STATISTICAL MECHANICS

Greiner, Neise, Stöcker (book, chapter 5)

- ✷ Microstates, entropy
- ✷ Ensemble theory -
  -microcanonical ..., -canonical ..., -grand ...
- ✷ Application to physical systems
  Harmonic oscillators,
  ideal gas, paramagnetism
- ✷ Quantum statistics
  ideal Bose and Fermi gas
- ✷ Phase transitions

Statistical mechanics

Microcanonical ensemble

Whole system

variables: E, V, N

Canonical ensemble

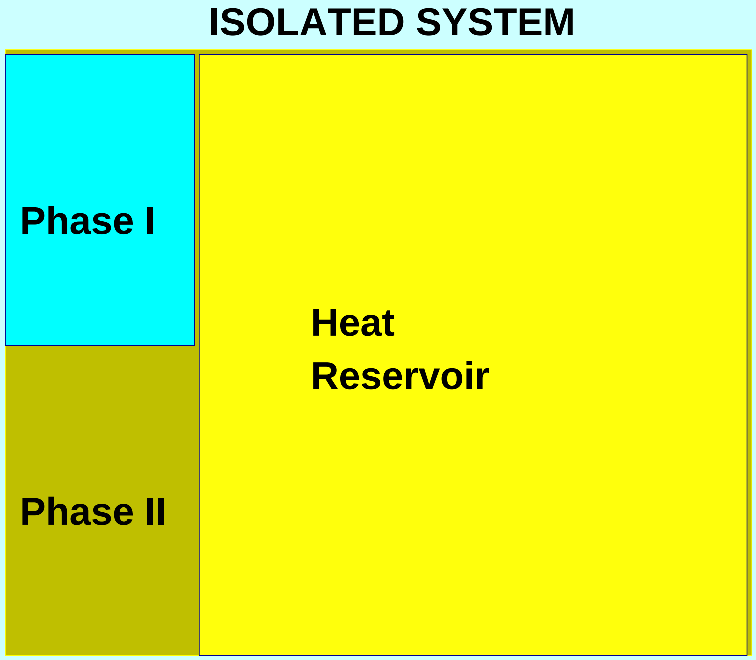
Phase I + II

variables: T, V, N

Grand canonical ensemble

Phase II

variables: T, V, μ



Microstates and Entropy (classical)

Phase space: $(q_\nu,\, p_\nu)$, $\nu = 1 \ldots 3N$

6 N dimensional space

Definite point in phase space is one **microstate** of the system

The phase space trajectory $(q_\nu(t), p_\nu(t))$ is determined by

$$\dot{q}_\nu = \frac{\partial H}{\partial p_\nu} \qquad \dot{p}_\nu = -\frac{\partial H}{\partial q_\nu}$$

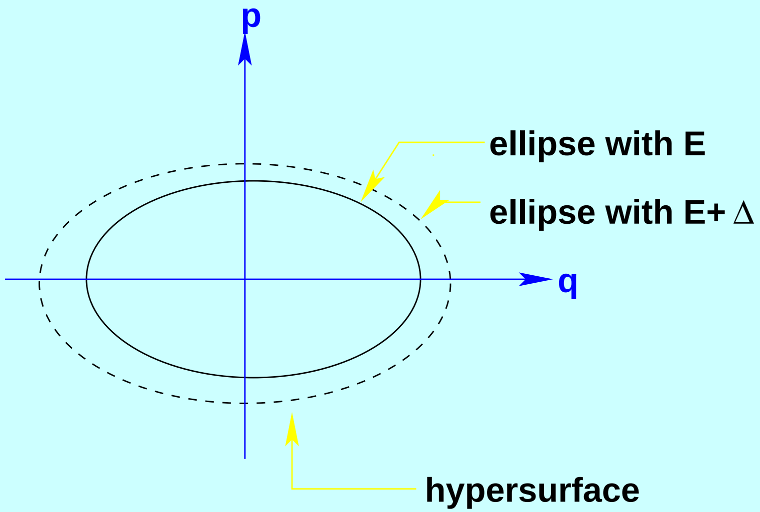
In a closed system

$$E = H(q_\nu(t), p_\nu(t))$$ 6N-1 hypersurface in phase space

is conserved along the trajectory

1D Harmonic Oscillator (example)

2d-phase space



$$H = \frac{p^2}{2m} + \frac{1}{2}kq^2$$

phase space distribution
of many equal systems
at one moment

Collection of phase space points
in $(E, E+\Delta E)$ is an **ensemble**

Phase space volume

$$\Delta\omega = \int_{E \leq H(q,p) \leq E+\Delta E} dqdp = \int_{\ldots} d\omega$$

Area of a hypersurface

$$\sigma(E) = \int_{E=H(q,p)} d\sigma$$

Closed system characterized by (E, V, N)

- V restricts q
- Only microstates on the E-surface are allowed

$$\Downarrow$$

Complicated surface

Thermodynamic limit: $V, N \to \infty$

Number of allowed microstates

$$\Omega(E, V, N) = \frac{\sigma(E, V, N)}{\sigma_0} = \frac{1}{\sigma_0} \int_{E=H(q_\nu, p_\nu)} d\sigma$$

σ_0: proportionality constant

Direct calculation of $\Omega\,(E, V, N)$ difficult

Often more convenient to use:

$$\Omega\,(E, V, N) = \frac{\sigma\,(E, V, N)}{\sigma_0} = \frac{1}{\sigma_0}\,\frac{\partial \omega}{\partial E}$$

with the volume

$$\omega(E, V, N) = \int_{H(q_\nu, p_\nu) \leq E} d^{3N}q\, d^{3N}p$$

Entropy

Thermodynamics ↘

equilibrium state

most probable macro state

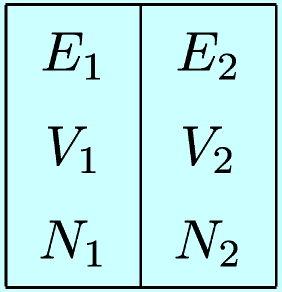
⇕

largest number of microstates

All microstates with same E **have the same probability**
(postulate)

Properties of the entropy

Closed system



E_1	E_2
V_1	V_2
N_1	N_2

$$\begin{array}{ll} E = E_1 + E_2 = \text{const} & dE_1 = -dE_2 \\ V = V_1 + V_2 = \text{const} & \bullet \\ N = N_1 + N_2 = \text{const} & \bullet \end{array}$$

$$\Omega(E, V, N) = \Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2)$$

$$\Omega(E,V,N) = \Omega_1(E_1,V_1,N_1)\Omega_2(E_2,V_2,N_2)$$

most probable state: $\quad \Omega = \Omega_{\mathrm{max}}, \quad d\Omega = 0$

$$d\Omega = \Omega_2 d\Omega_1 + \Omega_1 d\Omega_2$$

divide with $\Omega = \Omega_1\Omega_2$

$$\longrightarrow \qquad d\ln\Omega = d\ln\Omega_1 + d\ln\Omega_2$$

Equilibrium

$$d\ln\Omega = 0 \qquad \ln\Omega = \ln\Omega_{\mathrm{max}}$$

Closed system, internal energy $U = E$

$$S(E,V,N) = S_1(E_1,V_1,N_1) + S_2(E_2,V_2,N_2)$$

$$dS = dS_1 + dS_2$$

equilibrium $\longrightarrow \quad dS = 0 \quad , \quad S = S_{\max}$

Compare !

$$S(E,V,N) \quad = \quad k \ln \Omega(E,V,N)$$

$$\updownarrow$$

proportional

now macroscopic properties (equation of State ...)

$$\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{V,N} \quad , \quad \frac{P}{T} = \frac{\partial S}{\partial V}\Big|_{E,N} \quad , \quad -\frac{\mu}{T} = \frac{\partial S}{\partial N}\Big|_{E,V}$$

In principle: Calculate Ω from microscopic model → macroscopic properties (“through S”)

$$\boxed{\text{Difficult} \longrightarrow \text{ensemble theory}}$$

Example: Ideal gas

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{3N} \frac{p_\nu^2}{2m}$$

Calculate the phase space volume

$$\omega(E,V,N) = \int_{H(q_\nu,p_\nu)\leq E} d^{3N}q\,d^{3N}p = V^N \int_{\dots} d^{3N}p$$

The limit $H(q_\nu, p_\nu) \leq E$ defines
a $3N$-dimensional sphere with radius $\sqrt{2mE}$

$$\sum_{\nu=1}^{3N} p_\nu^2 \leq \left(\sqrt{2mE}\right)^2$$

The volume is

$$V_{3N}(R) = \frac{\pi^{3N/2}}{\frac{3N}{2}\,\Gamma\left(\frac{3N}{2}\right)}\, R^{3N}$$

and thus

$$\omega(E, V, N) = \frac{\pi^{3N/2}}{\frac{3N}{2}\,\Gamma\left(\frac{3N}{2}\right)}\,(2mE)^{3N/2}\, V^N$$

The number of possible microstates is thus

$$\Omega(E,V,N) = \frac{1}{\sigma_0}\,\frac{\partial\omega}{\partial E} = \frac{V^N}{\sigma_0}\,\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \cdot (2m)^{3N/2} E^{3N/2-1}$$

and the entropy

$$S(E,V,N) = k\ln\Omega(E,V,N) = k\ln\left\{\frac{V^N}{\sigma_0}\,\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}\,(2m)^{3N/2}\,E^{3N/2-1}\right\}$$

Use the asymptotic form

$$\ln\Gamma(n) \simeq n\ln n - n \qquad \text{if} \qquad n \ggg 1$$

and define $\sigma = \sigma_0^{1/N}$ and use $E^{3N/2-1} \sim E^{3N/2}$

$$\left\{ \dim\left(\frac{V^N\,(2mE)^{3N/2}}{\sigma_0 E}\right) = \dim\left(\frac{q^{3N}p^{3N}}{\sigma_0 E}\right) = 1 \right\}$$

$(\Delta\omega = \sigma(E)\Delta E)$

then

$$\begin{aligned} S(E,V,N) &\simeq Nk\ln\left\{\frac{V}{\sigma}\left(\frac{2\pi mE}{1}\right)^{3/2}\right\} - k\ln\Gamma\left(\frac{3N}{2}\right) \\ &= Nk\left\{\frac{3}{2} + \ln\left(\frac{V}{\sigma}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right)\right\} \end{aligned}$$

Now

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{3}{2}Nk\,\frac{1}{E} \quad \rightarrow \quad E = \frac{3}{2}NkT$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{Nk}{V} \quad \rightarrow \quad pV = NkT$$

So k can be identified as the Boltzmann constant k_B

(later σ is identified as $h^3 \ldots$dim)

But S here is not **extensive** (purly) (magnbundið)

Gibbs paradox: Two ideal gases A and B same T, p

A	B
T, p	T, p
$N_A,\ V_A$	$N_B,\ V_B$

$$
\begin{aligned}
\Delta S &= S^{(1)}_{\text{total}} - S^{(0)}_{\text{total}} \\
&= S^{(1)}_A\left(T, V_A + V_B, N_A\right) + S^{(1)}_B\left(T, V_A + V_B, N_B\right) \\
&\quad - S^{(0)}_A\left(T, V_A, N_A\right) - S^{(0)}_B\left(T, V_B, N_B\right) \\
\to \Delta S &= N_A k \ln\left\{\frac{V_A + V_B}{V_A}\right\} + N_B k \ln\left\{\frac{V_A + V_B}{V_B}\right\} > 0
\end{aligned}
$$

irreversible process, **mixing entropy**

If A and B same gas:

$S^{(0)}_{\text{total}}$ same as before

but now $S^{(1)}_{\text{total}} = S^{(1)}\left(T, V_A, +V_B, N_A + N_B\right)$

$\rightarrow \Delta S =$ (same as before with distinct gases) > 0

But the process is reversible!

Since quantum mechanically all the atoms are **completely indistinguishable**

Classically this is not the case!

We have to mend the classical way of enumeration of the particles

$$\Omega(E,V,N) = \frac{\sigma(E,V,N)}{\sigma_0} \to \frac{1}{N!}\frac{\sigma(E,V,N)}{\sigma_0}$$

Ω: number of microstates

σ: hypersurface area

$N!$: Gibbs correction

$$\begin{aligned} S(E,V,N) &= Nk\left\{\frac{3}{2} + \ln\left\{\frac{V}{\sigma}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right\}\right\} - k\ln N! \\ &\simeq Nk\left\{\frac{5}{2} + \ln\left\{\frac{V}{N\sigma}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right\}\right\} \end{aligned}$$

Now S is an extensive quantity
since $\frac{V}{N}$ and $\frac{E}{N}$ are intensive in the ln(...)

And $\Delta S = 0$ if gas $A =$ gas B

Read yourselves

Pseudo quantum mechanical counting of Ω

pp. 135 - 139

and example 5.3 p. 140 - 141

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Conclusion

The thermodynamic properties can be calculated from the microscopic H

The calculation of

$$\Omega(E,V,N) = \frac{\sigma}{\sigma_0} = \frac{1}{\sigma_0}\int_{E=H} d\sigma$$

or

$$\omega(E,V,N) = \int_{H\leq E} d^{3N}q\, d^{3N}p \quad \to \quad \Omega = \frac{1}{\sigma_0}\,\frac{\partial\omega}{\partial\Omega}$$

to get

$$S = k\ln\Omega$$

Complex geometry ⟶ **Ensemble theory**

Ensemble theory

- All microstates of the energy surface of a closed system are equally likely
- For open systems each microstate has a weight $\rho(q_\nu, p_\nu)$, a probability for the macro system to reach (q_ν, p_ν)
- In a closed system $\rho = 0$ outside the energy surface

The phase space density ρ is normalized

$$\int \frac{d^{3N}q d^{3N}p}{h^{3N}} \rho(q_\nu, p_\nu) = 1$$

(for convenience h^{3N} , $\rho =$ dimensionless)

Any observable of the system $f(q_\nu, p_\nu)$ will have a mean value

$$\langle f \rangle = \int \frac{d^{3N}q d^{3N}p}{h^{3N}} f(q_\nu, p_\nu)\rho(q_\nu, p_\nu)$$

f could be f. ex. $H(q_\nu, p_\nu)$, $\mathbf{L}(q_\nu, p_\nu)\ldots$

An average over a set of identical copies of the system at a fixed time

$\langle f \rangle$: ensemble average

For a closed system

$$\rho_{mc}(q_\nu, p_\nu) = \frac{1}{\sigma(E)}\delta(E - H(q_\nu, p_\nu))$$

ρ_{mc}: microcanonical ensemble phase space density

We have ignored time t!

The hope is that the time average

$$\overline{f} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, f(q_\nu(t), p_\nu(t))$$

(where the trajectory $(q_\nu(t), p_\nu(t))$ is determined by the Hamilton equations)

gives same results as $\langle f \rangle$

$\overline{f}$ and $\langle f \rangle$ are identical if the phase-space trajectory passes through each point of the energy surface an equal number of times (Ergodic hypothesis; Boltzmann 1871)

$1D$ Hamilton operator is such a system (ergodic), but ...

quasi ergodic hypothesis

The phase-space trajectory passes arbitrarily close to each point ...

Unsolved problem taken as an axiom!

Liouville's theorem

We do not need t for equilibrium thermodynamics,
generally $\rho = \rho(q_\nu, p_\nu, t)$

Elements of phase-space flow like incompressible fluid with t

- no points lost or gained
- no crossing of trajectories

$$\frac{\partial}{\partial t}\rho + \nabla \cdot (\rho \mathbf{v}) = 0 \quad \text{(equation of continuity)}$$

$$\frac{d}{dt}\rho = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

Liouville's equation. The total t derivative of the
phase space density ρ vanishes along a phase space trajectory

Lagrange Multipliers

We want to maximize $f(x, y)$, subject to the condition: $g(x, y) = c$, const.

- must satisfy: $f_x = 0,\ f_y = 0$
  Usually, but…

we set:

$$df = f_x dx + f_y dy = 0$$

If dx and dy were independent then we would conclude $f_x = 0$, $f_y = 0$, **but** they are not because

$$dg = g_x dx + g_y dy = 0$$

so we have

$$\begin{pmatrix} f_x & f_y \\ g_x & g_y \end{pmatrix} \begin{pmatrix} dx \\ dy \end{pmatrix} = 0$$

We are not seeking the trivial solution

$$\rightarrow \quad f_x g_y - g_x f_y = 0$$

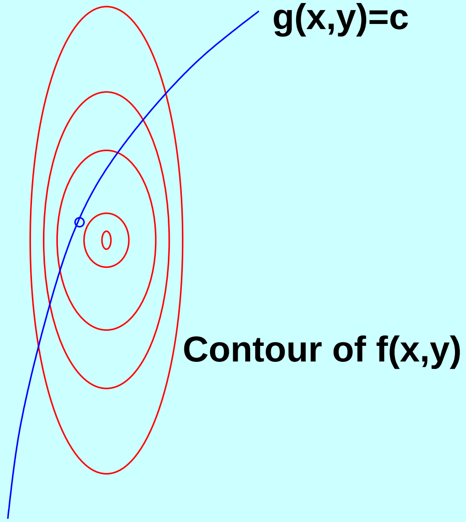
or $\quad \frac{f_x}{g_x} = \frac{f_y}{g_y} \equiv \lambda$ has to be const.

Then

$$f_x - \lambda g_x = 0, \quad f_y - \lambda g_y = 0$$

But these correspond to maximization of $f - \lambda g$

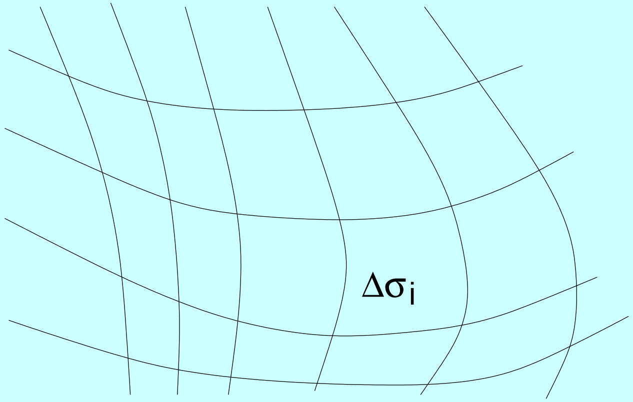
λ is a constant to be adjusted so that $g(x, y)$ takes on the correct value.



Microcanonical ensemble

We want to prove that a constant phase-space density on the energy surface is the most probable for a system.

Subdivide the energy surface into equally large surface elements $\Delta\sigma_i$



n_i microstates in $\Delta\sigma_i$

$\mathcal{N}$ identical copies of a closed system

$$\mathcal{N} = \sum_i n_i$$

p_i: probability for microstate i to lie in $\Delta\sigma_i$

$$p_i = n_i/\mathcal{N}$$

Corresponding to $\rho(q_\nu p_\nu) d^{3N}q d^{3N}p$ in the continuous formulation

The **total number** of ways to generate the distribution $\{n_1 n_2 \ldots\} = \{n_i\}$ of the $\mathcal{N}$ systems over the surface elements

$$w\{n_i\} = \frac{\mathcal{N}!}{\prod_i n_i!}$$

$\mathcal{N}!$ ways to enumerate the system differently

$n_i!$ exchanges in one cell do not give a new case

The **probability** of finding a distribution $\{n_i\}$ on the surface elements

$$w_{\text{tot}}\{n_i\} = \mathcal{N}! \prod_i \frac{(\omega_i)^{n_i}}{n_i!}$$

ω_i: The probability of finding **one** system within σ_i

What is the **most probable** distribution $\{n_i\}^*$ of the $\mathcal{N}$ systems over the phase space cells?

More convenient to use $\ln w_{\text{tot}}$ and $\ln n! \approx n \ln n - n$ for finite number of cells when $\mathcal{N} \to \infty$

$$\begin{aligned}\ln w_{\text{tot}} &= \ln \mathcal{N}! + \sum_i (n_i \ln \omega_i - \ln n_i!) \\ &\approx \quad \mathcal{N} \ln \mathcal{N} - \mathcal{N} + \sum_i \{ (n_i \ln \omega_i - (n_i \ln n_i - n_i)\}\end{aligned}$$

Most probable →

$$d \ln w_{\text{tot}} = -\sum_i (\ln n_i - \ln \omega_i) dn_i = 0$$

but all n_i are related since

$$\mathcal{N} = \sum_i n_i \qquad \text{is constant}$$

Use Lagrange multiplier λ:

Add $\lambda d\mathcal{N} = \lambda \sum_i dn_i = 0$

to $-\sum_i (\ln n_i - \ln \omega_i) dn_i = 0$

$$\rightarrow \quad \sum_i (\ln n_i - \ln \omega_i - \lambda) dn_i = 0$$

Consider all dn_i now independent

$$\rightarrow \quad \ln n_i - \ln \omega_i - \lambda = 0$$

or

$$n_i = \omega_i e^{\lambda} = \text{ constant}$$

Basic assumption of statistical physics

$$\boxed{\text{All microstates are equally likely}}$$

→ same ω_i

$$n_i = \omega_i e^{\lambda} = \text{ constant}$$

Constant phase-space density on the energy surface is the most probable possibility

$$p_i = \frac{n_i}{\mathcal{N}} \quad = \quad \begin{cases} \text{const} & H = E \\ 0 & \text{otherwise} \end{cases}$$

$$\Longrightarrow \rho_{mc} \quad = \quad \begin{cases} \text{const} & E < H \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

Read 149 + 150 to see that with

$$\rho_{mc} = \begin{cases} \frac{1}{\Omega} & E \leq H \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

The entropy can be expressed as

$$\begin{aligned} S(E,V,N) &= \int \frac{d^{3N}q\, d^{3N}p}{h^{3N}}\, \rho_{mc}(q_\nu, p_\nu)\ \{-k \ln \rho_{mc}(q_\nu, p_\nu)\} \\ &= < -k \ln \rho > \end{aligned}$$

i.e. the entropy is the ensemble average of the logarithm of the phase-space density.

The uncertainty function $H = H(p_i)$

Should only function of the probabilities p_i for $i = 1 \ldots$ possible outcome of exp

- ✓ when the outcome is certain $H = 0$
- ✓ order of independent experiments does not matter

$$H(\ldots p_i \ldots p_k \ldots) = H(\ldots p_k \ldots p_i \ldots)$$

- ✓ if all p_i are equal the outcome has max uncertainty

$$H = H_{\text{max}} \qquad \text{for all } p_i \text{ equal}$$

- ✓ if experiments I and II are independent then

$$H(I \text{ and } II) = H(I) + H(II)$$

for example I has sure outcome $H(I) = 0$

It can now be proven uniquely that

$$H = -\sum p_i \ln p_i$$

Many microstates larger entropy and uncertainty

Example

N classical distinguishable 1D H.O's. with frequency ω in the microcanonical ensemble

$$\Omega(E,V,N) = \frac{1}{h^N} \int_{E \leq H \leq E+\Delta E} d^N q d^N p$$

but it is convenient to find first

$$\sum(E,V,N) = \frac{1}{h^N}\int_{H\leq E} d^N q d^N p, \quad \text{(corresponding to } \omega\text{)}$$

No Gibbs factor ↔ distinguishability

Description of H.O. at certain sites in space … crystal lattice …

$$H(q_\nu, p_\nu) = \sum_{\nu=1}^{N}\left\{\frac{p_\nu^2}{2m} + \frac{1}{2}\,m\omega^2 q_\nu\right\}$$

With the substitution $x_\nu = m\omega q_\nu$

$$\sum(E,V,N) = \frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N \int_{\sum_{\nu=1}^N (p_\nu^2 + x_\nu^2) \leq 2mE} d^N x\, d^N p$$

an integral over a $2N$−dim sphere with radius $\sqrt{2mE}$

$$\begin{aligned} \to \sum(E,V,N) &= \frac{1}{h^N}\left(\frac{1}{m\omega}\right)^N \frac{\pi^N}{N\Gamma(N)} (2mE)^N \\ &= \frac{1}{N\Gamma(N)}\left(\frac{E}{\hbar\omega}\right)^N \end{aligned}$$

The mean number of states per energy interval

$$\begin{aligned} g(E,V,N) &= \frac{\partial}{\partial E} \sum(E,V,N) \\ &= \left(\frac{1}{\hbar\omega}\right)^N \frac{E^{N-1}}{\Gamma(N)} \end{aligned}$$

$g(E,V,N)$ corresponds to σ

Now

$$\Omega \simeq gE \qquad \text{and} \qquad \ln\Gamma(N) \eqsim N\ln N - N$$

so

$$\begin{aligned} S(E,V,N) = k\ln\Omega = k\ln & \left\{\left(\frac{1}{\hbar\omega}\right)^{N} \frac{E^{N}}{\Gamma(N)}\right\} \\ \eqsim \quad & Nk\left\{\ln\left(\frac{E}{\hbar\omega}\right) + 1 - \ln N\right\} \\ = \quad & Nk\left\{1 + \ln\left(\frac{E}{N\hbar\omega}\right)\right\} \end{aligned}$$

$\frac{E}{N\hbar\omega}$ ratio of the total energy $/N$ and

the oscillator energy $\hbar\omega_c$

$$\begin{aligned}\frac{1}{T} &= \left.\frac{\partial S}{\partial E}\right|_{V,N} = Nk\,\frac{1}{E} \rightarrow E = NkT \\ \frac{P}{T} &= \left.\frac{\partial S}{\partial V}\right|_{E,N} = 0 \qquad \rightarrow p = 0\end{aligned}$$

Oscillators fixed in space → $p = 0$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} = k\ln\left\{\frac{E}{N\hbar\omega}\right\}$$

Chemical potential

$$\mu = -kT\ln\left\{\frac{E}{N\hbar\omega}\right\}$$

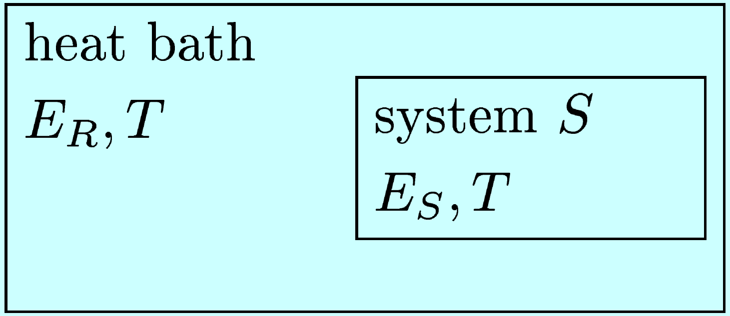
Heat capacity

$$C = \frac{\partial E}{\partial T} = Nk$$

The Canonical Ensemble

Microcanonical ensemble can be used for all systems, but …

Sometimes we want to describe only a subsystem, open system w.r.t. heat transfer



heat bath

E_R, T

system S

E_S, T

Read p. 159-160: Classical arguments comparing system sizes gives:

$$p_i = \frac{\exp\left(-\frac{E_i}{kT}\right)}{\sum_j \exp\left(-\frac{E_j}{kT}\right)}$$

as the **probability** for system S to be in microstate i

Here we follow ensemble theory

E_S is not fixed → all points in phase-space can be occupied

- ✷ Subdivide phase-space into equally sized cells $\Delta\omega_i$
- ✷ There are n_i systems in $\Delta\omega_i$
- ✷ $\mathcal{N}$ systems in the ensemble

$$\rightarrow \quad \mathcal{N} = \sum_i n_i$$

- ✷ $p_i = n_i/\mathcal{N}$ is the probability for the microstate i in the ensemble
- ✷ All possible energies E_i can be assumed with the probability p_i

But in **equilibrium** there must be certain **mean energy** U

$$\begin{aligned} U &= \langle E_i \rangle = \sum_i p_i E_i = \sum_i \frac{n_i}{\mathcal{N}} E_i \\ \rightarrow \quad \mathcal{N}U &= \sum_i n_i E_i \end{aligned}$$

There are thus **two conditions** on the distribution this time

$$\boxed{\begin{aligned} \mathcal{N} &= \sum_i n_i \\ \mathcal{N}U &= \sum_i n_i E_i \end{aligned} \qquad (*)}$$

The probability of the distribution $\{n_i\}$ is as in the microcanonical ensemble ($\Delta\omega_i$ is not a surface element here)

$$W\{n_i\} = \mathcal{N}! \prod \frac{(\omega_i)^{n_i}}{n_i!}$$

We have to find the most probable distribution $\{n_i\}^*$ subject to (*)

$$\ln W\{n_i\} = \mathcal{N} \ln - \mathcal{N} - \sum_i \{(n_i \ln n_i - n_i) - n_i \ln \omega_i\}$$

Due to (*) we need two Lagrange parameters

$$\begin{aligned} \lambda \sum_i dn_i &= 0 \\ -\beta \sum_i E_i \, dn_i &= 0 \end{aligned}$$

$$d \ln W = -\sum_i \{\ln n_i - \ln \omega_i - \lambda + \beta E_i\} \, dn_i = 0$$

Now dn_i are independent

$$\begin{aligned} \rightarrow \quad \ln n_i &= \lambda + \ln \omega_i - \beta E_i \\ \text{or} \quad n_i &= \omega_i e^{\lambda} e^{-\beta E_i} \end{aligned}$$

for equally sized phase-space cells all ω_i must be equal (the probability to find one system in $\Delta\omega_i$)

$$\begin{aligned} p_i &= \frac{n_i}{\mathcal{N}} = \frac{\omega_i e^{\lambda} e^{-\beta E_i}}{\omega_i e^{\lambda} \sum_j e^{-\beta E_j}} \\ &= \frac{\exp(-\beta E_i)}{\sum_j e^{-\beta E_j}} \end{aligned}$$

and

$$U = \frac{\sum_i E_i \, e^{-\beta E_i}}{\sum_j \, e^{-\beta E_j}} \qquad (**)$$

we still have to fix β ...

Introduce the **canonical partition function**

$$Z = \sum_i e^{-\beta E_i}$$

(Zustandssumme, ástandasumma)

In the continuous notation we have

$$Z = \frac{1}{h^{3N}} \int d^{3N}q d^{3N}p \, \exp\{-\beta H(q_\nu, p_\nu)\}$$

$$\rho_c(q_\nu, p_\nu) = \frac{\exp\{-\beta H(q_\nu, p_\nu)\}}{Z}$$

The entropy is the ensemble average of $-k \ln \rho_c$

$$\begin{aligned} S &= \langle -k \ln \rho_c \rangle = \frac{1}{h^{3N}} \int d\omega \, \rho_c(q_\nu, p_\nu) \cdot \{-k \ln \rho_c(q_\nu, p_\nu)\} \\ &= \frac{1}{h^{3N}} \int d\omega \, \rho_c(q_\nu, p_\nu) \, \{k\beta H(q_\nu, p_\nu) + k \ln Z\} \end{aligned}$$

$$\begin{aligned} \rightarrow \; S &= k\beta \, \langle H \rangle + k \ln Z \\ &= k\beta U + k \ln Z \end{aligned}$$

Obviously $\beta = \beta(U)$ (see (**))

$$\frac{1}{T} = \frac{\partial S}{\partial U} = kU \frac{\partial \beta}{\partial U} + k\beta + \frac{\partial}{\partial U}(k \ln Z)$$

but

$$\frac{\partial}{\partial U}(k \ln Z) = \frac{\partial \beta}{\partial U} \cdot \frac{\partial}{\partial \beta}(k \ln Z)$$

(since $Z = Z(\beta(U))$)

$$\frac{\partial}{\partial \beta}(k \ln Z) = \frac{k}{Z}\left\{-\sum_i E_i e^{-\beta E_i}\right\} = -kU$$

Thus

$$\frac{\partial S}{\partial U} = \frac{1}{T} = k\beta \rightarrow \boxed{\beta = \frac{1}{kT}}$$

But in addition we have

$$\begin{aligned} S &= k\beta U + k\ln Z \\ &= \frac{kU}{kT} + k\ln Z \end{aligned}$$

or

$$\begin{aligned} U - TS &= -kT\ln Z \\ &= F(T,V,N) \end{aligned}$$

with F the free energy of the system

micro → macro, convenience … $\boxed{F(T,V,N) = -kT\ln Z(T,V,N)}$

is **equivalent** to

$$S(E,V,N) = k\ln\Omega(E,N,V)$$

in the **micro canonical ensemble**

Gibbs correction

Read p. 164-166

Generally if the Hamiltonian is invariant under enumeration of the generalized coordinates then

$$Z_{nd}(T,V,N) = \int \frac{d^{3N}q d^{3N}p}{\mathcal{N}!\, h^{3N}} \exp\{-\beta H\}$$

non-distinguishable

Example: **The ideal gas in the canonical ensemble**

system in contact with a heat bath

$$H(q_\nu p_\nu) = \sum_{\nu=1}^{3N} \frac{p_\nu^2}{2m}$$

with Gibbs factor the partition function is

$$Z(T,V,N) = \frac{1}{\mathcal{N}! h^{3N}} \int d^{3N}q d^{3N}p \exp\Big\{ -\beta H(q_\nu, p_\nu)\Big\}$$

$H = H(p_\nu)$ only. Use $\exp\{\sum_i a_i\} = \prod_i \exp\{a_i\}$, then

$$Z(T,V,N) = \frac{1}{\mathcal{N}! h^{3N}} V^N \prod_{\nu=1}^{3N} \int_{-\infty}^{\infty} dp_\nu \exp\left\{-\beta \frac{p_\nu^2}{2m}\right\}$$

$$= \quad \frac{V^N}{\mathcal{N}! h^{3N}} \left(\frac{2m}{\beta}\right)^{3N/2} \prod_{\nu=1}^{3N} \int_{-\infty}^{\infty} dx\, e^{-x^2}$$

Since we used $x = \sqrt{\frac{\beta}{2m}}\, p_\nu$

giving

$$Z(T,V,N) = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

Use the thermal wavelength to get

$$\begin{aligned} \lambda &= \left(\frac{h^2}{2\pi mkT}\right)^{3/2} \\ Z(T,V,N) &= \frac{V^N}{\mathcal{N}!\lambda^{3N}} \end{aligned}$$

Using Stirlings formula the free energy is

$$\begin{aligned} F(T,V,N) &= -kT \ln Z(T,V,N) \\ &= -NkT \left\{1 + \ln\left(\frac{V}{N\lambda^3}\right)\right\} \end{aligned}$$

and the thermodynamic properties follow

$$\begin{aligned}
p &= -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{NkT}{V} \to pV = NkT \\
S &= -\frac{\partial F}{\partial T}\Big|_{V,N} = Nk\left[\frac{5}{2} + \ln\left\{\frac{V}{N\lambda^3}\right\}\right] \\
\mu &= -\frac{\partial F}{\partial N}\Big|_{T,V} = -kT\ln\left\{\frac{V}{N\lambda^3}\right\}
\end{aligned}$$

The internal energy U of the system is

$$U = F + TS = \frac{3}{2} NkT$$

and can be used to **replace** the T in S:

$$S(U, V, N) = Nk \left[\frac{5}{2} + \ln \left\{ \frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{3/2} \right\} \right]$$

same as in the microcanonical ensemble!

- F and S are equivalent thermodynamic potentials related by a legrende transformation

Later, we come back to this issue

Read Exercises 7.2 + 7.3 about the ultrarelativistic gas and the H.O's.

Noninteracting particles

If the Hamiltonian satisfies

$$H(q_1 \ldots q_{3N}, p_1 \ldots p_{3N}) = \sum_{\nu=1}^{N} h(q_\nu, p_\nu)$$

then

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N! h^{3N}} \int d^{3N}q d^{3N}p \, \exp\{-\beta H(q_\nu, p_\nu)\} \\ &= \frac{1}{N! h^{3N}} \prod_{\nu=1}^{N} \int d^3 q_\nu d^3 p_\nu \, \exp\{-\beta h(q_\nu, p_\nu)\} \\ &= \frac{1}{N!} \{Z(T,V,1)\}^N \end{aligned}$$

where

$$Z(T,V,1) = \frac{1}{h} \int d^3 q d^3 p \, \exp\{-\beta h(q,p)\}$$

is the partition function of a **one** particle system.

In an analogous way one often introduces (p. 171, read justification)

$$\rho_1(q,p) = \frac{\exp\{-\beta h(q,p)\}}{Z(T,V,1)}$$

Velocity in an ideal gas

$$\begin{aligned}
H(\mathbf{q}_i,\mathbf{p}_i) &= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \rightarrow h(q,p) = \frac{\mathbf{p}^2}{2m} \\
\rho(q,p) &= \frac{\exp\{-\beta h(q,p)\}}{Z(T,V,1)} \\
&= \frac{\lambda^3}{V} \exp\left\{-\frac{\beta}{2m}\,\mathbf{p}^2\right\}
\end{aligned}$$

The probability density for finding any particle in the one-particle phase-space with **p** and **q**

$$Z(T,V,1)=\frac{V}{\lambda^3}$$

independent particles: No correlation between q and p and position and momenta of other particles

interacting q_ν and p_ν are correlated

The probability of finding a particle with $\mathbf{p}$ between $\mathbf{p}$ and $\mathbf{p}+d\mathbf{p}$ and $\mathbf{q}$ and $\mathbf{q}+d\mathbf{q}$ is

$$\rho\cdot d^3q\,d^3p\,\frac{1}{h^3}$$

implying

$$
\begin{aligned}
& & f(\mathbf{p})d^3p &= \frac{d^3p}{h^3}\int d^3q\,\rho(q,p) \\
&\rightarrow & m^3 f\,(\mathbf{p})d^3v &= \frac{m^3}{h^3}\,d^3v\int d^3q\,\rho(q,p) \\
& & \text{or} & \\
& & f(\mathbf{v})d^3v &= \frac{m^3}{h^3}\,d^3v\int d^3q\,\frac{\lambda^3}{V}\,\exp\left\{-\frac{\beta m v^2}{2}\right\}
\end{aligned}
$$

normalization with dp or dv to 1

$$\rightarrow \quad f(\mathbf{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left\{-\frac{mv^2}{2kT}\right\}$$

$$f(\mathbf{v})d^3\mathbf{v} \equiv d^3w(\mathbf{v})$$

is the probability to find a particle with $\mathbf{v}$ between (v_x, v_y, v_z) and $(v_x + dv_x,\, v_y + dv_y,\, v_z + dv_z)$

find the probability for $|\mathbf{v}| \in (|\mathbf{v}|,\, |\mathbf{v} + d\mathbf{v}|)$

$|\mathbf{v}| \rightarrow$ polar coordinates

integrate $\mathbf{q}$ out (has been done)

$$dw(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{\beta m v^2}{2}\right\} 4\pi v^2 dv$$

Maxwell's velocity distribution

Most probable speed v^* corresponds to

$$F(v) = \frac{dw}{dv}$$

taking a maximum

$$F'(v)\Big|_{v^*} = 0$$

$$\Leftrightarrow 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left[-\frac{m}{kT}\exp\left\{-\frac{mv^2}{2kT}\right\}v^3+\exp\left\{-\frac{mv^2}{2kT}\right\}2v\right]_{v^*} = 0$$

$$\to\ v^* = \sqrt{\frac{2kT}{m}}$$

The mean speed

$$\langle|\mathbf{v}|\rangle = \int_0^\infty F(v)v dv = \sqrt{\frac{8kT}{m\pi}}$$

The mean square speed

$$\begin{aligned}\langle v^2\rangle &= \int_0^\infty F(v)v^2 dv = \frac{3kT}{m}\\ \langle\epsilon_{km}\rangle &= \frac{1}{2}m\langle v^2\rangle = \frac{3}{2}kT\end{aligned}$$

Read **Example 7.6**:

Velocity distribution of an evaporating gas

****

Observables as ensemble averages

The phase-space density $\rho(\mathbf{r}_i, \mathbf{p}_i)$ containes all information about the system, for example

$$S = \langle -k \ln \rho \rangle$$

and all thermodynamics follows.

But also

$$\rho(\mathbf{r}_1^1 \ldots \mathbf{r}_N^1, \mathbf{p}_1^1 \ldots \mathbf{p}_N^1,) = \langle h^{3N} \prod_{i=1} \delta(\mathbf{r}_i - \mathbf{r}'_i)\delta(\mathbf{p}_i - \mathbf{p}'_i) \rangle$$

The phase-space distribution for particle i in an ensemble of distinguishable particles is

$$\rho_i(\mathbf{r},\mathbf{p}) = \langle h^3 \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{p}_i - \mathbf{p}) \rangle$$

If there is *no interaction* then

$\rho_i(\mathbf{r},\mathbf{p})$ is identical with

$\rho(\mathbf{r}_1,\mathbf{p}_1)$ single-particle distribution

……

Total particle density

$$\rho(\mathbf{r}) = \langle \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}) \rangle$$

total momentum density

$$\rho(\mathbf{p}) = \langle \sum_{i=1}^{N} \delta(\mathbf{p}_i - \mathbf{p}) \rangle$$

$$\int d^3\mathbf{r}\, \rho(\mathbf{r}) = \int d^3\mathbf{p}\, \rho(\mathbf{p}) = N$$

Relative distance of two particles

Two particle correlation function

$$f_{ik}(r) = \langle \delta(r - |\mathbf{r}_i - \mathbf{r}_k|) \rangle$$

gives the mean distance of i and k

$$\begin{aligned}
\langle r_{ik} \rangle &= \langle |\mathbf{r}_i - \mathbf{r}_k| \rangle \\
&= \langle \int_0^\infty r\delta\left(r - |\mathbf{r}_i - \mathbf{r}_k|\right) dr \rangle \\
&= \int_0^\infty r \langle \delta\left(r - |\mathbf{r}_i - \mathbf{r}_k|\right) \rangle dr \\
&= \int_0^\infty r\, f_{ik}(r) dr
\end{aligned}$$

liquide, gas, solide, ...

Test on an ideal gas

$$
\begin{aligned}
\rho(\mathbf{r}_1 \ldots \mathbf{r}_N,\, \mathbf{p}_1 \ldots \mathbf{p}_N) &= N! \prod_{i=1}^{N} \frac{\exp\left\{-\frac{\beta}{2m}\,\mathbf{p}_i^2\right\}}{Z(T,V,1)} \\
&= N! \prod_{i=1}^{N} \rho_i(\mathbf{r}_1,\, \mathbf{p}_1)
\end{aligned}
$$

where ρ_i is the phase-space distribution for particle i, and

$$
Z(T,V,1) = \frac{1}{h^3} \int d\omega \, \exp\left\{-\frac{\beta \mathbf{p}^2}{2m}\right\} = \frac{V}{\lambda^3}
$$

Thus

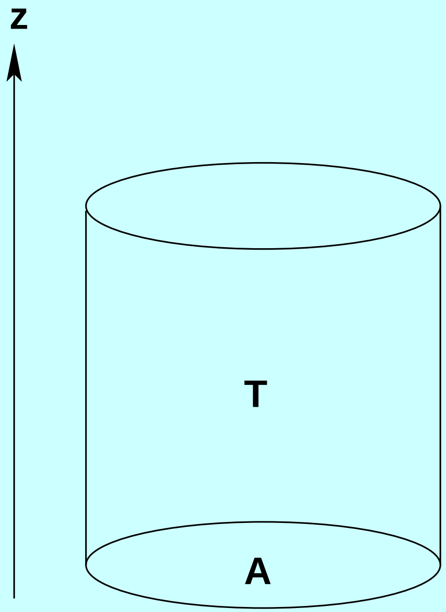
$$\begin{aligned}
\rho_i(\mathbf{r}) &= \langle\delta(\mathbf{r}_1 - \mathbf{r})\rangle \\
&= \frac{1}{N!h^{3N}} \int d^{3N}\mathbf{r}\, d^{3N}\mathbf{p}\, \rho(\mathbf{r}_1 \ldots, \mathbf{p}_1 \ldots)\delta(\mathbf{r}_i - \mathbf{r}) \\
&= \frac{1}{h^{3N}} \int d\omega \prod_{k=1}^{N} \rho_k(\mathbf{r}_k, \mathbf{p}_k)\delta(\mathbf{r}_i - \mathbf{r}) \\
&= \frac{1}{h^3} \int d^3\mathbf{p}_i\, d^3\mathbf{r}_i\, \frac{\lambda^3}{V} \exp\left\{-\frac{\beta\mathbf{p}_i^2}{2m}\right\} \delta(\mathbf{r}_i - \mathbf{r}) \\
&= \frac{\lambda^3}{Vh^3} \int d^3\mathbf{p}_i\, \exp\left\{-\frac{\beta\mathbf{p}_i^2}{2m}\right\} = \frac{1}{V}
\end{aligned}$$

So we have

$$\rho(\mathbf{r}) = \langle \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}) \rangle = \sum_{i=1}^{N} \rho_i(\mathbf{r}) = \frac{N}{V}$$

as expected !!

Example: The law of atmospheres



- Air column
- N: atoms
- Constant gravity

find $\rho(z)$

$$H(\mathbf{r}_i, \mathbf{p}_i) = \sum_{i=1}^{N} \left\{ \frac{\mathbf{p}_i^2}{2m} + mgz_i \right\} = \sum_{i=1}^{N} h_i(\mathbf{r}_i, \mathbf{p}_i)$$

$$\begin{aligned}\rho(\mathbf{r}_1\ldots,\mathbf{p}_1\ldots) &= N!\prod_{i=1}^{N}\frac{\exp\left\{-\beta h_i(\mathbf{r}_i,\mathbf{p}_i)\right\}}{Z(T,V,1)} \\ &= N!\prod_{i=1}^{N}\rho_i(\mathbf{r}_i,\mathbf{p}_i)\end{aligned}$$

One-particle partition function

$$\begin{aligned}Z(T,V,1) &= \frac{1}{h^3}\int d^3p\,\exp\left(-\frac{\beta\mathbf{p}^2}{2m}\right)\int d^3r\,\exp(-\beta mgz) \\ &= \frac{1}{\lambda^3}\cdot A\cdot\int dz\,\exp(-\beta mgz) \\ &= \frac{A}{\beta mg\lambda^3}\end{aligned}$$

Use the definition of a single-particle density

$$
\begin{aligned}
\rho_i(\mathbf{r}) &= \frac{1}{N!\,h^{3N}} \int d\omega \rho(\mathbf{r}_1 \ldots, \mathbf{p}_1 \ldots)\delta(\mathbf{r}_i - \mathbf{r}) \\
&= \frac{1}{h^{3N}} \int d\omega \prod_{k=1}^{N} \rho_k(\mathbf{r}_k, \mathbf{p}_k)\delta(\mathbf{r}_i - \mathbf{r})
\end{aligned}
$$

All integrals of $\rho_k(\mathbf{r}_k, \mathbf{p}_k)$ yield 1 expect the integral over $\mathbf{r}_i, \mathbf{p}_i$,

$$\begin{aligned}
\rightarrow \quad \rho_i(\mathbf{r}) &= \frac{\beta m g \lambda^3}{A h^3} \int d^3\mathbf{p}_i \, \exp\left\{-\frac{\beta \mathbf{p}_i^2}{2m}\right\} \\
&\quad \cdot \int d^3\mathbf{r}_i \, \exp\{-\beta m g z_i\} \, \delta(\mathbf{r}_i - \mathbf{r}) \\
&= \frac{\beta m g}{A} \int d^3\mathbf{r}_i \, \exp\{-\beta m g z_i\} \, \delta(\mathbf{r}_i - \mathbf{r}) \\
&= \frac{\beta m g}{A} \exp\{-\beta m g z\}
\end{aligned}$$

Thus for N atoms (independent)

$$\rho(\mathbf{r}) = \frac{N\beta mg}{A}\exp\{-\beta mgz\}$$

For an ideal gas we have

$$p = \frac{NkT}{V} = \rho kT = \rho/\beta$$

and thus the pressure is

$$\begin{aligned} p(z) &= \frac{Nmg}{A}\exp\{-\beta mgz\} \\ &= p(0)\exp\{-\beta mgz\} \end{aligned}$$

with the pressure $p(0) = \frac{Nmg}{A}$ at the surface!

Is the assumption about constant gravity important here? Is it ok?

Connection between microcanonical and canonical ensembles

The probability of finding a system of the canonical ensemble in microstate (q_ν, p_ν) is

$$dp = \frac{1}{h^{3N}}\,\rho(q_\nu, p_\nu)d\omega = \frac{1}{h^{3N}Z}\,e^{-\beta H(q_\nu, p_\nu)}d\omega$$

It is constant on the $H(q_\nu, p_\nu) = E$ surface

→ probability of finding the system with energy between E and $E + \Delta E$

$$dp(E) = \frac{\exp\{-\beta E\}}{Z\,h^{3N}} \int_{E \le H \le E + \Delta E} d\omega$$

Easier to calculate the volume

$$\sum(E, V, N) = \frac{1}{h^{3N}} \int_{H \le E} d\omega$$

and

$$\frac{1}{h^{3N}} \int_{E \le H \le E+\Delta E} d\omega = \frac{\partial \Sigma}{\partial E} dE \equiv g(E) dE$$

$g(E)$ is the density of states, (many-particle)

$$\begin{aligned} \rightarrow \quad dp(E) &= \frac{1}{Z} g(E) \exp\{-\beta E\} dE \\ &= p(E) dE \end{aligned}$$

In the same way we have

$$\begin{aligned} Z(T, V, N) &= \frac{1}{h^{3N}} \int d\omega \, \exp\{-\beta H(q_\nu, p_\nu)\} \\ &= \int dE \, g(E) \, \exp\{-\beta E\} \end{aligned}$$

in discrete systems (i.e. quantum)

$$g(E) \to g_E \qquad\qquad g_E: \text{ degeneracy factor}$$

and

$$p(E) = \frac{g_E}{Z}\, e^{-\beta E}$$

……

$$Z(T,V,N) = \int_0^\infty dE\, g(E)\, e^{-\beta E}$$

is a Laplace transform

$$\to \quad g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} d\beta\, e^{\beta E} Z(\beta)$$

Direct connection between $g(E)$, (i.e. Ω), and $Z(E)$

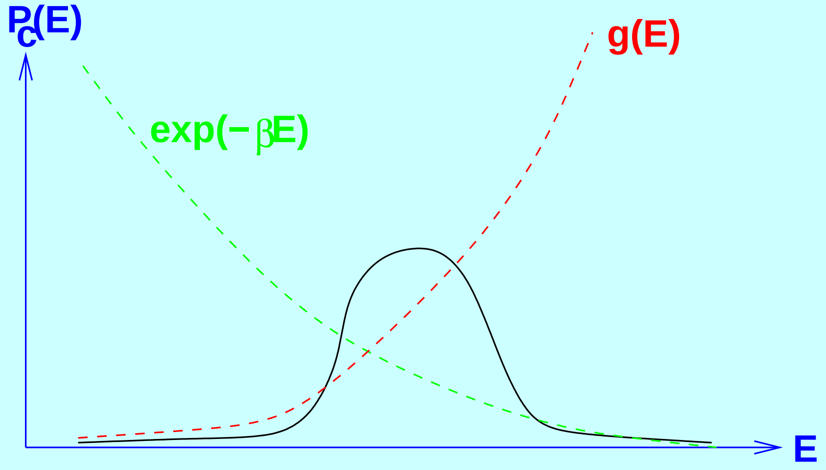
g: microcanonical . . . (used in both. . .); Z: canonical

Read Example 7.11 and Exercise 7.12

Fluctuations

The probability to find a canonical system at T and E

$$p_c(E) = \frac{g(E)}{Z}\, e^{-\beta E}$$



$g(E) \sim E^N$ as $N \to \infty$

find E^*

$$\begin{aligned} \frac{\partial}{\partial E} p_c(E) &= \frac{1}{Z}\left(\frac{\partial g}{\partial E} - g\beta\right) e^{-\beta E} = 0 \\ \rightarrow \quad \frac{\partial g}{\partial E} &= g\beta \\ \rightarrow \quad \frac{1}{g}\frac{\partial g}{\partial E}\bigg|_{E^*} &= \frac{1}{kT} \end{aligned}$$

but $\Omega = g\Delta E$ and $\frac{\partial \Delta E}{\partial E} = 0$

$$\begin{aligned} \frac{1}{g}\frac{\partial g}{\partial E}\bigg|_{E^*} &= \frac{\Delta E}{\Omega}\frac{1}{\Delta E}\frac{\partial \Omega}{\partial E}\bigg|_{E^*} = \frac{\partial \ln \Omega}{\partial E}\bigg|_{E^*} \\ &= \frac{1}{kT} \\ \text{or} \quad \frac{\partial S}{\partial E}\bigg|_{E^*} &= \frac{1}{T} \end{aligned}$$

The most probable energy E^* of the canonical ensemble is equal to E, the fixed energy of the microcanonical ensemble

We check the mean value

$$\begin{aligned}\langle E\rangle &= U = \frac{1}{Z}\int_0^\infty dE\, g(E)\, E\, \exp\{-\beta E\} \\ &= -\frac{1}{Z}\frac{\partial}{\partial\beta} Z = -\frac{\partial}{\partial\beta}\ \ln\ Z(\beta)\end{aligned}$$

now $\quad F = -kT\ln Z \quad$ and $\quad \beta = \frac{1}{kT}$

$$
\begin{aligned}
\rightarrow \quad \langle E \rangle &= U = + \frac{\partial}{\partial \beta}\left(\frac{F}{kT}\right) = -kT^2 \frac{\partial}{\partial T}\left(\frac{F}{kT}\right) \\
&= F - T\frac{\partial F}{\partial T} \\
&= F + TS
\end{aligned}
$$

$\langle E \rangle$ is also identical to E_0 of the microcanonical ensemble

+

The mean value $\langle E \rangle$ is the most probable value E^*

The distribution $p_c(E)$ is sharply peaked at this value

Standard deviation

$$
\begin{aligned}
\sigma^2 &= \langle E^2 \rangle - \langle E \rangle^2 \\
&= kT^2 C_V
\end{aligned}
$$

Relative width

$$\frac{\sigma}{\langle E\rangle} = \frac{\sqrt{\sigma^2}}{\langle E\rangle} = \frac{\sqrt{kT^2C_V}}{U}$$

but $U \sim N$ and $C_V \sim N$

$$\rightarrow \quad \frac{\sigma}{\langle E\rangle} \sim \frac{1}{\sqrt{N}} \quad \text{as} \quad N \rightarrow \infty$$

$$\text{or} \qquad p_{mc}(E) = \delta(E - E_0)$$

Virial theorem and equipartition theorem

Consider $H(q_\nu, p_\nu)$

$$\text{rename} \quad (q_\nu, p_\nu) \rightarrow x_i \qquad i = 1 \ldots 6N$$

$$\langle x_i \frac{\partial H}{\partial x_k} \rangle = \frac{1}{h^{3N}} \int d^{6N}x \, \rho(\mathbf{x}) \, x_i \frac{\partial H}{\partial x_k}$$

now select

$$\begin{aligned} \rho(\mathbf{x}) &= \rho_c(\mathbf{x}) = \frac{1}{Z} \, e^{-\beta H(\mathbf{x})} \\ \rightarrow \quad \langle x_i \, \frac{\partial H}{\partial x_k} \rangle &= \frac{1}{Z \, h^{3N}} \int d^{6N}x \, e^{-\beta H} x_i \, \frac{\partial H}{\partial x_k} \end{aligned}$$

we use

$$e^{-\beta H} \, \frac{\partial H}{\partial x_k} = -\frac{1}{\beta} \, \frac{\partial}{\partial x_k} \, e^{-\beta H}$$

for integration by parts

$$
\begin{aligned}
\langle x_i \frac{\partial H}{\partial x_k} \rangle \quad &= \quad \frac{1}{Z\, h^{3N}} \left\{ \int d^{6N-1}x\, x_i \left[-\frac{e^{-\beta H}}{\beta} \right]_{x_k^{\min}}^{x_k^{\max}} \right. \\
&\qquad \left. + \frac{\delta_{ik}}{\beta} \int d^{6N}x\, e^{-\beta H} \right\}
\end{aligned}
$$

the first terms vanishes

- if x_k is momentum $\rightarrow E_{kin} \rightarrow \infty$
  for $x_k^{\min} \rightarrow -\infty$ and $x_k^{\max} \rightarrow \infty$
- if x_k is spatial coordinate: $V \rightarrow \infty$ at walls

and $\int \frac{d^{6N}x}{h^{3N}}\, e^{-\beta H} = Z$

$$
\rightarrow \quad \langle x_i \frac{\partial H}{\partial x_k} \rangle = \frac{\delta_{ik}}{\beta} = \delta_{ik}\, kT
$$

Hamilton's equations

$$\begin{aligned}
\text{if} \quad \langle x_i \frac{\partial H}{\partial x_i} \rangle &= \langle p_i \, \dot{q}_i \rangle = 2 \langle E_{kin} \rangle \\
\text{if} \quad \langle x_i \frac{\partial H}{\partial x_i} \rangle &= -\langle p_i \, \dot{q}_i \rangle = -\langle q_i F_i \rangle \\
&= \alpha \langle V_i \rangle
\end{aligned}$$

$$\text{if} \quad V \sim r^\alpha$$

In the mean each degree of freedom of the system at T has the thermal energy $\frac{1}{2}kT$

Few examples of Boltzmann's statistics

N quantum mechanical harmonic oscillators

Energy of a single one

$$\epsilon_n = \hbar\omega \left(n + \frac{1}{2} \right) , \quad n = 0, 1, \ldots$$

Here, instead of a classical phase-space density

$$\rho_n = \frac{e^{-\beta \epsilon_n}}{Z(T, V, 1)}$$

with

$$Z(T, V, 1) = \sum_n e^{-\beta \epsilon_n}$$

ρ_n: is the probability for an h.o. to be in a quantum state n

Independent oscillators

$$\rightarrow \quad Z(T,V,N) = \{Z(T,V,1)\}^N$$

Assume the h.o. to be **distinguishable**

$$\begin{aligned}
Z(T,V,1) &= \sum_n \exp\{-\beta\epsilon_n\} \\
&= \sum_{n=0}^{\infty} \exp\left\{-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right\} \\
&= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} \Big(\exp\{-\beta\hbar\omega\}\Big)^n \\
&= \frac{\exp\left\{-\frac{\beta\hbar\omega}{2}\right\}}{1 - \ e^{-\beta\hbar\omega}} = \frac{1}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}} \\
&= \left\{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right\}^{-1}
\end{aligned}$$

$$\rightarrow \quad Z(T,V,N) = \left\{ 2\sinh\left(\frac{\beta\hbar\omega}{2}\right) \right\}^{-N}$$

Now

$$\begin{aligned} F(T,V,N) &= -kT \,\ln Z(T,V,N) \\ &= N\left[\frac{\hbar\omega}{2} + kT \,\ln\left\{1 - e^{-\beta\hbar\omega}\right\}\right] \end{aligned}$$

$\uparrow$ zero point energy

$\longrightarrow$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \frac{F}{N}$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = 0 \qquad \leftarrow \text{ as before}$$

The entropy is

$$S = -\frac{\partial F}{\partial T}\bigg|_{V,N} = Nk\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln\left\{1-e^{-\beta\hbar\omega}\right\}\right]$$

and the internal energy

$$U = F + TS = N\hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right]$$

Independent harmonic oscillators

$$\longrightarrow \quad U = N\langle\epsilon_n\rangle$$

with

$$\langle \epsilon_n \rangle = \hbar\omega \left[\langle n \rangle + \frac{1}{2} \right]$$

where

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

is the mean quantum number at T

For N classical oscillators the equipartion theorem gives

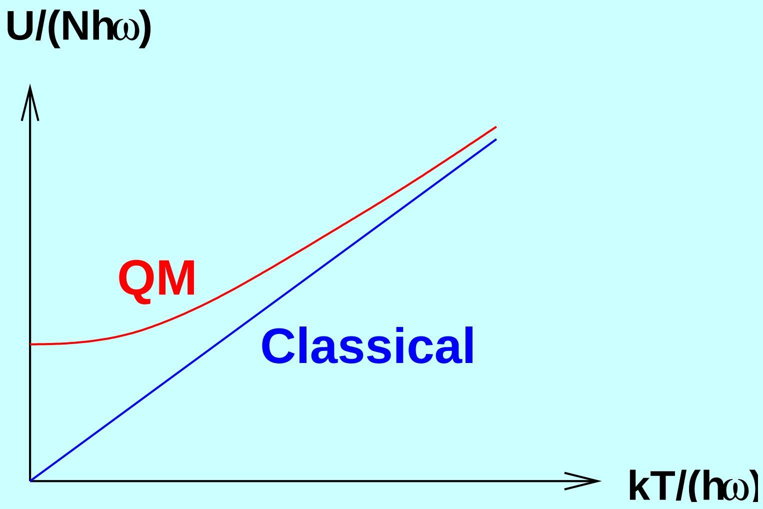
$$U_{cl} = NkT$$

obviously not true in the quantum case!

But as $T \to \infty$, $\beta\hbar\omega = \frac{\hbar\omega}{kT} \to 0$

$$U \simeq NkT + \ldots\ldots$$

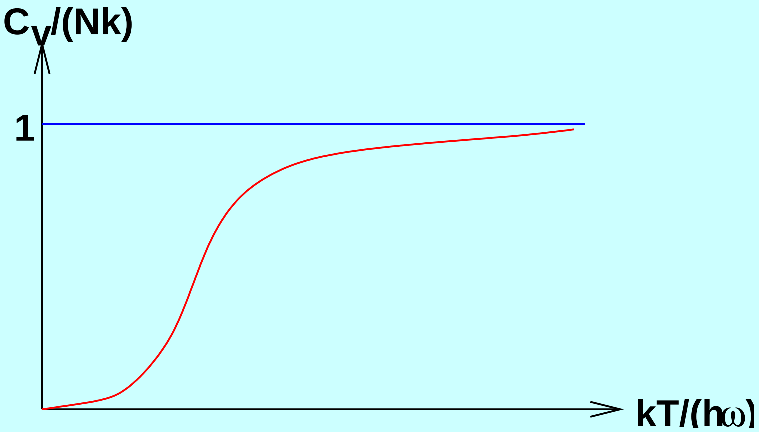
classical limit



classical $C_v^{cl} = C_p^{cl} = Nk$

but here

$$\begin{aligned} C_v &= \left.\frac{\partial U}{\partial T}\right|_{N,V} \\ &= Nk(\beta\hbar\omega)^2 \, \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \end{aligned}$$



For low T the thermal energy $kT \ll \hbar\omega$ has a very small possiblility to excite a h.o. because of the **discreteness** of the levels

……

Read carefully about the calculation of 9 in p. 213-214

……

Paramagnetism, (classical)

$$E = -\sum_{i=1}^{N} \boldsymbol{\mu_i} \cdot \mathbf{H}$$

$\boldsymbol{\mu_i}$: magnetic momentum

$\mathbf{H}$: external magnetic field

External **H** aligns the momenta
Thermal energy disaligns them
(maximum entropy), $\mathbf{H} = H\hat{z}$

$$Z(T,H,N) = \int d\Omega_1 \int d\Omega_2 \ldots \int d\Omega_N \, \exp\left\{\beta\mu H \sum_{i=1}^{N} \cos\theta_i\right\}$$

since $\boldsymbol{\mu_i} \cdot \mathbf{H} = \mu_z H_z = \mu H \cos\theta_i$

$$\begin{aligned} Z(T,H,1) &= \int d\Omega \, \exp\{\beta\mu H \cos\theta\} \\ &= 2\pi \int_{-1}^{1} dx \, \exp\{\beta\mu H x\} \\ &= 4\pi \, \frac{\sinh(\beta\mu H)}{\beta\mu H} \end{aligned}$$

The probability for the dipole to assume an orientation between $\theta, \theta + d\theta$ and $\varphi, \varphi + d\varphi$ is

$$\rho(\theta, \varphi) d\Omega = \frac{e^{\beta \mu H \cos\theta}}{Z(T, H, 1)} \sin\theta d\theta d\varphi$$

$\boldsymbol{\mu}$ in same coordinates, (θ, φ), $\boldsymbol{\mu} = \mu \hat{\Omega}$

$\rightarrow$ the mean magnetic moment in Cartesian coordinates is

$$\langle \boldsymbol{\mu} \rangle = \frac{\mu}{Z} \int \begin{pmatrix} \sin\theta \cos\varphi \\ \sin\theta \sin\varphi \\ \cos\theta \end{pmatrix} e^{\beta \mu H \cos\theta} \sin\theta d\theta d\varphi$$

φ-integration $\longrightarrow$ $\langle\mu_x\rangle = \langle\mu_y\rangle = 0$, left is

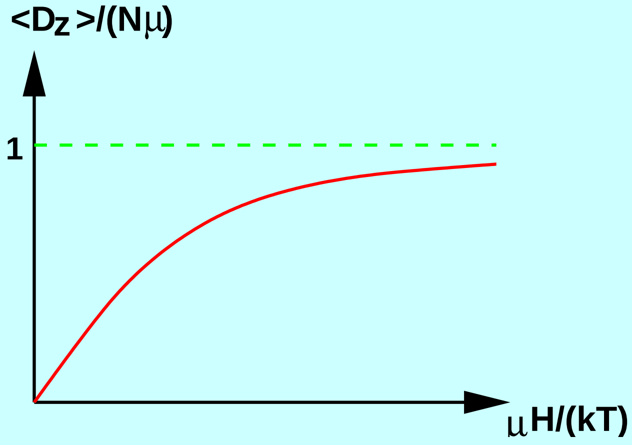
$$\begin{aligned}\langle\mu_Z\rangle &= \frac{\mu}{Z}\int \cos\theta e^{\beta\mu\cos\theta}\sin\theta d\theta d\varphi \\ &= 2\pi\int_{-1}^{1} dx\, e^{\beta\mu x} x\, dx \left(\frac{\mu}{Z}\right) \\ &= N_\mu\left\{\coth(\beta\mu H) - \frac{1}{\beta\mu H}\right\}\end{aligned}$$

or

$$\langle D_Z\rangle = N\langle\mu_Z\rangle = N\mu L\left(\beta\mu H\right)$$

L : Langevin function

Polarization, magnetization



linear with H for

constant T for small H

for

$$\frac{\mu H}{kT} \ll 1 \langle D_Z \rangle \simeq \frac{N\nu^2}{3kT} H - \dots$$

with the susceptibility

$$\chi = \lim_{H \to 0} \frac{\partial \langle D_Z \rangle}{\partial H}$$

$$= \frac{N\mu^2}{3kT} = \frac{C}{T}$$

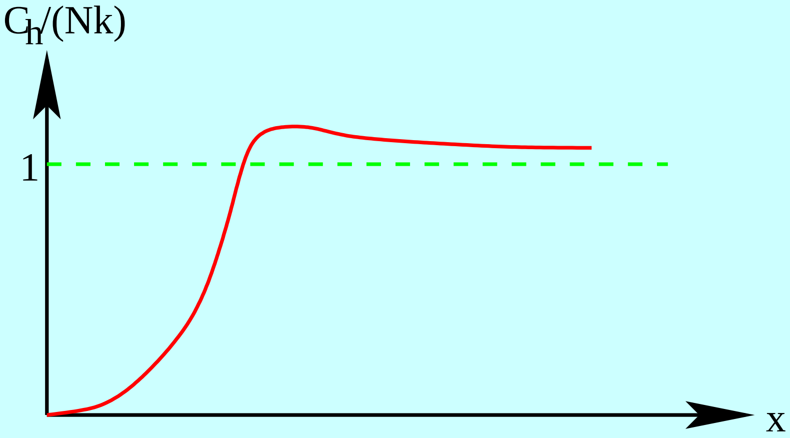
Curies law with Curie constant C

$$\begin{aligned} S(T,H,N) &= -\frac{\partial F}{\partial T}\bigg|_{H,N} \\ &= Nk \ln \left\{ 4\pi \frac{\sinh x}{x} \right\} \\ &\quad -\frac{N\mu H}{T} L(x) \end{aligned}$$

with $\quad x = \beta \mu H$

$$\rightarrow \boxed{U = F + TS = -\langle D_Z \rangle H}$$

$$C_H = \left.\frac{\partial U}{\partial T}\right|_{H,N} = \frac{Nk}{H}\left[1 - \frac{x^2}{\sinh^2 x}\right]$$



$$T \rightarrow \infty \quad \text{thus} \quad x \rightarrow 0$$

$$U \simeq 0 \qquad C_H \rightarrow 0$$

The external field can not align the dipoles at **high** **temperature**

The macrocanonical ensemble

Reservoir for heat and particles

Variables: $T, V, \mu \leftarrow$ chemical potential

μ can be fixed by the reservoir

{vapour, fluid .....}

in an analogous way to the canonical ensemble one finds

$$\rho_{gc}(N, q_\nu, p_\nu) = \frac{\exp\{-\beta H(q_\nu, p_\nu) + \alpha N\}}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d\omega \exp\{-\beta H(q_\nu, p_\nu) + \alpha N\}$$

↑ grand canonical partition function

$$\alpha = \frac{\mu}{kT}, \quad \beta = \frac{1}{kT}$$

The entropy

$$S = \langle -k \ln \rho_{gc} \rangle$$

gives

$$S(\beta, V, \alpha) = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d\omega\, \rho_{gc}(N, q_\nu, p_\nu) \left\{k \ln \mathcal{Z} + k\beta H(q_\nu, p_\nu) - k\alpha N\right\}$$

$$= k \ln \mathcal{Z}(\beta, V, \alpha) + k\beta \langle H \rangle - k\alpha \langle N \rangle$$

$$\longrightarrow U - TS - \mu \langle N \rangle = -kT \ln \mathcal{Z}(T, V, \mu)$$

To be compared with the grand thermodynamic potential

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

Thus

$$\boxed{\Phi(T, V, \mu) = -kT \ln \mathcal{Z}(T, V, \mu)}$$

The potential gives othe thermodynamic quantities

$$-S = \frac{\partial \Phi}{\partial T}\Big|_{V,\mu}, \qquad -p = \frac{\partial \Phi}{\partial V}\Big|_{T,\mu}$$

$$-N = \frac{\partial \Phi}{\partial \mu}\Big|_{T,V} \qquad \text{and} \quad \Phi = -pV$$

Comparable to

F for a system w. T, V, N

S — || — E, V, N

$\mathcal{Z}$ can be rewritten

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} \frac{1}{N!\,h^{3N}} \int d\omega \, \exp\left\{-\beta\left(H(q,p) - \mu N\right)\right\}$$

$$= \sum_{N=0}^{\infty} \left[\exp\left\{\frac{\mu}{kT}\right\}\right]^{N} \underset{\substack{\uparrow \\ \text{canonical partition function}}}{Z(T,V,N)}$$

---

a weighted sum of all canonical partition functions. Weighte with the fugacity

small z $\rightarrow z = e^{\mu/kT}$

But in a noninteracting system

$$Z(T,V,N) = \frac{1}{N!}\left\{Z(T,V,1)\right\}^{N}$$

$\rightarrow$

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} \frac{1}{N!}\left[\exp\left(\frac{\mu}{kT}\right) Z(T,V,1)\right]^{N}$$

$$= \exp\left[\exp\left(\frac{\mu}{kT}\right) Z(T,V,1)\right]$$

Ideal gas

before in the canonical ensemble

$$Z(T,V,1) = \frac{V}{\lambda^{3}}$$

$$\lambda = \left(\frac{h^{2}}{2\pi m kT}\right)^{1/2}$$

$$\mathcal{Z}(T,V,\mu) = \exp\left[\exp\left(\frac{\mu}{kT}\right)V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

$$\to \Phi(T,V,\mu) = -kT\ln\mathcal{Z}(T,V,\mu)$$

$$= -kT\exp\left\{\frac{\mu}{kT}\right\}V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$-\left.\frac{\partial\Phi}{\partial T}\right|_{V,\mu} = S(T,V,\mu) = \exp\left(\frac{\mu}{kT}\right)\left(\frac{2\pi mkT}{h^2}\right)^{3/2}k\left(\frac{5}{2}-\frac{\mu}{kT}\right)$$

$$-\left.\frac{\partial\Phi}{\partial V}\right|_{T,\mu} = p(T,V,\mu) = kT\exp\left(\frac{\mu}{kT}\right)\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$-\left.\frac{\partial\Phi}{\partial \mu}\right|_{T,V} = N(T,V,\mu) = \exp\left(\frac{\mu}{kT}\right)V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$p = \frac{kTN}{V}$$

$pV = kTN$ ideal gas equation

We had
$$\Phi = U - TS - \mu N$$

and the Euler relation gives

$$U = TS - pV + \mu N$$

$$\hookrightarrow -\frac{\Phi}{kT} = \boxed{\frac{pV}{kT} = \ln\mathcal{Z}}$$

Convenient for calculations

We have studied ensembles with variables
(E,V,N)
(T,V,N)
(T,V,μ)

We might have wanted (T,p,N)

$$\Xi(T,p,N) = \sum_V \exp(-\gamma V p)\,Z(T,V,N)$$

Laplace transf. Lagrange m.

Logarithms of partition functions are related to thermodynamic potentials

$$g \longleftrightarrow S = k \ln g$$

$$Z \longleftrightarrow F = -kT \ln Z$$

$$\mathcal{Z} \longleftrightarrow \Phi = -kT \ln \mathcal{Z}$$

and one can find

$$G = -kT \ln \Xi$$

the Gibbs free enthalpy

<u>Fluctuations</u> (read in book)

$$\frac{\sigma_N}{N} = \sqrt{\frac{kT}{V}\varkappa} \sim O\left(\frac{1}{\sqrt{V}}\right) \sim O\left(\frac{1}{\sqrt{N}}\right)$$

if $N \to \infty, V \to \infty, \frac{N}{V} = \text{const}$

<u>if $\varkappa$ is finite</u>

$$\varkappa = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_{T,N}$$

$$\varkappa = \frac{\partial N}{\partial \mu}\Big|_{T,V}$$

compressibility is not always

$$\frac{\sigma_E^2}{U^2} = \underbrace{\frac{kT^2}{U^2}C_V}_{= \frac{\sigma_{can}^2}{U^2}} + \frac{\sigma_N^2}{U^2}\left(\frac{\partial U}{\partial N}\Big|_{T,V}\right)^2$$

$$\sim O\left(\frac{1}{\sqrt{N}}\right) \quad \text{as } N \to \infty$$

In the thermodynamic limit all ensembles give the same results

---

If $\mathcal{Z}(T,V,z) = \sum_{N=1}^{\infty} z^N Z(T,V,N)$

is known then

$$Z(T,V,N) = \frac{1}{2\pi i}\oint_{\partial K} \frac{\mathcal{Z}(T,V,z)}{z^{N+1}}\,dz$$

on a circle around $z=0$ within the convergence radius of

Density operators

Eq. of motion for a system with N particles

$$i\hbar\partial_t \Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N, t) = \hat{H}(\boldsymbol{r}_i, \hat{\boldsymbol{p}}_i)\Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N, t)$$

Stationary states with definite energy

$$\hat{H}\,\Psi_E\,(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N) = E\,\Psi_E\,(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N)$$

Observable is an operator $\hat{f}(\hat{\boldsymbol{r}}_i, \hat{\boldsymbol{p}}_i)$ with eigenfunctions and values

$$\hat{f}\,\phi_f = f\,\phi_f$$

each eigenvalue has the probability

$$\langle \phi_f | \Psi_E^{(i)} \rangle \qquad \text{microstate i}$$

and the q.m. average of all measurements is

$$\langle\, \Psi_E^{(i)} \,|\, \hat{f} \,|\, \Psi_E^{(i)} \,\rangle = \langle\, \hat{f} \,\rangle$$

But often the microstate is uncertain

$$\rightarrow \quad \langle\, \hat{f} \,\rangle = \sum_i \rho_i \,\langle\, \Psi_E^{(i)} \,|\, \hat{f} \,|\, \Psi_E^{(i)} \,\rangle \quad (^*)$$

where ρ_i is the probability of state $\Psi_E^{(i)}$

In general we need

$$\langle\, \hat{f} \,\rangle = \sum_{ik} \rho_{ki} \,\langle\, \Psi_E^{(i)} \,|\, \hat{f} \,|\, \Psi_E^{(k)} \,\rangle$$

as can be seen by using

$$\Psi_E^{(i)} = \sum_k a_k^{(i)} \, \phi_k$$

in $(^*)$

ρ_{ki} is the probability with which $\langle\, \Psi_E^{(i)} \,|\, \hat{f} \,|\, \Psi_E^{(k)} \,\rangle$ contributes to $\langle\, \hat{f} \,\rangle$

. . . .

$$\begin{aligned}
\langle\, \hat{f} \,\rangle &= \sum_{ik} \rho_{ki} \,\langle\, \phi_i \,|\, \hat{f} \,|\, \phi_k \,\rangle \\
&\equiv \sum_{ik} \langle\, \phi_k \,|\, \hat{\rho} \,|\, \phi_i \,\rangle \langle\, \phi_i \,|\, \hat{f} \,|\, \phi_k \,\rangle
\end{aligned}$$

definition of the operator $\hat{\rho}$

$$= \sum_{k} \langle\, \phi_k \,|\, \hat{\rho}\; \hat{f} \,|\, \phi_k \,\rangle = T_r(\hat{\rho}\, \hat{f})$$

T_r is independent of basis

$\hat{\rho}$ is the density operator, ρ_{ik} the matrix elements of the density matrix

ρ_{ik} are basis dependent, can be diagonal

Pure and mixed states

If a system is described by a state vector $|\Psi^{(i)}\rangle$ it is in a pure state

If it is any of several different $|\Psi^{(i)}\rangle$ with probability ρ_i it is in a mixed state

$$\hat{\rho} = \sum_{kk'} |\phi_{k'}\rangle \, \rho_{k'k} \, \langle\phi_k|$$

which for a pure state reduces to the projection operator

$$\hat{\rho}^{\mathrm{pure}} = |\Psi^{(i)}\rangle\langle\Psi^{(i)}|$$

Hermitian $\hat{\rho}^{+} = \hat{\rho}, \quad T_r \hat{\rho} = 1$

and for a pure state $\hat{\rho}^2 = \hat{\rho}$

Equation of motion (von Neumann, Liouville ...)

$$i\hbar d_t \hat{\rho} = [\hat{H}, \hat{\rho}]$$

……

The density operators of quantum statistics

Microcanonical

Stationary ensemble $[\hat{H}, \hat{\rho}] = 0$

Use energy eigenvalues

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$$

→ diagonal $\rho_{mn} = \rho_n \delta_{m,n}$

$$\rho_n = \begin{cases} \frac{1}{\Omega} & E \leq E_n \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\hat{\rho} = \frac{\delta(\hat{H} - E \cdot \hat{I})}{Tr\{\delta(\hat{H} - E \cdot \hat{I})\}}$$

Canonical

In the energy representation

$$\rho_n = \frac{\exp\{-\beta E_n\}}{\sum_n \exp\{-\beta E_n\}}$$

with

$$Z(T, V, N) = \sum_n \exp\{-\beta E_n\}$$

$$\rightarrow \quad \hat{\rho} = \frac{\exp\{-\beta \hat{H}\}}{Tr(\exp\{-\beta \hat{H}\})}$$

and

$$\langle\hat{f}\rangle = Tr(\hat{\rho}\hat{f}) = \frac{Tr(\exp\{-\beta\hat{H}\}\hat{f})}{Tr(\exp\{-\beta\hat{H}\})}$$

Try

$$\begin{aligned} U = \langle\hat{H}\rangle &= \frac{Tr(\exp\{-\beta\hat{H}\}\hat{H})}{Tr(\exp\{-\beta\hat{H}\})} \\ &= -\frac{\partial}{\partial\beta}\,\ln\Big(Tr\,\exp\{-\beta\hat{H}\}\Big) \\ &= \frac{\partial}{\partial\beta}\,\ln\,Z(T,V,N) \end{aligned}$$

as in the classical case and

$$F = U - TS = -kT\,\ln\Big\{Tr(\exp\{-\beta\hat{H}\})\Big\}$$

Grand canonical

$$\hat{\rho} = \frac{\exp\{-\beta(\hat{H} - \mu\hat{N})\}}{Tr(\exp\{-\beta(\hat{H} - \mu\hat{N})\})}$$

$$\mathcal{Z}(T, V, \mu) = Tr(\exp\{-\beta(\hat{H} - \mu\hat{N})\})$$

But we still have to analyze the states with respect to particle distinguishability …

The symmetry of many particle wavefunctions

quantum theory

like particles are not to distinguish (wavefunctions, probability)

Particle exchange operator

$$\hat{P}_{ik}\Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_i \ldots \boldsymbol{r}_k \ldots \boldsymbol{r}_N) = \Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_k \ldots \boldsymbol{r}_i \ldots \boldsymbol{r}_N)$$

(change in the enumeration)

Quantum H are invariant under change in the enumeration

$$\rightarrow \quad \left[\hat{H}, \hat{P}_{ik}\right] = 0$$

for all $\qquad i, k = 1 \ldots N \qquad$ with $i \neq k$

$\hat{H}$ and $\hat{P}$ have common eigenfunctions

$$\begin{aligned}
\hat{P}_{ik}\Psi(\ldots\boldsymbol{r}_i\ldots\boldsymbol{r}_k\ldots) &= \lambda\Psi(\ldots\boldsymbol{r}_i\ldots\boldsymbol{r}_k\ldots) \\
=\Psi(\ldots\boldsymbol{r}_k\ldots\boldsymbol{r}_i\ldots) &= \lambda\Psi(\ldots\boldsymbol{r}_i\ldots\boldsymbol{r}_k\ldots) \\
\rightarrow \quad \left(\hat{P}_{ik}\right)^2\Psi(\ldots\boldsymbol{r}_i\ldots\boldsymbol{r}_k\ldots) &= \lambda^2\Psi(\ldots\boldsymbol{r}_i\ldots\boldsymbol{r}_k\ldots)
\end{aligned}$$

$$\rightarrow \quad \lambda^2 = 1 \quad \text{and} \quad \lambda \quad \text{is real}$$

$$\text{thus} \quad \lambda = \pm 1 \begin{array}{l} \text{symmetric wave function} \\ \text{antisymmetric}\ldots \end{array}$$

Generally “the permutation” operator

$$\hat{P}\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2\ldots\boldsymbol{r}_N) = \Psi(\boldsymbol{r}_{P_1}, \boldsymbol{r}_{P_2}\ldots\boldsymbol{r}_{P_N})$$

where $P_1\ldots P_N$ are permutations of $1\ldots N$

If H commutes with all $\hat{P}_{ik}$ or equivalently with $\hat{P}$ the energy eigenfunctions can be constructed completely symmetric or antisymmetric

$$\begin{aligned}
\Psi^S(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N) &= A \sum_P \hat{P}\Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N) \\
\Psi^A(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N) &= B \sum_P (-1)^P \hat{P}\Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N)
\end{aligned}$$

$\sum_P$ sum over all permutations $P_1 \ldots P_N$ of the indices $1 \ldots N$.

$$(-1)^P = \begin{cases} +1 & \text{even permutation} \\ -1 & \text{odd permutation} \end{cases}$$

A and B are normalization constants

Symmetric:	bosons	integer spin
Antisymmetric:	fermions	half integer spin

↓

experimental fact

(causality …)

Non-interacting system

$$\hat{H}(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N, \boldsymbol{p}_1 \ldots \boldsymbol{p}_N,) = \sum_{i=1}^{N} \hat{h}(\boldsymbol{r}_i, \boldsymbol{p}_i)$$

with

$$\hat{h}\, \phi_k(\boldsymbol{r}) = \epsilon_k\, \phi_k\,(\boldsymbol{r})$$

$$E = \sum_{i=1}^{N} \epsilon_k \qquad \text{(only for noninteracting)}$$

is the energy of the many-particle wavefunction

$$\Psi^{E}_{k_1\ldots k_N}(\boldsymbol{r}_1\ldots\boldsymbol{r}_N)=\prod_{i=1}^{N}\phi_i\left(\boldsymbol{r}_i\right)^{(*)}$$

In Dirac notation the state $^{(*)}$ is

$$\left|k_i\ldots k_N\right\rangle=\left|k_1\right\rangle\left|k_2\right\rangle\,\ldots\left|k_N\right\rangle$$

↰ here

particle 1 is in state k_1

$$\begin{aligned}
\langle k_1' \ldots k_N' \,|\, k_1 \ldots k_N \rangle &= \langle k_N' \,| \ldots \langle k_1' \,|\, k_1 \rangle \ldots |\, k_N \rangle \\
&= \langle k_1' \,|\, k_1 \rangle \ldots \langle k_N' \,|\, k_N \rangle \\
&= \delta(k_1' - k_1) \ldots \delta(k_N' - k_N)
\end{aligned}$$

Completeness relation

$$\mathbb{1} = \sum_{k_1 \ldots k_1} |k_1 \ldots k_N\rangle\langle k_1 \ldots k_N \,|$$

Arbitrary wavefunction, also interacting, can be expanded in $|k_1 \ldots k_N\rangle$

The wavefunction

$$\begin{aligned}\Psi^{E}_{k_1\dots k_N}(\boldsymbol{r}_1\dots\boldsymbol{r}_N) &= \langle \boldsymbol{r}_1\dots\boldsymbol{r}_N|k_1\dots k_N\rangle \\ &= \phi_{k_1}(\boldsymbol{r}_1)\dots\phi_{k_N}(\boldsymbol{r}_N)\end{aligned}$$

has no clear symmetry

Thus we can form

$$\begin{aligned}
\Psi^{S,E}_{k_1\ldots k_N}(\boldsymbol{r}_1\ldots\boldsymbol{r}_N) &= \text{Norm}\sum_P \hat{P}\,\phi_{k_1}(\boldsymbol{r}_1)\ldots\phi_{k_N}(\boldsymbol{r}_N) \\
\Psi^{A,E}_{k_1\ldots k_N}(\boldsymbol{r}_1\ldots\boldsymbol{r}_N) &= \frac{1}{\sqrt{N!}}\sum_P (-1)^P\,\hat{P}\,\phi_{k_1}(\boldsymbol{r}_1)\ldots\phi_{k_N}(\boldsymbol{r}_N) \\
& \quad \left\{\text{One can either permute } k_i\ldots \text{ or } r_i\ldots\right\} \\
&= \frac{1}{\sqrt{N!}}\det\begin{pmatrix} \phi_{k_1}(\boldsymbol{r}_1) & \ldots & \phi_{k_1}(\boldsymbol{r}_N) \\ \vdots & & \vdots \\ \phi_{k_N}(\boldsymbol{r}_1) & \ldots & \phi_{k_N}(\boldsymbol{r}_N) \end{pmatrix}
\end{aligned}$$

Slater determinant

Pauli principle obvious, and thus the normalization

In case of bosons k_i is occupied by n_i bosons

$$\begin{aligned} N &= \sum_i n_i \\ \rightarrow \quad \text{norm} &= \left\{ N! n_1! n_2! \ldots \right\}^{-1/2} \end{aligned}$$

……

$$\begin{aligned} |k_1 \ldots k_N\rangle^A &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \, |k_{p_1} \ldots k_{p_N}\rangle \\ |k_1 \ldots k_N\rangle^S &= \frac{1}{\sqrt{N!S}} \sum_P |k_{p_1} \ldots k_{p_N}\rangle \end{aligned}$$

……

It can now be shown (p. 290 - 292)

$$T_r\hat{O} = \frac{1}{N!} \sum_{k_1\ldots k_N} {}^{S,A}\langle k_1 \ldots k_N|\hat{O}|k_1 \ldots k_N\rangle^{A,S}$$

Read example 11.2   ideal gas

$${}^{A,S}\langle \boldsymbol{r}_1\boldsymbol{r}_2|\hat{\rho}|\boldsymbol{r}_1\boldsymbol{r}_2\rangle^{A,S} = \frac{1}{Z^{A,S}\lambda^6}\left\{1 \pm \exp\left\{-\frac{2\pi}{\lambda^2}\left(\boldsymbol{r}_1 - \boldsymbol{r}_2\right)^2\right\}\right\}$$

no more homogeneous as $\boldsymbol{r}_1 \rightarrow \boldsymbol{r}_2$

$$Z^{A,S} = \frac{1}{2}\frac{V^2}{\lambda^2}\left(1 \pm \frac{1}{2^{3/2}}\frac{\lambda^3}{V}\right)$$

bosons bunch together

but fermions avoid one another, $(- :$ A$)$, $(+ :$ S$)$

Ideal quantum systems
Grand canonical description

The canonical partition function is

$$\begin{aligned} Z(T,V,N) &= Tr\Big(\exp\{-\beta\hat{H}\}\Big) \\ &= \frac{1}{N!}\sum_{k_1\ldots k_N} {}^{S,A}\langle k_1\ldots k_N|\exp\{-\beta\hat{H}\}|k_1\ldots k_N\rangle^{S,A} \end{aligned}$$

Tr within any basis, but energy eigenstates are convenient $\hat{H}$

$$\hat{H}|k_1\ldots k_N\rangle^{S,A} = E|k_1\ldots k_N\rangle^{S,A}\,, \quad E = \sum_{i=1}^{N}\epsilon_{k_1}$$

no interaction

We consider 3 cases

$$\begin{aligned} \text{MB} &\rightarrow \text{Maxwell Boltzmann} \\ \text{FD} &\rightarrow \text{Fermi-Dirac} \\ \text{BE} &\rightarrow \text{Bose-Einstein} \end{aligned}$$

In the MB-case the wavefunction is a simple multiplication of single-particle wavefunctions, or

$$|k_1 \ldots k_N\rangle = |k_1\rangle \ldots |k_N\rangle$$

and thus

$$\begin{aligned} Z^{MB}(T,V,N) &= \frac{1}{N!} \prod_{i=1}^{N} \sum_{k_i} \langle k_i | \exp\{-\beta \hat{h}_i\} | k_i \rangle \\ &= \frac{1}{N!} \Big[Z(T,V,1) \Big]^N \end{aligned}$$

$\sum_{k_i}$ is superfluous

A fully symmetrized or antisymmetrized state is completely specified by occupation of the single-particle states $n_1 \ldots$

so instead of $|k_1 \ldots k_N\rangle^{S,A}$ labeling the state k_i of particle i (finite vector dim)

we use $|n_1\, n_2 \ldots\rangle$ (infinite dim) specifying the occupation of state i

$$\sum_{k=1}^{\infty} n_i = N \quad , \quad E = \sum_{k=1}^{\infty} n_k \epsilon_k$$

$$\begin{aligned} \hat{H}|n_1 n_2 \ldots\rangle^{S,A} &= E|n_1 n_2 \ldots\rangle^{S,A} \\ \hat{N}|n_1 n_2 \ldots\rangle^{S,A} &= N|n_1 n_2 \ldots\rangle^{S,A} \end{aligned}$$

and similarily

$$\hat{n}_k|n_1 n_2 \ldots\rangle^{S,A} = n_k|n_1 n_2 \ldots\rangle$$

$$n_k = \begin{cases} 0, 1 & \text{FD} \\ 0, 1, 2, \ldots & \text{BE} \end{cases}$$

$\{n_1 n_2 \ldots\}$ + symmetry specifies one microstate of the system

The occupation states are orthonomal

$$^{S,A}\langle n_1' n_2' \ldots | n_1 n_2 \ldots\rangle = \delta_{n_1' n_1} \delta_{n_2' n_2} \ldots$$

……

$$
\begin{aligned}
& {}^{S,A}\langle n_1' n_2' \ldots | \hat{\rho} | n_1 n_2 \ldots \rangle^{S,A} \\
& \quad = \quad \frac{1}{Z(T,V,N)} \, {}^{S,A}\langle n_1' n_2' \ldots | \exp\{-\beta \hat{H}\} | n_1 n_2 \ldots \rangle^{S,A} \\
& \quad = \quad \frac{1}{Z(T,V,N)} \exp\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\} \, \delta_{n_1' n_1} \delta_{n_2' n_2} \ldots
\end{aligned}
$$

where

$$
Z(T,V,N) = \sum_{\{n_k\}}{}' \exp\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\}
$$

$\sum'$ means the constraint

$\{n_k\}$ each set is one microstate

$$
\sum_{k=1}^{\infty} n_k = N
$$

The diagonal element of the density matrix

$$\begin{aligned} P\{n_k\} &= {}^{S,A}\langle n_1 n_2 \ldots | \hat{\rho} | n_1 n_2 \ldots \rangle \\ &= \frac{1}{Z} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k \epsilon_k \right\} \end{aligned}$$

is the probability of finding the special set $\{n_k\}$ of occupation numbers in the system

(The probability of that microstate)

. . . .

Analogously the matrix element of the grand canonical density op. is

$$
\begin{aligned}
&{}^{S,A}\langle n_1' n_2' \ldots | \hat{\rho} | n_1 n_2 \ldots \rangle^{S,A} \\
&= \frac{1}{\mathcal{Z}(T,V,\mu)} \, {}^{S,A}\langle n_1' n_2' \ldots | \exp\Big\{ -\beta(\hat{H} - \mu\hat{N}) \Big\} | n_1 n_2 \ldots \rangle^{S,A} \\
&= \frac{1}{\mathcal{Z}(T,V,\mu)} \exp\Big\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \Big\} \, \delta_{n_1' n_1} \delta_{n_2' n_2} \ldots
\end{aligned}
$$

with

$$\mathcal{Z}(T,V,\mu) = \sum_{\{n_k\}} \exp\Big\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\Big\}$$

$$n_k = \begin{cases} 0,1 & \text{FD} \\ 0,1,2\ldots & \text{BE} \end{cases}$$

But here is no constraint on N

(grand canonical . . . particle reservoir)

So

$$
\begin{aligned}
\mathcal{Z}(T,V,\mu) &= \sum_{N=0}^{\infty} z^N \, Z(T,V,N) \\
&= \sum_{N=0}^{\infty} z^N \sum_{\{n_k\}}^{\prime} \exp\Big\{-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\Big\} \\
&= \sum_{N=0}^{\infty} \sum_{\{n_k\}}^{\prime} \exp\Big\{-\beta \sum_{k=1}^{\infty} n_k (\epsilon_k - \mu)\Big\}
\end{aligned}
$$

since $z = e^{\mu/kT}$ $N = \sum_{k=1}^{\infty} n_k$

but

$$\sum_{N=0}^{\infty} \sum_{\{n_k\}}{}^{'}$$

is simly the sum over all sets of occupation numbers without a constraint

$\uparrow$

Makes the grand canonical ensemble very good for calculation

In this thermodynamic limit the GE is anyway a good description

(but small systems!!)

And again

$$\begin{aligned} P\{n_k\} &= {}^{S,A}\langle n_1 n_2 \ldots |\hat{\rho}| n_1 n_2 \ldots \rangle^{S,A} \\ &= \frac{1}{\mathcal{Z}} \exp\Big\{ -\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu) \Big\} \end{aligned}$$

is the probability of finding the special set $\{n_k\}$ in the system

Now we can unify the handeling of the 3-cases with different statistics

The MB-case reminds us of where quantum properties are important

The contrast

MB

- $\{n_1 n_2 \dots\}$ does not uniquely determine the state $|k_i \dots k_N\rangle$ corresponding to a simple product wavefunction
- $\{n_1 n_2 \dots\}$ no information about which particle is in which state
- **All product states compatible** to the set $\{n_1 n_2 \dots\}$ have **same energy** and **probability**
- There are $N!$ ways to permute the particles
- If there are n_k in state $|k\rangle$

  → $n_k!$ permutations give no new classical microstate

$$\rightarrow \quad \text{weight}\left(\{n_1 n_2 \dots\}\right) = \frac{N!}{n_1! n_2! \dots}$$

$$
\begin{aligned}
Z^{\mathrm{MB}}(T,V,N) &= \frac{1}{N!}\sum_{\{n_k\}}{}' \frac{N!}{n_1!n_2!\dots} \exp\left\{-\beta\sum_{k=1}^{\infty} n_k\epsilon_k\right\} \\
&\quad (\frac{1}{N!} \text{ was added by hand here }) \\
&= \frac{1}{N!}\sum_{n_1 n_2\dots=0}^{N} \frac{N!}{n_1!n_2!\dots}\Big(\exp\{-\beta\epsilon_1\}\Big)^{n_1}\Big(\exp\{-\beta\epsilon_2\}\Big)^{n_2}\dots \\
&= \frac{1}{N!}\left(\sum_{k=1}^{\infty}\exp\{-\beta\epsilon_k\}\right)^{N} \\
&= \frac{1}{N!}\Big[Z(T,V,1)\Big]^{N}
\end{aligned}
$$

→ The statistical weight of the set of occupation numbers $\{n_1 n_2 \ldots\}$ is

$$g^{\mathrm{MB}}\{n_k\} = \frac{1}{n_1! n_2! \ldots}$$

and for bosons

$$g^{\mathrm{BE}}\{n_k\} = 1$$

and Fermions

$$g^{\mathrm{FD}}\{n_k\} = \begin{cases} 1 & \text{If all } n_k = 0 \text{ or } 1 \\ 0 & \text{otherwise} \end{cases}$$

The three cases can be treated concurrently in the canonical ensemble

$$Z(T,V,N) = \sum_{\{n_k\}}{}^{'} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k \epsilon_k \right\}$$

or in the grand canonical ensemble

$$\mathcal{Z}(T,V,\mu) = \sum_{\{n_k\}} g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k (\epsilon_k - \mu) \right\}$$

The probability for a $\{n_k\}$ in the canonical ensemble is

$$P\{n_k\} = \frac{1}{Z}\, g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k \epsilon_k \right\}$$

and in the grand canonical ensemble

$$P\{n_k\} = \frac{1}{\mathcal{Z}}\, g\{n_k\} \exp\left\{ -\beta \sum_{k=1}^{\infty} n_k (\epsilon_k - \mu) \right\}$$

……

Now the expressions can be simplified in the grand canonical case for bosons and Fermions

The canonical expressions can only
be simplified for MB Statistics

↑

due to the constraint

$$N = \sum_{k=1}^{\infty} n_k$$

BE

$$\begin{aligned}\mathcal{Z}^{\mathrm{BE}}(T,V,\mu) &= \sum_{n_1 n_2 \cdots = 0}^{\infty} \Big(\exp\big\{-\beta(\epsilon_1-\mu)\big\}\Big)^{n_1} \\ &\qquad \Big(\exp\big\{-\beta(\epsilon_2-\mu)\big\}\Big)^{n_2} \\ &= \prod_{k=1}^{\infty}\sum_{n_k=0}^{\infty} \Big(\exp\big\{-\beta(\epsilon_k-\mu)\big\}\Big)^{n_k}\end{aligned}$$

but now

$$\sum_{n_k=0}^{\infty} \Big(\exp\big\{-\beta(\epsilon_k-\mu)\big\}\Big)^{n_k} = \frac{1}{1-ze^{-\beta\epsilon_k}}$$

with $z = e^{-\beta\mu}$

$$\rightarrow \quad \boxed{\mathcal{Z}^{\mathrm{BE}}(T,V,\mu) = \prod_{k=1}^{\infty} \frac{1}{1-ze^{-\beta\epsilon_k}}}$$

FD

Here the sum is only over two terms $n_r = 0, 1$

$$\rightarrow \quad \boxed{\mathcal{Z}^{\mathrm{FD}} = \prod_{k=1}^{\infty} \left(1 + z e^{-\beta \epsilon_k}\right)}$$

and **MB**-particles have

$$\mathcal{Z}^{\mathrm{MB}}(T, V, \mu) = \prod_{k=1}^{\infty} \exp\left\{ z e^{-\beta \epsilon_k} \right\}$$

> In principle the canonical ensemble partition functions can be derived from $\mathcal{Z}$, but the integrals are difficult

In the thermodynamic limit all the ensembles give the same results

……

The grand canonical potential is

$$\begin{aligned}\Phi(T,V,\mu) = -kT\,\ln\mathcal{Z}(T,V,\mu) &= U - TS - \mu N \\ &= -pV\end{aligned}$$

and

$$\begin{aligned}S(T,V,\mu) &= -\frac{\partial\Phi}{\partial T}\Big|_{V,\mu} \\ p(T,V,\mu) &= -\frac{\partial\Phi}{\partial V}\Big|_{T,\mu} \\ N(T,V,\mu) &= -\frac{\partial\Phi}{\partial \mu}\Big|_{T,V}\end{aligned}$$

It is possible to unify the notation for the potential

$$\ln \mathcal{Z} = \frac{pV}{kT} = \frac{1}{a} \sum_{k=1}^{\infty} \ln \left(1 + aze^{-\beta\epsilon_k}\right)$$

with

$$a = \begin{cases} +1 & \text{FD} \\ 0 & \text{MB} \\ -1 & \text{BE} \end{cases}$$

Thus

$$
\begin{aligned}
N(T,V,\mu) &= kT\,\frac{\partial}{\partial\mu}\,\ln\mathcal{Z}\Big|_{T,V} \\
&= \sum_{k=1}^{\infty}\frac{1}{z^{-1}e^{\beta\epsilon_k}+a}
\end{aligned}
$$

and

$$
\begin{aligned}
U(T,V,\mu) &= -\frac{\partial}{\partial\beta}\,\ln\mathcal{Z}\Big|_{Z,V} \\
&= \sum_{k=1}^{\infty}\frac{\epsilon_k}{z^{-1}e^{\beta\epsilon_k}+a}
\end{aligned}
$$

It can now be shown by considering

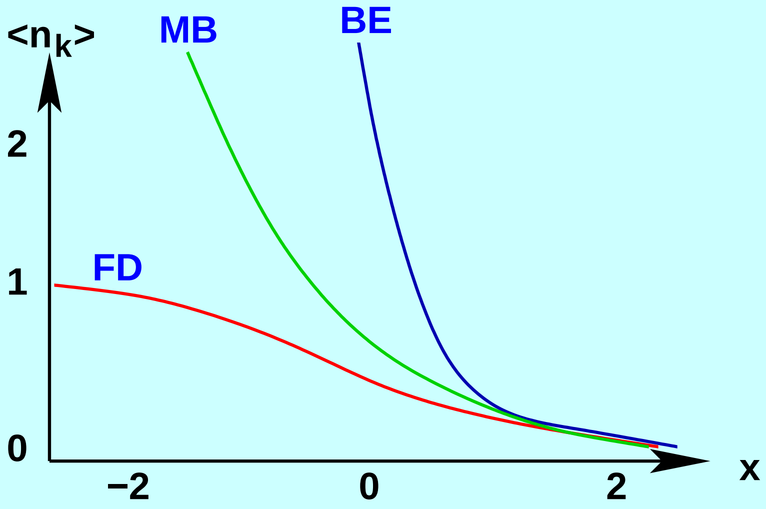
$$\langle \hat{N} \rangle = T_r \langle \hat{\rho} \hat{N} \rangle \quad \text{and} \quad \langle \hat{H} \rangle$$

that

$$\langle \hat{N} \rangle = \sum_{k=1}^{\infty} \langle \hat{n}_k \rangle \, , \, \langle \hat{H} \rangle = \sum_{k=1}^{\infty} \langle \hat{n}_k \rangle \, \epsilon_k$$

where $\hat{n}_k$ is the occupation operator for the one-particle state and its average is

$$\boxed{\begin{aligned} \langle \hat{n}_k \rangle &= \frac{1}{z^{-1} e^{\beta \epsilon_k} + a} \\ &= \frac{1}{z^{-1} e^{\{\beta(\epsilon_k - \mu)\}} + a} \end{aligned}}$$



The graph of $\langle \hat{n}_k \rangle$ is difficult to interprete since x is not a simple variable

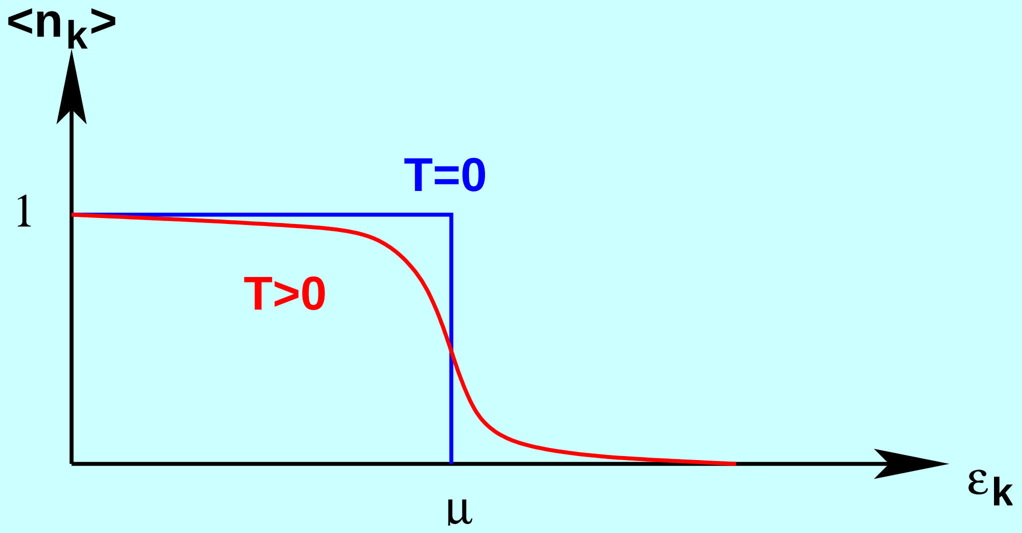
$$x = \frac{(\epsilon_k - \mu)}{kT}$$

and μ is a function of T also

But since $\langle \hat{n}_k \rangle$ diverges for bosons when $x = 0$, it is clear that

$$\mu < \epsilon_0 \qquad \text{for bosons}$$

for fermions at “constant μ”



If $T = 0$ then all levels with $\epsilon_k > \mu$ are empty
and $\mu = \epsilon_F$ the energy needed to add one fermion to the system

$\epsilon_F \sim \mu$ can be much larger than kT
In metals $kT_F = \epsilon_F$ gives $T_F \sim 10^5$ K
→ electron gas is degenerated, cold at room temperature

Excitations for fermions with $kT \ll \epsilon_F$ are just around $\epsilon \sim \mu$
Excitations at the fermi surface

Fluctuations

$$\frac{\sigma^2_{n_k}}{\langle \hat{n}_k \rangle^2} = \frac{1}{\langle \hat{n}_k \rangle} - a$$

gives the expected value in the MB-case

$a^{\mathrm{FD}} = +1$ **small** fluctuations

stiff system due to the Pauli principle

$a^{\mathrm{BE}} = -1$ **large** fluctuations

advantageous since particle bunch momentarly together

Ideal bose gas

non relativistic

We expect the $\boxed{\text{ideal bose gas}}$

if density is low $\Big\downarrow$ $T \to \infty$

$\boxed{\text{ideal MB gas}}$

Some bosons interact then the ideal boson gas is not a good model for high density

We shall check the range

$$n\lambda^3 \equiv \frac{N}{V}\lambda^3 = \frac{N}{V}\left(\frac{h^2}{2\pi m kT}\right)^{3/2} \ll 1$$

here. low density

We calculate the Logarithm of the partition function

$$q(T,V,z) \equiv \ln \mathcal{Z}(T,V,z) = -\sum_k \ln\left(1 - z e^{-\beta\epsilon_k}\right)$$

ϵ_k are here the single particle energies in a box of volume V

In such a system the number of particles is generally fixed

$$\Downarrow$$

z or μ is determined by

$$N = \sum_k \langle n_k \rangle^{BE} = \sum_k \frac{1}{z^{-1}e^{\beta\epsilon_k} - 1}$$

(an implicit equation)

Clearly $0 \le \langle n_k \rangle \le N$ for all k

$\rightarrow z^{-1} e^{\beta \epsilon_k} = \exp\{\beta(\epsilon_k - \mu)\} > 1$

$\rightarrow \epsilon_k > \mu$ for all k

— — — — —

If for example $\epsilon_0 = 0$ and $\mu \le 0$

and $\underline{0 \le z \le 1}$

$\rightarrow$ costs <u>no energy</u> to <u>add</u> a boson

use to convert sum to integral

$$\sum_k \rightarrow \frac{V}{(2\pi)^3} \int d^3k$$

use $\epsilon = \frac{\hbar^2 k^2}{2m}$

$$\| $$

$$\frac{2\pi V}{h^3} (2m)^{3/2} \int \sqrt{\epsilon}\, d\epsilon$$

$$g(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{\epsilon}$$

is the <u>one-particle</u> density of states

This $g(\epsilon)$ misses the fact that a state at $\epsilon = 0$ (or $\epsilon \to 0$) can be of singular importance

$\downarrow$

$$q(T,V,\mu) = -\frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty d\epsilon \sqrt{\epsilon} \ln(1 - z e^{-\beta\epsilon}) - \ln(1-z)$$

$$= \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} \beta \int_0^\infty \frac{d\epsilon\, \epsilon^{3/2}}{z^{-1} e^{\beta\epsilon} - 1} - \ln(1-z)$$

$$N(T,V,z) = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\sqrt{\epsilon}\, d\epsilon}{z^{-1} e^{\beta\epsilon} - 1} + \frac{z}{1-z}$$

The integrals can be related to

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}\,dx}{z^{-1}e^{x}-1} \qquad \begin{matrix} 0\le z\le 1 \\ n\in\mathbb{R} \end{matrix}$$

Since then

$$q(T,V,z) = \frac{V}{\lambda^3}\, g_{5/2}(z) - \ln(1-z)$$

$$N(T,V,z) = \frac{V}{\lambda^3}\, g_{3/2}(z) + N_0(z)$$

z has to be determined from this equation.

To do so we have to explore the functions $g_n(z)$

$$\frac{1}{z^{-1}e^{x}-1} = z e^{-x}\,\frac{1}{1-ze^{-x}}$$

$$= z e^{-x} \sum_{k=0}^{\infty} \{z e^{-x}\}^{k} = \sum_{k=1}^{\infty} z^{k} e^{-kx}$$

which gives

$$\boxed{g_n(z) = \frac{1}{\Gamma(n)} \sum_{k=1}^{\infty} z^{k} \int_0^\infty x^{n-1} e^{-kx}\,dx}$$

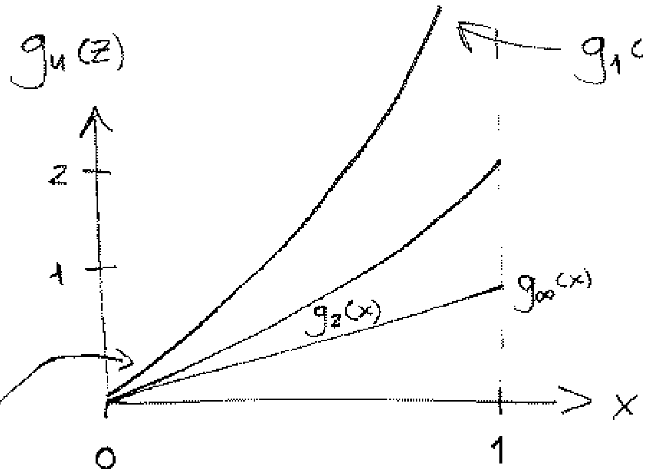
$$= \frac{1}{\Gamma(n)} \sum_{k=1}^{\infty} \frac{z^{k}}{k^{n}} \int_0^\infty y^{n-1} e^{-y}\,dy$$

$$\boxed{= \sum_{k=1}^{\infty} \frac{z^{k}}{k^{n}}} \qquad \underline{0\le z\le 1}$$

$g_n(1)$ is the Riemann's Zeta function

$$g_n(1) = \sum_{k=1}^{\infty} \frac{1}{k^{n}} = \zeta(n) \qquad \underline{n>1}$$

only convergent for



divergent for $n \leq 1$

all start at $x=0$ with slope 1

$$N = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1-z}$$

$$= \quad N_\epsilon \quad + \quad N_0$$

number of particles in excited states

number of particles in the lowest state $\epsilon = 0$

$$\lambda^3 = \left(\frac{h^2}{2\pi m k T}\right)^{3/2}$$

↳ in general $V/\lambda^3 \gg 1$

if T is not too small

$$0 \leq g_{3/2}(z) \leq \zeta(3/2) \approx 2.612$$

For a given V and T

$$N_\epsilon^{max} = \frac{V}{\lambda^3}\zeta(3/2) = V\left(\frac{2\pi m k T}{h^2}\right)^{3/2}\zeta(3/2)$$

$$\sim V T^{3/2}$$

The term

$$N_0 = \frac{z}{1-z}$$

can be neglected unless $z \sim 1$, then

$$\hookrightarrow N \approx N_0 = \frac{z}{1-z} \rightarrow z \approx \frac{N}{N+1} \simeq 1$$

Thermodynamic limit

$$\left(N \to \infty,\ V \to \infty,\ \frac{N}{V} = \text{const.} \right)$$

$$N = N_\epsilon + N_0$$

$$\to\ 1 = \frac{N_\epsilon}{N} + \frac{N_0}{N}$$

with

$$N_\epsilon = \frac{V}{\lambda^3} g_{3/2}(z)$$

$$N_0 = \frac{z}{1-z}$$

Two cases

1. $z \neq 1$ N_0 is finite $\to \frac{N_0}{N} \to 0$

the number of particles in the ground state (single-particle) is vanishingly small

$$1 = \frac{N_\epsilon}{N}, \quad \frac{N_0}{N} = 0$$

2. If $z = 1 \to N_\epsilon = N_\epsilon^{max}$

N_0 is divergent in principle, but $N_0 = N - N_\epsilon^{max}$

$$1 = \frac{N_\epsilon^{max}}{N} + \frac{N_0}{N}$$

macroscopic number of bosons condenses into the lowest state $\epsilon = 0$

$\to$ bose condensation!

explore further fix N, V, T

if $N < N_\epsilon^{max} = \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right)$

or $\boxed{\frac{N\lambda^3}{V} < \zeta\left(\frac{3}{2}\right)}$ (*)

all N particles can be in the excited states

$z \neq 1$ and has to be determined

by

$$\boxed{N = \frac{V}{\lambda^3} g_{3/2}(z)}$$

and the term N_0 can be neglected

If

$$\boxed{N > N_\epsilon^{max} = \frac{V}{\lambda^3} \zeta(3/2)} \quad (**)$$

then $z=1$ and

$$\boxed{N_0 = N - N_\epsilon^{max} = N - \frac{V}{\lambda^3}\zeta(3/2)}$$

condenses into the $\epsilon=0$ state

The transformation happens just when

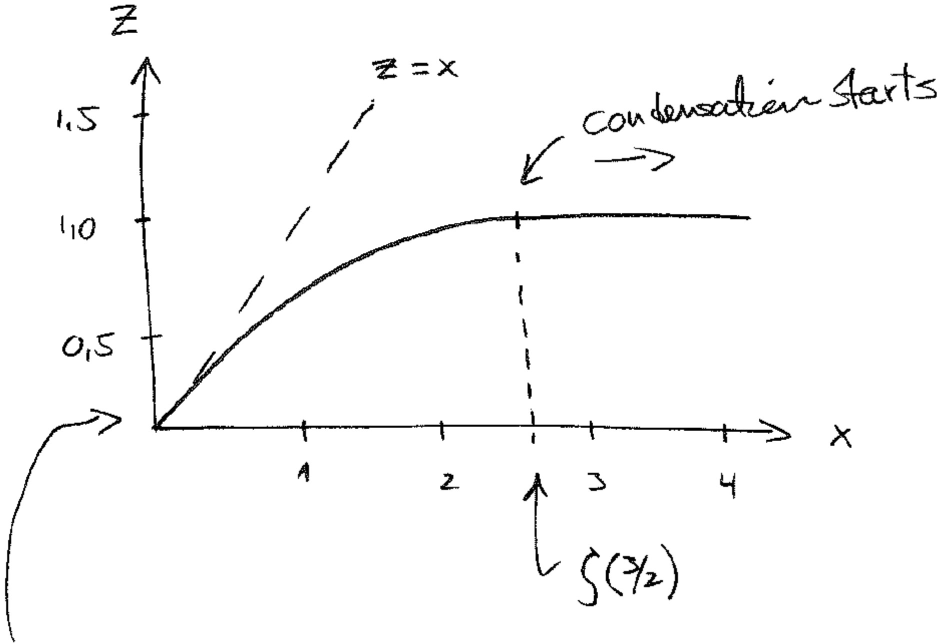
$$\frac{N\lambda^3}{V} = \zeta(3/2)$$

For large T and low $\frac{N}{V}$ we have (*), nearly all particles are excited into higher levels

for low T and high $\frac{N}{V}$ the positive statistical correlation gets a macroscopic number of bosons into the $\epsilon=0$ state

if $\quad x \equiv \frac{N\lambda^3}{V} \quad$ then

$$z = \begin{cases} 1 & \text{if } x \geqslant \zeta(3/2) \\ \text{sol}\{x = g_{3/2}(z)\} & \text{if } x < \zeta(3/2) \end{cases}$$



for $\underline{x \ll 1}$

$$x = z + \frac{z^2}{2^{3/2}} + \cdots \quad \text{or} \quad z \simeq x = \frac{N\lambda^3}{V}$$

The Bose condensation starts when

$$\frac{N\lambda^3}{V} = \zeta\left(3/2\right)$$

thus there is a critical temperature

$$kT_c = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi m \left\{\zeta(3/2)\right\}^{2/3}}$$

below which Bose-condensation occures

Now the expression $N_\epsilon^{\text{max}} = \frac{V}{\lambda^3}\,\zeta\left(3/2\right)$ can be used to express the occupation fractions in terms of T and T_c i.e.:

$$\frac{N_\epsilon}{N} = \begin{cases} 1 & \text{if} \quad x < \zeta(3/2) \quad \text{i.e.} \quad N < N_\epsilon^{\text{max}} \\ \\ \frac{N_\epsilon^{\text{max}}}{N} & \text{if} \quad x \geq \zeta(3/2) \quad \text{i.e.} \quad N \geq N_\epsilon^{\text{max}} \end{cases}$$

and

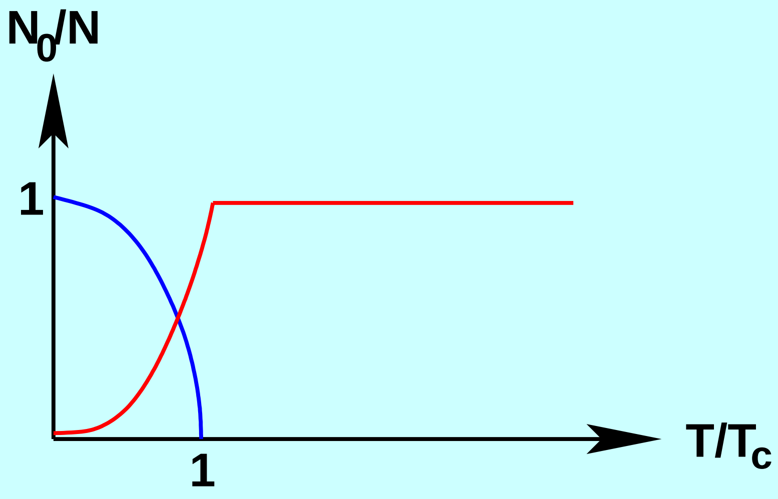
$$\frac{N_\epsilon^{\max}}{N} = \frac{\lambda_c^3}{\lambda^3} = \left(\frac{T}{T_c}\right)^{3/2}$$

Thus

$$\boxed{\frac{N_\epsilon}{N} = \begin{cases} 1 & T \geq T_c \\ \left(\frac{T}{T_c}\right)^{3/2} & T < T_c \end{cases}}$$

Or

$$\frac{N_0}{N} = \begin{cases} 0 & T \geq T_c \\ 1 - \left(\frac{T}{T_c}\right)^{3/2} & T < T_c \end{cases}$$



Later we introduce critical exponents at phase transitions. Here we have

$$\frac{N_\epsilon}{N} = \left(\frac{T}{T_c}\right)^{3/2}$$

In a finite system the kink at $T/T_c = 1$ does not exist

Pressure

$$pV = kT\, q(T, V, z)$$

$$\rightarrow \quad p = \frac{kT}{\lambda^3}\, g_{5/2}(z) - \frac{kT}{V}\, \ln(1 - z)$$

Thermodynamic limit

$$\text{if} \quad z < 1 \qquad \frac{\ln(1 - z)}{V} \rightarrow 0$$

Before we saw that when $z \approx 1$ then

$$z \approx \frac{N}{N + 1} \approx 1$$

$$\rightarrow \quad 1 - z \approx \frac{N + 1 - N}{N + 1} \approx \frac{1}{N + 1}$$

$$\rightarrow \quad \frac{-\ln(1 - z)}{V} \approx \frac{\ln N}{V} \rightarrow 0$$

Since $V, N \rightarrow \infty$, but $\frac{N}{V} = \text{const}$

$$\boxed{\text{Particle in the } \epsilon = 0 \text{ state with no kinetic energy do not contribute to pressure}}$$

$$\rightarrow \quad p = \frac{kT}{\lambda^3}\, g_{5/2}(z) \qquad (*)$$

For $T < T_c$ $\qquad z = 1$

$$\text{and} \quad p = \frac{kT}{\lambda^3}\, \zeta(5/2) \tag{1}$$

independent of V and N !

if a particle is added to the system $(T < T_c)$ it has to go to the $\epsilon = 0$ state

Volume decreases $\Longrightarrow$ more bosons get to the $\epsilon = 0$ state

We had a critical density

$$\left(\frac{N}{V}\right)_c = \frac{\zeta\,(3/2)}{\lambda^3}$$

which can be reinterpreted as

$$V_c = \frac{N\lambda^3}{\zeta\,(3/2)} \tag{2}$$

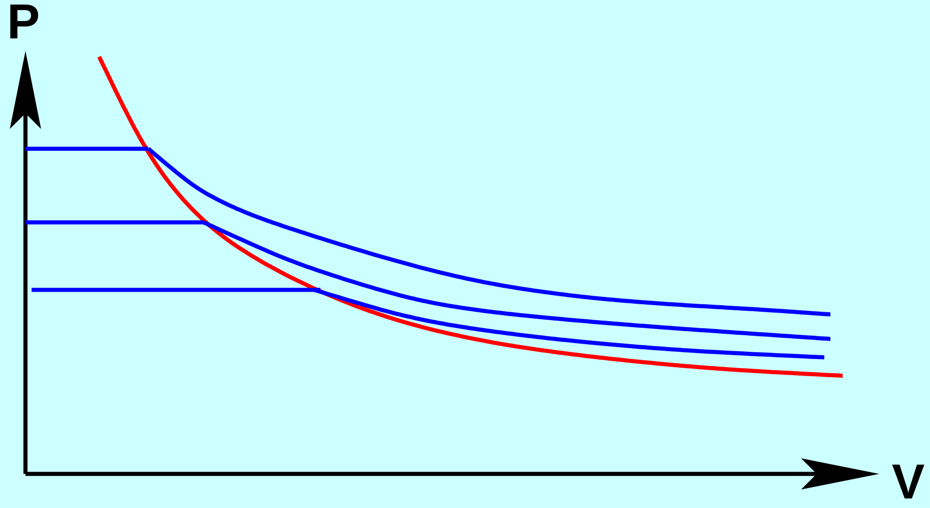
a critical volume below which the condensation starts

A phase transition in momentum space not in coordinate space as a liquid-vapor transition

A phase transition in momentum space not in coordinate space as a liquid-vapor transition

(1) and (2) can be combined to give

$$pV_c^{5/3} = \text{const} \; = \frac{h^2}{2\pi m}\,\frac{\zeta(5/2)N^{5/3}}{\Big(\zeta(3/2)\Big)^{5/3}}$$



For $x = \frac{N\lambda^3}{V} < 1$ one gets

$$\frac{pV}{NkT} = \sum_{\ell=1}^{\infty} a_\ell \, x^{\ell-1}$$

with

$$\begin{aligned} a_1 &= 1 \\ a_2 &= -\frac{1}{4\sqrt{2}} \\ a_3 &= -\Big(\frac{2}{9\sqrt{3}} - \frac{1}{8}\Big) \\ &\cdots\cdots \end{aligned}$$

……

Internal energy

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\,\ln\mathcal{Z}\Big|_{z,V} \\ &= \frac{3}{2}\,kT\,\frac{V}{\lambda^3}\,g_{5/2}(z) \end{aligned}$$

together with (*) yields

$$p = \frac{2}{3}\,\frac{U}{V} \qquad \text{for all } z's$$

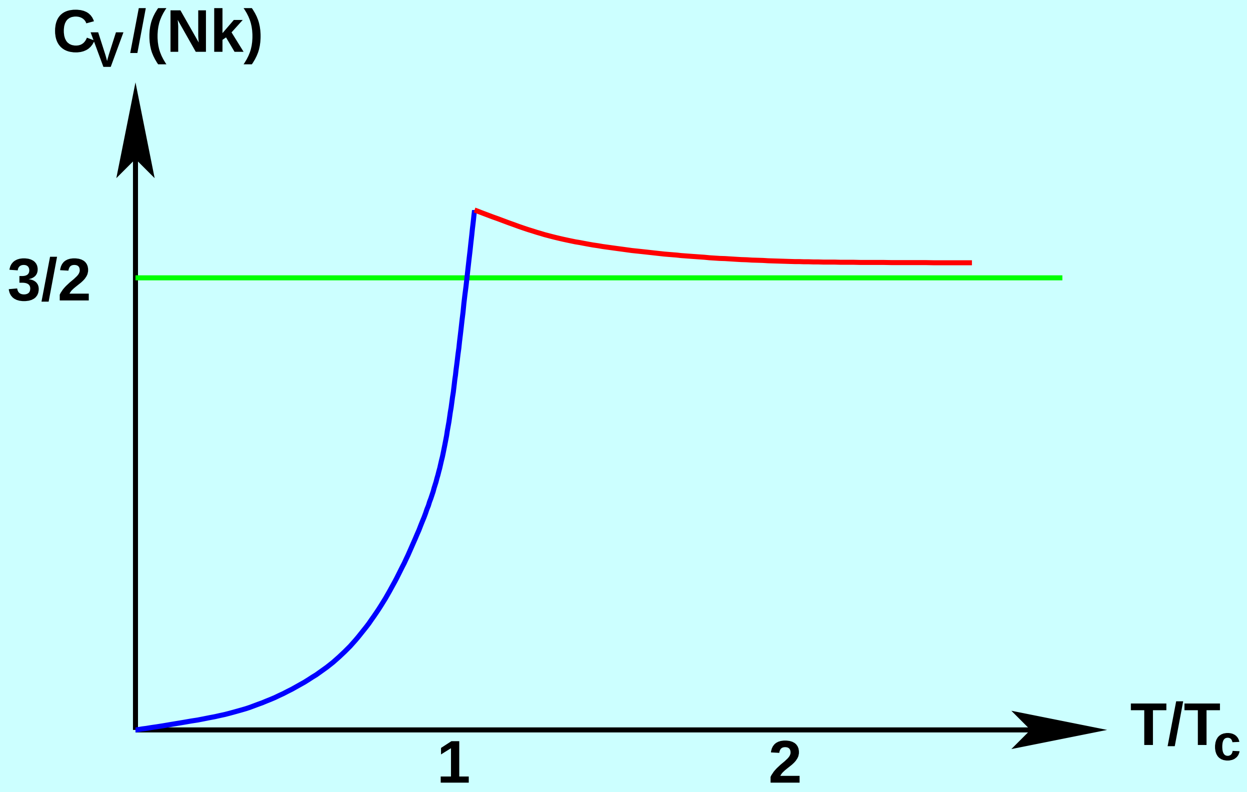
$$U = \frac{3}{2}\,pV = \frac{3}{2}\,kT\,\frac{V}{\lambda^3}\,g_{5/2}(z)$$

for $T < T_c \quad z = 1$

$$\begin{aligned}\frac{C_V}{Nk} &= \frac{1}{Nk}\,\frac{\partial U}{\partial T}\bigg|_{N,V} = \frac{3}{2}\,\frac{V}{N}\,\zeta(5/2)\,\frac{\partial}{\partial T}\left(\frac{T}{\lambda^3}\right) \\ &= \frac{15}{4}\,\zeta(5/2)\,\frac{V}{N\lambda^3} \;\propto T^{3/2}\end{aligned}$$

for $T > T_c$ now $N_0 \approx 0$

$$\frac{C_V}{Nk} = \frac{15}{4}\,\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\,\frac{g_{3/2}(z)}{g_{1/2}(z)}$$


$C_V/(Nk)$
3/2
T/T_c
1
2

Ideal Fermi Gas

$$q(T,V,z) = \ln \mathcal{Z} = \sum_k \ln(1 + ze^{-\beta\epsilon_k})$$

$$N(T,V,z) = \sum_k \langle n_k \rangle = \sum_k \frac{1}{z^{-1}e^{\beta\epsilon_k} + 1}$$

All values of z : $0 \leq z \leq \infty$

Large system

$$\begin{aligned} q(T,V,z) &= \int_0^\infty d\epsilon g(\epsilon) \ln(1 + ze^{-\beta\epsilon}) \\ N(T,V,z) &= \int_0^\infty d\epsilon g(\epsilon) \frac{1}{z^{-1}e^{\beta\epsilon} + 1} \end{aligned}$$

With

$$g(\epsilon) = g\,\frac{2\pi V}{h^2}\,(2m)^{3/2}\,\sqrt{\epsilon}$$

and

$$g = 2s + 1 \qquad \text{spin degeneracy factor}$$

with

$$f_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}dx}{z^{-1}e^x + 1}$$

we get

$$\begin{aligned} q(T,V,z) &= \frac{pV}{kT} = \frac{gV}{\lambda^3}\, f_{5/2}(z) \\ N(T,V,z) &= \frac{gV}{\lambda^3}\, f_{3/2}(z) \end{aligned}$$

$f_n(z)$ can be expanded as

$$f_n(z) = \sum_{k=1}^{\infty} (-1)^{k-1} \frac{z^k}{k^n}$$

(valid for small z)

and there is a useful recursion formula

$$\frac{\partial}{\partial z} f_n(z) = \frac{1}{z} f_{n-1}(z)$$

In a Fermi system with Pauli exclusion μ is often high, and

$$\rightarrow \quad z = e^{\beta\mu} = \exp\left\{\frac{\mu}{kT}\right\}$$

$z \rightarrow \infty$ as $T \rightarrow 0$

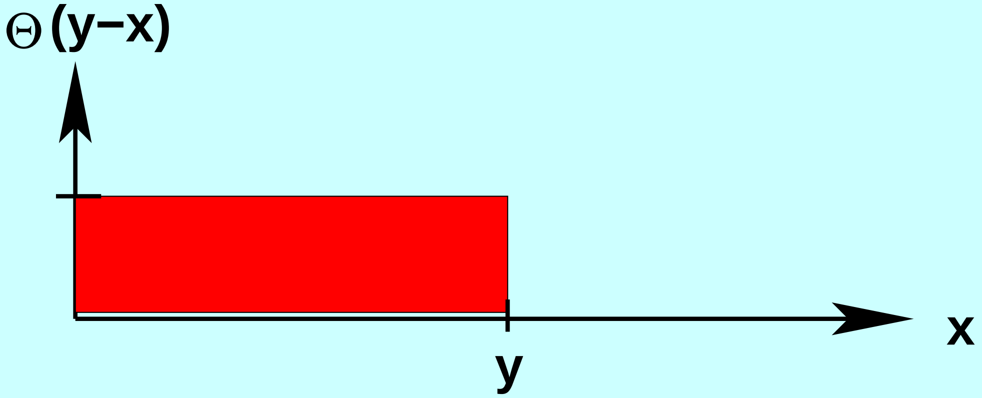
Then it is helpful to introduce $y = \beta\mu$ and consider $y \to \infty$

$$\frac{1}{z^{-1}e^{\beta\epsilon}+1} = \frac{1}{e^{x-y}+1} \quad \text{with } \; x = \beta\epsilon$$

$$\to \quad \begin{cases} 1 & \text{as} \quad x < y \quad \text{and} \quad y \to \infty \\ 0 & \text{as} \quad x > y \quad \text{and} \quad y \to \infty \end{cases}$$

$$\to \quad \ominus(y-x)$$

unit step function



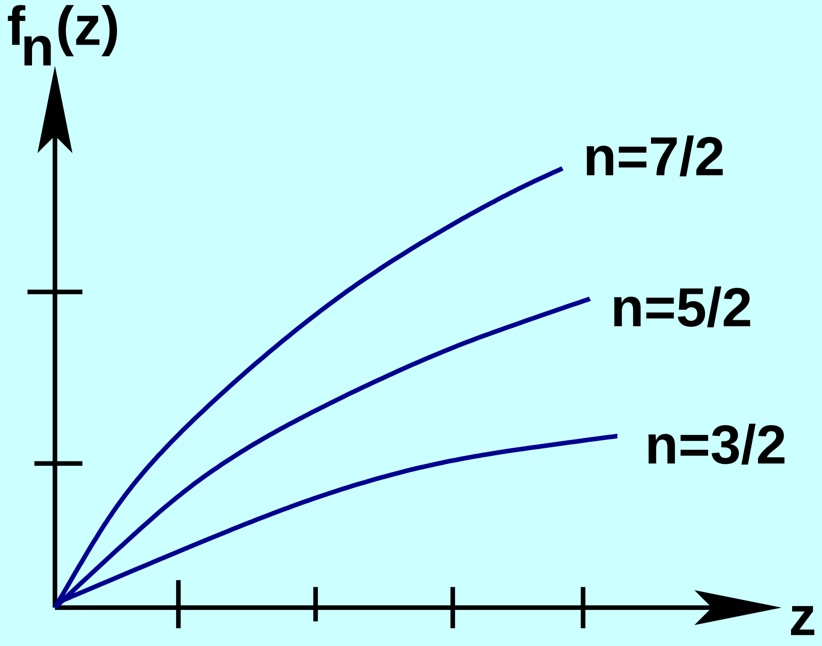
Define

$$F_n(y) = \Gamma(n) f_n(z) = \Gamma(n) f_n(y)$$

Sommerfeld found (1928)

$$\begin{aligned} f_n(y) &= \frac{y^n}{\Gamma(n+1)} \left\{ 1 + \sum_{j=1}^{\infty} 2 \begin{pmatrix} n-1 \\ 2j-1 \end{pmatrix} n y^{-2j} \right. \\ &\qquad \left. \cdot\, \Gamma(2j)\zeta(2j)\left(1 - \frac{1}{2^{2j-1}}\right) \right\} \end{aligned}$$

A low temperature expansion (works in 3D)
for $n = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots$ the expansion is good.



$$\text{for} \quad z \ll 1 \qquad f_n(z) \simeq z$$

and the Sommerfeld expansion shows that

$$f_n(z) \simeq \frac{(\ln\ z)^n}{n!}\ , \ \text{for} \quad z \gg 1$$

Thermodynamic of the Fermi gas

$$
\begin{aligned}
U &= -\frac{\partial}{\partial\beta}\,\ln\mathcal{Z}\Big|_{z,V} = kT^2\,\frac{\partial}{\partial T}\,\ln\mathcal{Z}\Big|_{z,V} \\
&= \frac{3}{2}\,kT\,\frac{gV}{\lambda^3}\,f_{5/2}(z) \\
&= \frac{3}{2}\,NkT\,\frac{f_{5/2}(z)}{f_{3/2}(z)}
\end{aligned}
$$

if

$$N = \frac{gV}{\lambda^3}\,f_{3/2}(z) \quad \text{is used}\ .$$

The classical limit

$$\frac{N\lambda^3}{Vg} \ll 1, \quad \begin{array}{l}\text{small density}\\ \text{high } T\end{array}$$

$$\frac{N}{V}\,\frac{\lambda^3}{g} = f_{3/2}(z) \ll 1 \rightarrow z \ll 1$$

$$U \rightarrow \frac{3}{2}NkT$$

$$\frac{pV}{kT} = \frac{gV}{\lambda^3}\,f_{5/2}(z) = \frac{U}{3kT/2}$$

$$\rightarrow p = \frac{2}{3}\,\frac{U}{V}$$

In general for all non-relativistic gases $p = \frac{2}{3}\,\frac{U}{V}$

Furthermore

$$\frac{C_V}{Nk} = \frac{15}{4}\,\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\,\frac{f_{3/2}(z)}{f_{1/2}(z)}$$

yielding the classical limit as $z \to 0$

The virial expansion of the equation of state is:

$$\frac{pV}{NkT} = \sum_{\ell=1}^{\infty} (-1)^{\ell-1} a_\ell x^{\ell-1}$$

with

$$x = \frac{\lambda^3}{gv} = \frac{N\lambda^3}{gV}$$

and a_ℓ are just the same as in the boson case

Degenerate Fermi gas

In many Fermi systems $\mu \gg kT$ at room temperature

$\rightarrow \quad T \approx 0$ can be used

$$\rightarrow \langle n_\epsilon \rangle_{T=0}^{FD} = \theta(\mu - \epsilon) = \begin{cases} 1 & \epsilon \leq \mu \\ 0 & \epsilon > \mu \end{cases}$$

$$
\begin{aligned}
N &= \int_0^\infty d\epsilon\, g(\epsilon)\theta(\mu-\epsilon) \\
&= g\,\frac{2\pi V}{h^3}\,(2m)^{3/2}\,\int_0^\mu \epsilon^{1/2} d\epsilon \\
&= gV\left(\frac{2\pi m}{h^2}\right)^{3/2}\,\frac{4}{3\sqrt{\pi}}\,\mu^{3/2}
\end{aligned}
$$

$$
U = \int_0^\infty d\epsilon\, g(\epsilon)\theta(\mu-\epsilon)\epsilon = gV\left(\frac{2\pi m}{h^2}\right)\,\frac{4}{5\sqrt{\pi}}\,\mu^{5/2}
$$

$$\rightarrow \quad \frac{U}{N} = \frac{3}{5}\mu\,, \quad \mu = \epsilon_f \text{ at } T = 0$$

mean energy per particle

And thus

$$\epsilon_f = \mu = \frac{\hbar^2}{2m} \underbrace{\left(\frac{6\pi}{g}\,\frac{N}{V}\right)^{2/3}}_{p_f^2}$$

and

$$\frac{U}{V} = \frac{3}{2}p = \frac{3}{5}\left(\frac{6\pi}{g}\right)^{2/3} \frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{5/3}$$

ϵ_f, $\frac{U}{V}$, $\frac{U}{N}$ all incease with $n = \frac{N}{V}$

E_{kin} grows with $\frac{N}{V}$

Define from $\frac{N}{V} = \frac{1}{v} = \frac{1}{\frac{4}{3}\pi r_0^3}$

$$r_s = \frac{r_0}{a_0} \qquad a_0 \text{ Bohr radius}$$

$$\rightarrow \quad E_{kin} \approx \frac{2.21}{r_s^2}$$

Coulomb interaction $\approx \frac{1}{r_s}$

$$\rightarrow \quad \text{as} \quad r_s \quad \ll \quad 1, \quad \text{large } n$$

$$E_{kin} \quad \gg \quad E_{int}$$

Coulomb interaction becomes **unimportant at high density**

We can check next order corrections by $(z \gg 1)$

$$
\begin{aligned}
f_{5/2}(z) &\simeq \frac{8}{15\sqrt{\pi}}(\ln z)^{5/2}\left\{1+\frac{5\pi^2}{8}(\ln z)^{-2}+\ldots\right\} \\
f_{3/2}(z) &\simeq \frac{4}{3\sqrt{\pi}}(\ln z)^{3/2}\left\{1+\frac{5\pi^2}{8}(\ln z)^{-2}+\ldots\right\} \\
f_{1/2}(z) &\simeq \frac{2}{\sqrt{\pi}}(\ln z)^{1/2}\left\{1-\frac{\pi^2}{24}(\ln z)^{-2}+\ldots\right\}
\end{aligned}
$$

Thus

$$\begin{aligned}\frac{N}{V} &= \frac{g}{\lambda^3} f_{3/2}(z) \simeq \frac{4\pi g}{3}\left(\frac{2m}{\hbar^2}\right)^{3/2} (kT\ln z)^{3/2} \\ &\cdot \left\{1+\frac{\pi^2}{8}(\ln z)^{-2}+\ldots\right\}\end{aligned}$$

We want to extract here an expression for z
(use here the 0^{th}-order for $\{\cdots\}$)

$$kT\ln z = \mu = \left(\frac{3N}{4\pi g V}\right)^{2/3} \frac{h^2}{2m} = \epsilon_f$$

$$
\begin{aligned}
\frac{N}{V} &= \frac{4\pi g}{3}\left(\frac{2m}{h^2}\right)^{3/2}(kT\ln z)^{3/2}\left\{1+\frac{\pi^2}{8}\frac{(kT)^2}{(kT\ln z)^2}+\ldots\right\} \\
&= \frac{4\pi g}{3}\left(\frac{2m}{h^2}\right)^{3/2}(kT\ln z)^{3/2}\left\{1+\frac{\pi^2}{8}\left(\frac{kT}{\epsilon_f}\right)^2+\ldots\right\}
\end{aligned}
$$

$$
\rightarrow kT\ln z = \mu \simeq \epsilon_f\left\{1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2\right\}
$$

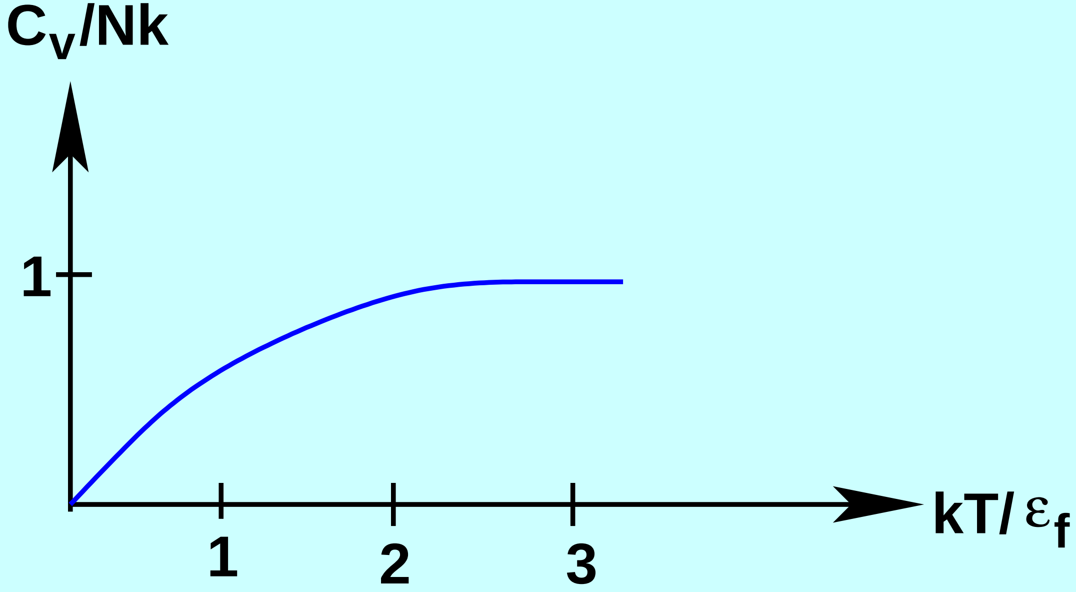
……

Similarily

$$
\frac{U}{N} \simeq \frac{3}{5}\epsilon_f\left\{1+\frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2+\ldots\right\}
$$

giving

$$\frac{C_V}{Nk} = \frac{1}{Nk}\,\frac{\partial V}{\partial T}\Big|_{V,N} = \frac{\pi^2}{2}\,\frac{kT}{\epsilon_f} + \ldots$$



Pauli paramagnetism

N electrons in a metal with magnetic moment

$$d_z = \gamma \mu_B m$$

with

$$m = \pm\frac{1}{2} \quad , \quad \gamma = 2 \quad , \quad \mu_B = \frac{e\hbar}{2mc}$$

γ can be quite different in materials

Neglect the influence of the magnetic field on the wavefunctions!!

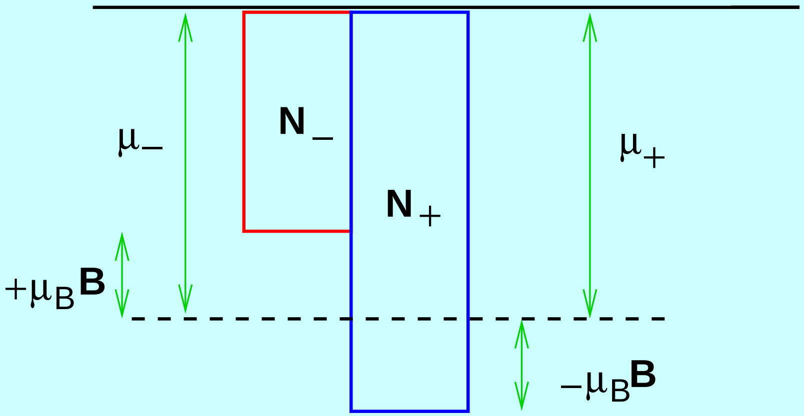
Limits to small B

$$\epsilon = \frac{\mathbf{p}^2}{2m} - d_z B$$

μ chemical potential of the free Fermi gas

equilibrium:

$\rightarrow \mu_+(N_+) = \mu_-(N_-)$



and

$$\begin{aligned} \mu_+(N_+) &= \mu(N_+) - \mu_B B \\ \mu_-(N_-) &= \mu(N_-) + \mu_B B \end{aligned}$$

$$\downarrow$$

$$\mu(N_+) - \mu(N_-) = 2\mu_B B$$

We know the function for μ from

$$f_{3/2}(z) = \frac{N}{V}\lambda^3 \quad , \quad z = e^{\mu\beta}$$

The total magnetic moment is

$$\langle D_z \rangle = \mu_B (N_+ - N_-)$$

and the susceptibility

$$\chi = \lim_{B\to 0} \frac{\partial \langle D_z \rangle}{\partial B}$$

For $kT \gg \epsilon_f$

$$\chi \simeq \chi_\infty \left(1 - \frac{n\lambda^3}{2^{5/2}}\right) \quad , \quad n = \frac{N}{V}$$

with

$$\chi_\infty = \frac{\mu_B^2 N}{kT}$$

For $kT \ll \epsilon_f$

True for metals at room temperature and lower (weak T dependence)

$$\chi \simeq \chi_0 \left\{1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_f}\right)^2\right\}$$

with

$$\chi_0 = \frac{3}{2} \frac{\mu_B^2 N}{\epsilon_f}$$

Landau diamagnetism

Diamagnetism of metals

B induces circular current opposing the external magnetic field

Landau levels

$$\epsilon = \epsilon_{jM} + \epsilon_z \qquad \overset{(c.g.s)}{\downarrow}$$

with

$$\begin{aligned} \epsilon_{jM} &= \hbar\omega_c \left(j + \frac{1}{2}\right) \quad , \quad \omega_c = \frac{\hbar B}{mc} \\ \epsilon_z &= \frac{p_z^2}{2m} \end{aligned}$$

ϵ_{jM}: the M-states are all (infinite) degenerate

$$g_j = V^{2/3}\frac{eB}{hc} = \frac{L^2}{\ell_B^2}$$

ℓ_B^2: magnetic length

$$\begin{aligned}\ln \mathcal{Z} \quad = \quad & \frac{V^{1/3}}{h}\int_{-\infty}^{\infty} dp_z \sum_{j=0}^{\infty} g_j \ln\Bigg[1 + z\exp\Big\{-\beta\big(\frac{p_z^2}{2m} \\ & +2\mu_B B(j+\frac{1}{2})\big)\Big\}\Bigg]\end{aligned}$$

The replacement $\omega_c \to \mu_B$ can not be done in materials where the electrons have an **effective mass** $m^* \neq m$

The chemical potential can be found from

$$N = \frac{V^{1/3}}{h} \int_{-\infty}^{\infty} dp_z \sum_{j=0}^{\infty} g_j \frac{1}{z^{-1} \exp\left\{\beta\left(\frac{p_z^2}{2m} + 2\mu_B B(j+\frac{1}{2})\right)\right\} + 1}$$

$$\begin{aligned} \langle D_z \rangle &= \frac{1}{\beta}\frac{\partial}{\partial B} \ln \mathcal{Z}\Big|_{Z,V,T} \\ &= -\frac{1}{2} N\mu_B \Big(\frac{\mu_B B}{\epsilon_f}\Big) \quad , \quad \epsilon_f \gg kT \gg \mu_B B \end{aligned}$$

and

$$\chi_0 = \lim_{B \to 0} \frac{\partial \langle D_z \rangle}{\partial B} = -\frac{1}{2} \frac{N \mu_B^2}{\epsilon_f}$$

For a metal

$$\begin{aligned} \chi_0^{\text{eff}} &= \chi_0^{\text{para}} + \chi_0^{\text{dia}} \\ &= \frac{1}{2} \frac{N}{\epsilon_f} \left(3\mu_B^2 - \mu_B^2 \right) \end{aligned}$$

If $m^* \neq m$!! …

Real gases

do interact →

$$H = \sum_{i=1}^{N} \frac{\bar{p}_i^{\,2}}{2m} + \sum_{\substack{i,k\\ i<k}} U_{ik}(|\bar{r}_i - \bar{r}_k|)$$

leading to a partition function

$$Z(T,V,N) = \frac{1}{N!\,h^{3N}} \int d^{3N}p \, \exp\left\{-\frac{\beta}{2m}\sum_{i=1}^{N} \bar{p}_i^{\,2}\right\}$$

$$\cdot \int d^{3N}r \, \exp\left\{-\beta \sum_{\substack{i,k\\ i<k}} U_{ik}\right\}$$

$$= \frac{1}{N!\,\lambda^{3N}} \int d^{3N}\bar{r} \prod_{\substack{i,k\\ i<k}} \exp\{-\beta U_{ik}\}$$

since the $\bar{p}$-integration could be performed

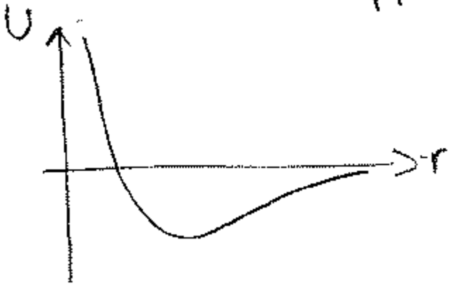
---

if $U_{ik} = 0$ for all i and k

then

$$Q_N(V,T) = \int d^{3N}r \prod_{\substack{i,k\\ i<k}} \exp\{-\beta U_{ik}\} = V^N$$

We need an approximation for Q_N



low $\frac{N}{V}$, → $U \to 0$

high T, → $E_{kin} \gg E_{pot}$

Introduce

$$f_{ik} = \{\exp(-\beta U_{ik}) - 1\}$$

Then $f_{ik} \ll 1$

$$\prod_{\substack{i,k\\ i<k}} (1 + f_{ik}) = 1 + \sum_{\substack{i,k\\ i<k}} f_{ik} + \sum_{\substack{i,k\\ l,m}} f_{ik} f_{lm} \cdots$$

$$Q_N(V,T) = \int d^{3N}r \left(1 + \sum_{\substack{i,k \\ i<k}} f_{ik} + \cdots \right)$$

$$= V^N + V^{N-2} \sum_{\substack{i,k \\ i<k}} \int d^3r_i \, d^3r_k \left\{ \exp(-\beta U_{ik}) - 1 \right\} + \cdots$$

Use center-of-mass coordinates

$$\bar{R} = \frac{1}{2}(\bar{r}_i + \bar{r}_k)$$

and relative coordinates

$$\bar{r} = (\bar{r}_i - \bar{r}_k)$$

$$Q_N(V,T) = V^N + V^{N-1} \frac{N(N-1)}{2} \int d^3r \left\{ \exp(-\beta U(r)) - 1 \right\}$$

that many pairs with $i<k$

use $\quad \underline{N(N-1)} \simeq \underline{N^2}$

Then

$$Z(T,V,N) = \frac{1}{N!} \frac{V^N}{\lambda^{3N}} \left[1 + \frac{N^2 a(T)}{2V} + \cdots \right]$$

with

$$a(T) = 4\pi \int_0^\infty r^2 dr \left\{ e^{-\beta U(r)} - 1 \right\}$$

and

$$p(T,V,N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{\partial}{\partial V}(kT \ln Z)$$

$$= \frac{NkT}{V} - kT \frac{\frac{aN^2}{2V^2}}{1 + \frac{aN^2}{2V}}$$

$$\rightarrow \quad p \simeq \frac{NkT}{V}\left(1 - \frac{aN}{2V}\right)$$

Mayer's cluster expansion

In

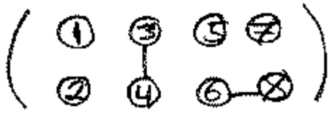
$$Q_N(V,T) = \int d^{3N}r \left(1 + \sum_{\substack{i,k \\ i<k}} f_{ik} + \cdots \right)$$

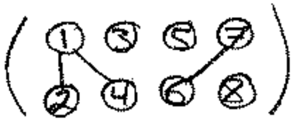
we can associate each term with a corresponding N-particle graph

for example if $N = 8$ then

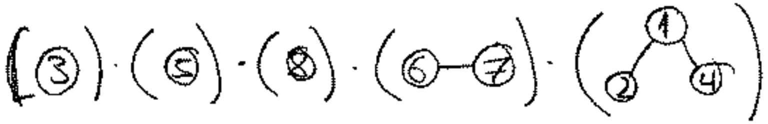
$$\int f_{34} f_{68} \, d^3r_1 \cdots d^3r_8 \qquad \int f_{12} f_{14} f_{67} \, d^3r_1 \cdots d^3r_8$$

$$\updownarrow \qquad\qquad\qquad\qquad \updownarrow$$





which can be factorized into clusters



$$\int d^3r_3 \int d^3r_5 \int d^3r_8 \int f_{12} f_{14} \, d^3r_1 d^3r_2 d^3r_4 \int f_{67} \, d^3r_6 d^3r_7$$

This leads to

$$Q_N(V,T) = N! \lambda^{3N} \sum_{\{m_\ell\}}{}' \prod_{\ell=1}^{N} \frac{1}{m_\ell!} \left(b_\ell \frac{V}{\lambda^3} \right)^{m_\ell}$$

with

$$b_\ell(V,T) = \frac{1}{\ell! \, \lambda^{3(\ell-1)} V} \left\{ \text{Sum of all types of } \ell\text{-clusters} \right\}$$

and

$$\sum_{\ell=1}^{N} \ell m_\ell = N \quad , \quad m_\ell = 0, 1, 2, \cdots N$$

b_ℓ are dimensionless number which do not depend on V in the thermodynamic limit, only T.

dilute gas → small clusters dominate

(far from phase transformation)

Grand canonical partition function

$$\mathcal{Z}(T,V,z) = \sum_{N=0}^{\infty} z^N Z(T,V,N)$$

use

$$z^N = z^{\sum_{\ell=1}^{N} \ell m_\ell} = \prod_{\ell=1}^{N} (z^\ell)^{m_\ell}$$

then

$$\mathcal{Z}(T,V,z) = \sum_{N=0}^{\infty} \sum_{\{m_\ell\}}{}' \prod_{\ell=1}^{\infty} \frac{1}{m_\ell!}\left(b_\ell z^\ell \frac{V}{\lambda^3}\right)^{m_\ell}$$

$$= \sum_{m_1 m_2 \cdots = 0}^{\infty} \prod_{\ell=1}^{\infty} \frac{1}{m_\ell!}\left(b_\ell z^\ell \frac{V}{\lambda^3}\right)^{m_\ell}$$

$$= \prod_{\ell=1}^{\infty}\left\{\sum_{m_\ell=1}^{\infty} \frac{1}{m_\ell!}\left(b_\ell z^\ell \frac{V}{\lambda^3}\right)^{m_\ell}\right\}$$

and

$$\phi = -kT \ln \mathcal{Z} = -kT \frac{V}{\lambda^3} \sum_{\ell=1}^{\infty} b_\ell z^\ell$$

giving the cluster expansions of Mayer

$$\boxed{\begin{aligned} \frac{p}{kT} &= \frac{1}{V}\ln \mathcal{Z} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell \\ \frac{N}{V} &= \frac{kT}{V}\frac{\partial}{\partial \mu}\ln \mathcal{Z}\Big|_{T,V} \\ &= \frac{z}{V}\frac{\partial}{\partial z}\ln \mathcal{Z}\Big|_{T,V} = \frac{1}{\lambda^3}\sum_{\ell=1} \ell b_\ell z^\ell \end{aligned}}$$

These can be compared to the virial expansion

$$\frac{pV}{NkT} = \sum_{\ell=1}^{\infty} a_\ell \left(\frac{\lambda^3 N}{V}\right)^{\ell-1}$$

the coefficient can be compared

$$a_1 = b_1 = 1$$

$$a_2 = -b_2 = -\frac{2\pi}{\lambda^3}\int_0^\infty \left(\exp\left\{-\frac{U(r)}{kT}\right\}-1\right) r^2 dr$$

$$a_3 = 4b_2^2 - 2b_3$$

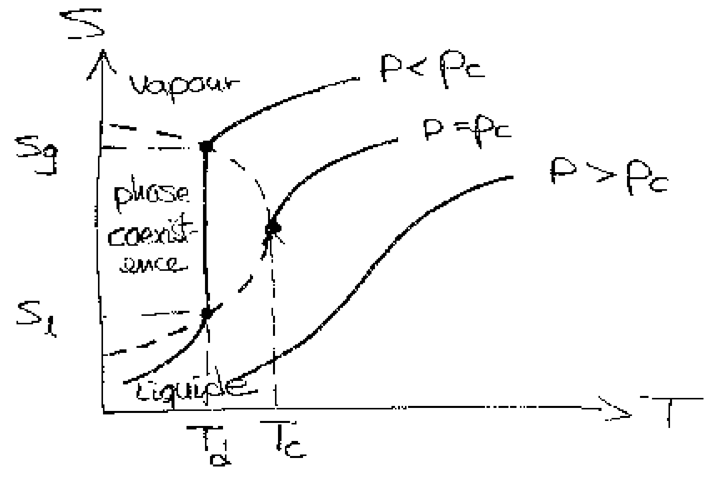
$$a_4 = -20b_2^3 + 18b_2b_3 - 3b_4$$

Phase transitions

Transitions can in most cases be described by order parameters (Landau '37)

small around the critical point where fluctuations on all length scales are strong <-> opalescence

Check liquide - vapour transition



Discontinuity of the entropy S at the transition $(T < T_c)$

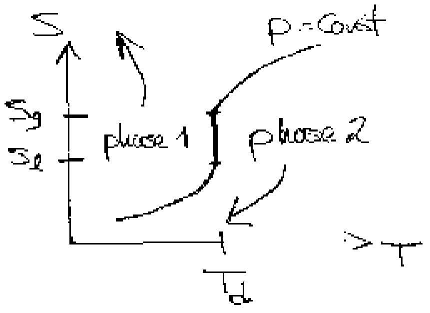
$$\Delta Q = T_d (S_g - S_l)$$

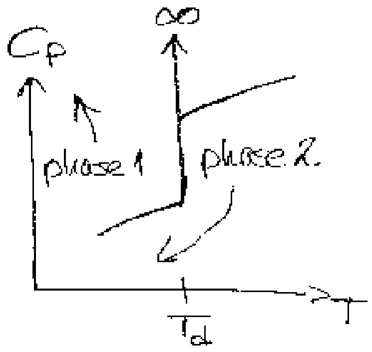
(Water at $p = 101$ kPa -> $T_d = 100°C$)

At constant p the heat ΔQ is needed to evapourate the liquide

latent heat

Infinit heat capacity $C_p = T \frac{\partial S}{\partial T}\Big|_p$ at T_d





Phase transitions with S-discontinuity are called „first order"

Ones with continuos-S are second or higher order

Closer Look

Gibbs free enthalpy $G(N, T, p, \vec{H}, E \cdots)$

for a first order phase transition one of the first derivatives of G with respect to the external fields is discontinuous

$$S = -\frac{\partial G}{\partial T}\Big|_{N,p,\cdots} , \quad V = \frac{\partial G}{\partial p}\Big|_{N,T\cdots}$$

$$d_z = -\frac{\partial G}{\partial H}\Big|_{N,T\ldots.}$$

magnetic dipole moment

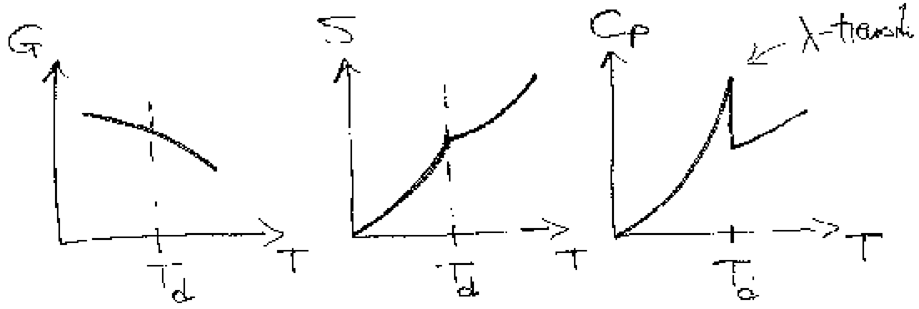
This discontinuity -> divergence in higher derivatives : $C_p, \kappa, \alpha, \chi$

$$C_p = T\frac{\partial S}{\partial T}\Big|_p = -T\frac{\partial^2 G}{\partial T^2}\Big|_p$$

compressibility $\kappa = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T = \frac{1}{V}\frac{\partial^2 G}{\partial p^2}$

expansion $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p = \frac{1}{V}\frac{\partial^2 G}{\partial p\,\partial T}$

$$\chi = \frac{\partial D_z}{\partial H}\Big|_T = -\frac{\partial^2 G}{\partial H^2}\Big|_T$$



Second order transition

Liquide-gas transition

C_p, κ, α diverge

Evaporation, melting, sublimation are first order

↑ latent heat

(Glass melting is not a phase transition)

↑ degree of order does not change

Superconductivity ($B=0$) is second order

superfluidity ^{4}He, alloys

1st order transitions can become 2nd order when $T \to T_c^-$

In any case, a phase transition is related to a nonanalytical behavior of the free enthalpy

↳ we need to find these points in G or Φ

$$\Phi = -pV = -kT \ln \mathcal{Z}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z(N,V,T)$$

An approximation scheme by Yang and Lee ('52) show this

In a potential with a strong hard core repulsion (and short range)

$$Z(T,V,N) = \frac{\lambda^{3N}}{N!} \int d^3r_1 \cdots d^3r_N \exp\left\{-\beta \sum_{i<k} U_{ik}\right\}$$

must vanish for high $\frac{N}{V}$ ($\underset{V}{N}$ given)

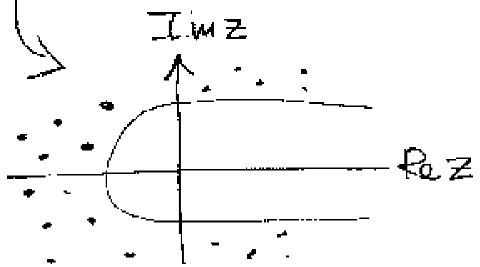
Thus → Φ or p must be analytic on the real z-axis

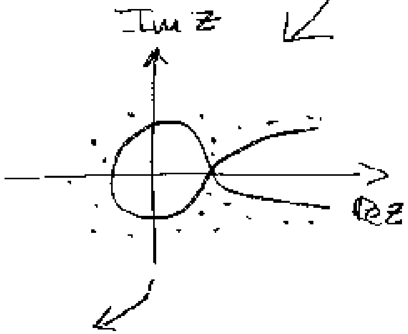
$$-\frac{\Phi}{V} = p = \frac{kT}{V}\ln \mathcal{Z} = \frac{kT}{V}\sum_{k=1}^{N_{max}} \ln\left(1-\frac{z}{z_k}\right)$$

is holomorphic for all $z \neq z_k$

when $N_{max} \to \infty$ (in the thermodynamic limit)

z_k become infinit and can approach the real z-axis.





Φ is then only piecewise analytical on the real z-axis

→ Phase transitions can happen at certain places

{ only in the thermodynamic limit,
but even small systems can show... }

$$F(z,T) = \lim_{V\to\infty}\left(\frac{1}{V}\ln\mathcal{Z}\right) = \frac{p(z,T)}{kT}$$

has the properties

① well defined for all positive real z

② Continuous, monotonously increasing function of z

③ Independent of V (as long as the surface does not grow faster than $V^{2/3}$)

④ The convergence is uniform in any region of analicity

⑤ The derivatives $\frac{\partial}{\partial \ln z} F(z)$ are analytical in the regions where $F(z)$ is.

↳ In regions of analicity the system has a single homogeneous phase

In regions where z_k approach the real axis

The "equation of state" $p = kT\, F(z,T)$ becomes unstable

↳ transition to another phase

Cluster expansion

$$b_\ell(V,T) = -\frac{\lambda^3}{V\ell} \sum_{k=1}^{N_{max}} \left(\frac{1}{z_k}\right)^\ell$$

fails near phase trans.

Corresponding States

→ $N_2, O_2, H_2, CO, \ldots$

All simple real gases obey the same equation of state if the variables are scaled in the critical param!

$$\bar p = \frac{p}{p_c}\ , \quad \bar v = \frac{v}{v_c}\ ; \quad \bar T = \frac{T}{T_c}$$

$$\hookrightarrow \left(\bar p + \frac{3}{\bar v}\right)(3\bar v - 1) = 8\bar T$$

(van der Waals) called the theorem of corresponding state

Experimentally the reduced evaporation heat $\Delta Q/T_c$ vs $p(v_g - v_e)/T$ gives

$$\frac{\Delta Q}{\frac{p(v_g - v_e)}{T}} = 5{,}4$$

for $0.5 < \frac{T}{T_c} < 1$

→ Clausius-Clapeyron equation for T dependence of vapor pressure p

$$\frac{dp}{dT} = \frac{s_g - s_e}{v_g - v_e} = \frac{\Delta Q/T}{v_g - v_e}$$

can be scaled as

$$\frac{\frac{dp}{p}}{\frac{dT}{T}} = \frac{\Delta Q}{\frac{p(v_g - v_e)}{T}} = \frac{\frac{\Delta Q\, T_c}{T_c}}{\frac{p(v_g - v_e)}{T}}$$

$$= 5.4\, T_c$$

$$\hookrightarrow \ln \frac{p}{p_c} = 5.4\left(1 - \frac{T_c}{T}\right) \qquad 0.5 < \frac{T}{T_c} < 1$$

this is integrated from T to T_c

Critical indices

The observed universality (classes) is expressed by critical indices in the neighbourhood of critical points

$$\alpha, \alpha', \beta, \gamma, \gamma', \delta$$

for liquid-vapor transition

The order parameter $\rho_l - \rho_g$ vanishes as $T \to T_c$ like

$$\Psi = \rho_l - \rho_g \sim \left(1 - \frac{T}{T_c}\right)^{\beta}$$

$$C_{V=V_c} \sim \begin{cases} \left(\frac{T}{T_c} - 1\right)^{-\alpha} & T|_{\rho=\rho_c} \to T_c^{+} \\ \left(1 - \frac{T}{T_c}\right)^{-\alpha'} & T|_{\rho=\rho_c} \to T_c^{-} \end{cases}$$

$$\kappa \sim \begin{cases} \left(\frac{T}{T_c} - 1\right)^{-\gamma} & T \to T_c^{+} \\ \left(1 - \frac{T}{T_c}\right)^{-\gamma'} & T \to T_c^{-} \end{cases}$$

and

$$p - p_c \sim |\rho - \rho_c|^{\delta} \qquad T = T_c$$

← critical isotherm

for simple real gases

$\alpha' \sim 0{,}1$

$\alpha \sim 0{,}1$

$\beta \sim 0{,}35$

$\gamma' \sim 1{,}2$

$\gamma \sim 1{,}3$

$\delta \sim 4{,}5$

Read yourself about examples of phase transitions p. 425-435

— — — —

The Ising model

A simple model that show phase transition. Was originally used to describe magnetism....

A lattice of spins that only assume two orientations $\sigma = \pm 1$ (with respect to z-axis)

$$H(\sigma_1 \dots \sigma_N) = -I \sum_{\underset{\nearrow}{n.n.}} \sigma_i \sigma_k$$

sum over nearest neighbours.

If $I > 0$ parallel spins are favored

{ normal exchange force between spins, short range. Can lead to ferro-magnetism at low T. }

If $I < 0$ anti parallel spins are favored

{ anti-ferro-magnetism }

↑ the spin flip energy has to be compared to the thermal energy kT.

At high T the interaction does not matter, higher entropy is attained through statistical distribution.

Exact solutions are known in 1D and 2D

Numerical approaches are common
approximations exist for 3D

In 1D there is no transition to ferromagnetism as $T \to 0$
i.e. $T_c = 0$

In higher dimensions there are phase transitions.

Related model is the Heisenberg model

$$\hat{H}(\bar{S}_1 \dots \bar{S}_N) = -2I \sum_{n.n.} \hat{\bar{S}}_i \cdot \hat{\bar{S}}_k$$

with quantum mechanical spins

$$2\bar{S}_i \cdot \bar{S}_k = \bar{S}^2 - \bar{S}_i^2 - \bar{S}_k^2 = S(S+1) - 2s(s+1)$$

$$= S(S+1) - \frac{3}{2}$$

$s = \pm 1/2$
$S = 0,1$

$$H_{\uparrow\uparrow} - H_{\uparrow\downarrow} = -2I$$

as for the Ising model

1D-Ising model

With an external magnetic field

$$H_N(\sigma_1 \dots \sigma_N) = -I \sum_{n.n.} \sigma_i \sigma_k - \mu B \sum_{i=1}^{N} \sigma_i$$

μ: magnetic moment

Assume periodicity $\sigma_{N+1} = \sigma_1$

Then the H_N can be written as

$$H_N(\sigma_1\cdots\sigma_N) = -I\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - \frac{1}{2}\mu B\sum_{i=1}^{N}(\sigma_i+\sigma_{i+1})$$

Thus

$$Z_N(B,T) = \sum_{\sigma_1=\pm1}\cdots\sum_{\sigma_N=\pm1}\exp\left\{\beta\sum_{i=1}^{N}\left[I\sigma_i\sigma_{i+1}+\frac{1}{2}\mu B(\sigma_i+\sigma_{i+1})\right]\right\}$$

Introduce a transfer matrix

$$\hat{P} = \begin{pmatrix}\exp\{\beta(I+\mu B)\} & \exp\{-\beta I\}\\ \exp\{-\beta I\} & \exp\{\beta(I-\mu B)\}\end{pmatrix}$$

and the states

$$\sigma_k = +1 \rightsquigarrow \begin{pmatrix}1\\0\end{pmatrix}$$

(single spin states)

$$\sigma_k = -1 \rightsquigarrow \begin{pmatrix}0\\1\end{pmatrix}$$

then

$$\langle\sigma_i|\hat{P}|\sigma_{i+1}\rangle = \exp\left\{\beta\left[I\sigma_i\sigma_{i+1}+\frac{1}{2}\mu B(\sigma_i+\sigma_{i+1})\right]\right\}$$

↑ site index, not spindirection index!

Now

$$Z_N(B,T) = \sum_{\sigma_1=\pm1}\cdots\sum_{\sigma_N=\pm1}\langle\sigma_1|\hat{P}|\sigma_2\rangle\cdots\cdots\langle\sigma_N|\hat{P}|\sigma_1\rangle$$

the single particle states $|\pm1\rangle$ form a complete basis

$$\to Z_N(B,T) = \sum_{\sigma_1=\pm1}\langle\sigma_1|\hat{P}^N|\sigma_1\rangle = \mathrm{Tr}\,\hat{P}^N$$

The trace can be found if $\hat{P}$ is diagonalized in order to compute the power

The diagonal form for $\hat{P}$ is

$$\hat{P} = \begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix}$$

with

$$\lambda_{1,2} = e^{\beta I}\cosh(\beta\mu B) \pm \left[e^{-2\beta I} + e^{+2\beta I}\sinh^2(\beta\mu B)\right]^{1/2}$$

$$Z_N(B,T) = \mathrm{Tr}\,\hat{P}^N = \mathrm{Tr}\begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix}^N = \lambda_1^N + \lambda_2^N$$

$$\rightarrow F(N,B,T) = -kT\ln Z_N(B,T) = -kT\ln(\lambda_1^N + \lambda_2^N)$$

Use the abbreviations

$$x = \beta\mu B \quad , \quad y = \beta I$$

giving

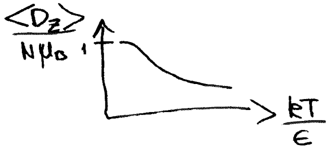
$$\lambda_{1,2} = e^{y}\cosh x \pm \left[e^{-2y} + e^{2y}\sinh^2 x\right]^{1/2}$$

Without an Interaction $(y=0)$

$$\lambda_{1,2} = \begin{cases} 2\cosh x \\ 0 \end{cases}$$

$$\rightarrow F(x,0) = -NkT\ln\{2\cosh x\}$$

agreeing with our earlier model of paramagnetism (8.55) without an interaction



With interaction

$$D_z(N,B,T) = -\left.\frac{\partial F}{\partial B}\right|_{N,T}$$

and

$$D_z(x,y) = N\mu\frac{\sinh x}{\{e^{-4y} + \sinh^2 x\}^{1/2}}\,\frac{\lambda_1^N - \lambda_2^N}{\lambda_1^N + \lambda_2^N}$$

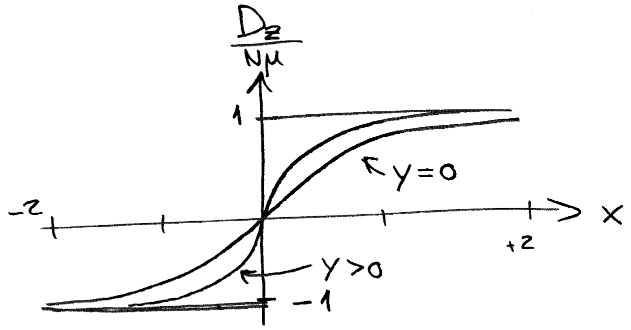
$$\lim_{x \to 0^+} D_z(x,y) = 0$$

The magnetization vanishes with the external field

$\downarrow$

no ferro-magnetism in 1D

$\boxed{D_z(x,0) = N\mu\tanh x}$ is paramagnetism



- if $y = \beta I \to \infty$, Strong interaction

$$\lambda_{1,2}(x, y \gg 1) \simeq e^{(y \pm x)}$$

$$\to D(x,y) \to N\mu \tanh \underset{\uparrow}{N} x$$

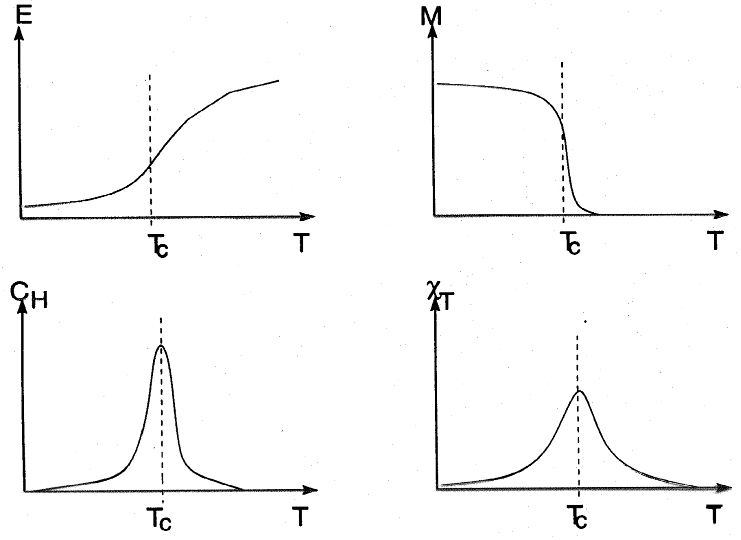
- around $x \approx 0$ $D(x,y) \to N\mu^2 \cdots$

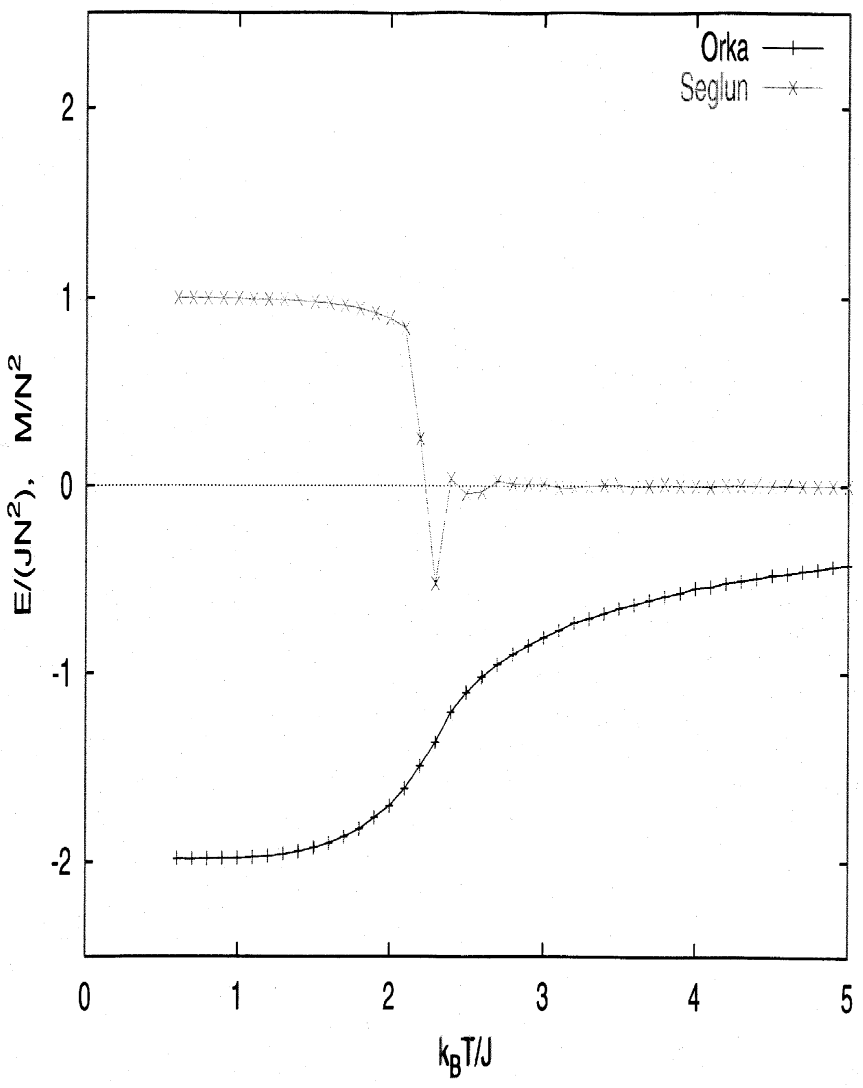
stronger than paramagnetism

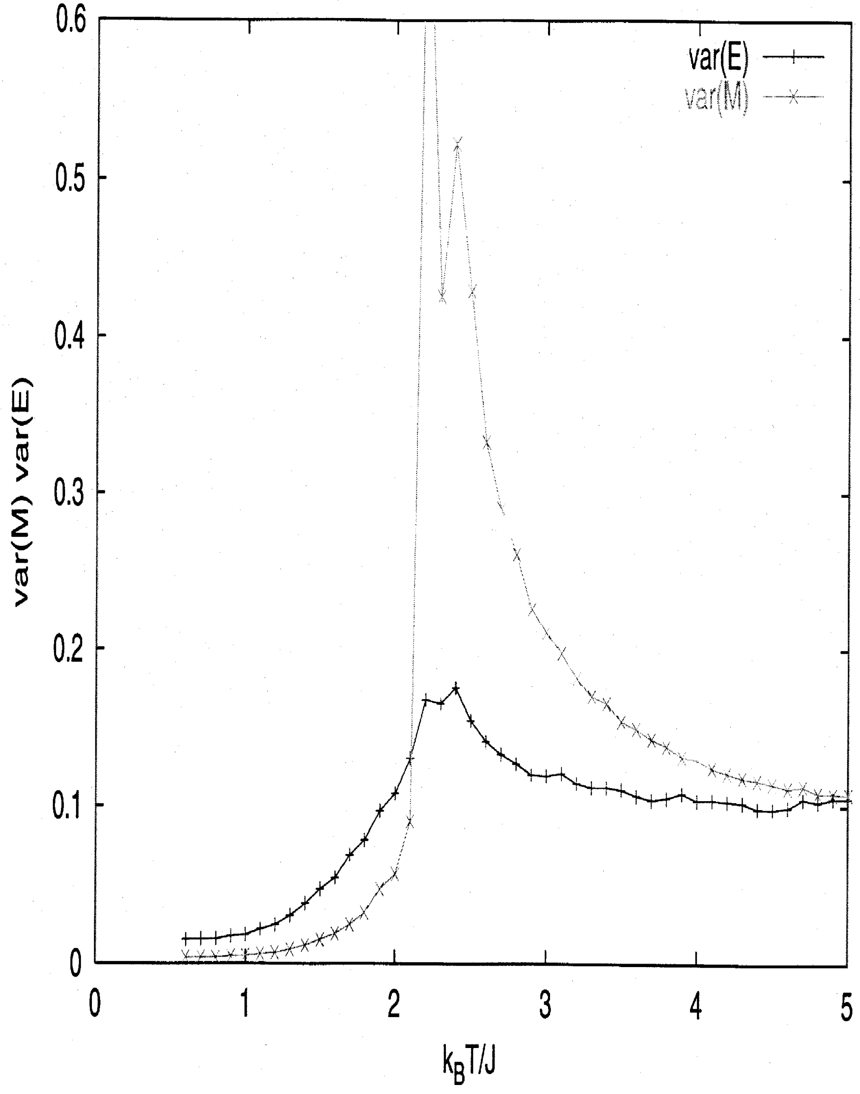
$\to$ supports $T_c = 0$

$y \gg 1$ spin correlation: antiparallel ordering is exponentially suppressed

blocks of parallel spin
but total magnetization vanishes




Orka
Seglun
2
1
0
-1
-2
0
1
2
3
4
5
$E/(JN^2)$, M/N^2
k_BT/J


var(E)
var(M)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
var(M) var(E)
k_BT/J

Mean field approach (Ising):

$\langle \sigma \rangle$: the mean value of σ

$$\sigma_i \sigma_k = \sigma_i \langle \sigma_k \rangle + \langle \sigma_i \rangle \sigma_k - \langle \sigma_i \rangle \langle \sigma_k \rangle$$
$$+ \left(\sigma_i - \langle \sigma_i \rangle\right)\left(\sigma_k - \langle \sigma_k \rangle\right)$$

Thus

$$H(\sigma_1 \dots \sigma_N) = - I \sum_{n.n.} \sigma_i \sigma_k$$

$$= - I \sum_{n.n.} \Big\{ \sigma_i \langle \sigma \rangle + \langle \sigma \rangle \sigma_k - \langle \sigma \rangle^2$$
$$+ \left(\sigma_i - \langle \sigma \rangle\right)\left(\sigma_k - \langle \sigma \rangle\right) \Big\}$$

identical terms

number of pairs

$$= - I q \langle \sigma \rangle \sum_{i=1}^{N} \sigma_i + I \boxed{\frac{q}{2} N} \langle \sigma \rangle^2 \qquad (*)$$
$$- I \sum_{n.n.} \left(\sigma_i - \langle \sigma \rangle\right)\left(\sigma_k - \langle \sigma \rangle\right)$$

q next neighbors (coordination number)

Mean field approximation:

Neglect the last term in $(*)$, the spin-spin correlation

$$H^{m.f.}(\sigma_1 \dots \sigma_N) = - I q \langle \sigma \rangle \sum_{i=1}^{N} \sigma_i + I \frac{q}{2} N \langle \sigma \rangle^2$$

each spin interacts with the mean field

$\langle \sigma \rangle$ has to be determined

$\Downarrow$

self-consistency problem to determine $\langle \sigma \rangle$

$$U = \langle H^{m.f.} \rangle = - I q N \langle \sigma \rangle^2 + I \frac{q}{2} N \langle \sigma \rangle^2$$
$$= - \frac{1}{2} q N I \qquad \text{if } \langle \sigma \rangle = 1$$

as expected

The average magnetic moment is

$$D = \mu \left\langle \sum_{i=1}^{N} \sigma_i \right\rangle = N\mu \langle \sigma \rangle$$

and can also be expressed as

$$D = -\frac{\partial}{\partial B} F(N,B,T,\langle\sigma\rangle)\Big|_{N,T,\langle\sigma\rangle}$$

if $\langle\sigma\rangle$ is considered a constant in the differentiation

can be used to obtain an implicit equation for $\langle\sigma\rangle$

External field

$$H^{m.f.}(\sigma_1 \cdots \sigma_N) = \frac{1}{2} I q N \langle\sigma\rangle^2 - \mu\left(B^{m.f.} + B\right)\sum_{i=1}^{N} \sigma_i$$

With

$$B^{m.f.} = \frac{qI\langle\sigma\rangle}{\mu}$$

caused by the spins

Now the partition function can be evaluated

$$Z(N,T,B,\langle\sigma\rangle) = \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} \exp\left\{-\frac{\beta q}{2} N I \langle\sigma\rangle^2\right\} \cdot \exp\left\{\beta\mu\left(B^{m.f.}+B\right)\sum_{i=1}^{N}\sigma_i\right\}$$

$$= \exp\left\{-\frac{1}{2}\beta q N I \langle\sigma\rangle^2\right\} \cdot \left[\sum_{\sigma=\pm1} \exp\left\{\beta\mu\left(B^{m.f.}+B\right)\sigma\right\}\right]^N$$

$$= \exp\left\{-\frac{1}{2}\beta q N I \langle\sigma\rangle^2\right\} \left[2\cosh\left\{\beta\mu\left(B^{m.f.}+B\right)\right\}\right]^N$$

→ can be treated as a sum of one particle Hamiltonians

Interacting H ⟶ effective H non-interacting

The free energy is then

$$F(N,T,B,\langle\tau\rangle) = \frac{1}{2}qNI\langle\tau\rangle^2$$

$$- NkT\ln\left[2\cosh\left\{\beta\mu(B^{m.f.}+B)\right\}\right]$$

so now the definition

$$D = -\frac{\partial}{\partial B}F(N,B,T,\langle\tau\rangle)\Big|_{N,T,\langle\tau\rangle} = N\mu\langle\tau\rangle$$

can be used to find

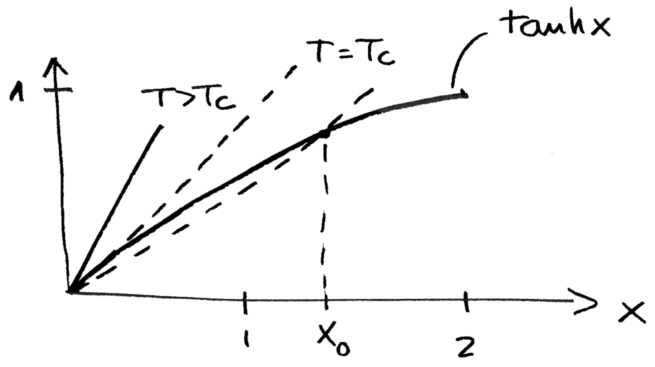
$$\langle\tau\rangle = \tanh\left\{\beta\mu\left(\frac{qI}{\mu}\langle\tau\rangle + B\right)\right\}$$

define

$$x = \beta qI\langle\tau\rangle + \beta\mu B$$

then

$$\frac{1}{\beta qI}(x-\beta\mu B) = \tanh x$$



if $B=0$

$$\frac{1}{\beta qI}\,x = \tanh x$$

Define $T\,T_c^{-1} = \dfrac{1}{\beta qI} = \dfrac{T}{T_c}$, $\left(T_c = \dfrac{qI}{k}\right)$

then if $T > T_c$ only $x=0$, $\langle\tau\rangle = 0$ is possible

if $T < T_c$ then there is $x = 0, x_0$

$x_0 \rightarrow \langle\tau\rangle \neq 0$

spontaneous magnetization.

This solution is also present for $q = 2$ (1D-system), where the mean field approach is not a good description.

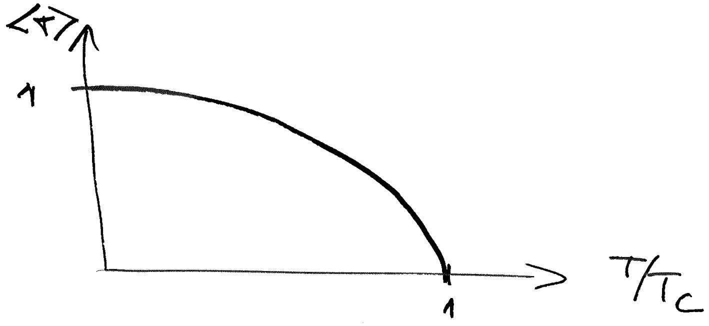
Expand the tanh x

$$\rightarrow \quad \frac{T}{T_c}x = x - \frac{x^3}{3} + \cdots$$

$$\rightarrow \quad x_0 = \left[3\left(1-\frac{T}{T_c}\right)\right]^{1/2} \qquad \text{for } T \le T_c$$

$$= \langle\tau\rangle \frac{T_c}{T}$$

the critical exponent for the order parameter $\langle\tau\rangle$ is exactly $\beta = 1/2$ here.



$T \rightarrow 0$

the slope of the straight line $\frac{1}{\beta q I}x$ is very small $\rightarrow$ intersection with tanh x at lage x

use

$$\frac{T}{T_c}x \simeq 1 - 2e^{-2x} + \cdots$$

$$\rightarrow \langle\tau\rangle = \frac{T}{T_c}x_0 \simeq 1 - 2\exp\left\{-\frac{2T_c}{T}\right\}$$

for $\frac{T}{T_c} \ll 1$

however experiment give

$$\langle\tau\rangle \simeq 1 - \text{cont.}\, T^{3/2}$$

Collective excitations of precession

: magnons

Internal energy $(\bar{B}=0)$

$$U_0 = -\frac{1}{2} q N I \langle\tau\rangle^2$$

$$\Rightarrow \quad C_0 = -qNI\langle\tau\rangle \frac{d\langle\tau\rangle}{dT}$$

$$= -NkT_c\langle\tau\rangle \frac{d\langle\tau\rangle}{dT}$$

use $\quad \langle\tau\rangle = \tanh\left\{\frac{T_c}{T}\langle\tau\rangle\right\}$

for the derivative

$$\frac{d\langle\tau\rangle}{dT} = \left(1-\tanh^2\left\{\frac{T_c\langle\tau\rangle}{T}\right\}\right) \cdot \left(-\frac{T_c}{T^2}\langle\tau\rangle + \frac{T_c}{T}\frac{d\langle\tau\rangle}{dT}\right)$$

$$= \left(1-\langle\tau\rangle^2\right)\left(-\frac{T_c\langle\tau\rangle}{T^2} + \frac{T_c}{T}\frac{d\langle\tau\rangle}{dT}\right)$$

giving

$$\frac{d\langle\tau\rangle}{dT} = \frac{\left(1-\langle\tau\rangle^2\right)\frac{T_c\langle\tau\rangle}{T^2}}{\left(1-\langle\tau\rangle^2\right)\frac{T_c}{T} - 1}$$

for $T<T_c$

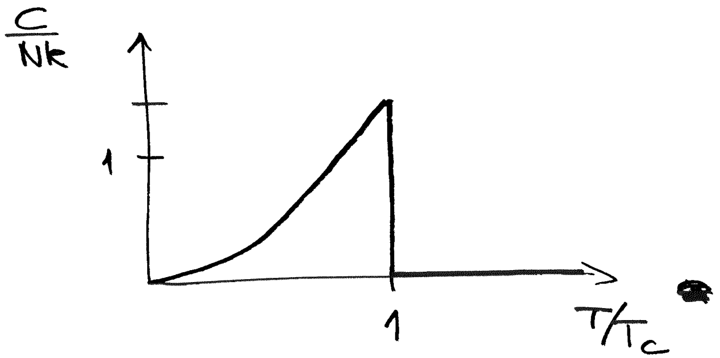
$$C_0(T) = -Nk\frac{T_c}{T}\langle\tau\rangle^2 \frac{1-\langle\tau\rangle^2}{1-\langle\tau\rangle^2-\frac{T}{T_c}}$$

$T \sim T_c$

$$C_0(T_c) = \frac{3}{2}Nk$$

$T>T_c$

$$C_0 = 0$$



$B \neq 0$

$T \gg T_c \;,\quad \beta \mu B \ll 1$

$$\langle \tau \rangle = \frac{\mu B}{k(T-T_c)}$$

$$D = N\mu \langle \tau \rangle = \frac{N\mu^2 B}{k(T-T_c)}$$

and the susceptibility

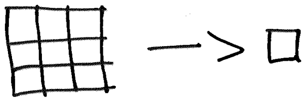
$$\chi = \frac{D}{B} = \frac{N\mu^2/k}{T-T_c}$$

Curie-Weiss law

①

Endurstuðlun

Höfum séð að „skölun" á Isinglíkaninu t.d.


(: meirihluti ræður)

Wilson, SciAm

→ breyti engu þegar $T = T_c$

þegar $T < T_c$ virðist T lækka

þegar $T > T_c$ virðist T hækka

flökt á öllum lengdarskölum

fylgnilengd → ∞

Hversvegna?

* .... ~~ger~~ verða fasabreytingar á altækan hátt sem lýsa má með markveldisvísum?

②

* .... eru til tengsl markveldisvísanna?

* .... eru sömu markveldisvísar fyrir $T < T_c$ og $T > T_c$?

* .... eru markveldisvísar oft ræð brot í 2D?

* .... er til markvídd d^* þ.a. þegar $d > d^*$ þá gilda meðalsviðslíkön.

Endurstuðlun, skölun

Athugum skalaðan Hamiltonvirkja

$$\tilde{H} = H/kT$$

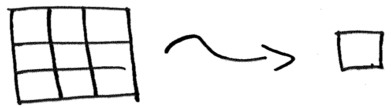
Við skölun eða endurstuðlun hann

$$\tilde{H}' = R\tilde{H}$$

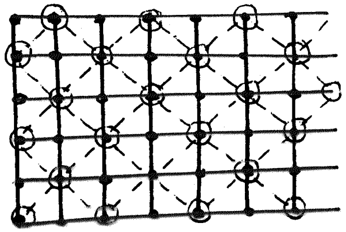
Aðgerðin fækkar frelsisgráðum

$$N \to N'$$

<u>dæmi</u>



eða



skölunarstuðull

$b = \sqrt{2}$

Í nýju grindinni er fjarlægð L (mæld í gömlu grindinni) $L/\sqrt{2}$

Skölun má gera í staðarrúmi, fjarlægja eða safna saman spunum, eða í nykurrúminu með brott heildun langra bylgjuvigra - - - - - -

Skölunarstuðull endurstöðlunar er $b^d = N/N'$

<u>Krafist er að</u> körsumman sé óbreytt

$$Z_{N'}(\tilde{H}') = Z_N(\tilde{H})$$

→ líka frjálsaorkan F

<u>F er magnbundin</u> (extensive)

Því ummyndast frjálsaorkan <u>á spuna</u>, skalaða

$$\tilde{f} = f/kT$$

eins og $\tilde{f}(\tilde{H}') = b^d \tilde{f}(\tilde{H})$

<u>Lengdir</u> mældar í <u>nýjugrindinni</u> skalast um b, verða

L/b

(5)

$$\bar{r} \to \bar{r}' = b^{-1} r$$

og skriðþungi

$$\bar{q} \to \bar{q}' = b\bar{q}$$

Til að fá rétta hegðun spunafylgni þarf að skala spuna

$$\bar{S}_r \to \bar{S}'_{r'} = c^{-1}\bar{S}_r$$

$$c^2\Gamma(b^{-1}r, \tilde{H}') = \Gamma(r, \tilde{H})$$

<u>Viljum finna stöðuga punkta</u> í endurstöðluninni

$$\tilde{H}' = \tilde{H} = \tilde{H}^*$$

Vitum að í stöðugum punkti mun fylgnilengdin varpast á sjálfa sig

$$\xi' = \xi = \xi^*$$

---

(6)

<u>En</u> lengdir breytast við endurstöðlun því fæst einnig

$$\xi' = b^{-1}\xi$$

Þetta tvennt gengur aðeins upp ef <u>$\xi = \infty$</u>

<u>Flæði í stikarúmi</u>

Köllum til sögunnar stikarúm:

<u>Almennt</u> má skrifa skalaðan Hamiltonvirkja sem

$$\tilde{H} = \sum_i \bar{\mu}\cdot\bar{f}$$

$\bar{f}$: er margfeldi virkja með gefna samhverfu. Í Ising-L. er t.d.

$\bar{f}$: "$\bar{S}$", "$\bar{S}_i\cdot\bar{S}_{i+1}$", "$\bar{S}_i\bar{S}_j\bar{S}\cdots$"

og $\bar{\mu}$ eru þar við tengdu sviðin

$\bar{\mu}$: "$\bar{B}$" . . . . - - - - -

* * *

Einfaldur $\tilde{H}$ getur orðinn flókinn eftir nokkrar endurstuðlanir

* * *

$\bar{\mu}$ er vigur sem táknar stöðu kerfisins í óendanlega víðu stikarúmi

Endurstuðlun flytur kerfið til í þessu rúmi

$$\bar{\mu}' = R\bar{\mu} \qquad (*)$$

Í stöðugum punkti gildir

$$\bar{\mu}' = \bar{\mu} = \bar{\mu}^*$$

Athugum smábreytingu um $\bar{\mu}^*$

$$\bar{\mu} = \bar{\mu}^* + \delta\bar{\mu}$$

$$\rightarrow \bar{\mu}' = \bar{\mu}^* + \delta\bar{\mu}'$$

Taylorliðun á $(*)$ tengir $\delta\bar{\mu}$ og $\delta\bar{\mu}'$

$$\delta\bar{\mu}' = \underset{\substack{\uparrow \\ \text{fylki fastra stuðla}}}{A}(\bar{\mu}^*)\,\delta\bar{\mu}$$

Eigingildi A, λ_i og eiginvigrar v_i segja til um eiginleika $\tilde{H}$ við markpunkta

(9)

λ_i eru föll af stökunarstikanum b.

Tvær endurstæðanir í röð :→

$$\lambda_i(b_1)\,\lambda_i(b_2) = \lambda_i(b_1 b_2)$$

$$\longrightarrow \quad \lambda_i(b) = b^{y_i}$$

með y_i óháð b

<u>y_i eru markveldisvísar og tengjast</u>

<u>$\alpha, \beta, \gamma \ldots$</u> (skýrist síðar)

Athugum fyrst flæði í stikarúminu

<u>Nærri</u> stöðugum punkti $\bar{\mu}^*$ má rita

$$\bar{\mu} = \bar{\mu}^* + \sum_i g_i \bar{v}_i$$

g_i: <u>línuleg stökunarsvið</u>

(10)

Við endurstæðum gildir

$$\bar{\mu}' = \bar{\mu}^* + \sum_i b^{y_i} g_i \bar{v}_i$$

eða einfaldlega

$$g_i' = b^{y_i} g_i$$

Hegðun $\tilde{H}$ undir endurstæðum nærri $\bar{\mu}^*$ ræðst af upphaflegu g_i og y_i

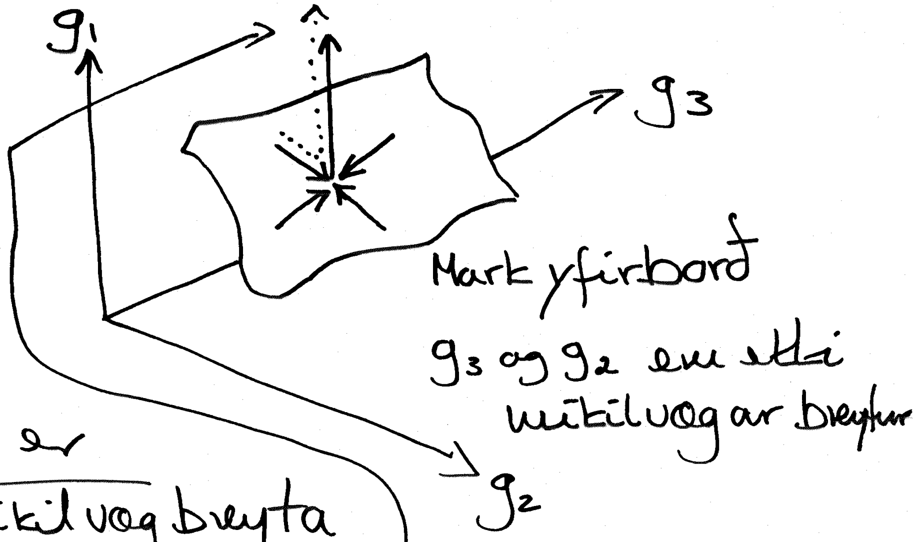
Fyrir $y_i > 0$ <u>vex</u> g_i og kerfið <u>fjarlægist</u> stöðugapunktinum $\bar{\mu}^*$

<u>mikilvæg breyta</u> (relevant)

Ef $Y_i < 0$ minnkar g_i og kerfið nálgast $\bar{\mu}^*$ við endurst. óháð upphafsgildi g_i

ekki mikilvæg breyta (irrelevant)

Stöðugleiki $\bar{\mu}^*$ byggist á fjölda breyta í þessum tveimur flokkum



hvað gerist rétt utan markyfirborðs

Á markyfirborðinu er mikilvæga breytan núll

Fyrir seglumarkerfi eru T og B venjulega mikilvægar breytur

↳ markyfirborðið hefur tveimur víddum færri en allir tengi (víxlverkunar) stuðlar sem taka verður með

Skölun og markveldisvísar

Höfðum áður fyrir frjálsu orkuna á spana

$$\tilde{f}_s(\bar{\mu}) = b^{-d}\tilde{f}_s(\bar{\mu}')$$

$\tilde{H}$: upprunalegur Hamiltonvirki

$\tilde{H}'$: endurstuðlaður —||—

Nærri föstum punkti eru $\bar{\mu}'$ og $\bar{\mu}$ táknuð við línulegu skölunarsviðin g_i' og g_i

$$\{ g_i' = b^{y_i} g_i \}$$

því verður (hér er föstum liðum f sleppt)

$$\tilde{f}_s(g_1, g_2, g_3 \cdots) \sim b^{-d}\tilde{f}_s(b^{y_1}g_1, b^{y_2}g_2, \dots)$$

þetta rétt fyrir hvaða b sem er

Dæmi um útvíkkað einsleitt fall (generalized homogeneous function).

t.d. $f(x,y) = x^3 + y^2$

$f(x,y) = x^3y^2 + x^2y^3$

um þau gildir $f(\lambda^a x, \lambda^b y) = \lambda f(x,y)$

þ.s. a og b þarf að ákveða

Við búumst við að í segulkerfi þurfi að stilla tvær breytur t.þ.a. ná markpunkti

$$\underset{\substack{\uparrow \\ \text{Hitastig}}}{T} \quad \text{og} \quad \underset{\substack{\uparrow \\ \text{ytra segulsvið (B)}}}{H}$$

Skölðu stærðirnar eru

$$h = H/kT \quad \text{og} \quad t = \frac{T-T_c}{T_c}$$

→ $g_1 = t$, $g_2 = h$

og allar aðrar breytur eru ekki mikilvægar

(*,*)

→ $$\tilde{f}_s(t, h, g_3 \cdots) \sim b^{-d} \tilde{f}_s(b^{y_1} t, b^{y_2} h, b^{y_3} g_3 \cdots)$$

þegar t, h og $g_3 \to 0$

Markvísirinn α — — — ↓

$$C \sim \left(\frac{\partial^2 \tilde{f}_s}{\partial t^2}\right) \sim |t|^{-\alpha}$$

$$L \equiv \tilde{f}_{tt}(h=0)$$

notum þetta á (**) og setjum $h, g_3 = 0$, þá fæst

$$\tilde{f}_{tt} \sim b^{-d+2y_1} \tilde{f}_{tt}(b^{y_1} t, 0)$$

b má velja frjálst → veljum $b^{y_1} |t| = 1$, þá verður

$$\tilde{f}_{tt}(t, 0) \sim |t|^{(d-2y_1)/y_1} \tilde{f}_{tt}(\pm 1, 0)$$

og því $\alpha = 2 - \frac{d}{y_1}$ (***)

Frekari athuganir gefur

$$\beta = (d - y_2)/y_1$$

$$\gamma = (2y_2 - d)/y_1$$

$$\delta = y_2/(d - y_2)$$

því fæst nákvæmt

$$\alpha + 2\beta + \gamma = 2$$

$$\gamma = \beta(\delta - 1)$$

í stað ójafna með varmafræðinni. Eins eru vísarnir eins ofan og neðan markpunktsins.

Fyrir fylgnifallið fæst

$$\Gamma(\bar{r}, t, h, g_3 \cdots) \sim c^2(b)\,\Gamma(b^{-1}\bar{r}, b^{y_1} t, b^{y_2} h, \ldots \qquad (4)$$

Setjum $h, g_3 \cdots = 0$ og veljum $b^{y_1}|t| = 1$

$$\rightarrow \Gamma(\bar{r}, t) \sim c^2(|t|^{-1/y_1})\,\Gamma(|t|^{1/y_1}\bar{r}, \pm 1)$$

allar lengdir skalast með $b \sim |t|^{-1/y_1}$

fylgnilengd hafði markhegðun

$$\xi \sim |t|^{-\nu}$$

$$\rightarrow \quad \nu = 1/y_1$$

sem saman með (***) gefur

$$2 - \alpha = d\nu$$

<u>Þurfum að finna c^2</u>

fyrir langar lengdir við markpunkt gildir

$$\Gamma(\bar{r}) \sim r^{-(d-2+\eta)}$$

Skoðum aftur (4) með $t, h, g_3 \cdots = 0$

$$\Gamma(\bar{r}) \sim c^2\,\Gamma(b^{-1}\bar{r})$$

eða

$$r^{-(d-2+\eta)} \sim c^2\left(\frac{r}{b}\right)^{-(d-2+\eta)}$$

$$\rightarrow \quad c^2(b) = b^{-(d-2+\eta)}$$

Skalaðar mælistærðir

Við höfðum

$$\tilde{f}_s(t,h,g_3\cdots)\sim b^{-d}\tilde{f}_s(b^{y_1}t,b^{y_2}h,b^{y_3}g_3,\cdots)$$

notum skilgreiningu á seglun

$$M = -\left(\frac{\partial F}{\partial B}\right)_{T,}$$

til þess að finna

$$M(t,h,g_3\cdots)\sim b^{-d+y_2}M(b^{y_1}t,b^{y_2}h,b^{y_3}g_{3,})$$

veljum $b^{y_1}|t|=1$ og $g_3\cdots \to 0$

$\to$

$$M(t,h)\sim|t|^{(d-y_2)/y_1}M(\pm 1,h|t|^{-y_2/y_1})$$

þekkjum y_1 og y_2

$$M(t,h)\sim|t|^{\beta}M(\pm 1,h|t|^{-\beta\delta})$$

Skilgreinum

$$\tilde{m}=\frac{M(t,h)}{|t|^{\beta}} \quad \text{og} \quad \tilde{h}=h|t|^{-\beta\delta}$$

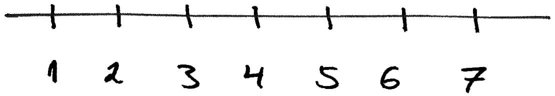
$\to$ $\tilde{m}\sim M(\pm 1,\tilde{h})$

$\to$ graf af $\tilde{m}$ vs. $\tilde{h}$

gefur eina kúrfu

óháð T!

Athugum eina staðarrúms endurstöðlun fyrir 1D Ising



byrjum með

$$\tilde{H} = -K\sum_{\{i,j\}} s_i s_j - h\sum_i s_i - \sum_i C$$

Víxlverkun við næstugranna

þannig liðir bætast alltaf seinna við í endurstöðlun

Í 1D-Ising er hægt að gera nákvæma endurstöðlun......

Ekki einfalt í fleiri víddum

Uppskrift

setjum $b=2$ með því að ljúka spor-aðgerðinni fyrir jöfn sæti

Fyrst er $\tilde{H}$ umritaður sem

$$Z = \sum_{\{s\}} \prod_{i=2,4,8,\ldots} \exp\Big\{K s_i (S_{i-1} + S_{i+1}) + h s_i + h(S_{i-1} + S_{i+1})/2 + 2C\Big\}$$

→ Hlutspor

~~$Z' = \sum_{\ldots S_1, S_3, S_5 \ldots} \prod_{i=2,4,8,} \Big\{ \exp\big[K(S_{i-1} + S_{i+1})$~~

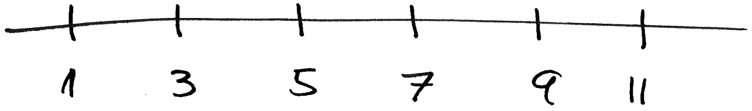
~~$+ \exp\big[-K(S_{i-1} + S_{i+1})$~~

~~$+h-h+h(S_{i-1}+S_{i+1})/2 + h(S_{i-1}+S_{i+1})/2$~~

~~$+ 2C\big]\Big\}$~~

$$Z' = \sum_{\ldots s_1 s_3 s_5 \ldots} \prod_{i=2,4,6\ldots} \Big\{ \exp\big[K(s_{i-1}+s_{i+1}) + h + h(s_{i-1}+s_{i+1})/2 + 2C\big]$$

$$+ \exp\big[-K(s_{i-1}+s_{i+1}) - h + h(s_{i-1}+s_{i+1})/2 + 2C\big]\Big\}$$



endurnefnum sætin t.þ.a. fá venjulega talnaröð $\rightarrow$

$$Z' = \sum_{\{s\}} \prod_i \Big\{ \exp\big[(K+\tfrac{h}{2})(s_i+s_{i+1}) + h + 2C\big]$$

$$+ \exp\big[-(+K-\tfrac{h}{2})(s_i+s_{i+1}) - h + 2C\big]\Big\}$$

Krefjumst þess að Z' hafi sama form og Z, en með nýjum tengistuðlum

$$Z' = \sum_{\{s\}} \prod_i \exp\{K' s_i s_{i+1} + h' s_i + C'\}$$

Því verður að gilda

$$\boxed{\begin{aligned} &\exp\{K' s_i s_{i+1} + h'(s_i+s_{i+1})/2 + C'\} \\ &= \exp\{(K+\tfrac{h}{2})(s_i+s_{i+1}) + h + 2C\} \\ &+ \exp\{-(K-\tfrac{h}{2})(s_i+s_{i+1}) - h + 2C\} \end{aligned}}$$

fyrir $S_i, S_{i+1} = \pm 1$ fáum
við 3 jöfnur

$$e^{K'+h'+C'} = e^{2K+2h+2C} + e^{-2K+2C} \quad \Bigg| \begin{matrix} S_i = 1 \\ S_{i+1} = 1 \end{matrix}$$

$$e^{K'-h'+C'} = e^{2K-2h+2C} + e^{-2K+2C} \quad \Bigg| \begin{matrix} -1 \\ -1 \end{matrix}$$

$$e^{-K'+C'} = e^{h+2C} + e^{-h+2C} \quad \Bigg| \begin{matrix} +1,-1 \\ -1,+1 \end{matrix}$$

því fást jöfnur fyrir endurstuðluðu tengistuðlana

$$e^{2h'} = \frac{e^{2h}\,\text{Cosh}(2K+h)}{\text{Cosh}(2K-h)}$$

$$e^{4K'} = \frac{\text{Cosh}(2K+h)\,\text{Cos}(2K-h)}{\text{Cosh}^2 h}$$

$$e^{4C'} = e^{8C}\,\text{Cosh}(2K+h)\,\text{Cosh}(2K-h)\,\text{Cosh}^2 h$$

Einstakt við 1D-Ising er að ekki verða til „hærri spunaliðir"

Fastir punktar

Skiptum um breytur í jöfnunum

$$\omega \equiv e^{-4C}, \quad x \equiv e^{-4K}, \quad y = e^{-2h}$$

Þar verða þá

$$\omega' = \frac{\omega^2 x y^2 (1+y)^2}{(x+y)(1+xy)}$$

$$x' = \frac{x(1+y)^2}{(x+y)(1+xy)} \leftarrow$$

$$y' = \frac{y(x+y)}{(1+xy)} \leftarrow$$

óháðar ω

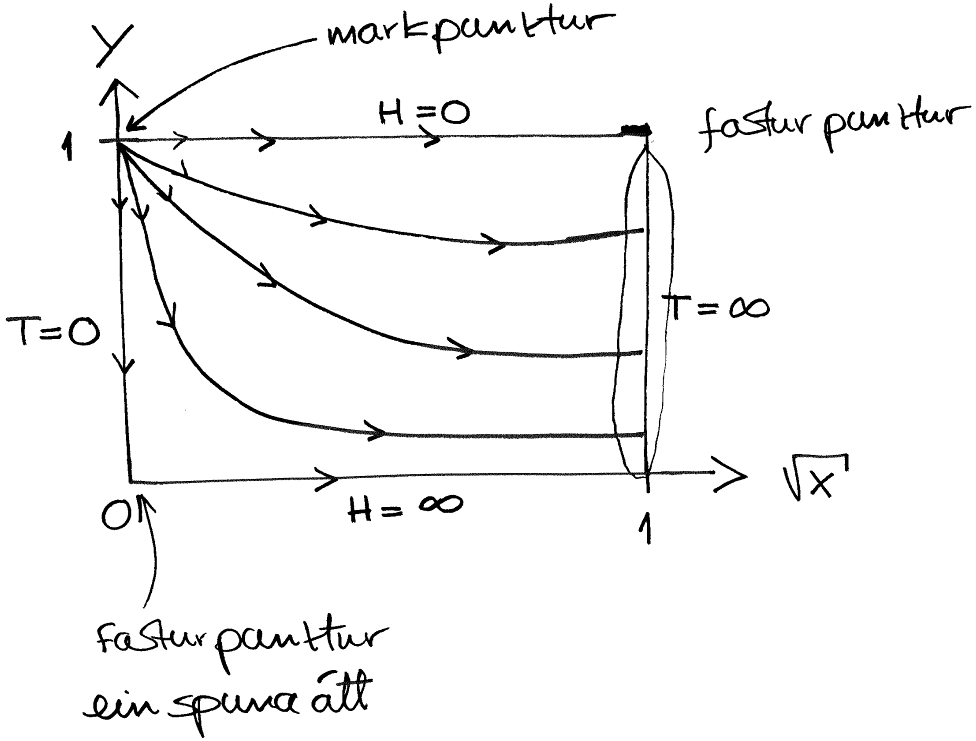
$\updownarrow$

tengist spuna

Athugum (x,y)-sléttuna

járnseglum $\rightarrow$ $K > 0$

$B \geq 0$



tvær mikilvægarbreytur, T, H

óstöðugur markpunktur

Athugum endurstöðlunar jöfnurnar

í kringum $(x^*, y^*) = (0,1)$

{fastur punktur fyrir járnseglum}

<u>línuleg nálgun</u>

$$x' \sim 4x$$

$$\epsilon' \sim 2\epsilon$$

með $\epsilon = y - y^* \equiv y - 1$

Eigingildi línulegu ummyndunarinnar

$$\lambda_1 = 4 \text{ og } \lambda_2 = 2$$

$b = 2$ og því verður

$$y_1 = 2 \text{ og } y_2 = 1$$

eða

$$\boxed{\tilde{f}_s(x,\epsilon) = b^{-1}\tilde{f}_s(b^2x, b\epsilon)}$$

b er hér aðeins 2 í heiltölu veldi, en fáguð framlenging er í lagi

veljum $b^2x = 1$

$$\tilde{f}_s(x,\epsilon) = \sqrt{x}\,\tilde{f}_s\left(1, \frac{\epsilon}{\sqrt{x}}\right) = \sqrt{x}\,\tilde{f}_s\left(\frac{\epsilon}{\sqrt{x}}\right) \qquad (*)$$

Áður höfðum við

$$f = -kT\ln\left\{e^{\beta J}\cosh\beta H + \sqrt{e^{2\beta J}\sinh^2\beta H + e^{-2\beta J}}\right\}$$

Sem þýtt í breyturnar hér og liðað fyrir smá x og ϵ verður

$$\tilde{f}(x,\epsilon) = -K - \sqrt{x}\sqrt{1+\frac{\epsilon^2}{x}}$$

Sem fellur saman við (*)

{sérstöðuhlutinn}

ef $\boxed{\tilde{f}(z) = \sqrt{1-z^2}}$

Endurstöðlunin gaf skölunarhegðun í markpunktinum, <u>en ekki fallið sjálft</u>