

Lecture 1

A Revising Classical Thermodynamics (partly TPI)

A.1 Basic Concepts and Definitions

=> handout

A.2 Thermodynamic Laws

=> handout

=> consequences of 3. law in lecture

A.1 Basic Concepts and Definitions

a) Thermodynamic System

Def: large, many-body system (number of particles in the system typically $N \gtrsim 10^{23}$) with clear distinction from surroundings/environment

- no hard walls required, defined borders are sufficient
- classification:
 - i) isolated / closed systems
 - no heat transfer or particle exchange with environment
 - MUST be classical
 - ii) systems with heat contact only
 - heat transfer between environment and system possible
 - no particle exchange between environment and system (N fixed)
 - iii) open systems
 - system and environment can exchange heat and particles
- remark: boundary conditions strongly influence system behaviour

b) Thermodynamic or State Functions

Def: define some property of the system and have a definitive value at each state

- can be mechanical, electro-magnetic or “truly” thermodynamical
- examples (gas): p, V, T, N, S, U
- examples (magnet): $H, m, M(r), T, N, S, U$
- classification:
 - i) extensive state functions
 - if quantity has the value A in a system with volume V , the quantity has the value αA in a system with the volume αV (IF both systems are in the same state, e.g., if we artificially split the system in two subsystems)
 - examples: V, N, U, S
 - ii) intensive state functions
 - the quantity does not depend explicitly on the volume, i.e., the quantity stays the same if we split the system
 - examples: $p, T, n = N/V$

c) Thermodynamic Limes

Def: we consider infinitely large systems with constant intensive variable, that is, $V \rightarrow \infty$ and $N \rightarrow \infty$, but $n = N/V = \text{const.}$

- all consideration in this course are done in the thermodynamic limes!

d) Thermodynamic State

Def: State of the system fully defined by a sufficiently large set of thermodynamic functions

- often only reduced sets of thermodynamic functions are quoted
- what is a “sufficiently large set” must be determined empirically

e) Equation of State

Def: connects a set of thermodynamic functions and reduces the number of state functions that fully define a state

- example (ideal gas): $pV = nk_B T$ (thermal)
- example (ideal gas): $U = \frac{3}{2} k_B T$ (caloric)

f) Thermodynamic Equilibrium

Def: special state of systems in which the state function do not change, that is for example, $U \neq U(t)$, $p \neq p(t)$, ...

- term is connected to the concept of equipartition and temperature (later more ...)
- all consideration in this course will concern systems in equilibrium

g) State Changes

Def: the way how the thermodynamic state changes

- classification
 - i) real nonequilibrium state changes
general case, but very hard to describe
 - ii) quasi-static changes (very slow)
system runs through a closely connected series of equilibrium states
all machines and motors in Thermal Physics I are based on that principle

A.2 Thermodynamic Laws

0th Law of Thermodynamic

- i) a state function temperature, T , exists.
- ii) two bodies in thermal contact and each in equilibrium are also in equilibrium with each other (they have the same T)
- temperature for now given by thermometer (later better)

1st Law of Thermodynamic

- i) a state function internal energy, U , exists.
- ii) a perpetuum mobile of the first kind does not exist
- iii) energy is conserved (in a very general sense)

$$\Delta U = Q + W = \text{heat} + \text{work}$$

$$dU = \delta Q + \delta W$$

- examples for work: pdV (mechanical), EdP (electrical), Hdm (magnetic)
- need to include all kinds of energy, including chemical ...
- law connects thermodynamic with other fields of physics

2nd Law of Thermodynamic

- i) a state function entropy, S , exists.
- ii) a perpetuum mobile of the second kind does not exist
heat flows spontaneously from hot to cold systems
- iii) the entropy in a close systems is increasing or constant

$$dS \geq \frac{\delta Q}{T} \quad \Leftrightarrow \quad \oint \frac{\delta Q}{T} \leq 0$$

“=” sign for reversible / quasi-static changes

- in open systems (earth), entropy export is possible !!!

Fundamental Law of Thermodynamic

- i) combines first and second law:

$$T dS \geq \delta Q = dU - \delta W$$

- basic relation for all technical applications

3rd Law of Thermodynamic (Nernst)

- i) the entropy at $T = 0$ is a unique function (does not depend on other state functions)
 $\Leftrightarrow S(T = 0) = 0$ per definition
- ii) states with $T = 0$ cannot be reached in experiments (record $T = 4.5 \times 10^{-10}$ K)
- consequences: see lecture or books

Mathematical Supplement: Exact Differentials ^(A)

Remark: Laws define therm. functions as exact differentials

↳ properties of such functions are needed

- consider $F(x, y)$ and changes in F if $x = x(t)$ and $y = y(t)$

$$\frac{dF}{dt} = \lim_{\Delta t \rightarrow 0} \frac{F(x(t+\Delta t), y(t+\Delta t)) - F(x(t), y(t))}{\Delta t}$$
$$= \left(\frac{\partial F}{\partial x}\right)_y \frac{dx}{dt} + \left(\frac{\partial F}{\partial y}\right)_x \frac{dy}{dt} + \frac{\partial F}{\partial t}$$

↑ often $\equiv 0$

- Def: exact differential

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

IF 1) $\left(\frac{\partial}{\partial y} \left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial F}{\partial y}\right)_x\right)_y$ mixed derivatives equal

2) $F(B) - F(A) = \int_A^B dF$ F given by dF (trout)

3) $\oint dF = 0$ no changes after return to initial values

- Notation: dF exact differential
 $\oint F$ not an exact --

• Examples

a) $df_1 = y dx - x dy$ [Lin. increase/decrease with x, y]

test: $\left(\frac{\partial f_1}{\partial x}\right)_y = y$; $\left(\frac{\partial f_1}{\partial y}\right)_x = -x$

$\Rightarrow \left(\frac{\partial}{\partial y} \left(\frac{\partial f_1}{\partial x}\right)\right) = 1 \neq -1 = \left(\frac{\partial}{\partial x} \left(\frac{\partial f_1}{\partial y}\right)\right)$

$\Rightarrow \oint df_1 \neq 0$

b) $df_2 = \frac{1}{y} dx - \frac{x}{y^2} dy$ [factor $\frac{1}{y^2}$ different]

test: $\left(\frac{\partial f_2}{\partial x}\right)_y = \frac{1}{y}$; $\left(\frac{\partial f_2}{\partial y}\right)_x = -\frac{x}{y^2}$

$\Rightarrow \left(\frac{\partial}{\partial y} \left(\frac{\partial f_2}{\partial x}\right)\right) = -\frac{1}{y^2} \equiv \frac{1}{y^2} = \left(\frac{\partial}{\partial x} \left(\frac{\partial f_2}{\partial y}\right)\right)$

$\Rightarrow df_2 \checkmark$

• Difference between $\oint df_1$ and df_2 is factor $\frac{1}{y^2}$

• Def: factor that creates exact differential is called "integrating factor"

• Thermodynamics: $\oint Q$ and $\oint W$,
 BUT $\frac{\partial Q}{T} = dS$ is exact differential

3rd law: $S(T=0) = 0$

①

Consequences:

a) heat capacities vanish at $T=0$

$$\lim_{T \rightarrow 0} C_q = \lim_{T \rightarrow 0} \left(\frac{\partial U}{\partial T} \right)_q \stackrel{\text{no work}}{=} \lim_{T \rightarrow 0} \left(\frac{\partial Q}{\partial T} \right)_q$$

$$\left(q = V, P, \mu, \dots \right) = \lim_{T \rightarrow 0} T \left(\frac{\partial S}{\partial T} \right)_q \equiv 0$$

proof: i) $C_q \geq 0 \Rightarrow T \left(\frac{\partial S}{\partial T} \right)_q \geq 0$

$$\Rightarrow \left(\frac{\partial S}{\partial \ln T} \right) \geq 0$$

ii) assume $\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial \ln T} \right) = \alpha > 0$

• set $x = \ln T = \lim_{T \rightarrow 0} x = -\infty$

means $\lim_{x \rightarrow -\infty} \left(\frac{\partial S}{\partial x} \right) = \alpha > 0$

$\Rightarrow \exists x_0$ with $-\infty < x' < x_0$ and

$$\left(\frac{\partial S}{\partial x} \right) \geq \frac{\alpha}{2} > 0 \quad \forall x' < x_0$$

(S is continuous fct.)

• use $S(x_0) - S(x) = \int_x^{x_0} \left(\frac{\partial S}{\partial \bar{x}} \right) d\bar{x}$ (2)

$$\geq \frac{\alpha}{2} (x_0 - x)$$

$$\Rightarrow S(x_0) - S(x) \leq \frac{\alpha}{2} x + \text{const}$$

$$S(x) \leq \frac{\alpha}{2} x + \text{const}'$$

$$\Rightarrow \lim_{x \rightarrow -\infty} S(x) = -\infty \quad \swarrow \text{3rd law}$$

$$\Rightarrow \lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial \ln T} \right) \neq 0$$

• combine i) and ii)

$$\left(\frac{\partial S}{\partial \ln T} \right) \neq 0 \quad \text{and} \quad \left(\frac{\partial S}{\partial \ln T} \right) \neq 0$$

$$\Rightarrow \left(\frac{\partial S}{\partial \ln T} \right) = c_g = 0 \quad \text{for } T \rightarrow 0$$

b) heat capacities fulfill

$$\lim_{T \rightarrow 0} \frac{c_p - c_v}{T} = 0 \quad (\text{gas})$$

proof @ HOME

G) $T=0$ cannot be reached

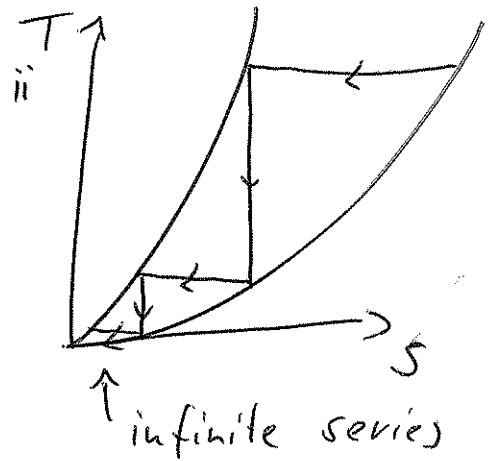
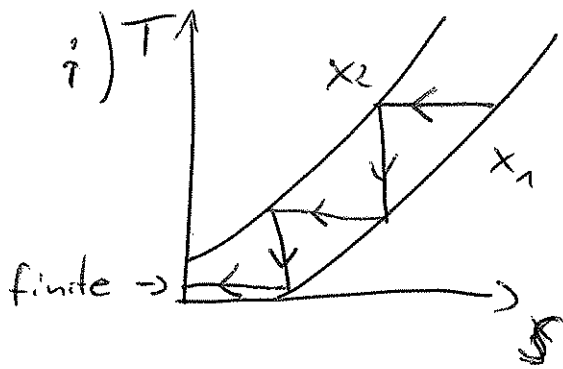
- How do we cool stuff?

- sequence of isothermal and adiabatic processes

- example gas: Linde procedure

- example magnet: magnetisation → demagnetisation →

possible paths



mathematical:

- assume 2 points $S(x_1, T_1), S(x_2, T_2)$

- adiabatic process $S(x_1, T_1) \rightarrow S(x_2, T_2)$

$\Rightarrow S(T_1, x_1) \leq S(T_2, x_2)$ 2nd law

- $S(T_1, x_1) = \int_0^{T_1} \frac{C(x_1, T_1')}{T_1'} dT_1'$

- IF $T_2 = 0 \Rightarrow S(T_2, x_2) = 0$

$\Rightarrow S(T_1, x_1) = \int_0^{T_1} \frac{C(x_1, T_1')}{T_1'} dT_1' \leq 0$

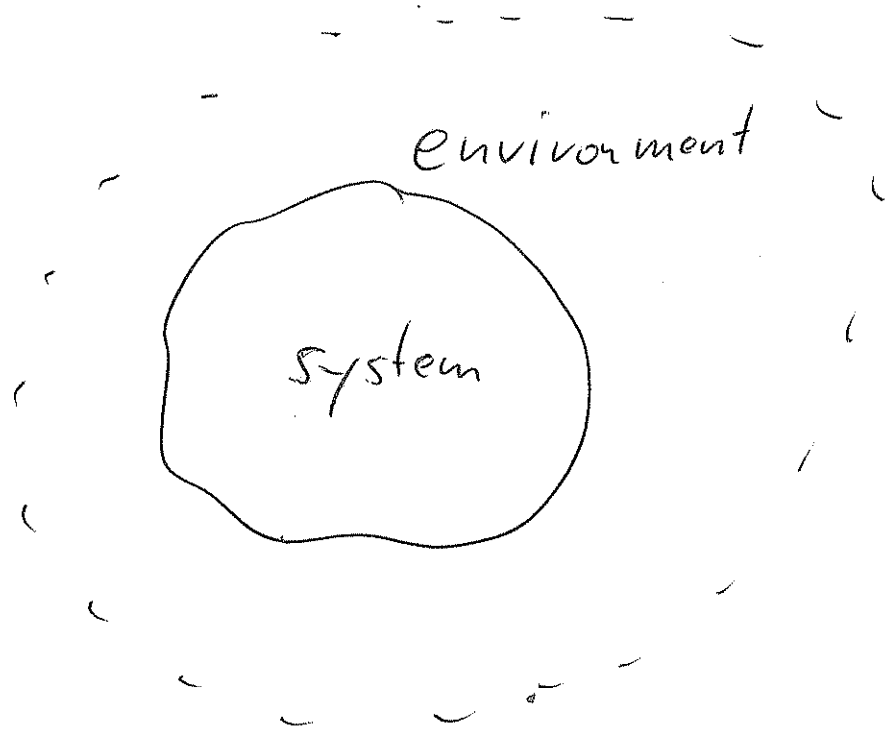
$\Rightarrow T_1 \neq 0$

↳ T, C positive

Lecture 2

Basic Problem for the course

(1)



Descriptions

phenomenologic

- based on empirical evidence like experiments and observations
- $TP I$ + extensions

statistical

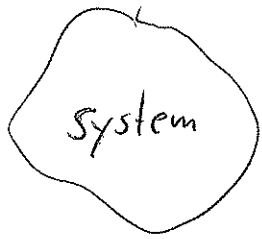
- based on the mechanics of the underlying many-body system
- Main point of $TP II$
 \Rightarrow EOS, measurable quantities
- possible?
- mainly in equilibrium

1. Isolated / Closed Systems (2)

- Micro-canonical ensemble

1.1. Basic definitions

Closed system:



- no heat transfer } between the
- no particle exchange } system and
the environment

=> properties of environment
not needed

=> $U = \text{const.}; N = \text{const.}$

Def: Macrostate: state of the macroscopic system defined by a set of thermodynamic functions
(T, p, N, U, \dots)

∴ very few variables needed

Def: Microstate : any microscopic configuration of the system's particles
consistent with restrictions:

E, V, N

∴ many variables

States that define a microstate: ③

• classical mechanics : state $\hat{=} \{ \vec{r}_N, \vec{p}_N \}$

• quantum mechanics : state $\hat{=} \Psi_N(s)$

s ... full set of variables,
e.g., positions & spins

• model systems:

state defined by
"relevant" variables, e.g.,
energy, sites, spins, ...

(show dices!)

Important: Many different microstates can
lead to the same macrostate \forall

Why do we care about microstates?

- Little as they are hard to measure

\forall but their number in a given
macrostate defines probabilities

phenomenology

Macrostate obeying
thermod. laws

goal
 \longleftrightarrow

statistical mechanics

Microstate following
from laws for particles

1.2. Thermodynamics of closed systems (4)

◦ central quantity: internal energy U

◦ 1st law: $dU = \delta Q + \delta W$

$$= T dS - p dV \quad (\text{quasi-static} \\ + \text{gas})$$

∴ U is an exact differential

$$\hookrightarrow U = U(S, V)$$

∴ independent variables are entropy S & volume V

a) internal energy acts as thermodynamic potential

∴ full thermodynamics follows from $U(S, V)$

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

$$ii) \left(\frac{\partial U}{\partial V} \right)_S = -p$$

$$\text{compare to } F = -\text{grad } V \stackrel{10}{=} - \frac{\partial V}{\partial x}$$

$U \leftrightarrow V$... potential

$T, p \leftrightarrow F$... "forces"

∴ U is ONLY thermodynamic potential in variables S, V

∴ $U(T, V)$ exists, but is not a potential

b) Maxwell - Relation

(connection between therm. functions in differential form)

- U is exact differential in S, V
 \hookrightarrow mixed derivatives must be equal

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right)_V$$

$$\text{iii) } \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial p}{\partial S}\right)_V$$

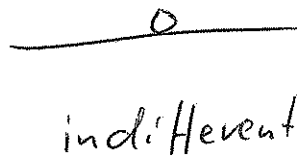
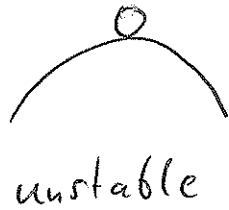
\Rightarrow find 3 relations from U being exact diff.

$$\checkmark \quad \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{act as } \underline{\text{Definition}}$$

for temperature

c) stability of thermodynamic equilibrium ⑥

Remark:



What is the criterion for stable equilibrium?

- apply 1st law for closed systems

$$\oint Q = 0 \quad \oint W = 0 \quad \Rightarrow \quad dU = 0 \quad ; \quad U = \text{const.}$$

- apply 2nd law

$$\oint Q \leq T dS$$

$$0 \leq T dS$$

$\Rightarrow dS \geq 0$: every irreversible process increases entropy S

\forall in equilibrium $\oint Q = T dS = 0$

\Rightarrow S at maximum in equilibrium
 $S \rightarrow$ maximum ... otherwise

HOME: Show that $S_{\text{tot}} = S_1 + S_2$, $T_1 = T_2$
and $p_1 = p_2$ for system

1	2
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Lecture 3

1.3. Fundamental Assumptions & Definitions (1)

of statistical descriptions

a) How often do special microstates occur?

• clue from experiments / simulations:

↳ it looks like that all complex systems of many particles move randomly between microscopic configurations

(available microstates)

↳ system explores all states compatible with constraints E, V, N

⇒ Equipartition Theorem:

All microstates of a closed system (fixed E, N) are equally likely to occur in the state of thermodynamic equilibrium

✓ Can be thought of as definition of equilibrium

2) Relation: measured value \leftrightarrow configuration ②

• clue: measurements are not instantaneous,
but sample configurations over some time.

↳ think of it as time average or series of many
measurements

• consequence: time average in measurements
is equal to an average over
configurations / ensembles

Def: average of quantity A

$$\langle A \rangle = \frac{1}{\Omega(E, N, V)} \sum_{\nu} A_{\nu}$$

Def.: # of states $\Omega = \Omega(E, N, V)$

Ω is the number of all states that are
consistent with constraints (E, N)

Def.: A_{ν} ... value of property "A" if
system is in microstate ν

ν labels all possible microstates

\Rightarrow time average $\hat{=}$ ensemble average

"If you want to study the growth of trees
over 100 years, study a forest!"

- Example: • 3 particles in a trap ③
- particles can have energies $0, \hbar\omega, 2\hbar\omega, \dots$
 - system energy is $E = U = 2\hbar\omega$

Configurations	energy of particle		
	①	②	③
a)	2	0	0
b)	1	1	0
c)	1	0	1
d)	0	2	0
e)	0	1	1
f)	0	0	2

\Rightarrow 6 possible configurations $\Omega(E=2, N=3) = 6$

\Rightarrow average energy of particle ①

$$\begin{aligned} \langle E_1 \rangle &= \frac{1}{6} \sum_V E_V = \frac{1}{6} [2 + 1 + 1 + 0 + 0 + 0] \\ &= \frac{4}{6} = \frac{2}{3} \hbar\omega \end{aligned}$$

\Rightarrow do time average by dices (experiment!)

$$\begin{aligned} 1 \hat{=} a) &= 2 & 4, 5, 6 \hat{=} d), e), f) &= 0 \\ 2 \hat{=} b) &= 1 \\ 3 \hat{=} c) &= 1 \end{aligned}$$

c) Probabilities for special states

(4)

Def.: probability that value "A" occurs

$$\lim_{N \rightarrow \infty} \frac{\# \text{ event } A}{\text{total } \# \text{ of events}} = p_A$$

Law of large numbers

\Rightarrow probability for microstate "a"

$$p_a = \frac{1}{\Omega} \quad \text{equipartition!}$$

$$\text{test: } \sum_a p_a = \sum_{a=1}^{\Omega} \frac{1}{\Omega} = 1$$

\Rightarrow probability of macrostate "A"

$$p_A = \frac{\# \text{ of all microstates leading to } A}{\Omega}$$
$$= \frac{p_a | A}{\Omega}$$

Example : • tossing a coin many times

(5)

• result: H T T H H T T T H T T H T ...

$\Rightarrow N$ independent tries : 2^N possible

arrangements of Hs and Ts

$\hookrightarrow 2^N$ possible microstates

$\hookrightarrow \Omega = 2^N$

Now fixing a macrostate: we want exactly N_1 heads ($N - N_1$ tails) out of N tries:

• # of arrangements with N_1 heads out of N is

$$\omega_N(N_1) = \frac{N!}{N_1! (N - N_1)!}$$

- $N!$ ways to arrange N (different) objects

- but order of Hs and Ts is not important
(look all the same)

- $N_1!$ possibilities to arrange the heads

- $(N - N_1)!$ - " - the tails

hint: $\omega_N(N_1)$ is number of special states,
not probability

$P_{N_1} = \frac{1}{\Omega} \omega_N(N_1)$ is the probability

tests: (maybe not doing if time problems occur) ⑥

- i) $N_1 = N \rightarrow \omega_N(N) = 1$
- ii) $N_1 = N-1 \rightarrow \omega_N(N-1) = N$
- iii) $N_1 = 0 \rightarrow \omega_N(0) = 1$
- iv) $N_1 = 1 \rightarrow \omega_N(1) = N$

$$\begin{aligned}
 v) \sum_{N_1=0}^N \frac{N!}{N_1! (N-N_1)!} &= \sum_{N_1=0}^N \frac{N!}{N_1! (N-N_1)!} 1^{N_1} \cdot 1^{N-N_1} \\
 &= \sum_{N_1=0}^N \binom{N}{N_1} 1^N 1^{N-N_1} = (1+1)^N = 2^N \quad \text{OK}
 \end{aligned}$$

math:

$$\begin{aligned}
 (a+b)^2 &= a^2 + 2ab + b^2 \\
 (a+b)^3 &= a^3 + 3a^2b + 3ab^2 + b^3 \\
 (a+b)^N &= \sum_{n=0}^N \binom{N}{n} a^n b^{N-n}
 \end{aligned}$$

binominal coefficients

Question: what is the average # of heads?

(... of course $\frac{1}{2}N$)

average value of quantity A

$$\langle A \rangle = \frac{1}{\Omega} \sum_v A_v \omega_N(A_v)$$

v... runs over all possible values

$$\langle N_1 \rangle = \frac{1}{\Omega} \sum_{N_1=0}^N N_1 \omega_N(N_1)$$

$$= \frac{1}{2^N} \sum_{N_1=0}^N N_1 \frac{N!}{N_1! (N-N_1)!} = \frac{1}{2} N$$

HOME

Lecture 4

1.4. Fluctuations in large systems

(1)

Question I: where is the maximum in the distribution (most likely event)?

Question II: how quickly does the distribution decay around maximum (width)?

$$a) w_N(N_1) = \frac{N!}{N_1! (N-N_1)!} \rightarrow \max$$

[coin tossing]
as example]

$$\text{search for: } \frac{dw_N(N_1)}{dN_1} = 0$$

$$\text{trick: } \frac{d \ln w_N(N_1)}{dN_1} = 0 \quad \text{is equivalent} \\ (\ln \text{ is monotone})$$

$$0 \stackrel{!}{=} \frac{d \ln w_N(N_1)}{dN_1} = \frac{d}{dN_1} \left(\ln \frac{N!}{N_1! (N-N_1)!} \right) \\ = \frac{d}{dN_1} \left(\ln N! - \ln N_1! - \ln(N-N_1)! \right)$$

Math: Stirlings formula: $\ln n! \approx n \ln n - n$

$$\frac{d \ln w_{N_1}(N_1)}{d N_1} = \frac{d}{d N_1} \left[N \ln N - N - N_1 \ln N_1 + N_1 - (N - N_1) \ln (N - N_1) + (N - N_1) \right] \quad (2)$$

$$= \frac{d}{d N_1} \left[N \ln N - N_1 \ln N_1 - (N - N_1) \ln (N - N_1) \right]$$

$$= -\ln N_1 - 1 + \ln (N - N_1) + 1$$

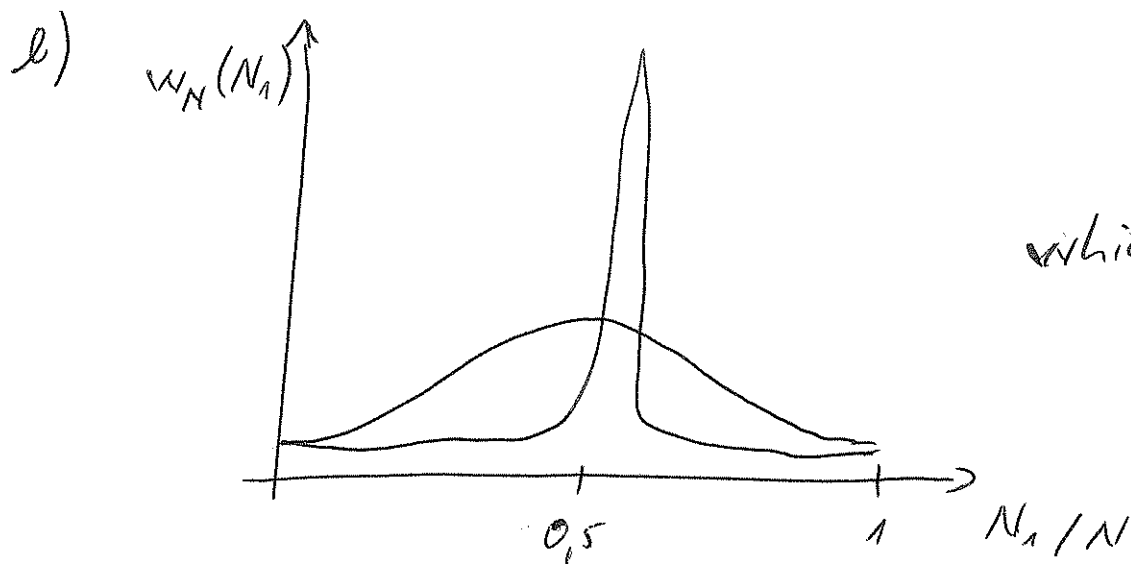
$$= -\ln N_1 + \ln (N - N_1)$$

$$= \ln \left(\frac{N - N_1}{N_1} \right) \stackrel{!}{=} 0$$

$$\Leftrightarrow \frac{N - N_1}{N_1} = 1$$

$$\Leftrightarrow N_1 = \frac{1}{2} N$$

$$\Rightarrow N_1^{\max} = \frac{1}{2} N = \langle N_1 \rangle$$



which one is true?

∅ predictability ~ width of the distribution

Question: where does the distribution fall to half the maximum value?

• N_1' such that $w_N(N_1') = \frac{1}{2} w(N_1^{\max})$

with $N_1^{\max} = \frac{1}{2} N$

$N_1' = N_1^{\max} - m = \frac{N}{2} - m$

$\Rightarrow w_N\left(\frac{N}{2} - m\right) = \frac{1}{2} w_N\left(\frac{N}{2}\right)$

$$\frac{N!}{\left(\frac{N}{2} - m\right)! \left(N - \frac{N}{2} + m\right)!} = \frac{1}{2} \frac{N!}{\left(\frac{N}{2}\right)! \left(N - \frac{N}{2}\right)!}$$

$\Rightarrow \left(\frac{N}{2} - m\right)! \left(\frac{N}{2} + m\right)! = 2 \left(\frac{N}{2}\right)!^2$

Math: $\left(\frac{N}{2} + m\right)! = \left(\frac{N}{2} + m\right) \left(\frac{N}{2} + m - 1\right) \dots \left(\frac{N}{2}\right)!$

$\left(\frac{N}{2}\right)! = \left(\frac{N}{2}\right) \left(\frac{N}{2} - 1\right) \left(\frac{N}{2} - 2\right) \dots \left(\frac{N}{2} - m\right)!$

$$\Rightarrow \left(\frac{N}{2} + m\right) \left(\frac{N}{2} + m - 1\right) \dots \left(\frac{N}{2} + 1\right) \quad (4)$$

$$= 2 \left(\frac{N}{2}\right) \left(\frac{N}{2} - 1\right) \dots \left(\frac{N}{2} - m + 1\right)$$

∴ take only the leading order terms in N
 $(N \gg m)$

$$\Rightarrow \left(\frac{N}{2}\right)^m + [1 + 2 + 3 + \dots + m] \left(\frac{N}{2}\right)^{m-1}$$

$$= 2 \left(\frac{N}{2}\right)^m - 2 [1 + 2 + 3 + \dots + (m-1)] \left(\frac{N}{2}\right)^{m-1}$$

.....

Math: $\sum_j^m j \approx \frac{m^2}{2}$ for $m \gg 1$

.....

- use summation
- divide by $\left(\frac{N}{2}\right)^{m-1}$

$$\Rightarrow \frac{N}{2} + \frac{m^2}{2} = 2 \frac{N}{2} - 2 \frac{(m-1)^2}{2}$$

$$\Rightarrow m^2 = N - 2(m-1)^2$$

$$m^2 \sim N$$

$$m \sim \sqrt{N}$$

∴ \sqrt{N} is also a large number, but we need
relative deviation from maximum $\sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$

\Rightarrow this relative deviation gets very small for $N \rightarrow \infty$

c) better definition of fluctuations

Def.: mean square deviation

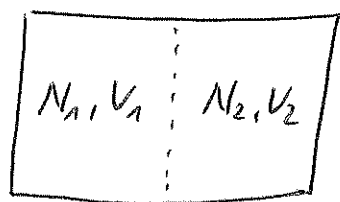
$$\begin{aligned} \sigma_A^2 &= \langle (A - \langle A \rangle)^2 \rangle \\ &= \langle A^2 \rangle - 2\langle A \rangle \langle A \rangle + \langle A \rangle^2 \\ &= \langle A^2 \rangle - \langle A \rangle^2 \end{aligned}$$

Def.: root mean square deviation

$$\sigma_A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

$\frac{\sigma_A}{N}$ is measure of fluctuations

example: gas in box that is divided into two (6)



• 1 particle: $p_1 = \frac{V_1}{V}$ and $p_2 = \frac{V_2}{V}$

• probability to find N_1 particles in V_1

$$P_N(N_1) = \frac{N!}{N_1! (N-N_1)!} p_1^{N_1} p_2^{N-N_1}$$

(we can almost copy from coin tossing...)

$$\Rightarrow \langle N_1 \rangle = N \cdot p_1 = N^{\max}$$

$$\Rightarrow \sigma_{N_1}^2 \sim 2 N p_1 (1-p_1)$$

$$\Rightarrow \frac{\sigma_{N_1}}{N} \sim \frac{\sqrt{2 N p_1 (1-p_1)}}{N} = \frac{\sqrt{2 p_1 (1-p_1)}}{\sqrt{N}}$$

✓ find typical $\frac{1}{\sqrt{N}}$ behaviour again ✓

example with numbers : gas in box

$$p_1 = \frac{1}{2}, p_2 = \frac{1}{2}, N = 10^{22} \text{ (1 l of air)}$$

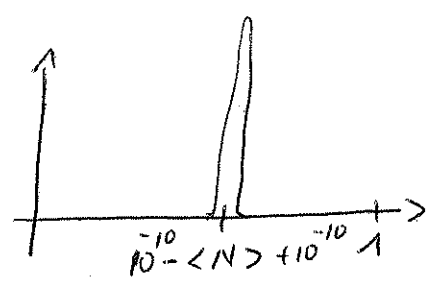
$$\Rightarrow \langle N_1 \rangle = 5 \times 10^{21} = N^{\max}$$

• consider probability to measure $N_1 = N_1^*$

with
$$\frac{N_1^* - N_1^{\max}}{N} = \frac{N_1^*}{N} - \frac{1}{2} = 10^{-10}$$

extremely small deviation

$$\Rightarrow \frac{W_N(N^*)}{W_N(N^{\max})} \approx e^{-1000} \hat{=} \text{non-existing}$$



\Rightarrow chances for total rest of distribution $< 10^{-4000}$

\Rightarrow for large N , we have extremely small deviations from average value

\Rightarrow measurement of quantity A gives (almost for sure) $\langle A \rangle$

✓ That's why statistical mechanics works ✓

Lecture 5

1.5. Micro-canonical ensemble

①

=> well suited for isolated / closed systems

Thermodynamics

$$\left. \begin{array}{l} N = \text{const.} \\ U = \text{const.} \end{array} \right\} \text{closed}$$

thermodynamic potential

$$\Rightarrow U = U(S, V, N)$$

stat. Mechanics

$$\begin{aligned} N &= \sum_i N_i = \text{const.} \\ E &= \sum_i N_i \epsilon_i = \text{const.} \end{aligned}$$

actually:

$$E - \Delta \leq E \leq E + \Delta$$

$$\text{with } \frac{\Delta}{E} \ll 1$$



$$\boxed{U = E}$$



identification needed

! connection $U = E$ is not sufficient

2 What is the additional connection between

$$U, S, T, V \quad \stackrel{?}{\Leftrightarrow} \quad \text{Number of states with energy } E$$

Boltzmann

$$\boxed{S^{\text{thermal}} = S^{\text{statistical}} = k_B \ln \Omega}$$

! relation is a postulate

=> no proof possible

=> justified by resulting, i.e. predicted, behaviour

other form for $S = k_B \ln \Omega$:

(2)

$$\begin{aligned} S &= k_B \ln \Omega = k_B \ln \Omega \underbrace{\sum_{v=1}^{\Omega} p_v}_{1 \hat{=} \text{sum of all probabilities}} \\ &= -k_B \ln \frac{1}{\Omega} \sum_{v=1}^{\Omega} p_v \\ &= -k_B \sum_{v=1}^{\Omega} \ln \frac{1}{\Omega} p_v \\ &= -k_B \sum_{v=1}^{\Omega} p_v \ln p_v \quad p_v = \frac{1}{\Omega} \text{ as all } p_v \text{ are equal} \end{aligned}$$

Arguments for $S = k_B \ln \Omega$

a) it works!

b) Similarities:

- S increases with heat input - Ω increases with energy available

$$dS \geq \frac{\delta Q}{T}$$

- heat leads to disorder
(melting, more chaos, ...)

- heat leads to more accessible states
 $\rightarrow p_v$ decreases

- S is a measure of disorder - Ω related to disorder

$$\Rightarrow S = f(\Omega)$$

what function?

c) extensive character of S

③

• consider system made out of two:
that are independent / isolated

①

②

$$\Rightarrow S_{1+2} = S_1 + S_2$$

(extensive)

$$\Rightarrow \Omega_{12} = \Omega_1 \cdot \Omega_2$$

(independent)

\Downarrow

$$S_{1+2} = f(\Omega_{12}) = f(\Omega_1) + f(\Omega_2)$$

\Downarrow

$$S_{1+2} = f(\Omega_{12}) = f(\Omega_1 \cdot \Omega_2)$$

\Downarrow

$$S_{1+2} = f(\Omega_1) + f(\Omega_2) = f(\Omega_1 \cdot \Omega_2)$$

\Leftarrow

\Rightarrow only true for logarithm

$$\begin{aligned} \Rightarrow S_{1+2} = S_1 + S_2 &= A \ln \Omega_1 + A \ln \Omega_2 \\ &= A \ln(\Omega_1 \cdot \Omega_2) = A \ln(\Omega_{12}) \end{aligned}$$

\Rightarrow need to fix constant : $A = k_B$

\Rightarrow units must be fixed with constant as well

$$\begin{aligned} k_B &= 1.381 \times 10^{-23} \text{ J/K} \\ &= 8.617 \times 10^{-5} \text{ eV/K} \end{aligned}$$

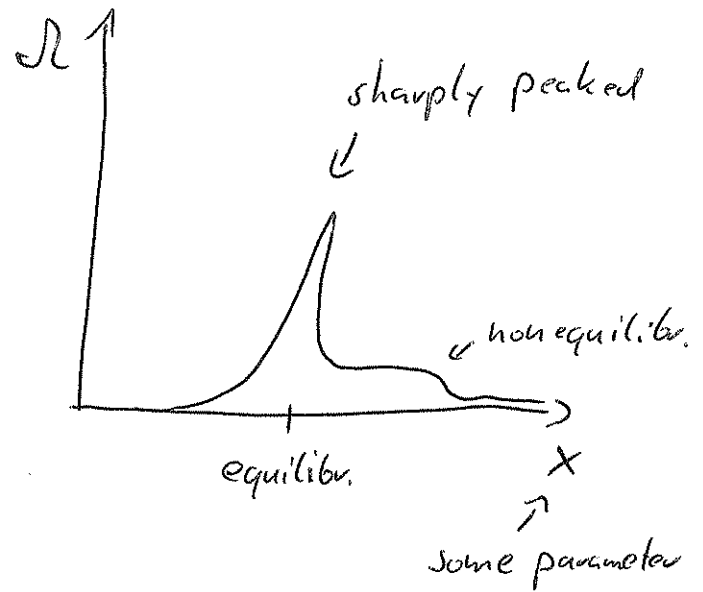
d) behaviour in nonequilibrium

(4)

→ relaxation towards equilibrium

$dS > 0$ non equilibrium

$S = S^{\max}$ equilibrium



in nonequilibrium:

$\Omega_1 \rightarrow \Omega_2 \rightarrow \dots$ randomly,

BUT much more states in the direction of equilibrium!

$\Omega \rightarrow \Omega^{\max}$

in equilibrium:

$S = S^{\max}$ and $\Omega = \Omega^{\max}$

⇒ $S = k_B \ln \Omega$ consistent with second law of thermodynamics

e) consistency with first law / equilibrium condition (5)

• consider system split into two: $\boxed{1 \mid 2}$

• first law + second law

$$U = U_1 + U_2 \\ = TdS - pdV$$

$$\hookrightarrow dS = \frac{1}{T} dU + \dots$$

$$= S(U, V, N)$$

• equilibrium: $T_1 = T_2$

• energy conservation

$$E = E_1 + E_2 \hookrightarrow dE_1 = -dE_2$$

• number of states

$$\Omega(E) \approx \Omega(E_1) \cdot \Omega(E_2)$$

• equilibrium: $\Omega(E) \rightarrow \max$

$$\frac{d\Omega(E)}{dE_1} \stackrel{!}{=} 0$$

$$\Rightarrow 0 = \frac{d \ln \Omega(E)}{dE_1} \quad \ln \dots \text{monoton}$$

$$= \frac{d \ln \Omega(E_1)}{dE_1} + \frac{d \ln \Omega(E - E_1)}{dE_1}$$

$$= \frac{d \ln \Omega(E_1)}{dE_1} - \frac{d \ln \Omega(E_2)}{dE_2}$$

Boltzmann

$$\Rightarrow 0 = \frac{1}{k_B} \left[\frac{\partial S(E_1)}{\partial E_1} - \frac{\partial S(E_2)}{\partial E_2} \right]$$

• identify: $E_1 = U_1, E_2 = U_2$

first law

$$\Rightarrow 0 = \frac{1}{T_1} - \frac{1}{T_2} \Rightarrow T_1 = T_2$$

$\Rightarrow S = k_B \ln \Omega$ is consistent with first law
+ equilibrium condition $T_1 = T_2$

Recipe for the micro-canonical description ⑥

- E, N given
- Identify: $U = E$
- Calculate: number of states $\Omega = \Omega(E, N)$
- Calculate: $S^{\text{stat}} = k_B \ln \Omega(E, N)$
- Identify: $S^{\text{therm.}} = S^{\text{stat.}}$

$$\Rightarrow S = S(E, N)$$

- Invert relation for $S(E, N)$ to obtain thermodynamic potential $U = U(S, N)$
- Use derivatives + Maxwell relations to obtain other thermodynamic functions

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad ; \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad ; \quad \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

✓ Problem: Calculate the number of states...

Lecture 6

Counting microstates for a given E & N ①

- in general: very problematic for large systems
- special cases: easier for systems with discrete energy levels (QM)

a) Notation

◦ $\Omega(E, N)$... # of all microstates with E, N

◦ $w_N(N_1)$... # of all microstates with E, N
under the restriction that N_1 particles are in the state " E_1 "
 \Rightarrow these microstates give the same macrostate (defined by " E_1 ")

general

◦ $w_N(n_1, \dots, n_j)$... # of all microstates with E, N
and n_1 particles in state E_1 ,
 n_2 particles in state E_2, \dots

$$\sum_k n_k = N \text{ must hold}$$

◦ p_r ... probability of microstate r $p_r = \frac{1}{\Omega}$

◦ $p(N_1)$... probability to find N_1 particles
in special state, e.g., E_1

◦ $p_N(n_1, \dots, n_j)$... probability to find N_1 particles
in E_1 , N_2 particles in E_2, \dots

b) Counting the states

(2)

- N independent particles that can occupy M states

$$\Rightarrow \Omega = \underbrace{M \cdot M \cdot \dots \cdot M}_N = M^N$$

- $w_N(N_1) = \frac{N!}{N_1! (N-N_1)!}$ $(N-N_1)$ particles in the other state

- $w_N(n_1, \dots, n_j) = \frac{N!}{n_1! n_2! \dots n_j!} = \frac{N!}{\prod_k n_k!}$

follows by splitting the system again, ...

- $p_N(n_1, \dots, n_j) = \frac{N!}{\prod_k n_k!} p_1^{n_1} p_2^{n_2} p_3^{n_3} \dots p_j^{n_j}$

c) Conditions to be hold:

- $\Omega = \sum_{n_k \geq 0} w_N(n_1, \dots, n_j)$ and $\sum_k n_k = N$

- $\sum_{n_k=0}^N p_N(n_1, \dots, n_j) = 1$ and $\sum_k p_k = 1$

1.5. Example: Einstein solid

(3)

- Lattice in 3D with N sites (atoms)
- 3 harmonic oscillators per site (one in each direction of space)
- Neither lattice sites nor oscillators couple in any way

\Rightarrow $3N$ independent oscillators

- energy of the system

$$E = N \frac{3}{2} \hbar \omega + \sum_{i=1}^{3N} n_i \hbar \omega$$

\uparrow
zero point energy

\uparrow
 n_i quanta of energy at site "i"

\Rightarrow total # of energy quanta

$$M = \sum_{i=1}^{3N} n_i$$

\Rightarrow M defines energy of the system ("quantum number")

$$E = \frac{3}{2} N \hbar \omega + M \hbar \omega \equiv U$$

o Count the microstates for $3N$ oscillators at E ⁽⁴⁾

trick: - oscillators are all independent, but they are distinguishable

=> arrange them in a line

=> represent boundaries between them by \bullet

=> represent quanta by symbols \circ

=> $3N-1$ symbols \bullet

and M symbols \circ

Question: In how many ways can we arrange M open and $3N-1$ full dots?

(Keep in mind: quanta are indistinguishable)

Answer:
$$\Omega = \frac{(3N-1+M)!}{M! (3N-1)!}$$

- $(3N-1+M)!$ is total # of symbols

- $M!$... # of same arrangements of M \circ 's

- $(3N-1)!$... # of same - " - of $(3N-1)$ \bullet 's

• calculate the entropy of the system (5)

$$S = k_B \ln \frac{(3N-1+M)!}{M! (3N-1)!}$$

Math: Stirling's formula: $\ln N! = N \ln N - N$

$$S = k_B \left[(3N-1+M) \ln (3N-1+M) - (3N-1+M) - M \ln M + M - (3N-1) \ln (3N-1) + (3N-1) \right]$$

Use the fact that $N \gg 1$ and $M \gg 1$

$$S = k_B \left[(3N+M) \ln (3N+M) - M \ln M - 3N \ln (3N) \right]$$

$$= k_B \frac{(3N+M)^{3N+M}}{M^M (3N)^{3N}}$$

• Invert $S = S(M)$

trick: write $S = S(T)$ and $M = M(T)$

$$\text{use: } \frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N = \left(\frac{\partial S}{\partial M} \right)_N \left(\frac{\partial M}{\partial E} \right)_N = \frac{1}{k_B T} \left(\frac{\partial S}{\partial M} \right)_N$$

$$\Rightarrow \frac{k_B T}{k_B T} = \frac{1}{k_B} \left(\frac{\partial S}{\partial M} \right)_N = \ln \left(\frac{3N}{M} + 1 \right)$$

check at HOME

cannot neglect "1" here
as $M \gg 3N$ (many quanta)

solve $\frac{\hbar\omega}{k_B T} = \ln\left(\frac{3N}{M} + 1\right)$ for M (6)

$$\Rightarrow 1 + \frac{3N}{M} = \exp(\beta\hbar\omega) \quad \beta = \frac{1}{k_B T}$$

$$\Rightarrow M = M(T, N) = \frac{3N}{\exp(\beta\hbar\omega) - 1}$$

calculate internal energy $U = U(T, N) = E(T, N)$

$$U = E = \frac{3}{2} N \hbar\omega + 3N \hbar\omega \left[\exp(\beta\hbar\omega) - 1 \right]^{-1}$$

$$= \frac{3}{2} N \hbar\omega + 3N \hbar\omega \frac{\exp(-\beta\hbar\omega)}{1 - \exp(-\beta\hbar\omega)}$$

internal energy at a given temperature

• calculate heat capacity

$$C_N = \left(\frac{\partial U}{\partial T} \right)_N = \frac{3N \hbar^2 \omega^2}{k_B T^2} \frac{\exp(-\beta\hbar\omega)}{[1 - \exp(-\beta\hbar\omega)]^2}$$

↑
can be measured
(comparison later)

• entropy follows to be

$$S = 3N k_B \ln(1 - e^{-\beta\hbar\omega}) + \frac{3N k_B \beta \hbar\omega e^{-\beta\hbar\omega}}{1 - \exp(-\beta\hbar\omega)}$$

... if time ...

Lecture 7

2 Systems in heat contact to environment ^① - the canonical ensemble

Problems with the micro-canonical ensemble

technical :

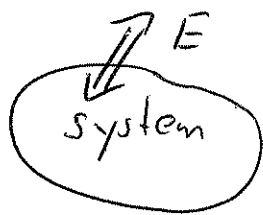
- calculations of Ω very difficult
- weird temperature definition: $T = \left(\frac{\partial U}{\partial S} \right)$
- independent variables S, V problematic

principal :

- no system is fully isolated; effect of energy fluctuations?

2.1. Systems under consideration

- describe system with heat contact to large reservoir, but no particle exchange allowed



- reservoir at constant temperature
- => system at same temperature (required by 0th law)

reservoir/environment

- system + reservoir are treated as isolated system

2.2. Thermodynamics for systems in heat contact ^② to environment

a) new thermodynamic potential

! T is defined by reservoir

$\Rightarrow T$ must be an independent variable,

but $U = U(S, V)$

\Rightarrow swap meaning of S and T

(who likes to use S anyway?)

• Moreover, U is not constant as heat is flowing from/to system to/from heat bath

• define Helmholtz free energy: $F = U - TS$

\Rightarrow exact differential: $dF = dU - d(TS)$

$$= dU - TdS - SdT$$

fundamental law \rightarrow

$$= TdS - pdV - TdS - SdT$$

$$= -SdT - pdV$$

\Rightarrow independent variables: $T, V \Leftrightarrow F = F(T, V)$

• transformation is called Legendre - transformation

(3)

\Rightarrow first derivatives of F

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

\Rightarrow second derivatives / Maxwell-relation

$$\left(\frac{\partial}{\partial V} \underbrace{\left(\frac{\partial F}{\partial T}\right)_V}_{-S}\right)_T = \left(\frac{\partial}{\partial T} \underbrace{\left(\frac{\partial F}{\partial V}\right)_T}_{-P}\right)_V$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

\forall 3 more relations between therm. functions

• Interpretation of U and F

U ... energy needed to create system
in vacuum

F ... energy needed to create system
in heat bath (energy can be extracted
from the reservoir)

b) equilibrium condition / stability criterion ⁽⁴⁾

• consider state changes without work: $dV=0$

$$\Rightarrow dU = \delta Q \leq T dS \quad \text{fundamental law}$$
$$\leq d(TS) \quad T = \text{const.}$$

$$\Rightarrow d(U - TS) \leq 0$$

$$\Rightarrow dF \leq 0$$

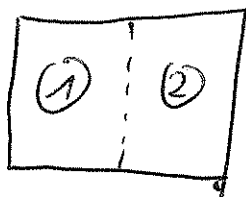
$dF < 0$ irreversible processes
(nonequilibrium)

$dF = 0$ quasi-static (reversible) processes
+ equilibrium

$F \rightarrow \min$ in nonequilibrium

$F = F_{\min}$ in equilibrium
(replaces condition $S \rightarrow \max$)

• consider system split into two parts



$\Rightarrow p_1 = p_2$ follows as for
isolated systems

$\forall_0 T_1 = T_2 = T_{\text{reservoir}}$ from
0th law of thermodynamics

Supplement: more therm. potentials (CHEMISTRY) ⁽⁵⁾

• can also swap $p \Leftrightarrow V$ to describe systems under constant pressure

• define Gibbs energy (enthalpy): $H = U + pV$

$$\begin{aligned}\Rightarrow \text{exact differential: } dH &= dU + d(pV) \\ &= TdS - pdV + pdV + Vdp \\ &= TdS + Vdp\end{aligned}$$

\Rightarrow independent variables: $S, p \Rightarrow H = H(S, p)$

$$\Rightarrow \text{first derivatives: } \left(\frac{\partial H}{\partial S}\right)_p = T \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

\Rightarrow second derivatives / Maxwell relation

$$\left(\frac{\partial}{\partial p} \underbrace{\left(\frac{\partial H}{\partial S}\right)_p}_T\right)_S = \left(\frac{\partial}{\partial S} \underbrace{\left(\frac{\partial H}{\partial p}\right)_S}_V\right)_p$$

$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

• interpretation: H is energy needed to create system under constant pressure

• we could also swap $S \Leftrightarrow T$ and $p \Leftrightarrow V$ ⑥

• define Gibbs free energy : $G = U - TS + pV$

=> exact differential :

$$dG = dU - d(TS) + d(pV)$$

$$= TdS - pdV - TdS - SdT + pdV + Vdp$$

$$= -SdT + Vdp$$

=> independent variables : $T, p \Rightarrow G = G(T, p)$

=> first derivatives : $\left(\frac{\partial G}{\partial T}\right)_p = -S$ $\left(\frac{\partial G}{\partial p}\right)_T = V$

=> second derivatives / Maxwell relation

HOME

• interpretation : G is energy needed to create system in heat bath under constant pressure

general :

	$-TS$				
	\longrightarrow				
$+pV$	\downarrow				
	<table border="1" style="display: inline-table;"><tr><td>U</td><td>F</td></tr><tr><td>H</td><td>G</td></tr></table>	U	F	H	G
U	F				
H	G				

schematic to obtain the therm. potentials

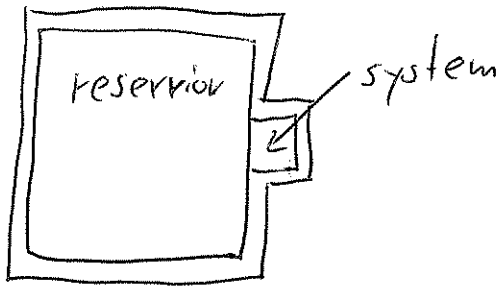
Lecture 8

2.3 The canonical ensemble

①

- appropriate for systems with heat contact to large reservoir

$\Rightarrow T = \text{const.}$ because of contact to reservoir



- reservoir + system are isolated
- no particle exchange

a) Boltzmann factor

- extreme example: system is single atom with discrete energies E_1, E_2, \dots

\Rightarrow energy conservation in $R+S$

$$E = E_R + E_S = \text{const.} \quad E_S = E_1, E_2, \dots$$

- number of states in $R+S$

$\Omega(E) \rightarrow \text{max}$ in equilibrium, but

$$\Omega(E) = \Omega_R(E_R) \cdot \Omega_S(E_S) \quad \text{for all } E_S$$

with $\Omega_R(E_R) \gg \Omega_S(E_S)$

here: $\Omega_S = 1$ as defined by energy E_S

- use equipartition theorem in $R+S$: (2)
 probability of state with $E_S = E_j$, that is $P(E_j)$
 is proportional to $\Omega \approx \Omega_R(E-E_R)$

V_0 probability for atom state related to
 # of states in the reservoir

- take ratio of probabilities

$$\frac{P(E_2)}{P(E_1)} = \frac{\Omega_R(E-E_2)}{\Omega_R(E-E_1)}$$

- relate # of states in reservoir to entropy

$$S_R = +k_B \ln \Omega_R(E-E_j)$$

$$\Rightarrow \frac{P(E_2)}{P(E_1)} = \frac{e^{S_R(E_2)/k_B}}{e^{S_R(E_1)/k_B}} = \exp\left(\frac{[S_R(E_2) - S_R(E_1)]}{k_B}\right)$$

- Thermodynamics (fundamental law)

$$dS_R = \frac{1}{T} [dU_R + p dV_R - \mu_R dN_R]$$

$$- dN_R = 0 \quad \text{no particle exchange}$$

$$- p dV_R \ll dU_R$$

$\nearrow \sim 10^{-25} \text{ J}$ for gases

$$\Rightarrow \Delta S_R = \frac{1}{T} \Delta U_R$$

$$\Rightarrow \Delta S_R = S_R(E_2) - S_R(E_1) = \frac{1}{T} [U_R(E_2) - U_R(E_1)] \quad (3)$$

$$E = U_R + E_j \rightarrow$$

$$\rightarrow U_R = E - E_j$$

$$= -\frac{1}{T} [E_2 - E_1]$$

$$\Rightarrow \frac{P(E_2)}{P(E_1)} = e^{-[E_2 - E_1]/k_B T} = \frac{e^{-\beta E_2}}{e^{-\beta E_1}}$$

• Def.: $e^{-\beta E_j}$... Boltzmann factor; $P(E_j) \sim e^{-\beta E_j}$

• separation of variables in ratio

$$\frac{P(E_2)}{\exp(-\beta E_2)} = \frac{P(E_1)}{\exp(-\beta E_1)} = \text{const.} = \frac{1}{Z}$$

$$\Rightarrow \boxed{P(E_j) = \frac{1}{Z} e^{-\beta E_j}}$$

! equipartition in $R+S$ yields different probabilities for states in the system S !

• derivation works also for larger systems as long as $E_R \gg E_S$ and $\Omega_R \gg \Omega_S$

b) Partition function

(4)

• $P(E_j)$ is probability to find system in state E_j

\Rightarrow sum over all probabilities must be unity

$$1 \stackrel{!}{=} \sum_j P(E_j) = \frac{1}{Z} \sum_j e^{-\beta E_j}$$

$$\Rightarrow \boxed{Z = \sum_{\text{states}} e^{-\beta E_j}} = \text{sum of all Boltzmann factors}$$

partition function

c) consider internal energy of the system

$$U = \langle E \rangle = \sum_j E_j P(E_j)$$

$$= - \frac{\partial}{\partial \beta} \ln Z$$

check at HOME

✓ Z defines thermodynamic quantity

✓ However, U is not therm. potential

for systems with heat contact to environment

d) Revealing thermodynamics from Z (5)

- unexpected idea: - Z was introduced as factor to yield $\sum p_j = 1$
- but Z contains all information on probabilities / system

• We are going to show

$$\boxed{F = -k_B T \ln Z} \quad \text{or} \quad Z = e^{-\beta F}$$

F... Helmholtz free energy = potential

Demonstrate that i) $F \sim \ln Z$ is extensive

ii) $F = U - TS$ holds with upper relation

i) consider two systems with no interaction

$$\Rightarrow E_{1+2} = E_1 + E_2$$

$$\Rightarrow Z_{1+2} = Z_1 \cdot Z_2 \quad \text{show at HOME}$$

$$\begin{aligned} \Rightarrow F_{1+2} &= -k_B T \ln Z_{1+2} = -k_B T \ln Z_1 \cdot Z_2 \\ &= -k_B T \ln Z_1 + (-k_B T) \ln Z_2 \\ &= F_1 + F_2 \end{aligned}$$

ii) thermodynamics : $dF = dU + SdT$ (6)

$$\Rightarrow \left(\frac{\partial F}{\partial T} \right)_V = -S = \frac{F-U}{T} \Leftrightarrow F = U - TS$$

• manipulating statistics side :

$$\left(\frac{\partial F}{\partial T} \right)_V = \frac{\partial}{\partial T} \left[-k_B T \ln Z \right] = -k_B \ln Z - k_B T \frac{\partial}{\partial T} \ln Z$$

① : this form is OK

$$\textcircled{2} : \frac{\partial}{\partial T} \ln Z = \frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{Z} \frac{\partial}{\partial T} \sum_j e^{-\beta E_j}$$

$$= \frac{1}{Z} \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \sum_j e^{-\beta E_j}$$

$$\beta = \frac{1}{k_B T}$$

$$= \frac{1}{Z} \left[-\frac{1}{k_B T^2} \right] \sum_j -E_j e^{-\beta E_j}$$

$$= \frac{1}{k_B T^2} \sum E_j P(E_j)$$

$$= \frac{1}{k_B T^2} \langle E \rangle = \frac{U}{k_B T^2}$$

$$\Rightarrow \overset{-\textcircled{1}-\textcircled{2}}{=} \frac{\partial}{\partial T} \left[-k_B T \ln Z \right] = -k_B \ln Z - k_B T \frac{U}{k_B T^2}$$

$$= \frac{1}{T} \left[-k_B T \ln Z - U \right]$$

$$= \frac{F-U}{T}$$

OK

Lecture 9

Recipe to obtain thermodynamics within the canonical ensemble ⑦ = ①

- Find all energy states of the system
- Calculate partition function $Z = \sum_j e^{-\beta E_j}$
- Calculate Helmholtz free energy:

$$F = -k_B T \ln Z$$

- Get thermodynamics from F

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N} \quad S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}$$

or use shortcut via internal energy

$$U = F + TS = - \frac{\partial \ln Z}{\partial \beta}$$

✓ no counting of states

✓ calculations often much more straight forward than in micro-canonical ensemble

✓ better suited for real systems

2.4. Examples

a) paramagnet (2 states)

- atoms have magnetic moments
 - magnetic moment in the direction of \vec{B} field can be $\pm \mu$
 - magnetic energy in \vec{B} field : $E = \mu B$
- $\Rightarrow E_{\uparrow} = -\mu B ; E_{\downarrow} = \mu B$

first one particle:

- partition function:

$$Z = \sum_s e^{-\beta E_s} = e^{\beta \mu B} + e^{-\beta \mu B}$$

$$= 2 \cosh(\beta \mu B)$$

- probabilities for states \uparrow and \downarrow :

$$P_{\uparrow, \downarrow} = \frac{1}{Z} e^{\pm \beta \mu B} = \frac{e^{\pm \beta \mu B}}{2 \cosh(\beta \mu B)}$$

- average energy:

$$\langle E \rangle = \sum_s E_s P_s = -\mu B \frac{e^{\beta \mu B} - e^{-\beta \mu B}}{2 \cosh(\beta \mu B)}$$

$$= -\mu B \frac{2 \sin(\beta \mu B)}{2 \cos(\beta \mu B)} = -\mu B \tanh(\beta \mu B)$$

- average magnetic moment

(3)

$$\langle \mu \rangle = \sum_s \mu_s P_s = \mu_{\uparrow} P_{\uparrow} + \mu_{\downarrow} P_{\downarrow} = \mu P_{\uparrow} - \mu P_{\downarrow} \\ = \mu \tanh(\beta \mu B)$$

Now N particles:

- all atoms have independent magnetic moments

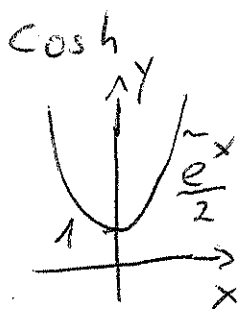
$$\Rightarrow \langle E \rangle = U = -N \mu B \tanh(\beta \mu B)$$

$$\text{test: } U = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta} \quad \text{HOME}$$

\Rightarrow all extensive quantities \times times N

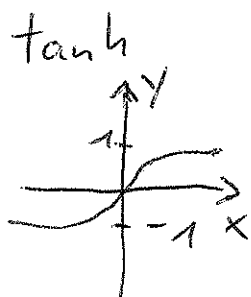
- heat capacity

$$C_B = \left(\frac{\partial U}{\partial T} \right)_B = -N \mu B \left(\frac{\partial}{\partial T} \left[\frac{e^A - e^{-A}}{e^A + e^{-A}} \right] \right)_B \quad A = \beta \mu B \\ = \frac{\mu B}{k_B T}$$



$$= -N \mu B \left[\frac{(e^A + e^{-A})(e^A - e^{-A})}{(e^A + e^{-A})^2} - \frac{(e^A - e^{-A})(e^A - e^{-A})}{(e^A + e^{-A})^2} \right] \left(- \frac{\mu B}{k_B T^2} \right)$$

$$= \frac{N}{k_B} \left(\frac{\mu B}{T} \right)^2 \frac{\cosh^2(A) - \sinh^2(A)}{\cosh^2(A)}$$



$$= k_B N (\beta \mu B)^2 \frac{1}{\cosh^2(A)}$$

$$= k_B N (2\beta \mu B)^2 \frac{\exp(2\beta \mu B)}{[\exp(2\beta \mu B) + 1]^2}$$

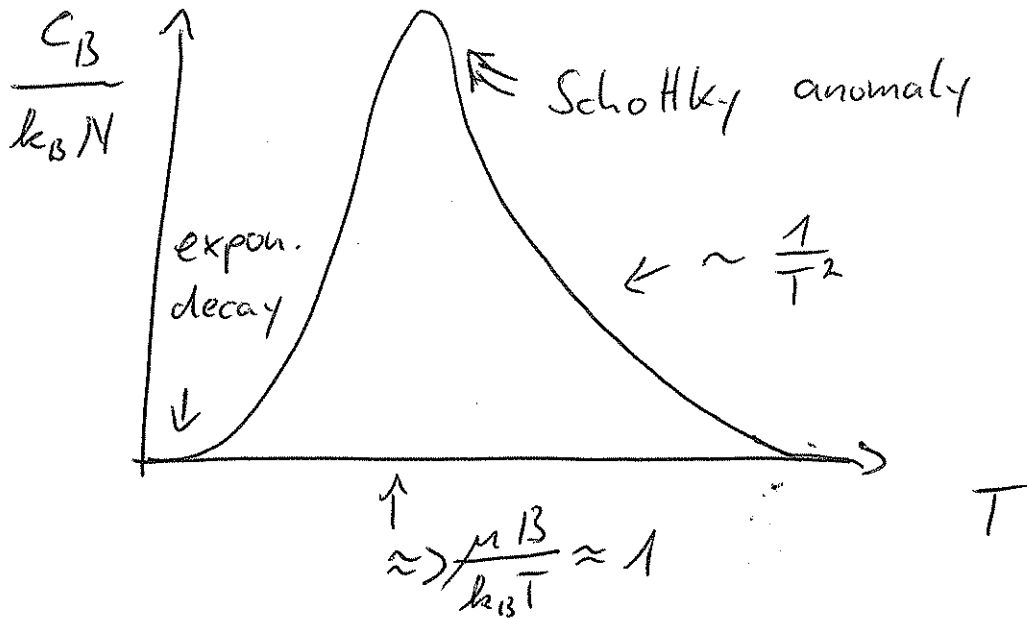
-high temperature limit : $\beta \mu B \ll 1$

$$\Rightarrow C_B = k_B N (2/\beta \mu B)^2 \sim \frac{1}{T^2} \rightarrow 0$$

-low temperature limit : $\beta \mu B \gg 1$

$$\Rightarrow C_B = k_B N (2/\beta \mu B)^2 \exp(-2\beta \mu B) \rightarrow 0$$

∇ third law fulfilled ∇



• Entropy

$$S = \frac{1}{T} [U - F] = k_B \beta U + k_B N \ln Z_1$$

$$= k_B N \left[-\beta \mu B \tanh(\beta \mu B) + \ln \left(2 \cosh(\beta \mu B) \right) \right]$$

-high temperatures ($\beta \mu B \ll 1$): $S \rightarrow k_B N \ln 2$

$\hat{=}$ coin tossing $\hookrightarrow \Omega = 2^N$ states

(fully chaotic) $\hookrightarrow S = k_B \ln \Omega = k_B N \ln 2$

-low temperatures : $S \rightarrow 0$

$\hat{=}$ fully ordered state with $\Omega = 1$

b) N harmonic oscillators in heat bath (Einstein solid) ⑤

• energies of oscillators

$$E_n = \left(\frac{1}{2} + n\right) \hbar \omega$$

n energy quanta $\hbar \omega$
+ zero point energy

first one oscillator →

• partition function

$$Z_1 = \sum_n \exp\left[-\beta \left(\frac{1}{2} + n\right) \hbar \omega\right]$$

$$= \exp\left(-\frac{1}{2} \beta \hbar \omega\right) \cdot \underbrace{\sum_{n=0}^{\infty} \exp(-n \beta \hbar \omega)}$$

$$= \sum_{n=0}^{\infty} \left[\exp(-\beta \hbar \omega)\right]^n$$

$$= \sum_{n=0}^{\infty} x^n \quad x = e^{-\beta \hbar \omega}$$

geometric series →

$$= \frac{1}{1-x} \quad \text{for } x < 1 \text{ OK}$$

$$Z_1 = \frac{\exp\left(-\frac{1}{2} \beta \hbar \omega\right)}{1 - \exp(-\beta \hbar \omega)}$$

• average energy $\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$

$$= \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1}$$

Low temp: $\langle E \rangle = \frac{1}{2} \hbar \omega$

high temp: $\langle E \rangle \rightarrow k_B T$ per particle

• heat capacity

$$C = \left(\frac{\partial U}{\partial T} \right) = k_B (\beta \hbar \omega)^2 \frac{\exp(\beta \hbar \omega)}{[\exp(\beta \hbar \omega) - 1]^2}$$

(6)

now N oscillators moving in 3 dimensions

$\Rightarrow 3N$ independent oscillators

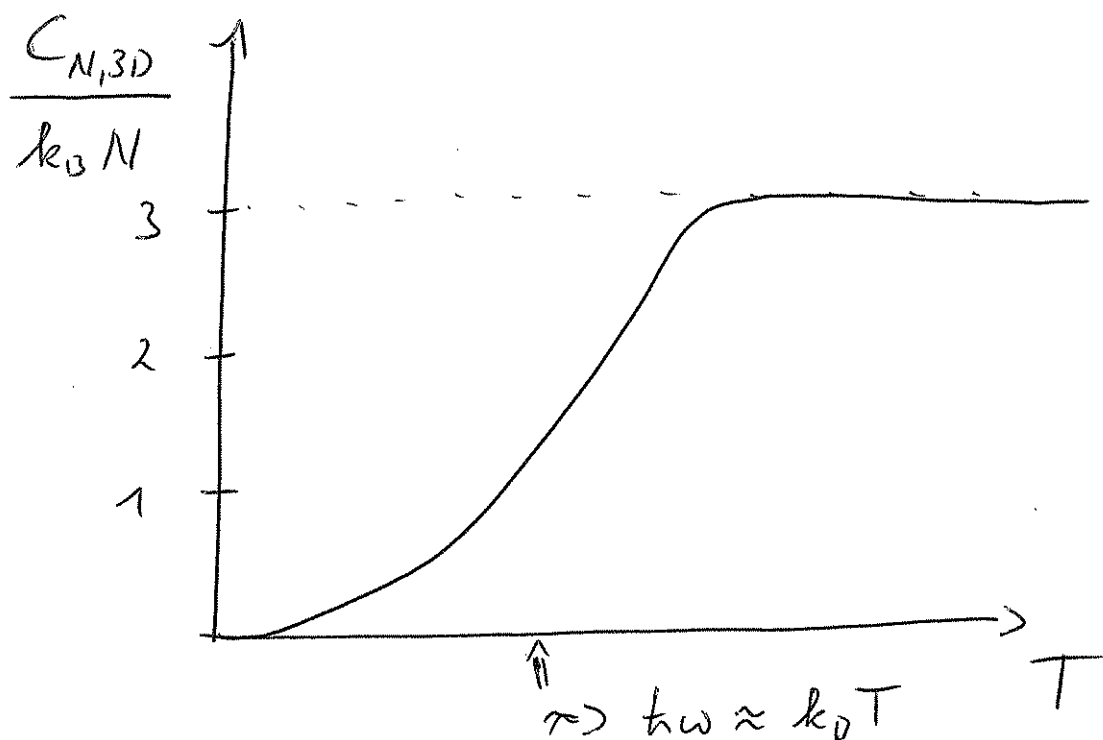
\Rightarrow partition function

$$Z_{3N} = (Z_x \cdot Z_y \cdot Z_z)^N = Z_1^{3N}$$

\Rightarrow all extensive quantities like U, F, C

have factors $3N$ compared to one oscillator

example: $C_{3D} = 3N k_B (\beta \hbar \omega)^2 \frac{\exp(\beta \hbar \omega)}{[\exp(\beta \hbar \omega) - 1]^2}$



Lecture 10

2.5. Energy fluctuations in the canonical ensemble ①

• fluctuations defined by: $\sigma_A^2 = \langle (A - \langle A \rangle)^2 \rangle$
 $= \langle A^2 \rangle - \langle A \rangle^2$
 $= \langle (\delta A)^2 \rangle$

or by standard deviation $\sigma_A = \sqrt{\sigma_A^2}$

• now energy fluctuations: $\langle (\delta E)^2 \rangle$?

Show that:

$$\sigma_E^2 = \langle (\delta E)^2 \rangle \stackrel{a)}{=} - \frac{\partial \langle E \rangle}{\partial \beta} \stackrel{b)}{=} k_B T^2 C_V$$

C_V ... heat capacity

$$\begin{aligned} \langle E \rangle &= \frac{1}{Z} \sum_s E_s e^{-\beta E_s} \\ &= - \frac{\partial \ln Z}{\partial \beta} \end{aligned}$$

proof a)

$$\begin{aligned} \bullet \text{ consider } \frac{\partial \langle E \rangle}{\partial \beta} &= \frac{\partial}{\partial \beta} \frac{1}{Z} \sum_s E_s e^{-\beta E_s} \quad (2) \\ &= \frac{1}{Z} \sum_s E_s e^{-\beta E_s} (-E_s) \\ &\quad - \frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \sum_s E_s e^{-\beta E_s} \\ &= -\frac{1}{Z} \sum_s E_s^2 e^{-\beta E_s} - \frac{1}{Z} \frac{\partial Z}{\partial \beta} \frac{1}{Z} \sum_s E_s e^{-\beta E_s} \\ &= -\langle E^2 \rangle - \frac{\partial \ln Z}{\partial \beta} \langle E \rangle \\ &= -\langle E^2 \rangle + \langle E \rangle^2 = -\langle (\delta E)^2 \rangle \\ \Rightarrow \sigma_E^2 = \langle (\delta E)^2 \rangle &= -\frac{\partial \langle E \rangle}{\partial \beta} \end{aligned}$$

proof b)

$$\begin{aligned} -\frac{\partial \langle E \rangle}{\partial \beta} &= -\frac{\partial T}{\partial \beta} \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial T}{\partial \beta} C_V \\ \hookrightarrow \frac{\partial T}{\partial \beta} &= \frac{\partial (k_B \beta)^{-1}}{\partial \beta} = -\frac{1}{k_B \beta^2} \\ &= -\frac{k_B^2 T^2}{k_B} = -k_B T^2 \\ -\frac{\partial \langle E \rangle}{\partial \beta} &= k_B T^2 C_V \end{aligned}$$

$$\bullet \text{ Combined: } \sigma_E^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 C_V$$

! amazing: $T \sim$ energy fluctuations V

• scaling with particle number

③

∴ C_V is extensive quantity

$$\Rightarrow C_V = C_V^s \cdot N$$

C_V^s ... specific heat capacity

$$\Rightarrow \sigma_E^2 = \langle (\delta E)^2 \rangle \sim N$$

$$\Rightarrow \sigma_E \sim \sqrt{N} \quad \Rightarrow \quad \frac{\sigma_E}{E} = \frac{\sigma_E}{N \cdot \epsilon} \sim \frac{1}{\sqrt{N}}$$

↑
average energy per particle

∴ scaling as in micro-canonical ensemble

example: N harmonic oscillators

$$\Rightarrow \langle E \rangle = \frac{N \hbar \omega}{\exp(\beta \hbar \omega) - 1} + \text{zero point energy}$$

$$\begin{aligned} \Rightarrow \sigma_E^2 &= - \frac{\partial \langle E \rangle}{\partial \beta} = \frac{N \hbar \omega}{[\exp(\beta \hbar \omega) - 1]^2} \hbar \omega e^{\beta \hbar \omega} \\ &= N \frac{(\hbar \omega)^2 e^{\beta \hbar \omega}}{[\exp(\beta \hbar \omega) - 1]^2} \end{aligned}$$

$$\Rightarrow \frac{\sigma_E}{\langle E \rangle} = \frac{N^{1/2} k\omega e^{\beta k\omega/2}}{[\exp(\beta k\omega) - 1]} \bigg/ \frac{N k\omega}{[\exp(k\omega\beta) - 1]} \quad (4)$$

$$= \frac{1}{\sqrt{N}} e^{\beta k\omega/2}$$

$$\Rightarrow \frac{\sigma_E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}$$

\checkmark for $N \rightarrow \infty$ very small fluctuations

\checkmark energy fluctuations become negligible in the thermodynamic limit ($N \rightarrow \infty, V \rightarrow \infty, n = \text{const.}$)

Comments: N -scaling like in micro-canonical ensemble

\Rightarrow for large systems, not much difference in

a) fixing $E \rightarrow \Omega(E, V, N)$ micro-can.

b) fixing $T \rightarrow Z(T, V, N)$ canonical

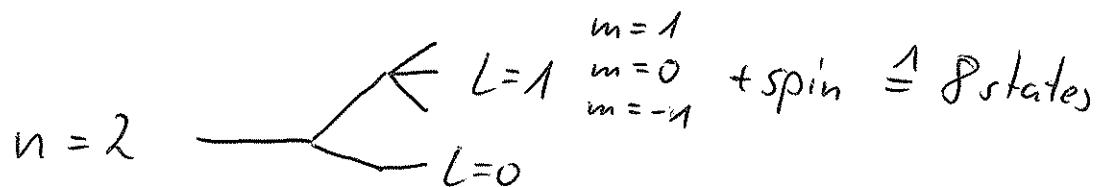
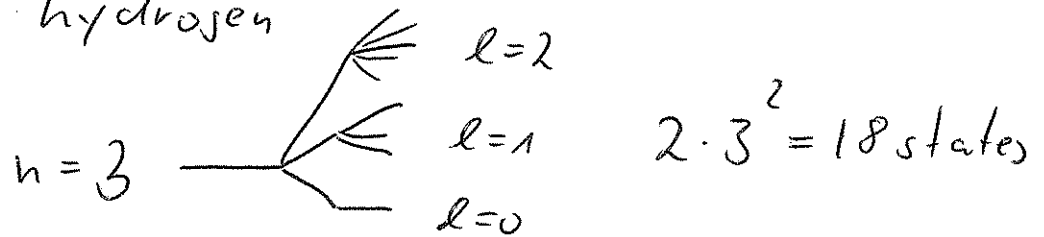
descriptions even as $\sigma_E \sim T$

2.6. Degenerate energy states

(5)

- Up to now : one energy \leftrightarrow one state
- But : QM shows that many states may have the same energy

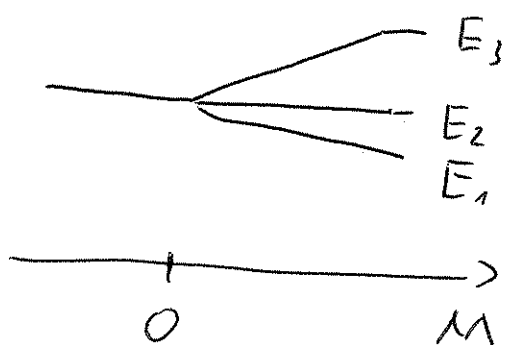
example : hydrogen



ground state $n=1$  $L=0$ 2 states $s = \pm \frac{1}{2}$

How do we know this?

\Rightarrow splitting of lines in magnetic field



\Rightarrow state 3 times degenerate without field

\Rightarrow 3 different states with magn. field

statistical treatment

⑥

- find degeneracy factor g_E
- count energy state E g_E - times

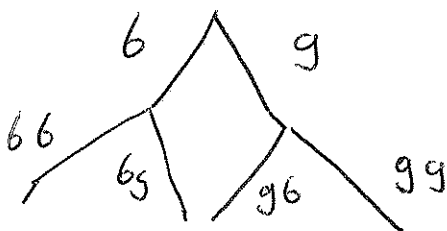
$\Rightarrow \Omega$ becomes larger in the micro-canonical ensemble

\Rightarrow canonical ensemble: new partition function

$$Z = \sum_s g_s e^{-\beta E_s}$$

s runs now over different energies

example from test (boys & girls)



1st child	b	b	g	g
2nd child	b	g	b	g

$\hat{=}$ 4 states

$bg + gb$ degenerate state $\hat{=}$ one boy, one girl

Lecture 11

2.7 Partition function for ideal gases ①

Up to now: $Z = \sum_s g_s e^{-\beta E_s}$

gives full thermodynamics

- for + systems with discrete energies
+ systems with distinguishable particles
- not for - systems with continuous energies
- indistinguishable particles
- Gases have continuous energies per particle
2 particles with $E = \text{const.} \Rightarrow E_1 + E_2 = E$
 \Rightarrow infinite solutions

? How can we count # of states?

How can we perform the sum in the partition function?

Are we stuck?

✓ new approach : using information from QM ②

$$\text{Heisenberg : } \Delta x \Delta p \geq \frac{\hbar}{2}$$

\Rightarrow for a given volume defining Δx ,
 Δp has a minimum
(cannot measure better than Δp)

$\Rightarrow \Delta p$ defines momentum bunch

\Rightarrow momentum bunch \Leftrightarrow energy bunch

? What is the g_E of an energy bunch?

move mathematically : each particle occupies
volume in phase space
(\vec{x}, \vec{p} are coordinates here)
• measurable volume elements
related to possible states

$$\Rightarrow \Omega = V \cdot V_p$$

Trick: consider one particle in cubic box
with length L
(later $L \rightarrow \infty$)

(3)

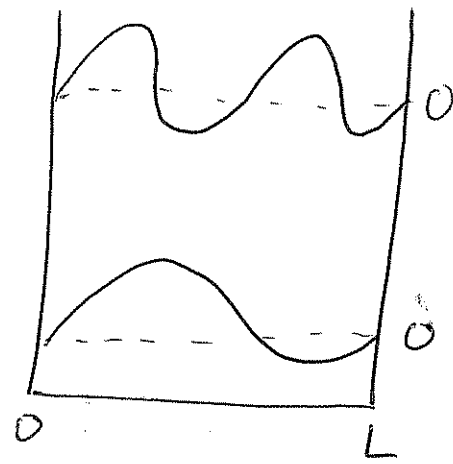
\Rightarrow wave function of particle must be zero
at boundary

• 3D: $\psi(\vec{r}) \sim \sin\left(\frac{2\pi x}{L} n_x\right) \sin\left(\frac{2\pi y}{L} n_y\right) \sin\left(\frac{2\pi z}{L} n_z\right)$

related energies
from QM

1D examples

$$E = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$



etc.

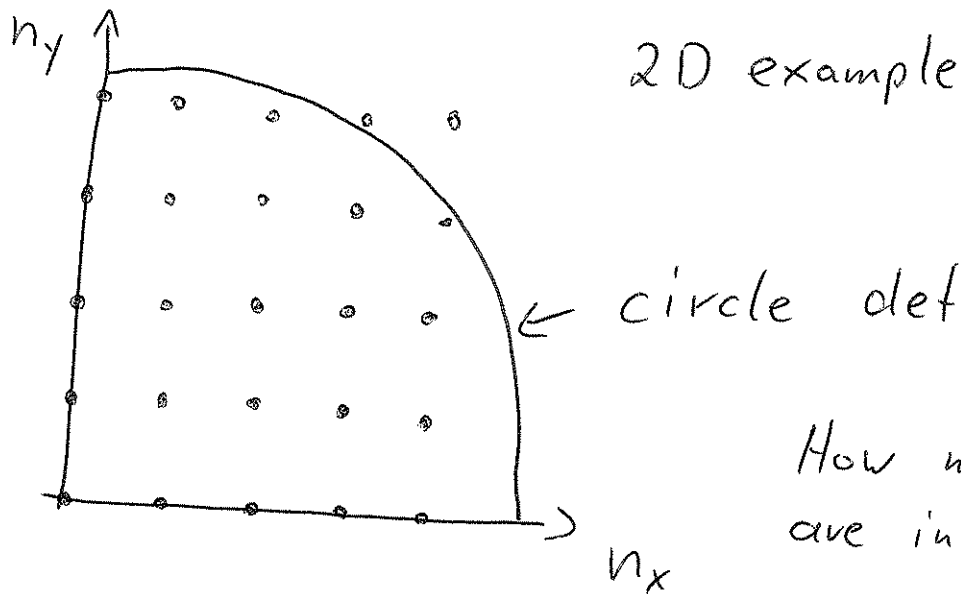
\Rightarrow energies are given by
quantum numbers n_x, n_y, n_z

? How many combinations of n_x, n_y, n_z
give the same (given, fixed) energy?

\Rightarrow this number is Ω in micro-can. ensemble

✓
0 solution: find all triples of integers
related to energies $0 \dots E$

trick 2: n_x, n_y, n_z define integer points in 3D space (4)



← circle defined by E

How many points are inside the circle?

⇒ 1 point per unit volume

∇ quantum numbers are large ⇒ boundary unimportant

$$\text{Def.: } R^2 = n_x^2 + n_y^2 + n_z^2 \stackrel{!}{=} \frac{8mL^2}{h^2} E$$

Largest radius with $E(R) \leq E$

⇒ # of states with energies 0... E

equals volume of sphere with radius R

divided by 8 (n_x, n_y, n_z are positive)

$$\begin{aligned} G(E) &= \frac{1}{8} \times \frac{4\pi}{3} R^3 \\ &= \frac{1}{8} \frac{4\pi}{3} \left(\frac{8mL^2}{h^2} E \right)^{3/2} \\ &= \frac{4\pi V}{3 h^3} (2mE)^{3/2} \end{aligned}$$

• $G(E)$... # of states between $0 \dots E$

⑤

• $G(E+\Delta) - G(E)$

... # of states between E and $E+\Delta$

\Rightarrow reduce Δ to differential

Def.: density of states

$$g(E) = \frac{dG(E)}{dE} = \frac{4\pi m V}{h^3} (2mE)^{1/2}$$

$g(E)dE$... # of states in energy bundle $E \dots E+dE$

• Now consider Boltzmann distribution for occupation of energy states

$$\Rightarrow n(E)dE = A \cdot g(E) e^{-\beta E} dE$$

... # of particles in energy bundle $E \dots E+dE$

• factor A is fixed by normalisation:

$$N = A \cdot \sum_s g_s(E) e^{-\beta E} = A \cdot Z$$

$$\Rightarrow A = N/Z$$

⇒ partition function for ideal gas

⑥

$$Z = \frac{N}{A} \int g(E) \exp(-\beta E) dE$$

Note: very dense energy levels

$$\Sigma \rightarrow \int dE$$

• calculate Z

$$Z_1 = \int_0^{\infty} \frac{4\pi m V}{h^3} (2mE)^{1/2} \exp(-\beta E) dE$$

$$\stackrel{\text{maths}}{=} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

Def.: thermal wave length

$$\Lambda_m = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} = \left(\frac{2\pi \hbar^2}{m k_B T} \right)^{1/2}$$

≙ de Broglie wave length for energy $k_B T$

$$\Rightarrow Z_1 = V \cdot \Lambda_m^{-3} = \frac{V}{V_{qm}}$$

$$\Rightarrow Z = \left(V \cdot \Lambda_m^{-3} \right)^N$$

Lecture 12

Thermodynamics for ideal gases

(1)

• We found : $Z_1 = V \cdot \Lambda_m^{-3} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$

$$Z = Z_1^N$$

=> Helmholtz free energy

$$F = -N k_B T \ln Z_1$$

$$= -N k_B T \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) \right]$$

C_1

Later :

all wrong!

• Entropy

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = N k_B \ln Z + N k_B T \frac{3}{2} \frac{\partial}{\partial T} \ln T$$
$$= N k_B \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{3}{2} \right]$$

• Internal energy ($F = U - TS$)

$$U = F + TS = N \frac{3}{2} k_B T$$

ideal gas law

$$\boxed{U = N \frac{3}{2} k_B T}$$

• Pressure

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = N k_B T \left(\frac{\partial \ln V}{\partial V} \right)_T = N k_B T \frac{1}{V}$$
$$\Rightarrow \boxed{pV = N k_B T}$$

2.8 Gibbs Paradox & Mixing Entropy (2)

(... and how to resolve it)

- Consider a container that is split in two parts by removable partition

gas A	gas B
P_A, T_A	P_B, T_B
$N_A = N$	$N_B = N$
$V_A = V$	$V_B = V$

$$P_A = P_B ; T_A = T_B$$

\Rightarrow all quantities equal in A and B except the type of the gas

\Rightarrow remove partition \Rightarrow mixing of the gases

- Calculate initial entropy

$$\begin{aligned} S_{\text{initial}} &= S_A + S_B \\ &= N k_B \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_A + \frac{3}{2} \right] \\ &\quad + N k_B \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_B + \frac{3}{2} \right] \end{aligned}$$

- Calculate entropy after mixing

$$\begin{aligned} S_{\text{mixing}} &= S_A(2V) + S_B(2V) = S_{\text{initial}} + N k_B \ln 2 \\ &= N k_B \left[\ln 2V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_A + \frac{3}{2} \right] \\ &\quad + N k_B \left[\ln 2V + \frac{3}{2} \ln T + \frac{3}{2} \ln C_B + \frac{3}{2} \right] \end{aligned}$$

✓ entropy increases by $Nk_B \ln 2$ when
the two gases mix

(3)

⇒ increase is called mixing entropy

Paradox: What happens if both gases
are the same?

↳ still an entropy increase of
 $Nk_B \ln 2$ follows from formula

↯ contradiction since nothing is mixing
(state unchanged)

↯ contradiction to second law

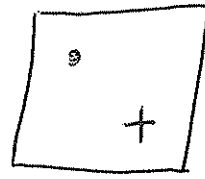
⇒ There must be something wrong here ✓

Resolving the paradox

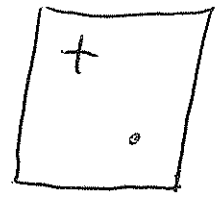
(4)

a) distinguishable particles

state a)

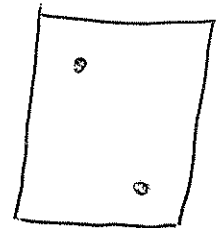
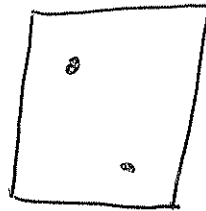


state b)



\Rightarrow two different states \checkmark

b) indistinguishable particles



\Rightarrow state really looks the same after swapping part.s

\Rightarrow same state that should only been counted once \checkmark

\checkmark gas particles are indistinguishable

\Rightarrow partition function:

$$Z_N = \frac{1}{N!} z_1^N$$

as we have $N!$ ways of arranging N gas particles on N positions

Correct thermodynamics for ideal gases (5)

- $Z_N = \frac{1}{N!} Z_1^N$

- Helmholtz free energy

$$F = -k_B T \ln Z_N \quad \text{Stirling: } \ln \frac{1}{N!} = -\frac{N \ln N}{N} + N$$

$$= -N k_B T \left[\ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{1}{2} \right]$$

is now extensive: $\ln V - \ln N = \ln \frac{V}{N}$
 \Rightarrow only N in pre factor is ext.

- Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N k_B \ln Z + N k_B T \frac{3}{2} \frac{\partial}{\partial T} \ln T$$
$$= N k_B \left[\ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2} \right]$$

- Internal energy

$$U = F + TS = \frac{3}{2} N k_B T \quad \text{unchanged}$$

- Pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = N k_B T V^{-1}$$

$$\Rightarrow pV = N k_B T \quad \text{unchanged}$$

Gibbs paradox again

(6)

- mixing of two identical gases in double the volume

$$Z_A = \frac{1}{N!} Z_A^N \equiv Z_B = \frac{1}{N!} Z_B^N$$

$$\Rightarrow S_{\text{initial}} = 2N k_B \left[\ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2} \right]$$

- entropy after "mixing" (partition removed)

$$Z_{\text{mix}} = \frac{1}{(2N)!} Z^{2N}$$

$$\Rightarrow S_{\text{mixing}} = 2N k_B \left[\ln 2V - \ln 2N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2} \right]$$

$$\text{with } \ln 2V - \ln 2N$$

$$= \ln \frac{2V}{2N} = \ln \frac{V}{N}$$

$$= \ln V - \ln N$$

$$\Rightarrow S_{\text{mixing}} = 2N k_B \left[\ln V - \ln N + \frac{3}{2} \ln T + \frac{3}{2} \ln C_1 + \frac{5}{2} \right]$$

$$= S_{\text{initial}}$$

\Rightarrow no entropy increase

\Rightarrow paradox resolved

Lecture 13

Revision of canonical treatment of gases

(if gap between terms occurs here)

Recipe :

- Find all energies of particles in the system
- Calculate partition function

$$Z = \sum_s g_s e^{-\beta E_s}$$

- Calculate Helmholtz free energy

$$F = -k_B T \ln Z$$

- Calculate internal energy / heat capacities

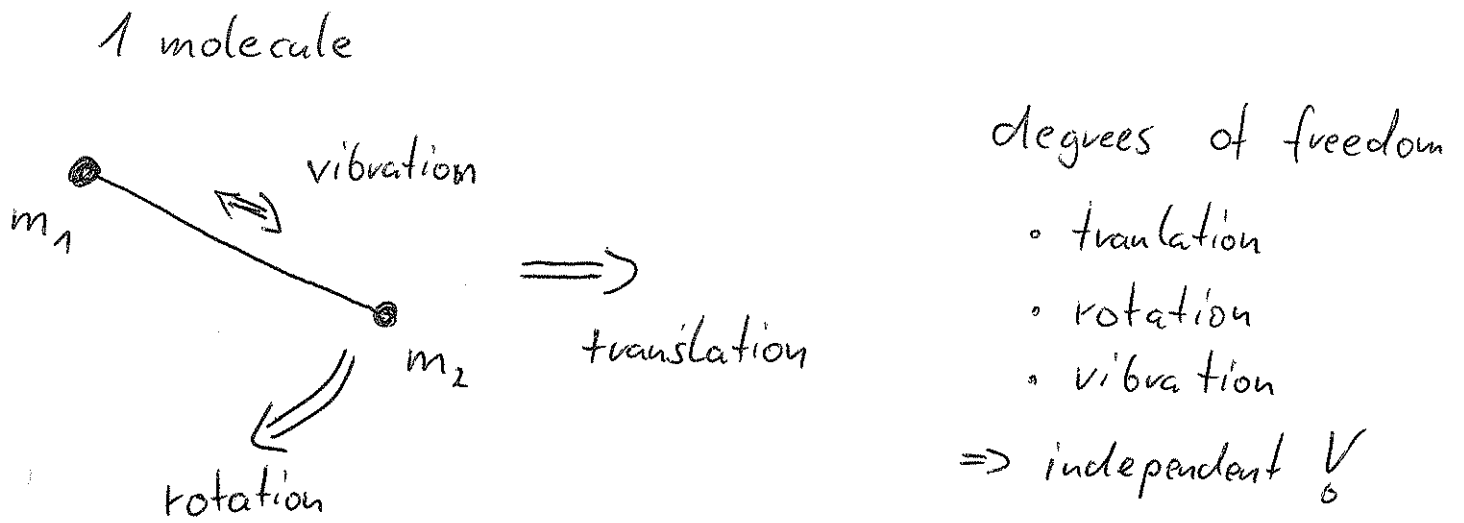
$$U = - \frac{\partial \ln Z}{\partial \beta} \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Gases: $Z_1 = V \Lambda_m^{-3}$

(idea) $Z_N = \frac{1}{N!} Z_1^N$

2.9 Heat capacity / thermodynamics of a diatomic gas

(1)



• first: 1 molecule (let the recipe work)

- Energy : $E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$

- partition function : $Z_{\text{total}} = Z_{\text{trans}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}}$

• now N molecules : $Z_N = \frac{1}{N!} Z_{\text{total}}^N$

• thermodynamics :

$$U = - \frac{\partial \ln Z_N}{\partial \beta} \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

(both were independent of $N!$ factor for ideal gases)

1) Translational degree of freedom

(2)

DONE $V \hat{=} \text{ideal gas of particles}$
with mass: $m = m_1 + m_2$

$$\Rightarrow Z_{\text{trans}} = V \Lambda_{\text{molecule}}^{-3} = V \left[\frac{2\pi (m_1 + m_2) k_B T}{h^2} \right]^{3/2}$$

2) Rotational degree of freedom

QM: $E_{\text{rot}} = \frac{\hbar^2}{2I_{\text{rot}}} J(J+1)$

$$g_J = 2J + 1$$

J ... quantum number
of rotation
($2J+1$)-z-projections
 $-J, \dots, J$ $\Delta J = \pm 1$

$$\Rightarrow Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\beta \frac{\hbar^2}{2I_{\text{rot}}} J(J+1)\right]$$

Def.: $k_B T_{\text{rot}} = \frac{\hbar^2}{2I_{\text{rot}}}$

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-J(J+1) T_{\text{rot}}/T\right]$$

remarks: • no general solution \rightarrow numerics needed

• limited cases interesting

Nitrogen: $T_{\text{rot}} = 2,8 \text{ K}$

Hydrogen: $T_{\text{rot}} = 82 \text{ K}$

i) high temperature limit ($T \gg T_{rot}$) (3)

\Rightarrow many states are occupied as enough energy available

\Rightarrow Levels are closely spaced compared to $k_B T$

$\Rightarrow \sum_J$ transformed into $\int dx$

$$\text{with } x = \sqrt{J(J+1)} = \sqrt{J^2 + J} = J\sqrt{1 + 1/J}$$

$\Rightarrow 2J+1 \approx 2x$ (for most J that are large numbers)

$$Z_{rot}^{highT} = \int_0^{\infty} \underbrace{2x}_{1/\alpha} \exp(-\alpha x^2) dx \quad \alpha = \frac{T_{rot}}{T}$$

$$\Rightarrow Z_{rot}^{highT} = \frac{1}{\alpha} = \frac{T}{T_{rot}}$$

$$\begin{aligned} \Rightarrow \langle E_{rot} \rangle &= - \frac{\partial \ln Z_{rot}}{\partial \beta} = k_B T^2 \frac{\partial \ln Z}{\partial T} \quad \beta = \frac{1}{k_B T} \\ &= k_B T^2 \frac{\partial \ln [T/T_{rot}]}{\partial T} = k_B T \end{aligned}$$

• N molecules

$$U_{rot} = N \langle E_{rot} \rangle = N k_B T$$

$$\Rightarrow C_V^{rot} = \left(\frac{\partial U}{\partial T} \right)_V = N k_B \quad \dots \quad k_B \text{ per molecule}$$

ii) Low temperature limit ($T_{\text{rot}} \gg T$)

(4)

\Rightarrow only a few states occupied [$P_s \sim e^{-E_s/k_B T}$]

\forall take only 2 levels into account

$$\bullet Z_{\text{rot}}^{T \rightarrow 0} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-J(J+1) \frac{T_{\text{rot}}}{T}\right]$$

$$\approx 1 + 3 \exp\left(-2 \frac{T_{\text{rot}}}{T}\right)$$

\forall second term much smaller than first term

$$\Rightarrow \ln Z_{\text{rot}}^{T \rightarrow 0} = \ln(1 + \varepsilon) \approx \varepsilon = 3 \exp\left(-2 \frac{T_{\text{rot}}}{T}\right)$$

$$\bullet \langle E_{\text{rot}} \rangle = k_B T^2 \frac{\partial \ln Z_{\text{rot}}}{\partial T} \\ = 6 k_B T_{\text{rot}} e^{-2 T_{\text{rot}}/T} \quad \text{for } T_{\text{rot}} \gg T$$

\bullet N molecules

$$U_{\text{rot}} = N \langle E_{\text{rot}} \rangle = 6 N k_B T_{\text{rot}} \exp\left(-2 \frac{T_{\text{rot}}}{T}\right)$$

$$\Rightarrow C_v^{\text{rot}} = \left(\frac{\partial U_{\text{rot}}}{\partial T}\right)_V = 12 N k_B \left(\frac{T_{\text{rot}}}{T}\right)^2 \exp\left(-\frac{2 T_{\text{rot}}}{T}\right)$$

$\Rightarrow C_v$ falls exponentially
when T approaches $T=0$

3) Vibrational degree of freedom (5)
(start the recipe...)

$$QM: E_{\text{vib}} = \left(n + \frac{1}{2}\right) h\nu$$

DONE $V \hat{=} \text{Einstein solid as we have}$
 N independent oscillators

$$\Rightarrow U_{\text{vib}} = N k_B T_{\text{vib}} \left[\frac{1}{2} + \frac{1}{\exp(T_{\text{vib}}/T) - 1} \right]$$

with $k_B T_{\text{vib}} = h\nu$... vibrational energy

examples: Hydrogen : $T_{\text{vib}} = 6210 \text{ K}$

Nitrogen : $T_{\text{vib}} = 3340 \text{ K}$

Chlorine : $T_{\text{vib}} = 810 \text{ K}$

$$\Rightarrow C_v^{\text{vib}} = \left(\frac{\partial U}{\partial T}\right)_v = N k_B \left(\frac{T_{\text{vib}}}{T}\right)^2 \frac{\exp(T_{\text{vib}}/T)}{[\exp(T_{\text{vib}}/T) - 1]^2}$$

i) high temperature limit ($T \gg T_{\text{vib}}$)

$$C_v^{\text{vib}} = N k_B \quad k_B \text{ per molecule}$$

ii) low temperature limit ($T \ll T_{\text{vib}}$)

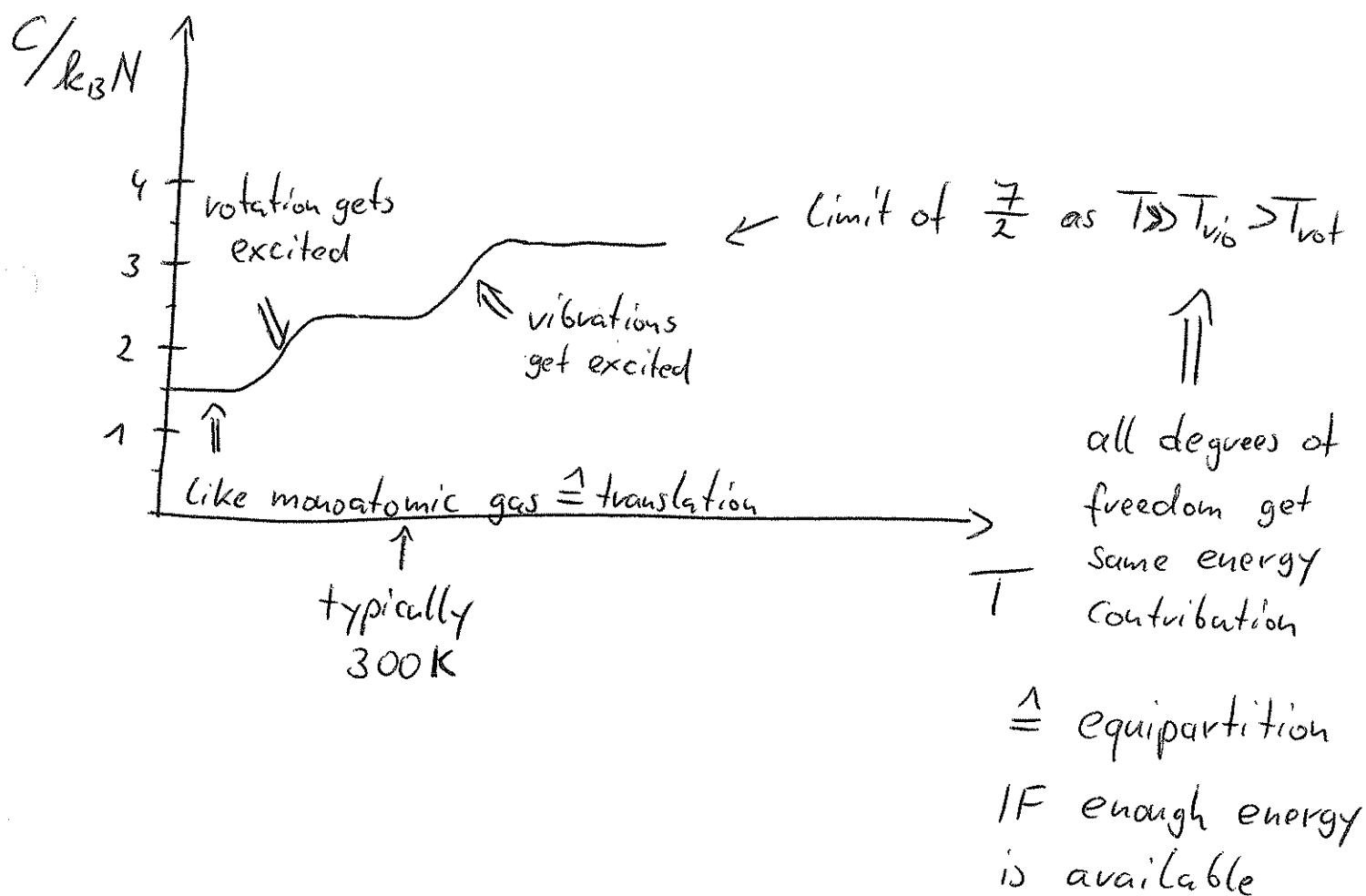
$$C_v^{\text{vib}} \rightarrow 0 \quad \text{exponential decay as } T \rightarrow 0$$

4) Putting it all together...

⑥

$$Z_N = \frac{1}{N!} [Z_{\text{trans}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}}]^N$$

$$\Rightarrow C_{\text{total}} = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}}$$



Questions: • What is S at $T = 300$ K (nitrogen)

• Show that for adiabatic processes in diatomic gases $VT^{5/2} = \text{const}$ holds

Lecture 14

3. Quantum Statistics

general remark: Quantum statistics is statistics
ON TOP of statistical
interpretation of quantum mechanics
→ statistics for quantum entities

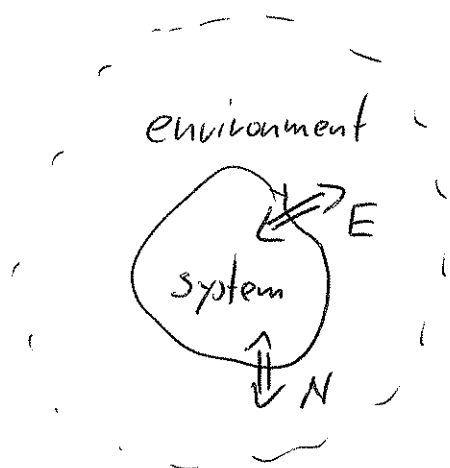
problems : a) quantum mechanical objects of the
same kind are indistinguishable
⇒ see $\frac{1}{N!}$ factor in Z_N of gases
⇒ different # of states Ω

b) quantum objects are small and can
tunnel through barriers
⇒ there are no 100% effective walls
⇒ particle numbers fluctuate
⇒ we have to deal with open systems

c) special QM laws might influence
statistics

3.1. Thermodynamics of open systems

①



- energy and particles can be exchanged / fluctuate

- adding particle exchange to internal energy

$$1. \text{ law: } dU = T dS - p dV + \sum_j \mu_j dN_j \quad (\text{gas})$$

$j \dots$ different species

$$\mu_j = \left(\frac{\partial U}{\partial N_j} \right)_{S, V} \dots \text{chemical potential of species } j$$

(better definition later)

! for open systems, we have to add the term $\sum_j \mu_j dN_j$ to every thermodynamic potential

\Rightarrow 2 more Maxwell-relations per potential
(3 mixed derivatives $\hat{=}$ 3 pairs to be equal)

HOME !

- Better definition for chemical potential μ_j

$$U = TS - pV + \sum_j \mu_j N_j$$

$$\Rightarrow \sum_j \mu_j N_j = \underbrace{U - TS + pV}_G$$

one component: $\mu = \frac{G}{N}$

$\Rightarrow \mu$ is Gibbs free energy per particle

- Thermodynamic potential for open systems

- Problem: U, F, G all depend on N ,
but N fluctuates now

- Solution: swap $\mu \leftrightarrow N$ (Legendre transformation)

$$\begin{aligned} \text{- Def.: } \Omega_{gr} &= U - TS - \mu N \\ &= TS - pV + \mu N - TS - \mu N \\ &= -pV \end{aligned}$$

$\Rightarrow \Omega_{gr} = -pV$ is new thermodynamic potential

- stability: $d\Omega_{gr} \leq 0$ "=" for equilibrium
 \Rightarrow minimum for equilibrium

9.2 Grand-canonical ensemble

(4)

9.2.1 Gibbs factor

hint: derivation is similar to Boltzmann factor,
but has additional μdN term in 1. law

notation: s_1 ... system is in state 1

s_2 ... - " - 2

$p(s_i)$... probability of state s_i

index R ... reservoir } properties
index S ... system }

start: • consider system to be a single atom

• describe system + environment micro-canonically

$$\Rightarrow \frac{p(s_2)}{p(s_1)} = \frac{\Omega(s_2)}{\Omega(s_1)} = \frac{\Omega_S(s_2)\Omega_R(s_2)}{\Omega_S(s_1)\Omega_R(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

1 atom either in state "1" or "2"

• use $S = k_B \ln \Omega$ (Boltzmann)

$$\Rightarrow \frac{p(s_2)}{p(s_1)} = \frac{\exp[S_R(s_2)/k_B]}{\exp[S_R(s_1)/k_B]} = \exp\left\{\frac{S_R(s_2) - S_R(s_1)}{k_B}\right\}$$

• changes due to $s_1 \leftrightarrow s_2$ in reservoir are small (5)

$$\Rightarrow S_R(s_2) - S_R(s_1) = dS_R$$

• use 1. + 2. law (fundamental law)

$$dU = TdS - pdV + \mu dN$$

$$dS = \frac{1}{T} [dU + pdV - \mu dN]$$

! pdV term extremely small \Rightarrow neglect

! keep μdN term here !

• $S + R \hat{=} \text{micro-canonical ensemble}$

$$\Rightarrow U = E = E_R + E_S = \text{const.}$$

$$\Delta E_R = -\Delta E_S$$

$$N = N_R + N_S = \text{const.}$$

$$\Delta N_R = -\Delta N_S$$

$$\begin{aligned} \Rightarrow S_R(s_2) - S_R(s_1) &= \frac{1}{T} [U_R(s_2) - U_R(s_1) - \mu N_R(s_2) + \mu N_R(s_1)] \\ &= -\frac{1}{T} [E_S(s_2) - E_S(s_1) - \mu N_S(s_2) + \mu N_S(s_1)] \end{aligned}$$

$$\Rightarrow \frac{p(s_2)}{p(s_1)} = \frac{\exp[-\beta E_S(s_2) + \beta \mu N_S(s_2)]}{\exp[-\beta E_S(s_1) + \beta \mu N_S(s_1)]}$$

$$\Rightarrow \boxed{p(s_i) \approx \exp[-\beta (E_i - \mu N_i)]}$$

$s_i \rightarrow E_i, N_i$

Gibbs factor

3.2.2 Grand partition function / partition sum (6)

- Gibbs factor shows only proportionality

$$P(E_s, N_s) = C_1 \exp[-\beta(E_s - \mu N_s)]$$

- Define constant via normalisation

$$\sum_{E_s} \sum_{N_s} P(E_s, N_s) = 1$$

... particle must be in one state

$$\Rightarrow \frac{1}{C_1} = \boxed{Z_{gr} = \sum_{E_s} \sum_{N_s} e^{-\beta(E_s - \mu N_s)}}$$

grand partition function

- Relation to canonical partition function

$$\begin{aligned} Z_{gr} &= \sum_N \sum_E e^{-\beta(E - \mu N)} \\ &= \sum_N e^{+\beta \mu N} \sum_E e^{-\beta E} = \sum_N z^N Z_{can} \end{aligned}$$

with $z = e^{\beta \mu}$... fugacity

⑦

- Physics missed by this easy derivation
(will be done more rigorously)

a) degeneracy of states

$$\Rightarrow Z_{gr} = \sum_{E,N} g(E,N) e^{-\beta(E-\mu N)}$$

b) indistinguishable particles

$$\Rightarrow Z_{gr} = \sum_N \frac{1}{N!} \sum_E g(E,N) e^{-\beta(E-\mu N)}$$

⇕

- to be done for each N separately ✓
- no problems to distinguish systems with different N ✓

OR

$$Z_{gr} = \sum_N z^N Z_{can}$$

⇕

put all of it
into canonical
partition function

Lecture 15

3.3 Relation Thermodynamics \Leftrightarrow Statistics ①

$$Z_{gr} = \sum_N \frac{1}{N!} \sum_E g(E, N) e^{-\beta(E - \mu N)}$$

- was introduced as normalisation factor
 - contains all information about the system
- $\Rightarrow Z_{gr}$ yields complete thermodynamics

How?

\Rightarrow clues via natural variables

- $Z_{gr} = Z_{gr}(T, \mu, V)$ while $Z_{can} = Z_{can}(T, N, V)$

- thermodynamic potential for open systems

$$-pV = \Omega_{gr} = \underbrace{U - TS}_{= F} - \mu N$$

(swap $\mu \Leftrightarrow N$
compared to F)

variables: $U = U(S, V, N)$

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

$$\Omega_{gr} = \Omega_{gr}(T, V, \mu) \Leftarrow \text{matches } Z_{gr}$$

\Rightarrow search for $\Omega_{gr} = f(Z_{gr})$

- relation is given by

$$-pV = \Omega_{gr} = -k_B T \ln Z_{gr}(T, V, \mu)$$

\Rightarrow complete thermodynamics follow from Ω_{gr}/Z_{gr}
(no proof here; similar to $F = -k_B T \ln Z_{can}$)

- review: relations between statistics and thermodynamics

MC: $S = k_B \ln \Omega$ (Boltzmann)

C: $F = -k_B T \ln Z_{can}$ \leftarrow follows

GC: $\Omega_{gr} = -k_B T \ln Z_{gr}$ \leftarrow follows

- short cut to particle number

$$\langle N \rangle = k_B T \frac{1}{Z_{gr}} \frac{\partial Z_{gr}}{\partial \mu}$$

proof: $\frac{\partial Z_{gr}}{\partial \mu} = \frac{\partial}{\partial \mu} \sum_{E, N} e^{-\beta(E - \mu N)}$

= ... HOME

3.4. Energy distributions for Fermions and Bosons

3.4.1 What are Fermion / Bosons?

- Nature: all particles have spins $S = n + \frac{1}{2}$ or $S = n$ where n is an integer
- observation / definition
 - $S = n + \frac{1}{2}$ particles are called Fermion
 - => they obey the Pauli exclusion principle: just one Fermion can occupy each state
 - $S = n$ particles are called Bosons (no exclusion principle)
 - rule for composite particles:
 - a) count # of Fermions contained
 - b) number even \rightarrow Boson
 - number odd \rightarrow Fermion

EXAMPLES

for real: symmetry postulate

- Fermions have antisymmetric wave function

$$\Psi(12) = \Psi_1(1)\Psi_2(2) - \Psi_1(2)\Psi_2(1) = -\Psi(21)$$
- Bosons have symmetric wave functions: $\Psi(12) = \Psi(21)$
- no other types!

3.4.2 Distributions for Fermions

given: - Gibbs factors / $p(E, N)$

- Pauli exclusion principle

wanted: - functions that allow to calculate thermodynamics: Ω , Z_{can} , Z_{gr}

- probabilities to calculate average quantities: $\langle E \rangle = \sum_s E_s p(E_s)$

() micro-canonical description: # of states, Ω , for a system with G states and N Fermions

• classical / distinguishable particles

$$\Omega = G \cdot G \cdot \dots \cdot G = G^N$$

• Fermions \forall indistinguishable

\forall obey Pauli principle

\Rightarrow we must have $G \geq N$

\Rightarrow we have N occupied and $(G-N)$ unoccupied states

\Rightarrow all occupied (unoccupied) states look the same

\forall # of configurations are identical to

G coin tossings with N heads and $(G-N)$ tails \forall

$$\Rightarrow \Omega = \frac{G!}{N! (G-N)!}$$

$G!$ configurations of G objects

$N!$ same - " - of filled states

$(G-N)!$ same - " - of unfilled states

b) Energy distribution

(5)

start: consider single energy state E_j and want probability that this state is occupied

• when state is unoccupied: $E = 0$

• when state is occupied by N particles:

$$E = N \cdot E_j$$

\Rightarrow probability that the state is occupied by N particles:

$$p(N) = \frac{1}{Z_{gr}} e^{-\beta(N \cdot E_j - \mu N)} = \frac{1}{Z_{gr}} e^{-\beta N(E_j - \mu)}$$

\forall Pauli principle: $N=0$ or $N=1$

$$\Rightarrow Z_{gr} = e^{-\beta \cdot 0} + e^{-\beta(E_j - \mu)} = 1 + e^{-\beta(E_j - \mu)}$$

\Rightarrow average number of particles in state E_j

$$\begin{aligned} \langle n \rangle &= \sum_{N=0,1} N p(N) = 0 \cdot p(0) + 1 \cdot p(1) \\ &= \frac{\exp[-\beta(E_j - \mu)]}{1 + \exp[-\beta(E_j - \mu)]} \end{aligned}$$

\forall works for all energy states

\Rightarrow

$$f_{FD}(E) = \langle n_{FD}(E) \rangle = \frac{1}{\exp[\beta(E - \mu)] + 1}$$

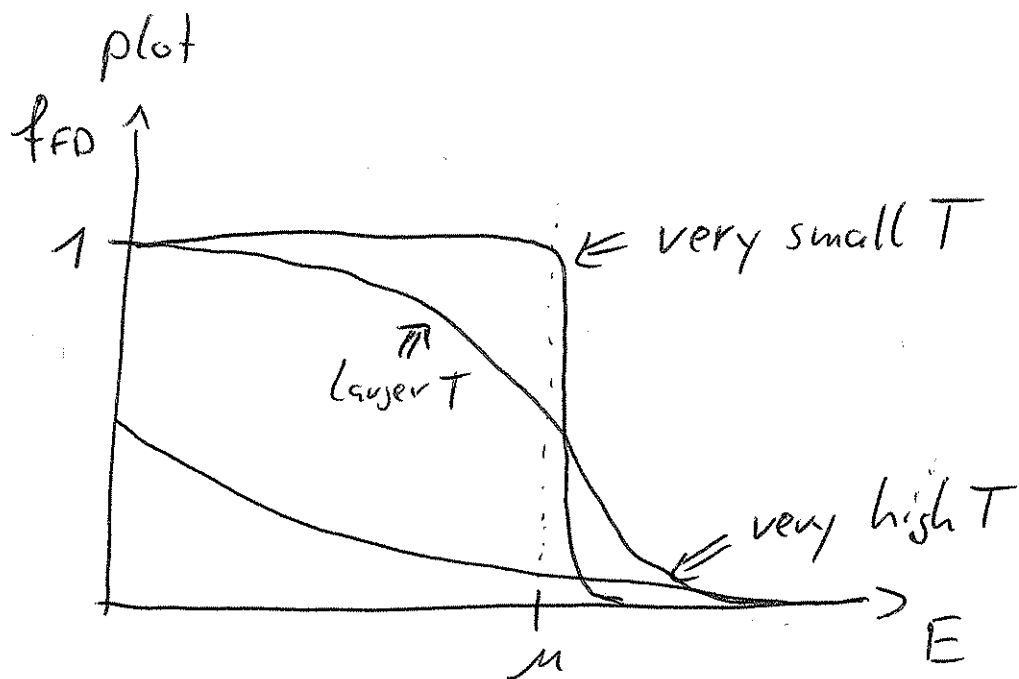
Fermi-Dirac distribution

• easy limit of the FD-distribution

(6)

$$E \gg \mu \Rightarrow f_{FD} \rightarrow 0$$

$$E \ll \mu \Rightarrow f_{FD} \rightarrow 1$$



• normalisation (without degeneracy)

$$\int dE f_{FD}(E) = \int dE \left[e^{\beta(E-\mu)} + 1 \right]^{-1} = N$$

\Rightarrow defines chemical potential $\mu = \mu(T, n = \frac{N}{V})$

• unfortunately, no analytic solution

• $-\infty \leq \mu \leq \infty$ is possible

Lecture 16

3.4.3 Distributions for Bosons

①

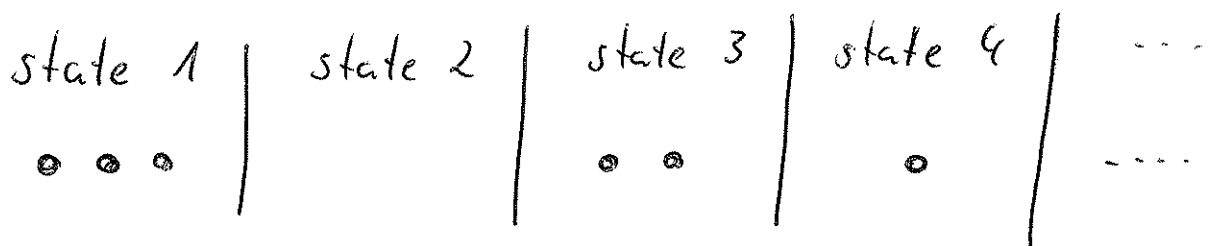
given : - Gibbs factors / $p(E, N)$
 - no Pauli principle

wanted : - Ω , Z_{can} , Z_{gr} , $f(E) \Rightarrow$ thermodynamics
 - probabilities / energy distribution

a) micro-canonical description : # of states, Ω ,
 for a system with G states and N Bosons

- classical / distinguishable particles : G^N
- Bosons \forall indistinguishable

Ω via trick : Label particles by \bullet
 label borders of states by $|$



\Rightarrow we have $(N + G - 1)$ objects : N objects \bullet (particles)
 $G - 1$ partitions $|$

$$\Rightarrow \Omega = \frac{(N + G - 1)!}{N! (G - 1)!} \dots \begin{array}{l} (N + G - 1)! \text{ configurations of} \\ (N + G - 1) \text{ objects} \\ N! \text{ same } \bullet \text{ configurations} \\ (G - 1)! \text{ same } | \text{ - " -} \end{array}$$

b) Energy distribution

(2)

start: consider a single energy state E_j and want probability that state is occupied by N Bosons

- energy of N particles: $E = N \cdot E_j$

- probability that state is occupied by N Bosons

$$p(N) = \frac{1}{Z_{gr}} e^{-\beta N (E_j - \mu)}$$

- partition function

$$Z_{gr} = \sum_N e^{-\beta N (E_j - \mu)} = 1 + e^{-\beta (E_j - \mu)} + e^{-2\beta (E_j - \mu)} + \dots$$

Def.: $x = e^{-\beta (E_j - \mu)}$

$$= 1 + x + x^2 + x^3 + \dots \quad \text{geometric series}$$

$$= \frac{1}{1-x} = [1 - \exp(-\beta (E_j - \mu))]^{-1}$$

- average number of particles in state E_j

$$\langle n \rangle = \sum_N N p(N) = p(1) + 2p(2) + 3p(3) + \dots$$

Def.: $\bar{x} = \beta (E_j - \mu)$

$$= \sum_N N \frac{1}{Z_{gr}} e^{-N\bar{x}} = -\frac{1}{Z_{gr}} \sum_N \frac{\partial}{\partial \bar{x}} e^{-N\bar{x}}$$

$$= -\frac{1}{Z_{gr}} \frac{\partial}{\partial \bar{x}} \sum_N e^{-N\bar{x}} = -\frac{1}{Z_{gr}} \frac{\partial}{\partial \bar{x}} Z_{gr}$$

$$= -(1 - e^{-\bar{x}}) \frac{\partial}{\partial \bar{x}} [1 - e^{-\bar{x}}]^{-1}$$

$$= -(1 - e^{-\bar{x}}) (-1) (1 - e^{-\bar{x}})^{-2} e^{-\bar{x}}$$

$$\Rightarrow \langle n \rangle = \frac{e^{-\bar{x}}}{1 - e^{-\bar{x}}} = \frac{1}{e^{\bar{x}} - 1}$$

$$= \frac{1}{e^{\beta(E_j - \mu)} - 1}$$

③

$$\Rightarrow f_{BE}(E) = \langle n_{BE}(E) \rangle = \frac{1}{\exp[\beta(E - \mu)] - 1}$$

Bose-Einstein distribution

• easy limits: $E \gg \mu \Rightarrow f_{BE} \rightarrow 0$

$E < \mu \Rightarrow f_{BE} \rightarrow \text{negative} \quad \downarrow$

$$\Rightarrow -\infty \leq \mu \leq E_{\min} (\text{gas: } E_m = 0)$$

$$E \rightarrow \mu \Rightarrow f_{BE} \rightarrow \infty$$

• normalisation (without degeneracy)

$$\int dE f_{BE}(E) = \int dE [\exp(\beta(E - \mu)) - 1]^{-1} = N$$

\Rightarrow defines chemical potential

Summary: Fermi / Bose distributions

$$f(E) = \frac{1}{e^{\beta(E-\mu)} \pm 1}$$

- +1 or -1 makes huge differences
- chemical potential :- any value (Fermions)
 - $\mu \leq E_{min}$ (Bosons)

• # of particles with energy E (including degeneracy)

$$N(E) = g(E) f(E) \quad g(E) \dots \text{density of states}$$

$$\Rightarrow N = \int dE g(E) f(E)$$

∴ ideal gases :

$$g(E) dE = (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

↑
spin degeneracy

which is the same for Fermions / Bosons ∴

3.4.4 Classical Limit

(5)

↳ new distributions for Fermions/Bosons

$$\Rightarrow p(E) \neq e^{-\beta E}$$

? Was it all wrong?

Where is the " ± 1 " term unimportant and Boltzmann statistics applicable?

a) for distinguishable particles (lattice position in solids)

b) for gases as well?

\Rightarrow consider gas within Boltzmann statistics (canonical) and see differences

• chemical potential?

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

$$\Rightarrow \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \frac{\partial}{\partial N} \left[-k_B T \ln Z_{\text{can}} \right]$$

$$Z_{\text{can}} = \frac{1}{N!} Z_1^N \quad Z_1 = V \Lambda_m^{-3} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

$$\hookrightarrow \ln Z_{\text{can}} = N \cdot \ln Z_1 - N \ln N + N$$

$$\begin{aligned} \hookrightarrow \mu &= \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \left[\ln Z_1 - \ln N - N \frac{1}{N} + 1 \right] \\ &= -k_B T \ln \frac{Z_1}{N} \end{aligned}$$

Consequences : • $\frac{z_1}{N} = e^{-\beta\mu}$ or $\frac{N}{z_1} = e^{\beta\mu} = z$ ⑥

• $e^{\beta\mu} = z = \frac{N}{z_1} = \frac{N}{V} \Delta_m^3 = n \Delta^3$ fugacity

$\Rightarrow \boxed{\beta\mu = \ln n \Delta^3}$ within Boltzmann statistics

• Boltzmann distribution

$$p(E) = \frac{1}{z} e^{-\beta E}$$

$$\langle n(E) \rangle = N p(E) = \frac{N}{z} e^{-\beta E} = e^{\beta\mu} e^{-\beta E}$$

$$= \frac{1}{e^{\beta(E-\mu)} \pm 0}$$

\Rightarrow Boltzmann distribution follows if

i) $e^{-\beta\mu} \gg 1 \Leftrightarrow \frac{z}{N} \gg 1 \Leftrightarrow z \gg N$

! much more states available than particles

ii) $e^{\beta\mu} \ll 1 \Leftrightarrow \boxed{n \Delta^3 \ll 1}$

- low density $n = \frac{N}{V}$
- high temperature $\Delta \sim T^{-\frac{1}{2}}$

Summary

Boltzmann statistics works for

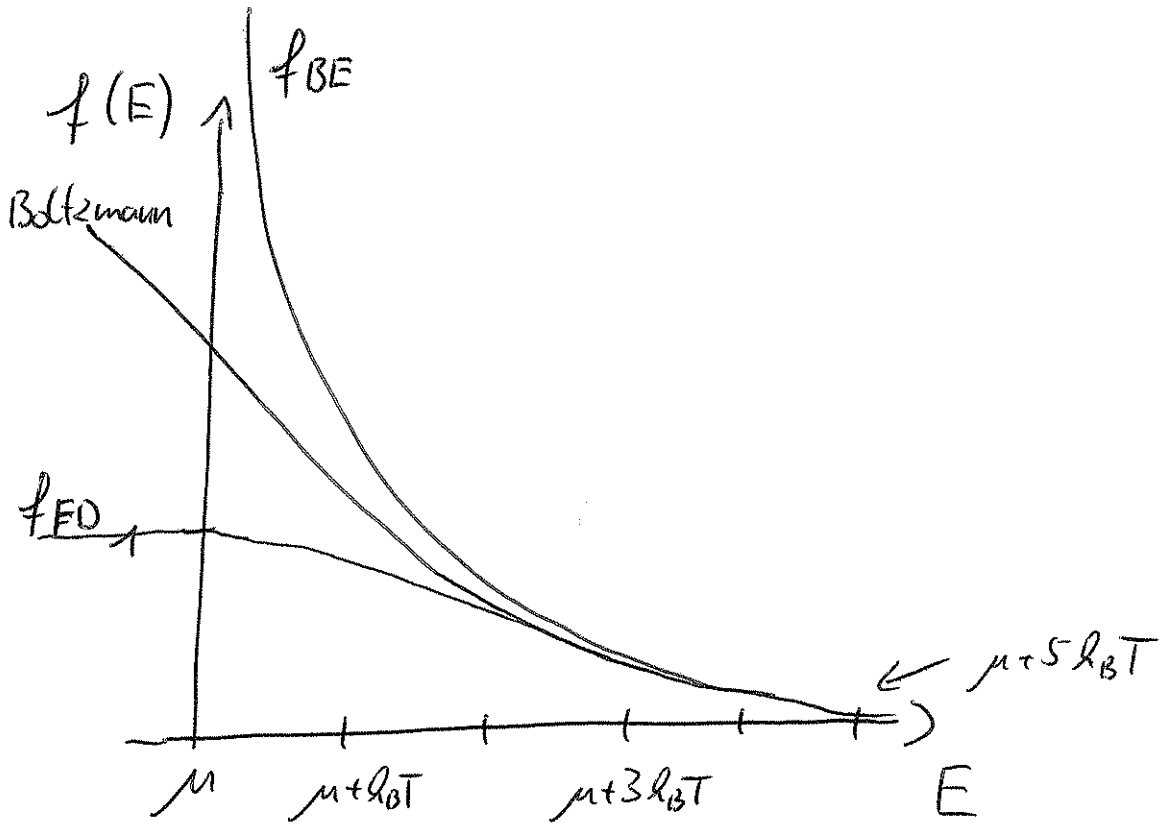
a) systems with distinguishable particles

b) gases with $n \Lambda_m^3 \ll 1$

→ in this case, "±1" term unimportant

$$\rightarrow \dots \quad f_{\text{Boltzmann}} = f_{\text{FD}} = f_{\text{BE}} = n \Lambda^3 e^{-\beta E}$$

c) for the high energy part of the distribution



Lecture 17

3.5 Ideal Quantum Gases

①

3.5.1 Fermions near $T=0$

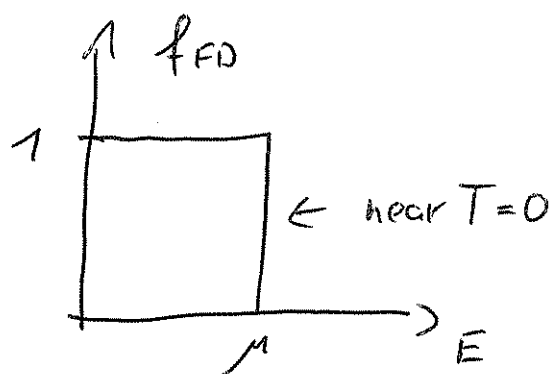
a) distribution function: $f_{FD}(E) = \frac{1}{e^{\beta(E-\mu)} + 1}$

Limits: $E > \mu$: $\beta(E-\mu) \xrightarrow{T \rightarrow 0} \infty$

$\Rightarrow \lim_{T \rightarrow 0} f(E) = 0$

$E < \mu$: $\beta(E-\mu) \xrightarrow{T \rightarrow 0} -\infty$

$\Rightarrow \lim_{T \rightarrow 0} f(E) = 1$



\Rightarrow special energy at highest occupied state
 $\equiv \mu$... chemical potential

Def.: $E_F = \mu(T=0)$... Fermi energy

b) relation: $n \Leftrightarrow \mu$ at $T=0$

(2)

$\hat{=}$ calculation of the Fermi energy

• use normalisation: $N = \int dE g(E) f(E)$

with $g(E) dE = (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$

$$\begin{aligned}\Rightarrow N &= \int_0^{\infty} dE (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} f(E) \\ &= (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_F} E^{1/2} dE \\ &= (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{3} E_F^{3/2} \quad \leftarrow \text{cut by } f(E)\end{aligned}$$

electrons: $(2s+1) = 2$ as $s = \frac{1}{2}$

$$\Rightarrow E_F^{3/2} = \frac{N}{(2s+1) 2\pi V} \frac{3}{2} \left(\frac{h^2}{2m}\right)^{3/2}$$

$$\Rightarrow E_F = \frac{h^2}{8m} \left(\frac{3}{\pi} \frac{N}{V}\right)^{2/3}$$

$$= \frac{h^2}{8m} \left(\frac{3}{\pi} n\right)^{2/3} \sim n^{2/3}$$

c) thermodynamic properties at $T=0$ (3)

$$\begin{aligned}
 \bullet U &= \int dE E g(E) f(E) \\
 &= (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_F} E^{3/2} dE \\
 e^- \rightarrow &= 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{5} E_F^{5/2} \\
 &= 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{5} \frac{N}{4\pi V} \frac{3}{2} \left(\frac{h^2}{2m}\right)^{3/2} E_F \quad \leftarrow E_F^{5/2} = E_F \cdot E_F^{3/2} \quad \text{use def.} \\
 &= \frac{3}{5} N E_F
 \end{aligned}$$

energy density: $\boxed{u = \frac{U}{N} = \frac{3}{5} E_F} \sim n^{2/3}$

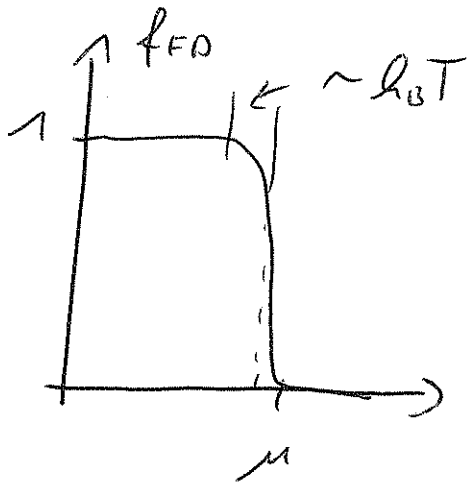
$$\begin{aligned}
 \bullet P &= - \left(\frac{\partial U}{\partial V} \right)_{S,N} = - \frac{\partial}{\partial V} \left[\frac{3}{5} N \frac{h^2}{8m} \left(\frac{3N}{\pi} \right)^{2/3} V^{-2/3} \right] \\
 &= - \frac{3}{5} N \frac{h^2}{8m} \left(\frac{3N}{\pi} \right)^{2/3} V^{-2/3} V^{-1} \left(-\frac{2}{3} \right) \\
 &= \frac{2}{5} N E_F \frac{1}{V} \\
 &= \frac{2}{5} n E_F = \frac{2}{3} \frac{U}{V} \sim n^{5/3}
 \end{aligned}$$

• bulk modulus:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T = -V \underset{\substack{\uparrow \\ \text{HOME}}}{C} \frac{\partial}{\partial V} \left(\frac{1}{V} \right)^{5/3} = \frac{10}{9} \frac{U}{V}$$

d) extension to small (non-zero) temperatures ⁽⁴⁾

- formally done by Sommerfeld expansion
- here: by arguments



- only few electrons near Fermi energy are affected by temperature
- # of e^- affected $\sim N k_B T$

• affected electrons can gain energy in the order of $k_B T$

\Rightarrow additional energy $\sim N (k_B T)^2$

$$\Rightarrow U = \frac{3}{5} N E_F + C N \frac{(k_B T)^2}{E_F}$$

$$= \frac{3}{5} N E_F + \frac{\pi^2}{4} N \frac{(k_B T)^2}{E_F}$$

by Sommerfeld expansion

$$\Rightarrow C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\pi^2 N k_B^2 T}{2 E_F} \sim T$$

e) examples for Fermions at "T=0"

i) conduction electrons in metals

→ very weak interactions due to Pauli principle and high average energies

? Why T=0 treatment?

$$n_e \approx n_{atom} \approx 10^{23} \text{ cm}^{-3}$$

$$\Rightarrow E_F \approx 8 \times 10^{-19} \text{ J} \approx 5 \text{ eV},$$

$$\text{but } k_B T \text{ (room temperature)} \approx \frac{1}{40} \text{ eV}$$

⇒ E_F much larger than thermal fluctuations $\sim k_B T$

⇒ E_F sets energy scale and T=0 treatment OK

- results:
- low T heat capacity described by model (higher T → lattice contribution larger)
 - bulk modulus within a factor of 3
 - How is the Fermi pressure compensated?

ii) electrons in white dwarf stars

• typical numbers (Sirius B): $V \approx 7 \times 10^{20} \text{ m}^3$
 $N \approx 7 \times 10^{56} \Rightarrow n \approx 10^{30} \text{ cm}^{-3}$

$$\Rightarrow E_F = 5.33 \times 10^{14} \text{ J} = 0.33 \text{ MeV}$$

$$p_F = 1.8 \times 10^{22} \text{ Pa} = 1.8 \times 10^{17} \text{ atm}$$

(balanced by gravity)

$$k_B T \approx 1 \text{ eV} \ll 0.33 \text{ MeV}$$

⇒ T=0 treatment appropriate

iii) even more extreme example:
gas of neutrons in neutron stars

iv) system of chemical elements
≡ electrons fill quantum levels around cores
=> discrete energy structure
=> integer number of states at a given energy

Why $T=0$?

• binding energies $|E_b|$ in the order of eV
(hydrogen: $E_b = -13,6 \text{ eV}$)

• room temperature: $k_B T \approx \frac{1}{40} \text{ eV}$

=> $k_B T \ll$ energy gaps between levels

=> electrons fill lower levels first

• energy structure

Level	n	l	$g = 2(2l+1)$
3d	3	2	10
3p	3	1	6
3s	3	0	2
2p	2	1	6
2s	2	0	2
1s	1	0	2

• Again, electrons at $T=0$ occupy lowest energy states possible, but they are restricted by the Pauli exclusion principle

⇒ Mendelejew periodic system

$$H : 1e^- \rightarrow 1s^1$$

$$He : 2e^- \rightarrow 1s^2$$

$$Li : 3e^- \rightarrow 1s^2 2s^1$$

$$Be : 4e^- \rightarrow 1s^2 2s^2$$

$$B : 5e^- \rightarrow 1s^2 2s^2 2p^1$$

⋮

$$Ne : 10e^- \rightarrow 1s^2 2s^2 2p^6$$

$$Na : 11e^- \rightarrow 1s^2 2s^2 2p^6 3s^1$$

⋮

$$Ar : 18e^- \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6$$

$$K : 19e^- \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$

carefull !

• $4s$ state lower than $3d$ state

Lecture 18

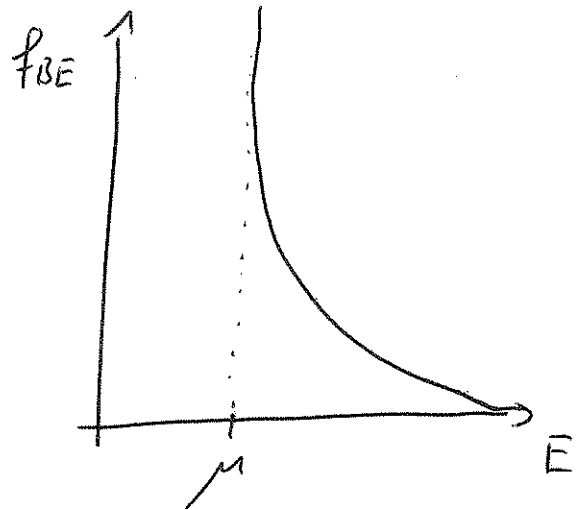
3.5.2 Bosons near $T=0$

①

a) distribution:

$$f(E) = \frac{1}{e^{\beta(E-\mu)} - 1}$$

$$\Rightarrow -\infty \leq \mu \leq 0 \text{ (gas)}$$



• reminder: $\beta\mu = \ln(n\Lambda_m^3)$ in the nondegenerate limit with $n\Lambda^3 \ll 1$ (does not work for $T \rightarrow 0$)

b) determination of μ for an ideal gas

• $\rho(E) = g(E) f_{BE}(E)$ with

$$g(E) dE = (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

• Bosons: s is integer ... $s=0$ important case
 $(2s+1) = 1$ - " -

• normalisation:

$$N = \sum_{\text{energies}} g(E) f_{BE}(E) \xrightarrow[\text{states}]{\text{many}} N = \int dE g(E) f_{BE}(E)$$

• fix $N, T \Rightarrow$ solve numerically

\Rightarrow outcome: $-\infty \leq \mu \leq 0$ possible,
 BUT cases with $\mu=0$
 are very problematic!

c) What happens at $\mu=0$?

(2)

• apply $\mu=0$ and see results

$$N = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} V \int_0^{\infty} dE \sqrt{E} \frac{1}{e^{\beta E} - 1}$$

$$\text{use: } x = E/k_B T = \beta E$$

$$N = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \int_0^{\infty} dx \frac{\sqrt{x}}{e^x - 1}$$

tables: 2.315

$$= 2.612 \frac{V}{\Lambda_m^3} = f(T)$$

∇ result must be wrong: # of particles does not depend on temperature ∇

• solution: $\sum_E \rightarrow \int dE$ works only for densely packed states

∇ integral does not include contributions from the ground state (usually small)

⇒ $N =$ particles in the ground state + part. in excited states

$$= N_0 + N_{ex}$$

$$\text{with } N_{ex} = \int dE g(E) f_{BE}(E)$$

⇒ start over again

(3)

• test 1: # particles in the ground state

$$N_0 = \frac{1}{e^{-\beta\mu} - 1} \Leftrightarrow -\beta\mu = \ln\left(1 + \frac{1}{N_0}\right) \approx \frac{1}{N_0}$$

⇒ $\mu=0$ IF many particles
(macroscopic number) in ground state

✓ OK, makes sense

• normalisation

$$N = \int dE g(E) f_{BE}(E) \quad \text{for } \mu < 0$$

or

$$N = N_0 + 2,612 V \Lambda_m^{-3} \quad \text{for } \mu = 0 \Leftrightarrow n_{ex} \Lambda_m^3 = 2,612$$

d) Bose-Einstein condensation

• phase transition at $n \Lambda^3 = 2,612$ is called
Bose-Einstein condensation

• for $\mu=0$, a macroscopic number of particles
occupies the ground state

• for $\mu=0$, system is a mixture of normal gas
(excited atoms) and gas with particles
in the ground state (condensate)

i) fix temperature & increase particle number

⇒ at $N_c = 2,612 V / \Lambda_m^3$ starts condensation

ii) fix particle number & reduce temperature

$$\Rightarrow \text{condensation at } N = N_{ox} = 2,612 V \left(\frac{2\pi m k_B T_c}{h^2} \right)^{3/2}$$

$$\Leftrightarrow T_c = \frac{h^2}{2\pi m k_B} \left(\frac{N}{V} \frac{1}{2,612} \right)^{2/3}$$

e) summary

(4)

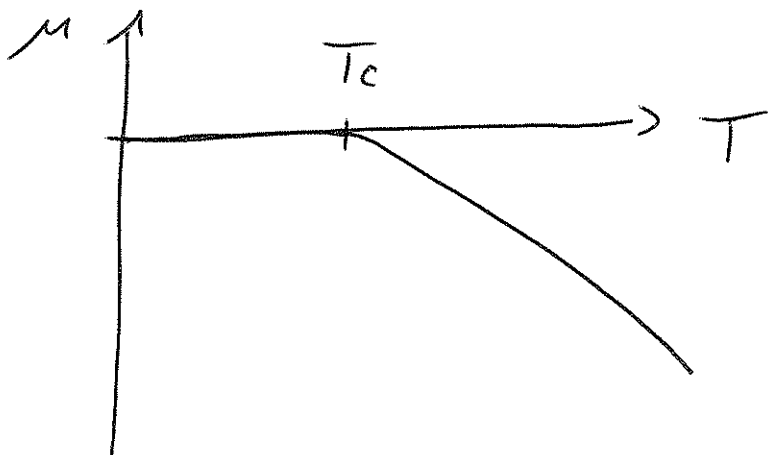
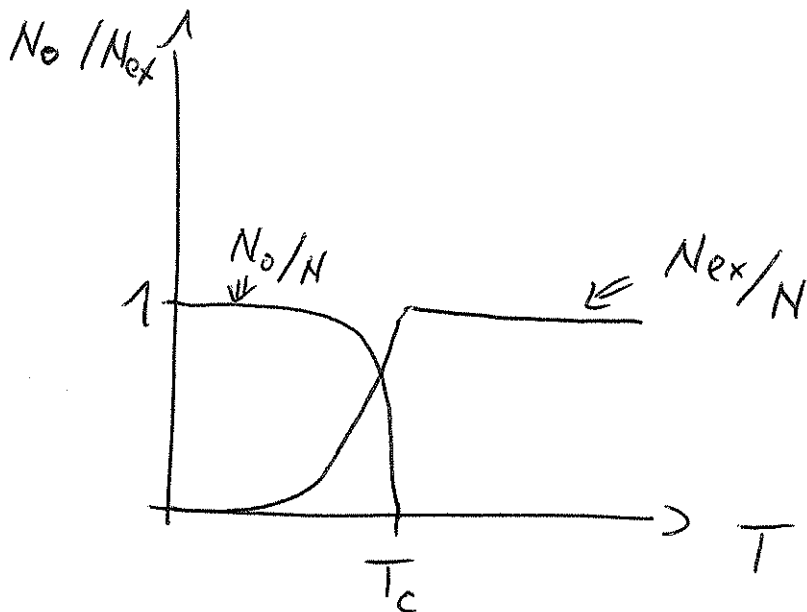
• for $T > T_c$: all Bosons in excited states (normal gas)
 $\mu < 0$

• for $T < T_c$: macroscopic # of Bosons in ground state
(BEC has occurred) and $\mu = 0$

• # of particles in the ground state

$$N = N_0 + N_{ex} \quad (\Leftrightarrow) \quad i) \quad N_0/N = 0 \quad \text{for } \mu < 0$$

$$ii) \quad N_0/N = 1 - \frac{N_{ex}}{N} \\ = 1 - \left(\frac{T}{T_c}\right)^{3/2} \quad \text{for } \mu = 0$$



1) thermodynamics of ideal Bose gases near $T=0$ ⑤

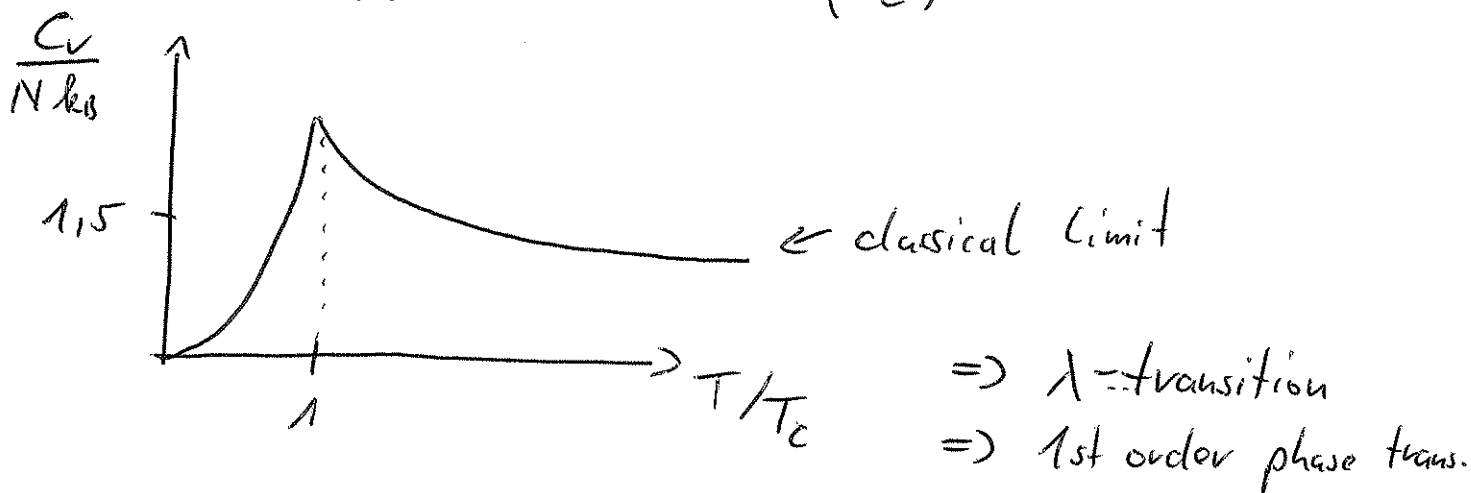
i) internal energy for $T < T_c$

• no contribution from Bosons in the ground state ($E=0$)

$$\begin{aligned} \Rightarrow U &= \int_0^{\infty} dE E N_{ex}(E) = \int_0^{\infty} dE E g(E) f_{BE}(E) \\ &= \frac{2}{\sqrt{\pi}} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \int_0^{\infty} \frac{x^{3/2}}{e^x - 1} dx \quad x = \beta E \\ &= 0,770 N k_B T \left(\frac{T}{T_c} \right)^{3/2} \quad \text{used: def. of } T_c \end{aligned}$$

ii) heat capacity ($T < T_c$)

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 1,92 N k_B \left(\frac{T}{T_c} \right)^{3/2} \Leftrightarrow C_V \sim T^{3/2}$$



iii) entropy ($T < T_c$)

$$S - S(T=0) = \int_0^T \frac{\delta Q}{T'} = \int_0^T \frac{C_V dT'}{T'} = 1,28 N k_B \left(\frac{T}{T_c} \right)^{3/2}$$

• for $T \rightarrow 0$, $S \sim T^{3/2} \xrightarrow{T \rightarrow 0} 0$ (3rd law OK)

g) examples

⑥

- i)
- ${}^4\text{He}$ becomes superfluid at $T = 2,18 \text{ K}$
 - heat capacity shows peak at $T = 2,18 \text{ K}$
 - for normal fluid density, BEC should occur at $T = 3,1 \text{ K}$

\Rightarrow special properties of the fluid below $2,18 \text{ K}$ are associated to BEC

\Rightarrow different transition temperature due to correlations (fluid) \rightarrow not perfect example

- ii)
- gases in laser traps (since 1998)
 - approx. $10^4 \dots 10^7$ atoms at low density being cooled down to $T \approx 10^{-7} \text{ K}$

\Rightarrow clear signature of BEC

at "correct = calculated" temperature

\Rightarrow Nobel price in 2001

Lecture 19

3.5.3 Photons as a Bose gas

- Blackbody Radiation

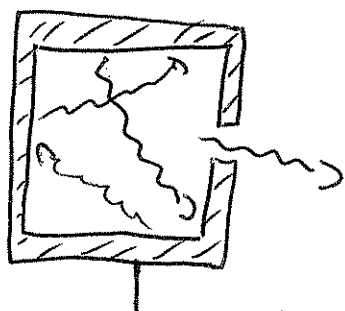
a) photon gas / distribution

- QM: radiation comes in chunks (photons) with energy $E = h\nu = \hbar\omega$ *
- a radiation field consists of many photons with (usually) different energies $\hat{=}$ gas
- photons barely interact with each other $\hat{=}$ ideal gas
- ! photons are Bosons

\Rightarrow # of photons per energy state / single state if radiation field is in equilibrium with "walls"

$$\langle n(E) \rangle = \frac{1}{e^{\beta(E-\mu)} - 1}$$

- Blackbody radiation $\hat{=}$ radiation field in cavity / hohlraum



walls at $T = \text{const}$

problem: explain spectrum + power of radiation that leaks out through small hole

summary photons: *

$$E = h\nu = \hbar\omega$$

$$= \frac{hc}{\lambda} = \hbar kc = pc \quad \text{ultra-relativistic}$$

$$p = \hbar k = \frac{h}{\lambda} = \frac{h\nu}{c} \quad k = \frac{2\pi}{\lambda}$$

b) chemical potential

! photon number is not constant even without transfer to environment

(photons can be emitted/absorbed by walls)

$$\Rightarrow \mu = 0$$

Why?

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

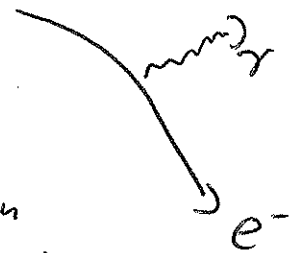
$F \rightarrow \min$ in equilibrium

$$\Rightarrow \left(\frac{\partial F}{\partial N} \right)_{T,V} = 0 = \mu \quad \text{at equilibrium}$$

ii) reaction, where photons are emitted/absorbed



\Rightarrow equilibrium condition (average photon number stays the same)



$$\mu_e = \mu_e + \mu_\gamma \quad \Leftrightarrow \quad \mu_\gamma = 0$$

c) density of states

③

- $\langle n(E) \rangle = f_{BE}(E)$ for single energy,
but energy states of photons are continuous

$$\Rightarrow \# \text{ of particles in energy band } dE \text{ at } E \dots E \\ n(E) dE = g(E) f_{BE}(E)$$

∇ need density of states $g(E)$

- Consider cubic container with length L

∇ Light must obey boundary conditions + wave equ.
(look for standing waves)

$$\Rightarrow \begin{aligned} E_x &= A_x \cos(k_x x) \sin(k_y y) \sin(k_z z) \\ E_y &= A_y \sin(k_x x) \cos(k_y y) \sin(k_z z) \\ E_z &= A_z \sin(k_x x) \sin(k_y y) \cos(k_z z) \end{aligned}$$

$$\text{fulfills: } \begin{aligned} \nabla^2 \vec{E} &= \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \\ \nabla \cdot \vec{E} &= 0 \end{aligned} \quad (\text{E-dynamics})$$

$$\text{IF } k_x = \frac{n_x \pi}{L}; \quad k_y = \frac{n_y \pi}{L}; \quad k_z = \frac{n_z \pi}{L} \\ \text{with } n_x, n_y, n_z \text{ integer}$$

$$\Rightarrow k^2 = \frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\text{Def.: } R^2 = (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2 L^2}{\pi^2}$$

(4)

\Rightarrow # of states with $\hbar k' = 0 \dots \hbar k$ is equal to $1/8$ volume of sphere with radius R

$$G(\hbar k) = \frac{1}{8} \frac{4}{3} \pi R^3 = \frac{1}{8} \frac{4}{3} \pi \left(\frac{\hbar k L}{\pi} \right)^3 = \frac{V \hbar^3 k^3}{6 \pi^2}$$

with $V = L^3$

\Rightarrow density of states

$$g(\hbar k) d\hbar k = \frac{\partial G(\hbar k)}{\partial \hbar k} d\hbar k = \frac{V \hbar^2}{2 \pi^2} d\hbar k$$

• transformation to energy space: $E = \hbar c k$
 $\hbar k = E / \hbar c$

$$\Rightarrow g(E) dE = 2 \times \frac{V E^2}{2 \pi^2 (\hbar c)^3} dE$$

• transformation to frequencies: $E = \hbar \omega$

$$\Rightarrow g(\omega) d\omega = 2 \times \frac{V \omega^2}{2 \pi^2 c^3} d\omega$$

\checkmark additional factor "2" due to polarisation

check: • derivation similar to particles

• what if $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$ (gas particles)

$$\Rightarrow g(E) dE = 2 \pi (2m)^{3/2} E^{1/2} \frac{V}{h^3} dE$$

OK

$\Rightarrow g(\hbar k)$ works for real and virtual particles \checkmark

d) frequency distribution of photon number & energy (5)

- spectrum : photon number per energy band

$$n(\omega) d\omega = g(\omega) f_{BE}^y(\omega) d\omega$$

$$= 2 \times \frac{V}{2\pi^2 c^3} \omega^2 \times \frac{d\omega}{\exp(\beta \hbar \omega) - 1}$$

- energy spectrum : energy per frequency band

$$u(\omega) d\omega = g(\omega) \times E(\omega) \times f_{BE}^y(\omega)$$

$$u(\omega) d\omega = 2 \times \frac{V}{2\pi^2 c^3} \omega^2 \times \hbar \omega \times \frac{d\omega}{\exp(\beta \hbar \omega) - 1}$$

Planck spectrum

$\hat{=}$ birthday of QM

- Limits

i) small frequencies $\Rightarrow \exp(\beta \hbar \omega) = 1 + \beta \hbar \omega + \dots$

$$\Rightarrow u(\omega) d\omega = 2 \times \frac{V}{2\pi^2 c^3} k_B T \omega^2 d\omega$$

- Rayleigh - Jeans Law

$\hat{=}$ exact classical derivation

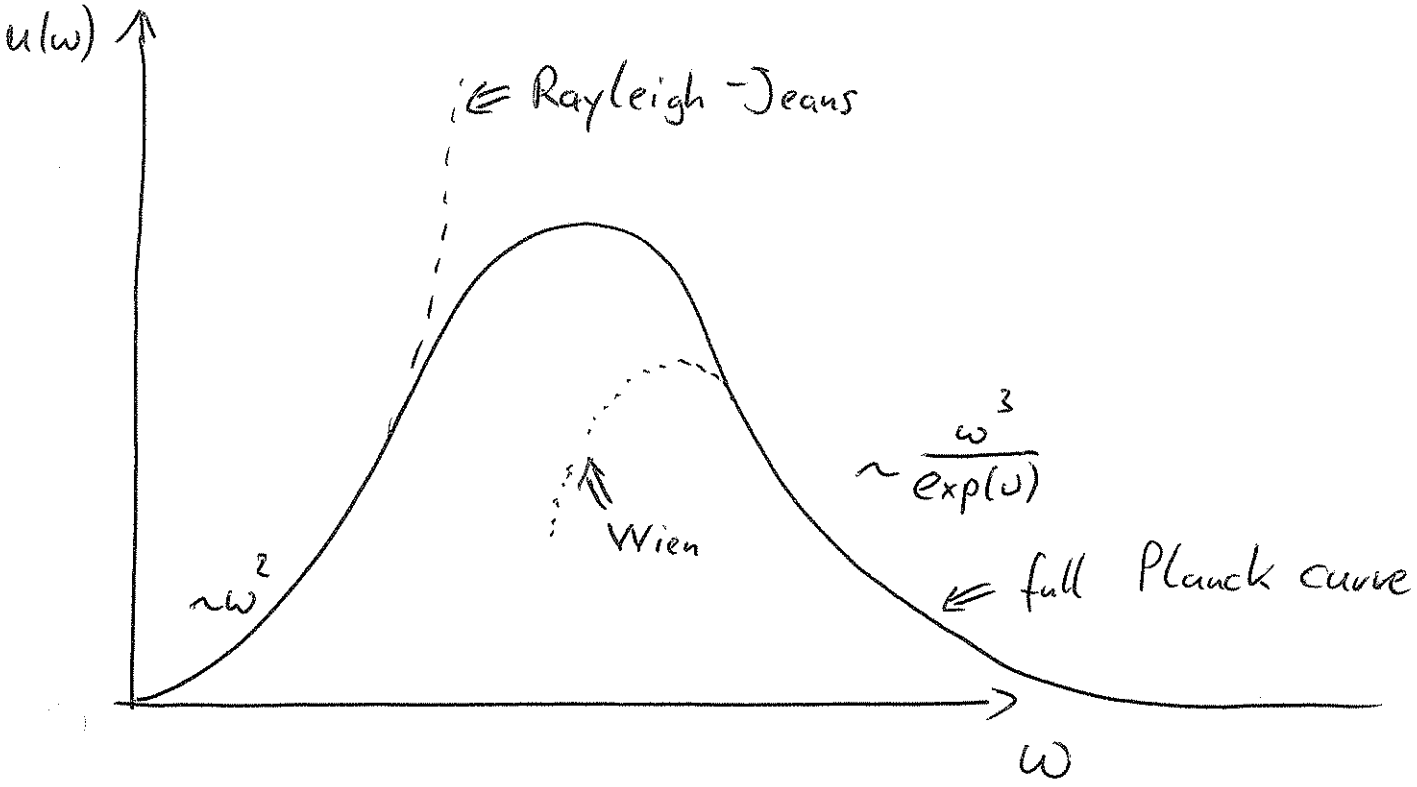
∇_0 cannot be true as $\int_0^{\infty} u(\omega) d\omega = \infty$

$\hat{=}$ ultra-violet catastrophe

ii) high frequencies $\Rightarrow \exp(\beta \hbar \omega) \gg 1$

$$\Rightarrow u(\omega) d\omega = 2 \times \frac{V}{2\pi^2 c^3} \frac{\omega^3 d\omega}{\exp(\hbar \omega / \beta)}$$

$\hat{=}$ Wien's Law



• maximum : $\lambda_{\max} T = \frac{c}{\nu_{\max}} T = \text{const.}$

Wien's displacement law
 ν_0 measured long before Planck

• example : Cosmic background radiation
 \Rightarrow excellent fit to Planck curve
 with $T = 2,735 \text{ K}$

e) thermodynamics of Blackbody radiation

⑥

i) internal energy

$$U = \int u(\omega) d\omega = \frac{V h}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3 d\omega}{\exp(\beta \hbar \omega) - 1}$$

$$= \frac{V h}{\pi^2 c^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^{\infty} \frac{x^3 dx}{e^x - 1} \quad \text{Def.: } x = \beta \hbar \omega$$

$\Rightarrow = \frac{\pi^4}{15}$

$$\Rightarrow U = \frac{\pi^2 V k_B^4}{15 \hbar^3 c^3} T^4 \sim T^4$$
$$= a T^4 V$$

ii) energy flux through a hole

$$\eta = \frac{1}{4} c \frac{U}{V} \quad \dots \text{ given by geometry}$$
$$= \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} T^4 = \sigma T^4 \quad \dots \text{ + kinetic behaviour}$$

Stefan's law

✓ can be experimentally confirmed
(measured before Planck's law)

iii) heat capacity (valid to $T=0$)

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 4aT^3V$$

iv) entropy T

$$S(T) = \int_0^T \frac{C_v(T')}{T'} dT' = 4aV \int_0^T T'^2 dT'$$
$$= \frac{4}{3} aT^3V$$

• $S \sim T^3$... 3rd Law OK: $S(T=0) = 0$

v) Light pressure

• Helmholtz free energy

$$F = U - TS = aT^4V - T \frac{4}{3} aT^3V$$
$$= -\frac{1}{3} aT^4V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3} aT^4$$

• Light pressure can exceed thermal pressure of gases ($p = n k_B T$) at high temperatures

Lecture 20

Appendix : Method of Lagrange Multipliers

①

Mathematical supplement

- problem : maximise / minimise a function $f(x, y, \dots)$ under some constraints

\Rightarrow without constrain : $\frac{\partial f}{\partial x_i} \stackrel{!}{=} 0$

- with constraints?

\Rightarrow extremum of $f(x, y)$ if exact differential is zero

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = 0$$

- constrain in the form : $g(x, y) = 0$

\Rightarrow differentiate constrain

$$dg = \frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy = 0 \quad \text{if } g(x, y) = 0 \text{ fulfilled}$$

- combine equation for df and dg

$$\left[\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} \right] dx + \left[\frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} \right] dy = 0$$

\forall dx and dy can be independently varied

$$\Rightarrow \frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0 \quad \& \quad \frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} = 0$$

- move free variables (dimensions) / more constraints

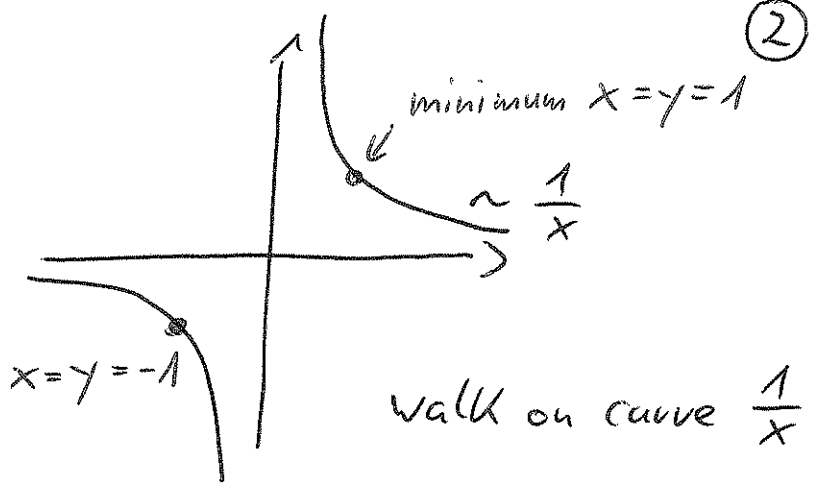
$$\Rightarrow \frac{\partial f}{\partial x_i} - \lambda_1 \frac{\partial g_1}{\partial x_i} - \lambda_2 \frac{\partial g_2}{\partial x_i} - \dots = 0$$

EXAMPLE:

$$f(x, y) = x^2 + y^2$$

$$g(x, y) = xy - 1 = 0$$

$$\Leftrightarrow y = \frac{1}{x}$$



• equations to solve

... show later

$$\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} = 2x - \lambda y \stackrel{!}{=} 0 \quad (1)$$

$$\frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} = 2y - \lambda x \stackrel{!}{=} 0 \quad (2)$$

$$xy - 1 = 0 \quad (3)$$

\Rightarrow 3 equations for variables x, y, λ

• combine (1) & (3) $\Rightarrow 2x - \lambda \frac{1}{x} = 0 \Rightarrow 2x^2 = \lambda$

• -u- (2) & (3) $\Rightarrow 2y - \lambda \frac{1}{y} = 0 \Rightarrow 2y^2 = \lambda$ (*)

• multiply (1) & (2)

$$\Rightarrow 4xy - 2x^2\lambda - 2y^2\lambda + xy\lambda^2 = 0$$

$$(*) \Rightarrow 4 - 2\lambda^2 + \lambda^2 = 0$$

$$\Rightarrow \lambda = 2$$

• from (*) with $\lambda = 2 \Rightarrow x = \pm 1 \quad y = \pm 1$

• from (1): $x = +y$

$$\Rightarrow x = y = 1 \\ \lambda = 2$$

and

$$x = y = -1 \\ \lambda = 2$$

Statistics using Lagrange Multipliers

③

a) micro-canonical ensemble

$$S = k_B \ln \Omega$$

Boltzmann

$$= -k_B \sum_V \rho_V \ln \rho_V$$

$\rho_V \dots$ probabilities

• $S \rightarrow \max$ in equilibrium

• subject to constrain $\sum_V \rho_V = 1$

• example: only two states: $\rho_V = \{ \rho_1, \rho_2 \}$

$$\Rightarrow 1 - \rho_1 - \rho_2 = 0$$

• use method to obtain ρ_V

$$\frac{\partial}{\partial \rho_1} [S - \lambda g] = \frac{\partial}{\partial \rho_1} \left[-k_B \sum_{i=1,2} \rho_i \ln \rho_i - \lambda (1 - \rho_1 - \rho_2) \right] \stackrel{!}{=} 0$$

$$= -k_B \ln \rho_1 - k_B + \lambda$$

$$= 0 \quad \textcircled{1}$$

$$\frac{\partial}{\partial \rho_2} [S - \lambda g] = -k_B \ln \rho_2 - k_B + \lambda$$

$$\textcircled{2}$$

• take $\textcircled{1} - \textcircled{2}$: $-k_B \ln \rho_1 + k_B \ln \rho_2 = 0$

$$\Leftrightarrow \rho_1 = \rho_2$$

equipartition

$\Rightarrow S \rightarrow \max$ is equivalent to equipartition theorem \checkmark

b) canonical ensemble

(4)

$$S = k_B \ln \Omega = -k_B \sum_v p_v \ln p_v \rightarrow \max$$

$$\text{constrains: i) } \sum_v p_v = 1$$

$$\text{ii) } \sum_v E_v p_v = \langle E \rangle = U$$

• apply method:

$$\frac{\partial}{\partial p_i} \left\{ -\sum_v p_v \ln p_v - \alpha \left[\sum_v p_v - 1 \right] - \beta \left[\sum_v E_v p_v - U \right] \right\} \stackrel{!}{=} 0$$

$$\alpha = \frac{\lambda_1}{k_B} \quad \beta = \frac{\lambda_2}{k_B}$$

$$\Rightarrow 0 = -\ln p_i - 1 - \alpha - \beta E_i$$

$$\Rightarrow \ln p_i = -1 - \alpha - \beta E_i$$

$$p_i = e^{-(1+\alpha)} e^{-\beta E_i}$$

... Boltzmann
distribution

BUT: what are α, β ?

• α from normalisation (constrain i)

$$\sum_v p_v = e^{-(1+\alpha)} \sum_v e^{-\beta E_v} = 1$$

$$\Rightarrow e^{-(1+\alpha)} = \frac{1}{Z_{\text{can}}} = \left[\sum_v e^{-\beta E_v} \right]^{-1}$$

β ... some number

• β from constrain ii)

5

- start with $\ln p_i = -(1+\alpha) - \beta E_i$
- multiply by $-k_B p_i$
- sum over all i

$$\Rightarrow -k_B \sum_i p_i \ln p_i = (1+\alpha) k_B \sum_i p_i + k_B \beta \sum_i E_i p_i$$
$$S = (1+\alpha) k_B + k_B \beta U \quad \leftarrow \text{constrain ii)}$$

- use thermodynamic relation : $F = U - TS$
 $TS = U - F$

$$\Rightarrow TS = (1+\alpha) k_B T + k_B T \beta U$$
$$= k_B T \ln Z_{can} + k_B T \beta U$$
$$\stackrel{!}{=} -F + U$$

\uparrow
OK, as
 $(1+\alpha) = \ln Z_{can}$

\uparrow
works IF
 $\beta = \frac{1}{k_B T}$

c) grand-canonical ensemble

(6)

$$S = -k_B \sum_v p_v \ln p_v \rightarrow \max$$

constrains: i) $\sum p_v = 1$

ii) $\sum E_v p_v = \langle E \rangle = U$

iii) $\sum N_v p_v = \langle N \rangle = N$

• apply method:

$$\frac{\partial}{\partial p_i} \left\{ -\sum_v p_v \ln p_v - \alpha \left[\sum_v p_v - 1 \right] - \beta \left[\sum_v E_v p_v - U \right] - \gamma \left[\sum_v N_v p_v - N \right] \right\} \stackrel{!}{=} 0$$

$$\Rightarrow 0 = -\ln p_i - 1 - \alpha - \beta E_i - \gamma N_i$$

$$\Rightarrow \ln p_i = -(1 + \alpha) - \beta E_i - \gamma N_i$$

$$\Rightarrow p_i = e^{-(1+\alpha)} e^{-\beta E_i - \gamma N_i} \quad \dots \text{Gibbs factors}$$

• obtain α, β, γ from constrains

i) $\Rightarrow e^{-(1+\alpha)} = \frac{1}{Z_{gv}}$

ii) $\Rightarrow \beta = \frac{1}{k_B T}$

iii) $\Rightarrow \gamma = -\beta \mu = -\mu / k_B T$ } use thermodynamics as well