Statistical Mechanics

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Abstract

The goal of this lecture and tutorial series is to introduce concepts and applications of statistical mechanics. We recommend the textbooks by Prof. Dr. R. Hentschke [1] and Prof. Dr. W. Nolting [2]. At `https://moodle.uni-wuppertal.de/course/view.php?id=19809`, you can find the syllabus, lecture notes and latest information.

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"Statistical mechanics is often thought of as the theory of how atoms combine to form gases liquids solids and even plasmas and black body radiation. But it is both much more and less than that. Statistical mechanics is a useful tools in many areas of science where a large number of variables has to be dealt with using statistical methods."

— Leonard Susskind, *Online Lectures*

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1 Two fundamental laws of Nature

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1.1.1 Mechanical work

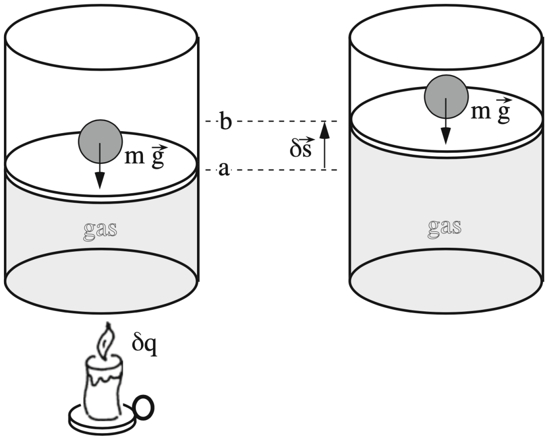


Figure 1: A gas confined to a cylinder absorbs a certain amount of heat δq and expands, pushing up a piston with a weight of mass m (from [1]).

δq = amount of heat absorbed by the gas in the cylinder
⇒ expansion of the gas $a \to b$
⇒ increase of volume $\delta V = V_b - V_a = A\delta s$
Some part of the heat is converted to mechanical work W to lift the piston and the weight ($m_{piston} << m_{weight}$, no friction):

$$\begin{aligned}\delta w_{done\ by\ gas} &= \int_a^b d\vec{s}\cdot\vec{f}_{done\ by\ gas} = \int_a^b d\vec{s}\cdot(-m\vec{g}) \\ &= \frac{mg}{A}\int_{V_a}^{V_b} dV = P_{ex}\delta V\end{aligned}$$

P_{ex} = external pressure exerted on the gas by the gravitational force mg

We define by E the internal (total) energy of the gas. Then

$$\delta E = \underbrace{\delta q}_{heat\ received} - \underbrace{P_{ex}\delta V}_{work\ done} \tag{1}$$

When the piston comes to rest, $P_{ex} = P$, where P is the gas pressure inside the cylinder. We know that $P = P(V)$, the gas pressure is a function fo the volume V occupied by the gas. We assume that the change of volume δV is small, such that we can neglect the change (second order effect) in gas pressure $\Rightarrow \boxed{\delta E = \delta q = P\delta V}$

1st law of thermodynamics: energy conservation for system (gas) during process (heat absorption and expansion), three cases of systems:

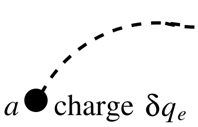
- isolated: no exchange with the exterior
- closed: no exchange of matter, but heat
- open: exchange everything

systems are sometimes divided into subsystems (= systems)
systems undergo changes (= process)
special case: system in thermal contact with reservoir, heat can be transferred from reservoir to system, however reservoir is so large that none of its physical properties change due to the heat exchange.

1.1.2 Electric work

Example: $\vec{F} = \delta q_e \vec{E}$

$\vec{E}$ = electric field = $-\vec{\nabla}\Phi$
Φ = electric potential



work done by the force when charge δq_e moves from a to b:

$$\delta w_q = \int_a^b d\vec{s}\vec{F} = -\delta q_e \int_a^b d\vec{s}\vec{\nabla}\Phi = -\delta q_e \Big(\Phi(b) - \Phi(a)\Big) = -\delta q_e \Phi_{ba}$$

Φ_{ba} is the potential difference between point b and a, the work depends only on this difference and not on the actual path from a to b
system = charge + field, change of internal energy

$$\delta E \;=\; -(\underbrace{-\delta q_e \Phi_{ba}}_{work\ done\ by\ the\ charge-field\ system}) = \delta q_e \Phi_{ba}$$

In terms of current $I = \delta q/\delta t$ (δt is a time interval) $\delta E_I = I\Phi_{ba}\delta t$. In presence of resistance R, the quantity $\delta q_{Joule} = RI^2\delta t$ is the Joule heat generated by the current.

We consider now continuous dielectric media and the following two Maxwell equations (in Gaussian units):

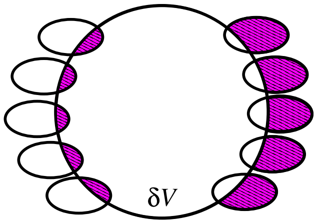
$$\vec\nabla \times \vec H = \frac{1}{c}\frac{\partial}{\partial t}\vec D + \frac{4\pi}{c}\vec j \qquad (2)$$

$$\vec\nabla \times \vec E = -\frac{1}{c}\frac{\partial}{\partial t}\vec B \qquad (3)$$

$\vec E(\vec r)$ = average electric field in a volume element at point $\vec r$
(size of volume element >> size of molecules)
$\vec D$ = $\vec E + 4\pi\vec P$ = electric displacement
$\vec P$ = macroscopic polarization = local electric dipole moment per volume

spatial variation of polarization:

⇒ more molecular charge may leave the volume element than enters it



$\vec H$ = $\vec B + 4\pi\vec M$ = magnetic field
$\vec M$ = macroscopic magnetization = local magnetic dipole moment per volume
$\vec B$ = average magnetic induction

Derivation of Eq. (2):
Consider a medium in which there is a macroscopic excess or free charge ρ_e. Associated to the ρ_e there is a current density $\vec j_e$. ρ_e and $\vec j_e$ satisfy the continuity equation

$$\frac{\partial\rho_e}{\partial t} + \vec\nabla\vec j_e = 0.$$

We also have the Maxwell equation $\vec\nabla\vec D = 4\pi\rho_e$ ($\vec\nabla\vec D = 4\pi\rho$ with $\rho = \rho_{molecules} + \rho_e = 0 + \rho_e$ since the average molecule charge is usually zero)

$$\Rightarrow \quad \frac{\partial}{\partial t}\vec\nabla\vec D = 4\pi\frac{\partial\rho_e}{\partial t} = -4\pi\vec\nabla\vec j_e \quad \text{or} \quad \vec\nabla\Bigg(\underbrace{\frac{\partial\vec D}{\partial t} + 4\pi\vec j_e}_{divergence-free\ vector}\Bigg) = 0$$

a divergence-free vector may be expressed as the curl of another vector $c'\vec{H}'$:

$$\vec{\nabla} \times \vec{H}' = \frac{1}{c'}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c'}\vec{j}_e$$

Comparison with Ampère's law in vacuum: $\vec{\nabla} \times \vec{B} = \frac{4\pi}{c}\vec{j}$ suggests $\vec{H}' = \vec{H}$ and $c' = c$, which leads to Eq. (2). $\square$

Derivation of Eq. (3):
Spatial averaging applied to Faraday's law in vacuum: $\vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$. We proceed by

$$\frac{c\vec{E}}{4\pi} \cdot (2) \quad : \quad \frac{c}{4\pi}\vec{E} \cdot (\vec{\nabla} \times \vec{H}) = \frac{1}{4\pi}\vec{E} \cdot \frac{\partial \vec{D}}{\partial t} + \vec{E} \cdot \vec{j} \tag{4}$$

$$-\frac{c\vec{H}}{4\pi} \cdot (3) \quad : \quad -\frac{c}{4\pi}\vec{H} \cdot (\vec{\nabla} \times \vec{E}) = \frac{1}{4\pi}\vec{H} \cdot \frac{\partial \vec{B}}{\partial t} \tag{5}$$

Using the vector identity $\vec{\nabla} \cdot (\vec{a} \times \vec{b}) = \vec{b} \cdot (\vec{\nabla} \times \vec{a}) - \vec{a} \cdot (\vec{\nabla} \times \vec{b})$:

$$\begin{aligned}(4) + (5) \quad : \quad & \frac{c}{4\pi}\left(\vec{E} \cdot (\vec{\nabla} \times \vec{H}) - \vec{H} \cdot (\vec{\nabla} \times \vec{E})\right) \\ = \quad & \frac{c}{4\pi}\vec{\nabla} \cdot (\vec{H} \times \vec{E}) = \frac{1}{4\pi}\vec{E} \cdot \frac{\partial \vec{D}}{\partial t} + \vec{E} \cdot \vec{j} + \frac{1}{4\pi}\vec{H} \cdot \frac{\partial \vec{B}}{\partial t}\end{aligned}$$

We use Green's theorem in space (divergence theorem):

$$\int_V dV \vec{\nabla} \cdot (\vec{H} \times \vec{E}) = \int_{\partial V = A} d\vec{A} \cdot (\vec{H} \times \vec{E})$$

where $d\vec{A} = dA\vec{n}$ is a surface element on $A = \partial V$ oriented towards the outside of V. If we choose the volume V such that the fields vanish on ∂V:

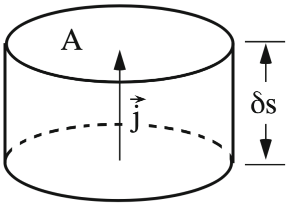
$$\int_{\partial V = A} d\vec{A} \cdot (\vec{H} \times \vec{E}) = 0 = \int_V dV \left(\frac{1}{4\pi}\vec{E} \cdot \frac{\partial \vec{D}}{\partial t} + \vec{E} \cdot \vec{j} + \frac{1}{4\pi}\vec{H} \cdot \frac{\partial \vec{B}}{\partial t}\right)$$

$$\frac{\partial \vec{D}}{\partial t} \approx \frac{\delta \vec{D}}{\delta t}, \quad \frac{\partial \vec{B}}{\partial t} \approx \frac{\delta \vec{B}}{\delta t}, \quad (\delta X = \text{ small change of } X)$$

$$0 = \int_V dV \left(\vec{E} \cdot \frac{\delta \vec{D}}{4\pi} + \underbrace{\delta t \vec{E} \cdot \vec{j}}_{\textit{work done by } \vec{E}-\textit{field during time } \delta t} + \vec{H} \cdot \frac{\delta \vec{B}}{4\pi}\right)$$

cylindrical volume element with $\delta\vec{s}\,||\,\vec{j}$:

$$\delta V = A\,\delta s$$
$$\delta V\,\vec{j} = A\,\delta\vec{s}\tfrac{q}{\delta t A} = \tfrac{q}{\delta t}\delta\vec{s}$$
$$\delta V\,\vec{j}\,\vec{E}\,\delta t = \underbrace{q\,\vec{E}}_{force\ of\ \vec{E}-field\ on\ charge\ q\ doing\ work}\,\delta\vec{s}$$



$\Rightarrow$ work done by the system (= charge + fields) $\delta w = \int_V dV\vec{j}\vec{E}\delta t$ can be expressed by

$$\delta w = -\int_V dV\left(\vec{E}\cdot\frac{\delta\vec{D}}{4\pi} + \vec{H}\cdot\frac{\delta\vec{B}}{4\pi}\right),$$

aka the change of the electromagnetic energy content of the system. For a process in which a system exchanges heat and performs electrical work

$$\boxed{\delta E = \delta q - \delta w = \delta q + \int_V dV\left(\vec{E}\cdot\frac{\delta\vec{D}}{4\pi} + \vec{H}\cdot\frac{\delta\vec{B}}{4\pi}\right)}$$

1.1.3 Chemical work

Consider an open system to which we can add material. Generally work must be done (chemical reactions, chemical conversions, spatial redistribution). If we add δn moles of a material, we write

$$\delta w_{done\ on\ system} = \mu\,\delta n$$

with μ the chemical potential (per mole added). One mole ($n = 1$) is the amount of substance of a system which contains as many elementary units as there are atoms of carbon in 12g of the pure nuclide carbon-12. The number of elementary units in one mole is $N_A = 6.0221\cdot 10^{23}$ mole^{-1} (Avogadro or Loschmidt). The elementary unit may be an atom, molecule, ion, electron, photon, or a specified group of such units. If the system contains different species i

$$\delta w_{done\ on\ system} = \sum_i \mu_i\,\delta n_i$$

For a process in which a system exchanges heat and performs chemical work

$$\boxed{\delta E = \delta q + \sum_i \mu_i\,\delta n_i}$$

1.1.4 The 1st law of thermodynamics

The first law expresses conservation of (internal) energy.

Examples:

- $\delta E = \delta q - P\delta V + \sum_i \mu_i \, \delta n_i$
  process with heat exchange and mechanical (volume) work and change of composition of system
- $\delta E = \delta q - \int_V dV \, \vec{j} \, \vec{E} \, \delta t$
  process involves heat exchange and electrical work
- $\delta E = \delta q - P\delta V + \int_V dV (\vec{E} \, \delta\vec{D} + \vec{H} \, \delta\vec{B})/4\pi$
  process with heat exchange and mechanical and electrical work

$$\begin{aligned} \delta E &= \delta q - \delta w_{done\ by\ the\ system} \\ &= \delta q + \delta w_{done\ on\ the\ system} \\ \delta &: \text{small change during a process (afterwards - before)} \\ \Delta &: \text{finite change} \\ d &: \text{exact differential} \end{aligned}$$

If a quantity changes during a process and the change only depends on the two end points of the path described by the process in the space of certain variables, *e.g.*, values of P and V, then the quantity possesses an exact differential and vice versa.

Example: piston moving in cylinder with friction

$$\underbrace{dE}_{\text{exact differential}} = \underbrace{\delta q - \delta w}_{\text{in general not exact differentials}}$$

1.2 The postulates of Kelvin and Clausius (2nd law)

The first law does not tell how much heat can be converted into work or exchanged between systems. This is the object of the following two postulates based on experiments which constitute the second law of thermodynamics.

1.2.1 Postulate of Lord Kelvin (K)

A complete transformation of heat (extracted from a uniform source) into work is impossible.

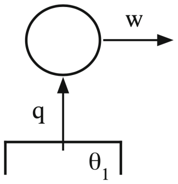
1.2.2 Postulate of Clausius (C)

It is impossible to transfer heat from a body at a given temperature to a body at higher temperature as the only result of a transformation.

Proof of equivalency of (K) and (C):

Θ = "temperature" (see section 1.3) of a reservoir → hotter or colder

(K) false ⇒ (C) false:

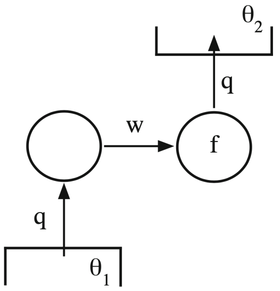


○ = device which converts heat in work at 100%, *i.e.*, $q = w$

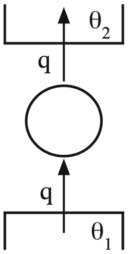
ⓕ = friction device which converts work in heat at 100%

⇒ net effect: heat is transferred to a second reservoir at $\Theta_2 > \Theta_1$

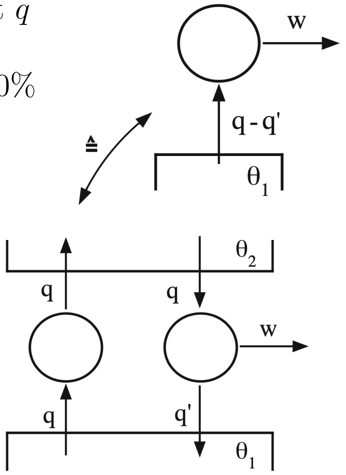
⇒ contradicts (C)



(C) false ⇒ (K) false:



device which transfers heat q from reservoir at Θ_1 to reservoir at $\Theta_2 > \Theta_1$ at 100%



the heat q is used by a second device to do work w leaving reservoir at Θ_2 unaltered ⇒ contradicts (K)

□

1.3 Carnot's engine and temperature

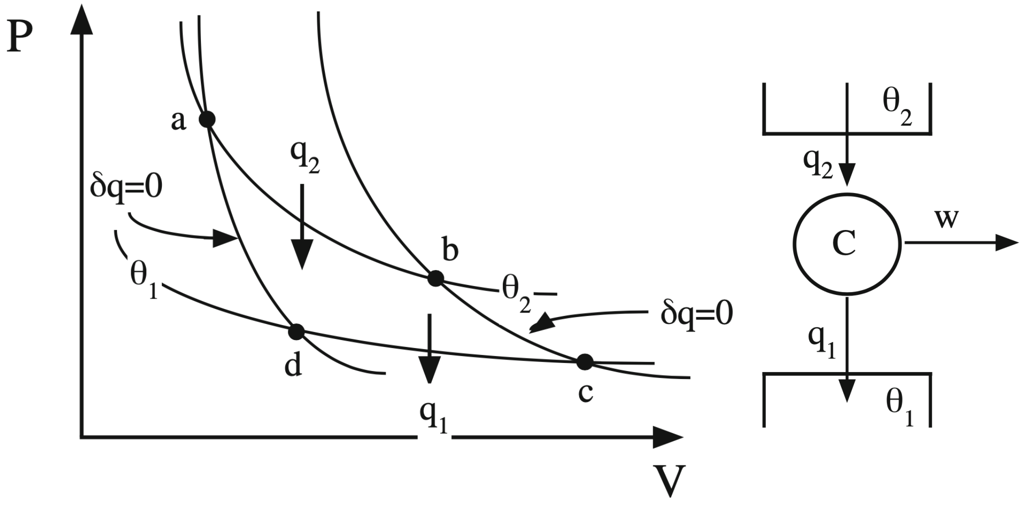


Figure 2: Fluid undergoing a cyclic transformation, from [1].

Carnot's engine:

$a \to b$ amount of heat q_2 is transferred from heat reservoir at temperature $\Theta_2 > \Theta_1$ to the device at temperature Θ_2: isothermal expansion.

$b \to c$ adiabatic ($\delta q = 0$) expansion to the temperature Θ_1 of a second reservoir

$c \to d$ isothermal compression, device releases heat q_1 to reservoir at temperature Θ_1

$d \to a$ adiabatic ($\delta q = 0$) compression to the temperature Θ_2

In addition, the device has done work w (= area of P-V loop). The cyclic transformation can be performed by the device in both directions (reversibility). If arrows are reverted: heat pump.

Carnot engine: $\Delta E = 0$
1st law of thermodynamics: $\delta E = \delta q - \delta w$
$\Rightarrow \Delta E = q_2 - q_1 - w = 0$ or $w = q_2 - q_1$

Thermal efficiency:

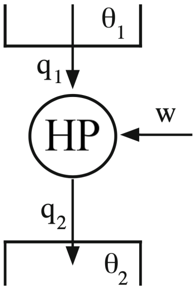
$$\eta = \frac{\text{work done}}{\text{heat absorbed}} = \frac{w}{q_2}$$

For the Carnot engine:

$\eta = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2}$

For a heat pump:

efficiency $= \frac{1}{\eta} = \frac{\text{heat transferred}}{\text{work received}}$



Carnot's theorem: the Carnot engine is the most efficient device operating between two temperatures

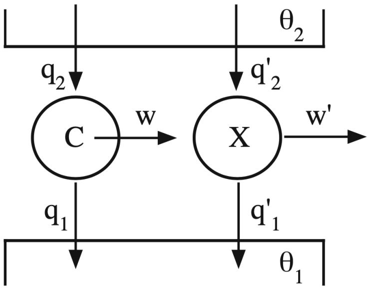
Proof:

X = competing device

we can arrange that $q_2 = q_2'$

(operate both devices many cycles

and add up the heat inputs)

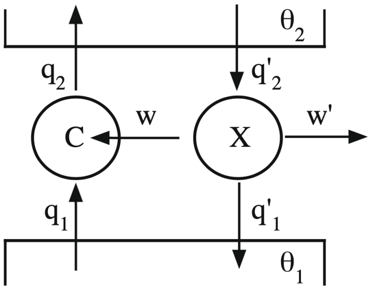


now reverse Carnot's engine:

again can assume $q_2 = q_2'$

$\Rightarrow$ reservoir at Θ_2

is completely unaltered



1st law (sign convention: q_i, q_i', w, $w' > 0$):

$$\begin{aligned} \text{C} &: \quad \Delta E_C = q_1 - q_2 + w = 0 \\ \text{X} &: \quad \Delta E_X = q_1' - q_2' + w' = 0 \end{aligned}$$

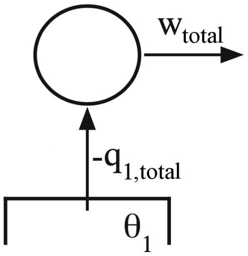
$$\Rightarrow w_{done\ in\ total} = w' - w = \underbrace{q_2' - q_2}_{q_{2,\,total}} - \underbrace{(q_1' - q_1)}_{q_{1,\,total}}$$

by assumption: $q_{2,\,total} = 0$

$\Rightarrow w_{total} = -q_{1,\,total}$

Kelvin postulate $\Rightarrow w_{total} \leqslant 0$

($w_{total} > 0$ is impossible)



$$\Rightarrow q_{1,\,total} \geqslant 0 \Rightarrow q_1' \geqslant q_1 \Rightarrow \frac{q_1'}{q_2'} \geqslant \frac{q_1}{q_2} \quad (q_2' = q_2)$$

$$\Rightarrow \eta_X = 1 - \frac{q_1'}{q_2'} \leqslant 1 - \frac{q_1}{q_2} = \eta_{Carnot} \quad \square$$

If the competing device is also reversible

$\Rightarrow$ repeat proof with the two engines interchanged

$\Rightarrow \eta_{Carnot} \leqslant \eta_{X,\,reversible} \Rightarrow \eta_{Carnot} = \eta_{X,\,reversible}$

Corollary: All Carnot engines operating between two given temperatures have the same efficiency.

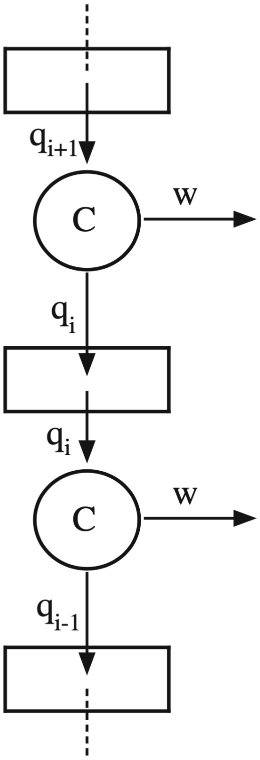
In the following define a temperature scale using

a sequence of Carnot engines:

each engine does the same amount of work w

each engine uses the heat produced by previous engine

first law: $w = q_{i+1} - q_i$



Definition of reservoir temperature: $\Theta_i = x \cdot q_i$

x is a proportionality constant independent of i

$\Rightarrow x \cdot w = \Theta_{i+1} - \Theta_i$

We may choose for example: $x \cdot w = 1\mathrm{K}$

$\Rightarrow$ the temperature difference between reservoirs is 1K.

This definition of temperature is independent of the fluid used.

efficiency is $\eta_i = 1 - \frac{\Theta_i}{\Theta_{i+1}} \quad (\Theta_{i+1} > \Theta_i)$

η_i grows if Θ_i decreases and Θ_{i+1} increases.

$\Theta_i = 0$ is not possible ($q_i = 0$ violates the postulate of Kelvin)

In section 2.2.1 we compute a Carnot engine's efficiency for an ideal gas as working medium $\Rightarrow$ ideal gas temperature $T \propto \Theta \Rightarrow$ from here on: $\Theta = T$

1.4 Entropy

Examples:

- gases escape from closed containers
- heat flows from a hot body to a colder environment

Spontaneous reversal of these processes is not possible (irreversible processes). This is the content of the

1.4.1 Theorem of Clausius

In any cyclic transformation throughout which the temperature is defined, the following inequality holds:

$$\boxed{\oint \frac{dq}{T} \leqslant 0} \qquad \oint = \text{integral over one cycle}$$

$\oint \frac{dq}{T} = 0 \Leftrightarrow$ the cyclic transformation is reversible.

Proof: assembly of Carnot engines ⓒ and reservoir $\boxed{T_i}$.

system = device which takes/gives heat q_i from/to reservoirs,
one after the other

at the end the system is in the same state as at the beginning:

$\sum_{i=1}^{n} q_i = 0 \Rightarrow$ in order to achieve this, not all Carnot engines operate
in the same direction, *i.e.*, q_i have different signs
$\frac{q_{i,0}}{T_0} = \frac{q_i}{T_i}$ (see section 1.3: $T_i = x\, q_i$)

$\Rightarrow$ total heat absorbed from reservoir at T_0 is $q_0 = \sum_{i=1}^{n} q_{i,0} = T_0 \sum_{i=1}^{n} \frac{q_i}{T_i}$

sign convention: $q_{i,0} > 0$: heat is taken from T_0-reservoir
$q_{i,0} < 0$: heat is given to T_0-reservoir

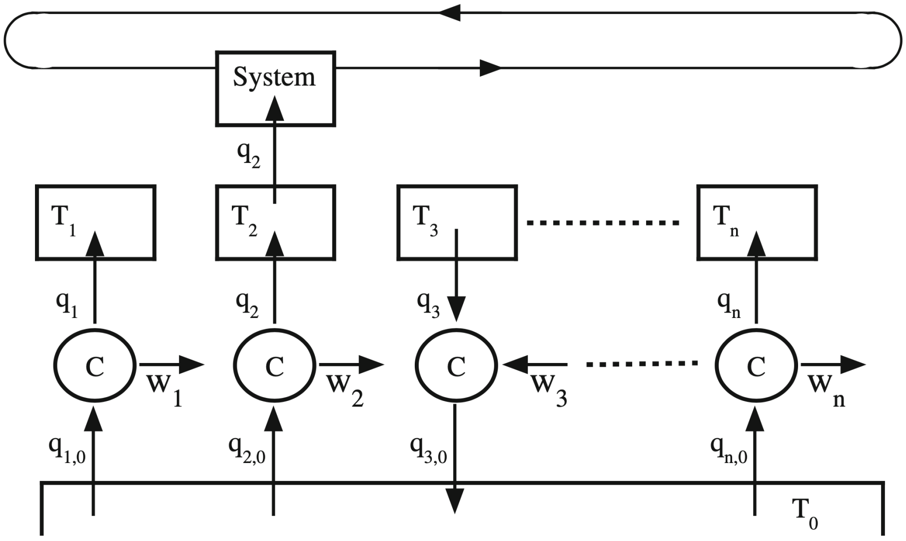


Figure 3: Assembly of Carnot engines and reservoirs, $T_0 > T_i$, $i = 1, \ldots, n$, from [1]

1st law for Carnot engines: $0 = \Delta E = \sum_{i=1}^{n} \Delta E_i = \underbrace{\sum_{i=1}^{n} q_{i,0}}_{q_0} - \underbrace{\sum_{i=1}^{n} q_i}_{=0} - w_{total}$

$\Rightarrow \; q_0 = w_{total}$

Kelvin postulate: $w_{total} \leqslant 0 \;\Rightarrow\; q_0 \leqslant 0 \;\Rightarrow\; \sum_{i=1}^{n} \frac{q_i}{T_i} \leqslant 0$

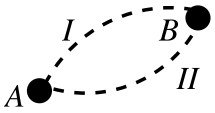
Limit $n \to \infty$ and $q_i \to dq$: $\oint \frac{dq}{T} \leqslant 0$

If the cycle is traversed in reversed order $q_i \to -q_i$ and $\sum_{i=1}^{n} \left(-\frac{q_i}{T_i}\right) \leqslant 0$

$\Rightarrow$ for a reversible cycle: $\sum_{i=1}^{n} \frac{q_i}{T_i} = 0.$ □

1.4.2 Consequences of Clausius' theorem

(i) If the transformations are reversible and I and II are two paths joining state A and B of the system:



$0 = \oint \frac{dq}{T} = \int_I \frac{dq}{T} - \int_{II} \frac{dq}{T}$

$\Rightarrow \int_A^B \frac{dq}{T}$ is independent of the paths $A \to B$ (if it is reversible)

(ii) Definition of **entropy S**:

O is an arbitrary, but fixed reference state.

The entropy $S(A)$ of any state A is defined via $S(A) = \int_O^A \frac{dq}{T}$.

The integration path is any reversible path joining O and A.

$S(A)$ depends on the reference state O through an additive constant.

Differences $S(B) - S(A) = \int_O^B \frac{dq}{T} - \int_O^A \frac{dq}{T} = \int_O^B \frac{dq}{T} + \int_A^O \frac{dq}{T} = \int_A^B \frac{dq}{T}$

of entropies are independent of the reference state O. Therefore,

$dS = \frac{dq}{T}$ holds for any infinitesimal reversible transformation.

1.4.3 Important properties of the entropy

(i) For an irreversible transformation from A to B: $\int_A^B \frac{dq}{T} \leqslant S(B) - S(A)$

Proof: consider a closed path composed by

$A \to B$ via irreversible transformation and

$B \to A$ via reversible path

Theorem of Clausius $\Rightarrow 0 \geqslant \oint \frac{dq}{T}$

$0 \geqslant \int_{\text{irreversible path } A\to B} \frac{dq}{T} - \underbrace{\int_{\text{reversible path } A\to B} \frac{dq}{T}}$

$\Rightarrow \int_{\text{irreversible path } A\to B} \frac{dq}{T} \quad \leqslant \quad S(B) - S(A)$ $\square$

(ii) The entropy of a thermally isolated system never decreases.

Proof: thermal isolation means $dq = 0$.

From (i) it follows $0 \leqslant S(B) - S(A)$ or $S(B) \geqslant S(A)$.

This is the manifestation of the thermodynamic arrow of time.

(iii) The entropy is a state function.

Proof: $S(A)$ depends only on the state A in which the system is, and not on the reversible path to define S. We know two state functions by now: entropy S and internal energy E, q is not a state function.

Combining the first law:

$dE = \delta q - \delta w$ for a reversible process, where $\delta q = dq = T\,dS$, we get

$$\boxed{dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{1}{T}\vec{H}\,d\vec{m} - \sum_i \frac{\mu_i}{T}dn_i + \dots}$$

where

$$\begin{aligned}
\left.\frac{\partial S}{\partial E}\right|_{V,\,\vec{m},\,n,\dots} &= \frac{1}{T}, \quad \text{thermodynamic definition of temperature } T \\
\left.\frac{\partial S}{\partial V}\right|_{E,\,\vec{m},\,n,\dots} &= \frac{1}{T}P, \\
\left.\frac{\partial S}{\partial \vec{m}}\right|_{E,\,V,\,n,\dots} &= -\frac{1}{T}\vec{H} \quad \text{and} \\
\left.\frac{\partial S}{\partial n_i}\right|_{E,\,V,\,\vec{m},\,n_j\neq n_i,\dots} &= -\frac{1}{T}\mu_i
\end{aligned}$$

Remark:

The $\vec{H}$ field is assumed to be constant, so $\int dV \frac{1}{4\pi}\vec{H}d\vec{B} = \vec{H}d\vec{m}$,

where $d\vec{m} = \int_V dV\,d\vec{M}$. In the analogous case of electric fields,

$\vec{H}\,d\vec{m}$ is replaced by $\vec{E}\,d\vec{p}$, where $d\vec{p} = \int_V dV\,d\vec{P}$.

There is a correspondence between pairs $(\vec{H},\vec{m})$, $(\vec{E},\vec{p})$ and $(P,-V)$.

Even more general is the mapping

$$(P,-V) \leftrightarrow (\vec{E}, V\tfrac{\vec{D}}{4\pi}) \quad \text{or} \quad (P,-V) \leftrightarrow (\vec{H}, V\tfrac{\vec{B}}{4\pi}),$$

where we assume homogeneous fields in (constant) volume V.

2 Thermodynamic functions

2.1 Internal energy and enthalpy

Consider internal energy to be a function of T and V: $E(V,T)$

$$dE = \underbrace{\left.\frac{\partial E}{\partial T}\right|_V}_{\equiv C_V = \text{isochoric heat capacity (heat capacity at constant volume)}} dT + \left.\frac{\partial E}{\partial V}\right|_T dV$$

(Greek: *ísos* = the same, *chṓra* = occupied space)

Definition: Enthalpy $H = E + PV$

On which variables does H depend? (is dH an exact differential?)

$$dH = dE + d(PV) = \left.\frac{\partial E}{\partial T}\right|_V dT + \left.\frac{\partial E}{\partial V}\right|_T dV + P\,dV + V\,dP$$

We use $V = V(T,P)$ and replace $dV = \left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP$

$$\begin{aligned} \Rightarrow dH &= \left(\left.\frac{\partial E}{\partial T}\right|_V + \left.\frac{\partial E}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P\right) dT \\ &\quad + \left(\left.\frac{\partial E}{\partial V}\right|_T \left.\frac{\partial V}{\partial P}\right|_T + P\left.\frac{\partial V}{\partial P}\right|_T + V\right) dP \end{aligned}$$

From Eq. (A.0.1):

$$\left.\frac{\partial E}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P = \left.\frac{\partial E}{\partial T}\right|_P - \left.\frac{\partial E}{\partial T}\right|_V \quad (A = E,\ x = T,\ y = V,\ z = P)$$

$$\Rightarrow (\ldots)dT = \left(\cancel{\left.\frac{\partial E}{\partial T}\right|_V} + \left.\frac{\partial E}{\partial T}\right|_P - \cancel{\left.\frac{\partial E}{\partial T}\right|_V} + P\left.\frac{\partial V}{\partial T}\right|_P\right) dT = \left.\frac{\partial (E+PV)}{\partial T}\right|_P dT$$

From Eq. (A.0.2):

$$\left.\frac{\partial E}{\partial V}\right|_T \left.\frac{\partial V}{\partial P}\right|_T = \left.\frac{\partial E}{\partial P}\right|_T \quad (A = E,\ x = V,\ y = T,\ z = P)$$

$$\Rightarrow (\ldots)dP = \left(\left.\frac{\partial E}{\partial P}\right|_T + P\left.\frac{\partial V}{\partial P}\right|_T + V\right) dP = \left.\frac{\partial (E+PV)}{\partial P}\right|_T dP$$

We get $dH = \left.\frac{\partial(E+PV)}{\partial T}\right|_P dT + \left.\frac{\partial(E+PV)}{\partial P}\right|_T dP$
and therefore this means $H = H(T, P)$.

We replaced the volume dependence by a pressure dependence. This is of great practical importance, working at fixed pressure is safer.

$$\left.\frac{\partial H}{\partial T}\right|_P \equiv C_P = \text{isobaric heat capacity (heat capacity at constant pressure)}$$

(Greek *báros* = weight)

Two other useful quantities:

$$\alpha_P \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P = \text{isobaric thermal expansion coefficient}$$
$$\kappa_T \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = \text{isothermal compressibility}$$

2.2 Simple applications

2.2.1 Ideal Gas Law

Often in applications we assume that the gases are ideal. This means that pressure P, volume V and temperature T are related by

$$\boxed{PV = nRT} \quad (n = \text{number of moles})$$

The quantity $R = 8.31447 m^3\, Pa\, K^{-1}\, mol^{-1}$ is called the gas constant ($1Pa = 1N\, m^{-2},\ 1N = 1kg\, m\, s^{-2}$)

For an ideal gas: $\left.\frac{\partial E}{\partial V}\right|_T = 0$.

Proof: In exercise 1.3 we prove the relation $\left.\frac{\partial E}{\partial V}\right|_T = T^2 \left.\frac{\partial (P/T)}{\partial T}\right|_V$.

Using the ideal gas law $\frac{P}{T} = \frac{nR}{V}$ and therefore $\left.\frac{\partial E}{\partial V}\right|_T = 0$. □

It follows that for an ideal gas $dE = \left.\frac{\partial E}{\partial T}\right|_V dT = C_V dT$.

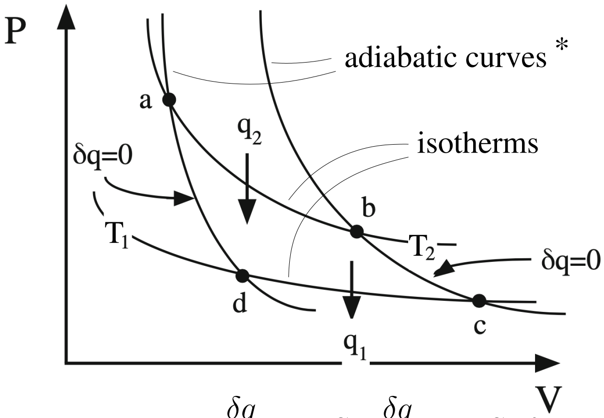
Further, for an ideal gas

$$\alpha_P = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_P = \frac{1}{V}\frac{nR}{P}\frac{\partial T}{\partial T}\bigg|_P = \frac{nR}{VP} = \frac{1}{T}.$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T = -\frac{1}{V}nRT\frac{\partial}{\partial P}\frac{1}{P}\bigg|_T = \frac{nRT}{VP^2} = \frac{1}{P}.$$

2.2.2 Isotherms and adiabatic curves

Carnot cycle:



* Clausius theorem $\Rightarrow \dfrac{\delta q}{T} \leqslant dS$. $\dfrac{\delta q}{T} = dS$ if the process is reversible.
Adiabatic curves in Carnot engines are **isentropic**: $dS = 0$.

Why are isotherms less steep than the adiabatic curves?

$$i.e., \frac{\partial P}{\partial V}\bigg|_T > \frac{\partial P}{\partial V}\bigg|_{\delta q=0} \text{ (the slopes } \frac{\partial P}{\partial V} \text{ are negative)}$$

Proof for an ideal gas: adiabatic curve: $\delta q = 0,\ dE = -\delta w = -P\,dV = C_V dT$

$$\text{using } T = \frac{PV}{nR} \Rightarrow dT = \frac{\partial T}{\partial V}\bigg|_P dV + \frac{\partial T}{\partial P}\bigg|_V dP = \frac{P}{nR}dV + \frac{V}{nR}dP$$

$$\Rightarrow \qquad -P\,dV = C_V\left(\frac{P}{nR}dV + \frac{V}{nR}dP\right)$$

$$-\left(1+\frac{C_V}{nR}\right)\cancel{P}\frac{dV}{V} = \frac{C_V}{nR}\cancel{V}\frac{dP}{P} \;\Rightarrow\; \left.\frac{d\ln P}{d\ln V}\right|_{\delta q=0} = -1-\frac{nR}{C_V}$$

$$\text{isotherm: } \left.\frac{dP}{dV}\right|_T = nRT\left.\frac{d\frac{1}{V}}{dV}\right|_T = -\frac{nRT}{V^2} = -\frac{P}{V}$$

$$\Rightarrow \left.\frac{d\ln P}{d\ln V}\right|_T = \frac{V}{P}\left.\frac{dP}{dV}\right|_T = -1$$

$$\Rightarrow \left.\frac{d\ln P}{d\ln V}\right|_T > \left.\frac{d\ln P}{d\ln V}\right|_{\delta q=0} \text{ or } \left.\frac{dP}{dV}\right|_T > \left.\frac{dP}{dV}\right|_{\delta q=0} \qquad \square$$

2.2.3 Efficiency of energies with ideal gas as working substance

Example (a) Carnot cycle:

Work done by the gas in the different sections of the cycle:

$$a\to b \;\; w_{a\to b} = \int_{V_a}^{V_b} P\,dV \overset{\delta T=0}{=} nRT_2\int_{V_a}^{V_b}\frac{dV}{V} = nRT_2\ln\frac{V_b}{V_a}$$

$$b\to c \;\; w_{b\to c} = \int_{V_b}^{V_c} P\,dV \overset{\delta q=0}{=} \int_{T_2}^{T_1}(-C_V)dT = -C_V(T_1-T_2)$$ (for an ideal gas $C_V = \#$ degrees of freedom $\times \frac{1}{2}nR$ by the equipartition theorem)

$$c\to d \;\; w_{c\to d} = \int_{V_c}^{V_d} P\,dV \overset{\delta T=0}{=} nRT_1\ln\frac{V_d}{V_c}$$

$$d\to a \;\; w_{d\to a} = \int_{V_d}^{V_a} P\,dV \overset{\delta q=0}{=} -C_V(T_2-T_1) = -w_{b\to c}$$

$\Rightarrow \underbrace{\text{total work}}$ done by the gas $w = w_{a\to b}+\cancel{w_{b\to c}}+w_{c\to d}+\cancel{w_{d\to a}} = w_{a\to b}+w_{c\to d}$
= area within the loop in the P-V plane

We now compute the heat absorbed q_2.
Along an isotherm $\Delta E_{\text{ideal gas}} = C_V\Delta T = 0 = q_2 - w_{a\to b} \;\Rightarrow\; q_2 = w_{a\to b}$

Thermal efficiency

$$\begin{aligned}\eta &= \frac{w}{q_2} = \frac{w_{a\to b} + w_{c\to d}}{w_{a\to b}} = 1 + \frac{w_{c\to d}}{w_{a\to b}} \\ &= 1 + \frac{T_1}{T_2}\frac{\ln(V_d/V_c)}{\ln(V_b/V_a)} = 1 - \frac{T_1}{T_2}\frac{\ln(V_c/V_d)}{\ln(V_b/V_a)}.\end{aligned}$$

along an adiabatic curve:

$$\begin{aligned}\underbrace{-P}_{=-\frac{nRT}{V}} dV = dE = C_V dT \Rightarrow \frac{dV}{V} &= -\frac{C_V}{nR}\frac{dT}{T} \\ \ln\frac{V'}{V} &= -\frac{C_V}{nR}\ln\frac{T'}{T} \\ \frac{V}{V'} &= \left(\frac{T'}{T}\right)^{\frac{C_V}{nR}}\end{aligned}$$

$$\Rightarrow \text{ adiabatic curve } b \to c: \; V_c = V_b\left(\frac{T_1}{T_2}\right)^{-\frac{C_V}{nR}} = V_b\left(\frac{T_2}{T_1}\right)^{\frac{C_V}{nR}}$$

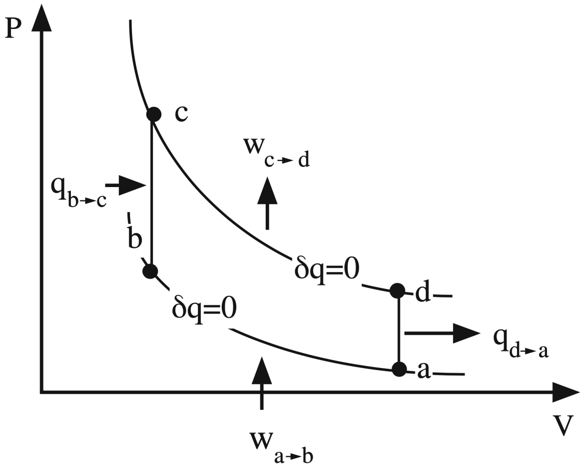
$$\text{adiabatic curve } d \to a: \; V_d = V_a\left(\frac{T_2}{T_1}\right)^{\frac{C_V}{nR}}$$

$\Rightarrow \dfrac{V_c}{V_d} = \dfrac{V_b}{V_a} \Rightarrow \eta = 1 - \dfrac{T_1}{T_2}$ in agreement with the result in section 1.3.

Example (b): Otto cycle

w = work done by gas

q = heat absorbed by gas



$a \to b$ $q_{a\to b} = 0$ $w_{a\to b} = \int_a^b P\,dV = -\int_a^b C_V dT = -C_V(T_b - T_a)$

$b \to c \;\; w_{b\to c} = 0 \quad q_{b\to c} = \int_b^c C_V dT = C_V(T_c - T_b)$

temperature $T = \frac{PV}{nR}$ increases, therefore heat must be absorbed

$c \to d \;\; q_{c\to d} = 0 \quad w_{c\to d} = -C_V(T_d - T_c)$

$d \to a \;\; w_{d\to a} = 0 \quad q_{d\to a} = C_V(T_a - T_d)$

Thermal efficiency $\eta = \dfrac{w}{q_{b\to c}} = \dfrac{-C_V(T_b - T_a) - C_V(T_d - T_c)}{C_V(T_c - T_b)} = 1 + \dfrac{T_a - T_d}{T_c - T_b}$

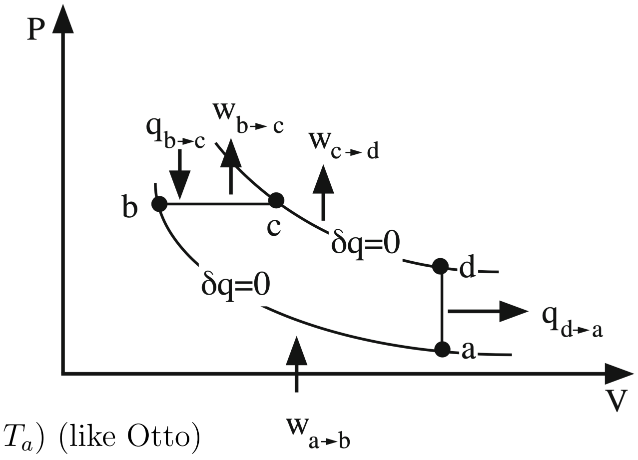
adiabatic curve $a \to b$: $\dfrac{V_a}{V_b} = \left(\dfrac{T_a}{T_b}\right)^{C_V/nR} \Rightarrow \dfrac{T_a}{T_b} = \left(\dfrac{V_b}{V_a}\right)^{nR/C_V} < 1$

adiabatic curve $c \to d$: $\dfrac{V_c}{V_d} = \left(\dfrac{T_d}{T_c}\right)^{C_V/nR} \Rightarrow \dfrac{T_d}{T_c} = \left(\dfrac{V_c}{V_d}\right)^{nR/C_V} < 1$

with $V_b = V_c$ and $V_a = V_d$ it follows $\dfrac{T_a}{T_b} = \dfrac{T_d}{T_c}$ or

$$\eta = 1 - \frac{T_a\frac{T_c}{T_b} - T_a}{T_c - T_b} = 1 - \frac{T_a}{T_b}\frac{T_c - T_b}{T_c - T_b} = 1 - \frac{T_a}{T_b}.$$

Example (c): Diesel cycle



$a \to b \;\; q_{a\to b} = 0 \quad w_{a\to b} = -C_V(T_b - T_a)$ (like Otto)

$b \to c \;\; w_{b\to c} = P_b(V_c - V_b) \quad q_{b\to c} = \int_b^c C_V dT + w_{b\to c} = C_V(\underbrace{T_c - T_b}_{>0}) + w_{b\to c}$

$(\delta E = \delta q - \delta w,\; \delta E = C_V \delta T)$

$c \to d \;\; q_{c\to d} = 0 \quad w_{c\to d} = -C_V(T_d - T_c)$ (like Otto)

$d \to a \;\; w_{d\to a} = 0 \quad q_{d\to a} = C_V(\underbrace{T_a - T_d}_{<0})$ (like Otto)

$$\text{Thermal efficiency } \eta = \frac{w}{q_{b\to c}} = \frac{-C_V(T_b - T_a) + P_b(V_c - V_b) - C_V(T_d - T_c)}{C_V(T_c - T_b) + P_b(V_c - V_b)}$$

$$= \frac{T_a - T_b + \frac{P_bV_b}{C_V}(\frac{V_c}{V_b} - 1) - T_d + T_c}{T_c - T_b + \frac{P_bV_b}{C_V}(\frac{V_c}{V_b} - 1)}$$

$$\eta = 1 - \frac{T_d - T_a}{T_c - T_b + \frac{P_bV_b}{C_V}(\frac{V_c}{V_b} - 1)}; \text{ using } P_bV_b = nRT_b:$$

$$\eta = 1 - \frac{T_a}{T_b}\frac{T_d/T_a - 1}{T_c/T_b - 1 + \frac{nR}{C_V}(\frac{V_c}{V_b} - 1)}; \text{ using } \frac{T_a}{T_b} = \left(\frac{V_a}{V_b}\right)^{nR/C_V}$$

$$\begin{aligned} \text{and } \frac{T_c}{T_b} &= \frac{T_d}{T_a}\frac{T_a}{T_b}\frac{T_c}{T_d} = \frac{T_d}{T_a}\left(\frac{V_b}{V_a}\right)^{nR/C_V}\left(\frac{V_c}{V_d}\right)^{-nR/C_V} \qquad \text{(see example (b))} \\ &= \frac{T_d}{T_a}\left(\frac{V_b\cancel{V_d}}{\cancel{V_a}V_c}\right)^{nR/C_V} \overset{(V_a=V_d)}{=} \frac{T_d}{T_a}\left(\frac{V_b}{V_c}\right)^{nR/C_V} \end{aligned}$$

$$\text{and } \left.\begin{array}{l} P_bV_b = nRT_b \\ P_bV_c = nRT_c \end{array}\right\} \Rightarrow \frac{T_c}{T_b} = \frac{V_c}{V_b},\ \frac{T_d}{T_a} = \left(\frac{V_c}{V_b}\right)^{nR/C_V+1}:$$

$$\eta = 1 - \left(\frac{V_b}{V_a}\right)^{nR/C_V}\frac{1}{\frac{V_c}{V_b} - 1}\frac{(\frac{V_c}{V_b})^{nR/C_V+1} - 1}{1 + \frac{nR}{C_V}}$$

$$\Rightarrow 1 - \eta = g\left(\frac{V_b}{V_a}\right)^{\gamma - 1} \text{ where } g = \left\{\begin{array}{l} 1 \text{ Otto example (b)} \\ \frac{1}{\gamma}\frac{x^\gamma - 1}{x - 1} \text{ Diesel ex. (c)} \end{array}\right.$$

$$\text{and } x = \frac{V_c}{V_b},\ \gamma = 1 + \frac{nR}{C_V}.$$

It can be shown: $g_{\text{Diesel}} > 1 = g_{\text{Otto}}$ for $x > 1$ and $\gamma > 1 \Rightarrow$ for the same compression ratio $\frac{V_a}{V_b}$, but, Diesel engines can operate at larger compression ratios and achieve greater efficiencies.

Remark: for both Otto and Diesel engines the relation $\eta = 1 - (-q_{d\to a}/q_{b\to c}$ holds in agreement with Carnot's theorem for reversible engines.

2.2.4 Temperature profile of the troposphere

Consider an air bubble rising in the atmosphere. We assume the air is an ideal gas and the process is adiabatic:

$$dE = \delta q - P\,dV \overset{\delta q=0}{=} -P\,dV \overset{\text{ideal gas}}{=} C_V dT$$

We replace $dV \overset{\text{ideal gas}}{=} d(\frac{nRT}{P}) = \frac{nR}{P}dT - \frac{nRT}{P^2}dP$

$$\begin{aligned} \Rightarrow C_V dT &= -nRdT + \frac{nRT}{P}dP \\ z\frac{dT}{T} &= \frac{dP}{P}, \quad z = \frac{C_V + nR}{nR} = \frac{C_V}{nR} + 1 \qquad (6) \\ z \ln \frac{T}{T_0} &= \ln \frac{P}{P_0}, \quad \text{or} \quad \frac{P}{P_0} = \left(\frac{T}{T_0}\right)^z \qquad (7) \end{aligned}$$

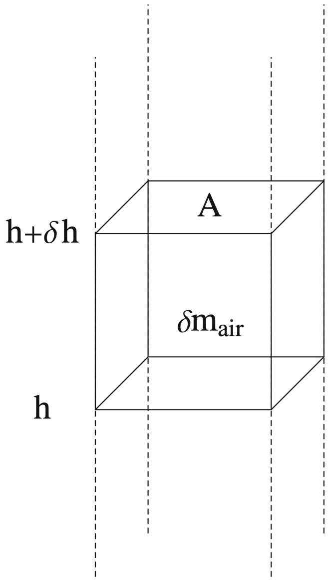
Now we want to express P in terms of the height h:

column of air parallel to gravitational field:

$$P(h) = P(h + \delta h) + g\delta m_{air}/A$$

$$\frac{dP}{dh} \approx \frac{P(h+\delta h) - P(h)}{\delta h} = -\frac{g\delta m_{air}}{A\delta h} = -cg$$

$$c = \frac{\delta m_{air}}{A\delta h} = \text{mass density, depends on } h$$



Assuming that in the column there are n moles of air:

$$\begin{aligned} c &= \frac{nm_{mol}}{V} \overset{\text{ideal gas}}{=} \frac{nm_{mol}}{nRT/P} \qquad m_{mol} = 0.029\text{kg (molar mass of air)} \\ \Rightarrow & \frac{dP}{P} = -\frac{m_{mol}g}{RT}dh \Leftrightarrow \frac{dP}{P} = -\frac{T_0}{T}\frac{dh}{H_0} \qquad (8) \end{aligned}$$

where $H_0 = \dfrac{RT_0}{m_{mol}g} \approx 29.2\text{mK}^{-1}T_0$, where T_0 is the air temperature at $h = 0$.

Usually $H_0 \approx 8500\text{m}$ ($T_0 = 300\text{K}$). Combining Eq. (6) with Eq. (8):

$$z\frac{dT}{\cancel{T}} = -\frac{T_0}{\cancel{T}}\frac{dh}{H_0} \Rightarrow z(T-T_0) = -\frac{T_0}{H_0}h \Leftrightarrow T = T_0\left(1-\frac{h}{H_0 z}\right) \tag{9}$$

In good approximation: $C_V = \frac{5}{2}nR$, thus $z \approx \frac{7}{2}$; the temperature decreases linearly with increasing h, we get a pressure profile from Eq. (8) and Eq. (9):

$$\frac{dP}{P} = -\frac{T_0}{T_0(1-\frac{h}{H_0 z})}\frac{dh}{H_0} = -z\frac{dh}{zH_0 - h}, \text{ if } \underbrace{zH_0 >> h}_{\overset{(9)}{\Rightarrow} T\approx T_0,\text{ isotherm}}, \text{ then}$$

$$\frac{dP}{P} \approx -\frac{dh}{H_0} \text{ or } \boxed{P = P_0 e^{-h/H_0}} \tag{10}$$

with $P_0 = 1\text{bar} = 10^5\text{Pa}$. Eq. (10) is called the barometric formula. The exact integration yields Eq. (7) (adiabatic). The two theoretical curves Eq. (10) and Eq. (7) bracket the measured pressure profile. The temperature behavior Eq. (9) applies only to the troposphere ($h \lesssim 10\text{km}$). Above other processes determine T. The ideal gas assumption applies well to the real data.

2.3 Free energy and free enthalpy

Definition: **Free energy** (or Helmholtz free energy) $F = E - TS$

Remark: $dE = \delta q - PdV \underbrace{=}_{\text{for reversible process: } \delta q = TdS} TdS - PdV \to E(S,V) \Rightarrow \left.\frac{\partial E}{\partial S}\right|_V = T$

$$\Rightarrow E - \left.\frac{\partial E}{\partial S}\right|_V S \text{ is the Legendre transform of } E(S,V)\text{, which}$$

defines a function $F(T,V)$ and replaces $S-$ with $T-$dependence.

Definition: **Free enthalpy** (or Gibbs free energy) $G = H - TS$

Remark: $dH = d(E+PV) = dE + VdP + PdV$
$= TdS - \cancel{PdV} + VdP + \cancel{PdV} = TdS + VdP \to H(S,P)$

$$\Rightarrow \left.\frac{\partial H}{\partial S}\right|_P = T$$

$\Rightarrow H - \left.\dfrac{\partial H}{\partial S}\right|_P S$ is the Legendre transform of $H(S,P)$, which

defines a function $G(T,P)$ and replaces $S-$ with $T-$dependence.

Total differentials:

$$\begin{aligned}
dF &= dE - d(TS) = \cancel{TdS} - PdV - \cancel{TdS} - SdT \\
&= -SdT - PdV \ (\Rightarrow F = F(T,V)) \\
dE &= \underbrace{\left.\frac{\partial E}{\partial T}\right|_V}_{=C_V \text{ this is not a simple thermodynamic variable}} dT + \left.\frac{\partial E}{\partial V}\right|_T dV \rightarrow E(T,V) \\
&= \underbrace{T}_{=\frac{\partial E}{\partial S}|_V} dS - PdV \quad \text{(1st law)} \quad \rightarrow E(S,V)
\end{aligned}$$

$\rightarrow$ Legendre transform $F = E - \left.\dfrac{\partial E}{\partial S}\right|_V dS = E - TS \rightarrow dF = -SdT - PdV$

similarly,

$$\begin{aligned}
dH &= \underbrace{\left.\frac{\partial H}{\partial T}\right|_P}_{=C_P} dT + \left.\frac{\partial H}{\partial P}\right|_T dP \rightarrow H(T,P) \\
&= d(E+PV) = TdS + VdP \rightarrow H(S,P)
\end{aligned}$$

Legendre transform: $G(T,P) = H - TS; \quad dG = -SdT + VdP$

$$\begin{aligned}
dG &= dH - d(TS) = \cancel{TdS} + VdP - \cancel{TdS} - SdT \\
&= -SdT + VdP \ (\Rightarrow G = G(T,P))
\end{aligned}$$

Remark: If there are other (than volume) types of work, for example chemical work, then $dE = \delta q - \delta w = TdS - PdV + \mu\, dn + \ldots$ and consequently

$$dF = -SdT - PdV + \mu\, dn + \ldots$$

$$dG = -SdT - VdP + \mu\, dn + \ldots$$

From total differentials we infer

$$\begin{aligned}
\left.\frac{\partial F}{\partial T}\right|_{V,n,\ldots} &= -S, & \qquad & \left.\frac{\partial G}{\partial T}\right|_{P,n,\ldots} = -S,\\
\left.\frac{\partial F}{\partial V}\right|_{T,n,\ldots} &= -P, & \text{and} \qquad & \left.\frac{\partial G}{\partial P}\right|_{T,n,\ldots} = V,\\
\left.\frac{\partial F}{\partial n}\right|_{T,V,\ldots} &= \mu, & \qquad & \left.\frac{\partial G}{\partial n}\right|_{T,P,\ldots} = \mu.
\end{aligned}$$

It is easy to see that $G = F + PV$. G is the Legendre transform of F:

$$G = F - \left.\frac{\partial F}{\partial V}\right|_{T,n,\ldots} V.$$

F is called a **thermodynamic potential** with respect to $T, V, n, \ldots$. The same is true for G with respect to $T, P, n, \ldots$. A thermodynamic quantity is called a thermodynamic potential if all other thermodynamic quantities can be derived from partial derivatives with respect to its variables.

2.3.1 Relation to second law

F and G possess a very important property, which determines the sign of their change under different irreversible processes.

first law: $dE = \delta q - \delta w$

Clausius' statement of second law:

for an irreversible process $\delta q < TdS$ or $dE - TdS < -\delta w$.

Assume that the process is isothermal and happens at constant volume ($T =$ const. and $V =$ const.), then

$$\begin{aligned}
&dF = d(E - TS) \overset{T=\text{const.}}{=} dE - TdS < -\delta w \underbrace{=}_{\text{assume w stands for volume work only}} -PdV \overset{V=\text{const.}}{=} 0\\
&\quad \Rightarrow dF|_{T,V} < 0
\end{aligned}$$

Irreversible processes, which happen at constant temperature and constant volume, are accompanied by a decrease of the free energy.

Assume that the process happens at $T = \text{const.}$ and $P = \text{const.}$, then

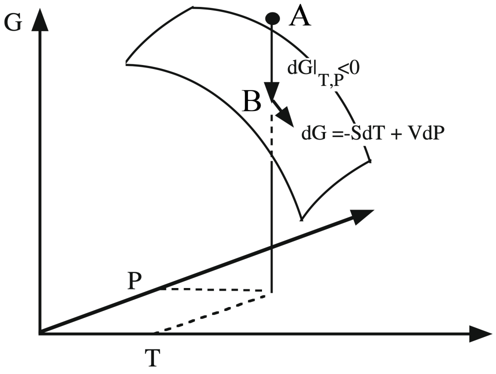
$$dG = d(H - TS) \overset{T=\text{const.},\ P=\text{const.}}{=} dE + PdV - TdS < -\delta w + PdV = 0$$

$$\Rightarrow dG|_{T,P} < 0$$

Irreversible processes, which happen at constant temperature and constant pressure, are accompanied by a decrease of the free enthalpy.

Remark: In both cases we consider processes, for example chemical reactions, in which the system is **not** in equilibrium and its state cannot be determined uniquely from its temperature and volume (or pressure).

A system prepared in state A lowers its free enthalpy as much as possible, which brings it down to state B on the surface, where $dG = -SdT + VdP$ holds.



Remark: If other (than volume) types of work are involved in the process and are controlled by variables X (other than V), then $dF|_{T,V,X} < 0$ and $dG|_{T,P,X} < 0$.

2.3.2 Maxwell relations

Take any state function $g(x, y)$. If $dg = pdx + qdy$, then

$$\left.\frac{\partial p}{\partial y}\right|_x = \left.\frac{\partial q}{\partial x}\right|_y \text{ yields a Maxwell relation.}$$

e.g., consider $S(T, V)$: $dS = \frac{1}{T}dE + \frac{P}{T}dV = \frac{1}{T}\left.\frac{\partial E}{\partial T}\right|_V dT + \frac{1}{T}\left(P + \left.\frac{\partial E}{\partial V}\right|_T\right)dV.$

$$\Rightarrow \frac{1}{T}\frac{\partial}{\partial V}\left(\left.\frac{\partial E}{\partial T}\right|_V\right)\Bigg|_T = \frac{\partial}{\partial T}\frac{1}{T}\left(P + \left.\frac{\partial E}{\partial V}\right|_T\right)\Bigg|_V$$

$$\Rightarrow \left.\frac{\partial E}{\partial V}\right|_T = T^2 \left.\frac{\partial(\frac{P}{T})}{\partial T}\right|_V \text{ (exercise 1.3)}$$

Example: Relation between $C_P = \left.\frac{\partial H}{\partial T}\right|_P$ and $C_V = \left.\frac{\partial E}{\partial T}\right|_V$

Using $G = H - TS$ and $-S = \left.\frac{\partial G}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P - S - T\left.\frac{\partial S}{\partial T}\right|_P$

as well as $F = E - TS$ and $-S = \left.\frac{\partial F}{\partial T}\right|_V = \left.\frac{\partial E}{\partial T}\right|_V - S - T\left.\frac{\partial S}{\partial T}\right|_V$

yields $C_P = T\left.\frac{\partial S}{\partial T}\right|_P$ and $C_V = T\left.\frac{\partial S}{\partial T}\right|_V$

With $\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P$ (Eq. (A.0.1), $A = S$, $x = T$, $y = V$, $z = P$)

we have $C_P - C_V = T\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P$.

Using $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$ (see below)

$$\text{we get } C_P - C_V = T \underbrace{\left.\frac{\partial P}{\partial T}\right|_V}_{\text{(Eq. (A.0.3)}, x=P, y=T, z=V) \rightarrow = -\frac{\partial P}{\partial V}|_T \frac{\partial V}{\partial T}|_P} \left.\frac{\partial V}{\partial T}\right|_P = -T \underbrace{\left.\frac{\partial P}{\partial V}\right|_T}_{= -\frac{1}{V\kappa_T}} \underbrace{\left(\left.\frac{\partial V}{\partial T}\right|_P\right)^2}_{= V^2\alpha_P^2} = TV\frac{\alpha_P^2}{\kappa_T}$$

We have to show $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$.

Free energy $dF = -SdT - PdV$

Maxwell relation: $\frac{\partial}{\partial V}(-S)|_T = \frac{\partial}{\partial T}(-P)|_V$.

Remark: One can prove the inequality $\left.\frac{\partial P}{\partial V}\right|_T < 0$.

Along an isothermal expansion the pressure always decreases $\Rightarrow C_P > C_V$.

Example: For an ideal gas $C_P - C_V = TV\frac{(1/T)^2}{1/P} = \frac{PV}{T} = nR$.

2.4 Extensive and intensive quantities

$$\begin{tikzcd}
\boxed{T, P, \ldots;\ V, n, \ldots} & & \boxed{T, P, \ldots;\ V, n, \ldots} \\
\text{container 1} \arrow[dr] & \text{(identical)} & \text{container 2} \arrow[dl] \\
& \boxed{T, V \ldots;\ 2V, 2n, \ldots} &
\end{tikzcd}$$

container 1 and 2 combined into one container

intensive quantities: $T, P, \ldots$ do not change

extensive quantities: $V, n, \ldots$ change proportionally to n

other intensive quantities: $\frac{V}{n}$, chemical potential μ

Implications for the free enthalpy G:

for a one-component system $dG|_{T,P,\underbrace{\ldots}_{\text{other intensive variables}}} = \mu dn \quad \Rightarrow \quad dG$ is extensive

Integration over sufficiently many differential amounts of matter,

$n = \int dn$ yields $\boxed{G(T, P, n, \ldots) = \mu n}$

Proof: T, P and other intensive quantities do not change when adding more material, so $G = \int dG|_{T,P,\ldots} = \mu \int dn = \mu n$ □

For a system with K components: $G(T, P, n_1, \ldots, n_K, \ldots) = \sum_{i=1}^{K} \mu_i n_i$.

Gibbs-Duhem equation:

equate the differentials

$$-SdT + VdP + \cancel{\mu dn} + \ldots = dG = d(\mu n) = nd\mu + \cancel{\mu dn}.$$

$$\boxed{-SdT + VdP + \ldots - nd\mu = 0}$$

For a system with K components: $-SdT + VdP + \ldots - \sum_{i=1}^{K} n_i d\mu_i = 0$.

Remark: We may be tempted to conclude similarly

$dF|_{T,V,\ldots} = \mu dn \to F = \mu n = G$ but this is wrong!

because we cannot keep $V =$ constant by integrating $\int dn = n$.

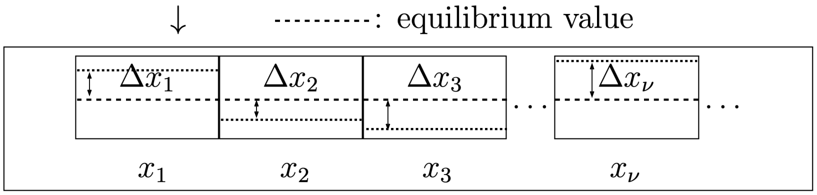
2.5 Chemical equilibrium

Isolated total system

$$\boxed{\boxed{E_1, V_1, n_1} \leftrightarrow \boxed{E_2, V_2, n_2} \leftrightarrow \boxed{E_3, V_3, n_3} \ldots \boxed{E_\nu, V_\nu, n_\nu} \ldots}$$

Identical systems differing only in $x_\nu = E_\nu, V_\nu, n_\nu$

$\leftrightarrow$: allow exchange of $x = E, V, n$



Exchange is an irreversible spontaneous process which maximizes the entropy, see 1.4.3 (ii). In equilibrium, $x_\nu = E^0_\nu, V^0_\nu, n^0_\nu$ which correspond to the maximum entropy S_0.

Taylor series of entropy $S = \sum_\nu S_\nu(E_\nu, V_\nu, n_\nu)$[1]:

$$\begin{aligned} S &= S^0 + \sum_\nu \left(\Delta E_\nu \frac{\partial S_\nu}{\partial E_\nu}\bigg|^0_{V_\nu, n_\nu} + \Delta V_\nu \frac{\partial S_\nu}{\partial V_\nu}\bigg|^0_{E_\nu, n_\nu} + \Delta n_\nu \frac{\partial S_\nu}{\partial n_\nu}\bigg|^0_{E_\nu, V_\nu} \right) \\ &\quad + \frac{1}{2} \sum_{\nu,\nu'} \left(\Delta E_{\nu'} \frac{\partial}{\partial E_{\nu'}}\bigg|^0_{V_{\nu'}, n_{\nu'}} + \Delta V_{\nu'} \frac{\partial}{\partial V_{\nu'}}\bigg|^0_{E_{\nu'}, n_{\nu'}} + \Delta n_{\nu'} \frac{\partial}{\partial n_{\nu'}}\bigg|^0_{E_{\nu'}, V_{\nu'}} \right) \\ &\quad \times \left(\Delta E_\nu \frac{\partial S_\nu}{\partial E_\nu}\bigg|^0_{V_\nu, n_\nu} + \Delta V_\nu \frac{\partial S_\nu}{\partial V_\nu}\bigg|^0_{E_\nu, n_\nu} + \Delta n_\nu \frac{\partial S_\nu}{\partial n_\nu}\bigg|^0_{E_\nu, V_\nu} \right) \end{aligned}$$

---

[1] the entropy S is extensive; if a system consists of several parts ν then $S_{\text{tot}} = \sum_\nu S_\nu$

total system is isolated: $\sum_\nu \Delta x_\nu = 0 \quad (\Delta x_\nu = \Delta E_\nu, \Delta V_\nu, \Delta n_\nu)$

For simplicity consider two subsystems $\nu = 1, 2$:

Maximum entropy ⇒ linear term of Taylor series vanishes:

$$\begin{aligned} 0 \;=\; & \Delta E_1 \left(\left.\frac{\partial S_1}{\partial E_1}\right|_{V_1,n_1}^{0} - \left.\frac{\partial S_2}{\partial E_2}\right|_{V_2,n_2}^{0} \right) \\ & + \Delta V_1 \left(\left.\frac{\partial S_1}{\partial V_1}\right|_{E_1,n_1}^{0} - \left.\frac{\partial S_2}{\partial V_2}\right|_{E_2,n_2}^{0} \right) \\ & + \Delta n_1 \left(\left.\frac{\partial S_1}{\partial n_1}\right|_{E_1,V_1}^{0} - \left.\frac{\partial S_2}{\partial n_2}\right|_{E_2,V_2}^{0} \right) \end{aligned}$$

With $dS_\nu = \frac{1}{T_\nu} dE_\nu + \frac{P_\nu}{T_\nu} dV_\nu - \frac{\mu_\nu}{T_\nu} dn_\nu$:

$$0 \;=\; \Delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \Delta V_1 \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) - \Delta n_1 \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right)$$

Because $\Delta E_1, \Delta V_1$ and Δn_1 are arbitrary ⇒ at equilibrium:

$$\boxed{T = T_1 = T_2, \quad P = P_1 = P_2, \quad \mu = \mu_1 = \mu_2}$$

These conditions can be generalized to an arbitrary number of subsystems:

subsystems ↗ different regions in space of a large system or
(phase = homogeneous state of matter)
subsystems ↘ different phases, *e.g.*, one region of ice and one adjacent region liquid water

The above conditions at equilibrium define the co-existence of two phases. Changing from one phase to another often, but not always, means a discontinuity in certain quantities, *e.g.*, ice has a lower density than liquid water.

For a K component system: $\mu_i^{(\mathrm{I})} = \mu_i^{(\mathrm{II})}$, $i = 1, \ldots, K$, where (I) and (II) refer to two subsystems, *e.g.*, two phases. At equilibrium the chemical potential of each component is continuous across the phase boundary. If we take the same amount of matter in each phase ⇒

$G^{(\mathrm{I})} = \sum_i \mu_i^{(\mathrm{I})} n_i = G^{(\mathrm{II})} = \sum_i \mu_i^{(\mathrm{II})} n_i$

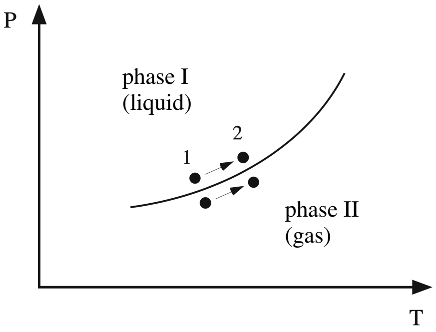
2.6 The Clausius-Clapeyron equation

Along the transition line separating phase I and II, we have

at "1": $\mu_{\rm I}^{(1)} = \mu_{\rm II}^{(1)}$

at "2": $\mu_{\rm I}^{(2)} = \mu_{\rm II}^{(2)}$

(chemical equilibrium or coexistence)



If "1" and "2" are infinitesimally close, the Gibbs-Duhem equation implies for the same amount of matter

$$n d\mu_{\rm I} = -S_{\rm I} dT + V_{\rm I} dP = -S_{\rm II} dT + V_{\rm II} dP = n d\mu_{\rm II}$$

or dividing by n ($s = S/n, v = V/n$):

$$\begin{aligned} d\mu_{\rm I} &= -s_{\rm I} dT + v_{\rm I} dP = -s_{\rm II} dT + v_{\rm II} dP = d\mu_{\rm II} \\ \Rightarrow \quad \left.\frac{dP}{dT}\right|_{\rm coexistence} &= \frac{s_{\rm II} - s_{\rm I}}{v_{\rm II} - v_{\rm I}} \end{aligned}$$

With $G = H - TS$: $G_{\rm I}(1) = H_{\rm I} - TS_{\rm I} = H_{\rm II} - TS_{\rm II} = G_{\rm II}(1)$

$$\Rightarrow \quad S_{\rm II} - S_{\rm I} = \frac{1}{T}(H_{\rm II} - H_{\rm I})$$

$$\Rightarrow \quad \left.\frac{dP}{dT}\right|_{\rm coexistence} = \frac{s_{\rm II} - s_{\rm I}}{v_{\rm II} - v_{\rm I}} = \frac{1}{T}\frac{h_{\rm II} - h_{\rm I}}{v_{\rm II} - v_{\rm I}} \quad (h = H/n)$$

$\Delta h = h_{\rm II} - h_{\rm I} = T(s_{\rm II} - s_{\rm I}) = T\Delta s$; enthalpy of vaporization "latent heat" (II = gas, I = liquid)

Example 1: Enthalpy of vaporization of water:

$$v_{\rm gas} - v_{\rm liquid} \approx v_{\rm gas} = RT/P \qquad (v = \text{molar volume})$$

Assuming $\Delta_{\text{vap}}h(T) = \text{const.}$:

$$\left.\frac{dP}{dT}\right|_{\text{coexistence}} \approx \frac{1}{T}\frac{\Delta_{\text{vap}}h}{RT/P} \text{ or } \frac{dP}{P} \approx \frac{\Delta_{\text{vap}}h}{R}\frac{dT}{T^2}$$

$$\Rightarrow \ln\frac{P}{P_0} \approx -\frac{\Delta_{\text{vap}}h}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \text{ or } P(T) \approx \text{ const. } e^{-\frac{\Delta_{\text{vap}}h}{R}\frac{1}{T}}$$

$$\text{Using: } \left.\begin{array}{ll} P = 4.246\text{kPa} & \text{at } T = 303.15\text{K} \\ P_0 = 0.6113\text{kPa} & \text{at } T = 273.15\text{K} \end{array}\right\} \Rightarrow \Delta_{\text{vap}}h = 45.5\frac{\text{kJ}}{\text{mol}}$$

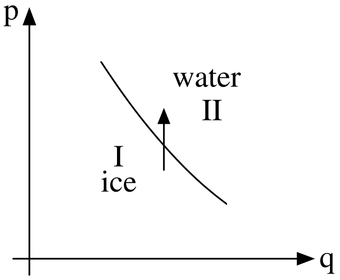
in good agreement with tabulated values in [3].

Example 2: Coexistence of ice and water:

II = water, I = ice: $\Delta h = h_{\text{II}} - h_{\text{I}} > 0$

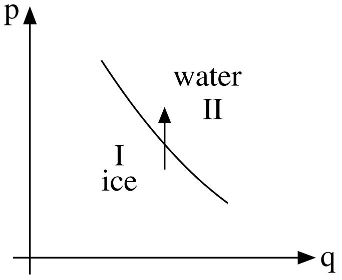
but $v_{\text{II}} - v_{\text{I}} < 0$

$$\Rightarrow \left.\frac{dP}{dT}\right|_{\text{coexistence}} < 0$$



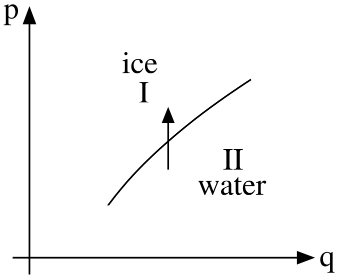
isothermal increase of pressure: ice can melt, glaciers flow on melted water

There would be two possibilities to get ice from water by decreasing the temperature:



$$\left.\frac{dP}{dT}\right|_{\text{coexistence}} < 0$$

nature



$$\cancel{\left.\frac{dP}{dT}\right|_{\text{coexistence}} > 0}$$

not realized in nature

3 Classical statistical physics

3.1 Microcanonical ensemble

3.1.1 State, phase space

We consider a system in classical mechanics, using the Hamilton formalism:

$$\pi = (q_1, \ldots, q_s, p_1, \ldots, p_s) \in \mathbb{R}^{2s}$$

$2s$ degrees of freedom, $2s = 6N$ for N particles in three dimensions.

$H(\pi) = H(p, q) = H(q_1, \ldots, q_s, p_1, \ldots, p_s) =$ Hamilton function

H generates the dynamics (time evolution). Equations of motion (EOMs) for an isolated (no explicit t-dependence of H) system:

$$\underbrace{\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = \frac{\partial H}{\partial p_i}}_{\dot{\pi} = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q}\right) = v(\pi)} \qquad i = 1, \ldots, s \qquad \dot{x} = \frac{dx}{dt}$$

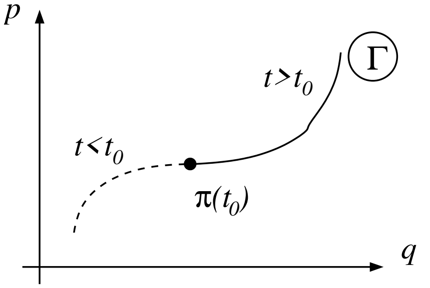
These are $2s$ ordinary differential equations of 1st order for $\pi(t) = (q_1(t), \ldots, q_s(t), p_1(t), \ldots, p_s(t))$ → they fix $\pi(t)\ \forall\ t$, if initial conditions $\pi(t_0)$ are given.

π: complete microcanonical description

$$\pi(t) \in \Gamma \in \mathbb{R}^{2s}$$

→ $\boxed{\textit{microstate}}$ (for any fixed t)

$\Gamma =$ phase space spanned by q, p



Energy conservation: $H(\pi(t)) = \text{const.}$

Proof: $\frac{d}{dt} H(\pi(t)) = \sum_{i=1}^{s} \left(\frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right) = 0$ (Hamilton EOMs) □

$H(\pi(t)) = E$ defines a $(2s-1)$-dimensional surface in Γ: energy shell

Observables: $F(\pi, t)$

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \textstyle\sum_{i=1}^{s} \left(\frac{\partial F}{\partial q_i} \dot{q}_i + \frac{\partial F}{\partial p_i} \dot{p}_i \right) = \frac{\partial F}{\partial t} + \{F, H\} \text{ (Hamilton EOMs)}$$

with the Poisson bracket $\{X, Y\} = \sum_{i=1}^{s} \left(\frac{\partial X}{\partial q_i} \frac{\partial Y}{\partial p_i} - \frac{\partial X}{\partial p_i} \frac{\partial Y}{\partial q_i} \right) = -\{Y, X\}$

Conserved quantities: $\frac{\partial F}{\partial t} = 0$ and $\{F, H\} = 0 \Rightarrow \frac{dF}{dt} = 0$

trivial case: $F = H(\pi)$ itself

Statistics: for $s \approx 10^{23} \approx N_A$

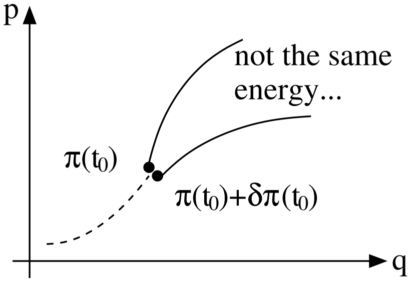
$$\left.\begin{array}{l} - \pi \text{ cannot be determined} \\ - \pi \text{ cannot be stored} \end{array}\right\} \text{missing initial conditions}$$

$-$ equations of motion for $\dot{\pi}$ cannot be solved

Moreover the system is chaotic:

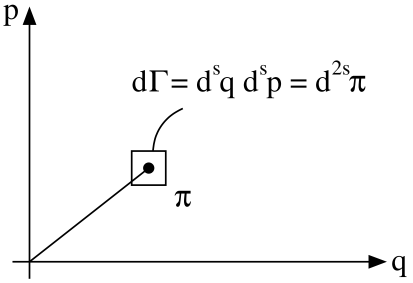
$\pi(t_0) \pm \delta\pi(t_0)$ yields trajectories in t which deviate exponentially

$\Rightarrow$ after a short time is $\pi(t)$ completely undetermined



Instead consider the probability density (classical!) in phase space $\rho(\pi, t) \equiv \rho(q, p, t)$, characterizing an ensemble of systems of the same type:

Consider n ($n \to \infty$) similar and independent systems, then $n\rho(\pi, t_0) d\Gamma$ is the fraction of systems which are in phase space volume $d\Gamma$ around the microstate π at time t_0.



We work with ρ instead of $\pi(t)$.

ρ is not determined from the microscopic dynamics, it is instead postulated (and verified experimentally).

> Postulate: For isolated systems ($E = H = \text{const.}$), ρ possesses a limit
>
> $$\lim_{t\to\infty} \rho(\pi, t) \to \tilde{\rho}(\pi)$$
>
> which is independent of $\rho(\pi, t_0)$. $\tilde{\rho}$ is called the equilibrium distribution. $t \to \infty$ means $t - t_0 >> \tau_{\text{relaxation}}$

This postulate cannot be proven. There are pathological exceptions (non-ergodic systems). If all systems have energy E, we must have that

$$\rho(\pi, t) = 0 = \tilde{\rho}(\pi) \text{ if } H(\pi) \neq E.$$

According to the postulate of same a priori probability:

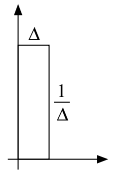
$$\boxed{\tilde{\rho}(\pi) = c\delta_\Delta(H(\pi) - E)}$$

The system can be in any of the microstates with $H(\pi) = E$ with the same probability.

In general we can only guarantee that $E \leqslant H \leqslant E + \Delta$, with $\Delta << E$:

$$\tilde{\rho}(\pi) = c\,\delta_\Delta(E - H(\pi))$$

$$\delta_\Delta(x) = \begin{cases} \frac{1}{\Delta} & \text{if } 0 \leqslant x \leqslant \Delta \\ 0 & \text{otherwise} \end{cases}$$



3.1.2 Ensemble, ensemble average

$\rho \leftrightarrow$ ensemble of systems. Why? Consider

- one system
- each macroscopic measurement of an observable $F(\pi, t)$ corresponds to an implicit integration of the microscopic equations of motion over time:

$$\frac{1}{T}\int_t^{t+T} F(\pi(\tau), \tau)d\tau = \bar{F}^T$$

Here the integration is over several microstates. Their distribution in equilibrium is given by the ensemble $\tilde{\rho}$:

$$\lim_{T\to\infty} \bar{F}^T = \int d\Gamma \tilde{\rho}(\pi) F(\pi) = \langle F \rangle \quad (T >> \tau_{\text{relax}})$$

$\Leftrightarrow$ time average = ensemble average

quasi ergodic hypothesis (quasi: $\exists$ pathological exceptions)

$\langle F \rangle$ is not a determined value of F. We require that the fluctuations

$$\sqrt{\langle (F - \langle F \rangle)^2 \rangle} \underbrace{<<}_{\text{for extensive ($\propto$ volume V) quantities ($\sqrt{V}<<V$)}} |\langle F \rangle|$$

Practically, $\langle F \rangle$ is determined.

3.1.3 Liouville equation

$\frac{\partial}{\partial t}\rho(\pi, t) \neq 0$ since all possible microstates π evolve in time according to Hamilton equations of motion:

$$\begin{aligned}
\dot{\pi}(t) = v(\pi) \quad &\Rightarrow \quad \pi(t+\epsilon) \simeq \pi(t) + \epsilon v(\pi) \\
\rho(\pi, t+\epsilon) \quad &= \quad \rho(\pi - \epsilon v(\pi), t) \quad \text{in equilibrium} \\
\cancel{\epsilon}\frac{\partial \rho}{\partial t} \quad &= \quad -\cancel{\epsilon} v \nabla_\pi \rho, \qquad \nabla_\pi = \left(\frac{\partial}{\partial q_1}, \dots \frac{\partial}{\partial q_s}, \frac{\partial}{\partial p_1}, \dots \frac{\partial}{\partial p_s}\right) \\
0 \quad &= \quad \frac{\partial \rho}{\partial t} + v \nabla_\pi \rho = \frac{\partial \rho}{\partial t} + \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q}\right)\left(\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right)\rho \\
&= \quad \frac{\partial \rho}{\partial t} + \{\rho, H\}
\end{aligned}$$

Liouville equation: $0 = \dfrac{d\rho}{dt} = \dfrac{\partial \rho}{\partial t} + \{\rho, H\}$

“induced equation of motion for ρ”, like “incompressible flow” in Γ!

We have that $\nabla_\pi v = 0$ (divergence of v)

$$\Rightarrow \frac{\partial \rho}{\partial t} + \nabla_\pi (\underbrace{v\rho}_{\text{“current” } j}) = 0 \text{ (continuity equation)}$$

$$\begin{aligned}\frac{d}{dt}\underbrace{\int_{G c \Gamma}\rho d\Gamma}_{\frac{n(G,t)}{n}} &= -\int_G \nabla_\pi(v\rho)d\Gamma \\ &= -\int_{\partial G} d\vec{S}(v\rho) = \text{ flux through } \partial G \text{ outwards}\end{aligned}$$

For $G \nearrow \Gamma \quad \int_{\partial G} d\vec{S}(v\rho) \to 0$ because $\rho \to 0$ for $|\pi| \to \infty$

$\Rightarrow \dfrac{d}{dt}\int_\Gamma d\Gamma \rho(\pi, t) = 0$

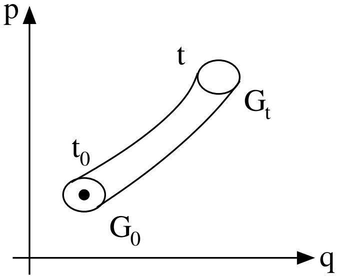
$\Rightarrow$ if $\int_\Gamma d\Gamma \rho(\pi, t_0) = 1$

then the same normalization condition holds for other times as well.

Liouville theorem of mechanics:

$$\underset{\nwarrow}{|G_0|} = \underset{\nearrow}{|G_t|}$$

volume in phase space



It is a direct consequence of Liouville equation for ρ:

$$\rho(\pi, t_0) = \Theta_{G_0}(\pi) = \begin{cases} 1 & \text{for } \pi \in G_0 \\ 0 & \text{otherwise} \end{cases}$$

$$\Rightarrow \rho(\pi, t) = \Theta_{G_t}(\pi) \text{ per construction}$$

$$\int d\Gamma \rho(\pi, t_0) = |G_0| = \int d\Gamma \rho(\pi, t) = |G_t|$$

Equilibrium distribution $\tilde{\rho}(\pi)$: if stationary $\dfrac{\partial \tilde{\rho}}{\partial t} = 0 \overset{\text{Liouville}}{\Rightarrow} \{\tilde{\rho}, H\} = 0$

Are stationary solutions compatible with Liouville equation?

OK for $\tilde{\rho} = f(c(\pi))$ with c a conserved quantity...

$$\{\tilde\rho, H\} = \sum_{i=1}^{s}\left(\underbrace{\frac{\partial f(c)}{\partial q_i}}_{f'(c)\frac{\partial c}{\partial q_i}}\frac{\partial H}{\partial p_i} - \underbrace{\frac{\partial f(c)}{\partial p_i}}_{f'(c)\frac{\partial c}{\partial p_i}}\frac{\partial H}{\partial q_i}\right) = f'(c)\{c, H\} = 0$$

Special case: $c = H,\ \tilde\rho = \tilde\rho(H(\pi))$.

3.1.4 Microcanonical ensemble

From now on: only equilibrium, we leave out the "∼"

$\tilde\rho \to \rho = K\delta_\Delta(H-E)$ with E fixed, given; $\Delta << E$

Normalized probability density:

$$1 = K\int_\Gamma d\Gamma\,\delta_\Delta(H-E) = \frac{K}{\Delta}\int_{E\leqslant H\leqslant E+\Delta} d\Gamma$$

Dimensions:

$d\Gamma = d^sq\,d^sp \qquad [d\Gamma] = [pq]^s = [h]^s \qquad h$: action, Planck

$p = \dfrac{\partial L}{\partial \dot q}, \quad \int L dt =$ action integral

$\Rightarrow [h] = [Lt] = [p\dot q t] = [pq]$

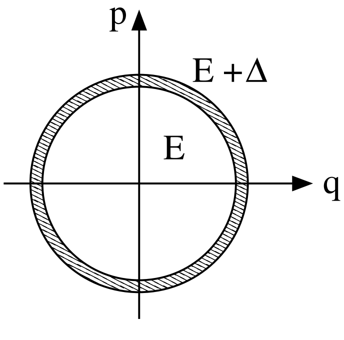
$[\Delta] =$ energy $\Rightarrow K = \Delta h^{-s}\times$(dimensionless quantity)

Definition:

$$\Gamma(E) = c_N\Delta\int_\Gamma \frac{d\Gamma}{h^s}\delta_\Delta(H-E)$$

$$= c_N\int_{E\leqslant H\leqslant E+\Delta}\frac{d\Gamma}{h^s}$$

$\Gamma(E) =$ number of microstates
in the energy shell $E \leqslant H \leqslant E+\Delta$



in principle: $\Gamma(E,\Delta) \sim \Delta$ for small Δ

Explanation: there are ∞-many mathematical points in the energy shell; quantum mechanics will show that one microstate has effectively volume h^s (uncertainty principle; h^s only plays a trivial role as normalization factor)

c_N is dimensionless, classically we would have $c_N = 1$, quantum mechanically, for identical particles, $c_N = 1/N!$, even in the classical limit.

States with $\vec{q}_1 = \vec{x}$, $\vec{q}_2 = \vec{y}$ and $\vec{q}_1 = \vec{y}$, $\vec{q}_2 = \vec{x}$ are connected in quantum mechanics as one state (see section 4).

$\rightarrow$ here again c_N is only a normalization factor.

Definition:

$$\lim_{\Delta \to 0} \frac{1}{\Delta} \Gamma(E) = c_N \int \frac{d\Gamma}{h^s} \delta(H - E) = D(E)$$

$$D(E) = \text{density of states} = \frac{\#\text{ states}}{\text{energy}}$$

$\Gamma(E) \approx \Delta D(E)$ since Δ is small.

Microcanonical average:

$$\langle F \rangle = \frac{\int d\Gamma F(\pi) \delta_\Delta(H - E)}{\int d\Gamma \delta_\Delta(H - E)} = \frac{\int d\Gamma F(\pi) \rho(\pi)}{\int d\Gamma \rho(\pi)}$$

is independent of normalization factors.

For example $U = \langle H \rangle \overset{\Delta \to 0}{\approx} E$ internal energy (thermodynamics!)

Example: ideal gas

$$H = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^{\,2}}{2m} + V_{\text{box}}(\vec{r}_i) \right) \qquad (N \text{ particles})$$

$$V_{\text{box}}(\vec{r}) = \begin{cases} 0 & \text{if } 0 \leqslant x, y, z \leqslant L \\ \infty & \text{otherwise} \end{cases}$$

Definition: $\varphi(E) = \#$ states with $H \leqslant E$

$$\Rightarrow \Gamma(E) = \varphi(E+\Delta) - \varphi(E) \simeq \Delta\varphi'(E)$$

$$\Rightarrow D(E) = \varphi'(E)$$

We first set $c_N = 1$: Heaviside function: $\Theta(x) = \begin{cases} 1 & \text{if } x \geqslant 0 \\ 0 & \text{if } x < 0 \end{cases}$

$$\begin{aligned}
\varphi(E) &= \int \prod_{i=1}^{N} \left(\frac{d^3p_i d^3r_i}{h^3}\right) \overbrace{\Theta(E-H)}^{=\Theta(1-H/E)} \\
&= \left(\frac{V}{h^3}\right)^N \int_{-\infty}^{\infty} \prod_i d^3p_i \Theta\Bigg(1 - \sum_i \frac{\vec{p}_i^2}{2mE}\Bigg) \qquad (V = \int d^3q_i) \\
&= \left(\frac{V}{h^3}\right)^N \sqrt{2mE}^{3N} \int d^{3N}\vec{X}\Theta(1-\vec{X}^2) \\
&= \left(\frac{V(2mE)^{3/2}}{h^3}\right)^N C_{3N} \qquad (\vec{X} = \frac{1}{\sqrt{2mE}}(\vec{p}_1, \vec{p}_2, \ldots) \in \mathbb{R}^{3N})
\end{aligned}$$

Volume of the n-dimensional unit ball $C_n = \dfrac{\pi^{n/2}}{\Gamma(\frac{n}{2}+1)} = \dfrac{\pi^{n/2}}{(\frac{n}{2})!}$

$(\frac{3}{2})! = \Gamma(\frac{5}{2}) = \frac{3}{2}\frac{1}{2}\Gamma(\frac{1}{2}) = \frac{3}{4}\sqrt{\pi}$ → exercise

$\Gamma(z) = \int_0^\infty dt e^{-t} t^{z-1},\ \Gamma(z+1) = z\Gamma(z),\ \Gamma(1) = 1,\ \Gamma(1/2) = \sqrt{\pi}$

$$D(E) = \varphi'(E) = \int \frac{d\Gamma}{h^s} \underbrace{\frac{d}{dE}\Theta(E-H)}_{\delta(E-H)}$$

We have $\varphi(E) = cE^{3N/2}$

$$\Rightarrow D(E) = \varphi'(E) = c\frac{3N}{2}E^{3N/2-1} = \frac{3N}{2}\frac{1}{E}\varphi(E)$$

$$\Gamma(E) = \Delta D(E) = \frac{3N}{2}\frac{\Delta}{E}\varphi(E) = \frac{3N}{2}\frac{\Delta}{E}\left(\frac{V(2mE)^{3/2}}{h^3}\right)^N C_{3N}$$

$N >> 1 \rightarrow$ Stirling formula: $\ln N! = N(\ln N - 1) + O(\ln N)$ as $N \rightarrow \infty$

$$\begin{aligned}\ln(C_{3N}) &= \frac{3N}{2}\ln\pi - \ln(\frac{3N}{2}!) \qquad\qquad (\rightarrow\ \text{exercise})\\ &= \frac{3N}{2}\ln\pi - \frac{3N}{2}(\ln\frac{3N}{2} - 1) + O(\ln N)\end{aligned}$$

$$\begin{aligned}\Rightarrow \ln\Gamma(E) &= N\ln\left(\frac{V(2mE)^{3/2}}{h^3}\right) + \ln(C_{3N}) + O(\ln N)\\ &= N\Bigg\{\ln\left(\frac{V(2mE)^{3/2}}{h^3}\right) + \ln(\pi^{3/2}) \underbrace{- \ln\left[\left(\frac{3N}{2}\right)^{3/2}\right]}_{=+\ln[(\frac{2}{3N})^{3/2}]} + \frac{3}{2}\Bigg\} + O(\ln N)\\ &= N\Bigg\{\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}\Bigg\} + O(\ln N)\end{aligned}$$

- leading term $\propto N$ is the same for $\underbrace{\ln\Gamma}_{E\leqslant H\leqslant E+\Delta}$, $\underbrace{\ln\varphi}_{H\leqslant E}$
- in high-dimensional bodies almost all of the volume is close to the surface of the bodies
- thermodynamic limit: $N \rightarrow \infty$, V/N, E/N fixed
  $\Rightarrow \ln\Gamma$ above grows $\propto N\ln N$
  $\Rightarrow \Gamma$ grows more than exponentially in N: Gibbs paradox
- with $c_N = 1/N! \leftrightarrow$ quantum mechanics, N identical particles
  $\ln\Gamma \rightarrow \ln\Gamma + \ln c_N = \ln\Gamma \underbrace{- \ln N!}_{\text{Stirling: } \simeq -N(\ln N - 1) = N(\ln[1/N]+1)}$
  $$\ln\Gamma = N\left\{\ln\left[\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{5}{2}\right\}$$
- now is $\ln\Gamma = \ln(\#\text{ states})$ extensive ($\propto N$) in the thermodynamic limit

Remark: Had we chosen a different value for the constant of dimension action = "volume of a microstate": $\int\frac{d\Gamma}{h^{3N}} \rightarrow \int\frac{d\Gamma}{(\alpha h)^{3N}}$ then: $\ln\Gamma \rightarrow \ln\Gamma - N\ln(\alpha^3)$

- change in $\ln\Gamma$ is proportional to N

- but it is only a constant, independent of E, V, N

3.1.5 Equilibrium, entropy, temperature

We will see that

$$k_B \ln \Gamma = S \quad (\propto N,\ \text{extensive})$$

can be identified with the phenomenologically motivated entropy

→ entropy changes are independent of the value of αh

$k_B = 1.3805 \times 10^{-23}\text{J/K}$ = Boltzmann constant = "trivial" constant factor ↔ definition of degree K

- consider two systems $N_i, V_i, E_i, \qquad i = 1, 2$
- $\Gamma_i(E_i, V_i, N_i) = \#$ microstates in system i
- each system (considered separately) is in equilibrium, $\tilde{\rho}_i \propto \delta(H_i - E_i)$ describes them
- the two systems are brought into contact $1 + 2$ with
  - exchange of energy → only $E = E_1 + E_2$ is conserved
  - no volume exchange, V_i is fixed
  - no particle exchange, N_i is fixed

For the total system: $\pi = (\pi_1, \pi_2)$ $(6(N_1 + N_2)$ components)

$$H(\pi) = H_1(\pi_1) + H_2(\pi_2) + V_{12}(\pi_1, \pi_2)$$

Remark: subtle point:

- $V_{12} \neq 0$ is necessary for energy exchange
- → new equilibrium of the total system for which we assume $|V_{12}| << H_1 + H_2 \rightarrow V_{12}$ can be neglected
- plausible: $H_i \sim N_i,\ V_{12} \sim N^{2/3}$ since the interaction happens on the contact surface

$$\Gamma_{1+2}(E) = \int \frac{dE_1}{\Delta} \Gamma_1(E_1) \times \Gamma_2(\underbrace{E - E_1}_{=E_2})$$

- # microstates is multiplied
- $E = E_1 + E_2$, in the exponent (entropy S) we sum over all possible ways to distribute E
- Δ is an energy scale, its value is irrelevant for $\ln \Gamma_{1+2} \propto N$ in the thermodynamic limit

Which values of E_1 give the dominant contribution?

$$\Gamma_{1+2} = \int \frac{dE_1}{\Delta} e^{(S_1+S_2)/k_B}$$

- exponent very large
- maximum:

$$0 = \frac{\partial}{\partial E_1}(S_1 + S_2) = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\bigg|_{E_2=E-E_1} \qquad \text{at } E_1 = \tilde{E}_1,\ \tilde{E}_2 = E - \tilde{E}_1$$

We have $\displaystyle\frac{\partial^2}{\partial E_1^2}(S_1 + S_2) = \frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}\bigg|_{E_2=E-E_1}$

In general: $\displaystyle\frac{\partial^k S}{\partial E^k} = O(N^{1-k})$ (S, E are both extensive $\propto N$)

→ Taylor expansion of the exponent about the maximum:

$$\begin{aligned}
\Gamma_{1+2} &= \int \frac{dE_1}{\Delta} e^{\frac{1}{k_B}\{S_1(\tilde{E}_1)+S_2(\tilde{E}_2)+\frac{1}{2}(E_1-\tilde{E}_1)^2(\frac{\partial^2 S_1}{\partial E_1^2}|_{\tilde{E}_1}+\frac{\partial^2 S_2}{\partial E_2^2}|_{\tilde{E}_2})+\ldots\}} \\
&= \underbrace{e^{\frac{1}{k_B}(S_1(\tilde{E}_1)+S_2(\tilde{E}_2))}}_{\Gamma_1(\tilde{E}_1)\Gamma_2(\tilde{E}_2)} \int \frac{dE_1}{\Delta} e^{\frac{1}{2k_B}(E_1-\tilde{E}_1)^2(\frac{\partial^2 S_1}{\partial E_1^2}|_{\tilde{E}_1}+\frac{\partial^2 S_2}{\partial E_2^2}|_{\tilde{E}_2})+\ldots}
\end{aligned}$$

- we have: $\displaystyle\frac{\partial^2 S_i}{\partial E_i^2} < 0$ (thermodynamic limit, E_i/N_i fixed)

  gas: $\displaystyle\frac{1}{k_B}\frac{\partial^2}{\partial E_i^2} S_i = \frac{\partial^2}{\partial E_i^2}\frac{3}{2} N_i \ln E_i = -\frac{3}{2}\frac{N_i}{E_i^2} \overset{\uparrow}{=} O(N_i^{-1})$

- in the integral only contribution with

$$\frac{1}{k_B}(E_1 - \tilde{E}_1)^2\left(\frac{\partial^2 S_1}{\partial E_1^2}\bigg|_{\tilde{E}_1} + \frac{\partial^2 S_2}{\partial E_2^2}\bigg|_{\tilde{E}_2}\right) = O(1) \Rightarrow |E_1 - \tilde{E}_1| = O(N^{1/2})$$

- higher order terms in the exponent

$$\frac{1}{k_B}\frac{1}{k!}(E_1-\tilde{E}_1)^k\frac{\partial^k S_1}{\partial E_1^k}\sim N^{k/2}\times N^{1-k}=N^{1-k/2}<<1 \text{ for } k\geqslant 3$$

- performing the Gauss integral: $\int_{-\infty}^{\infty}dx\,e^{-tx^2}=\sqrt{\frac{\pi}{t}},\ t=\frac{1}{2k_b}\frac{\partial^2 S}{\partial E_1^2}$

$$\Gamma_{1+2}=\Gamma_1(\tilde{E}_1)\Gamma_2(\tilde{E}_2)\times\frac{\sqrt{2\pi}}{\Delta}\underbrace{\left(\left|\frac{1}{k_B}\frac{\partial^2 S_1}{\partial E_1^2}\bigg|_{\tilde{E}_1}+\frac{1}{k_B}\frac{\partial^2 S_2}{\partial E_2^2}\bigg|_{\tilde{E}_2}\right|\right)^{-1/2}}_{O(N^{1/2})}$$

$$\Rightarrow \ln\Gamma_{1+2}(E)=\underbrace{\ln\Gamma_1(\tilde{E}_1)}_{\sim N}+\underbrace{\ln\Gamma_2(\tilde{E}_2)}_{\sim N}+O(\ln N)$$

- instead of the integral: value of the integrand at the maximum
- $\ln\Gamma$ and S respectively are additive in equilibrium and in the thermodynamic limit
- after the contact the entropy $S_1(E_1)+S_2(E-E_1)$ increases until it reaches its maximum $S(E)=S_1(\tilde{E}_1)+S_2(E-\tilde{E}_1)$ in equilibrium
- after equilibrium in the total system only contribution with $|E_1-\tilde{E}_1|\sim N^{1/2},\ \tilde{E}_1\sim N\Rightarrow E_1=\tilde{E}_1(1\pm O(10^{-11}))$ is fixed in practice
- at $E_1=\tilde{E}_1:\ \dfrac{\partial S_1}{\partial E_1}=\dfrac{\partial S_2}{\partial E_2}\Leftrightarrow$ the same temperature $\dfrac{1}{T_1}=\dfrac{\partial S_i}{\partial E_i}$ in both (→ all of the) subsystems in equilibrium
- here: $T_i=T_i(E_i,\,V_i,\,N_i)$

$$\text{gas: }\frac{1}{T}=k_B\frac{\partial}{\partial E}\underbrace{N\{\ln E^{3/2}+\ldots\}}_{\ln\Gamma}=k_B\frac{3}{2}N\frac{1}{E}$$

$$\Rightarrow E=\frac{3}{2}Nk_BT\text{ energy of the gas at temperature }T$$

Fluctuation:

$$\langle(H_1-\tilde{E}_1)^2\rangle_{1+2}=\frac{\int d\Gamma_{1+2}\delta(E-H_1-H_2)(H_1-\tilde{E}_1)^2}{\int d\Gamma_{1+2}\delta(E-H_1-H_2)}$$

Numerator:

$$\int d\Gamma_1 d\Gamma_2 \underbrace{\int dE_1 \delta(E_1 - H_1)}_{=1} \delta(E - H_1 - H_2)(H_1 - \tilde{E}_1)^2$$

$$= \int dE_1 \int d\Gamma_1 \delta(E_1 - H_1)(E_1 - \tilde{E}_1)^2 \int d\Gamma_2 \delta(E - E_1 - H_2)$$

$$= \int dE_1 (E_1 - \tilde{E}_1)^2 D_1(E_1) \frac{h^{3N_1}}{c_{N_1}} D_2(E - E_1) \frac{h^{3N_2}}{c_{N_2}}$$

$$\begin{aligned} \langle (H_1 - \tilde{E}_1)^2 \rangle_{1+2} &= \frac{\int dE_1 (E_1 - \tilde{E}_1)^2 D_1(E_1) D_2(E - E_1)}{\int dE_1 D_1(E_1) D_2(E - E_1)} \\ &\simeq \frac{\int \frac{dE_1}{\Delta} (E_1 - \tilde{E}_1)^2 \Gamma_1(E_1) \Gamma_2(E - E_1)}{\underbrace{\int \frac{dE_1}{\Delta} \Gamma_1(E_1) \Gamma_2(E - E_1)}_{\Gamma_{1+2}(E)}} \qquad (\Gamma_i \simeq \Delta D_i) \end{aligned}$$

- integral like before, only $|E_1 - \tilde{E}_1| = O(N^{1/2})$ contributes

$\sqrt{\langle (H_1 - \tilde{E}_1)^2 \rangle} = O(\sqrt{N})$ = observable $H_1(\pi_1)$ sharply peaked at $\tilde{E}_1$

3.1.6 Second law

Like before $\Gamma_1(E_1)$, $\Gamma_2(E_2)$ (N_i, V_i fixed)

Before thermal contact:

$$\begin{aligned} \Gamma(E) &= \Gamma_1(E_1) + \Gamma_2(E_2) \quad (E = E_1 + E_2) \\ S(E) &= S_1(E_1) + S_2(E_2) \\ &\quad \downarrow \text{ irreversible process} \end{aligned}$$

total system in equilibrium:

$$\Gamma(E) = \int \frac{dE_1}{\Delta} \Gamma_1(E_1) \Gamma_2(E_2)$$

is dominated by $E_1 = \tilde{E}_1,\ E_2 = E - \tilde{E}_1$

$$\begin{aligned} \ln\Gamma(E) &\approx \ln\Gamma_1(\tilde{E}_1) + \ln\Gamma_2(E-\tilde{E}_1) = \frac{1}{k_B}(S_1(\tilde{E}_1) + S_2(E-\tilde{E}_1)) \\ &= \ln(\text{maximum of the integrand}) \end{aligned}$$

- Entropy has increased through thermal contact till $\dfrac{\partial S_1}{\partial E_1} = \dfrac{1}{T_1} = \dfrac{\partial S_2}{\partial E_2} = \dfrac{1}{T_2}$ holds at $E_1 = \tilde{E}_1$
- for $E_1 \neq \tilde{E}_1$ we have:

$$\begin{aligned} \frac{\partial}{\partial E_1}[S_1(E_1) + S_2(E-E_1)] &= \frac{1}{T_1} - \frac{1}{T_2} \\ 0 < \Delta[S_1(E_1) + S_2(E-E_1)] &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta E_1 \end{aligned}$$

  which means if $T_1 < T_2 \Rightarrow E_1$ increases, $T_1 > T_2 \Rightarrow E_1$ decreases.

Remark: $\dfrac{\partial S}{\partial E} > 0$, since $\dfrac{\partial \Gamma}{\partial E} > 0$,

the volume in phase space increases with $E \Rightarrow T > 0$.

$\Rightarrow$ the proposed statistical definition of entropy $S = k_B \ln\Gamma$ ($\Gamma\ldots$volume in phase space, # microstates at energy E) is consistent with the thermodynamic empirical definition of entropy and of temperature $\frac{1}{T} = \frac{\partial S}{\partial E}|_{V,N}$.

3.1.7 Chemical potential, pressure

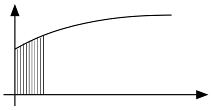
Now consider $1+2$ with

- energy exchange: $E = E_1 + E_2$, only E conserved
- particle exchange: $N = N_1 + N_2$, only N conserved
- no volume exchange: V_1 and V_2 fixed

In equilibrium (thermal + chemical):

$$\Gamma(E,N) = \sum_{N_1} \int \frac{dE_1}{\Delta} \Gamma_1(E_1,N_1)\Gamma_2(E-E_1,N-N_1)$$

$\sum_{N_1} \to \int dN_1$, because Γ_i changes by small amount if $N_1 \to N_1 + 1 \to N_1 + 2 \ldots$



Considerations about dominant contributions are completely analogous to the case of energy exchange only

$$\Rightarrow \ln \Gamma(E, N) \simeq \ln \Gamma_1(\tilde{E}_1, \tilde{N}_1) + \ln \Gamma_2(\underbrace{\tilde{E}_2}_{E-\tilde{E}_1}, \underbrace{\tilde{N}_2}_{N-\tilde{N}_1}) + O(\ln N)$$

$\tilde{E}_1$ and $\tilde{N}_1$ are given by ($\leftrightarrow$ S maximal)

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{\tilde{E}_1,\tilde{N}_1} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E-\tilde{E}_1,N-\tilde{N}_1} \text{ and } \left.\frac{\partial S_1}{\partial N_1}\right|_{\tilde{E}_1,\tilde{N}_1} = \left.\frac{\partial S_2}{\partial N_2}\right|_{E-\tilde{E}_1,N-\tilde{N}_1}$$

Definition: $\mu_i = -T_i \left.\frac{\partial S_i}{\partial N_i}\right|_{E_i,V_i}$ = chemical potential

In chemical equilibrium both ($\to$ all of the) macroscopic ($N \to \infty$) subsystems have the same chemical potential: $\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2} \Rightarrow \mu_1 = \mu_2$ if $T_1 = T_2 = T$.

$$0 < \Delta S = \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)\Delta N_1 + \left(\underbrace{\frac{\partial S_1}{\partial E_1}}_{=\frac{1}{T}} - \underbrace{\frac{\partial S_2}{\partial E_2}}_{=\frac{1}{T}}\right)\Delta E_1 = -\left(\frac{\mu_1}{T} - \frac{\mu_2}{T}\right)\Delta N_1$$

N_1 grows $\Leftrightarrow \mu_1 < \mu_2$; $\qquad \sqrt{\langle (N_1 - \tilde{N}_1)^2 \rangle} = O(\sqrt{N})$

Now consider in addition mechanical exchange, only $V = V_1 + V_2$ is conserved $\Rightarrow$ in mechanical equilibrium $V = \tilde{V}_1 + \tilde{V}_2$ such that

$$\left.\frac{\partial S_1}{\partial V_1}\right|_{\tilde{E}_1,\tilde{N}_1,\tilde{V}_1} = \left.\frac{\partial S_2}{\partial V_2}\right|_{E-\tilde{E}_1,N-\tilde{N}_1,V-\tilde{V}_1} \leftrightarrow S \text{ maximal}$$

Definition: $\left.\frac{\partial S_i}{\partial V_i}\right|_{E_i,N_i} = \frac{P_i}{T_i}$ with P_i = pressure

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_1 = P_2 \text{ if } T_1 = T_2 = T; \qquad 0 < \Delta S = \frac{P_1 - P_2}{T}\Delta V_1$$

V_1 grows $\Leftrightarrow P_1 > P_2$; $\qquad \sqrt{\langle (V_1 - \tilde{V}_1)^2 \rangle} = O(\sqrt{N})$

It can be shown that the statistical definition of pressure agrees with the mechanical definition: $\langle -\frac{\partial H}{\partial V} \rangle = T\frac{\partial S}{\partial V}$ ($\langle \ldots \rangle$ microcanonical ensemble average)

3.1.8 Basic relations of thermodynamics

Quasistatic reversible transformation: external parameters are varied slowly, such that at any time the system can be considered in equilibrium, sign of all changes can be reversed ⇒ description by a microcanonical ensemble is always valid, entropy is defined

For such a transformation: $S = S(E, V, N)$

$$dS = \underbrace{\left.\frac{\partial S}{\partial E}\right|_{V,N}}_{\frac{1}{T}} dE + \underbrace{\left.\frac{\partial S}{\partial V}\right|_{E,N}}_{\frac{P}{T}} dV + \underbrace{\left.\frac{\partial S}{\partial N}\right|_{E,V}}_{-\frac{\mu}{T}} dN$$

$\leftrightarrow TdS = dE + PdV - \mu dN$ energy conservation ↔ 1st law of TD

If the transformation is not reversible

→ entropy increase during thermalization
(*e.g.*, energy exchange between subsystems)

$\rightarrow TdS > dE + PdV - \mu dN$ ↔ 2nd law of TD (Clausius: $\delta q < TdS$)

3rd law of TD → quantum statistics, later...

Summary: Statistical mechanics ⇒ thermodynamics

- $H(q, p, z)$ $\quad z$: external parameters, like $V, \ldots$
- compute $\varphi(E) = c_N \int \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \Theta(E - H)$ (ball)
  or $D = \varphi'(E)$ (sphere) or $\Gamma = \Delta D$ (shell) phase-space volume
- $S = k_B \ln \Gamma$
- $\rightarrow T, \mu, P$ as functions of (E, V, N)
- internal energy $U = \langle H \rangle = E$ (trivial, microcanonical ensemble)
  $S(E, V, N)$, solve for $E \rightarrow E(S, V, N) \equiv U(S, V, N)$
- U central quantity of phenomenological thermodynamics

- other thermodynamic potentials are obtained through Legendre transformation (compare mechanics $L(q,\dot{q},t) \to H(q,p,t) = p\dot{q} - L,\ p = \frac{\partial L}{\partial \dot{q}}$, equivalent description)

Example: free energy $F = U - TS$

Derivation from the microcanonical ensemble:

$$\frac{1}{T} = \frac{\partial S}{\partial E}(E,V,N),\ T = \frac{\partial E}{\partial S}(S,V,N) = T(S,V,N) \text{ solve to get } S(T,V,N)$$

$\Rightarrow F = U(S,V,N) - TS$, replace S with $S(T,V,N) \Rightarrow F(T,V,N)$.

3.1.9 Equipartition theorem

Compute for a system in microcanonical ensemble

$$\langle \pi_i \frac{\partial H}{\partial \pi_j} \rangle \qquad \pi = (q_1, \dots, q_s, p_1, \dots, p_s)$$

$0 = \int_{H \leqslant E} d\Gamma \frac{\partial}{\partial \pi_j} \pi_i (E - H)$ from Gauss theorem (*)

more precisely: $\sum_i M_{ji} \pi_i (E - H(\pi)) = D_j(\pi)$ vector field,

$$M_{ij}:\ 2s \times 2s \text{ matrix}$$

$$B = \{\pi | H(\pi) \leqslant E\}$$

$\int_B d\Gamma \nabla_\pi D = \int_{\partial B} dF\, D = 0$ (since $E = H$ on $\partial B \Rightarrow D_j = 0$)

$= \sum_{j,i} M_{ji} \int_{H \leqslant E} d\Gamma \frac{\partial}{\partial \pi_j} \pi_i (E - H) = 0, \quad M_{ji}$ arbitrary $\Rightarrow$ (*)

$$\begin{aligned} \Rightarrow 0 &= \delta_{ij} \int_{H \leqslant E} d\Gamma (E - H) - \int_{H \leqslant E} d\Gamma \pi_i \frac{\partial H}{\partial \pi_j} \\ &= \delta_{ij} \int d\Gamma \Theta(E - H)(E - H) - \int d\Gamma \Theta(E - H) \pi_i \frac{\partial H}{\partial \pi_j} \end{aligned}$$

$$\frac{\partial}{\partial E}: \qquad 0=\delta_{ij}\Bigg(\int d\Gamma\,\underbrace{\delta(E-H)(E-H)}_{=0}+\underbrace{\int d\Gamma\Theta(E-H)}_{=\varphi(E)h^{3N}/c_N}\Bigg)$$

$$-\int d\Gamma\delta(E-H)\pi_i\frac{\partial H}{\partial \pi_j}$$

$$\Rightarrow \quad \int d\Gamma\delta(E-H)\pi_i\frac{\partial H}{\partial \pi_j}=\delta_{ij}\varphi(E)\frac{h^{3N}}{c_N}$$

With $\varphi'(E)=D(E)=\int d\Gamma\delta(E-H)\dfrac{c_N}{h^{3N}}$:

$$\Rightarrow \langle\pi_i\frac{\partial H}{\partial \pi_j}\rangle=\frac{\int d\Gamma\delta(E-H)\pi_i\frac{\partial H}{\partial \pi_j}}{\int d\Gamma\delta(E-H)}=\delta_{ij}\frac{\varphi(E)}{\varphi'(E)}=\frac{\delta_{ij}}{\frac{\partial}{\partial E}\ln\varphi}.$$

In the TD limit we found $\ln\varphi\approx\ln\Gamma$, hence

$$\frac{\partial}{\partial E}\ln\varphi=\frac{\partial}{\partial E}\ln\Gamma=\frac{\partial}{\partial E}\frac{S}{k_B}=\frac{1}{k_BT}\ \Rightarrow\ \langle\pi_i\frac{\partial H}{\partial \pi_j}\rangle=\delta_{ij}k_BT$$

$$\Rightarrow \langle p_i\frac{\partial H}{\partial p_i}\rangle=\langle p_i\dot{q}_i\rangle=\langle -q_i\dot{p}_i\rangle=\langle q_i\frac{\partial H}{\partial q_i}\rangle=k_BT \text{ for each } i=1,\dots,s$$

(Generalized) Equipartition theorem:

For $H=\sum_{i=1}^N\dfrac{\vec{p}_i^2}{2m}+V(\vec{r}_1,\dots,\vec{r}_N)\ \Rightarrow\ \sum_{i=1}^N\langle\underbrace{\vec{r}_i\vec{\nabla}_iV}_{\text{average virial }=\vec{r}_i\frac{\partial H}{\partial\vec{r}_i}}\rangle=\underbrace{3N}_{\#\text{ degrees of freedom}}k_BT$

Kinetic energy: $\langle T\rangle=\left\langle\sum_{i=1}^N\dfrac{\vec{p}_i^2}{2m}\right\rangle=\left\langle\sum_{i=1}^N\dfrac{1}{2}\vec{p}_i\dfrac{\partial H}{\partial\vec{p}_i}\right\rangle=\dfrac{3N}{2}k_BT$

equipartition theorem of the energy "$\frac{1}{2}k_BT$ per degrees of freedom"

together: $\langle T\rangle=\frac{1}{2}\langle\sum_{i=1}^N\vec{r}_i\vec{\nabla}_iV\rangle$ ↔ virial theorem of mechanics

- mechanics: time average over trajectory

- statistics: (microcanonical) ensemble average

consistent with postulate time average = ensemble average

3.1.10 Ideal gas

We already computed $S(E, V, N) = k_B \ln \Gamma$

$$= Nk_B \left\{ \ln \left[\frac{V}{Nh^3} \left(\frac{4\pi}{3} m \frac{E}{N} \right)^{3/2} \right] + \frac{5}{2} \right\} + O(\ln N)$$

Sackur-Tetrode equation

S is extensive $\propto N$ in the TD limit $N \to \infty$ ($\frac{V}{N}$, $\frac{E}{N}$ fixed). This result is obtained with $c_N = 1/N!$, otherwise ($c_N = 1$) term $\propto N \ln N$.

For the ideal gas it follows

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{\partial}{\partial E} Nk_B \left(\frac{3}{2} \ln E + \ldots \right) = \frac{3}{2} \frac{Nk_B}{E}$$

$$\Rightarrow U = E = \frac{3}{2} Nk_B T$$

- internal energy of the ideal gas
- thermal equation of state

$$P = T \left.\frac{\partial S}{\partial V}\right|_{E,N} = T \frac{\partial}{\partial V} Nk_B (\ln V + \ldots) = T \frac{Nk_B}{V}$$

$\Rightarrow PV{=}Nk_BT{=}nRT$ ($n{=}N/N_A$ moles, 1 mole: $N{=}N_A \Rightarrow R{=}N_A k_B$)

- caloric equation of state, solve $S(E = U, V, N)$ for U:

$$U(S, V, N) = N \left(\frac{3h^2}{4\pi m} \right) \left(\frac{N}{V} \right)^{2/3} e^{\frac{2S}{3Nk_B} - \frac{5}{3}}$$

everything is consistent with thermodynamics (where S is defined up to a constant)

$$\begin{aligned} \mu &= -T \left.\frac{\partial S}{\partial N}\right|_{E,V} = -T \frac{\partial}{\partial N} k_B N (\ln N^{-5/2} + \ldots) \\ &= T(k_B \ln N^{5/2} + k_B N \frac{5}{2} \frac{1}{N}) \\ &= k_B T \frac{5}{2} (\ln N + 1) = \frac{5}{2} k_B T \ln(eN) \end{aligned}$$

Entropy of mixing

- 2 identical gases with E_i, V_i, N_i are brought into contact, entropies $S_i(E_i, V_i, N_i)$
- pressure and temperature are the same: $\dfrac{\partial S_1}{\partial E_1} = \dfrac{\partial S_2}{\partial E_2}, \quad \dfrac{\partial S_1}{\partial V_1} = \dfrac{\partial S_2}{\partial V_2}$ (dividing partition can freely move $\Rightarrow$ same pressure)
- energy, volume and particle exchange are possible, but only particles are exchanged
  $\boxed{E_1,\, V_1,\, N_1}\boxed{E_2,\, V_2,\, N_2} \quad E = E_1 + E_2,\ V = V_1 + V_2,\ N = N_1 + N_2$
  $\rightarrow$ remove dividing partition, reversible when particles are identical (if the gases are identical we cannot distinguish "mixed" from "unmixed")
  Since $PV_i = N_i k_B T,\ PV = N k_B T \Rightarrow \dfrac{N_1}{V_1} = \dfrac{N_2}{V_2} = \dfrac{N}{V} = \dfrac{P}{k_B T}$
  With $E_i = \dfrac{3}{2} N_i k_B T: \quad \dfrac{E_1}{N_1} = \dfrac{E_2}{N_2} = \dfrac{E}{N} = \dfrac{3}{2} k_B T$
- Since $S = N k_B f(\frac{E}{N}, \frac{V}{N})$:
  $S_1 + S_2$ (with dividing partition) $= N_1 k_B f(\frac{E_1}{N_1}, \frac{V_1}{N_1}) + N_2 k_B f(\frac{E_2}{N_2}, \frac{V_2}{N_2})$
  $= (N_1 + N_2) k_B f(\frac{E}{N}, \frac{V}{N}) = S_{1+2}$ (without dividing partition)
- necessary property in order that $S =$ state function, uniquely defined, independent of the history!
- result with $c_N = 1$ was different: $\Gamma' = N!\Gamma$
  $S' = N k_B [f(\frac{E}{N}, \frac{V}{N}) + \ln N - 1]$, hence

$$\begin{aligned} S_1' + S_2' &= S_{1+2} + N_1 k_B (\ln N_1 - 1) + N_2 k_B (\ln N_2 - 1) \\ &= S_{1+2}' - N k_B (\ln N \cancel{-1}) + N_1 k_B (\ln N_1 \cancel{-1}) + N_2 k_B (\ln N_2 \cancel{-1}) \\ &= S_{1+2}' + \underbrace{N_1 k_B \ln \frac{N_1}{N} + N_2 k_B \ln \frac{N_2}{N}}_{-\Delta S < 0} \qquad (11) \end{aligned}$$

$\Delta S =$ entropy of mixing > 0, entropy increases when two **different** gases mix and expand ($V_i \to V$) in the total volume:
$\Delta S = \sum_{i=1}^{2} [S(E_i, V, N_i) - S(E_i, V_i, N_i)] = \sum_{i=1}^{2} N_i k_B \ln \overset{= \frac{N}{N_i}}{\frac{V}{V_i}}$ (exercise 1)
But Eq. (11) is wrong for identical gases $\rightarrow$ **Gibbs paradox**
(imagine we have divided the gas volume in many small volumes $\rightarrow$ can generate arbitrarily large ΔS!)

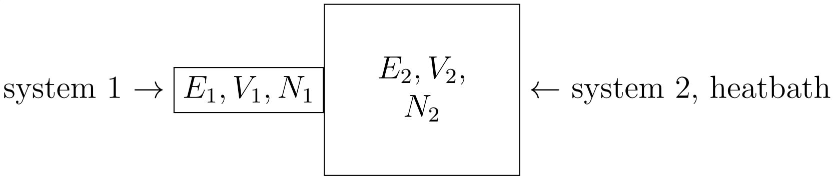
- we need from quantum mechanics:
  - dimensionful constant h, its value $\leftrightarrow$ additive constant in S $\rightarrow$ irrelevant for classical TD
  - avoid multiple counting of states, which differ by exchange of identical particles $\rightarrow$ important for consistency

3.2 Canonical ensemble

Microcanonical ensemble: $E \approx$ const. (uncertainty $\Delta << E$),
$V =$ const., $N =$ const. $\rightarrow S(E, V, N)$

Canonical ensemble: $T =$ const., $V =$ const., $N =$ const.

Physical realization:



- thermal contact ($\leftrightarrow$ energy exchange, no volume or particle exchange)
- both subsystems are macroscopic
- system 1 << system 2 $\Rightarrow \dfrac{1}{T} = \dfrac{\partial S_2}{\partial E_2} = \dfrac{\partial S_1}{\partial E_1}$ (see section 3.1.4)
- since system 2 is large, T cannot be practically changed through the energy exchange ($E_2 \approx$ const.) $\rightarrow$ heatbath
- total system is described by a microcanonical ensemble

3.2.1 Partition function

$$\rho(\underset{\text{system 1}}{\underset{\swarrow}{\pi_1}}, \underset{\text{system 2}}{\underset{\searrow}{\pi_2}}) = \text{const.} \times \rho(E - H_{1+2})$$

$$\int d\Gamma \rho = \int d\Gamma_1 d\Gamma_2 \rho = 1 \qquad \text{normalized}$$

$$d\Gamma_1 = d^{f_1}q_1\, d^{f_1}p_1, \quad d\Gamma_2 = d^{f_2}q_2\, d^{f_2}p_2$$

$$H = H_1 + H_2 + \cancel{H_{12}} \qquad (H_{12} \text{ is negligible})$$

For observables which are only defined on the small subsystem we have

$$\langle F(\pi_1)\rangle_{1+2} \propto \int d\Gamma_1 F(\pi_1) \int d\Gamma_2 \delta(E - H_1 - H_2)$$

prefactor can be reconstructed through $\langle 1\rangle = 1$ → temporarily ignored

$$\langle F(\pi_1)\rangle_{1+2} \propto \int d\Gamma_1 F(\pi_1) \int dE_1 \delta(E_1 - H_1) \underbrace{\int d\Gamma_2 \delta(E - E_1 - H_2)}_{\sim\Gamma_2(E-E_1)}$$

integral is dominated by values of E_1, such that $|E - E_1| \approx E$ (little exchange) (ideal gas: $\tilde{E}_1/E = N_1/N << 1$)

$$\text{there } \ln\Gamma_2(E - E_1) \simeq \ln\Gamma_2(E) - E_1 \frac{\partial}{\partial E}\ln\Gamma_2(E)$$

$$\simeq \frac{S_2}{k_B} - E_1\frac{1}{k_B T} + O(E_1^2)$$

$$\Rightarrow \Gamma_2(E - E_1) \simeq e^{S_2/k_B - E_1/k_B T} \propto e^{-E_1/k_B T}$$

(e^{S_2/k_B} is independent on system 1!)

$$\langle F(\pi_1)\rangle_{1+2} \propto \int d\Gamma_1 F(\pi_1) \int dE_1 \delta(E_1 - H_1) e^{-E_1/k_B T} = \int d\Gamma_1 F(\pi_1) e^{-H_1/k_B T}$$

Normalization: $\langle F(\pi_1)\rangle_{1+2} = \int d\Gamma_1 \rho_1(\pi_1) F(\pi_1)$

$$\rho_1(\pi_1) = \frac{1}{Z}\frac{c_{N_1}}{h^{f_1}} e^{-H_1(\pi_1)/k_B T}$$

$$\langle 1\rangle = 1 = \int d\Gamma_1 \rho_1(\pi_1) \Leftrightarrow \boxed{Z = c_{N_1}\int \frac{d\Gamma_1}{h^{f_1}} e^{-H_1(\pi_1)/k_B T}}$$

- discussion exact for $N_2 \to \infty$
- when ρ_1 is known we can neglect system 2, only dependence on T
- suppress index 1

- $\rho(\pi_1)$ = probability for π_1 in the canonical ensemble at temperature T

Example:

$H = \sum_{i=1}^{N} \dfrac{\vec{p}_i^2}{2m} + V(\vec{r}_1, \ldots, \vec{r}_N)$

$Z = \dfrac{1}{N!} \int \prod_i \dfrac{d^3p_i \, d^3r_i}{h^3} e^{-\beta(\sum_i \frac{\vec{p}_i^2}{2m} + V(\vec{r}_1,\ldots,\vec{r}_N))}; \; \beta = \dfrac{1}{k_B T}$

$\int d^3p \, e^{-\frac{\beta}{2m}\vec{p}^2} = \prod_{i=1}^{3} \int dp_i \, e^{-\frac{\beta}{2m}p_i^2} = \left(\dfrac{2\pi m}{\beta}\right)^{3/2}$

$\sqrt{\dfrac{2\pi m}{\beta}} = \dfrac{h}{\lambda_T}$ (dimension = momentum)

λ_T: thermal de Broglie wavelength

$$Z = \frac{1}{\lambda_T^{3N} N!} \int \prod_{i=1}^{N} d^3r_i \, e^{-\beta V(\vec{r}_1,\ldots,\vec{r}_N)}$$

With $D(E,V) = \dfrac{1}{N!} \int \dfrac{d\Gamma}{h^{3N}} \delta(E - H)$ (density of states) we can write

$$Z = \int dE \, D(E,V) \, e^{-\beta E}$$

3.2.2 Free energy

Microcanonical ensemble: internal energy $U = \underset{\text{independent parameter}}{\underset{\swarrow}{E}} = \underset{\text{no fluctuations for } \Delta \to 0}{\underset{\searrow}{\langle H \rangle}}$

$\Rightarrow$ in general we define $U = \langle H \rangle = U(T,V,N)$ also in canonical ensemble:

$$\begin{aligned} U &= \frac{\int d\Gamma e^{-\beta H(\pi)} H(\pi)}{\int d\Gamma e^{-\beta H(\pi)}} = -\frac{\partial}{\partial \beta} \ln[\text{const.} \times \int d\Gamma e^{-\beta H(\pi)}] \\ &= -\frac{\partial}{\partial \beta} \ln Z = k_B T^2 \frac{\partial}{\partial T} \ln Z(T,V,N) \qquad \left(\frac{\partial T}{\partial \beta} = -k_B T^2\right) \end{aligned}$$

Here $\langle H \rangle$ fluctuates, but as we will show, in the TD limit canonical and microcanonical ensembles become equivalent and the fluctuations in H are $\propto 1/\sqrt{N}$ and become irrelevant.

Analogously: $P = -\left\langle \frac{\partial H}{\partial V} \right\rangle = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z(T,V,N)$ (first law: $\delta U = -P\delta V$)

$U(T,V,N)$ is not a thermodynamical potential with respect to the variables T, V, N, since

$$dU = TdS - PdV \text{ (at fixed } N) \to U(S,V,N)$$

But via Legendre: $F = U - TS$

$$\begin{aligned} dF &= dU - TdS - SdT = -PdV - SdT \to F(T,V,N) \\ d(-\beta F) &= \frac{1}{k_B T}(PdV + SdT) + F\frac{1}{k_B T^2}dT \\ &= \frac{1}{k_B T}(PdV + (S + \frac{U-TS}{T})dT) = \frac{1}{k_B T}(PdV + \frac{U}{T}dT) \end{aligned}$$

From statistics we had

$$d\ln Z = \frac{\partial \ln Z}{\partial T}dT + \frac{\partial \ln Z}{\partial V}dV = \frac{\overset{\langle H\rangle}{\overset{\nearrow}{U}}}{k_B T^2}dT + \frac{\overset{\langle -\frac{\partial H}{\partial V}\rangle}{\overset{\nearrow}{P}}}{k_B T}dV$$

A comparison yields $-\beta F = \ln Z$ (+ const.)

$$\boxed{Z(T,V,N) = e^{-\beta F(T,V,N)}}$$

⇒ statistical expression for F from the canonical partition function

It is easy to show that $\ln Z = -\frac{1}{k_B T}F$ is extensive:

$N = N_1 + N_2$, $V = V_1 + V_2$, $T = T_1 = T_2$ (thermal contact)

$1 \leftrightarrow 2$ are two distinguishable systems

$F(T,V,N) = F_1(T,V_1,N_1) + F_2(T,V_2,N_2)$, because

$$e^{-\beta F} = \frac{1}{h^{3N}N_1!\,N_2!}\int d\Gamma_1 d\Gamma_2 e^{-\beta(H_1+H_2)} = e^{-\beta F_1} \times e^{-\beta F_2}$$

S from F: since $\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S$

$$\Rightarrow S = k_B \frac{\partial}{\partial T} T \ln Z(T, V, N) = S(T, V, N)$$

$\Rightarrow$ all thermodynamical potentials can be derived from Z

$\Rightarrow Z$ is essential for statistical physics.

3.2.3 Fluctuations

The property $\left.\frac{\partial^2 S}{\partial E^2}\right|_{V,N} < 0$ was needed in order that $\tilde{E}_1 =$ maximum.

$$-\left.\frac{\partial^2 S}{\partial E^2}\right|_{V,N} = -\frac{\partial}{\partial E}\frac{1}{T} = \frac{1}{T^2}\left.\frac{\partial T}{\partial E}\right|_{V,N} = \frac{1}{T^2 \frac{\partial U}{\partial T}|_{V,N}} = \frac{1}{T^2 C_V}$$

$> 0 \leftrightarrow$ thermal stability

$C_V =$ heat capacity at fixed volume (isochoric)

With statistical definition:

$$\begin{aligned}
C_V &= \frac{\partial U}{\partial T} = -\frac{\partial}{\partial T}\underbrace{\frac{\partial}{\partial \beta}\ln Z}_{=-U} = k_B \beta^2 \frac{\partial^2}{\partial \beta^2}\ln Z \\
&= k_B \beta^2 \frac{\partial}{\partial \beta}\frac{\frac{\partial Z}{\partial \beta}}{Z} = k_B \beta^2 \left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{\frac{\partial Z}{\partial \beta}}{Z}\right)^2\right) \\
&= k_B \beta^2 (\langle H^2 \rangle - \langle H \rangle^2) \qquad (Z \propto \int d\Gamma e^{-\beta H}) \\
&= k_B \beta^2 \langle (H - \langle H \rangle)^2 \rangle \geqslant 0
\end{aligned}$$

For the relative fluctuations it follows

$$\frac{\sqrt{\langle (H - \langle H \rangle)^2 \rangle}}{\langle H \rangle} = \frac{\sqrt{C_V/(k_B \beta^2)}}{U} \propto \frac{1}{\sqrt{N}}$$

in the TD limit, where $U \sim N$ and $C_V \sim N$.

$\Rightarrow$ although in the canonical ensemble all values of H contribute, only $H = \langle H \rangle = U$ plays a role in the TD limit → like microcanonical

3.2.4 Equivalence M-ensemble (microcanonical) and K-ensemble (canonical) in the TD limit

M: free input parameters: E, V, N

$\rightarrow$ computed: $\ln\Gamma = \ln(D\Delta) \simeq \ln D$ ("$\simeq$" $\leftrightarrow$ TD limit)

$$S_M(E,V,N) = k_B \ln\Gamma, \quad \frac{1}{T_M} = \frac{\partial S_M}{\partial E}$$

K: free input parameters: T, V, N

$\rightarrow$ computed: $Z(T_K,V,N),\ U = \langle H\rangle_K$

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

$$\left.\frac{\partial F}{\partial T_K}\right|_{V,N} = -S_K(T_K,V,N)$$

We require $E = \langle H\rangle_M = \langle H\rangle_K = U \quad (\langle H\rangle_K$ implicitly fixes $T_K(E))$

does it follow a) $T_M = T_K$ or b) $S_M = S_K$?

We have

$$Z = \int dE' D(E',V,N) e^{-\beta E'} = \int dE' e^{+\ln D - \beta E'}$$

recall: $D(E') = C_N \int \frac{d\Gamma}{h^{3N}} \delta(E' - H)$

$De^{-\beta E'}$ has a sharp peak at $\tilde{E}$, in TD limit only contributions from $E' = \tilde{E} \ \Rightarrow \ \tilde{E} = U$

$$\begin{aligned} 0 &= \frac{\partial}{\partial E'}(\ln D - \beta E')|_{\tilde{E}=U} \ \Rightarrow \\ \beta &= \frac{1}{k_B T_K} = \frac{\partial}{\partial E'} \ln D_{E'=U} = \frac{\partial}{\partial E'} \frac{1}{k_B} S_M|_U = \frac{1}{k_B T_M} \\ &\Rightarrow T_K = T_M \end{aligned}$$

Expansion around $E' = U$:

$$\ln D - \beta E' = \ln D|_U - \beta U + \frac{1}{2}(E'-U)^2 \left.\frac{\partial^2 \ln D}{\partial E^2}\right|_U \tag{12}$$

$$\frac{\partial^2 \ln D}{\partial E^2} = \frac{1}{k_B}\frac{\partial}{\partial E}\frac{1}{T_M} = -\frac{1}{k_B T_M^2}\frac{\partial T_M}{\partial E} = -\frac{1}{k_B T_M^2}\underset{\substack{\uparrow \\ \text{(U and T are already identified)}}}{\frac{1}{\frac{\partial U}{\partial T}}} = -\frac{1}{k_B T_M^2}\frac{1}{C_V}$$

$$\begin{aligned}
&D(E', V, N)e^{-\beta E'} = D(U, V, N)e^{-\beta U}e^{-\frac{k_B\beta^2}{2C_V}(E'-U)^2} \\
&\textstyle\int dE' \ldots \Rightarrow Z = D(U, V, N)e^{-\beta U}\int dE' e^{-\frac{k_B\beta^2}{2C_V}(E'-U)^2} \\
&\qquad\qquad\quad = D(U, V, N)e^{-\beta U}\left(\frac{2\pi C_V}{k_B\beta^2}\right)^{1/2} \\
&\Rightarrow F = -\frac{1}{\beta}\ln Z = U - \frac{1}{\beta}\ln D + O(\ln N = \ln C_V) = U - TS_M
\end{aligned}$$

We had identified:

$$\begin{aligned}
&S_K = -\frac{\partial F}{\partial T} \\
&-\beta F(T, V, N) = \sup_{E'}[-\beta E' + \ln D(E', V, N)] \quad (\text{at } E' = U) \\
&\frac{\partial}{\partial \beta}\sup_{E'}[\qquad] \underset{\substack{\uparrow \\ \text{(D does not depend on β explicitly)}}}{=} -E' = -U
\end{aligned}$$

Explanation: if we change $T \to T + \delta T$ or $\beta \to \beta + \delta\beta$ respectively

- value of sup changes because of explicit β-dependence

- position $E' = U \to E' = U + \delta U$,
  but the value of sup only changes by δU^2, see Eq. (12)

$$\begin{aligned}
S_K &= -\frac{\partial}{\partial T}F = \frac{\partial}{\partial T}k_B T \sup[\qquad] \\
&= -\frac{1}{T}F - k_B T U\frac{\partial \beta}{\partial T} = -\frac{1}{T}(F - U) = S_M
\end{aligned}$$

3.3 Grand-canonical ensemble

To change microcanonical → canonical ensemble we substituted $E = U \to T$

According to Legendre transformation

$$S - \frac{\partial S}{\partial E}E = S - \frac{U}{T} = -\frac{1}{T}F \ \ (\text{cf. } L - p\dot{q},\ p = \tfrac{\partial L}{\partial \dot{q}}) \ \Leftrightarrow F = U - TS$$

Now we want to substitute $N \to \mu$ as well:

$$\text{grand-canonical potential } \Omega = F - \mu N = F - G \quad (\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V})$$

Why? often N is not fixed (for example photons!) or it can be freely chosen

Natural dependency: $\Omega = \Omega(T, V, \mu)$

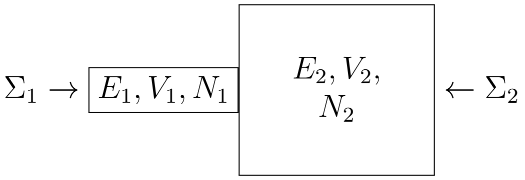
$$\Omega = U - TS - \mu N$$

$dU = TdS - PdV + \mu dN$ (1st law of TD, we derived it from M-ensemble)

$$\Rightarrow d\Omega = TdS - PdV + \mu dN - d(TS) - d(\mu N) = -SdT - PdV - Nd\mu$$

$$\left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu} = -S, \quad \left.\frac{\partial \Omega}{\partial V}\right|_{T,\mu} = -P, \quad \left.\frac{\partial \Omega}{\partial \mu}\right|_{T,V} = -N$$

Consider again two subsystems Σ_1, Σ_2:



- $\Sigma_1 << \Sigma_2$
- both macroscopic
- energy + particle exchange
- $\Sigma_1 + \Sigma_2$ is isolated $\Rightarrow$
  $E = E_1 + E_2 = \text{const.}$
  $N = N_1 + N_2 = \text{const.}$

$$\Gamma_{1+2} = \frac{1}{N!}\int \frac{d\Gamma_{1+2}}{h^{3N}}\delta(E - H_1(\pi_1) - H_2(\pi_2))$$

Formula:

$$\int_{V_1 \cup V_2} \prod_{i=1}^{N} d^3 r_i f(\underbrace{\vec{r}_1, \ldots, \vec{r}_N}_{\substack{\text{symmetric,} \\ \text{like } H_1 + H_2 + \ldots + H_N}}) = \sum_{N_1=0}^{N} \begin{pmatrix} N \\ N_1 \end{pmatrix} \int_{V_1} d^3 r_1 \ldots d^3 r_{N_1} \int_{V_2} d^3 r_{N_1+1} \ldots d^3 r_N f(\vec{r}_1, \ldots, \vec{r}_N)$$

Example: $N = 2$

$$\begin{aligned}
I &= \int_{V_1\cup V_2} d^3r_1 d^3r_2 f(\vec{r}_1,\vec{r}_2) = \left(\int_{V_1} d^3r_1 + \int_{V_2} d^3r_1\right)\left(\int_{V_1} d^3r_2 + \int_{V_2} d^3r_2\right) f(\vec{r}_1,\vec{r}_2) \\
&= \int_{V_1} d^3r_1 \int_{V_1} d^3r_2 f + \int_{V_1} d^3r_1 \int_{V_2} d^3r_2 f + \int_{V_2} d^3r_1 \int_{V_1} d^3r_2 f + \int_{V_2} d^3r_1 \int_{V_2} d^3r_2 f \\
&\qquad \text{3rd term = 2nd term: } \int_{V_2} d^3r_1 \int_{V_1} d^3r_2 f(\vec{r}_1,\vec{r}_2) = \int_{V_1} d^3r_1 \int_{V_2} d^3r_2 \underbrace{f(\vec{r}_2,\vec{r}_1)}_{=f(\vec{r}_1,\vec{r}_2)} \\
&= \left(\int_{V_1}\int_{V_1} d^3r_1 d^3r_2 + 2\int_{V_1} d^3r_1 \int_{V_2} d^3r_2 + \int_{V_2}\int_{V_2} d^3r_1 d^3r_2\right) f(\vec{r}_1,\vec{r}_2)
\end{aligned}$$

In analogy with section 3.2.1:

$$\langle \underbrace{F_1}_{\substack{\text{only}\\ \text{in } \Sigma_1}} \rangle_{1+2} \propto \sum_{N_1=0}^{N} \underbrace{\frac{1}{N!}\begin{pmatrix} N \\ N_1 \end{pmatrix}}_{\frac{1}{N_1!(N-N_1)!}} \int_{N_1} d\Gamma_1 F_{N_1}(\pi_1) \int_{N-N_1} d\Gamma_2 \delta(E - H_1 - H_2)$$

$\int_{N_1} d\Gamma_1 \ldots$: phase-space integral for N_1 particles in V_1

F_1 has contributions only from particles in V_1

$F_{N_1}(\pi_1)$: for each value of N_1, $F_{N_1}(\cdot)$ is a function of $\{\vec{p}_i,\vec{r}_i\}_{i=1,\ldots,N_1}$.

$$\langle F_{N_1}(\pi_1) \propto \sum_{N_1} \frac{1}{N_1!} \int dE_1 \int_{N_1} d\Gamma_1 F_{N_1} \delta(E_1 - H_1) \underbrace{\frac{1}{(N-N_1)!} \int_{N-N_1} d\Gamma_2 \delta(E - E_1 - H_2)}_{\propto \Gamma_2(E-E_1,V_2,N-N_1)}$$

- integral over E_1/sum over N_1 is dominated by a pair (E_1, N_1) such that $|E - E_1| \approx E$, $|N - N_1| \approx N$

- there $\ln \Gamma_2(E - E_1, V_2, N - N_1)$

$$\simeq \ln \Gamma_2(E, V_2, N) - E_1 \underbrace{\frac{\partial}{\partial E} \ln \Gamma_2(E, V_2, N)}_{\frac{1}{k_BT}} - N_1 \underbrace{\frac{\partial}{\partial N} \ln \Gamma_2(E, V_2, N)}_{-\frac{\mu}{k_BT}}$$

$$\Rightarrow \Gamma_2(E - E_1, V_2, N - N_1) \simeq e^{\frac{S_2}{k_B} - \frac{E_1}{k_BT} + \frac{\mu N_1}{k_BT}}$$

Hence (rotation: $N_1 \to N$, $E_1 \to E$, drop index 1):

$$\langle F_N(\pi)\rangle_{1+2} = \frac{1}{\Xi}\sum_{N=0}^{\infty}\frac{1}{N!}\int_N \frac{d\Gamma}{h^{3N}} e^{-\beta(H_N(\pi)-\mu N)} F_N(\pi)$$

$\to$ Grand-canonical partition function:

$$\boxed{\Xi = \sum_{N=0}^{\infty}\frac{1}{N!}\int_N \frac{d\Gamma}{h^{3N}} e^{-\beta(H_N(\pi)-\mu N)}} \;\leftrightarrow\; \langle 1\rangle_{1+2} = 1$$

Remark: e^{S_2/k_B} drops, common factor numerator and denominator

$\langle F\rangle = \frac{\int d\Gamma_{1+2\ldots}F}{\int d\Gamma_{1+2\ldots}}$

$\Sigma_2 \to \infty$ leaves behind only β and $\mu\ldots$

Remark: $N \to \infty$ since Σ_2 (heatbath + particle reservoir) is arbitrarily large.

Using the density of states: $D(E,V,N) = \frac{1}{N!}\int_N \frac{d\Gamma}{h^{3N}}\delta(E-H) \;\Rightarrow$

$$\begin{aligned}\Xi &= \sum_{N=0}^{\infty}\int dE\, D(E,V,N)e^{-\beta(E-\mu N)} = \Xi(T,V,\mu)\\ &= \sum_{N=0}^{\infty} z^N Z(T,V,N) \quad \text{with} \quad z = e^{\beta\mu} \quad \text{fugacity}\end{aligned}$$

Z: canonical partition function

With the definition $\langle F_N(\pi)\rangle = \sum_N \int_N d\Gamma F_N(\pi)\delta_N(\pi)$

$\leftrightarrow$ grand-canonical probability density $\delta_N = \dfrac{1}{\Xi(T,V,\mu)}\dfrac{1}{N!h^{3N}}e^{-\beta(H-\mu N)}$

3.3.1 Relation to thermodynamics

It can be shown in a similar way as it was done for the canonical ensemble in section 3.2.4 that:

- sums over N are dominated by a few terms in the TD limit:

$$\langle N\rangle = \frac{1}{\Xi}\sum_{N=0}^{\infty} N\frac{1}{N!}\int\frac{d\Gamma}{h^3N}e^{-\beta(H-\mu N)} = \frac{1}{\Xi}\sum_{N=0}^{\infty} N z^N Z(T,V,N)$$

$\ln(z^N Z(T,V,N)) = N\beta\mu - \beta F(T,V,N)$
maximum at $N = \tilde{N}$: $\mu = \dfrac{\partial F}{\partial N}(T,V,\tilde{N})$
gives the dominant contribution: $\langle N \rangle \simeq \tilde{N}$

- if we choose μ such that $\langle N \rangle_G$ ($G \leftrightarrow$ grand-canonical) is equal to the fixed value of N in the canonical ensemble (and T, V are the same), then G-ensemble and K-ensemble are equivalent in the TD limit

Thermodynamics in the G-ensemble is described by the grand-canonical potential $\Omega(T,V,\mu)$.

By comparing $d\Omega$ and $d\ln\Xi$ we find:

$$\Omega = -k_B T \ln \Xi (+\, const.) \Leftrightarrow \boxed{\Xi = e^{-\beta\Omega}}$$

cf. the relation $Z = e^{-\beta F}$ in the K-ensemble

Application: ideal gas

$$Z(T,V,N) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N; \qquad \lambda_T = h\sqrt{\tfrac{\beta}{2\pi m}} \text{ (see section 3.2.1)}$$

$$\Xi = \sum_{N=0}^{\infty} z^N Z = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{zV}{\lambda_T^3}\right)^N = e^{zV/\lambda_T^3} = e^{-\beta\Omega} \qquad (z = e^{\beta\mu})$$

$$\Rightarrow \Omega = -k_B T \frac{zV}{\lambda_T^3} = \Omega(T,V,\mu)$$

$$\begin{aligned} \langle N \rangle &= \frac{1}{\Xi}\sum_{N=0}^{\infty} N \underbrace{z^N}_{=e^{N\ln z}} Z = \frac{\partial}{\partial \ln z}\ln\Xi \\ &= -\beta \frac{\partial}{\partial \ln z}\Omega = -\beta\Omega \quad \text{(only for the ideal gas!)} \end{aligned}$$

$$\Rightarrow \Xi = e^{\langle N \rangle} \qquad\qquad \tfrac{\partial}{\partial \ln z} = z\tfrac{\partial}{\partial z}$$

In general:

$$\begin{aligned}\langle F(N)\rangle &= \frac{1}{\Xi}\sum_{N=0}^{\infty}F(N)z^N Z = \frac{1}{\Xi}\sum_{N=0}^{\infty}\frac{1}{N!}F(N)\left(\frac{zV}{\lambda_T^3}\right)^N\\ &= e^{-\langle N\rangle}\sum_{N=0}^{\infty}F(N)\frac{1}{N!}(-\beta\Omega)^N = \sum_{N=0}^{\infty}F(N)e^{-\langle N\rangle}\frac{1}{N!}(\langle N\rangle)^N\end{aligned}$$

$W_N(T,V,\mu) = e^{-\langle N\rangle}\dfrac{1}{N!}(\langle N\rangle)^N$ probability to find N particles in the system = Poisson distribution for N: $W_N = e^{-\lambda}\dfrac{1}{N!}\lambda^N$,

normalized: $\sum_{N=0}^{\infty} W_N = e^{-\lambda}\sum_{N=0}^{\infty}\dfrac{1}{N!}\lambda^N = 1$ and

$\langle N\rangle = \sum_{N=0}^{\infty} N\, W_N = e^{-\lambda}\sum_{N=1}^{\infty}\dfrac{1}{(N-1)!}\lambda^N = \lambda$ and

$\langle N^2\rangle - \langle N\rangle^2 = \lambda = \langle N\rangle$ (variance = mean)

For the ideal gas: $\dfrac{\sqrt{\langle (N-\langle N\rangle)^2\rangle}}{\langle N\rangle} = \dfrac{1}{\sqrt{\langle N\rangle}} \overset{\text{"}N\to\infty\text{"}}{\underset{\text{macroscopic}}{\longrightarrow}} 0$

It can be shown (see [2] p.92) that for any macroscopic system $\dfrac{\sqrt{\langle (N-\langle N\rangle)^2\rangle}}{\langle N\rangle} \overset{\text{"}N\to\infty\text{"}}{\longrightarrow} 0$, the fluctuations of the particle number becomes arbitrarily small as $N\to\infty$ (almost all of the macroscopic systems in the grand-canonical ensemble have the same number of particles equal to $\langle N\rangle$) $\Rightarrow$ equivalence of G-ensemble and K-ensemble.

M-ensemble → $S(E,V,N)$

K-ensemble → $F(T,V,N)$

G-ensemble → $\Omega(T,V,\mu)$

are all equivalent in the TD limit, when $\langle H\rangle$ (trivial in M) and $\langle N\rangle$ (trivial in M, K) have the same value respectively.

4 Quantum statistics

So far: classical mechanics in Hamilton formulation was the basis

- state ↔ $\pi = (q_1, \ldots, q_s, p_1, \ldots, p_s) \in \Gamma \subseteq \mathbb{R}^{2s}$
- in principle deterministic trajectories
- incomplete information → ensemble (= time) average
- in practice sharp values $(\pm\frac{1}{\sqrt{N}})$ for specific macroscopic observables ↔ thermodynamics

In reality: microscopic theory = quantum mechanics (QM): there even for complete set of information: probabilities

We will see that QM yields the same thermodynamics as its classical limit in many situations.

Exceptions: low temperatures, for example 3rd law of thermodynamics

We already "borrowed" from QM:

- $\frac{1}{N!}$ ↔ phase space of identical particles
- h dimensionful constant (its precise value $\neq 0$ is classically irrelevant)

4.1 Statistical operator, density matrix

4.1.1 Pure state

QM observable: $\hat{F}$, hermitian operator in Hilbert space

Eigenstates $\hat{F}|f_n\rangle = f_n|f_n\rangle$

f_n : possible values of measurement of $\hat{F}$

$\{|f_n\rangle\}$: orthonormal basis (ONB) $\langle f_n|f_m\rangle = \delta_{mn}$

$\Rightarrow |\Psi\rangle = \sum_n c_n|f_n\rangle$ with $c_n = \langle f_n|\Psi\rangle$ for any state vector $|\Psi\rangle$

- in general an infinite sum $\sum_{n=0}^{\infty}$ (convergence assumed)
- eigenstates are countable and normalizable, this can be achieved through finite volume, periodic boundary conditions
- generalization to states $\langle x|y\rangle = \delta(x-y)$ possible

$|\Psi\rangle = \int dx |x\rangle \Psi(x), \qquad \Psi(x) = \langle x|\Psi\rangle$

If $|\Psi\rangle$ is normalized: $1 = \langle\Psi|\Psi\rangle = \sum_{m,n} c_m^* c_n \langle f_m|f_n\rangle = \sum_n |c_n|^2$

$|c_n|^2$ = probability for a state $|\Psi\rangle$ to measure the value f_n for $\hat{F}$

Remark: $|\Psi\rangle$ and $e^{i\alpha}|\Psi\rangle$ are equivalent, in reality a physical state is $\{|\Psi\rangle z,\ z \in \mathbb{C}\backslash\{0\}\} = 1-D$ subspace of the Hilbert space (and not one vector)

4.1.2 Mixed state

Less information is available, compared to what is in principle possible in QM; classical probability superimposed to the intrinsic probability of QM

System with probability p_m in the state $|\Psi_m\rangle$, $0 \leqslant p_m \leqslant 1$, $\sum_m p_m = 1$

For simplicity we assume: $\langle\Psi_m|\Psi_n\rangle = \delta_{nm}$

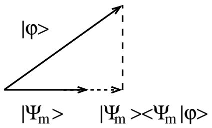
Average value of $\hat{F}$ is now:

$$\begin{aligned} \hat{F} &= \sum_m p_m \langle\Psi_m|\hat{F}|\Psi_m\rangle \\ &= \sum_m p_m \sum_n \langle\Psi_m|\hat{F}|f_n\rangle\langle f_n|\Psi_m\rangle \qquad (\sum_n |f_n\rangle\langle f_n| = 1) \\ &= \sum_m p_m \sum_n f_n \underbrace{|\langle\Psi_m|f_n\rangle|^2}_{\text{QM probability to measure value } f_n \text{ there}} \end{aligned}$$

p_m... classical probability for $|\Psi_m\rangle$

$\langle\hat{F}\rangle = \mathrm{Tr}(\hat{\rho}\hat{F})$ with $\hat{\rho} = \sum_m p_m |\Psi_m\rangle\langle\Psi_m|$

$|\Psi_m\rangle\langle\Psi_m|$ is a projector:



Definition of Tr: in any ONB $\{|i\rangle\}$:

$\mathrm{Tr}(\hat{\rho}\hat{F}) = \sum_i \langle i|\hat{\rho}\hat{F}|i\rangle = \sum_{i,m} p_m \langle i|\Psi_m\rangle\langle\Psi_m|\hat{F}|i\rangle = \sum_m p_m \langle\Psi_m|\hat{F}|\Psi_m\rangle$

because $\sum_i |i\rangle\langle i|\Psi_m\rangle = |\Psi_m\rangle$

$\mathrm{Tr}(\hat{\rho}\hat{F}) = \mathrm{Tr}(\hat{F}\hat{\rho})$ even when $[\hat{\rho}, \hat{F}] \neq 0$

Properties of the density matrix $\hat{\rho}$:

- $\hat{\rho}^\dagger = \hat{\rho}$ hermitian
- $\mathrm{Tr}\hat{\rho} = \sum_m p_m \mathrm{Tr}|\Psi_m\rangle\langle\Psi_m| = \sum_m p_m = 1$ because $\mathrm{Tr}|\Psi_m\rangle\langle\Psi_m| = 1$
- non-negative: $\langle\varphi|\hat{\rho}|\varphi\rangle \geqslant 0$ for all $|\varphi\rangle$
  $\langle\varphi|\hat{\rho}|\varphi\rangle = \sum_m p_m \langle\varphi|\Psi_m\rangle\langle\Psi_m|\varphi\rangle = \sum_m p_m |\langle\Psi_m|\varphi\rangle|^2 \geqslant 0$
- eigenvalues: $\hat{\rho}|\Psi_m\rangle = p_m|\Psi_m\rangle$ only valid for $\langle\Psi_m|\Psi_n\rangle = \delta_{mn}$
- special case: pure state

  $\hat{\rho} = |\Psi\rangle\langle\Psi|,\ \mathrm{Tr}(\,\hat{\rho}\hat{F}) = \sum_i \langle i|\Psi\rangle\langle\Psi|\hat{F}|i\rangle = \langle\Psi|\hat{F}|\Psi\rangle$
- $\hat{\rho}^2 = \sum_{m,n} p_m p_n |\Psi_m\rangle\langle\Psi_m|\Psi_n\rangle\langle\Psi_n| = \sum_m p_m^2 |\Psi_m\rangle\langle\Psi_m|$

  $\mathrm{Tr}(\,\hat{\rho}^2) = \sum_m p_m^2 \leqslant \sum_m p_m = 1$

  "$=$" $\Leftrightarrow p_m^2 = p_m$ for all $m \Rightarrow p_m = 0, 1$

  since $\sum_m p_m = 1$ exactly one $p_m = 1 \Leftrightarrow$ pure state (see ex.7b)
- $\hat{\rho}^2 \leqslant \hat{\rho}$ ($\leftrightarrow \hat{\rho} - \hat{\rho}^2 = \hat{\rho}(1 - \hat{\rho})$ non-negative)
- time evolution: $\hat{\rho}(t)$
  $i\hbar\dfrac{d}{dt}|\Psi_m\rangle = \hat{H}|\Psi_m\rangle$ Schrödinger picture (here: $\dfrac{d}{dt} = \dfrac{\partial}{\partial t}$)
  $\Rightarrow -i\hbar\dfrac{d}{dt}\langle\Psi_m| = \langle\Psi_m|\hat{H}$

$$\begin{aligned}\Rightarrow i\hbar\,\hat{\rho} &= i\hbar\sum_m p_m \frac{d}{dt}|\Psi_m\rangle\langle\Psi_m| \\ &= \sum_m p_m(\hat{H}|\Psi_m\rangle\langle\Psi_m| - |\Psi_m\rangle\langle\Psi_m|\hat{H}) \\ &= \hat{H}\,\hat{\rho} - \,\hat{\rho}\hat{H} = [\hat{H},\,\hat{\rho}] \quad \text{(von Neumann equation)}\end{aligned}$$

System is at time $t = t_0$ in state $|\Psi_n(t_0)\rangle$ with probability $p_n \;\Rightarrow$ at time t in state $|\Psi_n(t)\rangle$ with probability p_n, where $|\Psi_n(t)\rangle$ is the solution of $i\hbar\frac{d}{dt}|\Psi_n(t)\rangle = \hat{H}|\Psi_n(t)\rangle$ with initial condition $|\Psi_n(t_0)\rangle$.
Formally: $|\Psi_n(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}|\Psi_n(t_0)\rangle \qquad (\frac{\partial}{\partial t}\hat{H} = 0)$

formal solution of von Neumann equation: $\hat{\rho}(t) = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}\,\hat{\rho}(t_0)e^{\frac{i}{\hbar}(t-t_0)\hat{H}}$

$$\begin{aligned}\Leftrightarrow \hat{\rho}(t+\epsilon) &= \hat{\rho}(t) + \epsilon\frac{d}{dt}\,\hat{\rho}(t) \;=\; \hat{\rho}(t) + \frac{\epsilon}{i\hbar}[\hat{H},\,\hat{\rho}] \\ &\simeq (1 + \frac{\epsilon}{i\hbar}\hat{H})\,\hat{\rho}(t)(1 - \frac{\epsilon}{i\hbar}\hat{H}) \;\simeq\; e^{\frac{\epsilon}{i\hbar}\hat{H}}\,\hat{\rho}(t)e^{-\frac{\epsilon}{i\hbar}\hat{H}}\end{aligned}$$

iterate, many steps ϵ_k, $\sum_k \epsilon_k = t - t_0$

4.1.3 Correspondence principle

- formal similarity between classical mechanics and QM in suitable formulation
- QM "translation" of statistics can be guessed/proposed
- ultimately test by experiment, in particular where there are deviations from classical behavior

Classical mechanics:

$\langle F\rangle = \int d^sqd^sp\rho(q,p)F(q,p)$
Normalization of ρ : $\quad \langle 1\rangle = 1 = \int d^s_qd^sp\rho(q,p)$

QM: $\langle\hat{F}\rangle = \mathrm{Tr}(\,\hat{\rho},\hat{F}) \quad \langle 1\rangle = 1 = \mathrm{Tr}(\,\hat{\rho})$

Time evolution of ρ:

$$\frac{\partial\rho}{\partial t} = \{H,\rho\}_{\text{Poisson}} \qquad (\rho, H \text{ functions of } q,p)$$

$$\frac{\partial\,\hat\rho}{\partial t} = \frac{1}{i\hbar}[\hat H,\,\hat\rho]_{\text{commutator}} \quad (\,\hat\rho, \hat H \text{ operators, Schrödinger picture!})$$

Dictionary:

classical mechanics:	**QM:**
phase-space function $F(\pi)$	observable $\hat F$ (for example $\hat F(\hat q_i, \hat p_j)$)
density $\rho(\pi)$	density matrix $\hat\rho$
Poisson bracket $\{F,G\} = \sum_i \left(\frac{\partial F}{\partial q_i}\frac{\partial P}{\partial p_i} - \frac{\partial G}{\partial q_i}\frac{\partial F}{\partial p_i}\right)$	commutator $\frac{1}{i\hbar}[\hat F,\hat G] = \frac{1}{i\hbar}(\hat F\hat G - \hat G\hat F)$
Γ-integral $\frac{1}{h^{3N}N!}\int d^sq d^sp \ldots$	trace Tr$(\ldots)$ (QM trace will automatically yield factor $\frac{1}{N!}$ for identical particles)
stationary ensemble: $\{\rho,H\}=0$	$[\,\hat\rho,\hat H]=0$

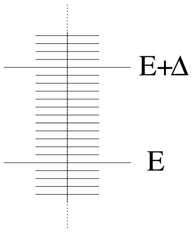
4.2 Microcanonical ensemble

- principle of same a priori probabilities, only constrained by energy
- stationary: $[\hat H,\,\hat\rho]=0 \;\Rightarrow$ QM: common eigenstates

  assumption: all discrete (finite volume), normalizable

  $\hat H|E_n\rangle = E_n|E_n\rangle \qquad \langle E_n|E_m\rangle = \delta_{nm}$

  $\langle E_m|\hat H|E_n\rangle = E_m\delta_{mn}$ diagonal



often: dense energy levels in interval

$E,\ E+\Delta$ for macroscopic system

$\to$ continuous spectrum for volume $\to \infty$

Ansatz for density matrix of microcanonical ensemble:

$$\hat{\rho}_M = \textstyle\sum_m p_m |E_m\rangle\langle E_m| \qquad (\Rightarrow [\,\hat{\rho}_M, \hat{H}] = 0)$$

$$p_m = \begin{cases} \frac{1}{\Gamma(E)} & \text{if } E < E_m < E+\Delta \\ 0 & \text{otherwise} \end{cases}$$

$$\Gamma(E) = \sum_{\substack{m \\ E<E_m<E+\Delta}} 1 = \text{number of states with } E_m \in (E, E+\Delta)$$

$$\begin{aligned} \Rightarrow \operatorname{Tr} \hat{\rho}_M &= \sum_n \langle E_n|\,\hat{\rho}_M|E_n\rangle = \sum_{n,m} p_m \langle E_n|E_m\rangle\langle E_m|E_n\rangle \\ &= \frac{1}{\Gamma(E)} \sum_{\substack{m \\ E<E_m<E+\Delta}} 1 = 1 \end{aligned}$$

Remark: to be precise $\Gamma(E, V, N, \Delta)$

$$\begin{aligned} \langle \hat{F} \rangle &= \operatorname{Tr} \hat{\rho}_M \hat{F} = \sum_{m,n} p_m \langle E_n|E_m\rangle\langle E_m|\hat{F}|E_n\rangle \\ &= \sum_m p_m \langle E_m|\hat{F}|E_m\rangle = \frac{1}{\Gamma(E)} \sum_{\substack{m \\ E<E_m<E+\Delta}} \langle E_m|\hat{F}|E_m\rangle \\ &\Rightarrow U = \langle \hat{H} \rangle = \frac{1}{\Gamma(E)} \sum_{\substack{m \\ E<E_m<E+\Delta}} E_m \approx E \end{aligned}$$

Entropy: $S = k_b \ln \Gamma(E) = S(E, V, N)$

Remark: factor $c_N = 1/N!$ is automatic in $\operatorname{Tr}(\,\hat{\rho}\hat{F})$:

Tr only over a ONB $\{|i\rangle\}$ in the (anti-/)symmetric (fermions/bosons) tensor product-space of the one-particle theory (details see section 5 Fermi-/Bose-gas)

Example: N distinguishable harmonic oscillators of the same frequency ω

$\hat{H} = \sum_{i=1}^{N} \hbar\omega(a_i^+ a_i + 1/2)$ (see also appendix C)

$E_{n_1,\ldots,n_N} = \sum_{i=1}^{N} \hbar\omega(n_i + 1/2)$

$\hat{H}|n_1,\ldots,n_N\rangle = E_{n_1,\ldots,n_N}|n_1,\ldots,n_N\rangle$

Microcanonical ensemble: $E = \underbrace{\frac{N}{2}\hbar\omega}_{\text{zero-point}} + N_0\hbar\omega$

How many states $|n_1,\ldots,n_N\rangle$ have $\sum_i n_i = N_0$?

$$\begin{array}{ccccccccccccc} \text{x x x} & | & \text{x x} & | & & | & \text{x x x} & | & \ldots & | & \text{x} & | & \text{x} \\ n_1 & & n_2 & & n_3 & & n_4 & & \ldots & & n_{N-1} & & n_N \end{array}$$

N_0 times x, $N-1$ times $|$, number of different configurations:

$$\binom{N_0+N-1}{N_0} = \frac{(N_0+N-1)!}{N_0!(N-1)!} = \Gamma(E,N)$$

...if positions of N_0 x are chosen, the rest are $|$; permutations of x ($N_0!$) or $|$ ($(N-1)!$) do not produce a new configuration

Stirling $(N_0, N >> 1!)$: $\ln M! = M(\ln M - 1) + O(\ln M)$

$$\begin{aligned} S &= k_B \ln\Gamma \simeq k_B[(N_0+N)\ln(N_0+N) - N_0\ln N_0 - N\ln N] \\ &= k_B N[(1+f)\ln(1+f) - f\ln f] \text{ with } f = \frac{N_0}{N}, N_0 = \frac{E}{\hbar\omega} - \frac{N}{2} \end{aligned}$$

$$N[(1+f)\ln(1+f) - f\ln f] = (N+N_0)\ln\left[\frac{N+N_0}{N}\right] - N_0\ln\left[\frac{N_0}{N}\right]$$

$$= (N+N_0)\ln(N+N_0) - N\ln N - \cancel{N_0\ln N} - N_0\ln N_0 + \cancel{N_0\ln N}$$

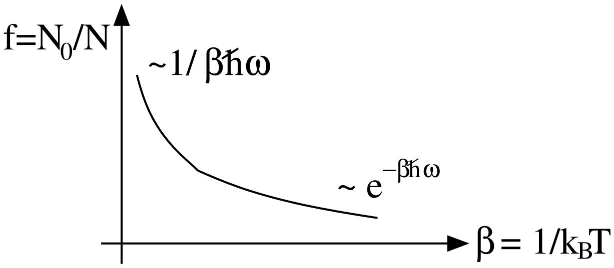
$\lim_{f\to 0} S = 0$! (3rd law of thermodynamics, see below)

Temperature:

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial E} = \frac{\partial S}{\partial N_0}\overbrace{\frac{\partial N_0}{\partial E}}^{=\frac{1}{\hbar\omega}} = \frac{k_b}{\hbar\omega}[\ln(N_0+N) - \ln(N_0)] = \frac{k_B}{\hbar\omega}\ln(1+\frac{1}{f})\\ &\Leftrightarrow 1+\frac{1}{f} = e^{\frac{\hbar\omega}{k_BT}}\end{aligned}$$

$$T \to 0: \; f \simeq e^{-\frac{\hbar\omega}{k_BT}} \to 0 \Leftrightarrow \frac{E}{N} \searrow \tfrac{1}{2}\hbar\omega$$

$$T \to \infty: \; e^{\frac{\hbar\omega}{k_BT}} \simeq 1 + \frac{\hbar\omega}{k_BT} \to 1 \Leftrightarrow f = \frac{k_BT}{\hbar\omega} \approx \frac{E}{N\hbar\omega} \to \infty \Leftrightarrow \frac{E}{N} \approx k_BT$$



Remark: the 3rd law of thermodynamics states: The entropy of a thermodynamical system goes for $T \to 0$ to a universal constant which can be chosen to be zero. This holds independently of the values of other state variables.

Classical ideal gas (Sackur-Tetrode) violates the 3rd law:

$$E_{\min} = 0, \; \lim_{E\to 0} S = -\infty \quad (S \propto \ln E, \; E = \tfrac{3}{2}Nk_BT)$$

The 3rd law originates from QM (but it cannot be proved for all systems, see Nolting p.112, $C_V = T\frac{\partial S}{\partial T}|_V$)

In QM one finds that for small E or small T respectively the number of states becomes so small due to Fermi/Bose statistics that $\lim_{T\to 0} S = 0$ ($T \to 0 \Leftrightarrow f \to 0$, see example)

4.3 Canonical ensemble

Effective theory for:

- system in thermal contact with heatbath
- isolated total system in thermodynamical equilibrium, microcanonical

$\Rightarrow\ \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}} = \frac{1}{Z} \sum_n e^{-\beta E_n} |n\rangle\langle n| \quad (\hat{H}|n\rangle = E_n|n\rangle,\ \sum_n |n\rangle\langle n| = 1)$

$Z = \mathrm{Tr} e^{-\beta \hat{H}} = \sum_n e^{-\beta E_n} = e^{-\beta F}$ canonical partition function

$F(T, V, N)$ free energy $\qquad \beta = 1/k_B T$

$S = -\frac{\partial F}{\partial T}, \quad P = -\frac{\partial F}{\partial V}, \quad \mu = \frac{\partial F}{\partial N}$

Example: N distinguishable harmonic oscillators of the same frequency ω

$\hat{H} = \sum_{i=1}^N \hbar\omega (a_i^+ a_i + 1/2)$ $\qquad$ (see also appendix C)

$$\begin{aligned}
Z &= \sum_{\{n_1,\ldots,n_N=0,\ldots,\infty\}} e^{-\beta E_{n_1,\ldots,n_N}} = \sum_{\{\ldots\}} e^{-\beta\hbar\omega \sum_{i=1}^N (n_i+1/2)} \\
&= \left(\sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} \right)^N = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^N = \left(\frac{1}{2\sinh(\beta\hbar\omega/2)} \right)^N = e^{-\beta F}
\end{aligned}$$

$$F = \frac{1}{\beta} N \ln[2\sinh(\beta\hbar\omega/2)]$$

$$\begin{aligned}
U &= \langle \hat{H} \rangle = \mathrm{Tr}(\hat{\rho}\hat{H}) = \sum_{\{\ldots\}} \langle n_1, \ldots, n_N | \hat{\rho}\hat{H} | n_1, \ldots, n_N \rangle \\
&= \frac{1}{Z} \sum_{\{\ldots\}} E_{n_1,\ldots,n_N} e^{-\beta E_{n_1,\ldots,n_N}} = -\frac{\partial}{\partial\beta} \ln Z \\
&= N \frac{\partial}{\partial\beta} \ln[2\sinh(\frac{\beta\hbar\omega}{2})] = N \frac{\cosh(\frac{\beta\hbar\omega}{2})}{\sinh(\frac{\beta\hbar\omega}{2})} \frac{\hbar\omega}{2} = N \coth\left(\frac{\beta\hbar\omega}{2}\right) \frac{\hbar\omega}{2}
\end{aligned}$$

Defining $U = \hbar\omega(\frac{N}{2} + \bar{N}_0) \rightarrow \frac{U}{N} = \hbar\omega(\frac{1}{2} + \bar{f}) \quad (\bar{f} = \frac{\bar{N}_0}{N})$

$$\coth\left(\frac{\beta\hbar\omega}{2}\right)\frac{\hbar\omega}{2} = \hbar\omega(\tfrac{1}{2}+\bar{f}) \Leftrightarrow \coth\left(\frac{\beta\hbar\omega}{2}\right) = 1+2\bar{f} = \frac{e^{\beta\hbar\omega/2}+e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}}$$

$$1+2\bar{f} = \frac{e^{\beta\hbar\omega}+1}{e^{\beta\hbar\omega}-1} \Rightarrow e^{\beta\hbar\omega}+1 = (1+2\bar{f})(e^{\beta\hbar\omega}-1)$$

$$e^{\beta\hbar\omega}2\bar{f} = 2+2\bar{f} \Rightarrow e^{\beta\hbar\omega} = 1+1/\bar{f}$$

→ identical result as microcanonical
(there f given → β computed, here reverse)

fluctuations of $\bar{f}$: $\dfrac{\sqrt{\langle(\hat{H}-U)^2\rangle}}{U} \sim \dfrac{1}{\sqrt{N}}$
(like classical, $C_V = k_B\beta^2\langle(\hat{H}-U)^2\rangle = \dfrac{\partial U}{\partial T} \propto N$)

4.4 Grand-canonical ensemble

We need particle number operator $\hat{N}$

Definition of $\hat{N}$, Hilbert space → section 5

$$[\hat{H},\hat{N}] = 0 \quad \Rightarrow \quad \text{eigenstates } |E_k, N\rangle$$

$$\hat{H}|E_k,N\rangle = E_k(N)|E_k,N\rangle \qquad \hat{N}|E_k,N\rangle = N|E_k,N\rangle$$

- microcanonical total system $\sum_1 + \sum_2$, $|\sum_1| << |\sum_2|$
- energy and particle exchange
- large system ("bath") defines T and μ

Result: density matrix of the grand-canonical ensemble ($\beta = 1/k_BT$)

$$\begin{aligned}\hat{\rho} &\propto \sum_N\sum_k e^{-\beta(E_k(N)-\mu N)}|E_k,N\rangle\langle E_k,N| \\ &= e^{-\beta(\hat{H}-\mu\hat{N})}\sum_N\sum_k |E_k,N\rangle\langle E_k,N| = \frac{1}{\Xi(T,V,\mu)}e^{-\beta(\hat{H}-\mu\hat{N})}\end{aligned}$$

(k range can depend on N; $\{|E_k,N\rangle\}$ ONB)

Relation to canonical ensemble:

$$\begin{aligned}\Xi(T,V,\mu) &= \sum_N \sum_k \langle E_k, N| e^{-\beta(\hat{H}-\mu\hat{N})} |E_k, N\rangle \\ &= \sum_N \sum_k e^{-\beta(E_k(N)-\mu N)} \quad \text{grand-canonical partition function} \\ &= \sum_{N=0}^{\infty} z^N \sum_k e^{-\beta E_k(N)} = \sum_{N=0}^{\infty} z^N Z(T,V,N)\end{aligned}$$

$z = e^{\beta\mu}$ fugacity; Z: canonical partition function

Analogously:

$$\begin{aligned}\langle \hat{O} \rangle_G &= \text{Tr}(\,\hat{\rho}\hat{O}) = \frac{1}{\Xi} \sum_N z^N \underbrace{\sum_k e^{-\beta E_k(N)} \langle E_k, N|\hat{O}|E_k, N\rangle}_{\underset{\text{(canonical)}}{\langle \hat{O}\rangle_{K,N}}\; Z(T,V,N)} \\ &= \frac{\sum_N z^N Z(T,V,N) \langle \hat{O}\rangle_{K,N}}{\sum_N z^N Z(T,V,N)}\end{aligned}$$

Special case: $\langle \hat{N} \rangle_G = \frac{1}{\beta} \frac{\partial}{\partial\mu} \ln \Xi|_{T,V} = z \frac{\partial}{\partial z} \ln \Xi$

It can be shown: $\frac{\sqrt{\langle (\hat{N} - \langle \hat{N}\rangle)^2\rangle_G}}{\langle \hat{N} \rangle_G} \sim N^{-1/2} \overset{N\to\infty}{\longrightarrow} 0$

Therefore $N = \langle \hat{N} \rangle$ dominates the sum

$$\Xi(T,V,\mu) \approx \underbrace{e^{\beta\mu\langle\hat{N}\rangle}}_{z^{\langle\hat{N}\rangle}} Z(T,V,\langle\hat{N}\rangle) \quad \text{on the right: } \langle\hat{N}\rangle = f(T,V,\mu)$$

in principle can be solved for $\mu = \mu(T,V,\langle\hat{N}\rangle)$

Grand-canonical and canonical (and microcanonical) ensembles are equivalent in TD limit.

Finally, like classical theory: $\Xi = e^{-\beta\Omega}$; Ω: grand-canonical potential

$$\left.\frac{\partial\Omega}{\partial T}\right|_{V,\mu} = -S, \quad \left.\frac{\partial\Omega}{\partial V}\right|_{T,\mu} = -P, \quad \left.\frac{\partial\Omega}{\partial \mu}\right|_{T,V} = -N$$

4.5 Extremal properties of entropy S, free energy F and grand-canonical potential Ω

4.5.1 Entropy and statistical operator

The relation is $\boxed{S = -k_B \mathrm{Tr}(\hat{\rho} \ln \hat{\rho}) = -k_B \langle \ln \hat{\rho} \rangle}$ for $\hat{\rho} = \hat{\rho}_M,\ \hat{\rho}_K,\ \hat{\rho}_G$,

M: microcanonical, K: canonical, G: grand-canonical ensemble

$S \geqslant 0$, since eigenvalues of $\hat{\rho}$ are in $[0,1]$, probabilities $\Rightarrow -\ln \hat{\rho} > 0$

M: $\hat{\rho}_M = \dfrac{1}{\Gamma(E)} \sum_{E<E_m<E+\Delta} |E_m\rangle\langle E_m|$

$$\hat{\rho}_M |E_n\rangle = \begin{cases} \dfrac{1}{\Gamma(E)} |E_n\rangle, & \text{if } E < E_n < E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

$$\begin{aligned} -\langle \ln \hat{\rho}_M \rangle_M &= -\sum_n \langle E_n | \hat{\rho}_M \ln \hat{\rho}_M | E_n \rangle \\ &= -\frac{1}{\Gamma(E)} \sum_{E<E_m<E+\Delta} \ln\left(\frac{1}{\Gamma(E)}\right) = \ln(\Gamma(E)) = \frac{1}{k_B} S \end{aligned}$$

K: $\hat{\rho}_K = \dfrac{1}{Z} e^{-\beta \hat{H}} = e^{-\beta(\hat{H}-F)} \qquad (Z = e^{-\beta F})$

$$\begin{aligned} -\langle \hat{\rho}_K \rangle_K &= \beta(\langle \hat{H} \rangle_K - F) \qquad (F = U - TS) \\ &= \beta(U - F) = \beta T S = \frac{1}{k_B} S \end{aligned}$$

G: $\hat{\rho}_G = \dfrac{1}{\Xi} e^{-\beta(\hat{H}-\mu\hat{N})} = e^{-\beta(\hat{H}-\mu\hat{N}-\Omega)} \qquad (\Xi = e^{-\beta\Omega})$

$$\begin{aligned} -\langle \ln \hat{\rho}_G \rangle_G &= \beta(\langle \hat{H} - \mu\hat{N} \rangle_G - \Omega) = \beta(U - \mu N - \Omega) \\ &= \beta(U - F) = \frac{1}{k_B} S \quad (\Omega = F - \mu N) \end{aligned}$$

- general definition of S from $\hat{\rho}$
- holds for any density matrix also outside of equilibrium, statistical or Gibbs entropy

4.5.2 Boltzmann *H*-function (Eta)

$\hat\rho$: density matrix, equilibrium (M, K, G)

$\hat\rho'$: arbitrary mixed state, in general not in equilibrium, in general $\hat\rho' = \hat\rho'(t)$

Both statistical operators are hermitian, normalized:

$\hat\rho' = \sum_n \rho'_n |\rho'_n\rangle\langle\rho'_n| \quad 0 \leqslant \rho_n \leqslant 1, \quad \{|\rho'_n\rangle\}$ ONB:

$\hat\rho|\rho'_n\rangle = \rho'_n|\rho'_n\rangle, \quad \mathrm{Tr}\,\hat\rho' = 1, \quad \hat\rho'^{+} = \hat\rho'$, etc.

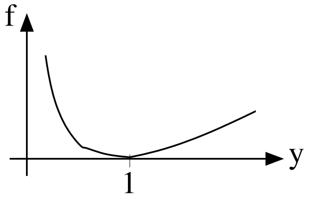
similarly: $\hat\rho = \sum_n \rho_n |\rho_n\rangle\langle\rho_n|$

Definition of *H*-function:

$$\begin{aligned}
H &= \mathrm{Tr}[\,\hat\rho'(\ln\,\hat\rho - \ln\,\hat\rho')] = \sum_m \langle\rho'_m|[\,\hat\rho'(\ln\,\hat\rho - \ln\,\hat\rho')]|\rho'_m\rangle \\
&= \sum_m \rho'_m(\langle\rho'_m|\ln\,\hat\rho|\rho'_m\rangle - \ln\rho'_m \underbrace{\langle\rho'_m|\rho'_m\rangle}_{=1}) \\
&= \sum_{m,n} \rho'_m(\langle\rho'_m|\underbrace{\ln\,\hat\rho}_{=\ln\rho_n}|\rho_n\rangle\langle\rho_n|\rho'_m\rangle - \ln\rho'_m \underbrace{|\langle\rho'_m|\rho_n\rangle|^2}_{=\langle\rho'_m|\rho_n\rangle\langle\rho_n|\rho'_m\rangle}) \\
&= \sum_{m,n} \rho'_m \ln\frac{\rho_n}{\rho'_m}|\langle\rho'_m|\rho_n\rangle|^2
\end{aligned}$$

Inequality: $y - 1 \geqslant \ln y$ for $y \in [0, \infty)$

proof:
$$\begin{aligned}
&f(y) = y - 1 - \ln y \\
&\left.\begin{aligned} &f(1) = 0 \\ &f'(1) = 0 \\ &f''(y) = 1/y^2 \end{aligned}\right\} \text{minimum at } y = 1
\end{aligned}$$



$$\begin{aligned}
H &\leqslant \sum_{m,n} \rho'_m(\frac{\rho_n}{\rho'_m} - 1)|\langle\rho'_m|\rho_n\rangle|^2 = \sum_{m,n}(\rho_n - \rho'_m)|\langle\rho'_m|\rho_n\rangle|^2 \\
&= \sum_n \rho_n \underbrace{\sum_m |\langle\rho'_m|\rho_n\rangle|^2}_{=1} - \sum_m \rho'_m \underbrace{\sum_n |\langle\rho'_m|\rho_n\rangle|^2}_{=1}
\end{aligned}$$

$$\begin{aligned} &= \sum_m (\rho_m - \rho'_m) = \mathrm{Tr}\,\hat\rho - \mathrm{Tr}\,\hat\rho' = 0 \\ 0 &\geqslant H = \mathrm{Tr}[\,\hat\rho'(\ln\,\hat\rho - \ln\,\hat\rho')] \end{aligned}$$

4.5.3 Statistical entropy

$$\begin{aligned} S &= -k_B \mathrm{Tr}(\,\hat\rho \ln\,\hat\rho) \qquad \hat\rho = \,\hat\rho_M \text{ microcanonial in } [E, E+\Delta] \\ S' &= -k_B \mathrm{Tr}(\,\hat\rho' \ln\,\hat\rho') \qquad \hat\rho'|E_k\rangle = 0 \text{ if } E_k \notin [E, E+\Delta] \\ k_B H &= S' + k_B \mathrm{Tr}(\,\hat\rho' \ln\,\hat\rho) \end{aligned}$$

$$\begin{aligned} k_B \mathrm{Tr}(\,\hat\rho' \ln\,\hat\rho) &= k_B \sum_n \langle \rho_n|\,\hat\rho'|\rho_n\rangle \underbrace{\ln\rho_n}_{=-\ln\Gamma(E)} \\ &= k_B \underbrace{\mathrm{Tr}\,\hat\rho'}_{=1}(-\ln\Gamma(E)) = -S \end{aligned}$$

- $\rho_n \in \{\emptyset, 1/\Gamma(E)\}$
- if $\rho_n = 0 \Rightarrow\, \hat\rho'|\rho_n\rangle = 0$ because of assumption
  $\hat\rho'$: not equilibrium, but constrained on the energy shell

$\Rightarrow k_B H = S' - S \leqslant 0 \Rightarrow S' \leqslant S \Rightarrow dS \geqslant 0$ (2nd law of TD)

When $\hat\rho'(t) \underset{\substack{\text{irreversible}\\\text{process}}}{\overset{t\to\infty}{\longrightarrow}} \hat\rho_M$ (energy $\in [E, E+\Delta]$) the statistical entropy never decreases.

4.5.4 Free energy

Now: $\hat\rho = \,\hat\rho_K = \frac{1}{Z} e^{-\beta\hat H} \to \ln\,\hat\rho_K = -\ln Z - \beta\hat H$

$$\begin{aligned} k_B \mathrm{Tr}(\,\hat\rho' \ln\,\hat\rho) &= k_B(-\ln Z - \beta \mathrm{Tr}(\,\hat\rho'\hat H)) \\ &= -k_B \ln Z - \frac{1}{T}U' = \frac{1}{T}(F - U') \qquad (\ln Z = -\beta F) \end{aligned}$$

$$\begin{aligned} k_B H &= k_B \mathrm{Tr}(\,\hat\rho' \ln\,\hat\rho) - k_B \mathrm{Tr}(\,\hat\rho' \ln\,\hat\rho') \\ &= \frac{1}{T}(F - U') + S' = \frac{1}{T}(F - F') \leqslant 0 \qquad (F = U - TS) \end{aligned}$$

$\Rightarrow F \leqslant F', \quad dF \leqslant 0$

For processes at T = const., V = const., N = const., the free energy does not increase $\Rightarrow F$ minimal in equilibrium.

We used: temperature T is defined also for $\hat{\rho}'$ system, which is in contact with heatbath as well, but not (yet) in TD equilibrium.

4.5.5 Grand-canonical potential

Analogously: $k_B H = S' + \frac{1}{T}(\Omega - \Omega') - S' \leqslant 0 \Rightarrow \Omega \leqslant \Omega',\ d\Omega \leqslant 0$

For processes at T = const., V = const., μ = const., the grand-canonical potential does not increase $\Rightarrow \Omega$ minimal in equilibrium.

5 Quantum gases

5.1 Foundations

5.1.1 Identical particles

a) State space

$\mathcal{H}_1$: Hilbert space for one particle

$|\Psi_1\rangle = \int d^3r |\vec{r}\rangle \Psi_1(\vec{r}) \quad \in \quad \mathcal{H}_1$ or

$|\Psi_1\rangle = \sum_n c_n |E_n\rangle$ with $\hat{H}_1 |E_n\rangle = E_n |E_n\rangle$

State space for N particles: tensor product

$\mathcal{H}_N = \mathcal{H}_1 \otimes \mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_1$ (N factors)

Basis: $\{|E_{n_1}\rangle |E_{n_2}\rangle \ldots |E_{n_N}\rangle \equiv |E_{n_1}\rangle \otimes |E_{n_2}\rangle \otimes \ldots \otimes |E_{n_N}\rangle\}$

or $\{|\vec{r}_1\rangle |\vec{r}_2\rangle \ldots |\vec{r}_N\rangle \equiv |\vec{r}_1\rangle \otimes |\vec{r}_2\rangle \otimes \ldots \otimes |\vec{r}_N\rangle\}$

N-particle state in position space basis:

$$|\Psi\rangle = \int d^3r_1 \dots d^3r_N |\vec{r}_1\rangle|\vec{r}_2\rangle \dots |\vec{r}_N\rangle \underbrace{\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}_{\text{N-particle wave function}}$$

Symmetric observable:

Example: total energy (without interactions)

$$\hat{H}_N = \hat{H}_1 \otimes 1 \otimes \dots \otimes 1 + 1 \otimes \hat{H}_1 \otimes 1 \otimes \dots \otimes 1 + \dots + 1 \otimes 1 \otimes \dots \otimes \hat{H}_1$$

each term has N factors!

$$\begin{aligned} \hat{H}_N|E_{n_1}\rangle|E_{n_2}\rangle \dots |E_{n_N}\rangle &= (\hat{H}_1|E_{n_1}\rangle) \dots |E_{n_N}\rangle + \dots + |E_{n_1}\rangle \dots (\hat{H}_1|E_{n_N}\rangle) \\ &= (E_{n_1} + E_{n_2} + \dots + E_{n_N})|E_{n_1}\rangle|E_{n_2}\rangle \dots |E_{n_N}\rangle \end{aligned}$$

In nature for identical particles there is no way to distinguish for example states $|\vec{r}_1\rangle|\vec{r}_2\rangle$ and $|\vec{r}_2\rangle|\vec{r}_1\rangle$

⇒ observables for identical particles have to be symmetric under permutation of particle indices

⇒ in $\mathcal{H}_N$ there exist operators which represent these permutations and commute with all observables

Permutations can be built from transpositions:

$$\hat{T}_{ij}(1\;2 \dots i \dots j \dots N) = (1\;2 \dots j \dots i \dots N)$$

⇒ representation $\hat{T}_{ij}$ in $\mathcal{H}_N$:

$$\hat{T}_{ij}|\vec{r}_1 \dots \vec{r}_i \dots \vec{r}_j \dots \vec{r}_N\rangle = |\vec{r}_1 \dots \vec{r}_j \dots \vec{r}_i \dots \vec{r}_N\rangle$$

For example $N = 2$:

$$\begin{aligned} \hat{T}_{12}|\Psi\rangle = \hat{T}_{12} \int d^3r_1 d^3r_2 |\vec{r}_1\rangle|\vec{r}_2\rangle\Psi(\vec{r}_1\vec{r}_2) &= \int d^3r_1 d^3r_2 |\vec{r}_2\rangle|\vec{r}_1\rangle\Psi(\vec{r}_1\vec{r}_2) \\ \dots\text{change of variables}\dots &= \int d^3r_1 d^3r_2 |\vec{r}_1\rangle|\vec{r}_2\rangle\Psi(\vec{r}_2\vec{r}_1) \end{aligned}$$

obviously, $\hat{T}_{12}^2 = 1$; $\hat{T}_{12}^\dagger = \hat{T}_{12}$ hermitian

$\Rightarrow$ eigenvalues of $\hat{T}_{ij}$ in $\mathcal{H}_N$: $\hat{T}_{ij}|\Psi\rangle = \lambda|\Psi\rangle$ with $\lambda^2 = 1$, $\lambda = \pm 1$

for a symmetric observable $\hat{F}$: $[\hat{F}, \hat{T}_{ij}] = 0$

Bosons, fermions:

- all observables are symmetric
- subspaces of $\mathcal{H}_N = \mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_1$, where
  $\hat{T}_{ijj}|\Psi\rangle = |\Psi\rangle$ or $\hat{T}_{ijj}|\Psi\rangle = -|\Psi\rangle$
  for a general permutation π:
  unitary representation $P(\pi)|\Psi\rangle = \lambda|\Psi\rangle,\ \lambda \in \mathbb{C}$
  $\Rightarrow \mathcal{H}_{N\pm} = \{|\Psi\rangle \in \mathcal{H}_N$ with $\hat{T}_{ij}|\Psi\rangle = \pm|\Psi\rangle\}$
  symmetric observable $\hat{F}$: $|\Psi\rangle \in \mathcal{H}_{N\pm} \ \Rightarrow\ \hat{F}|\Psi\rangle \in \mathcal{H}_{N\pm}$
- N bosons: state space $\mathcal{H}_{N+}$
- N fermions: state space $\mathcal{H}_{N-}$
- spin-statistics theorem of relativistic quantum field theory (Wolfgang Pauli, 1940):
  - bosons ↔ integer spin (photon, mesons, Higgs,...)
  - fermions ↔ half-integer spin (e^-, p, n, ν all 1/2)

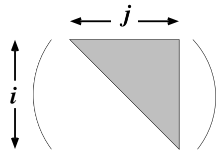
$|\Psi\rangle = \int d^3r_1 \ldots d^3r_N |\vec{r}_1\rangle|\vec{r}_2\rangle \ldots |\vec{r}_N\rangle \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ is in $\mathcal{H}_{N+}$ ($\mathcal{H}_{N-}$) if $\Psi(\vec{r}_1, \ldots, \vec{r}_N)$ is symmetric (anti-symmetric) with respect to its arguments $\vec{r}_1, \ldots, \vec{r}_N$.

$\mathcal{H}_{N\pm}$ are strictly "smaller" subspaces than $\mathcal{H}_N$:

Example: $\mathcal{H}_1$ with basis $\{|1\rangle, \ldots, |k\rangle\}$ of finite dimension k

$\mathcal{H}_2 = \mathcal{H}_1 \otimes \mathcal{H}_1$ has dimension k^2

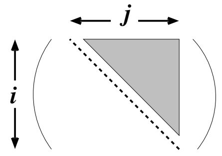
$\mathcal{H}_{2+}$



basis $\{\frac{1}{\sqrt{2}} * (|i\rangle|j\rangle + (|i\rangle|j\rangle)\}$

$\dim\mathcal{H}_{2+} = \dfrac{k(k+1)}{2}$

$\mathcal{H}_{2-}$



basis $\{\frac{1}{\sqrt{2}} * (|i\rangle|j\rangle - (|j\rangle|i\rangle)\}$, no states with $i = j$

$\dim\mathcal{H}_{2-} = \dfrac{k(k-1)}{2}$

In general: $\dim\mathcal{H}_N = k^N$ numerical example: $k = 10, N = 5 : 10000$

$$\dim\mathcal{H}_{N+} = \begin{pmatrix} N+k-1 \\ N \end{pmatrix} \qquad 2002$$

$$\dim\mathcal{H}_{N-} = \begin{pmatrix} k \\ N \end{pmatrix} \qquad 252$$

b) Bases of $\mathcal{H}_{N+}$, $\mathcal{H}_{N-}$

$\{|1\rangle, |2\rangle, \ldots\} = \{|\alpha\rangle,\ \alpha = 1, 2 \ldots\}$ orthonormal basis of $\mathcal{H}_1$

$|\alpha_1\alpha_2\ldots\alpha_N\rangle = |\alpha_1\rangle|\alpha_2\rangle\ldots|\alpha_N\rangle$ is a state vector in $\mathcal{H}_N$, but in general not in $\mathcal{H}_{N\pm}$ if it is not an eigenstate of $\hat{T}_{ij}$

Projection onto $\mathcal{H}_{N+}$:

$|\alpha_1\alpha_2\ldots\alpha_N\rangle_+ = C\sum_{\pi\in S_N} |\alpha_{\pi(1)}\rangle|\alpha_{\pi(2)}\rangle\ldots|\alpha_{\pi(N)}\rangle$

S_N ...permutation group

Example: $N = 3 :$ $|\alpha_1\rangle, |\alpha_2\rangle, |\alpha_3\rangle$ arbitrary one-particle states

$$\begin{aligned} |\alpha_1\alpha_2\alpha_3\rangle_+ \ = \ & C\{|\alpha_1\rangle|\alpha_2\rangle|\alpha_3\rangle + |\alpha_2\rangle|\alpha_3\rangle|\alpha_1\rangle + |\alpha_3\rangle|\alpha_1\rangle|\alpha_2\rangle + \\ & |\alpha_2\rangle|\alpha_1\rangle|\alpha_3\rangle + |\alpha_1\rangle|\alpha_3\rangle|\alpha_2\rangle + |\alpha_3\rangle|\alpha_2\rangle|\alpha_1\rangle\} \end{aligned}$$

$\hat{T}_{12}|\alpha_1\alpha_2\alpha_3\rangle_+ = |\alpha_1\alpha_2\alpha_3\rangle_+$ etc.

in general: $|\alpha_1\alpha_2\ldots\alpha_N\rangle_+$ is invariant under all permutations of the one-particle indices $\{\alpha_1,\alpha_2,\ldots,\alpha_N\}$

<u>Projection onto $\mathcal{H}_{N-}$:</u>

$$|\alpha_1\alpha_2\ldots\alpha_N\rangle_- = C\sum_{\pi\in S_N}\mathrm{sig}(\pi)|\alpha_{\pi(1)}\rangle|\alpha_{\pi(2)}\rangle\ldots|\alpha_{\pi(N)}\rangle$$

$\mathrm{sig}(\pi)=+1(-1)$ if π is composed of an even(odd) number of transpositions

decomposition of π in transpositions is not unique, but $\mathrm{sig}(\pi)$ is unique (→ theory of permutation group S_N)

Now $\hat{T}_{ij}|\alpha_1\ldots\alpha_N\rangle_- = -|\alpha_1\ldots\alpha_N\rangle_-$

Example: $N=3$:

$$\begin{aligned}|\alpha_1\alpha_2\alpha_3\rangle_- &= C\{|\alpha_1\rangle|\alpha_2\rangle|\alpha_3\rangle+|\alpha_2\rangle|\alpha_3\rangle|\alpha_1\rangle+|\alpha_3\rangle|\alpha_1\rangle|\alpha_2\rangle\\ &\quad -|\alpha_2\rangle|\alpha_1\rangle|\alpha_3\rangle-|\alpha_1\rangle|\alpha_3\rangle|\alpha_2\rangle-|\alpha_3\rangle|\alpha_2\rangle|\alpha_1\rangle\}\end{aligned}$$

$\hat{T}_{12}|\alpha_1\alpha_2\alpha_3\rangle_- = -|\alpha_1\alpha_2\alpha_3\rangle_-$ etc.

⇒ in particular: $|\alpha_1\alpha_2\alpha_3\rangle_- = 0$ if $\alpha_1=\alpha_2$ etc.

in general: $|\alpha_1\ldots\alpha_N\rangle_- \neq 0$ only when all indices $\{\alpha_i\}$ are different

Slater determinant:

$$\det M = \begin{vmatrix} M_{11} & \ldots & M_{1N} \\ & & \\ M_{N1} & \ldots & M_{NN}\end{vmatrix} = \sum_{\pi\in S_N}\mathrm{sig}(\pi)M_{\pi(1)1}M_{\pi(2)2}\ldots M_{\pi(N)N}$$

$$|\alpha_1\ldots\alpha_N\rangle_- = C\begin{vmatrix} |\alpha_1\rangle & |\alpha_1\rangle & \ldots & |\alpha_1\rangle \\ |\alpha_2\rangle & |\alpha_2\rangle & \ldots & |\alpha_2\rangle \\ & & & \\ |\alpha_N\rangle & |\alpha_N\rangle & \ldots & |\alpha_N\rangle \end{vmatrix}\downarrow \text{index of the state}$$

$\rightarrow$ position in the tensor product

Consequences:

- $|\alpha_1 \ldots \alpha_N\rangle_\pm$ do not depend on the order of the indices $\{\alpha_1, \alpha_2, \ldots, \alpha_N\}$ (except for the sign for fermions → but the physical state is the same irrespectively of the overall sign)

- in $|\alpha_1 \ldots \alpha_N\rangle_-$ each α_i can appear at most once (Pauli principle for fermions)

- after normalization: $\{|\alpha_1 \ldots \alpha_N\rangle_\pm\}$ complete orthonormal set in $\mathcal{H}_\pm$
  Example: $N = 3$, $|\alpha_1\alpha_2\alpha_3\rangle_\pm$ (see above), if $|\alpha_i\rangle \neq |\alpha_j\rangle \Rightarrow$
  ${}_\pm\langle\alpha_1\alpha_2\alpha_3|\alpha_1\alpha_2\alpha_3\rangle_\pm \overset{!}{=} 1 = |C|^2\{\langle\alpha_1\alpha_2\alpha_3|+\ldots\}\{|\alpha_1\alpha_2\alpha_3\rangle+\ldots\} = 6|C|^2$
  $\Rightarrow C = 1/\sqrt{6} = 1/\sqrt{3!}$

- everything can be repeated for $|\alpha\rangle \to |\vec{r}\rangle$

c) Fock space

Occupation numbers:

Instead of $\{\alpha_1\alpha_2 \ldots \alpha_N\}$ we specify how many times each one-particle state $|\alpha\rangle$ appears in the (anti-)symmetric tensor product:

$$|\alpha_1\alpha_2 \ldots \alpha_N\rangle_\pm = |n_1 n_2 n_3 \underset{\substack{\nwarrow \\ \text{in general } \infty\text{-many}}}{\ldots}\rangle_\pm \in \mathcal{H}_{N\pm}, \quad N = \textstyle\sum_\alpha n_\alpha$$

Example: $N = 3$, $|\alpha_i\rangle \neq |\alpha_j\rangle$

$$|\alpha_1\alpha_2\alpha_3\rangle_\pm = |00\ldots\underset{\substack{\uparrow \\ \text{position of } \alpha_1}}{1}\ldots 0\ldots\underset{\substack{\uparrow \\ \alpha_2}}{1}\ldots 0\ldots\underset{\substack{\uparrow \\ \alpha_3}}{1}\ldots 0\ldots\rangle_\pm$$

case $-$ (fermions): $n_\alpha = 0, 1$

case $+$ (bosons): $n_\alpha = 0, 1, 2, 3, \ldots$

State space with arbitrary number of particles: Fock space

$\mathcal{F}_+ \;=\; \mathcal{H}_0 \;\oplus\; \mathcal{H}_1 \;\oplus\; \mathcal{H}_{2+} \;\oplus\; \mathcal{H}_{3+} \;\oplus\; \dots$

$\oplus$: direct sum: state has components in each $\mathcal{H}_{N\pm}$

$\mathcal{H}_0$: one-dimensional space $|v\rangle = |00\dots0\dots\rangle_+$, all $n_\alpha = 0$, "empty" state, Fock vacuum, not the zero vector!

$\mathcal{H}_1$: original one-particle space

Example of direct sum:

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \in \mathbb{R}^2 \quad \begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix} \in \mathbb{R}^3 \quad \to \quad \begin{pmatrix} x_1 \\ x_2 \\ y_1 \\ y_2 \\ y_3 \end{pmatrix} \in \mathbb{R}^2 \otimes \mathbb{R}^3 = \mathbb{R}^5$$

$$\begin{aligned} \underline{\mathcal{F}_+ \ni |B\rangle} \;&=\; c^{(0)}|v\rangle + \sum_\alpha c^{(1)}_\alpha |\alpha\rangle + \frac{1}{2}\sum_{\alpha,\beta} c^{(2)}_{\alpha\beta}|\alpha\beta\rangle_+ + \frac{1}{3!}\sum_{\alpha,\beta,\gamma} c^{(3)}_{\alpha\beta\gamma}|\alpha\beta\gamma\rangle_+ + \dots \\ &=\; \sum_{\{n_\alpha=0,1,2,\dots\}} b(n_1, \underset{\nwarrow \text{different } N=\sum_\alpha n_\alpha \text{ contribute}}{n_2}, n_3,\dots)|n_1 n_2 n_3\dots\rangle_+ \end{aligned}$$

$c^{(2)}_{\alpha\beta}$ and $c^{(3)}_{\alpha\beta\gamma}$ are symmetric

$\{b(n_1,n_2,n_3,\dots)\} \leftrightarrow \{c^{(0)}, c^{(1)}_\alpha, c^{(2)}_{\alpha\beta}, \dots\}$

Example: $|\underset{n_1}{1}\,\underset{n_2}{1}\,00\dots0\dots\rangle_+ = c(|1\rangle|2\rangle + |2\rangle|1\rangle) \in \mathcal{H}_{2+}$

$|200\dots0\dots\rangle_+ = |1\rangle|1\rangle$

$$\begin{aligned} \big||1100\dots0\dots\rangle\big|^2 \;&=\; |c|^2(\langle1|\langle2| + \langle2|\langle1|)(|1\rangle|2\rangle + |2\rangle|1\rangle) \\ &=\; 2|c|^2 \Rightarrow \text{ choose } c = 1/\sqrt{2} \end{aligned}$$

Normalization in general:

$|n_1 n_2\dots\rangle_+ \in \mathcal{H}_{N=\sum n_\alpha +}$ should be normalized

$|n_1 n_2 \ldots\rangle_+ = c \sum_{\pi \in S_N} |\alpha_{\pi(1)}\rangle |\alpha_{\pi(2)}\rangle \ldots |\alpha_{\pi(N)}\rangle$

where the index set $\{\alpha_1 \alpha_2 \ldots \alpha_N\}$, which is permuted contains: n_1 times $\alpha = 1$, n_2 times $\alpha = 2$, etc.

$$||n_1 n_2 \ldots\rangle_+|^2 = |c|^2 N! \underbrace{\sum_{\pi \in S_N} \langle\alpha_1|\alpha_{\pi(1)}\rangle\langle\alpha_2|\alpha_{\pi(2)}\rangle \ldots \langle\alpha_N|\alpha_{\pi(N)}\rangle}_{n_1! n_2! n_3! \ldots} \Rightarrow c = (N! \textstyle\prod_\alpha n_\alpha!)^{-1/2}$$

$\underline{\mathcal{F}_- \ni |F\rangle} = \sum_{\{n_\alpha = 0,1\}} f(n_1, n_2, n_3, \ldots) |n_1 n_2 n_3 \ldots\rangle_-$

$$|n_1 n_2 n_3 \ldots\rangle_- = c \sum_{\substack{\pi \in S_N \\ N = \sum_\alpha n_\alpha}} \mathrm{sig}(\pi) |\alpha_{\pi(1)}\rangle |\alpha_{\pi(2)}\rangle \ldots |\alpha_{\pi(N)}\rangle$$

$$||n_1 n_2 n_3 \ldots\rangle_-|^2 = 1 \Rightarrow c = (N!)^{-1/2} \quad (0! = 1,\ 1! = 1)$$

here also: Fock vacuum $|00 \ldots 0 \ldots\rangle_- \in \mathcal{F}_-$ (all $n_\alpha = 0$)

Complete orthonormal set in $\mathcal{F}_+$ resp. $\mathcal{F}_-$:

$\{|n_1 n_2 \ldots\rangle_\pm\}$ with ${}_\pm\langle m_1 m_2 \ldots | n_1 n_2 \ldots\rangle_\pm = \prod_\alpha \delta_{m_\alpha, n_\alpha}$

d) Creation and annihilation operators

Creation operator $\hat{a}^+_\alpha$:

- adds the one-particle state $|\alpha\rangle$
- position in tensor product irrelevant (possibly up to a phase) because of (anti-)symmetrization
- augments $n_\alpha \to n_\alpha + 1$, therefore: $\hat{a}^+_\alpha :\ \mathcal{H}_{N\pm} \to \mathcal{H}_{N+1\pm}$ resp. $\mathcal{F}_\pm \to \mathcal{F}_\pm$

case $\mathcal{F}_+$:

$$\hat{a}^+_\alpha |n_1 \ldots n_{\alpha-1} n_\alpha n_{\alpha+1} \ldots\rangle_+ = \sqrt{n_\alpha + 1} |n_1 \ldots n_{\alpha-1} (n_\alpha + 1) n_{\alpha+1} \ldots\rangle_+$$

→ all matrix elements in $\mathcal{F}_+$ are determined

→ normalization $\sqrt{n_\alpha + 1}$ like the harmonic oscillator

$${}_+\langle m_1 m_2 \ldots | \hat{a}_\alpha^+ | n_1 n_2 \ldots \rangle_+ = \sqrt{n_\alpha + 1}\,\delta_{m_\alpha, n_\alpha + 1} \prod_{\beta \neq \alpha} \delta_{m_\beta n_\beta}$$

<u>adjoint operator</u>:

in general: $\langle \phi | \hat{A} | \chi \rangle = (\langle \chi | \hat{A}^+ | \phi \rangle)^*$

$$\Rightarrow\ {}_+\langle m_1 m_2 \ldots | \hat{a}_\alpha | n_1 n_2 \ldots \rangle_+ = \underbrace{\sqrt{m_\alpha + 1}\,\delta_{n_\alpha, m_\alpha + 1}}_{= \sqrt{n_\alpha}\,\delta_{m_\alpha, n_\alpha - 1}} \prod_{\beta \neq \alpha} \delta_{n_\beta m_\beta}$$

$$\Rightarrow \hat{a}_\alpha | n_1 \ldots n_{\alpha-1} n_\alpha n_{\alpha+1} \ldots \rangle_+ = \sqrt{n_\alpha} | n_1 \ldots n_{\alpha-1} (n_\alpha - 1) n_{\alpha+1} \ldots \rangle_+$$

- $\hat{a}_\alpha$ eliminates $|\alpha\rangle$, $n_\alpha \to n_\alpha - 1$
- $\hat{a}_\alpha | n_1 \ldots n_{\alpha-1} 0 n_{\alpha+1} \ldots \rangle_+ = 0$
- annihilation operator

<u>algebra</u>:

trivial: $[\hat{a}_\alpha, \hat{a}_\beta] = [\hat{a}_\alpha^+, \hat{a}_\beta^+] = 0$

$[\hat{a}_\alpha, \hat{a}_\beta^+] = 0$ if $\alpha \neq \beta$

$$\hat{a}_\alpha^+ \hat{a}_\alpha | \ldots n_\alpha \ldots \rangle_+ = \sqrt{n_\alpha} | \ldots n_\alpha - 1 \ldots \rangle_+ = n_\alpha | \ldots n_\alpha \ldots \rangle_+$$

$\Rightarrow$ - $\hat{n}_\alpha = \hat{a}_\alpha^+ \hat{a}_\alpha$ = occupation number operator

- $\hat{N} = \sum_\alpha \hat{n}_\alpha = \sum_\alpha \hat{a}_\alpha^+ \hat{a}_\alpha$ = particle number operator
- $\hat{a}_\alpha \hat{a}_\alpha^+ - \hat{a}_\alpha^+ \hat{a}_\alpha = 1$

$$\Rightarrow [\hat{a}_\alpha, \hat{a}_\beta^+] = \delta_{\alpha\beta}, \quad [\hat{a}_\alpha, \hat{a}_\beta] = 0 = [\hat{a}_\alpha^+, \hat{a}_\beta^+]$$

canonical (fundamental) commutation relation

<u>case $\mathcal{F}_-$</u>:

$$\hat{a}_\alpha^+ | n_1 \ldots n_{\alpha-1} n_\alpha n_{\alpha+1} \ldots \rangle_- = \begin{cases} 0 & \text{if } n_\alpha = 1 \\ (-1)^{n_1 + n_2 + \ldots + n_{\alpha-1}} | n_1 \ldots n_\alpha + 1 \ldots \rangle_- & \text{if } n_\alpha = 0 \end{cases}$$

- adds $|\alpha\rangle$ if it was absent before
- position is irrelevant, phase is chosen to be consistent with anti-symmetrization
- $(\hat{a}^+_\alpha)^2 = 0$ (nilpotent)

it holds: $\{\hat{a}^+_\alpha, \hat{a}^+_\beta\} = \hat{a}^+_\alpha \hat{a}^+_\beta + \hat{a}^+_\beta \hat{a}^+_\alpha = 0$

Proof: let $\alpha < \beta$: $\hat{a}^+_\alpha \hat{a}^+_\beta$ (or $\hat{a}^+_\beta \hat{a}^+_\alpha$) $\neq 0$ when

$$\begin{aligned}
\hat{a}^+_\alpha \hat{a}^+_\beta |n_1 \dots \underset{\substack{\uparrow \\ \alpha}}{0} \dots \underset{\substack{\uparrow \\ \beta}}{0} \dots\rangle_- &= \hat{a}^+_\alpha (-1)^{n_1 + \dots + \underset{\substack{\uparrow \\ \alpha}}{0} + \dots n_{\beta-1}} |n_1 \dots 0 \dots 1 \dots\rangle_- \\
&= (-1)^{n_1 + \dots + n_{\alpha-1}} (-1)^{n_1 + \dots + \underset{\uparrow}{0} + \dots n_{\beta-1}} |n_1 \dots 1 \dots 1 \dots\rangle_-
\end{aligned}$$

Conversely:

$$\begin{aligned}
\hat{a}^+_\beta \hat{a}^+_\alpha |n_1 \dots 0 \dots 0 \dots\rangle_- &= \hat{a}^+_\beta (-1)^{n_1 + \dots + n_{\alpha-1}} |n_1 \dots 1 \dots 0 \dots\rangle_- \\
&= (-1)^{n_1 + \dots + n_{\alpha-1}} (-1)^{n_1 + \dots + \underset{\uparrow}{1} + \dots n_{\beta-1}} |n_1 \dots 1 \dots 1 \dots\rangle_-
\end{aligned}$$

$\Rightarrow$ $\hat{a}^+_\alpha \hat{a}^+_\beta$ and $\hat{a}^+_\beta \hat{a}^+_\alpha$ yield the same state with a relative minus sign

$\Rightarrow \{\hat{a}^+_\alpha \hat{a}^+_\beta\} = 0 \quad \square$

adjoint operator:

$$\hat{a}_\alpha |n_1 \dots n_{\alpha-1} n_\alpha n_{\alpha+1} \dots\rangle_- = \begin{cases} 0 & \text{if } n_\alpha = 0 \\ (-1)^{n_1 + n_2 + \dots + n_{\alpha-1}} |n_1 \dots n_{\alpha-1}\, 0\, n_{\alpha+1} \dots\rangle_- & \text{if } n_\alpha = 1 \end{cases}$$

algebra: canonical anti-commutation relations:

$$\{\hat{a}^+_\alpha, \hat{a}^+_\beta\} = 0 = \{\hat{a}_\alpha, \hat{a}_\beta\} \qquad \{\hat{a}_\alpha, \hat{a}^+_\beta\} = \delta_{\alpha\beta}$$

occupation number operator $\hat{n}_\alpha = \hat{a}^+_\alpha \hat{a}_\alpha$

$$\hat{n}^2_\alpha = \hat{a}^+_\alpha \hat{a}_\alpha \hat{a}^+_\alpha \hat{a}_\alpha = \hat{a}^+_\alpha \underbrace{(\hat{a}_\alpha \hat{a}^+_\alpha + \hat{a}^+_\alpha \hat{a}_\alpha)}_{=1} \hat{a}_\alpha = \hat{n}_\alpha$$

$\Rightarrow$ eigenvalues λ of $\hat{n}_\alpha$: $\lambda^2 = \lambda \;\Rightarrow\; \lambda = 0, 1$ fermions

For $\mathcal{F}_+$ and $\mathcal{F}_-$ it holds:

$$|n_1 n_2 \ldots\rangle_\pm = (\textstyle\prod_\alpha n_\alpha!)^{-1/2} (\underset{\substack{\uparrow \\ \text{one factor for each one-particle state}}}{\hat{a}_1^+})^{n_1} (\hat{a}_2^+)^{n_2} \ldots |\underset{\substack{\uparrow \\ \text{empty Fock state}}}{0}\rangle_\pm$$

- the manipulation of the (anti-)symmetrized tensor product states is shifted to the algebra of $\hat{a}_\alpha^+, \hat{a}_\beta$
- <u>bosons</u>: like a harmonic oscillator degree of freedom for each one-particle state, which is occupied with $n_\alpha = 0, 1, 2, \ldots$ quanta: "second quantization"
- <u>fermions</u>: ladder operators with anti-commutation relations lead to $n_\alpha = 0, 1$

Example: one degree of freedom

fermion: $\{\hat{a}, \hat{a}^+\} = 1,\ \hat{a}^2 = (\hat{a}^+)^2 = 0$

$|0\rangle,\ |1\rangle = \hat{a}^+|0\rangle$ 2-dim Hilbert space

boson: $|n\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^+)^n|0\rangle,\ n \in \mathbb{N},\ \infty$-dimensional

e) Operators in second quantization

One-particle operators like the Hamiltonian $\hat{H}_1$ can act as operators in $\mathcal{H}_N$ via $\hat{H}_N = \hat{H}_1 \otimes 1 \otimes \ldots \otimes 1 + 1 \otimes \hat{H}_1 \otimes 1 \otimes \ldots \otimes 1 + 1 \otimes \ldots \otimes 1 \otimes \hat{H}_1$ (each term has N factors)

$$\hat{H}_N|\alpha_1\rangle|\alpha_2\rangle \ldots |\alpha_N\rangle = (\hat{H}_1|\alpha_1\rangle)|\alpha_2\rangle \ldots |\alpha_N\rangle + \ldots |\alpha_1\rangle \ldots |\alpha_{N-1}\rangle(\hat{H}_1|\alpha_N\rangle)$$

Similarly: $\hat{H}_N$ acts on $|\Psi\rangle_\pm \in \mathcal{H}_{N\pm}$

Since $\hat{H}_N$ is symmetric $\Rightarrow \hat{H}_N|\Psi\rangle_\pm \in \mathcal{H}_{N\pm}$

Shorthand: $\hat{H}_N\mathcal{H}_{N\pm} \subseteq \mathcal{H}_{N\pm}$

- from this it follows: $\hat{H} = \underset{\substack{\uparrow \\ N=1}}{\hat{H}_1} \oplus \underset{\substack{\uparrow \\ N=2}}{\hat{H}_2} \oplus \underset{\substack{\uparrow \\ N=3}}{\hat{H}_3} \oplus \ldots$

  $\hat{H}\mathcal{F}_\pm \subseteq \mathcal{F}_\pm, \qquad \hat{H}|0\rangle_\pm = 0$

- similarly for all one-particle operators

Proposition: The result holds (in second quantization)

$\hat{H} = \sum_{\alpha,\beta} \hat{a}^+_\alpha h_{\alpha\beta} \hat{a}_\beta$ with $h_{\alpha\beta} = \langle\alpha|\hat{H}_1|\beta\rangle$

Special case 2 bosons:

$|\Psi\rangle \propto (|\alpha_1\rangle|\alpha_2\rangle + |\alpha_2\rangle|\alpha_1\rangle) \propto \hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}|0\rangle$

($n_{\alpha_1} = n_{\alpha_2} = 1$, other n_α's $= 0$)

$\hat{H}\hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}|0\rangle = [\hat{H}, \hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}]|0\rangle \quad (\hat{a}_\beta|0\rangle = 0)$

Important formula: for operators A, B_1, B_2:

$$[A, B_1B_2] = [A, B_1]B_2 + B_1[A, B_2] = AB_1B_2 - B_1AB_2 + B_1AB_2 - B_1B_2A \quad (*)$$

$$\hat{H}\hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}|0\rangle \overset{(*)}{=} [H, \hat{a}^+_{\alpha_1}]\hat{a}^+_{\alpha_2}|0\rangle + \hat{a}^+_{\alpha_1}[H, \hat{a}^+_{\alpha_2}]|0\rangle$$

It holds:

$$\begin{aligned} [\hat{H}, \hat{a}^+_\gamma] &= \sum_{\alpha,\beta} h_{\alpha\beta}[\hat{a}^+_\alpha\hat{a}_\beta, \hat{a}^+_\gamma] \text{ ... similar formula to (*) ...} \\ &= \sum_{\alpha,\beta} h_{\alpha\beta}(\hat{a}^+_\alpha \underbrace{[\hat{a}_\beta, \hat{a}^+_\gamma]}_{=\delta_{\beta\gamma}} + \underbrace{[\hat{a}^+_\alpha, \hat{a}^+_\gamma]}_{=0}\hat{a}_\beta) \end{aligned}$$

$\Rightarrow [\hat{H}, \hat{a}^+_\gamma] = \sum_\alpha h_{\alpha\gamma}\hat{a}^+_\alpha$

$$\begin{aligned} \Rightarrow \hat{H}\hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}|0\rangle &= \sum_\gamma (h_{\gamma\alpha_1}\hat{a}^+_\gamma\hat{a}^+_{\alpha_2}|0\rangle + h_{\gamma\alpha_2}\hat{a}^+_{\alpha_1}\hat{a}^+_\gamma|0\rangle) \\ &\propto \sum_\gamma h_{\gamma\alpha_1}|\gamma\alpha_2\rangle_+ + \sum_\gamma h_{\gamma\alpha_2}|\gamma\alpha_1\rangle_+ \end{aligned}$$

It holds:

$$\begin{aligned} \sum_\gamma \langle\gamma|\hat{H}_1|\alpha_1\rangle|\gamma\rangle|\alpha_2\rangle &= \sum_\gamma (|\gamma\rangle\langle\gamma|\hat{H}_1|\alpha_1\rangle)|\alpha_2\rangle \\ &= (\hat{H}_1|\alpha_1\rangle)|\alpha_2\rangle = (\hat{H}_1 \otimes 1)|\alpha_1\rangle|\alpha_2\rangle \text{ etc.} \end{aligned}$$

$\Rightarrow \sum_{\alpha,\beta} \hat{a}^+_\alpha \langle\alpha|\hat{H}_1|\beta\rangle$ embeds the one-particle observable correctly into $\mathcal{H}_{2+}\ldots\mathcal{H}_{N+}\ldots\mathcal{F}_+$.

Simple special case:

$$h_{\alpha\beta} = \langle\alpha|\hat{H}_1|\beta\rangle = E_\alpha\delta_{\alpha\beta}$$

$$\Rightarrow \hat{H} = \sum_{\alpha,\beta} h_{\alpha\beta}\hat{a}^+_\alpha\hat{a}_\beta = \sum_\alpha E_\alpha\hat{n}_\alpha$$

$$\Rightarrow \hat{H}|n_1n_2\ldots\rangle_+ = \sum_\alpha E_\alpha n_\alpha|n_1n_2\ldots\rangle_+$$

E_α: energy of oscillator α

n_α: number of excited quanta

In short: what is different for special case: 2 fermions ($\{\hat{a}_\alpha,\hat{a}^+_\beta\} = \delta_{\alpha\beta}$ etc.)

$$\hat{H}\hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}|0\rangle = [\hat{H},\hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}]|0\rangle = [\hat{H}\hat{,}a^+_{\alpha_1}]\hat{a}^+_{\alpha_2}|0\rangle + \hat{a}^+_{\alpha_1}[\hat{H},\hat{a}^+_{\alpha_2}]|0\rangle$$

Now: important formula

$$\begin{aligned} [A_1A_2,B] &= A_1\{A_2,B\} - \{A_1,B\}A_2 \\ &= A_1A_2B + A_1BA_2 - A_1BA_2 - BA_1A_2 \end{aligned}$$

$$\sum_{\alpha,\beta} h_{\alpha\beta}[\hat{a}^+_\alpha\hat{a}_\beta,\hat{a}^+_{\alpha_1}] = \sum_{\alpha,\beta} h_{\alpha\beta}(\hat{a}^+_\alpha \underbrace{\{\hat{a}_\beta,\hat{a}^+_{\alpha_1}]}_{=\delta_{\beta\alpha_1}} + \underbrace{[\hat{a}^+_\alpha,\hat{a}^+_{\alpha_1}]}_{=0}\hat{a}_\beta) = \sum_\alpha h_{\alpha\alpha_1}\hat{a}^+_\alpha$$

- reduce to fundamental anti-commutations
- other steps analogous to bosons
  $\rightarrow \hat{H} = \sum_{\alpha,\beta}\hat{a}^+_\alpha h_{\alpha\beta}\hat{a}_\beta$ with $h_{\alpha\beta} = \langle\alpha|\hat{H}_1|\beta\rangle$ holds also for 2 fermions
- everything goes through analogously for $N > 2$

f) Position space representation, interaction

$\hat{a}^+_{\alpha_1}\hat{a}^+_{\alpha_2}|0\rangle \rightarrow \hat{a}^+(\vec{x})\hat{a}^+(\vec{y})|0\rangle \qquad \{|\alpha\rangle\} \rightarrow \{|\vec{x}\rangle\}$

$[\hat{a}(\vec{x}),\hat{a}^+(\vec{y})] = \delta^{(3)}(\vec{x}-\vec{y})$ bosons

$$[\hat{a}(\vec{x}), \hat{a}(\vec{y})] = 0 = [\hat{a}^+(\vec{x}), \hat{a}^+(\vec{y})]$$

$\hat{H}_1 \to \langle \vec{x}|\hat{H}_1|\vec{y}\rangle$ one-particle Hamiltonian

$\to \hat{H} = \int d^3x d^3y \langle \vec{x}|\hat{H}_1|\vec{y}\rangle \hat{a}^+(x)\hat{a}(\vec{y})$ embedded in $\mathcal{F}_+$

What is $\langle \vec{x}|\hat{H}_1|\vec{y}\rangle$?

If $\hat{H}_1 = \frac{1}{2m}\hat{\vec{p}}^2 + \hat{V}(\hat{\vec{x}})$:
$\langle \vec{x}|\hat{\vec{p}}^2|\vec{y}\rangle = \int \dfrac{d^3p}{(2\pi\hbar)^3}\vec{p}^2 e^{\frac{i}{\hbar}\vec{p}(\vec{x}-\vec{y})}$

$\langle \vec{x}|\hat{V}|\vec{y}\rangle = V(\vec{x})\delta^{(3)}(\vec{x}-\vec{y})$

$$\begin{aligned}
\Rightarrow \hat{H} &= \int d^3x d^3y \hat{a}^+(\vec{x}) \Bigg[\int \frac{d^3k}{(2\pi)^3} \frac{(\hbar\vec{k})^2}{2m} e^{i\vec{k}(\vec{x}-\vec{y})} + V(\vec{x})\delta^{(3)}(\vec{x}-\vec{y}) \Bigg] \hat{a}(\vec{y}) \\
&= \int d^3x \, \underbrace{\hat{a}^+(\vec{x}) \quad \underbrace{\left[-\frac{\hbar^2}{2m}\Delta + V(\vec{x}) \right]}_{\text{first quantization: } \hat{H}_1 \text{ in position space}} \quad \hat{a}(\vec{x})}_{\text{second quantization: } \hat{H} \text{ operator in Fock space}}
\end{aligned}$$

fermions: replace everywhere $[,] \to \{,\}$ (anti-commutator)

<u>interaction</u>:
consider simple case of two-particle interaction: construct operator $\hat{V}_I$ s.t.

$$\hat{V}_I|\vec{r}_1\vec{r}_2\rangle_\pm = V(\vec{r}_1 - \vec{r}_2)|\vec{r}_1\vec{r}_2\rangle_\pm$$

with $V(\vec{r}) = V(-\vec{r}) \Leftrightarrow \hat{V}_I$ symmetric, $[\hat{V}_I, \hat{T}_{12}] = 0$

$\Rightarrow \hat{V}_I$ does not change symmetry ($\pm$) of states

In second quantization:

$$\hat{V}_I = \frac{1}{2}\int d^3x d^3y V(\vec{x}-\vec{y}) \underbrace{\hat{a}^+(\vec{x})\hat{a}^+(\vec{y})\hat{a}(\vec{y})\hat{a}(\vec{x})}_{\text{hermitian operator}}$$

Example: 2 fermions $|\Psi\rangle_- = \hat{a}^+(\vec{r}_1)\hat{a}^+(\vec{r}_2)|0\rangle_-$

$$\begin{aligned}\hat{a}(\vec{x})|\Psi\rangle_- &= [\hat{a}(\vec{x}), \hat{a}^+(\vec{r}_1)\hat{a}^+(\vec{r}_2)]|0\rangle_- \\ &= \{\hat{a}(\vec{x}), \hat{a}^+(\vec{r}_1)\}\hat{a}^+(\vec{r}_2)|0\rangle_- - \hat{a}^+(\vec{r}_1)\{\hat{a}(\vec{x}), \hat{a}^+(\vec{r}_2)\}|0\rangle_- \\ &= \delta^{(3)}(\vec{x}-\vec{r}_1)\hat{a}^+(\vec{r}_2)|0\rangle_- - \delta^{(3)}(\vec{x}-\vec{r}_2)\hat{a}^+(\vec{r}_1)|0\rangle_-\end{aligned}$$

$$\begin{aligned}\hat{a}(\vec{y})\hat{a}(\vec{x}) &= \delta^{(3)}(\vec{x}-\vec{r}_1)\{\hat{a}(\vec{y}), \hat{a}^+(\vec{r}_2)\}|0\rangle_- - \delta^{(3)}(\vec{x}-\vec{r}_2)\{\hat{a}(\vec{y}), \hat{a}^+(\vec{r}_1)\}|0\rangle_- \\ &= \Big(\delta^{(3)}(\vec{x}-\vec{r}_1)\delta^{(3)}(\vec{y}-\vec{r}_2) - \delta^{(3)}(\vec{x}-\vec{r}_2)\delta^{(3)}(\vec{y}-\vec{r}_1)\Big)|0\rangle_-\end{aligned}$$

$$\begin{aligned}\hat{V}_I|\Psi\rangle_- &= \frac{1}{2}\int d^3x d^3y V(\vec{x}-\vec{y})\Big(\delta^{(3)}(\vec{x}-\vec{r}_1)\delta^{(3)}(\vec{y}-\vec{r}_2) - \delta^{(3)}(\vec{x}-\vec{r}_2)\delta^{(3)}(\vec{y}-\vec{r}_1)\Big)\hat{a}^+(\vec{x})\hat{a}^+(\vec{y})|0\rangle_- \\ &= \frac{1}{2}V(\vec{r}_1-\vec{r}_2)\Big(\hat{a}^+(\vec{r}_1)\hat{a}^+(\vec{r}_2) - \underbrace{\hat{a}^+(\vec{r}_2)\hat{a}^+(\vec{r}_1)}_{=-\hat{a}^+(\vec{r}_1)\hat{a}^+(\vec{r}_2)}\Big)|0\rangle_- = V(\vec{r}_1-\vec{r}_2)|\Psi\rangle_-\end{aligned}$$

on a N-particle state: $V_I|\vec{r}_1 \ldots \vec{r}_N)\rangle_- = \sum_{i<j} V(\vec{r}_i - \vec{r}_j)|\vec{r}_1 \ldots \vec{r}_N\rangle_-$

This can be generalized to 2 (or N) bosons.

Remark: $\hat{V}_I$ (interaction) is quartic in $\hat{a}^+$, $\hat{a}$.

5.1.2 Partition function of ideal quantum gases

$\Xi = \mathrm{Tr} e^{-\beta(\hat{H}-\mu\hat{N})}$ (grand-canonical)

2nd quantization, $\hat{a}_\alpha, \hat{a}^+_\beta$ acting on one-particle basis of energy eigenstates

$\hat{N} = \sum_\alpha \hat{n}_\alpha \qquad \hat{n}_\alpha = \hat{a}^+_\alpha \hat{a}_\alpha$ occupation number

$\hat{H} = \sum_\alpha E_\alpha \hat{n}_\alpha$ no interaction! ↔ ideal gas

$$\begin{aligned}\Xi &= \mathrm{Tr} e^{-\beta(\hat{H}-\mu\hat{N})} \\ &= \sum_{\{n_\alpha\}} {}_\pm\langle n_1 n_2 \ldots | e^{-\beta(\hat{H}-\mu\hat{N})} | n_1 n_2 \ldots\rangle_\pm = \sum_{\{n_\alpha\}} e^{-\beta\sum_\alpha (E_\alpha - \mu) n_\alpha}\end{aligned}$$

bosons: $n_\alpha = 0, 1, 2, \ldots, \infty$ for each state
fermions: $n_\alpha = 0, 1$ for each state

$$\begin{aligned}
\Xi &= \prod_\alpha \Big(\sum_n e^{-\beta(E_\alpha - \mu)n} \Big) \\
&= \begin{cases} \prod_\alpha \Big(1 + e^{-\beta(E_\alpha-\mu)}\Big) & \text{fermions (-)} \\ \prod_\alpha \Big(1 - e^{-\beta(E_\alpha-\mu)}\Big)^{-1}_{\text{(from geometric series)}} & \text{bosons (+)} \end{cases}
\end{aligned}$$

$$\begin{aligned}
\Xi &= e^{-\beta\Omega}; \quad \Omega = \Omega(T, V, \mu) \\
\Omega_+ &= \frac{1}{\beta} \sum_\alpha \ln(1 - e^{-\beta(E_\alpha-\mu)}) \\
\Omega_- &= -\frac{1}{\beta} \sum_\alpha \ln(1 + e^{-\beta(E_\alpha-\mu)})
\end{aligned}$$

Remark: V goes in through the structure of $\{E_\alpha\}$, see below.

Number of particles $\leftrightarrow$ μ:

$$\begin{aligned}
N_\pm = \langle \hat{N} \rangle_\pm &= -\frac{\partial}{\partial\mu}\Omega_\pm - = \sum_\alpha \frac{e^{-\beta(E_\alpha-\mu)}}{1 \mp e^{-\beta(E_\alpha-\mu)}} \\
&= \sum_\alpha \frac{1}{e^{\beta(E_\alpha-\mu)} \mp 1}
\end{aligned}$$

solve for $\mu - = \mu(T, V, N_\pm)$ with this: thermal equation of state

$\Omega = -PV$ (Gibbs-Duhem) $\rightarrow P(T, V, N_\pm)$

caloric equation of state:

$U = \langle \hat{H} \rangle = -\frac{\partial}{\partial\beta} \ln \Xi|_z \qquad z = e^{\beta\mu},\ z$ fixed $\Leftrightarrow \beta\mu$ fixed

$U_\pm = \pm\frac{\partial}{\partial\beta} \sum_\alpha \ln(1 \mp z e^{-\beta E_\alpha})|_z = \sum_\alpha \dfrac{E_\alpha}{e^{\beta(E_\alpha-\mu)} \mp 1}$ with $\mu(T, V, N_\pm)$

$\rightarrow U_\pm = U_\pm(T, V, N_\pm)$ caloric equation of state

Key quantity:

$$\begin{aligned}\langle\hat{n}_\alpha\rangle_\pm &= \frac{1}{\Xi}\mathrm{Tr}(\hat{n}_\alpha e^{-\beta(\hat{H}-\mu\hat{N})}) \\ &= \frac{\sum_{\{n_\beta\}} n_\alpha e^{-\beta\sum_\beta(E_\beta-\mu)n_\beta}}{\sum_{\{n_\beta\}} e^{-\beta\sum_\beta(E_\beta-\mu)n_\beta}} = -\frac{1}{\beta}\frac{\partial}{\partial E_\alpha}\ln\Xi \\ &= \frac{\partial}{\partial E_\alpha}\Omega = \frac{1}{e^{\beta(E_\alpha-\mu)}\mp 1} = \text{ occupation probability for state } \alpha\end{aligned}$$

Fermi-distribution function: $\langle\hat{n}_\alpha\rangle_- = (e^{\beta(E_\alpha-\mu)}+1)^{-1}$

$0 \leq \langle\hat{n}_\alpha\rangle_0 - \leq 1$ for all real $\beta, \mu \leftrightarrow$ structure of state space

Bose-distribution function: $\langle\hat{n}_\alpha\rangle_+ = \frac{1}{e^{\beta(E_\alpha-\mu)}-1}$

$E_\alpha - \mu \geq 0$ must hold for all α, otherwise μ is not physically meaningful:

- $\langle\hat{n}_\alpha\rangle_+ < 0$ possible ↯
- operator $\hat{H} - \mu\hat{N}$ has arbitrary negative eigenvalues

Let E_0 be the smallest energy

In order that $\langle\hat{N}\rangle \geq \langle\hat{n}_0\rangle < \infty$ we even need $E_0 - \mu > 0 \Leftrightarrow \mu \in (-\infty, E_0)$

But then $\langle\hat{n}_\alpha\rangle_+ \to 0$ for $T \to 0 \Leftrightarrow \beta \to \infty$ and hence $\langle\hat{N}\rangle \to 0$

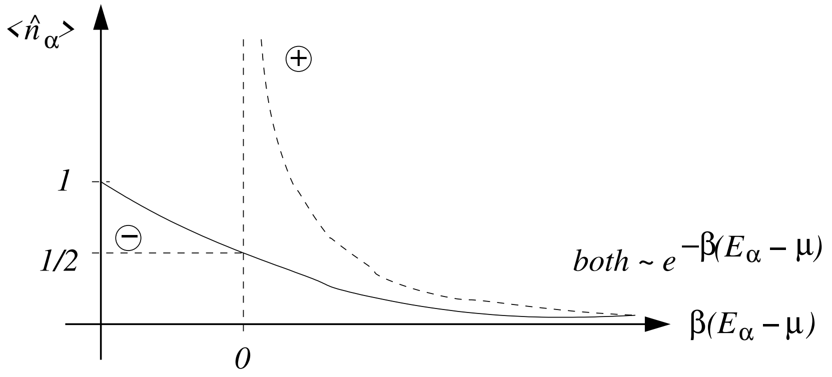
Does a limit $T \to 0$ with $N_+ = \langle\hat{N}\rangle_+$ finite exist?

- at the same time we must have $\mu \nearrow E_0$
- $\leftrightarrow$ Bose-Einstein condensation, phase transition, macroscopic occupation number $\langle\hat{n}_0\rangle_+$ (ground state)
- $\to$ details later

We found:

$N_\pm = \langle\hat{N}\rangle_\pm = \sum_\alpha\langle\hat{n}_\alpha\rangle_\pm$

$U_\pm = \langle \hat{H} \rangle_\pm = \sum_\alpha E_\alpha \langle \hat{n}_\alpha \rangle_\pm$



Remark: spin statistics theorem (Wolfgang Pauli, relativistic quantum field theory)

bosons ↔ integer spin values (photon, mesons, Higgs, ...)

fermions ↔ half-integer spin values (e^-, p, n, ν all 1/2)

5.2 Ideal Fermi gas

Non-interacting fermions

Dominant effect: Pauli principle, $n_\alpha = 0, 1$

Particularly relevant for $\mu >> k_B T \Leftrightarrow \beta\mu >> 1$

- degenerate case
- tendency to populate states with small E_α

5.2.1 Equations of state

Which one-particle states?

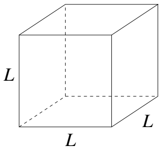
- momentum $\vec{p} = \hbar\vec{k}$
- spin: $m_s = -S, -S+1, \ldots, S-1, S$ (electron: $S = 1/2, m_S = -1/2, +1/2$)

The values of $\vec{k}$ become countable in finite volume with periodic boundary conditions: $V = L^3$

$$e^{i\vec{k}\vec{r}} \overset{!}{=} e^{i\vec{k}(\vec{r}+L\vec{e}_i)} \quad i = 1,2,3 \quad V = L^3$$

$$\Rightarrow k_i L = 2\pi n_i, \quad \vec{k} = \tfrac{2\pi}{L}\vec{n}, \quad n_i \in \mathbb{Z}$$

$$|\alpha\rangle \to |\vec{k}m_s\rangle,\ \langle\vec{k}m_s|\vec{k}'m_s'\rangle = \delta_{\vec{k},\vec{k}'}\delta_{m_s,m_s'}$$



For free particles:

$$\hat{H}_1|\vec{k}m_s\rangle = E_{\vec{k}}|\vec{k}m_s\rangle, \quad E_{\vec{k}} = \tfrac{\hbar^2\vec{k}^2}{2m}$$

$$\{\hat{a}(\vec{k},m_s), \hat{a}^+(\vec{k}',m_s')\} = \delta_{\vec{k},\vec{k}'}\delta_{m_s,m_s'}$$

$$\{\hat{a},\hat{a}\} = 0 = \{\hat{a}^+,\hat{a}^+\}$$

$$\hat{n}(\vec{k},m_s) = \hat{a}^+(\vec{k},m_s)\hat{a}(\vec{k},m_s)$$

$$\Xi = \textstyle\sum_{\{n(\vec{k},m_s)=0,1\}} e^{-\beta\sum_{\vec{k},m_s}(E_{\vec{k}}-\mu)n(\vec{k},m_s)} = \prod_{\vec{k}}(1+ze^{-\beta E_{\vec{k}}})^{2S+1},\ z = e^{\beta\mu}$$

$$-\beta\Omega = (2S+1)\sum_{\vec{k}}\ln(1+ze^{-\beta E_{\vec{k}}}$$

$k_i = \frac{2\pi}{L}n_i$, step-size in k_i: $\frac{2\pi}{L} = \Delta k$, very small for $L \to \infty$ (macroscopic)

$$\begin{aligned} -\beta\Omega &= (2S+1)\left(\frac{L}{2\pi}\right)^3\sum_{\vec{k}}\ln(1+ze^{-\beta E_{\vec{k}}}) \\ &\approx (2S+1)\frac{V}{(2\pi)^3}\int d^3k\,\ln(1+ze^{-\beta E_{\vec{k}}}) \\ &= (2S+1)\frac{V}{(2\pi)^3}4\pi\int_0^\infty dkk^2\ln(1+ze^{-\frac{\beta\hbar^2}{2m}k^2}) \end{aligned}$$

Change of variable: $\sqrt{\frac{\beta}{2m}}\hbar k = u = \frac{\lambda_T}{2\sqrt{\pi}}k$

$\lambda_T = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$ thermal de Broglie wavelength

$$-\beta\Omega := (2S+1)\tfrac{4}{\sqrt{\pi}}\tfrac{V}{\lambda_T^3}\int_0^\infty duu^2\ln(1+ze^{-u^2}) =: (2S+1)\tfrac{V}{\lambda_T^3}f_{5/2}(z)$$

Using the series $\ln(1+y) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{y^n}{n}$:

$f_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^{\infty} duu^2 \ln(1+ze^{-u^2}) = \frac{4}{\sqrt{\pi}}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{z^n}{n}\int_0^{\infty} duu^2 e^{-nu^2}$

$\int_0^{\infty} duu^2 e^{-nu^2} = n^{-3/2}\int_0^{\infty} duu^2 e^{-u^2} = n^{-3/2}\frac{\sqrt{\pi}}{4}$

$\Rightarrow f_{5/2}(z) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{z^n}{n^{5/2}}$, in general: $f_k(z) = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{z^n}{n^k}$

$\Omega = -PV$ (Gibbs Duhme) $\Rightarrow \beta P = \frac{2S+1}{\lambda_T^3} f_{5/2}(z)$, here $P(T,V,\mu)$

$\langle \hat{N} \rangle = -\frac{\partial}{\partial \mu}\Omega = z\frac{\partial}{\partial z}\underbrace{\ln \Xi}_{=\beta PV} = zV\beta\frac{\partial P}{\partial z}|_{T,V}$

$\beta z \frac{\partial P}{\partial z} = \frac{2S+1}{\lambda_T^3} z\frac{\partial}{\partial z} f_{5/2}(z) = \frac{2S+1}{\lambda_T^3} f_{3/2}(z)$

→ density $n = \frac{\langle \hat{N} \rangle}{V} = \frac{2S+1}{\lambda_T^3} f_{3/2}(z)$ → solve for $z(n)$, insert into $P(T,\cancel{V},n)$

→ thermal equation of state (in general not explicit)

caloric equation of state:

$$\begin{aligned} U &= \frac{1}{\Xi}(-1)\frac{\partial}{\partial \beta}\mathrm{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})})|_{z,V} \\ &= -\frac{\partial}{\partial \beta}\ln \Xi|_{z,V} = (2S+1)Vf_{3/2}(z)(-\frac{\partial}{\partial \beta}\frac{1}{\lambda_T^3}) \\ \lambda_T^{-3} &\sim \beta^{-3/2} \to -\frac{\partial}{\partial \beta}\lambda_T^{-3} = \frac{3}{2}\frac{1}{\beta\lambda_T^3} \end{aligned}$$

$\Rightarrow U = \frac{3}{2}PV$ same as for classical ideal gas, no QM correction

5.2.2 Classical limit

- explicit equations of state for $z = e^{\beta\mu} << 1$

  (cf. virial expansion, homework 7)

  $\langle \hat{n}_\alpha \rangle_- = \frac{1}{e^{\beta(E_\alpha-\mu)}+1} = \frac{1}{\frac{e^{\beta E_\alpha}}{z}+1} \approx ze^{-\beta E_\alpha}$

- Maxwell Boltzmann distribution

- not degenerate, $\langle \hat{n}_\alpha \rangle << 1$, small effects from the Pauli principle

  Approximations: $f_k(z) = z - \frac{z^2}{2^k} + O(z^3) \qquad k = 3/2, 5/2$

  Remark: neglecting spin ($S = 0$)

- $-\beta\Omega = \frac{V}{\lambda_T^3} f_{5/2}(z) = \frac{V}{\lambda_T^3} z(1 - \frac{z}{2^{5/2}}{}_{O}(z^2))$

  Compare with classical expression 13:

- $-\beta\Omega \underset{\uparrow}{=} \frac{zV}{\lambda_T^3} =$ $\underset{\Downarrow}{\text{leading}}$ term of QM expression

  $c_N = \frac{1}{N!},\ h^{-3N}$ confirm these factors

We had for the density

$$n = \frac{2S+1}{\lambda_T^3} f_{3/2}(z) = \frac{2S+1}{\lambda_T^3}(z - \frac{z^2}{2^{3/2}} + \ldots) \approx \frac{2S+1}{\lambda_T^3} z(1 - \frac{z}{2^{3/2}})$$

and for the pressure

$$\beta P = \frac{2S+1}{\lambda_T^3} f_{5/2}(z) = \frac{2S+1}{\lambda_T^3}(z - \frac{z^2}{2^{5/2}} + \ldots) \approx \frac{2S+1}{\lambda_T^3} z(1 - \frac{z}{2^{5/2}})$$

Combine the two equations, eliminate z:

$$\beta P(1 - \frac{z}{2^{5/2}})^{-1} = n(1 - \frac{z}{2^{3/2}})^{-1}$$

$$\beta P \approx n(1 - \frac{z}{2^{3/2}})^{-1}(1 - \frac{z}{2^{5/2}}) = n(1 + z\underbrace{(2^{-3/2} - 2^{-5/2})}_{\frac{1}{4\sqrt{2}}} + O(z^2))$$

$$n = \frac{2S+1}{\lambda_T^3} z + O(z^2) \leftrightarrow z = \frac{\lambda_T^3}{2S_1} n + O(n^2)$$

$$\beta P = n(1 + \frac{\lambda_T^3 n}{4(2S+1)\sqrt{2}}) + O(n^3) \quad |V k_B T$$

$$PV \approx \langle \hat{N} \rangle \underset{\uparrow}{k_B} T(1 + \underset{\uparrow}{\frac{n\lambda_T^3}{4\sqrt{2}(2S+1}})$$

classical ideal gas   leading QM correction

- expansion in the dimensionless quantity $n\lambda_T^3 << 1$
- classical limit $\leftrightarrow$ small density and small λ_T

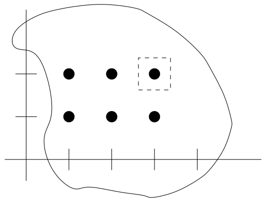
- $\lambda_T = \sqrt{2\pi\beta\hbar^2/m} \to 0$ at large temperature

5.2.3 Density of states, Fermi function

$\vec{k} = \frac{2\pi}{L}\vec{n}$

$\to$ each state in $\vec{k}$-space has a

"cell volume" $\Delta k^3 = (\frac{2\pi}{L})^3$



$$\begin{aligned}\phi(E) &= \sum_{\vec{k},m_s} \Theta\left(E - \frac{\hbar^2\vec{k}^2}{2m}\right) \equiv (2S+1)\sum_{\vec{k}} \Theta\left(\sqrt{\frac{2mE}{\hbar^2}} - |\vec{k}|\right) \\ &\approx (2S+1)\frac{4\pi}{3}\left(\frac{\sqrt{2mE}}{\hbar\Delta k}\right)^3 = (2S+1)\frac{4\pi}{3}\left(\frac{2mE}{\hbar^2}\right)^{3/2}\frac{V}{(2\pi)^3} \quad \text{for } L \geq 0\end{aligned}$$

Remark: This result justifies the factor $\hbar^{-3N}$, which was introduced in classical statistics.

Density of states:

$$D(E) = \tfrac{d}{dE}\phi(E) = \begin{cases} 0 & \text{for } E \leq 0 \\ d \cdot \underset{\swarrow}{E^{1/2}} & \text{for } E > 0 \end{cases}$$

$\leftrightarrow$ non-relativistic kinetic energy

$d = (2S+1)\frac{V}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}$

$[d] = (\text{energy})^{-3/2}$

- $D(E)$ number of one-particle states (Fermi + Bose)
- occupation: Fermi $\langle \hat{n}_{\vec{k},m_s}\rangle_- = f_-(E_{\vec{k}})$

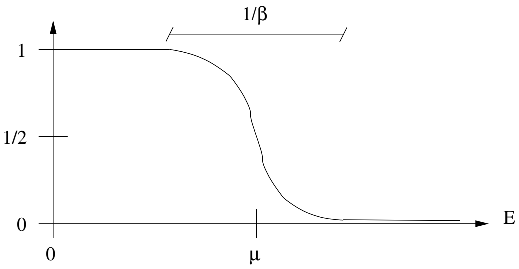
Definition of Fermi-(Dirac)-function:

$f_-(E) = (e^{\beta(E-\mu)} + 1)^{-1} \in [0,1]$

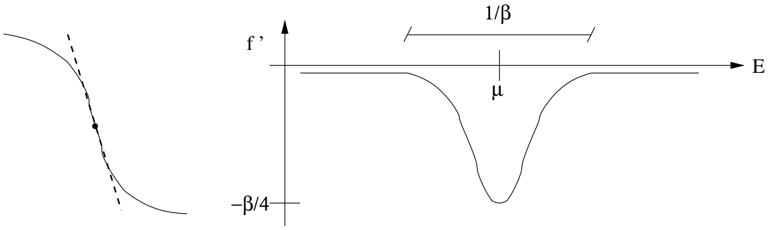
$D(E)f_-(E)$: density of $\underline{\text{occupied}}$ states at T, μ ($\beta = \frac{1}{k_B T}$)

$U = \int_{-\infty}^{\infty} dE f_-(E)D(E)E$

$\bar{N} = \langle \hat{N} \rangle = \int_{-\infty}^{\infty} dE f_-(E) D(E)$



- $f_- \overset{\beta\to\infty}{\longrightarrow} \Theta(\mu - E)$
- $\beta < \infty$ "regularized step function"
- $f_-(\mu + \Delta) = \frac{1}{e^{\beta\Delta}+1} = 1 - \frac{e^{\beta\Delta}}{e^{\beta\Delta}+1} = 1 - \frac{1}{e^{-\beta\Delta}+1} = 1 - f_-(\mu - \Delta)$ "symmetry"
- $f_-(\mu) = 1 - f_-(\mu) \Rightarrow f_-(\mu) = 1/2$
- width $\propto$ $\Delta = 1/\beta$
- $f_-'(E) = -\frac{1}{4}\frac{\beta}{\cosh^2(\beta(E-\mu)/2)} \overset{\beta\to\infty}{\longrightarrow} -\delta(E - \mu)$



$f_-'(\mu) = -\beta/4$

degenerate Fermi gas at $\underline{T = 0,\ \beta \to \infty}$:

- lowest lying states with $\langle \hat{n}_{\vec{k},m_s} \rangle = 1$ occupied for $E_{\vec{k}} \leq \mu$, higher states unoccupied
  $\bar{N} = \int_{-\infty}^{\infty} dE \underbrace{f_-(E)}_{\Theta(\mu-E)} D(E) = \int_{-\infty}^{\mu} dE D(E) \overset{\text{here}}{=} \int_0^{\mu} dE D(E)$
- for given $\bar{N}$, the energy threshold μ at $\beta = \infty$: $\bar{N} = \int_{-\infty}^{\mu=E_F} dE D(E)$ is called Fermi energy, $\mu|_{\beta=\infty} = E_F = \frac{\hbar^2 k_F^2}{2m}$.

- states in the Fermi ball in $\vec{k}$-space with radius k_F are occupied

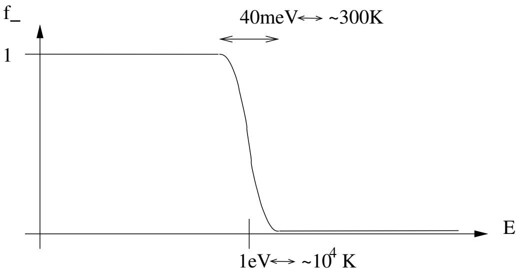
  $$\bar{N} = \textstyle\int_0^{E_F} dE d\sqrt{E} = d\frac{2}{3}E_F^{3/2} = (2S+1)\frac{V}{6\pi^2}\left(\frac{2mE_F}{\hbar^2}\right)^{3/2}$$

  $$\Rightarrow E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}n\right)^{3/2}, \quad n = \frac{\bar{N}}{V}$$

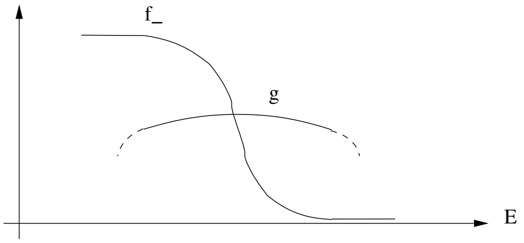
  $$\frac{\mu}{\bar{N}} = \frac{\int_0^\mu dED(E)E}{\int_0^\mu dED(E)} = \frac{\frac{2}{5}\mu^{5/2}}{\frac{2}{3}\mu^{3/2}} = \frac{3}{5}\mu = \frac{3}{5}E_F \text{ (at } T=0)$$

Definition: Fermi temperature $E_F = k_B T_F$

Electrons in metals at room temperature are approximately a degenerate Fermi gas with $T_F \sim 10^4 K \gg 300K$ (definition of <u>degenerate</u>: $25 \precsim \mu\beta \gg 1$)



5.2.4 Sommerfeld expansion



$I = \int_{-\infty}^{\infty} dEg(E)f_-(E)$

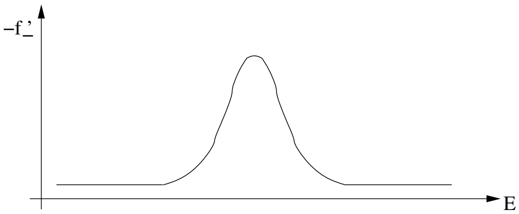
approximation if $g(E)$ smooth at $E = E_F \approx \mu$:

$p(E) = \int_{-\infty}^{E} dE'g(E')$

$$I = \underbrace{p(E)f_-(E)_{-\infty}^{\infty}}_{\substack{=0 \text{ since} \\ p(-\infty)=0,\, f_-(\infty)=0}} - \int_{-\infty}^{\infty} dEg(E)f_-'(E)$$

(p should be $\propto E^k$ for $E \to \infty$)

$-f'_- \sim$ smeared δ-function, width $\sim k_B T$



$$\begin{aligned} p(E) &= \sum_{n=0}^{\infty} \frac{1}{n!} p^{(n)}(\mu)(E-\mu)^n \quad \text{Taylor} \\ &= p(\mu) + \sum_{n=1}^{\infty} \frac{1}{n!} g^{(n-1)}(\mu)(E-\mu)^n \end{aligned}$$

$$\begin{aligned} I &= I_0 + \beta \sum_{n=1}^{\infty} \frac{1}{n!} g^{(n-1)}(\mu)(E-\mu)^n I_n \\ I_0 &= -p(\mu) \int_{-\infty}^{\infty} f'_-(E) dE = -p(\mu) \underbrace{f_-|_{-\infty}^{\infty}}_{-1} = p(\mu) \\ I_n &= -\frac{1}{\beta} \int_{-\infty}^{\infty} (E-\mu)^n f'_-(E) dE : \ \text{moments of } f'_- \end{aligned}$$

because of symmetry: $f_-(\mu+E) = 1 - f_-(\mu-E) \Rightarrow f'_-(\mu+E) = f'_-(\mu-E) \Rightarrow$ $I_n = 0$ for n odd

$$\begin{aligned} I &= \int_{-\infty}^{\mu} dE g(E) + \beta \sum_{n=1}^{\infty} \frac{1}{(2n)!} g^{(2n-1)}(\mu) I_{2n} \\ I_{2n} &= \frac{1}{4} \int_{-\infty}^{\infty} dE (E-\mu)^{2n} \cosh^{-2}(\beta(E-\mu)/2) \\ &= \frac{1}{4} \beta^{-(2n+1)} \int_{-\infty}^{\infty} du u^{2n} \cosh^{-2}(u/2) = \ldots \text{integral tables} \ldots \\ &= 2(1-2^{1-2n}) \beta^{-(2n+1)} (2n)! \xi(2n) \end{aligned}$$

$\xi(n) = \sum_{k=1}^{\infty} \frac{1}{k^n}$: Riemann Zeta function ($n \geq 2$)

$\xi(2) = \frac{\pi^2}{6}, \ \xi(4) = \frac{\pi^4}{90}, \ \xi(6) = \frac{\pi^6}{945}, \ldots$

Sommerfeld expansion:

$$I = \int_{-\infty}^{\infty} g(E) f_-(E) = \underset{\overset{\updownarrow}{I_0}}{\int_{-\infty}^{\mu} dE g(E)} + \underset{\overset{\updownarrow}{I_2}}{\tfrac{\pi^2}{6}(k_B T)^2 g'(\mu)} + \underset{\overset{\updownarrow}{I_4}}{\tfrac{7\pi^4}{360}(k_B T)^4 g'''(\mu)} + ...$$

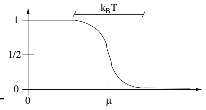
If μ is the only energy scale in g, then order of magnitude $g^{(n)}(\mu) \sim \mu^{-n} g(\mu) \ \Rightarrow$ fast convergence, expansion in $(\frac{k_B T}{\mu})^2 \sim \frac{1}{(25)^2}$

5.2.5 Thermodynamical properties of the degenerate Fermi gas

N fixed → corresponding T-dependent μ:

$$\begin{aligned} \langle \hat{N} \rangle &= N = \int_{-\infty}^{\infty} dE D(E) f_-(E) \qquad (g(E) = D(E)) \\ &= \int_{-\infty}^{\mu} dE D(E) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu) + \dots \end{aligned}$$

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



D: density of states

$$D(E) = d\sqrt{E} \quad (\text{for } E = \tfrac{\hbar^2 k^2}{2m},\ d = \dots)$$

From the definition of E_F : $(D(E) = 0$ for $E \le 0)$

$$T = 0 : N = \int_{-\infty}^{E_F} D(E) dE = \tfrac{2}{3} d E_F^{3/2} \rightarrow d = \tfrac{3}{2} N E_F^{-3/2}$$

For general T:

$$N = \underbrace{\frac{3}{2} N E_F^{-3/2}}_{d} (\tfrac{2}{3}\mu^{3/2} + \tfrac{\pi^2}{6}(k_B T)^2 \tfrac{1}{2}\mu^{-1/2} + \dots)$$

$$1 = (\tfrac{\mu}{E_F})^{3/2}[1 + \tfrac{\pi^2}{8}(\tfrac{k_B T}{\mu})^2] \text{ fixes } \mu(T, n) \leftrightarrow E_F = \tfrac{\hbar^2}{2m}(\tfrac{6\pi^2}{2S_1} n)^{2/3},\ n = N/V$$

$$\begin{aligned} (...)^{2/3} : 1 &= \frac{\mu}{E_F}[1 + \frac{\pi^2}{12}(\frac{k_B T}{\mu})^2 + \dots] \quad (\Rightarrow E_F = \mu + \dots) \\ &\approx \frac{\mu}{E_F}[1 + \frac{\pi^2}{12}(\frac{k_B T}{E_F})^2 + \dots] \end{aligned}$$

$\Rightarrow \mu = E_F[1 - \frac{\pi^2}{12}(\frac{k_BT}{E_F})^2 + O(\frac{k_BT}{E_F})^4]$

$\Rightarrow \mu$ is well approximated by E_F, correction is negative

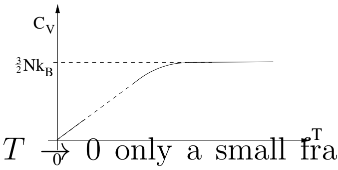
$E_F = \frac{\hbar^2}{2m}(\frac{6\pi^2}{2S+1}\frac{N}{V})^{2/3}$ (exact) $\quad \mu \leftrightarrow N$

Similarly:

$U(T) = U(0)[1 + \frac{5\pi^2}{12}(\frac{k_BT}{E_F})^2 + \ldots]$, $U(0) = d\frac{2}{5}E_F^{5/2} = \frac{3}{5}NE_F$

$C_V = \frac{\partial U}{\partial T}|_{V,N} \ll C_V^{\text{cl.}} = \frac{3}{2}Nk_B = \lim_{T\to\infty} C_V$

For the ideal Fermi gas:



$C_V \overset{T\to\infty}{\longrightarrow} C_V^{\text{cl.}}$

$C_V \gamma T$ $(T \to 0)$

for $T \to 0$ only a small fraction $\sim N\frac{k_BT}{E_F}$ of the electrons can absorb the energy k_BT (and change to an unoccupied nearby energy level)

For real metals: $C_V^* = \gamma T + \underbrace{\alpha T^3}$

phonons ($\leftrightarrow$ oscillation of crystal of ions, Debye law)

Thermal equation of state: from $U = \frac{3}{2}PV$ (exact, ideal Fermi gas)

$\Rightarrow PV = \frac{2}{3}U = \frac{2}{5}NE_F[1 + \frac{5\pi^2}{12}(\frac{k_BT}{E_F})^2 + \ldots]$

- weak T-dependence
- $P(T=0) = \frac{2}{5}\frac{N}{V}E_F = \frac{2}{5}\frac{\hbar^2}{2m}(\frac{6\pi^2}{2S+1})^{2/3}(\frac{N}{V})^{5/3}$
- $P(T=0)$ from e^- in states $\vec{k} \neq 0$ (Pauli principle)
- compensates the attraction of ions

Entropy: $S(T,V,\mu) = -\frac{\partial\Omega}{\partial T}|_{V,\mu}$

$\Xi = e^{-\beta\Omega} = \prod_{\vec{k}}(1 + e^{-\beta(E_{\vec{k}}-\mu)})^{2S+1}$

$$\Rightarrow S = -k_B(2S+1)\sum_{\vec{k}}[\langle\hat{n}_{\vec{k}}\rangle \underset{\overset{\uparrow}{\text{particles}}}{\ln(\langle\hat{n}_{\vec{k}}\rangle)} + (1-\langle\hat{n}_{\vec{k}}\rangle)\underset{\overset{\uparrow}{\text{“holes”}}}{\ln(1-\langle\hat{n}_{\vec{k}}\rangle)}]$$

$\langle\hat{n}_{\vec{k}}\rangle = (e^{\beta(E_{\vec{k}}-\mu)}+1)^{-1}$

for $T\to 0$:

$E_{\vec{k}} > E_F:\ \langle\hat{n}_{\vec{k}}\rangle \to 0$, $\ln(1-\langle\hat{n}_{\vec{k}}\rangle)\to 0$

$E_{\vec{k}} < E_F:\ \langle\hat{n}_{\vec{k}}\rangle \to 1$, $\ln(\langle\hat{n}_{\vec{k}}\rangle)\to 0$

$\Rightarrow S\to 0$ for $T\to 0 \leftrightarrow$ 3rd law of TD

5.3 Ideal Bose gas

5.3.1 Equations of state

One-particle energies: $|\vec{k}m_s\rangle \quad m_s = -S\ldots,S$

$\epsilon(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m};\quad \vec{k} = \frac{2\pi}{L}\vec{n};\quad \epsilon(\vec{k})\geq 0 \Rightarrow \mu\in(-\infty,0)$ is physical

$\langle\hat{n}_{\vec{k}=0,m_s}\rangle = \frac{1}{e^{-\beta\mu}-1} \overset{-\beta\mu<<1(\mu\nearrow 0)}{\approx} \frac{1}{-\beta\mu}$ (notation: $\langle\ldots\rangle_+ \equiv \langle\ldots\rangle$, we drop subscript “+”)

can be macroscopically large ($O(N)$) unlike for fermions $\langle\hat{n}_{\vec{k}=-0,m_s}\rangle_- \leq 1$

density of states $D(E)\propto\sqrt{E}\to D(0)=0$

problem when $(2S_1)\sum_{\vec{k}}\ldots \overset{L\to\infty}{\to} \int dE\, D(E)\ldots$: ground state is macroscopically occupied, but has weight 0 ↯

$\to$ need special treatment of $\vec{k}=0$

$$\begin{aligned} e^{-\beta\Omega} &= \sum_{\{n_{\vec{k},m_s}\}} e^{-\beta\sum_{\vec{k},m_s}(\epsilon(\vec{k})-\mu)n_{\vec{k},m_s}} \\ &= \prod_{\vec{k}}(1-e^{-\beta(\epsilon(\vec{k})-\mu)})^{-(2S+1)} \end{aligned}$$

$$\begin{aligned}\beta\Omega &= (2S+1)\sum_{\vec{k}}\ln(1-ze^{-\beta\epsilon(\vec{k})})\\ &= (2S+1)\{\ln(1-z)+\sum_{\vec{k}\neq 0}\ln(1-ze^{-\beta\epsilon(\vec{k})})\}\\ &= (2S+1)\{\ln(1-z)-\frac{V}{\lambda_T^3}g_{5/2}(z)\}\end{aligned}$$

with $g_m(z) = -f_m(-z) = \sum_{n=1}^{\infty}\frac{z^n}{n^m}$

Remarks:

- replacement $\sum_{\vec{k}\neq 0}\ldots \to \frac{V}{(2\pi)^3}\int d^3k$ completely analogous to Fermi gas (the missing term $\vec{k}=0$ does not play a role)
- it is justified to single out $\vec{k}=0$ contribution only; for $-\beta\mu = c/N$ as $N, L\to\infty$ at fixed $N/L^3 = n$; $c = 0(1)$
  $\langle\hat{n}_{\vec{k}_1,m_s}\rangle = \frac{1}{e^{\beta(\epsilon_1-\mu)}-1}\approx\frac{1}{\beta(\epsilon_1-\mu)}$

  $\beta\epsilon_1 = \beta\frac{\hbar^2}{2m}(\frac{2\pi}{L})^2 = \frac{\alpha}{N^{2/3}}$

  $\frac{\langle\hat{n}_{\vec{k}_1,m_s}\rangle}{\langle\hat{n}_{\vec{k}_0,m_s}\rangle}\approx\frac{1}{-\frac{\beta\epsilon_1}{\beta\mu}+1} = \frac{1}{\frac{\alpha}{c}N^{1/3}+1} = \mathcal{O}(N^{-1/3})\approx\mathcal{O}(10^{-7})$

Gibbs-Duhem: $\Omega = -PV$

(1) $\beta P = \frac{-\beta\Omega}{V} = (2S+1)\{\frac{g_{5/2}(z)}{\lambda_T^3}-\frac{\ln(1-z)}{V}\}$
Thermal equation of state: replace $z\to N = \langle\hat{N}\rangle$ using

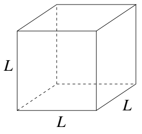
(2) $n = \frac{N}{V} = -\frac{1}{V}\frac{\partial\Omega}{\partial\mu} = \frac{1}{V}\,z\underbrace{\frac{\partial}{\partial z}}_{\frac{1}{\beta}\frac{\partial}{\partial\mu}}\underbrace{(-\beta\Omega)}_{\ln\Xi}|_{T,V} = (2S+1)\{\frac{g_{3/2}(z)}{\lambda_T^3}+\frac{1}{V}\frac{z}{1-z}\}$
combine (1) and (2) $\to P(T,V,n)$ $\qquad z\frac{d}{dz}g_m(z) = g_{m-1}(z)$
caloric equation of state $U = -\frac{\partial}{\partial\beta}\ln\Xi|_{z,V}\to$

(3) $U = \frac{3}{2}k_BTV\frac{2S+1}{\lambda_T^3}g_{5/2}(z)$ $\qquad(-\frac{\partial}{\partial\beta}\lambda_T^{-3} = \frac{3}{2}\frac{1}{\beta\lambda_T^3})$
combine (3) and (1):

$$U = \underbrace{\frac{3}{2}PV}_{\substack{\text{classical,}\\ \text{Fermi}}}+\underbrace{\frac{3}{2}k_BT(2S+1)\ln(1-z)}_{\substack{\text{additional term}\\ \text{for bosons}}}$$

Addendum:

- one-particle states $|\vec{k}, m_s\rangle \quad m_s = -s, -s+1, \ldots, s-1, s$
  - momentum $\vec{p} = \hbar\vec{k}$, energy $\epsilon(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m}$
  - spin S integer
  - finite volume with periodic boundary conditions:
    $e^{i\vec{k}\vec{r}} \overset{!}{=} e^{i\vec{k}(\vec{r}+L\vec{e}_i)} \quad i = 1,2,3 \quad V = L^3$
    $\Rightarrow k_i L = 2\pi n_i, \quad \vec{k} = \frac{2\pi}{L}\vec{n}, \quad n_i \in \mathbb{Z}$



- density of states:

  each state in $\vec{k}$-space occupies a cell of volume $\Delta k^3 = (2\pi/L)^3$

  number of states with energy $E = \frac{\hbar^2\vec{k}^2}{2m}$:

$$\begin{aligned}\varphi(E) &= \sum_{\vec{k},m_s} \Theta(E - \frac{\hbar^2\vec{k}^2}{2m}) = (2S+1)\sum_{\vec{k}} \Theta(\sqrt{2mE/\hbar^2} - |\vec{k}|^2) \\ &\cong (2S+1)\frac{4\pi}{3}\left(\frac{\sqrt{2mE}}{\hbar}\right)^3 (\Delta k)^{-3} = (2S+1)\frac{4\pi}{3}\left(\frac{2mE}{\hbar^2}\right)^{3/2}\frac{V}{(2\pi)^3}\end{aligned}$$

  Remark: this result justifies factor h^{-3N} for phase space volume in classical statistics

  density of states (Fermi + Bose):

$$D(E) = \frac{d}{dE}\varphi(E) = \begin{cases} 0 & \text{for } E \leq 0 \\ dE^{1/2} & \text{for } E > 0 \end{cases}$$

  $d = (2S+1)\frac{V}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}, \quad [d] = (\text{energy})^{-3/2}$

-

$$\begin{aligned}\beta\Omega &= (2S+1)\sum_{\vec{k}} \ln(1 - ze^{-\beta\epsilon(\vec{k})}), \quad z = e^{\beta\mu} \\ &= (2S+1)\{\ln(1-z) + \sum_{\vec{k}\neq 0}\} \ln(1 - ze^{-\beta\epsilon(\vec{k})})\}\end{aligned}$$

$$\begin{aligned}
\sum_{\vec{k}\neq 0} \ln(1 - ze^{-\beta\epsilon(\vec{k})}) &= \frac{V}{(2\pi)^3}\sum_{\vec{k}\neq 0}(\Delta k)^3 \ln(1 - ze^{-\beta\epsilon(\vec{k})}) \\
&\cong \frac{V}{(2\pi)^3}\int d^3k \ln(1 - ze^{-\beta\epsilon(\vec{k})}) \\
&= \frac{V}{(2\pi)^3}4\pi\int_0^\infty dk k^2 \ln(1 - ze^{-\beta\hbar^2k^2/2m}) \\
&= \frac{4}{\sqrt{\pi}}\frac{V}{\lambda_T^3}\int_0^\infty du u^2 \ln(1 - ze^{-u^2})
\end{aligned}$$

last line: change of variable: $\sqrt{\frac{\beta}{2m}}\hbar k = u = \frac{\lambda_T}{2\sqrt{\pi}}k$

$\lambda_T = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$ thermal de Broglie wavelength

series expansion: $\ln(1-y) = -\sum_{n=1}^\infty \frac{y^n}{n} \quad (|y| < 1)$

definitions:

$$\begin{aligned}
g_{5/2}(z) &:= -\frac{4}{\sqrt{\pi}}\int_0^\infty du u^2 \ln(1 - ze^{-u^2}) = \frac{4}{\sqrt{\pi}}\sum_{n=1}^\infty \int_0^\infty du u^2 \frac{(ze^{-u^2})^n}{n} \\
&= \frac{4}{\sqrt{\pi}}\sum_{n=1}^\infty \frac{z^n}{n} \underbrace{\int_0^\infty du u^2 e^{-nu^2}}_{=n^{-3/2}\int_0^\infty dx x^2 e^{-x^2} = n^{-3/2}\frac{\sqrt{\pi}}{4}} = \sum_{n=1}^\infty \frac{z^n}{n^{5/2}}
\end{aligned}$$

$g_{3/2}(z) := z\frac{d}{dz}g_{5/2}(z) = \sum_{n=1}^\infty \frac{z^n}{z^{3/2}}$ in general: $g_m(z) = \sum_{n=1}^\infty \frac{z^n}{n^m}$

$\Rightarrow \beta\Omega = (2S+1)\{\ln(1-z) - \frac{V}{\lambda_T^3}g_{5/2}(z)\}$

5.3.2 Classical limit

$\langle \hat{n}_{\vec{k},m_s}\rangle = \frac{1}{z^{-1}e^{\beta\epsilon(\vec{k})}-1} \approx ze^{-\beta\epsilon(\vec{k})} << 1$

for small z:

- $n_\alpha \geq 2$ does not occur → occupation numbers like for fermions
- $\vec{k} = 0$ special term irrelevant, because not $z \nearrow 1$

- analogous calculation to fermions

$$\Rightarrow PV = \underbrace{Nk_BT}_{\substack{\text{classical}\\ \text{ideal gas}}}(1 - \underbrace{\frac{n\lambda_T^3}{4\sqrt{2}(2S+1)}}_{\substack{\text{quantum}\\ \text{correction}}})$$

- opposite sign as for fermions
- quantitatively small effect compared to other van der Waals terms

5.3.3 Bose Einstein condensation

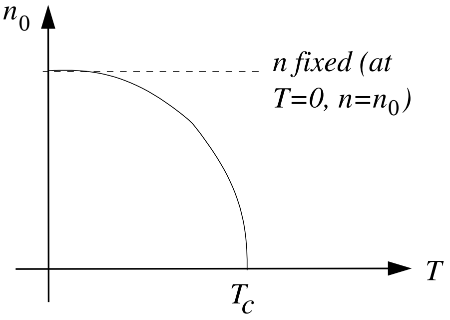
degenerate Bose gas: high density (↯ classical), low temperatures

phase transition:

$$n_0 = \frac{\langle \hat{n}_{\vec{k}=0,m_s}\rangle}{V}(2S+1)$$

$$= \frac{1}{V}\frac{1}{\frac{1}{z}-1}(2S+1)$$

$$= \frac{1}{V}\frac{z}{1-z}(2S+1)$$



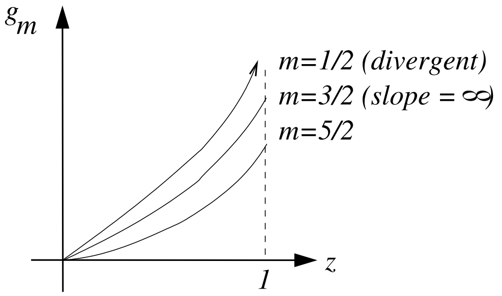
- density $n \cong n_0$ is expected for $k_BT < \epsilon_1 - \epsilon(\vec{k}=0) \sim \frac{\hbar^2}{2m}(\frac{2\pi}{L})^2$
  $\Rightarrow T \sim 10^{-20}$K ($\langle \hat{n}_{\vec{k}_1,m_s}\rangle = \frac{1}{e^{\beta(E_1-\mu)}-1} \approx \frac{1}{\beta(\epsilon_1-\epsilon(0))} < 1$)
- Bose-Einstein condensation: $n \cong n_0$ at $T_c = \mathcal{O}(1\text{K})$!

Properties of $g_m(z) = \sum_{n=1}^{\infty}\frac{z^n}{n^m} \quad z \in (0,1) \Leftrightarrow \mu \in (-\infty, 0)$

$$g_{5/2}(1) = \xi(\tfrac{5}{2}) = 1.342\ldots$$

$$g_{3/2}(1) = \xi(\tfrac{3}{2}) = 2.612\ldots$$

$$zg'_{3/2}(z) = g_{1/2}(z) \to \infty \text{ for } z \nearrow 1$$



eq. (2) sec. 5.3.1 : $n = n_0 + (2S+1) g_{3/2}(z)/\lambda_T^3$

For $n > (2S+1)\xi(3/2)/\lambda_T^3$ it must be: $n_0 > 0$

Limiting case: $n\lambda_T^3 = (2S+1)\xi(3/2)$

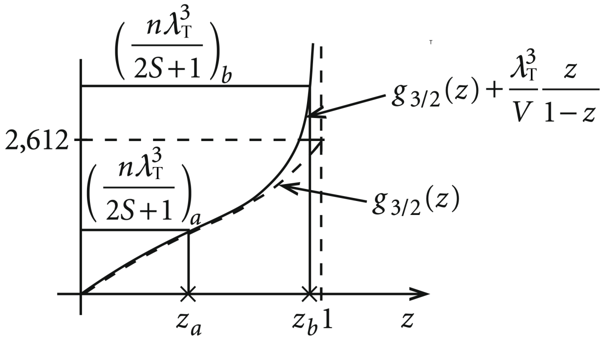
$\Rightarrow k_B T_c = \frac{2\pi\hbar^2}{m}(\frac{n}{(2S+1)\xi(3/2)})^{3/2} \to T_c(n) \qquad (\lambda_T = \sqrt{\frac{2\pi\beta\hbar^2}{m}})$

respectively $n_c = (2S+1)\xi(3/2)\lambda_T^{-3} = (2S+1)\xi(3/2)(\frac{mk_BT}{2\pi\hbar^2})^{3/2} = n_c(T)$

condensation happens for $T \leq T_c$ or $n \geq n_c$ resp. $\Leftrightarrow n\lambda_T^3 = \mathcal{O}(1) \leftrightarrow$

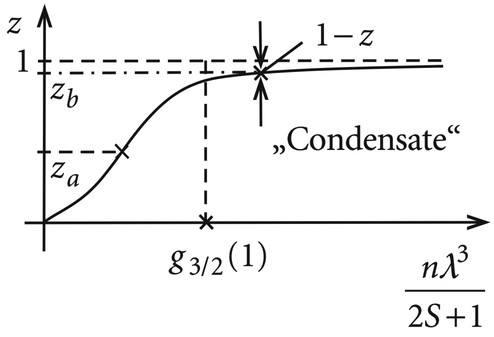
average particle distance $= \mathcal{O}(\lambda_T)$

Relation $n \leftrightarrow z$ at fixed T, λ_T and V large, but finite



eq.(2): $\frac{n\lambda_T^3}{2S+1} = \frac{n_0\lambda_T^3}{2S+1} + g_{3/2}(z) \qquad n_0 = \frac{1}{V}\frac{z}{1-z}(2S+1)$

inverted:



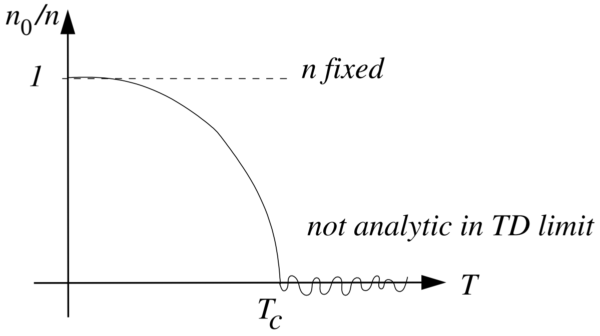
$(\frac{n\lambda_T^3}{2S+1})_b > \xi(3/2) \Leftrightarrow n_0 > 0$

In thermodynamic limit $N \to \infty, V \to \infty, n = N/V$ fixed

$$z = \begin{cases} 1 & \text{if } n\lambda_T^3 \geq (2S+1)\xi(3/2) \quad (*) \\ \text{solution of } g_{3/2}(z) = \frac{n\lambda_T^3}{2S+1} & \text{if } n\lambda_T^3 < (2S+1)\xi(3/2) \quad (**) \end{cases}$$

In the "condensation region" (*):

$$\begin{aligned} \frac{n_0}{n} &\cong 1 - \frac{2S+1}{n\lambda_T^3}\xi(3/2) = 1 - (\frac{\lambda_T(T_c)}{\lambda_T})^3 \\ &= 1 - (\frac{T}{T_c})^{3/2} \qquad (\lambda_T \propto T^{-1/2}) \\ \frac{n_0}{n} &= 0 \text{ outside (**)} \end{aligned}$$



$\frac{n_0}{n}$: "order parameter"

terminology in analogy to liquid-gas transition:

n_0: liquid phase $\quad n_0 = n(1 - (T/T_c)^{3/2})$ in $\vec{k} = 0$ state

$n - n_0$: gas phase $\quad n - n_0 = n(T/T_c)^{3/2}$ in excited $\vec{k} \neq 0$ states

→ Bose-Einstein condensation

Remark: for $T < T_c$ the $n - n_0$ bosons have an asymptotically thin distribution $\frac{\langle \hat{n}_{\vec{k}_1} \rangle}{\langle \hat{n}_{\vec{k}=0} \rangle}$ $N^{-1/3}$
Addendum: Experimental realization of a Bose-Einstein condensate:

dilute (↔ weakly interacting) alkali gases:

- Wieman and Cornell (University of Colorado, Boulder), 1995:
  rubidium-87 atoms, $T = 20$nK, $N = 2000$ atoms
- Ketterle (MIT), 1995:
  sodium-23 atoms, $T = 2\mu$K, $N = 5 \times 10^5$ atoms

Nobel prize in physics 2001

Remark 1:

- superconductivity, superfluidivity happen for strongly interacting systems
- Bose-Einstein condensation happen for ideal (non-interacting) systems

Remark 2: experimental signature of Bose-Einstein condensate:

- anisotropy in the velocity distribution
- interference

5.3.4 Photons

Photons: quantum electrodynamics, relativistic quantum field theory classical: electromagnetic waves = solutions of Maxwell's equations in empty space:

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i(\vec{k}\vec{r}-\omega t)} \quad \vec{B} = (\tfrac{\vec{k}}{\omega} \times \vec{E}_0) e^{i(\vec{k}\vec{r}-\omega t)}$$

with $\omega^2 = c^2\vec{k}^2$, $\vec{E}_0$: two independent polarizations

quantized: particles with $E = \hbar\omega$, $\vec{p} = \hbar\vec{k}$

$$\Rightarrow E^2 - c^2p^2 = \hbar^2(\omega^2 - c^2\vec{k}^2) = 0 \overset{\text{in general}}{=} (mc^2)^2$$

$$\Rightarrow m = 0 \text{ particles, spin } S = 1 \rightarrow m_s = -1, \cancel{0}, 1$$

Lorentz group ⇒ only $m_s = -s, s$ for massless particles

$m_s = -1, +1 \leftrightarrow$ classical: left/right circularly polarized

second quantization as bosons ($S = 1$!)

$$[\hat{a}_{\vec{k},\sigma}, \hat{a}^+_{\vec{k}',\sigma'}] = \delta_{\vec{k},\vec{k}'}\delta_{\sigma,\sigma'} \qquad \sigma, \sigma' = \pm 1$$

$\vec{k} = \frac{2\pi}{L}\vec{n}$ in <u>cavity</u>

$$\hat{H} = \sum_{\vec{k},\sigma} \hbar\underset{\substack{\nearrow \\ \text{associated energy}}}{\omega(\vec{k})}\underset{\substack{\nwarrow \\ \text{\# photons in mode } \vec{k}\text{, spin } \sigma}}{\hat{n}_{\vec{k},\sigma}}$$

$\hat{N} = \sum_{\vec{k},\sigma} \hat{n}_{\vec{k},\sigma}$ does not commute with the interactions which thermalize cavity ↔ radiation, $\langle\hat{N}\rangle$ is not conserved (unlike e in solid bodies)

Thermodynamics of photons: only V, T can be chosen, not $N = \langle\hat{N}\rangle$, $N(V,T)$ is adjusted by the condition that the free energy is minimal: $\frac{\partial F}{\partial N}|_{T,V} = 0$

Respectively, in the microcanonical description: E, T can be chosen $E = \sum_{\vec{k}} n_{\vec{k},\sigma}\hbar\omega(\vec{k})$

Distribution of E on photons is chosen by the system, photons are created/annihilated during thermalization.

We found the change of F by adding a photon $\frac{\partial F}{\partial N}|_{T,V} \overset{\text{def.}}{=} \mu \Rightarrow \mu = 0$

$\Rightarrow$ compute Ω only for $\mu = 0$ (here not variable)

$$\begin{aligned}\beta\Omega(T,V) &= 2\sum_{\vec{k}} \ln(1 - e^{-\beta\hbar\omega(\vec{k})}) \cong 2\frac{V}{(2\pi)^3}\int d^3k \ln(1 - e^{-\beta\hbar\omega(\vec{k})}) \\ &= \frac{V}{\pi^2}\int_0^\infty dk k^2 \ln(1 - e^{-\beta\hbar ck}) =: \frac{V}{\pi^2}\mathcal{J}(\beta)\end{aligned}$$

$$\mathcal{J}(\beta) \underset{\text{by parts}}{\overset{\text{integration}}{=}} -\frac{1}{3}\int_0^\infty dk k^3 \frac{\beta\hbar c e^{-\beta\hbar ck}}{1 - e^{-\beta\hbar ck}} = -\frac{1}{3(\beta\hbar c)^3}\int_0^\infty du \frac{u^3}{e^u - 1}$$

general formula: $\int_0^\infty du \frac{u^{\alpha-1}}{e^u - 1} = \Gamma(\alpha)\xi(\alpha);\qquad \Gamma(4) = 3! = 6;\qquad \xi(4) = \frac{\pi^4}{90}$

$\Rightarrow \Omega(T,V) = -\frac{\pi^2 V}{45(\hbar c)^3}(k_B T)^4 = -PV$

$\Rightarrow P(T) = \frac{1}{3}\alpha T^4$ Stefan-Boltzmann law with Stefan-Boltzmann constant

$\alpha = \frac{\pi^2 k_B^4}{15(\hbar c)^3} \approx 7.6 \cdot 10^{-16} \frac{J}{m^3 K^4}$

Since $\Omega = F - \mu N$ (Legendre) $\Omega(T,V) = F(T,V)$ identical

Entropy: $S(T,V) = -\frac{\partial \Omega}{\partial T}|_V = \frac{4}{3}\alpha V T^3$

Photon number (self-adjusting) $N = \langle \hat{N} \rangle = \int_{-\infty}^\infty dE D(E) f_+(E)$

with $f_+ = 1/(e^{\beta E} - 1)$

$D(E)$ for photons? $E = \hbar\omega(\vec{k}) = \hbar c|\vec{k}|$

$$\begin{aligned}\phi(E) &= 2\frac{\frac{4\pi}{3}(\frac{E}{\hbar c})^3}{(\frac{2\pi}{L})^3} = \frac{VE^3}{3\pi^2(\hbar c)^3} \\ D &= \begin{cases}\phi' = \frac{VE^2}{\pi^2(\hbar c)^3} & \text{for } E \geq 0 \\ 0 & \text{otherwise}\end{cases}\end{aligned}$$

Remark: compare $D \propto \sqrt{E}$ non-relativistic case.

$$\begin{aligned} \Rightarrow N &= \frac{V}{\pi^2(\hbar c)^3}\int_0^\infty dE \frac{E^2}{e^{\beta E}-1} = \frac{V}{\pi^2(\beta\hbar c)^3}\int_0^\infty dE \frac{u^2}{e^u - 1} = \\ &= \frac{V}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3 \Gamma(3)\xi(3) \approx 2\cdot 10^7 \frac{VT^3}{[m^3K^3]} \end{aligned}$$

Similarly:

$U = \int_{-\infty}^{\infty} dE\, E\, D(E)\, f_+(E) = \alpha V T^4 \Rightarrow \epsilon(T) = \frac{U}{V} = \alpha T^4$

$P(T) = \frac{1}{3}\epsilon(T)$

Spectral energy density $\hat{\epsilon}(\omega, T)$:

$U =: V \int_0^\infty \hat{\epsilon}(\omega, T) d\omega$ with $E = \hbar\omega$, $dE = \hbar d\omega \Rightarrow$

Planck radiation formula: $\hat{\epsilon}(\omega, T) d\omega = \frac{E}{V} D(E) f_+(E) dE = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{d\omega}{e^{\beta\hbar\omega}-1}$

For $\hbar\omega << k_B T$: Rayleigh-Jeans limit: $e^{\beta\hbar\omega} - 1 \approx \beta\hbar\omega$

$\hat{\epsilon} d\omega \to \frac{\omega^2}{\pi^2 c^3} k_B T d\omega$

- no $\hbar$ anymore
- classical result $\int_0^\infty d\omega \hat{\epsilon}_{RJ} = \infty$!

For $\hbar\omega >> k_B T$: $\hat{\epsilon}(\omega, T) \to \frac{\hbar\omega^3}{\pi^2 c^3}$ = Wien radiation formula

A Mathematical Intermezzo: exact differentials

Consider functions of two variables: $f = f(x,y)$

Definition of differential: $df(x,y) = \frac{\partial f}{\partial x}\Big|_y dx + \frac{\partial f}{\partial y}\Big|_x dy$

$\frac{\partial f}{\partial x}\Big|_y dx$ is the partial derivative of f with respect to x at constant y

The expression $dg(x,y) = p\,dx + q\,dy$ is called an **exact differential**,

provided that $\displaystyle \frac{\partial p}{\partial y}\bigg|_x = \frac{\partial q}{\partial x}\bigg|_y$.

The above $df(x,y)$ is an exact differential, because the partial derivatives may be exchanged (if they are continuous)

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\bigg|_y\right)\bigg|_x = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\bigg|_x\right)\bigg|_y \qquad \left(p = \frac{\partial f}{\partial x}\bigg|_y,\ q = \frac{\partial f}{\partial y}\bigg|_x\right)$$

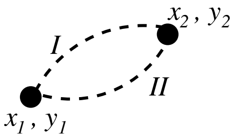
Green's Theorem: Let $dA(x,y) = P\,dx + Q\,dy$, where P, Q, $\frac{\partial P}{\partial y}$ and $\frac{\partial Q}{\partial x}$ are single-valued and continuous in a simply- (or multiply-) connection region $\mathcal{M}$, bounded by a simple (or more) closed curve(s) $\mathcal{C}$. Then

$$\oint_{\mathcal{C}} dA = \int_{\mathcal{M}} dx\,dy\left(\frac{\partial Q}{\partial x}\bigg|_y - \frac{\partial P}{\partial y}\bigg|_x\right)$$

Corollary: If $dA(x,y)$ is an exact differential, we have

$\oint_{\mathcal{C}} dA = 0.$ $\qquad \displaystyle\left(\text{Proof: } \frac{\partial Q}{\partial x}\bigg|_y = \frac{\partial P}{\partial y}\bigg|_x\right)$

If $\mathcal{C} = (x_1, y_2) \xrightarrow{\text{path } I} (x_2, y_2) \xrightarrow{-\text{path } II} (x_1, y_1)$
then $\int_{\text{path } I} dA = \int_{\text{path } II} dA$.



Therefore, the value of $A(x_2, y_2)$ does not depend on the path along which (x_2, y_2) is reached (at fixed reference point (x_1, y_1)). Every function possessing this property is called a **state function**.

Corollary: $dA(x,y)$ exact differential $\Leftrightarrow$ $A(x,y)$ state function

Examples: $E(T,V)$ and $S(E,V)$ are state functions

Example: $dq = dE + P\,dV$ is not an exact differential.

Proof: $dq \overset{(*)}{=} \underbrace{\left.\frac{\partial E}{\partial T}\right|_V}_{=p(T,V)} dT + \underbrace{\left(\left.\frac{\partial E}{\partial V}\right|_T + P\right)}_{=q(T,V)} dV$

For an exact differential: $\underbrace{\left.\frac{\partial}{\partial V}\left(\left.\frac{\partial E}{\partial T}\right|_V\right)\right|_T}_{\overset{(*)}{=}\left.\frac{\partial}{\partial T}\left(\left.\frac{\partial E}{\partial V}\right|_T\right)\right|_V} \overset{!}{=} \left.\frac{\partial}{\partial T}\left(\left.\frac{\partial E}{\partial V}\right|_T + P\right)\right|_V$

$(\frac{\partial p}{\partial V}|_T = \frac{\partial q}{\partial T}|_V)$

$^{(*)}$ dE is an exact differential: $dE(T,V) = \frac{\partial E}{\partial T}|_V dT + \frac{\partial E}{\partial V}|_T dV$

$\Rightarrow \frac{\partial P}{\partial T}|_V = 0$ cannot be correct, e.g., ideal gas: $PV = nRT$: $\frac{\partial P}{\partial T}|_V = \frac{nR}{V}$. $\square$

Lemma: Consider $A = A(x,y)$ and $z = z(x,y)$

$$\left.\frac{\partial A}{\partial x}\right|_z = \left.\frac{\partial A}{\partial x}\right|_y + \left.\frac{\partial A}{\partial y}\right|_x \left.\frac{\partial y}{\partial x}\right|_z \tag{A.0.1}$$

$$\left.\frac{\partial A}{\partial z}\right|_y = \left.\frac{\partial A}{\partial x}\right|_y \left.\frac{\partial x}{\partial z}\right|_y \tag{A.0.2}$$

$$\left.\frac{\partial x}{\partial y}\right|_z = -\left.\frac{\partial x}{\partial z}\right|_y \left.\frac{\partial z}{\partial y}\right|_x \tag{A.0.3}$$

Proof: $dA = \left.\frac{\partial A}{\partial x}\right|_y dx + \left.\frac{\partial A}{\partial y}\right|_x dy$

$$\overset{(*)}{\Rightarrow} \left.\frac{\partial A}{\partial x}\right|_z = \left.\frac{\partial A}{\partial x}\right|_y \underbrace{\left.\frac{\partial x}{\partial x}\right|_z}_{=1} + \left.\frac{\partial A}{\partial y}\right|_x \left.\frac{\partial y}{\partial x}\right|_z \Rightarrow (A.0.1)$$

$$\text{or } \left.\frac{\partial A}{\partial z}\right|_y = \left.\frac{\partial A}{\partial x}\right|_y \left.\frac{\partial x}{\partial z}\right|_y + \left.\frac{\partial A}{\partial y}\right|_x \underbrace{\left.\frac{\partial y}{\partial z}\right|_y}_{=0} \Rightarrow (A.0.2)$$

$^{(*)}$ consider finite differences:

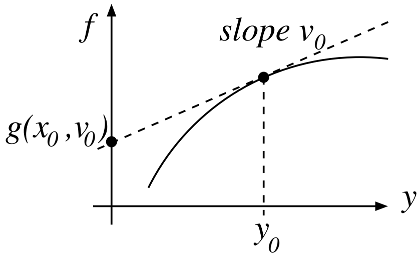
$$\Delta A = \left.\frac{\partial A}{\partial x}\right|_y \Delta x + \left.\frac{\partial A}{\partial y}\right|_x \Delta y \Rightarrow \frac{\Delta A}{\Delta x} = \left.\frac{\partial A}{\partial x}\right|_y \frac{\Delta x}{\Delta x} + \left.\frac{\partial A}{\partial y}\right|_x \frac{\Delta y}{\Delta x} \text{ etc.}$$

Now take Eq. (A.0.1) and set $z = A$:

$$\underbrace{\left.\frac{\partial z}{\partial x}\right|_z}_{=0} = \left.\frac{\partial z}{\partial x}\right|_y + \left.\frac{\partial z}{\partial y}\right|_x \left.\frac{\partial y}{\partial x}\right|_z$$

Using $\left.\frac{\partial z}{\partial x}\right|_y = \frac{1}{\frac{\partial x}{\partial z}|_y}$ and $\left.\frac{\partial y}{\partial x}\right|_z = \frac{1}{\frac{\partial x}{\partial y}|_z} \Rightarrow (A.0.3)$

Legendre transformation: Consider $df = u\,dx + v\,dy$, where $v = \frac{\partial f}{\partial y}|_x$. We define a new function g via $g = f - vy$.



one-dimensional sketch $(x = x_0)$

$g(x_0, v_0)$ intercept of tangent of f at y_0

$$dg = df - d(vy)$$
$$= u\,dx + v\,dy - v\,dy - y\,dv$$

$\Rightarrow\ dg = u\,dx - y\,dv$

$\Rightarrow$ g is a function of x and v, i.e., $g(x, v)$, which is called the Legendre transform of $f(x, y)$. It replaces the dependence of y by a dependence of v. It assumes the validity of $v = \frac{\partial f}{\partial y}|_x$.

Example: $dE = dq - P\,dV = T\,dS + (-P)dV \qquad \left.\frac{\partial E}{\partial V}\right|_S = -P$

Legendre transform $H = E - \left.\frac{\partial E}{\partial V}\right|_S V = E + PV$ replaces dependence on V by dependence on P, see section 2.1.

B Question on internal energy

From the first law of thermodynamics Eq. (1) the variation of the internal energy is given by

$$dE = \underbrace{dq}_{\textit{absorbed heat}} - \underbrace{P\,dV}_{\textit{work done}}$$

The second law of thermodynamics for reversible processes reads

$$\begin{aligned} & dq = T\,dS \\ \Rightarrow\quad & \boxed{dE = T\,dS - P\,dV} \text{ is an exact differential,} \\ & \left.\frac{\partial E}{\partial S}\right|_V = T; \quad \left.\frac{\partial E}{\partial V}\right|_S = -P \end{aligned}$$

$E = E(S,V)$ is a state function of S and V.

Legendre Transformation: $[x = S,\ y = V,\ v- = P]$

$$\begin{aligned} & H = E(S,V) - \left.\frac{\partial E}{\partial V}\right|_S V = E + PV \\ \Rightarrow\quad & \boxed{dH = dE + d(PV) = T\,dS + V\,dP} \quad \text{(exact differential)} \\ & \left.\frac{\partial H}{\partial S}\right|_P = T; \quad \left.\frac{\partial H}{\partial P}\right|_S = V \end{aligned}$$

$H = H(S,P)$ is a state function of S and P.

We can also look at $E = E(T,V)$:

$$dE = \underbrace{\left.\frac{\partial E}{\partial T}\right|_V} dT + \left.\frac{\partial E}{\partial V}\right|_T dV$$

$= C_V =$ isochore heat capacity, which is not a thermodynamic function, *e.g.*, for an ideal gas with point-like particles $C_V = \frac{3}{2}nR$ is a constant.

The thermodynamic function of T and V is the free energy F.

C N identical harmonic oscillators

$\hat{H} = \sum_{i=1}^{N} \hbar\omega(a_i^+ a_i + 1/2)$

Bosons: $[a_i, a_j^+] = \delta_{ij}$, all other commutators vanish

Energies: $E_{n_1,\dots,n_N} = \sum_{i=1}^{N} \hbar\omega(n_i + 1/2)$

Eigenstates: $|n_1, \dots, n_N\rangle$, $\hat{H}|n_1, \dots, n_N\rangle = E_{n_1,\dots,n_N}|n_1, \dots, n_N\rangle$

Since the oscillators are identical we cannot distinguish which oscillator is in which eigenstate $\leftrightarrow n_i$

$$\begin{aligned} |n_1, \dots, n_N\rangle &\equiv |n_1, \dots, n_N\rangle_+ \text{ (symmetric)} \\ &= c_+ \sum_{\pi \in S_N} |n_{\pi(1)}, \dots, n_{\pi(N)}\rangle \end{aligned}$$

$\{\pi(1), \dots, \pi(N)\}$: permutation of $1, \dots, N$

all the states $|n_{\pi(1)}, \dots, n_{\pi(N)}\rangle$ have the same energy

If all n_i's are different*: $c_+ = 1/\sqrt{N!} \leftrightarrow$ origin of the factor $c_+ = 1/N!$

in classical statistical mechanics which automatically appears in

$\mathrm{Tr}(\cdot) = \sum_{\{n_i\}} {}_+\langle n_i, \dots, n_N| \cdot |n_1, \dots, n_N\rangle_+$

* in general: $c_+ = (N! \prod_{m=0}^{\infty} N_m!)^{-1/2}$

N_m = number of oscillators with $n_i = m$ $(0! = 1)$

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