

I Review of Statistical Physics

Stat phys: study of macroscopic systems with $N \gtrsim 10^{23}$ particles.
 system is characterized by a microstate and a macrostate

microstate: defined by the location and momenta of all N particles (classical systems) or the N -body wave function (for qm systems).

macrostate: characterizes system by a few macroscopic observables like energy (E), volume (V), pressure (P), temp (T), ...

* microstate is practically impossible to determine, even if we would know the state, how shall we solve the system of $N \sim 10^{23}$ coupled equations?

* in addition microstate changes all the time due to interaction processes with environment, usually interaction processes are weak enough so that ^{only} the microstate changes, but the macrostate remains the same

Strategy in statistical physics: consider all microstates at the same time that are consistent with certain values of macro observable
 \Rightarrow ensembles

ensembles: a large number of virtual copies of a system, where each copy represents a possible ^{micro}state the system can be in

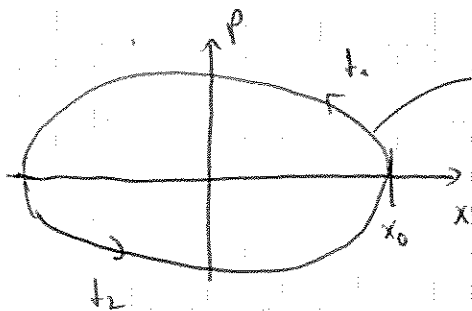
1) phase space in classical physics

I/2

consider one particle in one dimension

harmonic oscillator: $x = x_0 \cos \omega t$

$$p = -m \dot{x} = m \omega x_0 \sin \omega t$$



phase space trajectory corresponds to a fixed energy of the system

$$E = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$
$$= \frac{1}{2} x_0^2 \omega^2 m$$

at a given time

state of system ψ is a point in a 2-dim (x, p) phase space

for N particles in 3 dimensions phase space has ~~6N~~ ^{6N} dimensions, many (!) different points (microstates) correspond to a microstate of a given energy

introduce probability distribution in phase space

$$g(x, p, t) dx dp = g(x_{11}, x_{21}, \dots, x_{3N}, p_{11}, \dots, p_{3N}) \prod_{i=1}^{3N} dx_i dp_i$$

conservation laws for g : $\frac{\partial g}{\partial t} = -\text{div } v g$ (Liouville equation)

what is $g(x, p, t)$?

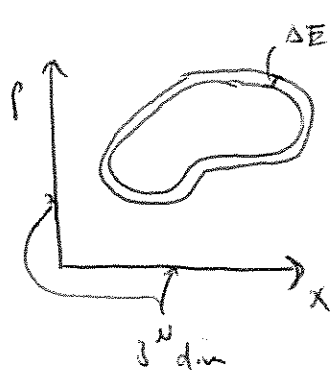
2) microcanonical ensemble

consider isolated macroscopic system with N particles, volume V and energy E

N, V, E

in reality the total energy is given by a range $[E - \Delta E, E]$

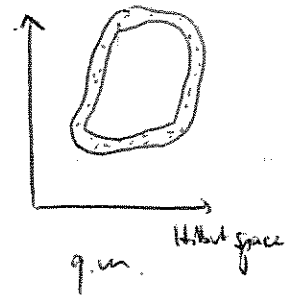
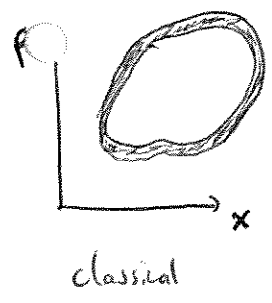
macroscopic \uparrow microscopic
 (e.g. fluctuations due to interaction with env.)



Fundamental postulate of statistical physics:

All microstates with energy in the range $[E - \Delta E, E]$ have the same probability (density)

$$P_{mc} = \begin{cases} \frac{1}{Z_{mc}} & E - \Delta E < H(p, x) \leq E \\ 0 & \text{else} \end{cases}$$



Z_{mc} a phase space volume in classical physics and a discrete ^{number} sum of states in q.m.

It turns out that Z_{mc} is ^{basically} independent of ΔE since the phase space increases very rapidly $Z_{mc} \sim E^N$. For $N \sim 10^{23}$ entire phase space is dominated by the ~~energy~~ upper limit of energy shell.

↳ exercise

3. density matrix ~~and~~, entropy and expectation values

Consider a system in a microstate $|\psi_i\rangle$ with probability p_i . Then the density matrix is defined by

$$\rho = \sum_i p_i |\psi_i\rangle \langle \psi_i|$$

↓
 ↳ contain inherent q.m. uncertainties
 describe statistical uncertainties (cf. ensembles)

Then the expectation value of an operator A can be expressed in I/4 the form

$$\begin{aligned}
 \langle A \rangle &= \sum_i p_i \langle \psi_i | A | \psi_i \rangle \\
 &= \sum_i p_i \sum_n \langle \psi_i | n \rangle \langle n | A | \psi_i \rangle \\
 &= \sum_i p_i \sum_n \langle n | A | \psi_i \rangle \langle \psi_i | n \rangle \\
 &= \sum_n \langle n | A \rho | n \rangle = \sum_n \langle n | \rho A | n \rangle = \text{Tr}(\rho A)
 \end{aligned}$$

Tr: short-hand notation for sum over complete set of N -body states.

microcanonical density matrix

$$\rho_{mc} = \sum_n p_{mc}(E_n) |n\rangle\langle n| = \sum_n \frac{1}{Z_{mc}(E_n)} |n\rangle\langle n|$$

for classical systems of identical particles

$$\text{Tr} = \int \frac{d^{3N}x d^{3N}p}{h^{3N} N!}$$

 semiclassical approx.

normalization: $\text{Tr} \rho_{mc} = 1$ (probabilities add up to one)

entropy def: $S = -k_B \text{Tr}(\rho \log \rho) = -k_B \langle \log \rho \rangle$
 (general)

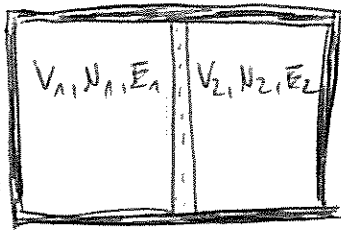
i.e. for microcanonical ensemble:
$$\begin{aligned}
 S_{mc} &= -k_B \sum_n p(E_n) \log(p(E_n)) \\
 &= -k_B \sum_n Z_{mc}^{-1}(E_n) \log Z_{mc}^{-1}(E_n) \\
 &= +k_B \log(Z(E_n))
 \end{aligned}$$

↳ Boltzmann entropy
 see also Shannon entropy in information theory
 measure of information content of a string of numbers/characters

a function of the form $\sim \log Z$ is called a "state function", hence the state function of the microcanonical ensemble is the entropy

4. Temperature and Pressure

consider a system consisting of two subsystems, total system isolated



Hamiltonian: $H = H_1 + H_2 + W$

↑
small correction to H_1 and H_2 , but allows energy exchange between systems

density matrix of total system $\rho_{mc}^{(1+2)}$ probabilities of microstates of system 1+2:

$$\rho_{mc}^{(1+2)}(E) = \begin{cases} \frac{1}{Z_{mc}^{(1+2)}(E_0)} & \text{for } E_0 - \Delta E \leq H_1 + H_2 + W \leq E_0 \quad (\text{ie } H_1 + H_2 \approx E_0) \\ 0 & \text{else} \end{cases}$$

probability for subsystem 1 to have energy in the range $[E_1^0 - \Delta E_1^0, E_1^0]$ (and hence system 2 energy $[E_2^0 - \Delta E_2^0, E_2^0]$)

$$\begin{aligned} \rho(E_1) &= \text{Tr}_{E_1} \rho_{mc}^{(1+2)} = \text{Tr} \rho_{mc}^{(1+2)} \int_{E_1, H_1 = (E_1 - \Delta E_1^0 \leq H_1 \leq E_1)} \\ &= \text{Tr} \frac{1}{Z_{mc}^{(1+2)}} \int_{E_1, H_1} \int_{E_2, H_2} \\ &= \text{Tr}_1 \text{Tr}_2 \frac{1}{Z_{mc}^{(1+2)}} \int_{E_1, H_1} \int_{E_2, H_2} \\ &= \frac{Z_{mc}^{(1)}(E_1) Z_{mc}^{(2)}(E - E_1)}{Z_{mc}^{(1+2)}} \int_{E - E_1, H_2} \end{aligned}$$

determine most probable energy \bar{E}_1 , $\frac{d\rho(E_1)}{dE_1} = 0$

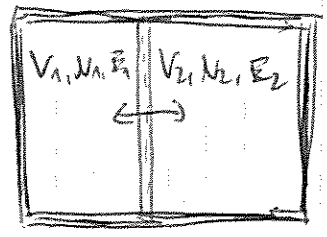
$$\begin{aligned} \frac{\partial Z_{mc}^{(1)}(E_1)}{\partial E_1} \Big|_{E_1 = \bar{E}_1} Z_{mc}^{(2)}(E - \bar{E}_1) + Z_{mc}^{(1)}(\bar{E}_1) \frac{\partial Z_{mc}^{(2)}(E - \bar{E}_1)}{\partial E_1} \Big|_{E_2 = \bar{E}_2} &= 0 \\ \Rightarrow \frac{\partial \log Z_{mc}^{(1)}(E_1)}{\partial E_1} &= \frac{\partial \log Z_{mc}^{(2)}(E_2)}{\partial E_2} \end{aligned}$$

$$\Rightarrow \frac{\partial S_1(E_1)}{\partial E_1} \Big|_{E_1 = \bar{E}_1} = \frac{\partial S_2(E_2)}{\partial E_2} \Big|_{E_2 = \bar{E}_2}$$

definition: $T_1^{-1} = T_2^{-1}$

$$T^{-1} = \frac{\partial S(E)}{\partial E} \quad \text{Temperature}$$

Following the same arguments if we allow the dividing wall to be ~~not~~ ^{flexible} ~~fixed~~ i.e. allow for variable V_1, V_2 with $V_1 + V_2 = V$ we obtain



$$\frac{\partial S_1(E_1, V_1)}{\partial V_1} = \frac{\partial S_2(E_2, V_2)}{\partial V_2}$$

$\frac{P_1}{T} = \frac{P_2}{T}$ pressure

pressure: $p = T \frac{\partial S(E, V)}{\partial V} \Big|_E$

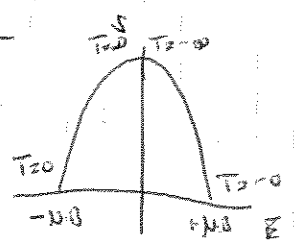
Finally, if we also allow for variable number of particles N_1 and N_2 we obtain

$$\frac{\partial S_1(E_1, V_1, N_1)}{\partial N_1} = \frac{\partial S_2(E_2, V_2, N_2)}{\partial N_2} \Rightarrow \mu_1 = \mu_2$$

Definition of chemical potential $\mu = T \frac{\partial S(E, V, N)}{\partial N} \Big|_{E, V}$

discuss negative temperature, ~~negative chemical potential~~

show paramagnetic system



free gas: $S(E) \sim \log(E^{3N/2})$

$$\Rightarrow T \sim \frac{3}{2} EN k_B$$

energy bounded from above!

$$S = \frac{k_B N}{2} \left(-(1+c) \log\left(\frac{1+c}{2}\right) - (1-c) \log\left(\frac{1-c}{2}\right) \right)$$

~~But~~ $c = \frac{E}{NB}$ $H_2 = \vec{B} \cdot \vec{S}$

ω $0 \rightarrow 0$ $\rightarrow -\omega \mu = \frac{1}{T}$ continuous

5. First law of thermodynamics

question: how are changes of S, E, V and N related?

consider a Hamiltonian $H(a)$, where a is an external parameter, e.g. $a=V$

study change of partition function when a is changed:

$$dZ_{mc} = d \text{Tr} \left[\Theta(E - H(a)) - \Theta(H(a) - (E - \Delta E)) \right]$$

$$= \text{Tr} \left[\delta(E - H(a)) + \delta(E - \Delta E - H(a)) \right] \cdot \left[dE - \frac{\partial H}{\partial a} da \right]$$

can be neglected
since phase space increases
rapidly with E

$$= \text{Tr} \left[\delta(E - H(a)) \left(dE - \frac{\partial H}{\partial a} da \right) \right]$$

$$dZ_{mc} \approx \left[\text{Tr} \delta(E - H(a)) \right] \left(dE - \left\langle \frac{\partial H}{\partial a} \right\rangle da \right)$$

energy "surface" in
phase space

averaged over energy
surface

$$\Rightarrow dS = k_B d \log Z_{mc} = k_B \frac{dZ_{mc}}{Z_{mc}} = k_B \frac{\text{Tr} \delta(E - H(a))}{Z_{mc}} \left[dE - \left\langle \frac{\partial H}{\partial a} \right\rangle da \right]$$

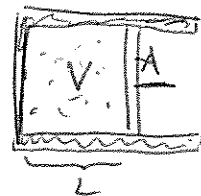
since $\frac{\partial S}{\partial E} = T^{-1}$ we have $\Rightarrow = T^{-1}$

$$\Rightarrow dS = \frac{1}{T} dE - \left\langle \frac{\partial H}{\partial a} \right\rangle da$$

consider $a=V$, what is $\left\langle \frac{\partial H}{\partial V} \right\rangle$?

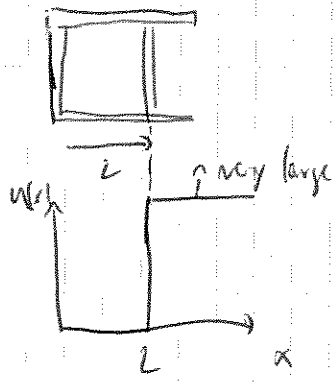
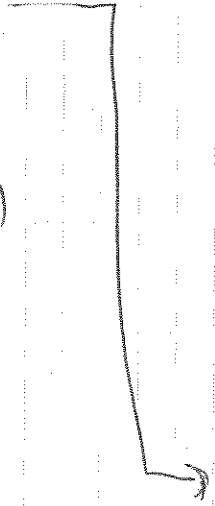
if $H(V)$ contains a potential term $U(x)$ that prevents particles from penetrating the walls then the force the

particles apply to the wall is given by



$$\begin{aligned}
 \vec{F} &= \sum_i^N \vec{F}_i = \sum_{i=1}^N -\frac{\partial u(x_i, L)}{\partial x_i} \\
 &= \sum_{i=1}^N +\frac{\partial u(x_i, L)}{\partial L} \\
 &= \sum_i^N \frac{\partial H(x_i, L, p_i)}{\partial L}
 \end{aligned}$$

$$P = -\frac{\langle \vec{F} \rangle}{A} = -\left\langle \frac{\partial H}{\partial V} \right\rangle$$



$$\frac{\partial u(x, L)}{\partial x} = \delta(x-L) \cdot c = -\frac{\partial u(x, L)}{\partial L}$$

$$\Rightarrow dS = T^{-1}(dE + p dV)$$

$$\text{or } dE = T dS - p dV$$

allowing also the number of particles to vary $a=N$, gives

$$dE = T dS - p dV + \mu dN$$

↓ heat
↓ mechanical work
↓ adding/removing matter

First law of thermodynamics
energy balance between different states

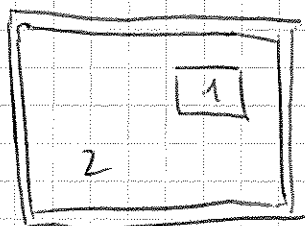
\Rightarrow the state variables of the microcanonical ensemble are
 $S = S(E, V, N)$ or $E = E(S, V, N)$
 \uparrow
state function $S = \log \Omega$

6. Canonical ensemble

[15]

- in practice it is not easy to fix or determine the entropy of a system, the temperature is a more accessible variable
- theoretical calculations of microcanonical partition functions sometimes complicated by sharp cutoffs/restrictions of phase space

consider an isolated system consisting of a small subsystem 1 and a large subsystem 2 ("heatbath")



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

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

$$V = V_1 + V_2, \quad V_2 \gg V_1$$

Hamiltonian:

$$H = H_1 + H_2 + V$$

$$\approx H_1 + H_2$$

↑
allows energy transfer between system 1 and 2

expectation value of an operator A :

$$\langle A \rangle = \text{Tr}(\rho A) = \text{Tr}\left(\frac{1}{Z^{(1+2)}} A\right) = \text{Tr}_1 \text{Tr}_2 \left(\frac{1}{Z^{(1+2)}} A\right) = \text{Tr}_1 \left(\rho^{(1)} A\right)$$

↑
integrated out states of system 2

derive explicit form of $\rho^{(1)}$.

$$\rho^{(1)} = \text{Tr}_2 \frac{e^{-\beta H^{(1+2)}}}{Z^{(1+2)}} = \text{Tr}_2 \left[\frac{e^{-\beta H^{(1+2)}}}{Z^{(1+2)}} \right]^{-1} \sum_{i_1, i_2} |i_1\rangle \langle i_2| \langle i_1, i_2| = \sum_{i_1} \frac{Z^{(2)}(E - E_{i_1})}{Z^{(1+2)}(E)} |i_1\rangle \langle i_1|$$

now use that $\frac{E_1}{E} \ll 1$ and expand:

$$Z^{(2)}(E - E_1) \approx Z^{(2)}(E) + \frac{\partial Z^{(2)}(E)}{\partial E} (-E_1)$$

note that $Z^{(2)}(E)$ is a rapidly varying function: ~~not~~
(typically $Z(E) \sim E^\alpha$)

⇒ it is much more clever and useful to expand the logarithm $\log(Z^{(2)})$ instead

$$\log z^{(2)}(E-E_1) \approx \log z^{(2)}(E) + \frac{\partial \log z^{(2)}(E)}{\partial E} (-E_1)$$

$$= \log z^{(2)}(E) - \frac{E_1}{k_B T}$$

I/10

$$\Rightarrow z^{(2)}(E-E_1) \approx z^{(2)}(E) e^{-\frac{E_1}{k_B T}}$$

$$p^{(1)} = \frac{z^{(2)}(E)}{z_{\text{enc}}^{(1+2)}(E)^n} \sum_n e^{-\frac{E_{1n}}{k_B T}} \ln |n\rangle \langle n| = c \sum_n e^{-\frac{E_{1n}}{k_B T}} \ln |n\rangle \langle n|$$

$$= c \cdot e^{-\frac{E_1}{k_B T}}$$

determine c by normalization condition

$$\text{Tr}_1 p^{(1)} = 1$$

$$Z_c \equiv \text{Tr}_1 e^{-\frac{H_1}{k_B T}}$$

canonical partition function

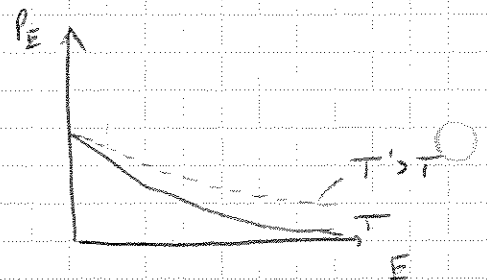
$$\Rightarrow \rho_c^{(1)} = Z_c^{-1} e^{-\frac{H_1}{k_B T}}$$

canonical density matrix

probability that system 1 has energy E_1 .

$$p^{(1)} = \sum_n p_{E_n} |n\rangle \langle n| = Z_c^{-1} \sum_n e^{-\frac{E_n}{k_B T}} |n\rangle \langle n|$$

$$p_{E_n} = \frac{e^{-\frac{E_n}{k_B T}}}{Z_c}$$



entropy in canonical ensemble (start from original def. previous lectures)

$$S_c = -k_B \text{Tr}(\rho_c \cdot \log \rho_c)$$

$$= -k_B \text{Tr} \left[\rho_c \cdot \left(\log Z_c^{-1} - \frac{H}{k_B T} \right) \right]$$

$$= +k_B \log Z_c \text{Tr}(\rho_c) + k_B \text{Tr} \left(\rho_c \frac{H}{k_B T} \right)$$

$$= k_B \log Z_c + \frac{1}{T} \langle H \rangle$$

$$= k_B \log Z_c + \frac{E}{T}$$

remark: E in canonical ensemble not fixed externally, given by ensemble average of Hamiltonian

entropy not of the form $S = k_B \log Z$ anymore ~~at~~ (additional term)
 define a new state function of the canonical ensemble

$$F = -k_B T \log Z_c \quad \text{free energy}$$

that means $S_c = -\frac{F}{T} + \frac{E}{T} \Rightarrow \boxed{F = E - TS_c}$

$P_c = P_c(T, V, N)$
 ↑ ↑ in Hamiltonian
 explicitly (via lattice spacing or hard wall interaction of boundaries)

hence $F = F(T, V, N)$

$$dF = dE - T dS - S dT = -p dV - S dT \quad (dN=0)$$

Legendre transformation
 to exercise

7. various ensembles and its properties

ensemble system	microcanonical isolated	canonical energy transfer with bath	grand canonical energy- and particle exchange with heat + particle reservoir
density matrix	$Z_{micro}^{-1} \sum_{i \in \Omega(E, V, N)} \delta(E - \hat{H}_i - \epsilon) \delta(V - \hat{V}_i) \delta(N - \hat{N}_i)$	$Z_c^{-1}(T, V, N) e^{-\frac{\hat{H}}{k_B T}}$	$Z_{gc}^{-1}(T, V, \mu) e^{-\frac{\hat{H} - \mu \hat{N}}{k_B T}}$
state variables	E, V, N	T, V, N	T, V, μ
state function	$S = k_B \log Z_{micro}$	$F = -k_B T \log Z_c$	$\Phi = -k_B T \log Z_{gc}$

all thermodynamic quantities follow from the state function and its derivatives

⇒ central goal of statistical physics is evaluation of the partition function Z , usually Z_c in this course

Legendre Transformation

the microcanonical and canonical ensemble are related by a Legendre transformation

by going from the ~~can~~ microcan to the can ensemble the variable S is traded for the variable T
↳ exercise

8. Derivatives of thermodynamic quantities

$$dE = \delta Q + \delta A + \delta E_N$$

↳ $T dS$

heat capacity: $C = \frac{\delta Q}{dT} = T \frac{dS}{dT} \Rightarrow C_V = T \left. \frac{\partial S}{\partial T} \right|_{V,N} = \frac{\partial E}{\partial T} \Big|_{V,N}$

"how much heat is needed to increase temperature by fixed amount"

$$C_P = T \left. \frac{\partial S}{\partial T} \right|_{P,N}$$

compressibility: $\kappa = -\frac{1}{V} \frac{dV}{dP}$ (e.g. for gases and fluids)

"how much pressure is needed to change volume by fixed amount"

Magnetic systems are described on a fixed lattice in an external magnetic field B and a magnetization M . $E \sim -\vec{M} \cdot \vec{B}$
(replace $V \rightarrow \vec{B}$, $P \rightarrow \vec{M}$ in the relation for gas)

$$dE = T dS - \vec{M} \cdot d\vec{B} \quad (\text{microcan.})$$

$$dF = -S dT - \vec{M} \cdot d\vec{B} \quad (\text{can.})$$

instead of compressibility, def susceptibility $\chi = \frac{\partial M}{\partial B}$ (later more!)

9. Ergodicity

consider a classical system, then the system is ergodic if

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(x_i(t), p_i(t)) = \int \frac{d^{3N}x \int d^{3N}p}{h^{3N} N!} P_{eq}(\{x, p\}) A(x, p)$$

\downarrow 3N variables \downarrow 3N variables \downarrow probability distribution
 equilibrium distribution

basic statement: time average = ensemble average

over time ^{microscopic} configuration of system approaches every point of phase space; discuss some analogous examples (human behavior, restaurants in a city)

is this always fulfilled? No! For phase transitions and the corresponding symmetry breaking leads to a breaking of ergodicity

human behavior and ergodicity

restaurants 1 2 3 4 ... n "phase space"

ensemble of people 1 2 3 4 ... N all possible

time average: pick one person and measure how often given restaurants have been visited (assume infinite life time)

ensemble average: snapshot of all people of ensemble at a given time

results will typically not be the same, e.g. vegetarians \leftrightarrow many veg restaurants

