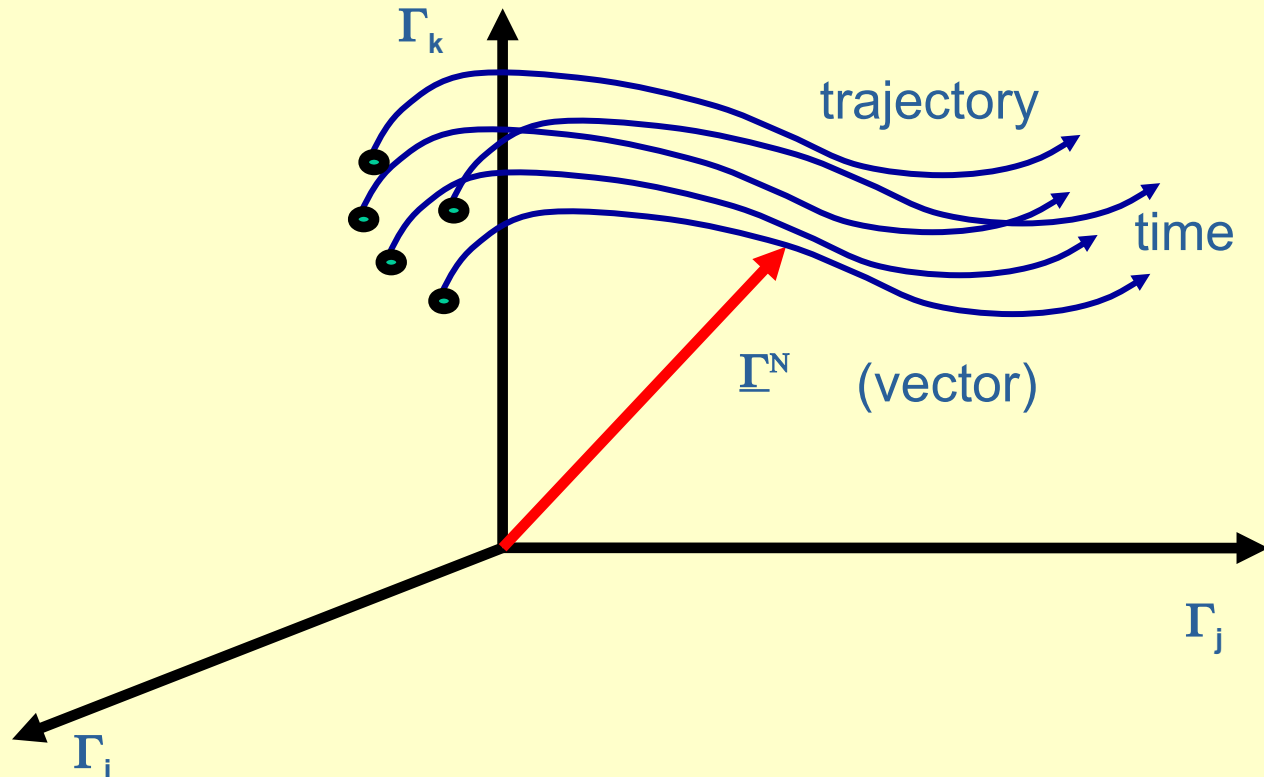After differentiation – revert to original variables.

Application:
All systems!

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The Ensemble in Phase Space

The ensemble samples phase space, generating a sequence of points:

Γ_k

$\underline{\Gamma^N}$ (vector)

Γ_j

Γ_i

If the number of points is large it is meaningful to speak of the density in a volume $d\,\vec{\Gamma}^{N}$ at $\vec{\Gamma}^{N}$.

Phase Space Evolution

Γ_k

trajectory

time

$\underline{\Gamma}^N$ (vector)

Γ_j

Γ_i

- Each point evolves in time along a trajectory governed by the equations of motion of the system.
- Trajectories cannot have same positions and momenta at the same moment in time. So can never cross.
- However they may stay local to each other.

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The Total Time Derivative of f_N

The time derivative of the distribution function $f_N(\vec{\Gamma}^N)$ has the form:

$$\frac{df_N}{dt} = \left(\frac{\partial f_N}{\partial t}\right) + \sum_{i=1}^{3N}\left(\dot{x}_i\frac{\partial f_N}{\partial x_i} + \dot{p}_i\frac{\partial f_N}{\partial p_i}\right).$$

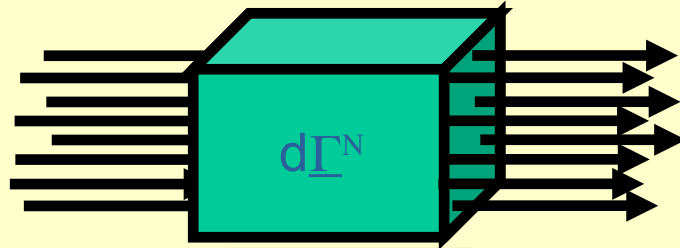The equilibrium distribution function is constant in time so

$$\frac{df_N}{dt} = 0.$$

This shows that the density of phase points around any moving phase point is constant. Trajectories are conserved and the integral of the probability density is constant in time. i.e. like an incompressible fluid.

Liouville Theorem (i)

Occupancy: $\delta N = f_N \, \delta \vec{\Gamma}^N$

Rate of trajectories in

$d\underline{\Gamma}^N$

Fixed Location

Rate of trajectories out

$\dot{x}_i f_N \, \delta \vec{\Gamma}^{N'}$

$\left\{ \dot{x}_i + \dfrac{\partial \dot{x}_i}{\partial x_i} \delta x_i \right\} \left\{ f_N + \dfrac{\partial f_N}{\partial x_i} \delta x_i \right\} \delta \vec{\Gamma}^{N'}$

$$\frac{d(\delta N)}{dt} \approx - \left(f_N \frac{\partial \dot{x}_i}{\partial x_i} + \dot{x}_i \frac{\partial f_N}{\partial x_i} \right) \delta \vec{\Gamma}^N, \qquad \text{and similarly:}$$

$$\frac{d(\delta N)}{dt} \approx - \left(f_N \frac{\partial \dot{p}_i}{\partial p_i} + \dot{p}_i \frac{\partial f_N}{\partial r_i} \right) \delta \vec{\Gamma}^N.$$

Liouville Theorem (ii)

Generally, for all phase variables:

$$\frac{d(\delta N)}{dt} = -\sum_{i=1}^{3N}\left(f_N\left(\frac{\partial \dot{x}_i}{\partial x_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + \left(\dot{x}_i\frac{\partial f_N}{\partial x_i} + \dot{p}_i\frac{\partial f_N}{\partial p_i}\right)\right)\delta\vec{\Gamma}^N,$$

so $\left(\dfrac{\partial f_N}{\partial t}\right) = -\sum_{i=1}^{3N}\left(f_N\left(\dfrac{\partial \dot{x}_i}{\partial x_i} + \dfrac{\partial \dot{p}_i}{\partial p_i}\right) + \left(\dot{x}_i\dfrac{\partial f_N}{\partial x_i} + \dot{p}_i\dfrac{\partial f_N}{\partial p_i}\right)\right).$

Since $\dot{x}_i = \dfrac{\partial H}{\partial p_i}$ & $\dot{p}_i = -\dfrac{\partial H}{\partial x_i}$ (after Hamilton) this becomes

$$\left(\frac{\partial f_N}{\partial t}\right) = -\sum_{i=1}^{3N}\left(\frac{\partial H}{\partial p_i}\frac{\partial f_N}{\partial x_i} - \frac{\partial H}{\partial x_i}\frac{\partial f_N}{\partial p_i}\right).$$

$\boxed{\text{The Liouville Equation}}$

Formal Solution of Liouville's Equation

Define the *Liouville Operator* $\hat{L}$ as:

$$i\hat{L} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i} \frac{\partial}{\partial x_i} - \frac{\partial H}{\partial x_i} \frac{\partial}{\partial p_i} \right).$$

Then the Liouville equation can be written as

$$\frac{\partial f_N}{\partial t} = -i\hat{L} f_N.$$

This has the formal solution

$$f_N(\vec{\Gamma}^N; t) = \exp(-it\hat{L}) f_N(\vec{\Gamma}^N; 0),$$

where the *propagator* $\exp(-it\hat{L})$ can be expanded as:

$$\exp(-it\hat{L}) \approx 1 - it\hat{L} + \frac{1}{2}(it\hat{L})^2 - \frac{1}{3!}(it\hat{L})^3 + O(t^4)$$

This can be used to derive symplectic MD algorithms.

Propagation of System Variables

If $A \equiv A(\vec{r}^N, \vec{p}^N)$, then

$$\frac{dA}{dt} = \sum_{i=1}^{3N} \left(\dot{x}_i \frac{\partial A}{\partial x_i} + \dot{p}_i \frac{\partial A}{\partial p_i} \right),$$
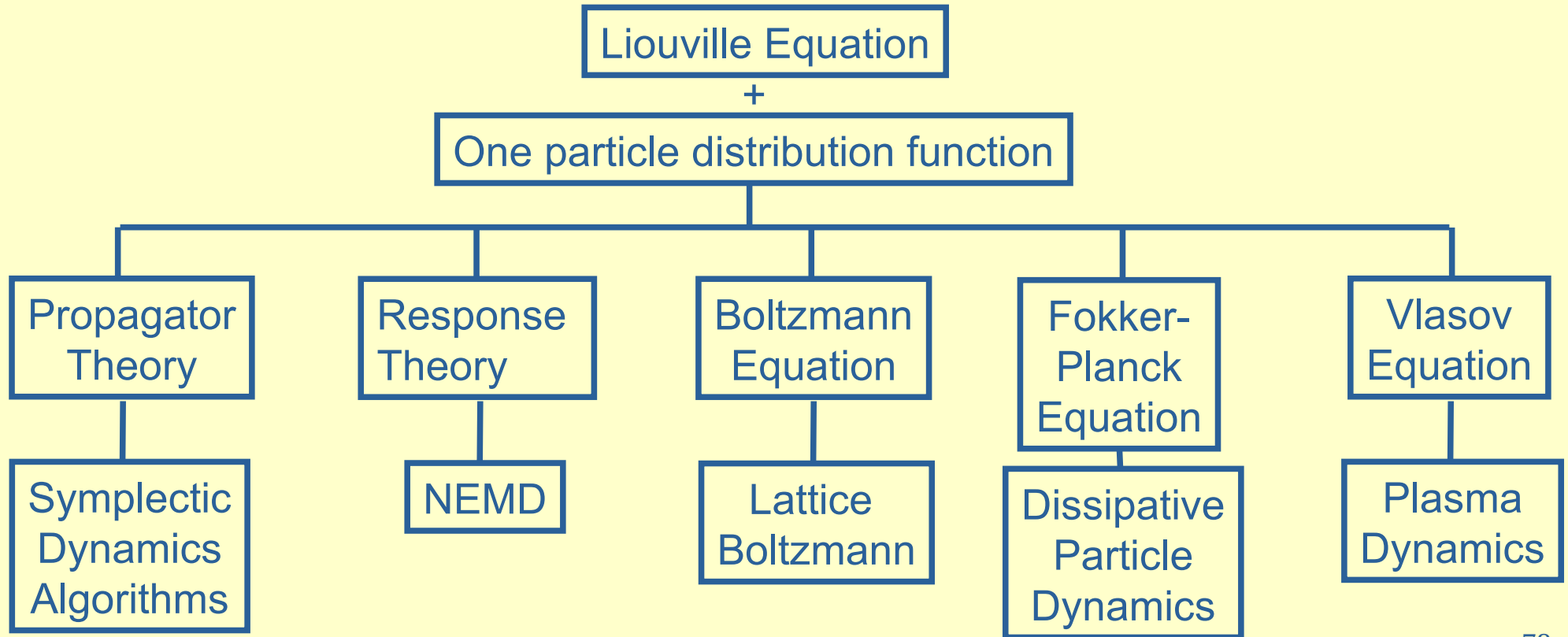
or $\quad \displaystyle\frac{dA}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i} \frac{\partial A}{\partial x_i} + \frac{\partial H}{\partial p_i} \frac{\partial A}{\partial p_i} \right).$

$$\therefore \frac{dA}{dt} = i \hat{L} A.$$

$$\therefore A(t) = \exp(i t \hat{L}) A(0).$$

Property $A(t)$ at time t is uniquely determined by the initial value $A(0)$ and the propagator.

Liouville Equation - Connections

Fluctuation and Dissipation

- How do (slightly) perturbed systems relax to equilibrium?

- Onsager hypothesis: assume the process is the same as normal relaxation from a fluctuation:

$$\frac{\Delta A_{\text{exp}}(t)}{\Delta A_{\text{exp}}(0)} = \frac{\left(A_{\text{exp}}(t) - \bar{A}\right)}{\left(A_{\text{exp}}(0) - \bar{A}\right)} = \frac{\langle \delta A(t)\, \delta A(0)\rangle_0}{\langle \delta A^2 \rangle_0} = \frac{C(t)}{C(0)}.$$

- Formally proved by the Fluctuation-Dissipation theorem.

- Applications: Linear response theory of spectroscopy; transport properties; and stochastic processes.

Fluctuation Dissipation Theorem (i)
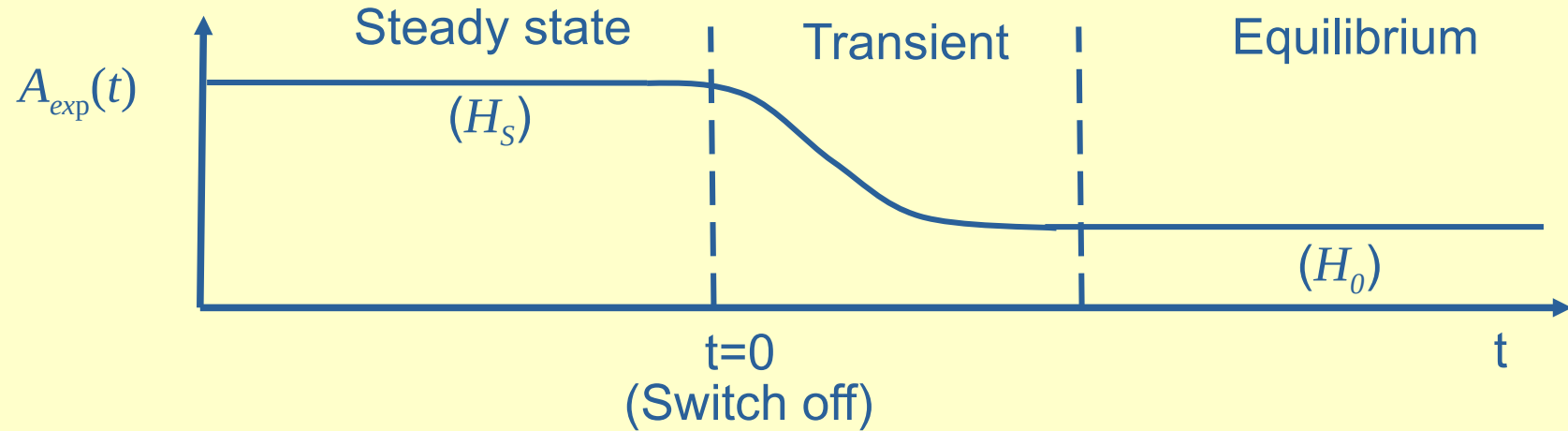
Equilibrium Hamiltonian: H_0.

Field F, coupling variable A: $H_1=-AF$.

Steady state Hamiltonian :
$$H_s=H_0+H_1=H_0-AF.$$

Fluctuation Dissipation Theorem (ii)

Note that: $A_{\exp}(0) \equiv \langle A(0) \rangle_S$ and $A_{\exp}(t) \equiv \langle A(t) \rangle_S$.

From perturbation theory (TOTT2):

$$\langle A \rangle_S = \langle A \rangle_0 - \beta \left(\langle A H_1 \rangle_0 - \langle A \rangle_0 \langle H_1 \rangle_0 \right) + O\left((\beta H_1)^2 \right).$$

Since $H_1 = -AF$ (values fixed at $t=0$):

$$\Delta A_{\exp}(t) = \langle A \rangle_S - \langle A \rangle_0 = \beta F \langle \delta A(0) \delta A(t) \rangle_0 + O(F^2).$$

Also $\Delta A_{\exp}(0) = \beta F \langle \delta A^2 \rangle_0$ so

$$\frac{\Delta A_{\exp}(t)}{\Delta A_{\exp}(0)} = \frac{\langle \delta A(t) \delta A(0) \rangle_0}{\langle \delta A^2 \rangle_0} = \frac{C(t)}{C(0)}.$$

This is the result obtained by Onsager.

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