Lecture 1: Introduction

Lecturer: Jeffrey Everts, 5.32 jeffrey.everts@fuw.edu.pl

Tutor: Reinier van Buel, 5.63, r.van-buel@uw.edu.pl.

Material: Lecture notes (in progress), books (see website).

Website: www.fuw.edu.pl/~jeverts/teaching/statphysb

Organisation: Lectures on Wednesday, 12:15-15:00, room 2.06.

Tutorials on Thurstay, 16:15-19:00, room 1.38

Examination: Mid-term (20%), Final (60%), hand-ins (20%)

What is Statistical Physics about?

Microscopic interpretation:

Typical physical system can be described by a Hamiltonian, e.g.

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

$$\vec{p}^N := (\vec{p}_1, \ldots, \vec{p}_N)$$

$$\vec{r}^N := (\vec{r}_1, \ldots, \vec{r}_N)$$

For a classical system, we would like to know $\{\vec{p}^N(t), \vec{r}^N(t)\}$ (phase space)

determined by $\dot{\vec{r}}_i = \frac{\partial H}{\partial \vec{p}_i}$; $\dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{r}_i}$ Hamilton equations of motion.

+ 6N initial conditions.

In the case of quantum system: $i\hbar \frac{d}{dt}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$

Schrödinger equation (Hilbert space)

However, only limited number of problems are "solvable"

- Single particle ($\Phi = 0$)
- Particle in external potential
- Two-particle problems with radial potential.

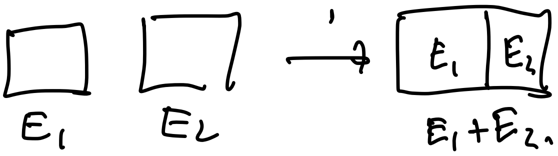
Classical mechanics, quantum mechanics.

However, macroscopic systems $N \sim 10^{23}$ ...

Macroscopic interpretation:

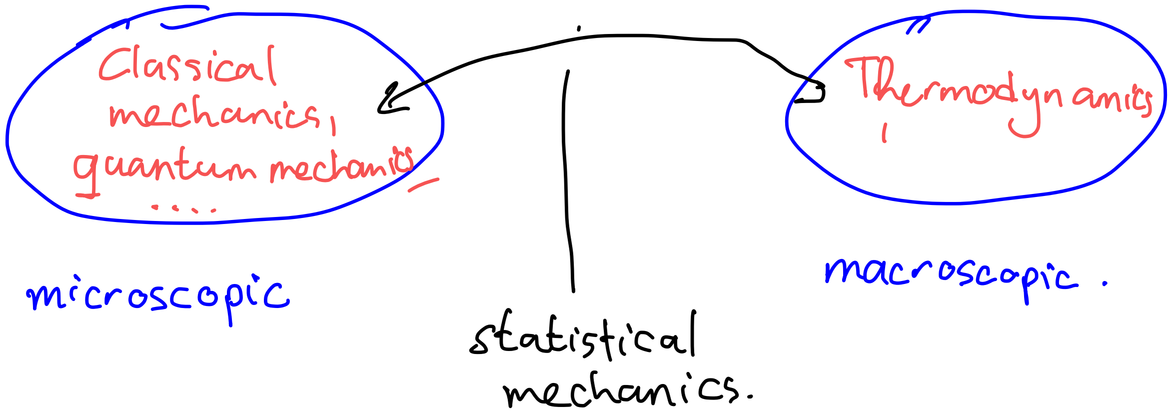
Instead of $\{\vec{p}^N(t), \vec{r}^N(t)\}$ (classical) or $|\Psi(t)\rangle$ (quantum) the macroscopic state is determined by just a few variables.

Examples:			
N	μ	μN	(chemical work, mass transport)
V	p	$-pV$	(mechanical)
S	T	TS	(heat)
$\vec{M}$	$\vec{H}$	$\vec{M}\cdot\vec{H}$	(magnetic).
$\vec{P}$	$\vec{E}$	$\vec{P}\cdot\vec{E}$	(electric)
extensive variables	intensive variables		



This is the field of (equilibrium) thermodynamics.

⇝ Roughly speaking how the available energy of a system is redistributed between heat and work.

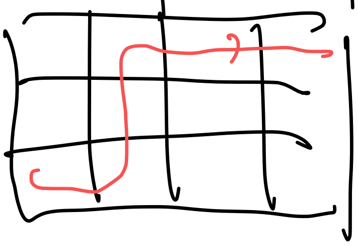


Pragmatic view on statistical mechanics:

(Recall we assume elementary knowledge on stat mech)

Consider time evolution $(\vec{p}^N(t), \vec{r}^N(t))$ or $|\Psi(t)\rangle$.

⇝ "line" in phase space / Hilbert space. $\Big\{$ system with some variables controlled. E.g. E, N, V fixed.



$\mathcal{N}$ independent measurements of observable $\mathcal{O}$

$O_{obs} = \frac{1}{\mathcal{N}} \sum_{a=1}^{\mathcal{N}} O_a$ where we measure long enough ($\mathcal{N} \to \infty$)

↳ system will flow arbitrarily close to all microscopic states consistent with constraints.

Then

$$O_{obs} = \sum_{\nu} \underbrace{\left[\frac{1}{\mathcal{N}} \left(\begin{array}{c} \text{Number of times state } \nu \text{ is} \\ \text{observed in the } \mathcal{N} \text{ observations} \end{array} \right) \right]}_{:= P_\nu} O_\nu$$

with $O_\nu = \langle \nu | \hat{O} | \nu \rangle$.

↳ probability / fraction of time spent in state ν.

$\Rightarrow$ $O_{obs} = \sum_{\nu} P_\nu O_\nu =: \langle O \rangle$ Ensemble average.

Continuous case: $\Gamma := (\vec{p}^{N}, \vec{r}^{N})$.

$$\bar{O} = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt \, O(\Gamma(t))$$

For τ sufficiently long $\bar{O} = \langle O \rangle$

$$\langle O \rangle = \int d\Gamma \, f(\Gamma) \, O(\Gamma)$$

Ergodic system (not obvious!)

How do we construct P_ν / $f(\Gamma)$?

Fundamental assumption of statistical mechanics (cannot be proven)

> For an isolated system with fixed E, V, N all microscopic states are equally likely at thermodynamic equilibrium.

↳ Uniform distribution of microscopic states with same energy and system size. Equilibrium is the most "random" state.

For example for discrete energy levels $P_\nu = \frac{1}{\Omega(N,V,E)} \delta_{E,E_\nu}$.

Normalisation: $\sum_\nu P_\nu = 1. \Leftrightarrow \Omega(N,V,E) = \sum_\nu \delta_{E,E_\nu}.$

Continuous (classical) case: $f_m(\Gamma) = \dfrac{\delta(E-H(\Gamma))}{\omega(E,V,N)}$

where $\omega(E,V,N) = \int d\Gamma\, \delta(E-H(\Gamma)).$

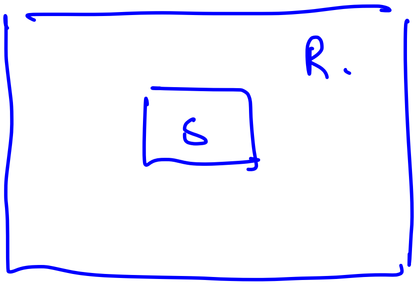
Link to thermodynamics $S = k_B \ln \Omega(N,V,E).$

↳ The collection of microstates subjected to macroscopic constraints is called an ensemble. E.g. (N,V,E) fixed ~~is~~ called microcanonical ensemble.

From the microcanonical ensemble other ensembles can be derived

For example, canonical ensemble. (N,V,T) fixed.

States given by $\hat{H}|\psi_\nu\rangle = E_\nu|\psi_\nu\rangle$



$N_S + N_R = N$

$E_S + E_R = E$ (N,V,E) fixed.

$V_S + V_R = V.$

System is in equilibrium with bath: $\beta := \dfrac{1}{k_B T} = \left(\dfrac{\partial \ln \Omega}{\partial E}\right)_{N,V}.$

We take reservoir in thermodynamic limit:

$$\frac{N_R}{N_S}, \frac{V_R}{V_S}, \frac{E_R}{E_S} \longrightarrow \infty$$

Suppose $E_S = E_\nu.$

$$\Rightarrow \Omega(N,V,E)\Big|_{E_S=E_\nu} = \overbrace{\Omega_S(N_S,V_S,E_\nu)}^{=1}\,\Omega_R(N_R,V_R,E-E_\nu).$$

Fundamental assumption: $P_\nu \propto \Omega_R(N_R,V_R,E-E_\nu)$
of stat mech

$= \exp[\ln \Omega_R(N_R,V_R,E-E_\nu)]$

$E_\nu \ll E$

$$\Rightarrow \ln\Omega_R(E-E_\nu) = \ln\Omega_R(E) - \underbrace{\left(\frac{\partial \ln\Omega_R}{\partial E}\right)_{N_R,V_R}}_{\rightarrow \left(\frac{\partial \ln\Omega}{\partial E}\right)_{N,V} = \beta.} E_\nu + \dots$$

Higher order derms vanish:

E.g. $\frac{\partial^2 \ln\Omega_R}{\partial E^2} \rightarrow \left(\frac{\partial\beta}{\partial E}\right)_{N,V} = -k_B\beta^2 C_V^{-1} \rightarrow 0$

$\Updownarrow$ extensive.

$$\Rightarrow P_\nu \propto \exp(-\beta E_\nu)$$

$$\sum_\nu P_\nu = 1 \Leftrightarrow P_\nu = \frac{1}{Z(N,V,T)} e^{-\beta E_\nu}.$$

$$Z(N,V,T) = \sum_\nu e^{-\beta E_\nu}$$

Canonical partition function.

Remark: $Z(N,V,T) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right].$

& trace over complete set of states.

Also note that:

$$\langle E\rangle = \sum_\nu P_\nu E_\nu = \frac{1}{Z}\sum_\nu e^{-\beta E_\nu} E_\nu = \frac{1}{Z}\sum_\nu \frac{\partial}{\partial(-\beta)} e^{-\beta E_\nu}$$

$$= \frac{1}{Z}\frac{\partial}{\partial(-\beta)}\sum_\nu e^{-\beta E_\nu} = \frac{1}{Z}\frac{\partial Z}{\partial(-\beta)} = -\frac{\partial \ln Z}{\partial\beta}.$$

uniform convergent.

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

$(dF = -SdT - pdV + \mu dN)$

$$= \left(\frac{\partial \beta F}{\partial\beta}\right)_{N,V}.$$

$$\Rightarrow \beta F = -\ln Z(N,V,T)$$

Link to thermodynamics.

Other ensembles:

Grand canonical ensemble (μ, V, T) fixed.

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, V, T) \quad \text{(grand-canonical partition function)}$$

with link to thermodynamics: $\beta \Omega(\mu, V, T) = -\ln \Xi(\mu, V, T)$,

$$\Omega(\mu, V, T) = F(\langle N \rangle, V, T) - \mu \langle N \rangle \quad \text{(grand potential)}$$

So we see always that:

$$\beta \begin{pmatrix} \text{Thermodynamic} \\ \text{potential} \end{pmatrix} = -\log \begin{pmatrix} \text{partition} \\ \text{function} \end{pmatrix},$$

complete thermodynamics

via e.g. $d\Omega = -S\,dT - p\,dV - N\,d\mu$.

So we could say, the main problem of stat mech is to compute the partition function.

In elementary course of stat mech, you have seen how to compute partition functions for simple cases.

- Ideal systems (classical and quantum)
  - Bosons
  - Fermions.
- Some simple models, like

  (1D) Lattice gases, Ising model.

In Stat Phys B we take it a step further:

- Partition functions of interacting systems
  - ⤳ mostly classical because for quantum systems more tools are needed, eg. second quantisation.
- Phase transitions.
- Some elementary concepts in non-equilibrium systems.

Placement

- Quantum many-body theory.
- Critical Phenomena.
- Non-eq. stat phys.