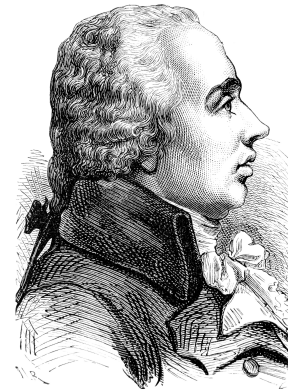


Electronic Structure Methods for Materials Modelling

Ensembles Medley

- Learning Outcomes
 - Changing the *state* function: ***Legendre Transform***
 - Changing the *partition* function: ***Laplace Transform***

- The need for something other than NVE
- How to switch from one ensemble to another: the two L_s
 - Changing the state function: Legendre transform
 - Changing the partition function: Laplace transform
- NVT: the canonical ensemble
 - State and partition functions
 - Thermostats
- NPT: the isobaric (and isobaric/isothermal) ensemble
 - State and partition functions
 - NO Barostats
- η V T: the gran-canonical ensemble
 - State and partition functions
 - NO dealing with a variable number of particles
- Next: Free energy calculations...



Beyond the NVE

Why do we need more?

The NVE ensemble



- A lot of statistical mechanics is strictly valid in the NVE only
- It is the computationally cheapest ensemble
- In NVE the dynamics is as close as possible to the actual evolution of the system (with respect to any other ensemble)
- It is - in principle - possible to simulate a system at a given temperature and pressure
- Experiments are never performed in NVE conditions (constant energy)
- In practice, one has to equilibrate the system at the conditions of interest before attempting a successful (energy properly conserved) MD run
- Many interesting phenomena require the ability of simulating the system along a temperature or pressure gradient (phase transitions)
- You maybe have to enforce a certain temperature or pressure - against the will of the NVE system (exothermic reactions)
- NVE cannot deal with open systems (where the number of particles is not constant anymore)

Ensembles other than NVE allow us to simulate the system within certain conditions, much as a truly computer experiment

The ability to use - but not abuse! - ensembles beyond NVE opens many possibilities
This is true for classical as well as ab-initio MD

Switching ensembles

A couple of - powerful - StatMech tricks...

The two main quantities that characterise an ensemble are its **state function** and its **partition function**

The thermodynamic potential that rules the ensemble (Entropy for NVE)

The phase space volume accessible to the system

Luckily, once you have derived those two for the microcanonical NVE ensemble...

NVE state function

Legendre transform

(~) State function of any other ensemble

With respect to the same (well, almost the same...) variable

NVE partition function

Laplace transform

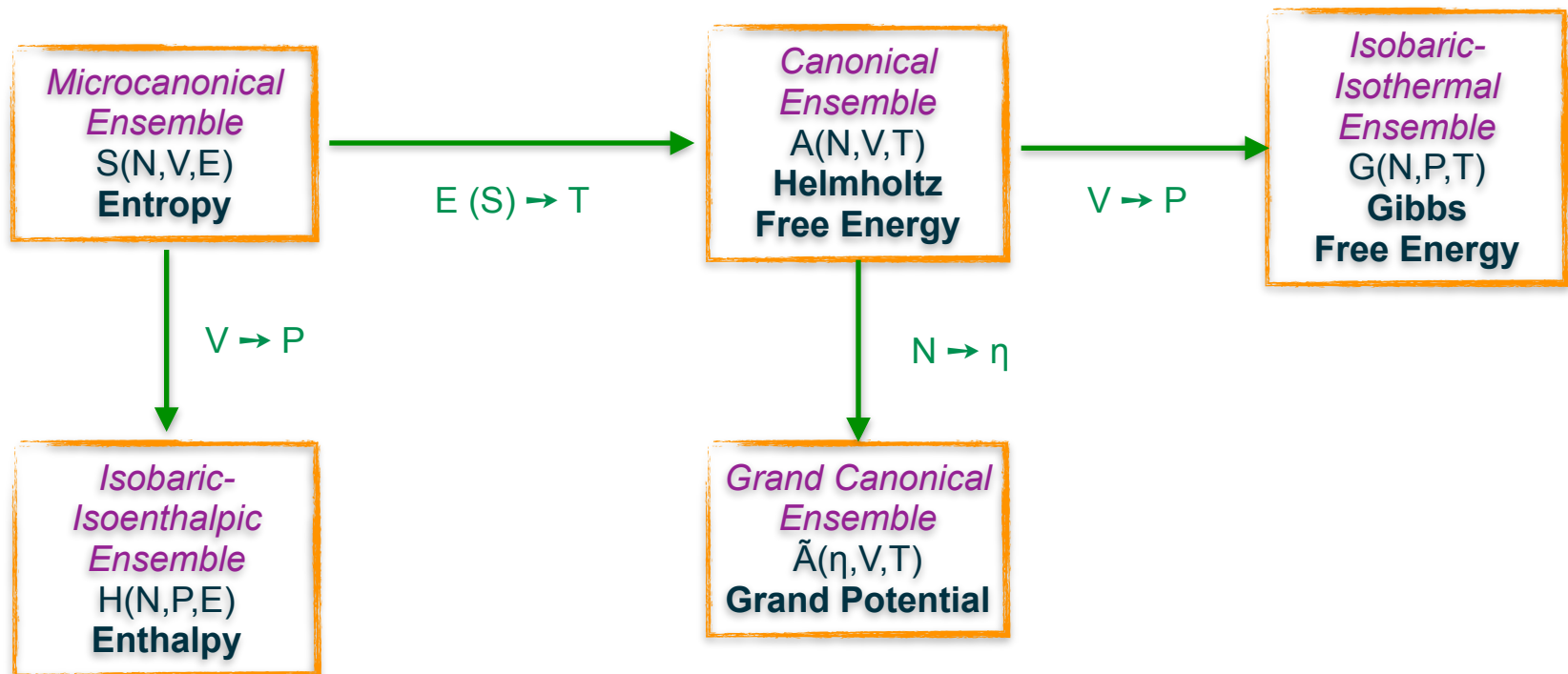
(~) Partition function of any other ensemble

Switching ensembles

The state function

The tool: Legendre transform

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

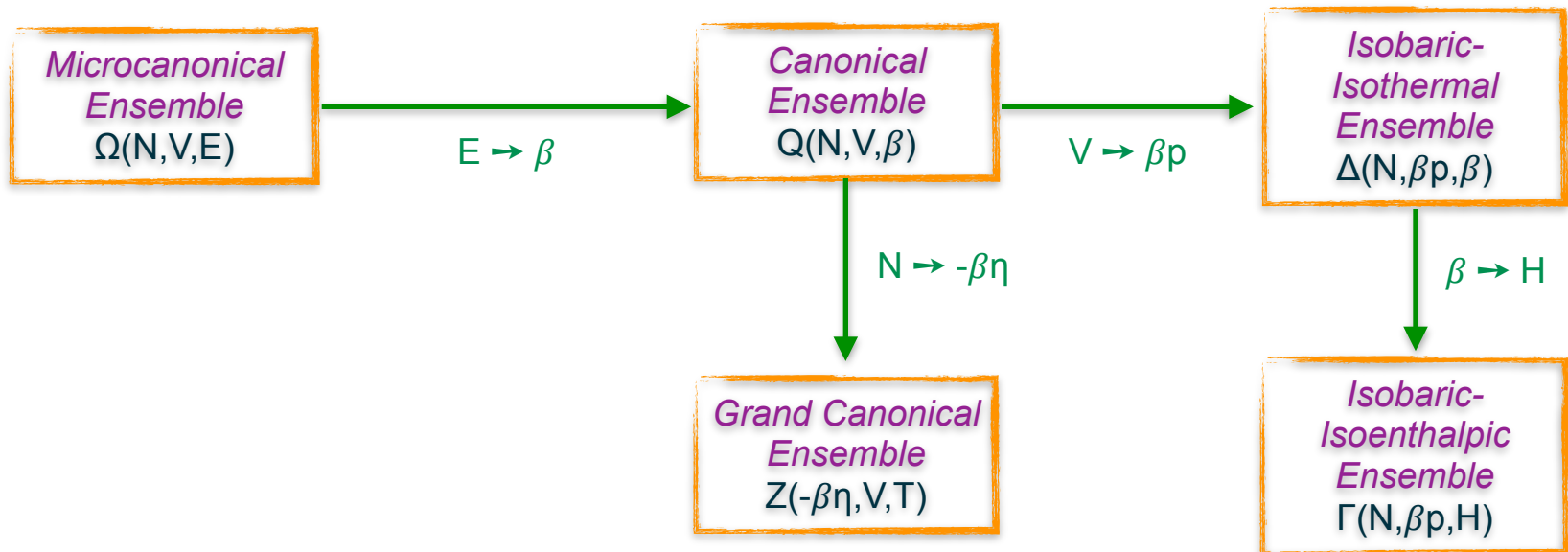


Switching ensembles

The partition function

The tool: Laplace transform

$$\hat{f}(s) = \int_0^\infty e^{-sx} f(x) dx$$

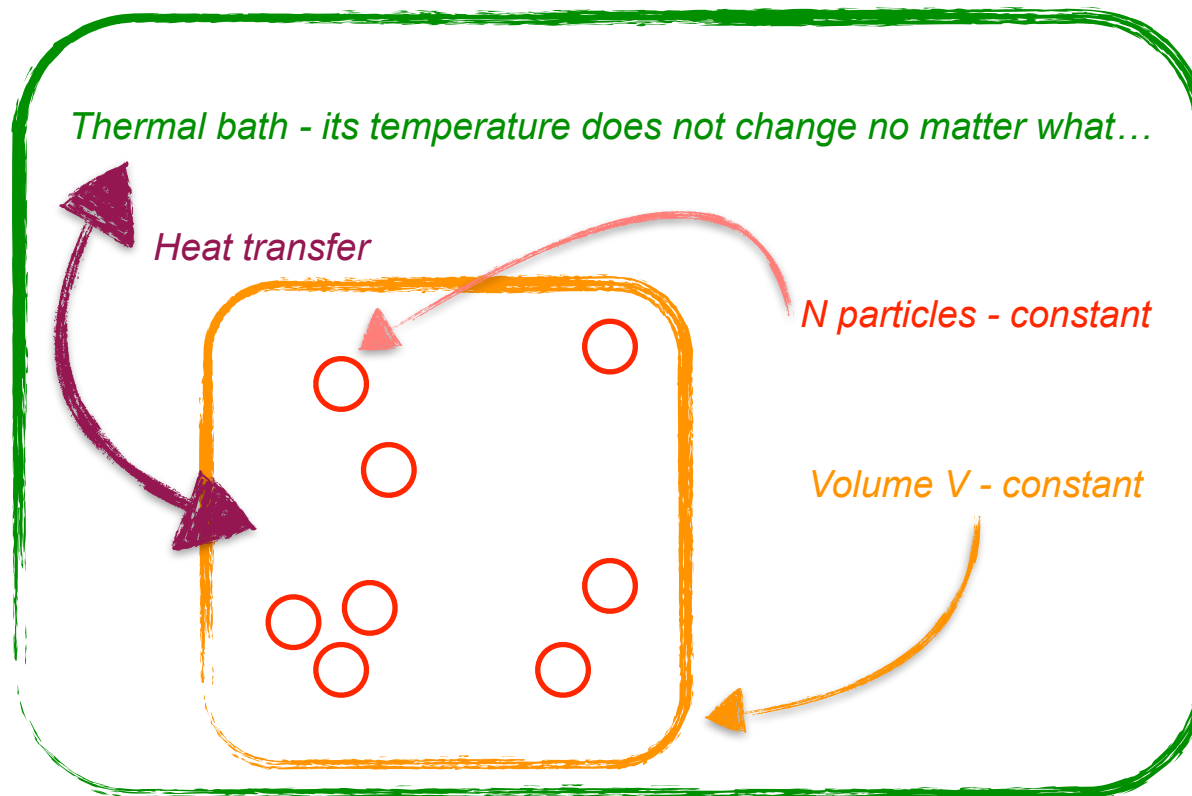


The canonical (N, V, T) ensemble

The idea

The microcanonical ensemble NVE can be imagined as an isolated system

In the NVT ensemble N and V are still fixed, but the system can exchange heat with its surrounding, typically approximated as a thermal bath, or thermal reservoir



The temperature of the system is “constant”
If you do things right, the energy will behave nicely as well...

The canonical (N,V,T) ensemble

Changing the state function

The state function of the NVE ensemble is $S(N, V, E)$ and $\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}$

In NVT we are interested in a state function such as: $A(N, V, T)$

Thus, we rewrite the NVE state function as $E(N, V, S)$ so that $T = \left(\frac{\partial E}{\partial S} \right)_{N,V}$

Now, recall the general formulation of the Legendre transform:

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

In this case, we aim at: $S \rightarrow T$ so that: $\tilde{f} = A$, $f(x) = E(N, V, S)$, $x = S$, $s = T$



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

The state function of the NVT ensemble is the Helmholtz free energy

Not to be confused with the Gibbs free energy!

A is a very useful quantity: for instance, it tells you whether a certain process is thermodynamically favourable or not

However, remember: thermodynamics means very little without kinetics! (More on that in the next Lecture...)

The canonical (N,V,T) ensemble

Changing the partition function

We need another mathematical tool: the Laplace transform: $\hat{f}(s) = \int_0^\infty e^{-sx} f(x) dx$

The variables involved are -almost- the same we have used for the Legendre transform! Thus:

$$\hat{f}(s) = Q(N, V, \beta), \quad f(x) = \Omega(N, V, E), \quad x = E, \quad s = \beta$$



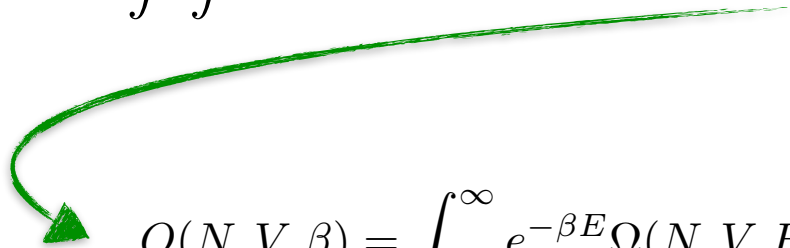
Recall (1)

$$\begin{aligned} \Omega(N, V, E) &= \int \delta(\mathcal{H}(x) - E) dx \\ &= \int \int \delta(\mathcal{H}(x, p) - E) dx dp \end{aligned}$$

Recall (2)

$$\int_0^\infty f(y) \delta(a - y) dy = f(a)$$

As in NVE, Q represents the total number of accessible microscopic states.



$$\begin{aligned} Q(N, V, \beta) &= \int_0^\infty e^{-\beta E} \Omega(N, V, E) dE \\ &= \int_0^\infty dE \int dx [\delta(\mathcal{H}(x) - E) e^{-\beta E}] \\ &= \int dx e^{-\beta \mathcal{H}(x)} \end{aligned}$$



In NVT the Hamiltonian is **not** conserved. Rather, it obeys the Boltzmann distribution as a consequence of the fact that the system can exchange energy with its surroundings.

How do we keep the temperature constant within an MD simulation?

We apply algorithms known as *thermostats*



- Not all the thermostat allow for an actual sampling of the NVT ensemble
- There are many properties that in principle the ideal thermostat should satisfy

We usually come to a compromise...

(Too) many choices available. In this lecture:

From the first thermostat ever (velocity rescaling)...



...to (in my very personal opinion) the best option you have these days
(Bussi-Donadio thermostat)

Thermostats

Velocity rescaling

The naive - also the first one ever - way to do it: **velocity rescaling**

Every n MD steps

$$\mathbf{v}_i^*(t) = \mathbf{v}_i(t) \cdot \alpha, \quad \alpha = \sqrt{\frac{\langle K \rangle_{NVT}}{\langle K \rangle(t)}}$$

recall... $\langle K \rangle_{NVT} = \sum_{i=1}^N \frac{1}{2} m_i v_i^2 = \frac{3}{2} N k_B T$

In an ideal world...

Actual temperature of the system at time t

Target temperature



- Fast
- Obviously very effective

- Literally no fluctuations (worst approach ever)
- Not clear what you are sampling, surely not the NVT ensemble
- Trajectories are strongly discontinuous, particles jump away at every rescaling.

Berendsen thermostat: a smoother evolution of the bare velocity rescaling

We change the temperature (or kinetic energy, equivalent...) according to how far away we are from the target value

$$\frac{d\langle K \rangle(t)}{dt} = \frac{1}{\tau} (\langle K \rangle_{NVT} - \langle K \rangle(t))$$

Implies an exponential decay of the system toward the target temperature

$$\langle K \rangle(t) = \langle K \rangle_{NVT} - c \cdot e^{-\frac{t}{\tau}}$$



* *The Hidden Math* - on Moodle



- One of the best ways to equilibrate (even massive) systems very far away from equilibrium in a very short time
- Wrong fluctuations
- No proper NVT sampling (close enough for some systems, tragic for others)
- Hot solvent-cold solute issue

Bussi-Donadio thermostat: still a (sort of) velocity rescaling!

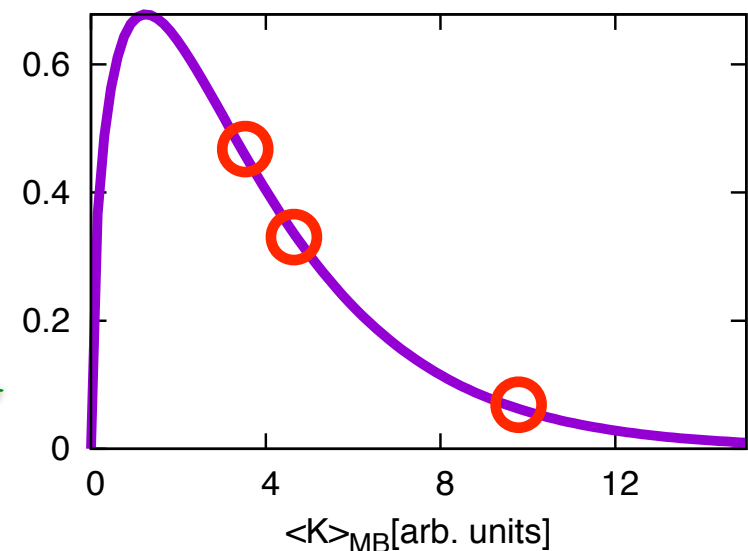


Instead of getting the exact value of the kinetic energy we want (as for the bare velocity rescaling), we pick a **random value** consistent with the canonical distribution for the kinetic energy:

$$\alpha(\text{velocity rescaling}) = \sqrt{\frac{\langle K \rangle_{NVT}}{\langle K \rangle(t)}} \Rightarrow \alpha(\text{Bussi-Donadio}) = \sqrt{\frac{\langle K \rangle_{MB}}{\langle K \rangle(t)}}$$

$$P(\langle K \rangle_{MB}) \propto \sqrt{\langle K \rangle_{MB}} \cdot \exp\left(-\frac{\langle K \rangle_{MB}}{k_B T}\right)$$

$P(\langle K \rangle_{MB})$

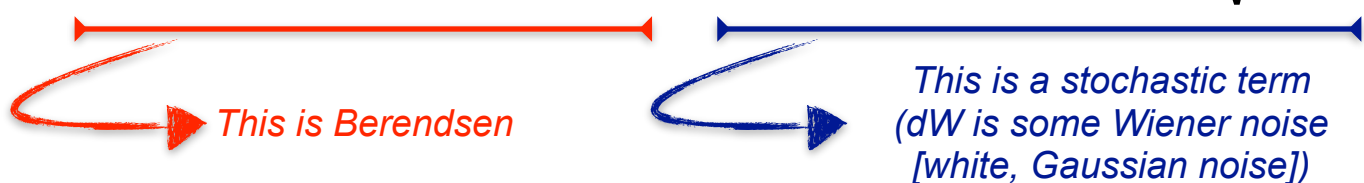


However, this is not smooth enough (discontinuous trajectories are bad...).

We can make it smoother by using the value of $\langle K \rangle(t-1)$ (previous step) to get $\langle K_{MB} \rangle(t)$ (current step):

$$\langle K \rangle(t-1) \Rightarrow \langle K \rangle_{MB}(t)$$

This - evolution/prediction - of K_{MB} is done via a flavour of stochastic dynamics which basically adds a stochastic term to the Berendsen thermostat

$$\frac{d\langle K \rangle(t)}{dt} = \frac{1}{\tau} (\langle K \rangle_{NVT} - \langle K \rangle(t)) + 2\sqrt{\frac{\langle K \rangle(t) \langle K \rangle_{NVT}}{3}} \frac{dW}{\sqrt{\tau}}$$


This is Berendsen

*This is a stochastic term
(dW is some Wiener noise
[white, Gaussian noise])*

That is, the Bussi-Donadio thermostat is an extension of the Berendsen thermostat in which a random force is added to ensure the correct kinetic energy distribution.

Why the Bussi-Donadio thermostat is a flexible tool:

$\lim_{\tau \rightarrow 0} \rightarrow$ The system is instantly thermalised $\langle K \rangle(t) = \langle K \rangle_{NVT} - c \cdot e^{-\frac{t}{\tau}}$

$\lim_{\tau \rightarrow \infty} \rightarrow$ NVE dynamics

Far from equilibrium, the Berendsen, deterministic part dominates and quickly brings the system where you want to.

At equilibrium the stochastic part kicks in, allowing for a proper sampling of the NVT ensemble via stochastic fluctuations consistent with the canonical distribution



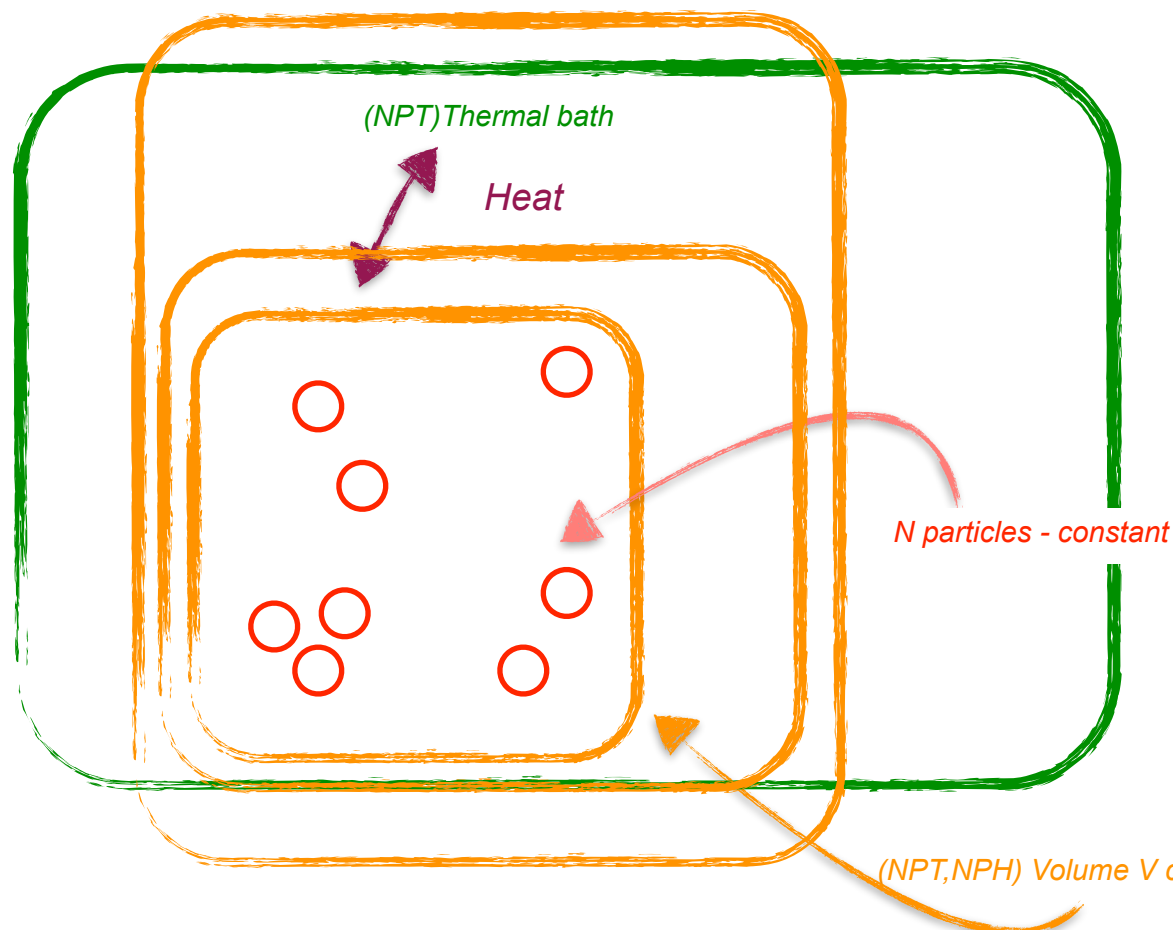
- But for crazily small coupling constants (never good in any case...) one can sample **dynamical properties within the NVT ensemble**.
- It's in CP2K, and I'd would say it's always the best choice

The isobaric ensembleS

Dealing with constant pressure (AND temperature?)

Constant pressure: getting closer to most of the experimental conditions

The volume is not constant anymore!



Two choices:

- **NPT ensemble** - rather popular
- **NPH ensemble** - rather unpopular

Doing this require a barostat (possibly on top of a thermostat)

Isobaric-Isothermal (N,P,T) ensemble

Changing the state function

Legendre once more, this time starting from the NVT state function (the Helmholtz free energy)

$$A(N, V, T) \rightarrow G(N, P, T)$$

We aim at: $V \rightarrow P$ so that:

$$\tilde{f} = G, \quad f(x) = A(N, V, T), \quad x = V, \quad s = P$$



$$G(N, P, T) = H(N, V(P), T) - TS(N, V(P), T)$$

The state function of the NPT ensemble is the Gibbs free energy.
Particularly famous thermodynamics variable...

Isobaric-Isothermal (N,P,T) ensemble

Changing the partition function

Laplace transform of the canonical partition function $Q(N, V, \beta)$

$$V \rightarrow \beta P$$

$$\Delta(N, \beta p, \beta) = \int_0^\infty dV e^{-\beta p V} \cdot Q(N, V, \beta) = \int_0^\infty dV \int dx e^{-\beta \cdot (H(x) + PV)}$$

A not-so-silly detail (apparently lost in many Stat Mech. books):

$$P \text{ vs } \beta p$$

Extensive variables vs conjugate intensive variables

$$V \rightarrow \beta p \quad \text{and} \quad N \rightarrow -\beta \mu$$

Isobaric-Isoenthalpic (N,P,H) ensemble

Changing the state function

Once more - start from NVE and perform a Legendre transform for $V \rightarrow P$

$$E(N, V, S) \quad \tilde{f}(s) = f(x(s)) - sx(s), \quad s = f'(x)$$

In this case, we aim at: $V \rightarrow P$ so that:

$$\tilde{f} = E^*, \quad f(x) = E(N, V, S), \quad x = V, \quad s = P$$



$$E^*(N, P, S) = E(N, V(P), S) - PV(P) = H(N, P, S)$$

The state function of the NPH ensemble (isoenthalpic-isobaric ensemble) is enthalpy

Isobaric-Isoenthalpic (N,P,H) ensemble UCI

Changing the partition function

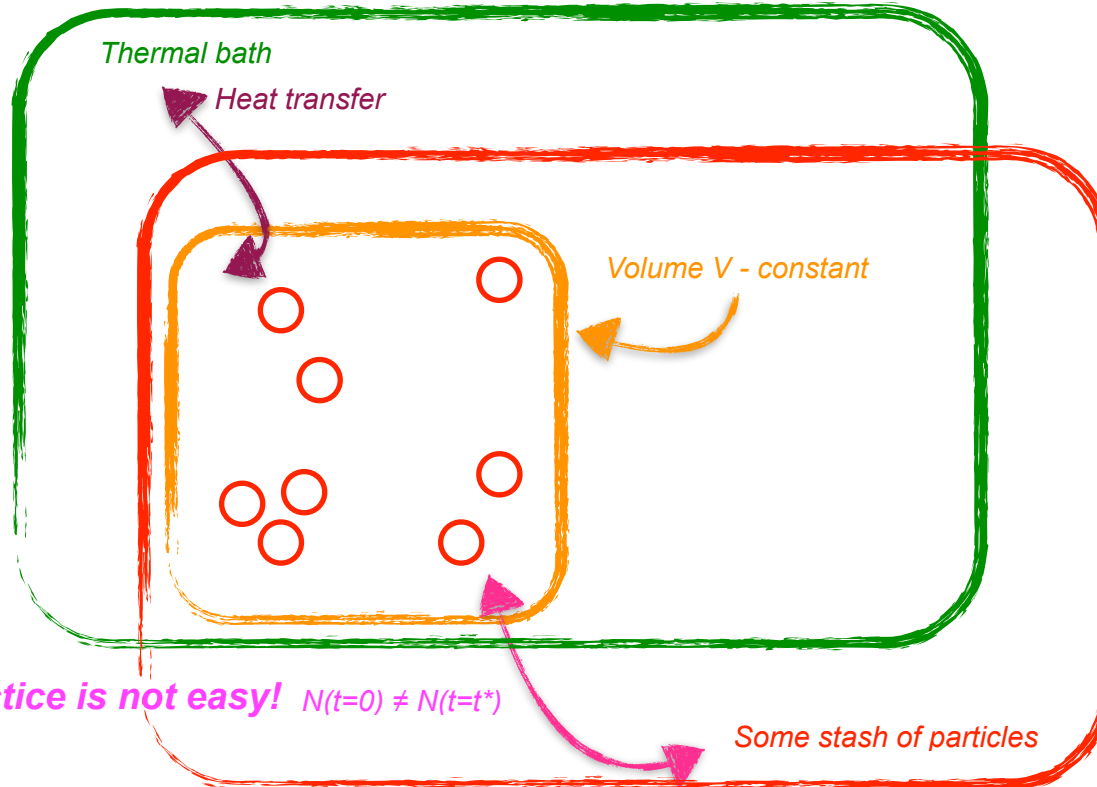
Exercise!



Grand canonical (μ, V, T) ensemble

The idea

In the (μVT) ensemble, the number of particles is not a constant anymore



The chemical potential μ is

$$\mu_i(\mu, V, T) = \left(\frac{\partial A}{\partial N_i} \right)_{V, T, N_{j \neq i}} \quad \text{or...} \quad \mu_i(\mu, P, T) = \left(\frac{\partial G}{\partial N_i} \right)_{P, T, N_{j \neq i}}$$

Yes, there is a (μ, P, T) ensemble...

The chemical potential can be thought of as a measure of how much do you pay to insert an additional particle in the system

Grand canonical (μ, V, T) ensemble

Changing the state function

Legendre again, this time starting from the canonical ensemble.
Instead of conserving the number of particles we want to conserve the chemical potential μ

$$N \rightarrow \mu$$

$$\tilde{f}(s) = \tilde{A}(\mu, V, T), \quad f(x) = A(N, V, T), \quad x = N, \quad s = \mu$$



$$\tilde{A}(\mu, V, T) = A(N(\mu), V, T) - \mu N(\mu)$$

The state function of the Grand Canonical ensemble is known as “the Grand Potential”

Grand canonical (μ, V, T) ensemble

Changing the partition function

Laplace transform of the canonical partition function $Q(N, V, \beta)$

$$N \rightarrow -\beta\mu$$

Some would say it's an inverse Laplace transform,
but in here everything is real, so it's just the sign, really...

$$\begin{aligned}\mathcal{Z}(-\beta\mu, V, \beta) &= \int_0^\infty e^{\beta\mu N} \cdot Q(N, V, \beta) \\ &= \sum_{N=0}^{\infty} \int dx \, e^{\beta(\mu N - \mathcal{H}(x))}\end{aligned}$$

The quantum case

Long & easy ways...

We *could* derive the (quantum) NVE ensemble from the Liouville(-Von Neumann) equation - exactly as we did for the classical case

And, we *could* derive all the other (quantum) ensembles from the quantum NVE ensemble



That would be a long way to go...

The easy way:


Classical equilibrium phase space distribution functions




Quantum operators

Recall how do we perform an ensemble average...

Classical Statistical Mechanics


$$\begin{aligned}\langle p \rangle &= \frac{1}{N_\lambda} \sum_{\lambda=1}^{N_\lambda} p(x_\lambda, t = t^*) \\ &= \frac{1}{\int F(\mathcal{H}(x)) dx} \int F(\mathcal{H}(x)) p(x) dx\end{aligned}$$

Quantum Statistical Mechanics


$$\langle \hat{p} \rangle = \frac{1}{N_\lambda} \sum_{\lambda=1}^{N_\lambda} \langle \psi^\lambda | \hat{p} | \psi^\lambda \rangle$$

The quantum case

Long & easy ways...

For instance...

Classical Statistical Mechanics

$$\langle p \rangle_{NVT} = \frac{1}{Q(N, V, T)} \int e^{-\beta H(x)} p(x) dx$$

$$\langle p \rangle_{NPT} = \frac{1}{\Delta(N, P, T)} \int e^{-\beta(H(x) + PV)} p(x) dx$$

$$\langle p \rangle_{\mu VT} = \frac{1}{\mathcal{Z}(\mu, V, T)} \int e^{-\beta(H(x) - \mu N)} p(x) dx$$

Quantum Statistical Mechanics

$$\langle \hat{p} \rangle_{NVT} = \frac{1}{Q(N, V, T)g(E_k)} \sum_k g(E_k) e^{-\beta \hat{\mathcal{H}}} \langle E_k | \hat{p} | E_k \rangle$$

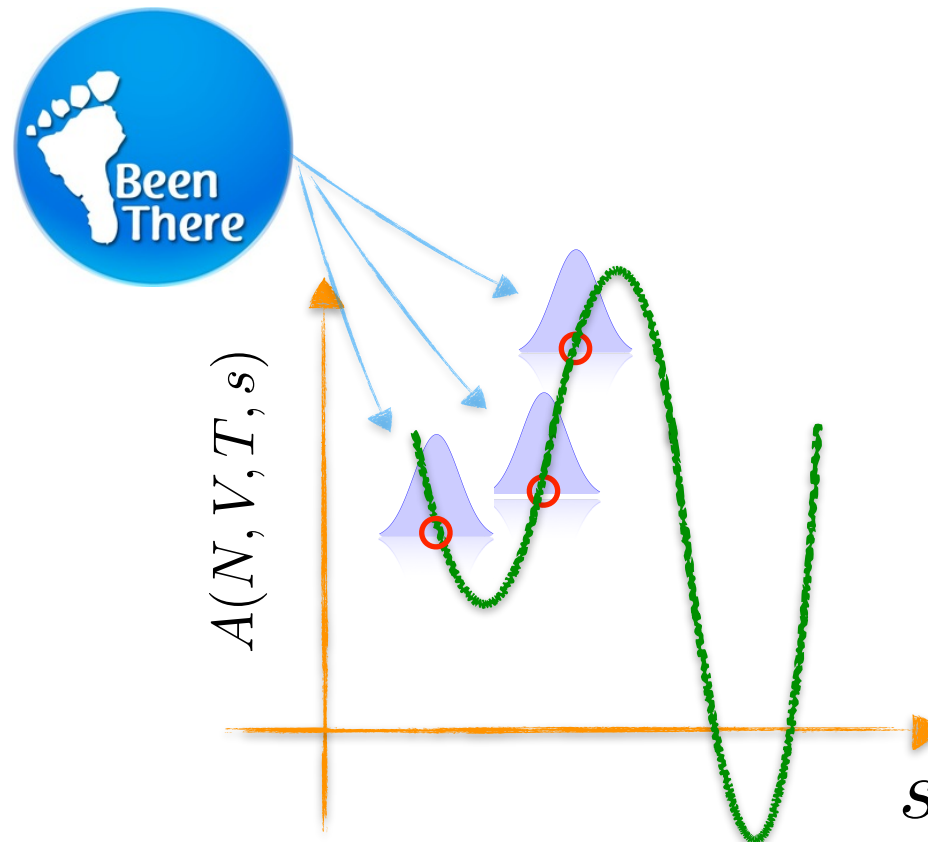
$$\langle \hat{p} \rangle_{NPT} = \frac{1}{\Delta(N, P, T)g(E_k)} \sum_k g(E_k) e^{-\beta(\hat{\mathcal{H}} + PV)} \langle E_k | \hat{p} | E_k \rangle$$

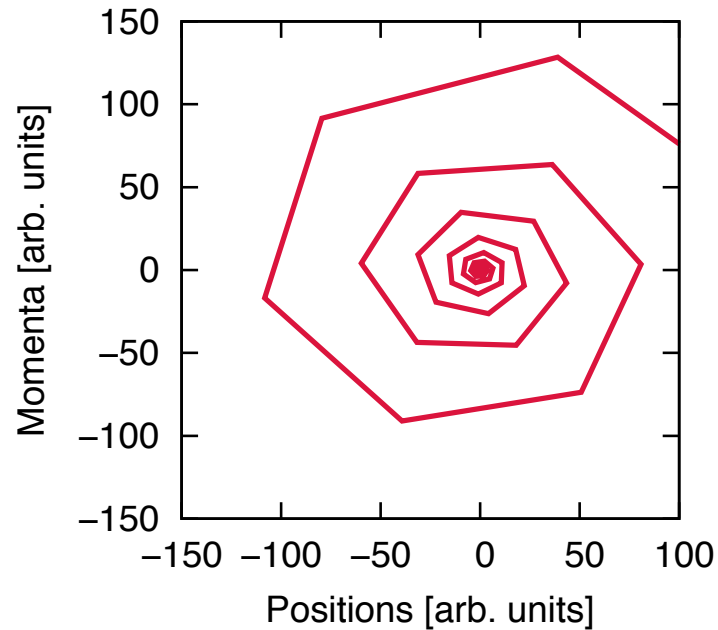
$$\langle \hat{p} \rangle_{\mu VT} = \frac{1}{\mathcal{Z}(\mu, V, T)g(E_k)} \sum_k g(E_k) e^{-\beta(\hat{\mathcal{H}} - \mu N)} \langle E_k | \hat{p} | E_k \rangle$$

- Learning Outcomes
 - Changing the *state* function: ***Legendre Transform***
 - Changing the *partition* function: ***Laplace Transform***

A peek into the wondrous realm of the

Enhanced Sampling (Vol.1)





- Exercises!
 - Remember Moodle
 - Drop me a line
 - Additional session