Statistical Physics

Lecture Notes

Abstract

These notes represent the material covered in the Part II lecture *Statistical Physics*. They are largely based on the more extended lecture notes by David Tong [2]. The main purpose of these notes to provide as close as possible a one-to-one representation of the course as it appears on the black board in the lecture room. This comes, at times, at the expanse of uniformly using complete sentences and instead using short phrases and the like.

Readers interested in more details as well as a wider range of subjects, will find David Tong's lecture notes an excellent source and may also find the following books of interest.

- E. Mandl, "Statistical Physics" .
- L. D. Landau & E. M. Lifshitz, "Statistical Physics" .
- F. Reif, "Fundamentals of Statistical and Thermal Physics" .
- M. Kardar, "Statistical Physics of Particles", "Statistical Physics of Fields"; see also Kardar's webpage [3].
- A. B. Pippard, "The Elements of Classical Thermodynamics" .

Example sheets for this course will be available on the web page

`http://www.damtp.cam.ac.uk/user/examples`

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Contents

A The fundamentals of statistical physics

A.1 Introduction

Science works in layers, e.g.:

History
Economy
Psychology
Biology
Chemistry
Atomic Physics
Nuclear Physics
Particle Physics

Choose one area, consider the neighbours, ignore the rest.

Fundamental laws, large numbers
→ emergent phenomena, e.g. traffic jams, temperature

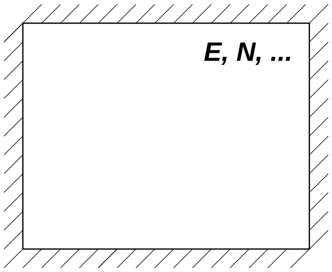
Statistical Physics: translate microphyics (fundamental laws)
→ macrophysics (temperature, color, . . .)

We will see that this can be done quite rigorously for many laws: *ideal gas law*, *Wien's displacement*, . . .

Not all macrosystems are understood at micro level: *black holes*, *high T super conductors*

Note: We have large numbers $\boxed{N \sim 10^{23} \neq 1}$

A.2 The microcanonical ensemble



Isolated system: no exchange of energy, particles with outside world

We do this QM, but applies to classical systems as well ($\sum \to \int$)

time independent Schrödinger eq.: $\hat{H}|\psi\rangle = E|\psi\rangle$

ψ Eigenstate

E Eigenvalue

For $N \sim 10^{23}$ degrees of freedom:
- impossible to solve
- unnecessary to solve: system jumps from state to state …

our view: **mixed state** with probability $p(n)$ for state $|n\rangle$

expectation value $\langle\hat{\mathcal{O}}\rangle = \sum_n p(n)\langle n|\hat{\mathcal{O}}|n\rangle$

equilibrium: probability distribution is time independent!

e.g. leave system for a while

> **Fundamental assumption**: For an isolated system in equilibrium, all accessible microstates are equally likely

"accessible" = same energy E (for now)

$$\boxed{\begin{aligned} &\Omega(E) = \#\text{ of states with energy } E \\ \Rightarrow\quad &p(n) = \begin{cases} \frac{1}{\Omega(E)} & \text{if } |n\rangle \text{ has energy } E \\ 0 & \textit{otherwise} \end{cases}\end{aligned}}$$

Comments:
- $\Omega(E)$ is absurdly large! E.g. 10^{23} 2-state particles $\Rightarrow$ $\Omega(E) = 2^{(10^{23})}$
- In QM, energy levels are discrete. For $N \sim 10^{23}$ they are finely spaced → almost like continuum.

  We implicitly define $\Omega(E)$ as the # of states with energy $\in [E,\ E + \Delta E)$; $\Delta E \ll$ measurement accuracy, $\gg$ level spacing

A.2.1 Entropy and the 2nd law of thermodynamics

<u>Def.:</u> Entropy of system $\boxed{S(E) = k_B \ln \Omega(E)}$

$k_B = 1.381 \cdot 10^{-23}\ \frac{\mathrm{J}}{\mathrm{K}}$ "Boltzmann's constant"

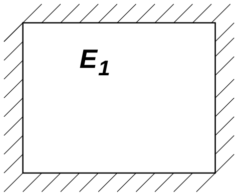
Recall: N 2-state particles $\Rightarrow$ $\Omega = 2^N$

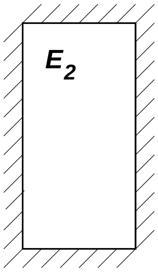
$\Rightarrow$ $S \sim N$

additive: consider 2 separate systems

$$\Rightarrow \quad \Omega(E_1, E_2) = \Omega_1(E_1)\,\Omega_2(E_2)$$

$$\Rightarrow \quad S(E_1, E_2) = S_1(E_1) + S_2(E_2)$$



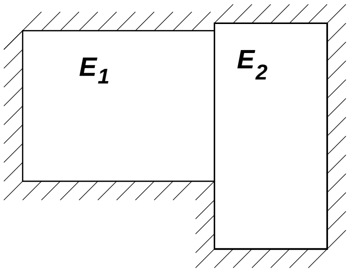


<u>**The second law**</u>

bring the two systems together

They exchange energy: $E_1 \to \tilde{E}_1, \quad E_2 \to \tilde{E}_2$

$E_{\text{tot}} = E_1 + E_2 = \tilde{E}_1 + \tilde{E}_2$



$$\begin{aligned} \Rightarrow \Omega(E_{\text{tot}}) &= \sum_{\{\tilde{E}_i\}} \Omega_1(\tilde{E}_1^i)\,\Omega_2(E_{\text{tot}} - \tilde{E}_1^i) \\ &= \sum_{\{\tilde{E}_i\}} \exp\left[\frac{S_1(\tilde{E}_1^i)}{k_B} + \frac{S_2(E_{\text{tot}} - \tilde{E}_1^i)}{k_B}\right] \end{aligned}$$

discreteness of QM energy levels: see comment above!

when the systems were separate, we had $\Omega(E_1, E_2)$ states.
each such state is also one of the $\Omega(E_{\text{tot}})$ states when the system is combined!

$\Rightarrow \Omega(E_{\text{tot}}) \geq \Omega(E_1, E_2)$

$\Rightarrow S(E_{\text{tot}}) \geq S(E_1, E_2) = S_1(E_1) + S_2(E_2)$

$\Rightarrow \boxed{\Delta S \geq 0}$

For large N: recall that $S \sim N$

$\Rightarrow$ the above sum $\displaystyle \Omega(E_{\text{tot}}) = \sum_{\{\tilde{E}_1^i\}} \exp\left[\frac{S_1(\tilde{E}_1^i)}{k_B} + \frac{S_2(E_{\text{tot}} - \tilde{E}_1^i)}{k_B}\right]$

is a sum of exponentials of $N \sim 10^{23}$.
Such sums are dominated by their maximum value!
Say, for some energy $\tilde{E}_1^i = E_*$, the exponent $\dfrac{S_1 + S_2}{k_B}$ is twice as large as for any other E.
Then this term is $\sim e^N$ times larger than all other terms.

$\Rightarrow$ All terms but the one with $\tilde{E}_1^i = E_*$ are negligible

Setting $\tilde{E}_1 = \tilde{E}_1^i$, $\tilde{E}_2 = E_{\text{tot}} - \tilde{E}_1^i$, the exponent is

$$\frac{1}{k_B}\left[S_1(\tilde{E}_1) + S_2(\tilde{E}_2)\right],$$

and it is maximal for $\tilde{E}_1^i = E_*$ if

$$\frac{\partial}{\partial \tilde{E}_1^i}\left[S_1(\tilde{E}_1) + S_2(\tilde{E}_2)\right] = \frac{\partial S_1}{\partial \tilde{E}_1} - \frac{\partial S_2}{\partial \tilde{E}_2} = 0$$

$$\Rightarrow \boxed{\left.\frac{\partial S_1}{\partial E}\right|_{E_*} - \left.\frac{\partial S_2}{\partial E}\right|_{E_{\text{tot}}-E_*} = 0} \qquad (*)$$

Then the total entropy is

$$S(E_{\text{tot}}) \approx S_1(E_*) + S_2(E_{\text{tot}} - E_*) \geq S_1(E_1) + S_2(E_2)$$

$\Rightarrow$ Subsystems 1 and 2 have nearly determined energies E_*, $E_{\text{tot}} - E_*$ after contact.

Note: If $E_1 \neq E_*$, subsystem 1 will hardly ever return from energy E_* to E_1

"contact vastly enhances the number of accessible states"

Second Law: energy is rearranged such that $S_1(\tilde{E}_1) + S_2(\tilde{E}_2)$ is maximal

A.2.2 Temperature

Note: We are slightly departing here from the microcanonic assumption $E = \text{const.}$ This is to be viewed as an ensemble of systems with different E.

<u>Def.:</u> Temperature T: $\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}}$

Why is this a good definition?

Does it describe coffee?

1) Units ok thanks to Boltzmann's constant
2) Consider Eq. $(*)$: Energy rearranged such that $S_1(\tilde{E}_1) + S_2(\tilde{E}_2)$ max.
   Now assume $E_1 = \tilde{E}_1$, $E_2 = \tilde{E}_2$, i.e. no energy transfer at all

$$\Rightarrow \quad \left.\frac{\partial S_1}{\partial E}\right|_{E_1} - \left.\frac{\partial S_2}{\partial E}\right|_{E_2} = 0 \Rightarrow \quad T_1 = T_2$$

$\Rightarrow$ No energy transfer corresponds to equal $T_1 = T_2$ (before contact) as expected.

3) Let us assume small energy transfer: $\delta E_1 = -\delta E_2$

$$\Rightarrow \delta S \approx \left.\frac{\partial S_1}{\partial E}\right|_{E_1} \delta E_1 + \left.\frac{\partial S_2}{\partial E}\right|_{E_2} \delta E_2 = \left(\left.\frac{\partial S_1}{\partial E}\right|_{E_1} - \left.\frac{\partial S_2}{\partial E}\right|_{E_2} \right) \delta E_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1$$

$\delta S > 0$ because S maximized

if $T_1 > T_2 \quad \Rightarrow \quad \delta E_1 < 0$

$\Rightarrow$ energy goes from hot to cold

Summary: T looks a good definition

equal $T \quad \Rightarrow$ equilibrium

we will evaluate T for ideal gas later; our def. is correct

Heat capacity

Def.: $C \equiv \dfrac{\partial E}{\partial T}$

Comments:

- we should call this “energy capacity”
- C is nice: can be measured!
- consider E a function of T

$$\Rightarrow \quad \frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{C}{T}$$

$$\Rightarrow \quad C = T\frac{\partial S}{\partial T}$$

we will see this as $C = \dfrac{\delta Q}{\delta T}$ in thermodynamics

where we also specify what’s kept constant: C_V, C_P, ...

we can measure entropy differences: $\Delta S = \displaystyle\int_{T_1}^{T_2} \frac{C(T)}{T} dT$

...beats counting $\sim \exp(10^{23})$ states

Def.: specific heat capacity $c = \dfrac{C}{N}$

Note: $$\frac{\partial S}{\partial E} = \frac{1}{T} \quad \Rightarrow \quad \frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\frac{1}{T} = \frac{\partial T}{\partial E}\frac{\partial}{\partial T}\frac{1}{T} = -\frac{1}{T^2 C}$$

Almost all substances have $C > 0 \quad \Rightarrow \quad \dfrac{\partial^2 S}{\partial E^2} < 0$

⇒ The extremum in Eq. $(*)$ is really a max.

⇒ "thermodynamically stable systems"

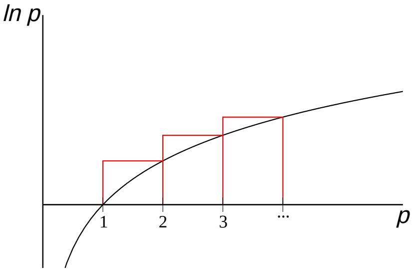
Exception: black holes; Hawking radiation

A.2.3 The Two-State system

Stirling's formula

We often have $\ln N!$

Stirling: $\ln N! = N \ln N - N + \dfrac{1}{2}\ln(2\pi N) + \mathcal{O}\left(\dfrac{1}{N}\right)$ (Examples)



For now: $$\ln N! = \sum_{p=1}^{N} \ln p \approx \int_1^N \ln p \, dp = \int_1^N 1 \, \ln p \, dp = [p \, \ln p]_1^N - \int_1^N \frac{p}{p} dp = N \, \ln N - (N-1)$$

$$\Rightarrow \quad \boxed{\ln N! \approx N \, \ln N - N} \qquad \text{(lower limit!)}$$

Two-spin-state system

N particles: non-interacting, 2 states: $\uparrow, \downarrow$

Let $E_\downarrow = 0$, $E_\uparrow = \epsilon$

$N_\uparrow$ particles with spin up $\Rightarrow$ $N_\downarrow = N - N_\uparrow$

$\Rightarrow$ $E = N_\uparrow \epsilon$

what is $\Omega(E)$?

pick $N_\uparrow$ particles from N

$$\Rightarrow \quad \Omega(E) = \tbinom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\,(N - N_\uparrow!)}$$

$$\Rightarrow \quad S(E) = k_B \ln \frac{N!}{N_\uparrow!\,(N - N_\uparrow)!} = k_B \left[\ln N! - \ln N_\uparrow! - \ln(N - N_\uparrow)!\right]$$

$$\approx k_B \left[N \ln N - N - N_\uparrow \ln N_\uparrow + N_\uparrow - (N - N_\uparrow)\ln(N - N_\uparrow) + N - N_\uparrow\right]$$

$$= k_B \left[(N - N_\uparrow)\ln N + N_\uparrow \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow)\ln(N - N_\uparrow)\right]$$

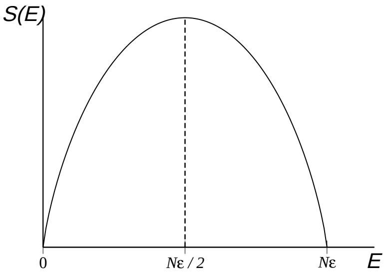
$$= -k_B \left[(N - N_\uparrow)\ln \frac{N - N_\uparrow}{N} + N_\uparrow \ln \frac{N_\uparrow}{N}\right] \qquad \Big| N_\uparrow = \frac{E}{\epsilon}$$

$$= -k_B N \left[\left(1 - \frac{E}{N\epsilon}\right)\ln\left(1 - \frac{E}{N\epsilon}\right) + \frac{E}{N\epsilon}\ln \frac{E}{N\epsilon}\right]$$

special cases: $S(0) = 0$

$S\left(\dfrac{N\epsilon}{2}\right) = k_B N \ln 2$ maximum

$S(N\epsilon) = 0$



Temperature: $\dfrac{1}{T} = \dfrac{\partial S}{\partial E} = \ldots = \dfrac{k_B}{\epsilon} \ln\left(\dfrac{N\epsilon}{E} - 1\right)$

$$\Rightarrow \quad \frac{N_\uparrow}{N} = \frac{E}{N\epsilon} = \frac{1}{e^{\epsilon/(k_B T)} + 1}$$

For $T \to \infty$: $\dfrac{N_\uparrow}{N} = \dfrac{1}{2}$

What happens for $E > \dfrac{N\epsilon}{2}$?

$T < 0 \;\Rightarrow$ as we increase E, $\Omega(E)$ decreases

view as $\dfrac{1}{T}$ going through 0 to negative values

Heat capacity: $C = \dfrac{\partial E}{\partial T} = \dfrac{\partial}{\partial T}\left(\dfrac{N\epsilon}{e^{\epsilon/(k_B T)} + 1}\right) = \dfrac{N\epsilon^2}{k_B T^2} \dfrac{e^{\epsilon/(k_B T)}}{\left(e^{\epsilon/(k_B T)} + 1\right)^2}$

- C max near $T \sim \dfrac{\epsilon}{k_B}$
- $T \to 0 \;\Rightarrow\; C \sim e^{-\epsilon/(k_B T)} \to 0$

  "gap to first excited state"

  $\Rightarrow$ heating "a bit" does nothing
- $T \to \infty \;\Rightarrow\; C \sim \dfrac{1}{T^2} \to 0$ "half the states are already ↑"

Schottky anomaly

for normal substances: C dominated by phonons or free electrons; spin negligible

$\Rightarrow$ C increases with T.

for special cases at low T: e.g. paramagnetic salts

spin contribution significant $\Rightarrow$ C like Fig.

A.2.4 Pressure, Volume, 1^{st} law of thermodynamics

Consider volume V of system

$\Rightarrow \quad S(E,V) = k_B \ln \Omega(E,V)$

$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$; "keep V constant"

Recall: we defined $\frac{1}{T} = \frac{\partial S}{\partial E}$ and concluded that
2 systems keep their energies E_1, E_2 if they have same T

__**Def:**__ "Pressure": $\boxed{p \equiv T\left(\frac{\partial S}{\partial V}\right)_E}$

Repeat the argument for T equilibrium

$\Rightarrow$ 2 systems keep their volume if they have the same p

First Law: from our definitions: $dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV = \frac{1}{T}dE + \frac{p}{T}dV$

$$\Rightarrow \boxed{dE = TdS - pdV}$$

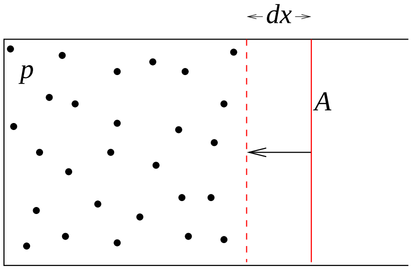
Note: $pdV = p\,A\,dx = F\,dx$

= work done by system

sign: $dV < 0$

$\Rightarrow$ we work on the system

$\Rightarrow$ $dE > 0$



energy conservation: $TdS =$ heat δQ added to the system; cf. Sec. **D**

$pdV =$ work done by the system

$\Rightarrow$ The system's change in energy is equal to the heat added plus the work done on the system heat capacity: we now write $C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

$\uparrow$

Strictly $\left(\frac{\delta Q}{\delta T}\right)_V$ but it's the same since $dV = 0$

analagously: $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ (don't use $\frac{\partial E}{\partial T}$ here!)

Ludwig Boltzmann: did a lot of this in the absence of proof for atoms!

$S = k_B \ln \Omega$ on his tomb stone

his work received a lot of criticism;

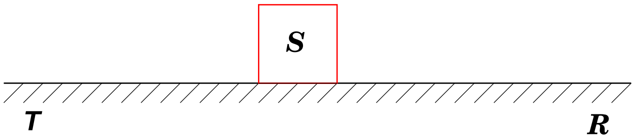
truely appreciated after his suicide in Trieste in 1906

A.3 The canonical ensemble

Closed system: can exchange energy, but no matter, with outside world

- closed system $\mathcal{S}$
- at equilibrium temperature T
- coupled to *large* reservoir $\mathcal{R}$

↳ changes in T of reservoir negligible



What is the number of states of the total system $\mathcal{S} + \mathcal{R}$?

$$\Omega(E_{\text{tot}}) = \sum_n \Omega_{\mathcal{R}}(E_{\text{tot}} - E_n) = \sum_n \exp\left[\frac{S_{\mathcal{R}}(E_{\text{tot}} - E_n)}{k_B}\right]$$

where $n =$ state of system $\mathcal{S}$ with energy E_n

$\Omega_{\mathcal{R}} =$ # of states of reservoir; $S_{\mathcal{R}} = k_B \ln \Omega_{\mathcal{R}}$

Note: We sum over all states n, not over the energies E_n of $\mathcal{S}$!

Otherwise: degeneracy factor $g(E_n)$

$\mathcal{R}$ large $\Rightarrow$ $E_n \ll E_\text{tot}$

$$\Rightarrow \quad \Omega(E_\text{tot}) = \sum_n \exp\left[\frac{S_\mathcal{R}(E_\text{tot} - E_n)}{k_B}\right] \approx \sum_n \exp\left[\frac{S_\mathcal{R}(E_\text{tot})}{k_B} - \underbrace{\frac{\partial S_\mathcal{R}}{\partial E_\text{tot}}}_{=\frac{1}{T}} \frac{E_n}{k_B}\right]$$

$$\Rightarrow \quad \Omega(E_\text{tot}) \approx e^{S_\mathcal{R}(E_\text{tot})/k_B} \sum_n e^{-E_n/(k_B T)}$$

$\Rightarrow$ # of states where $\mathcal{S}$ sits in state $|n\rangle$: $e^{S_\mathcal{R}/k_B}\ e^{-E_n/(k_B T)}$

Each of the $\Omega(E_\text{tot})$ states equally likely

$\Rightarrow$ probability that $\mathcal{S}$ is in state $|n\rangle$: $\boxed{p(n) = \dfrac{e^{-E_n/(k_B T)}}{\sum_m e^{-E_m/(k_B T)}}}$

"Boltzmann distribution", "canonical ensemble"

Comments:

- Reservoir only plays a role through T
- $p \sim e^{-E/(k_B T)}$ $\Rightarrow$ high-energy states unlikely
- E of system large $\Rightarrow$ fewer states of reservoir to distribute its energy
- $T \to 0$ forces system into ground state (lowest E)

A.3.1 The partition function

Def.: $\boxed{\beta \equiv \dfrac{1}{k_B T}}$

Def.: "partition function" $\boxed{Z \equiv \sum_n e^{-\beta E_n}}$

= sum of probabilities of $|n\rangle$ up to normalization

$\Rightarrow$ Boltzmann distribution: $\boxed{p(n) = \dfrac{e^{-\beta E_n}}{Z}}$

Z is the most important quantity in statistical physics!

Z is multiplicative: Consider two systems 1, 2

$$\Rightarrow \quad Z = \sum_{n,m} e^{-\beta[E_m^{(1)}+E_n^{(2)}]} = \sum_{n,m} \left[e^{-\beta E_m^{(1)}} \; e^{-\beta E_n^{(2)}} \right]$$

$$= \sum_m \left[e^{-\beta E_m^{(1)}} \right] \; \sum_n \left[e^{-\beta E_n^{(2)}} \right] = Z_1 \; Z_2$$

In QM we have 2 probabilities:
- QM
- our ignorance of the system

$\Rightarrow$ density matrix: $\hat{\rho} = \dfrac{e^{-\beta \hat{H}}}{Z}$

$\Rightarrow \quad p(\phi) = \langle \phi | \hat{\rho} | \phi \rangle =$ probability of state $|\phi\rangle$

We won't use that

Derivations from Z

average energy: $\langle E \rangle = \sum_n (p_n E_n) = \sum_n \dfrac{E_n e^{-\beta E_n}}{Z}$

$$\Rightarrow \quad \boxed{\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z}$$

energy fluctuations: $\Delta E^2 = \left\langle (E - \langle E \rangle)^2 \right\rangle = \langle E^2 \rangle - \langle E \rangle^2$

$$\Rightarrow \ldots \Rightarrow \quad \boxed{\Delta E^2 = \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial}{\partial \beta} \langle E \rangle}$$

heat capacity: $C_V = \left. \dfrac{\partial \langle E \rangle}{\partial T} \right|_V = \dfrac{\partial \beta}{\partial T} \dfrac{\partial \langle E \rangle}{\partial \beta} = \dfrac{1}{k_B T^2} \Delta E^2$

$$\Rightarrow \quad \Delta E^2 = k_B T^2 \, C_V$$

Comments:

1) large fluctuations $\sim$ large heat capacity:
manifestation of "fluctuation-dissipation theorem"

2) Recall: $C_V \sim N$, $E \sim N \;\Rightarrow\; \dfrac{\Delta E}{E} \sim \dfrac{1}{\sqrt{N}}$

$\Rightarrow$ for large N: E peaked near $\langle E \rangle$, essentially constant

in thermodynamic limit: microcanonic $\approx$ canonic; $E = \langle E \rangle$

The two-spin-state system revisited

single particle: $$Z_1 = \sum_n e^{-\beta E_n} = 1 + e^{-\beta\epsilon} = 2e^{-\beta\epsilon/2}\,\cosh\frac{\beta\epsilon}{2}$$

$$\Rightarrow Z = \prod_{k=1}^{N} Z_k = 2^N e^{-N\beta\epsilon/2}\,\cosh^N\frac{\beta\epsilon}{2}$$

$$\Rightarrow \langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \ldots = \frac{N\epsilon}{2}\left(1-\tanh\frac{\beta\epsilon}{2}\right) = \frac{N\epsilon}{1+e^{\beta\epsilon}} \qquad \Bigg|\ \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

$$C_V = \ldots$$

Note: the partition function automatically handles the combinatorics

A.3.2 Entropy

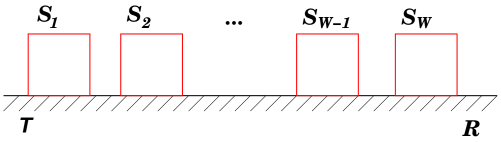
MiCE: $S = k_B \ln\Omega(E) = k_B$ ln of # states

Now: probability distribution over states with different E

Trick: take W identical systems, all coupled to $\mathcal{R}$

For each system: states $|n\rangle$, say $n = 1\ldots N$

$\Rightarrow$ # of systems in state $|n\rangle$: $p(n)\,W$, if W large



Consider reservoir + all systems as microcanical (E_{tot} fixed)

$\Rightarrow \quad \Omega_{\text{tot}} = \Omega_{\mathcal{R}}\,\Omega_{\mathcal{S}}$

what is $\Omega_{\mathcal{S}}$?

1) List all states $n = 1 \dots N$

2) create $p(n)\,W$ slots for state n

3) $\sum$ of all slots $= W$

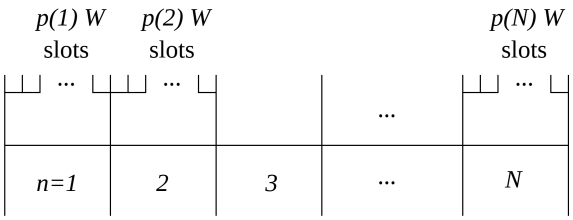
4) $W! =$ # of permutations of W systems

$=$ # of ways to put them into slots

5) $[p(n)\,W]! =$ # of permutations of $p(n)\,W$ systems

$=$ # of ways to reshuffle systems in state n

without changing the physical setup



$$\Rightarrow \quad \Omega_{\mathcal{S}} = \frac{W!}{\prod_n [p(n)W]!} = $$ # of different ways to get $p(1)\,W$ systems in state $|1\rangle$, $p(2)\,W$ systems into state $|2\rangle$, etc.

$\Rightarrow \quad S_{\text{tot}} = k_B(\ln\Omega_{\mathcal{R}} + \ln\Omega_{\mathcal{S}}) \qquad \Big|$ we ignore $S_{\mathcal{R}}$

$$\Rightarrow \quad S_{\mathcal{S}} = k_B \ln\Omega_{\mathcal{S}} = \overset{\text{(Stirling)}}{\dots} = -k_B W \sum_n p(n)\ln p(n) = \text{entropy of } W \text{ systems}$$

$\Rightarrow$ one system: $\boxed{S = -k_B \sum_n p(n)\ln p(n)}$ due to Gibbs

Comments:

- $S =$ function of probability distribution
- MiCE: prob. distr. $= f(\text{Energy}) \quad \Rightarrow \quad S = S(E)$
- CE: prob. distr. $= f(T)$
- $p(n) = \dfrac{1}{\Omega(E)} \quad \Rightarrow \quad \dots \quad \Rightarrow \quad S = k_B \ln\Omega(E)$
- $p(n) = \dfrac{e^{-\beta E_n}}{Z} \quad \Rightarrow \quad S = -\dfrac{k_B}{Z}\sum_n e^{-\beta E_n} \ln\dfrac{e^{-\beta E_n}}{Z} = \left[\dfrac{k_B\beta}{Z}\sum_n E_n e^{-\beta E_n}\right] + k_B \ln Z$

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

MiCE vs. CE

$S = k_B \, \ln \Omega(E) \qquad \text{vs.} \qquad S = -k_B \sum_n p(n) \, \ln p(n)$

different probability distributions!

But for $N \to \infty$ physical observables agree in both ensembles. How?

Consider $Z = \sum_n e^{-\beta E_n} = \sum_{\{E_i\}} \Omega(E_i) \, e^{-\beta E_i}$

$N \to \infty \;\Rightarrow\; \Omega(E_i) \, e^{-\beta E_i}$ is strongly peaked at $E_i = E_*$ "$e^{\pm N}$ effect"

$\Rightarrow$ sum in Z dominated by E_* term with max. condition

$$\left\{ \frac{\partial}{\partial E} \left[\Omega(E) e^{-\beta E} \right] \right\}_{E_*} = 0$$

$\Rightarrow \; Z \approx \Omega(E_*) e^{-\beta E_*}$

We'll need: $\dfrac{1}{T} = \dfrac{\partial S}{\partial E} = k_B \dfrac{\partial \ln \Omega}{\partial E} \quad \Rightarrow \quad \beta = \dfrac{\partial \ln \Omega}{\partial E}$

$$\begin{aligned} \Rightarrow \; \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z \\ &= -\frac{\partial}{\partial \beta} \left[\ln \Omega - \beta E_* \right] \\ &= -\frac{\partial E_*}{\partial \beta} \frac{\partial \ln \Omega}{\partial E_*} + E_* + \beta \frac{\partial E_*}{\partial \beta} \\ &= E_* \qquad (!) \end{aligned}$$

entropy: $S = k_B \dfrac{\partial}{\partial T} (T \, \ln Z) = k_B \dfrac{\partial}{\partial T} \left[T (\ln \Omega - \beta E_*) \right] \qquad \Big| \quad \dfrac{\partial}{\partial T} = -k_B \beta^2 \dfrac{\partial}{\partial \beta}$

$$\begin{aligned} &= k_B \ln \Omega - k_B \beta E_* - k_B T \, k_B \beta^2 \underbrace{\frac{\partial}{\partial \beta} (\ln \Omega - \beta E_*)}_{=-E_*} \\ &= k_B \ln \Omega(E_*) \end{aligned}$$

$\Rightarrow$ CE like MiCE at energy E_* !

Maximizing entropy

both MiCE and CE can be obtained from a variational principle

MiCE: Consider Gibbs entropy $S = -k_B \sum_n p(n) \ln p(n)$

with $p(n) \neq 0$ for states $|n\rangle$ with energy E

constraint: $\sum_n p(n) = 1$

vary $S + \alpha k_B \left[\sum_n p(n) - 1 \right]$; $\alpha =$ Lagrange multiplier

$$\Rightarrow \quad \frac{\partial}{\partial p(m)} \left[- \sum_n p(n) \ln p(n) + \alpha \sum_n p(n) - \alpha \right] = 0$$

$$\Rightarrow \quad - \ln p(m) - p(m) \frac{1}{p(m)} + \alpha = 0$$

$$\Rightarrow \quad \ln p(m) = \alpha - 1$$

$$\Rightarrow \quad p(m) = e^{\alpha - 1} = \text{const} \qquad \text{MiCE!}$$

CE: keep $\langle E \rangle$ fixed (example sheet)

A.3.3 Free energy

Def.: Free energy $\boxed{F := E - TS}$ "available energy"

Mathematically: *Legendre trafo*

$$\Rightarrow \quad dF = dE - d(TS) = TdS - pdV - TdS - SdT = -SdT - pdV$$

$$\Rightarrow \quad S = - \left. \frac{\partial F}{\partial T} \right|_V , \qquad p = - \left. \frac{\partial F}{\partial V} \right|_T$$

Recall $E = -\frac{\partial}{\partial \beta} \ln Z \,, \quad S = k_B \frac{\partial}{\partial T} (T \ln Z) \,, \quad \frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$

$$\Rightarrow \quad F = E - TS = k_B T^2 \frac{\partial}{\partial T} \ln Z - k_B T \ln Z - k_B T^2 \frac{\partial}{\partial T} \ln Z$$

$$\Rightarrow \quad \boxed{F = -k_B T \ln Z}$$

A.4 The grand canonical ensemble

A.4.1 The chemical potential

Consider additional quantities of the system: particle number N, electric charge q

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

recall: $\dfrac{1}{T} = \left.\dfrac{\partial S}{\partial E}\right|_{V,N}, \qquad p = T \left.\dfrac{\partial S}{\partial V}\right|_{E,N}$

Def.: chemical potential $\boxed{\mu = -T \left.\dfrac{\partial S}{\partial N}\right|_{V,E}}$

repeat argument for T-equilibrium

$\Rightarrow$ systems do not (net-)exchange particles if $\mu_1 = \mu_2$ "chemical equilibrium"

1st law: $dS = \dfrac{1}{T}dE + \dfrac{p}{T}dV - \dfrac{\mu}{T}dN \quad \Rightarrow \quad \boxed{dE = TdS - pdV + \mu dN}$

$\Rightarrow \quad \mu =$ "energy cost to add one particle"

For electric charge we would get the electrostatic potential

Comment: $\mu = -T \left.\dfrac{\partial S}{\partial N}\right|_{V,E}$, but from first law: $\mu = \left.\dfrac{\partial E}{\partial N}\right|_{S,V}$ Why?

in general: let x, y, z be variables with one constraint

$$\Rightarrow \quad \boxed{\left.\frac{\partial x}{\partial y}\right|_z \cdot \left.\frac{\partial y}{\partial z}\right|_x \cdot \left.\frac{\partial z}{\partial x}\right|_y = -1}$$

for us: $x = E$, $y = N$, $z = S$, constraint: $V = \text{const}$; use $\left.\dfrac{\partial y}{\partial z}\right|_x = \left(\left.\dfrac{\partial z}{\partial y}\right|_x\right)^{-1}$

If we work at constant temperature rather than energy:

we use $dF = -SdT - pdV + \mu dN \quad \Rightarrow \quad \mu = \left.\dfrac{\partial F}{\partial N}\right|_{T,V}$

A.4.2 The grand canonical ensemble

GrCE: We now let the system also exchange particles with its environment

$\Rightarrow$ fixed T and μ

Def.: Let a state $|n\rangle$ correspond to energy E_n and particle number N_n

Grand canonical partition function $\boxed{\mathcal{Z}(T,\mu,V) = \sum_n e^{-\beta(E_n-\mu N_n)}}$

$$\Rightarrow \overset{\text{(Sec. 3)}}{\ldots} \Rightarrow \quad \boxed{p(n) = \frac{e^{-\beta(E_n-\mu N_n)}}{\mathcal{Z}}}$$

Entropy: $S = -k_B \sum_n p(n)\, \ln p(n) \quad \Rightarrow \ldots \Rightarrow \quad \boxed{S = k_B \frac{\partial}{\partial T}(T\, \ln \mathcal{Z})}$

one also gets:

$$\boxed{\begin{aligned} &\langle E\rangle - \mu\langle N\rangle = -\frac{\partial}{\partial\beta}\ln\mathcal{Z} \\ &\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} \\ &\Delta N^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln\mathcal{Z} = \frac{1}{\beta}\frac{\partial\langle N\rangle}{\partial\mu} \end{aligned}}$$

A.4.3 The grand canonical potential

Def.: Grand canonical potential $\boxed{\Phi = F - \mu N}$

$d\Phi = -SdT - pdV - Nd\mu$

View $\Phi = \Phi(T,V,\mu)$

with $F = E - TS\,, \quad \Phi = E - TS - \mu N\,, \quad \frac{\partial}{\partial\beta} = -k_B T^2 \frac{\partial}{\partial T}$

$$\Rightarrow \Phi = -\frac{\partial}{\partial\beta}\ln\mathcal{Z} - Tk_B\frac{\partial}{\partial T}(T\ln\mathcal{Z})$$

$$\Rightarrow \boxed{\Phi = -k_B T\ln\mathcal{Z}}$$

Def.: "extensive" quantities scale as system size: E, N, V, S

"intensive" quantities size independent: $\frac{1}{T} = \frac{\partial S}{\partial E}\,, \quad p = T\frac{\partial S}{\partial V}\,, \quad \mu = -T\frac{\partial S}{\partial N}$

F is extensive: $F(T, \lambda V, \lambda N) = \lambda\, F(T, V, N)$

Φ is extensive: $\Phi(T, \lambda V, \mu) = \lambda\, \Phi(T, V, \mu)$:

only one extensive independent variable!

$\Rightarrow$ Φ must be $\sim V$!

We know $\left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu} = -p \quad \Rightarrow \quad \boxed{\Phi = -p(T, \mu)\, V}$

A lot of this developed by Josiah Willard Gibbs (1839-1903)

B Classical Gases

gas = particles flying around in a box

classical, but QM is often “there” in the background

we’ll typically use the CE

one particle: $H = \dfrac{\vec{p}^2}{2m} + U(\vec{q}) = E_{\text{kin}} + E_{\text{pot}}$

state = point in phase space $\{(q_i,\, p_i)\}$

$\sum \to \int \Rightarrow$ partition function for one particle $\quad Z_1 = \dfrac{1}{h^3}\displaystyle\int e^{-\beta H(\vec{p},\vec{q})} d^3p\, d^3q$

$$h = 6.6 \cdot 10^{-34}\ \mathrm{J\,s}$$

why h in a classical formula?

B.1 From QM to classical

One particle in 1 dim. in QM: Hamilton operator: $\hat{H} = \dfrac{\hat{p}^2}{2m} + U(\hat{q})$

$$\hat{H}\,\underset{\substack{\uparrow\\ \text{Eigenstate}}}{|n\rangle} = \underset{\substack{\nwarrow\\ \text{energy}}}{E_n}\,|n\rangle$$

Recall identity operator: $\mathbb{1} = \displaystyle\int dq\,|q\rangle\langle q|\,, \qquad \mathbb{1} = \int dp\,|p\rangle\langle p|$

$$\begin{aligned}
\Rightarrow Z_1 &= \sum_n e^{-\beta E_n} = \sum_n \langle n|e^{-\beta\hat{H}}|n\rangle \\
&= \sum_n \langle n| \int dq\,|q\rangle\langle q|e^{-\beta\hat{H}} \int dq'\,|q'\rangle\langle q'|n\rangle \\
&= \int dq\,dq' \left\{ \langle q|e^{-\beta\hat{H}}|q'\rangle \sum_n \left[\langle q'|n\rangle\langle n|q\rangle\right] \right\} \qquad \Bigg|\, \sum_n |n\rangle\langle n| = \mathbb{1}\,, \quad \langle q'|q\rangle = \delta(q-q') \\
\Rightarrow Z_1 &= \int dq \langle q|e^{-\beta\hat{H}}|q\rangle \quad \text{“} = \mathrm{Tr}\, e^{-\beta\hat{H}}\ \text{”}
\end{aligned}$$

Recall from QM: $e^{\hat{A}}\, e^{\hat{B}} = e^{\hat{A}+\hat{B}+\frac{1}{2}[\hat{A},\hat{B}]+\dots}$

for us: $\hat{A} = \hat{q},\ \ \hat{B} = \hat{p},\ \ [\hat{q},\hat{p}] = i\hbar$

$$\Rightarrow e^{-\beta\hat{H}} = e^{-\beta\left[\frac{\hat{p}^2}{2m}+U(\hat{q})\right]} = e^{-\beta\frac{\hat{p}^2}{2m}}\cdot e^{-\beta U(\hat{q})} + \mathcal{O}(\hbar)$$

Classical limit: $\hbar \to 0$!

$$\Rightarrow Z_1 = \int dq \langle q| e^{-\beta\frac{\hat{p}^2}{2m}} e^{-\beta U(\hat{q}}|q\rangle \qquad \Big| \ |q\rangle \text{ eigenstates to } \hat{q} \ \ \Rightarrow \ \ \underset{\substack{\uparrow \\ \text{operator}}}{U(\hat{q})}|q\rangle = \underset{\substack{\uparrow \\ \text{number}}}{U(q)}|q\rangle$$

$$\begin{aligned}\Rightarrow Z_1 &= \int dq\, e^{-\beta U(q)} \langle q|e^{-\beta\frac{\hat{p}^2}{2m}}|q\rangle \\ &= \int dq\, dp\, dp' \left\{ e^{-\beta U(q)} \langle q|p\rangle \langle p|e^{-\beta\frac{\hat{p}^2}{2m}}|p'\rangle \langle p'|q\rangle \right\}\end{aligned}$$

Note: $\langle q|p\rangle = \langle p|q\rangle^* = \dfrac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}pq}$, $\qquad \langle p|p'\rangle = \delta(p-p')$

In 3 dims.: $\boxed{Z_1 = \dfrac{1}{(2\pi\hbar)^3}\displaystyle\int d^3q\, d^3p e^{-\beta H(\vec{p},\vec{q})}}$

B.2 Ideal gas

Def.: gas = N particles trapped in box of volume V

"ideal" = particles do not interact, i.e. $U(q) = 0$

"monatomic" = particles have no structure (i.e. no vibration, rotation)

$$\Rightarrow \quad Z_1(V,T) = \frac{1}{(2\pi\hbar)^3}\int d^3q\, d^3p e^{-\beta\frac{\vec{p}^2}{2m}} \qquad \Big| \int d^3q = V$$

We'll often use $\boxed{\displaystyle\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}}$

$$\Rightarrow Z_1(V,T) = \frac{V}{(2\pi\hbar)^3}\int dp_x\, dp_y\, dp_z\, e^{-\beta\frac{p_x^2}{2m}}\, e^{-\beta\frac{p_y^2}{2m}}\, e^{-\beta\frac{p_z^2}{2m}} = V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \qquad \Big| \ a = \frac{\beta}{2m} = \frac{1}{2mk_BT}$$

<u>**Def.:**</u> thermal de Broglie wavelength $\boxed{\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}}$

"average de Broglie wavelength at T"

$$\Rightarrow \quad \boxed{Z_1 = \frac{V}{\lambda^3}}$$

N indistinguishable particles: $\boxed{Z(N,V,T) = \frac{Z_1^N}{N!} = \frac{V^N}{\lambda^{3N} N!}}$

exchange two particles → no new state! Hence $N!$

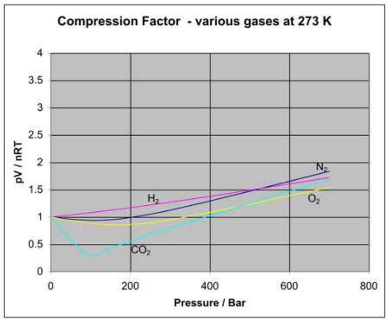
Recall: $F = -k_B T \ln Z = -k_B T \left[N \ln V - 3N \ln \lambda - \ln N! \right]$

$$p = -\left.\frac{\partial F}{\partial V}\right|_T = +\frac{N k_B T}{V} \quad \Rightarrow \quad \underline{\textbf{ideal gas law:}} \quad \boxed{pV = N k_B T}$$

Comments:

- all $\hbar$ have disappeared!
- equations linking p, T, V are called "equations of state" (EOS)
- T as defined above $\left(\frac{\partial S}{\partial E}\right)$ is really a "good" temperature!
- in the lab: deviations at higher densities

  expected: $U \neq 0$



B.2.1 Equipartition of energy

energy: $E = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \left[-3N \ln \lambda \right] = 3N \frac{\partial}{\partial \beta} \left[\frac{1}{2} \ln \beta \right] = \frac{3}{2} N k_B T$

Assume the gas existed in D spatial dimensions

$$\Rightarrow \ldots \Rightarrow \quad Z = \frac{V^N}{\lambda^{DN} N!} \quad \Rightarrow \quad E = \frac{D}{2} N k_B T$$

$\Rightarrow$ D degrees of freedom; each contributes $\frac{N k_B T}{2}$ to E

<u>**equipartition of energy:**</u> each degree of freedom contributes $\frac{N k_B T}{2}$ to E

breaks down for QM systems at small T

For one particle: $\langle E\rangle = \frac{p^2}{2m} \quad \Rightarrow \quad p \sim \sqrt{mE} \sim \sqrt{mk_BT}$

de Broglie wavelength $\lambda_{\text{dB}} = \frac{h}{p} \sim \lambda$ up to factors of 2 or π

heat capacity: $C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{3}{2}Nk_B$

Comment on k_B: Why is it so small?

energy of gas $E \sim Nk_BT$

E, T have units where numbers are $\mathcal{O}(1) \quad \Rightarrow \quad Nk_B = \mathcal{O}(1)$

stars in universe $\sim 10^{22} < N$ (!) $\Rightarrow \quad k_B \sim \frac{1}{N} \sim 10^{-23}$

Chemist Notation

Def.: Avogadro's number $N_A \equiv$ # atoms in 12 g of Carbon^{12}

1 mol $\equiv N_A$ atoms

ideal gas law: $pV = Nk_BT = n\mathcal{R}T$

with: $n \equiv \frac{N}{N_A}, \qquad \mathcal{R} \equiv N_A k_B \approx 8\ \frac{\text{J}}{\text{K mol}}$ "Universal gas constant"

B.2.2 Entropy

Recall entropy for CE: $S = k_B \frac{\partial}{\partial T}(T \ln Z)$

$$\frac{\partial}{\partial T}\ln\lambda = \frac{\partial}{\partial T}\ln\sqrt{\frac{2\pi\hbar^2}{mk_BT}} = \frac{\partial}{\partial T}\ln T^{-1/2} = -\frac{1}{2T}$$

$$\Rightarrow S = k_B \ln Z + k_BT\frac{\partial}{\partial T}\left[N\ln V - 3N\ln\lambda - \ln N!\right]$$

$$= k_B\left[\ln\frac{V^N}{\lambda^{3N}} - \ln N!\right] + k_BT\frac{3N}{2T} \qquad \Big| \text{Stirling}: \ \ln N! \approx N\ln N - N$$

$$\approx k_B\left[\ln\frac{V^N}{\lambda^{3N}N^N} + N\right] + \frac{3}{2}Nk_B$$

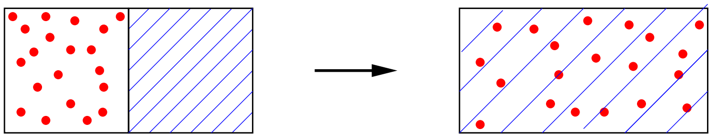
$$\Rightarrow \boxed{S = Nk_B\left(\ln\frac{V}{\lambda^3 N}+\frac{5}{2}\right)} \quad \text{“Sackur-Tetrode equation”}$$

Comments:

- S has $\hbar$; classically we only measure ΔS $\Rightarrow$ $\hbar$ drops out
- S measures the factor $N!$ in Z

  Gibbs noticed this before QM:

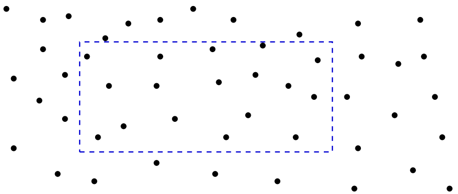
  Mix “red” and “blue” gas $\Rightarrow$ entropy increases



  Mix “red” and “red” gas $\Rightarrow$ entropy does not increase $\rightarrow$ $N!$

B.2.3 The ideal gas in the GrCE

view as subvolume inside larger gas



$$\mathcal{Z}_{\text{ideal}}(\mu,V,T) = \sum_n\left(e^{\beta N_n\mu}\,e^{-\beta E_n}\right) = \sum_N\left[e^{\beta N\mu}\sum_m e^{-\beta E_m}\right]$$

↖states for fixed N

$$= \sum_{N=0}^{\infty}\left[e^{\beta\mu N}Z_{\text{ideal}}(N,V,T)\right] = \sum_{N=0}^{\infty}\left[\left(e^{\beta\mu}\right)^N\left(\frac{V}{\lambda^3}\right)^N\frac{1}{N!}\right]$$

$$= \exp\left(\frac{e^{\beta\mu}V}{\lambda^3}\right)$$

$$\Rightarrow \langle N\rangle = N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} = \frac{e^{\beta\mu}V}{\lambda^3}$$

$$\Rightarrow \mu = k_BT\,\ln\left(\frac{\lambda^3 N}{V}\right)$$

$\dfrac{V}{N}$ = average volume per particle

$\lambda \approx$ average de Broglie wavelength of particle

$\lambda^3 \approx \frac{V}{N} \quad \Rightarrow$ QM effects important

classical limit $\Rightarrow \ \lambda^3 \ll \frac{V}{N} \quad \Rightarrow \ \mu < 0$

Comments:

- $\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}$ = energy cost of adding particle at <u>constant S, V !</u>

  extra particle $\Rightarrow$ more ways of distributing energy

  $\Rightarrow$ S would increase unless E decreases

  $\Rightarrow$ E decreases $\Rightarrow$ $\mu < 0$

- $\mu > 0$ possible for some special cases

Fluctuations: $\quad \Delta N^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2} \ln \mathcal{Z} = N$

$$\Rightarrow \frac{\Delta N}{N} = \frac{1}{\sqrt{N}} \quad \to 0 \text{ in thermodynamic limit}$$

Recall: $pV = -\Phi = k_B T \ln \mathcal{Z} = k_B T \frac{e^{\beta\mu} V}{\lambda^3} = k_B T N$ ideal gas law !

B.3 Maxwell distribution

Goal: velocity distribution

1 particle, ideal gas: $Z_1 = \frac{1}{(2\pi\hbar)^3} \int e^{-\frac{\beta \vec{p}^2}{2m}} d^3q\, d^3p \qquad \Big| \ \vec{v} = \frac{\vec{p}}{m}$

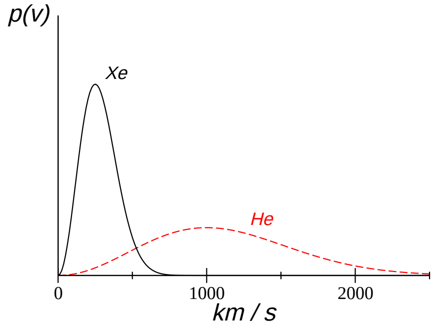
$$= \frac{m^3 V}{(2\pi\hbar)^3} \int e^{-\beta \frac{m\vec{v}^2}{2}} d^3v$$

$$= \frac{4\pi m^3 V}{(2\pi\hbar)^3} \int v^2 e^{-\beta\frac{mv^2}{2}} dv$$

$\Rightarrow$ probability that atom speed in $[v, v + dv]$: $\boxed{\begin{array}{l} p(v) = \mathcal{N} v^2 e^{-\frac{mv^2}{2k_BT}} \\ \mathcal{N} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \end{array}}$ "Maxwell distribution"

$$\Rightarrow \; \langle v^2 \rangle = \int_0^\infty p(v)\, v^2 dv = \ldots = \frac{3k_BT}{m}$$

equipartition of energy



Maxwell's argument: prob. distribution in x dir.: $\phi(v_x)$

rotational symmetry $\Rightarrow$ same in y, z dir.

+ distribution cannot depend on direction

$$\Rightarrow \; p(\vec{v}) = p\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right) = p(v)$$

$$\Rightarrow \; p(v)\, dv_x\, dv_y\, dv_z = \phi(v_x)\, \phi(v_y)\, \phi(v_z)\, dv_x\, dv_y\, dv_z$$

It can be shown that the only solution is $\phi(v_x) = Ae^{-Bv_x^2}$

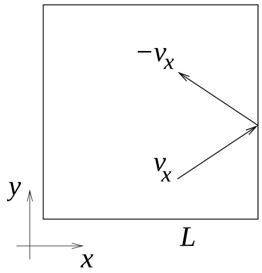
$$\Rightarrow \; p(v)\, dv_x\, dv_y\, dv_z = 4\pi v^2\, p(v) dv = 4\pi A^3 v^2\, e^{-Bv^2}\, dv$$

equipartition of energy $\Rightarrow$ $B = \dfrac{m}{2k_BT}$

History of kinetic theory

kinetic theory = understanding gas properties through atoms

1783 Bernoulli: pressure = bombardment of atoms



$$\Delta p_x = 2mv_x$$

next "hit" after $\Delta t = \dfrac{2L}{v_x}$

$$\Rightarrow \; F = \frac{\Delta p_x}{\Delta t} = \frac{mv_x^2}{L}$$

all atoms: $F = \dfrac{Nm\langle v_x^2 \rangle}{L} = \dfrac{Nm\langle v^2 \rangle}{3L}$

$$\Rightarrow \; \text{pressure } p = \frac{F}{A} = \frac{Nm\langle v^2 \rangle}{3L^3} = \frac{Nm\langle v^2 \rangle}{3V} \overset{!}{=} \frac{Nk_BT}{V} \qquad \text{(gas law)}$$

$$\Rightarrow \; \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

1843: Waterson: rejected paper “Thoughts on Mental Functions”

1857: Clausius: rotating, vibrating modes

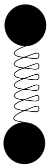
1859: Maxwell: distribution, gas viscosity independent of density

→ experiment, Cavensdish Lab

Boltzmann Eq.: dynamics in phase space → non-equilibrium

B.4 Diatomic gas

Molecules with 2 atoms ≈ 2 masses attached to spring



⇒ i) Rotation about 2 axes (ignore symmetry axis)

ii) vibration

⇒ $Z_1 = Z_{\text{trans}}\, Z_{\text{rot}}\, Z_{\text{vib}}$

i) Rotation

Lagrangian: $L_{\text{rot}} = \frac{1}{2} I \left(\dot\theta^2 + \sin^2\theta\, \dot\phi^2\right)$

⇒ conjugate momenta: $p_\theta = \frac{\partial L_{\text{rot}}}{\partial \dot\theta} = I\dot\theta\,, \qquad p_\phi = \frac{\partial L_{\text{rot}}}{\partial \dot\phi} = I\, \sin^2\theta\, \dot\phi$

⇒ Hamiltonian: $H_{\text{rot}} = p_\theta\dot\theta + p_\phi\dot\phi - L_{\text{rot}} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$

$$\Rightarrow\ Z_{\text{rot}} = \frac{1}{(2\pi\hbar)^2} \int e^{-\beta H_{\text{rot}}} dp_\theta\, dp_\phi\, d\theta\, d\phi \qquad \Bigg| \int e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

$$= \frac{2\pi I}{\beta(2\pi\hbar)^2} \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = \frac{2I}{\beta\hbar^2}$$

$$\Rightarrow\ E_{\text{rot}} = -\frac{\partial}{\partial\beta} \ln Z_{\text{rot}} = -\frac{\partial}{\partial\beta}\left[-\ln\beta \pm \ldots\right] = \frac{1}{\beta} = k_B T$$

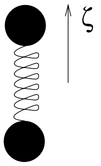
$\Rightarrow$ gas with rotation: $Z_1 = Z_{\text{trans}}\, Z_{\text{rot}} \sim (k_B T)^{5/2}$

$$Z = \frac{Z_1^N}{N!} \quad \Rightarrow \quad E = \frac{5}{2} N k_B T$$

$$C_V = \frac{5}{2} N k_B \ : \ 3 + 2 \text{ deg. of freedom}$$

ii) vibration

harmonic oscillator with frequency ω



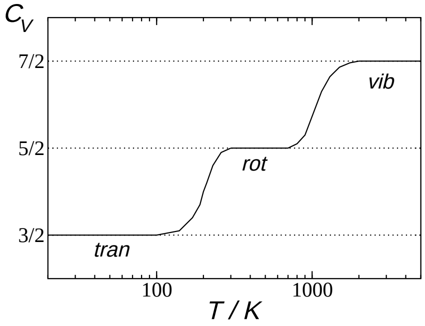
$$\Rightarrow \quad H_{\text{vib}} = \frac{p_\zeta^2}{2m} + \frac{1}{2} m\omega^2 \zeta^2$$

$$\Rightarrow \quad Z_{\text{vib}} = \frac{1}{2\pi\hbar} \int e^{-\beta H_{\text{vib}}} dp_\zeta \, d\zeta$$

$$= \frac{1}{2\pi\hbar} \int e^{-\beta \frac{p_\zeta^2}{2m}} \ e^{-\beta \frac{m\omega^2 \zeta^2}{2}} dp_\zeta \, d\zeta = \frac{1}{\hbar\beta\omega} = \frac{k_B T}{\hbar\omega}$$

$\Rightarrow \quad E_{\text{vib}} = k_B T$: 2 degrees of freedom! potential + motion

diatomic gas: $C_V = \frac{7}{2} N k_B$



Note:
- I, ω dropped out
- at lower T: dof's frozen out, e.g. H_2 :

  QM effect; visible in *hot gas*!

B.5 Interacting gas

Consider monatomic gas

ideal gas good for small $\frac{N}{V}$

Virial expansion: $$\frac{p}{k_B T} = \frac{N}{V} + \underbrace{B_2(T)}_{} \frac{N^2}{V^2} + \underbrace{B_3(T)}_{} \frac{N^3}{V^3} + \dots$$

virial coefficients

goal: get $B_i(T)$ from first principals, i.e. potential $U(r)$ between atoms

2 features of $U(r)$:
- attractive $\frac{1}{r^6}$: dipols p_1, p_2 $\Rightarrow$ pot. energy $\frac{p_1 p_2}{r^3}$

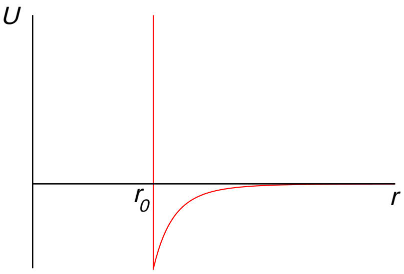
  instantaneous dipol p_1 $\Rightarrow$ electr. field $E \sim \frac{p_1}{r^3}$

  $\Rightarrow$ induced dipol $p_2 \sim E \sim \frac{p_1}{r^3}$

  "van der Waals interaction"
- strong repulsion from Pauli exclusion

Lennard-Jones potential: $U(r) \sim \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6$; $12 = 6 \cdot 2$ chosen for convenience

hard-core potential: $U(r) = \begin{cases} \infty & r < r_0 \\ -U_0 \left(\frac{r_0}{r}\right)^6 & r \geq r_0 \end{cases}$



hard-core easier! Take that...

B.5.1 Mayer f function and B_2

Notation: $\vec{r}$ = particle position (instead of $\vec{q}$)

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \underbrace{\sum_{i>j}}_{\text{count pairs once!}} U(r_{ij}) \, ; \qquad r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$$

$$\Rightarrow \; Z(N,V,T) = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int \prod_{i=1}^{N} d^3 p_i \, d^3 r_i \, e^{-\beta H}$$

$$= \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \left[\int \prod_i d^3 p_i e^{-\beta \sum_j \vec{p}_j^2/(2m)} \right] \cdot \left[\int \prod_i d^3 r_i e^{-\beta \sum_{j<k} U(r_{jk})} \right]$$

$$= \frac{1}{\lambda^{3N} N!} \underbrace{\int \prod_i d^3 r_i e^{-\beta \sum_{j<k} U(r_{jk})}}_{\text{hard!}}$$

1st try: Taylor: $e^{-\beta\sum_{j<k}U(r_{jk})} = 1 - \beta\sum_{j<k}U(r_{jk}) + \frac{\beta^2}{2}\sum_{j<k,\,l<m,\,l>j}U(r_{jk})\,U(r_{lm}) \pm \dots$

problem: for $r_{ij} \to 0$: $U(r_{ij}) \to \infty$ not good expansion parameter

2nd try: Mayer f function: $f(r) = e^{-\beta U(r)} - 1$

$$r \to \infty \quad \Rightarrow \quad f(r) \to 0\,, \qquad r \to 0 \quad \Rightarrow \quad f(r) \to -1$$

Def.: $f_{ij} \equiv f(r_{ij}) \quad \Rightarrow \quad e^{-\beta\sum_{j<k}U(r_{jk})} = \prod_{j<k}(1 + f_{jk})$

$$\Rightarrow \quad Z(N,V,T) = \frac{1}{N!\,\lambda^{3N}}\int\prod_i d^3r_i\left(1 + \sum_{j>k}f_{jk} + \sum_{j>k,\ l>m,\ l>j}f_{jk}\,f_{lm} + \dots\right)$$

1st term: $1 \to V^N$, ideal gas

2nd term: sum of terms like

$$I_{12} \equiv \int\prod_i d^3r_i\,f_{12} = V^{N-2}\int d^3r_1\,d^3r_2\,f(r_{12}) = V^{N-1}\int d^3r\,f(r)$$

where $\vec{r} = \vec{r}_1 - \vec{r}_2\,, \quad \vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$

we were a bit sloppy with limits of integration

but this only matters near the boundary of the system

because $f(r)$ has contributions only for $r \approx$ atomic distances

We have $\frac{1}{2}N(N-1) \approx \frac{N^2}{2}$ terms of type I_{12}

$$\Rightarrow Z(N,V,T) = \frac{V^N}{N!\,\lambda^{3N}}\left[1 + \frac{N^2}{2V}\int d^3r\,f(r) + \dots\right] \qquad \Big| \ (1+\epsilon)^N \approx 1 + N\epsilon$$

$$\approx Z_{\text{ideal}}\left[1 + \frac{N}{2V}\int d^3r\,f(r)\right]^N$$

$$\Rightarrow \boxed{F = -k_BT\,\ln Z = F_{\text{ideal}} - \underbrace{Nk_BT\ln\left[1 + \frac{N}{2V}\int d^3r\,f(r)\right]}_{\to B_2(T)}}$$

What do we mean with low density?

For Lennard-Jones or hard-core potential one can show: $\int f(r) d^3r \sim r_0^3$

$$\begin{aligned} \text{where } r_0 &\sim \text{ location of min. of potential} \\ &\approx \text{ atom size} \end{aligned}$$

The expansion is valid if higher-order terms are small

$$\Leftrightarrow \quad \frac{N}{V} r_0^3 \ll 1 \quad \Rightarrow \quad \frac{N}{V} \ll \frac{1}{r_0^3}$$

For liquids: atoms packed $\Rightarrow \frac{N}{V} \approx \frac{1}{r_0^3}$

$\Rightarrow$ expansion good for gases at densities much below liquid state

B.5.2 Van der Waals equation of state

With $\ln(1+x) \approx x$ in F $\Rightarrow p = -\frac{\partial F}{\partial V} = \ldots = \frac{N k_B T}{V}\left(1 - \frac{N}{2V}\int f(r) d^3r + \ldots\right)$

$$\Rightarrow \frac{pV}{N k_B T} = 1 - \frac{N}{2V}\int f(r) d^3r\ ; \qquad f(r) = e^{-\beta U(r)} - 1$$

Cases:

1) repulsion: $U(r) > 0 \ \forall_r$ and $U(r \to \infty) = 0 \quad \Rightarrow \quad f(r) < 0 \quad \Rightarrow p > p_{\text{ideal}}$

2) attraction: $U(r) < 0 \quad \Rightarrow \ldots \Rightarrow \quad p < p_{\text{ideal}}$

3) hard-core: $\int f(r) d^3r = \int_0^{r_0} -1 d^3r + \int_{r_0}^{\infty} d^3r \left[e^{+\beta U_0 (r_0/r)^6} - 1\right]$

high T limit: $\beta U_0 \ll 1 \quad \Rightarrow \quad e^{\beta U_0 (r_0/r)^6} \approx 1 + \beta U_0 \left(\frac{r_0}{r}\right)^6$

$$\begin{aligned} \Rightarrow \int f(r) d^3r &\approx -4\pi \int_0^{r_0} r^2 dr + \frac{4\pi U_0}{k_B T}\int_{r_0}^{\infty} \frac{r_0^6}{r^4} dr \\ &= \frac{4\pi r_0^3}{3}\left(\frac{U_0}{k_B T} - 1\right) \end{aligned}$$

$$\Rightarrow \quad \boxed{\frac{pV}{Nk_BT} = 1 - \frac{N}{V}\left(\frac{a}{k_BT} - b\right)}\,; \qquad a = \frac{2\pi r_0^3 U_0}{3}\,, \quad b = \frac{2\pi r_0^3}{3}$$

$$\Rightarrow \ldots \Rightarrow \quad k_BT = \frac{V}{N}\left(p + \frac{N^2}{V^2}a\right)\left(1 + \frac{N}{V}b\right)^{-1} \approx \left(p + \frac{N^2}{V^2}a\right)\left(\frac{V}{N} - b\right)$$

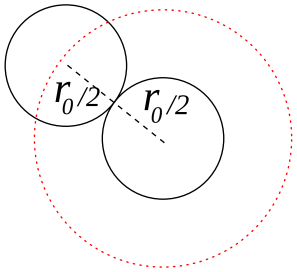
"van der Waals EOS": valid at low $\frac{N}{V}$, high T

$$\Rightarrow p = \frac{Nk_BT}{V - bN} - a\frac{N^2}{V^2}$$

Comments:

- a depends on U_0 $\Rightarrow$ attractive large r effects → smaller p
- b only function of r_0 → hard-core repulsion → reduces V
- one atom blocks volume $\frac{4}{3}\pi r_0^3$

  but $b = \frac{2}{3}\pi r_0^3$ Why?

  1st atom has space V,

  2nd atom has space $V - \Omega$, $\Omega = 2b$

  etc.

  whole configuration space: $$\prod_{m=0}^{N-1}(V - m\Omega) \approx V^N\left(1 - \frac{N^2}{2}\frac{\Omega}{V} + \ldots\right) \Bigg|\ \Omega \ll V$$

  $$\approx \left(V - N\frac{\Omega}{2}\right)^N = (V - Nb)^N$$

- Our method can only handle potentials

  $U(r) \sim \frac{1}{r^n}$ with $n > 3$. Otherwise divergent integral of $f(r)$

- 2nd virial term of van der Waals EOS: $B_2(T) = -\left(\frac{a}{k_BT} - b\right)$
- Higher-order virial coefficients: e.g. *cluster expansion*,

  cf. Sec. 2.5.3 in David Tong's notes [2]

- More on van der Waals in Sec. E (Phase transitions)

C Quantum Gases

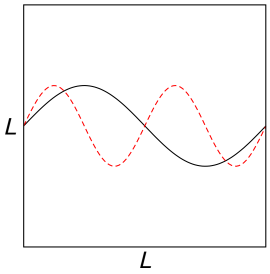
gases where QM effects are important; includes light, phonons,…

C.1 Density of states

often convenient to $\sum_n \to \int \ldots dE$; requires density of states

ideal QM gas: no interaction

model particles as plane waves $\psi = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{x}}$



impose periodic boundary conditions

(the physics can be shown not to depend on the BCs)

$$\Rightarrow k_i = \frac{2\pi n_i}{L} \,, \quad n_i \in \mathbb{Z}$$

$$\wedge \quad E_{\vec{n}} = \frac{\hbar^2 \vec{k}^2}{2m} = \frac{4\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2) \,, \quad k = |\vec{k}| \,, \quad \hat{p} = -i\hbar\frac{\partial}{\partial x_i}$$

one particle: $Z_1 = \sum_{\vec{n}} e^{-\beta E_{\vec{n}}}$

recall $\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$ $\Rightarrow$ exponent $\frac{E_{\vec{n}}}{k_BT} = \beta\frac{\hbar^2\vec{k}^2}{2m} \sim \frac{\lambda^2\vec{n}^2}{L^2}$

for macroscopic box: $\lambda \ll L$ $\Rightarrow$ many $\vec{n}$ with $E_{\vec{n}} \leq k_BT$

$$\Rightarrow \quad \sum_{\vec{n}} \approx \int d^3n = \frac{L^3}{(2\pi)^3}\int d^3k = \frac{4\pi V}{(2\pi)^3}\int k^2 dk$$

$$E = \frac{\hbar^2k^2}{2m} \quad \Rightarrow \quad dE = \frac{\hbar^2 k}{m}dk$$

$$\Rightarrow \sum_{\vec{n}} \approx \frac{V}{2\pi^2}\int \sqrt{\frac{2mE}{\hbar^2}}\frac{m}{\hbar^2}dE =: \int g(E)dE \,,$$

$$\boxed{g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}}$$

Comments:
- $g(E)dE =$ # of states in energy interval $[E,\, E+dE)$
- looks classical, but useful for many QM systems!

C.1.1 Relativistic systems

all that changes is $E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$ instead of $\dfrac{\hbar^2 k^2}{2m}$

$$\Rightarrow\ dE = \frac{\hbar^2 k c^2}{E} dk$$

$$\Rightarrow \ldots \Rightarrow \quad k^2 dk = \frac{E\, dE}{\hbar^2 c^2} \frac{\sqrt{E^2 - m^2 c^4}}{\hbar c}$$

$$\Rightarrow \ldots \Rightarrow \quad \boxed{g(E) = \frac{VE}{2\pi^2 \hbar^3 c^3} \sqrt{E^2 - m^2 c^4}}$$

for massless particles: $g(E) = \dfrac{VE^2}{2\pi^2 \hbar^3 c^3}$

C.2 Photons: Blackbody Radiation

light = gas of photons

color of light at $T =$ color of any object at T (equilibrium!)

if we ignore the atomic makeup (absorption lines, emission lines),

→ “blackbody radiation” because at $T = 0$ such a body is black

Photons: wavelength λ, frequency $\omega = \dfrac{2\pi c}{\lambda} = kc$

energy $E = \hbar\omega$; $m = 0$

2 polarization states (transverse) $\Rightarrow$ $g(E)$ picks up extra factor of 2

$$\Rightarrow\ g(E)\, dE = \frac{VE^2}{\pi^2 \hbar^3 c^3} dE = \underbrace{\frac{V\omega^2}{\pi^2 c^3}}_{=:\tilde{g}(\omega)} d\omega$$

$\tilde{g}(\omega) =$ # states for a single photon with frequency $\in [\omega,\, \omega + d\omega)$

Note: photons are not conserved! Unlike atoms

→ one could work in GrCE with $\mu = 0$. In this case $\Phi = F$

and our above relations of E, F, Φ to Z or $\mathcal{Z}$ become the same.

We'll stick with CE notation.

partition function for photons in fixed state n with ω_n:

$$Z_{\omega_n} = 1 + e^{-\beta\hbar\omega_n} + e^{-2\beta\hbar\omega_n} + \ldots = \text{“summing over all } N\text{”}$$
$$= \frac{1}{1 - e^{-\beta\hbar\omega_n}}$$

take all frequencies ⇒ the Z multiply ⇒ the $\ln Z$ add up

$$\Rightarrow \ln Z = \int_0^\infty \tilde{g}(\omega)\, \ln Z_\omega d\omega = -\frac{V}{\pi^2 c^3}\int_0^\infty \omega^2 \,\ln\left(1 - e^{-\beta\hbar\omega}\right) d\omega$$

C.2.1 Planck distribution

energy: $E = -\dfrac{\partial}{\partial\beta}\ln Z = \dfrac{V\hbar}{\pi^2 c^3}\displaystyle\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega = \int_0^\infty E(\omega)d\omega$

$$\Rightarrow \quad E(\omega) = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1} = \text{ photon energy density in frequency space}$$

Comments:

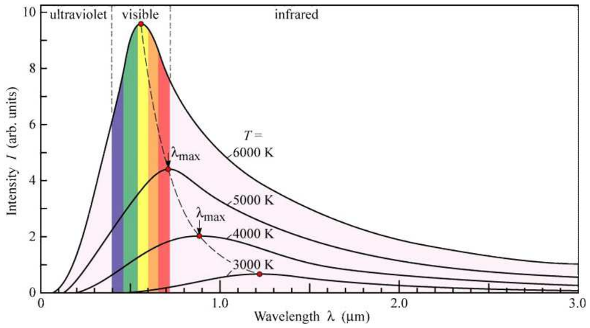
- as T decreases:

  $\omega_{\max}$ decreases, $\lambda_{\max}$ increases
- $\omega_{\max} = \zeta\frac{k_B T}{\hbar}$,

  where $3 - \zeta = 3e^{-\zeta}$ ⇒ $\zeta \approx 2.822$

  “Wien's displacement law”

  → color of object at T



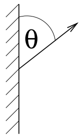
total energy: $$E = \frac{V}{\pi^2 c^3}\frac{(k_B T)^4}{\hbar^3}\underbrace{\int_0^\infty \frac{x^3}{e^x - 1}dx}_{= \, ... \, = \frac{\pi^4}{15}} \qquad \Big| \; x = \beta\hbar\omega$$

$$\Rightarrow \quad \boxed{\frac{E}{V} = \frac{\pi^2 k_B^4}{15\hbar^3 c^3}T^4}$$

energy flux from object = luminosity: $$\boxed{L = \frac{E}{V}\frac{c}{4} = \sigma T^4 \; ; \qquad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} = 5.67 \times 10^{-8}\frac{\mathrm{J}}{\mathrm{m^2\,s\,K}}}$$

"Stefan-Boltzmann law" (cf. Reif [1] for details)

Comments:
- factor c because it is flux
- 2 factors of $\frac{1}{2}$: a) flux goes only away from object, not into it
  b) angular factor in integral



pressure: $$F = -k_B T \ln Z = \frac{V k_B T}{\pi^2 c^3}\int_0^\infty \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right) d\omega \qquad \Big| \text{int. by parts}$$

$$= -\frac{V\hbar}{3\pi^2 c^3}\int_0^\infty \frac{\omega^3 e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}d\omega$$

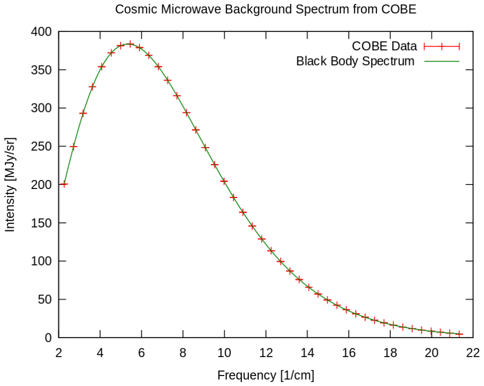
$$= -\frac{V\hbar}{3\pi^2 c^3}\frac{1}{\beta^4\hbar^4}\int_0^\infty \frac{x^3}{e^x - 1} = -\frac{V\pi^2}{45\hbar^3 c^3}(k_B T)^4$$

$$\Rightarrow \quad p = -\left.\frac{\partial F}{\partial V}\right|_T = \frac{1}{3}\frac{E}{V} = \frac{4}{3}\frac{\sigma}{c}T^4$$

Note: photon pressure = $\frac{1}{3}$ photon energy; important in cosmology!

We also get: $$S = -\left.\frac{\partial F}{\partial T}\right|_V = \frac{16V\sigma}{3c}T^3 \, , \qquad C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{16V\sigma}{c}T^3$$

C.2.2 Cosmic Microwave Background (CMB)



CMB = afterglow after big bang

measured by COBE, WMAP, PLANCK

CMB $\approx$ 2.725 K blackbody radiation (within 10^{-5})

photons have travelled for ~ 13.7 billion years

the disagreement → exciting physics

C.2.3 The birth of QM

Consider the classical limit of Planck's formula:

$$E(\omega) = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \approx \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{\beta\hbar\omega} = \underbrace{\frac{V\omega^2 k_B T}{\pi^2 c^3}}_{= E_{\mathrm{RJ}}(\omega)} \qquad \Big| \; x \ll 1 \Rightarrow e^x \approx 1 + x$$

"Rayleigh-Jeans"

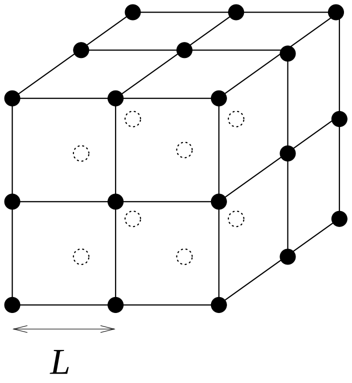
Problem: $\int_0^\infty E_{\mathrm{RJ}}(\omega)\, d\omega$ diverges: "ultraviolet catastrophe"

QM: for $\hbar\omega \gg k_B T$, the temperature cannot excite even one photon.

states "frozen out"

Planck used $E = \hbar\omega$ and Boltzmann statistics $\Rightarrow$ first hint of QM

C.3 Phonons



vibrations of crystal = sound waves

QM: electromagnetic waves ↦ photons

QM: sound waves ↦ phonons

phonon energy: $E = \hbar\omega = \hbar k c_s$ (speed of sound)

differences from photons:

- c_s instead of c
- 3 polarization states; also longitudinal
- upper frequency limit:

  $\lambda = \dfrac{2\pi c_s}{\omega} < L \quad \Rightarrow$ no shaking possible

  $\Rightarrow \omega < \omega_D$ "Debye frequency"

We expect $\omega_D \sim \left(\dfrac{N}{V}\right)^{1/3} c_s$, but what is the prop. constant?

Debye: total number of atoms: N ; each atom has 3 directions of movement

$\Rightarrow$ $3N$ ways of moving

set $3N = \int_0^{\omega_D} \tilde{g}(\omega)\, d\omega$ which is the number of states available for one phonon

$$\Rightarrow \quad 3N = \int_0^{\omega_D} \frac{3}{2}\frac{V\omega^2}{\pi^2 c_s^3} d\omega = \frac{V\omega_D^3}{2\pi^2 c_s^3} \quad \Rightarrow \quad \boxed{\omega_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3} c_s}$$

Def.: Debye temperature $T_D = \dfrac{\hbar\omega_D}{k_B} =$ temperature at which highest-frequency states become excited

$T_D \approx 100$ K for lead, 2 000 K for diamond, $\approx 200 \ldots 400$ K for many materials phonons are not conserved → same game as for photons:

$$Z_\omega = \frac{1}{1-e^{-\beta\hbar\omega}}\,, \qquad \ln Z_{\text{phonon}} = \int_0^{\omega_D} \tilde{g}(\omega)\,\ln Z_\omega\, d\omega$$

$$\Rightarrow E = \int_0^{\omega_D} \hbar\omega \frac{\tilde{g}(\omega)}{e^{\beta\hbar\omega}-1}\,d\omega = \frac{3V\hbar}{2\pi^2 c_s^3}\int_0^{\omega_D}\frac{\omega^3}{e^{\beta\hbar\omega}-1}\,d\omega \qquad \Big| \quad x=\beta\hbar\omega$$

$$\Rightarrow E = \frac{3V(k_BT)^4}{2\pi^2(\hbar c_s)^3}\int_0^{T_D/T}\frac{x^3}{e^x-1}\,dx$$

no analytic solution

Limits: 1) $T \ll T_D \quad\Rightarrow\quad$ upper int. limit $\approx \infty$: $\displaystyle\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}$

$$\Rightarrow C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{2\pi^2 V k_B^4}{5(\hbar c_s)^3}T^3 = Nk_B\frac{12\pi^4}{5}\left(\frac{T}{T_D}\right)^3$$

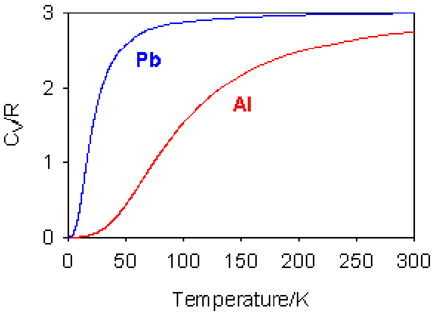
2) $T \gg T_D \quad\Rightarrow\quad$ Taylor expand integrand

$$\Rightarrow \int_0^{T_D/T}\frac{x^3}{e^x-1}dx \approx \int_0^{T_D/T}(x^2+\ldots)\,dx = \frac{1}{3}\left(\frac{T_D}{T}\right)^3+\ldots$$

$$\Rightarrow E\sim T \quad\wedge\quad C_V = \frac{Vk_B^4T_D^3}{2\pi^2\hbar^3c_s^3} = 3Nk_B \qquad \text{(with } N \text{ above)}$$

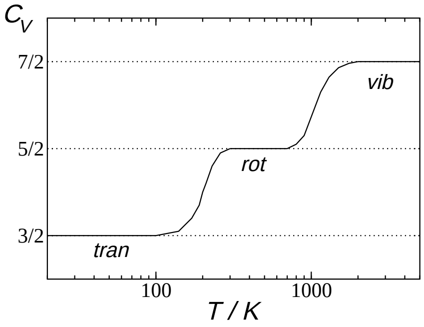
Comments:

- The high T behaviour known since early 1800s: "Dulong-Petit law"
- Debye's ω_D reproduces the "$3N$"
- Debye's new contribution was limit 1)



C.4 The diatomic gas revisited

Recall Figure for C_V: rotation, vibration frozen out at low T



1) Rotation

$$H = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\,\sin^2\theta}$$

QM $\Rightarrow$ E levels: $E = \frac{\hbar^2}{2I} j(j+1)\,;\quad j = 0,\,1,\,2,\,\ldots$

degeneracy $2j+1$ (L_z quantum numbers)

$$\Rightarrow\quad Z_{\text{rot}} = \sum_{j=0}^{\infty}(2j+1)e^{-\beta\hbar^2 j(j+1)/(2I)}$$

a) $T \gg \frac{\hbar^2}{2Ik_B} \quad\Rightarrow\quad \frac{\beta\hbar^2}{2I} \ll 1$

$$\Rightarrow\quad Z_{\text{rot}} \approx \int_0^\infty (2x+1)e^{-\beta\hbar^2 x(x+1)/(2I)}dx = \frac{2I}{\beta\hbar^2} = Z_{\text{classic}}$$

b) $T \ll \frac{\hbar^2}{2Ik_B} \quad\Rightarrow\quad Z_{\text{rot}} \approx 1$

T insufficient to excite even the 1^{st} state above ground level.

Also explains why monatomic gas has no rot. degree of freedom:

I tiny $\to T \ll \frac{\hbar^2}{2Ik_B} \quad\Rightarrow\quad$ "frozen out for almost all T"

2) Vibration

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

$$\Rightarrow\quad Z_{\text{vib}} = \sum_n e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = e^{-\beta\hbar\omega/2}\sum_n e^{-\beta\hbar n\omega} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{1}{2\sinh\frac{\beta\hbar\omega}{2}}$$

a) $T \gg \dfrac{\hbar\omega}{k_B} \quad \Rightarrow \quad Z_{\text{vib}} \approx \dfrac{1}{\beta\hbar\omega} = Z_{\text{class}}$

b) $T \ll \dfrac{\hbar\omega}{k_B} \quad \Rightarrow \quad Z_{\text{vib}} \approx e^{-\beta\hbar\omega/2} =$ contribution from zero-point energy

$\Rightarrow$ energy offset $E_{\text{vib}} = -\dfrac{\partial}{\partial\beta} \ln Z_{\text{vib}} = \dfrac{\hbar\omega}{2}$, but no contribution to C_V

C.5 Bosons

QM: 2 types of particles: 1) bosons: integer spin: $\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$

2) fermions: $\frac{1}{2}$-integer spin: $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$

p, n, e fermions $\Rightarrow$ odd # of p, n → fermions, e.g. He^3

even # of p, n → bosons, e.g. He^4

thermal de Broglie $\lambda = \sqrt{\dfrac{2\pi\hbar^2}{mk_BT}}$

T small $\Rightarrow$ λ large; eventually $\approx$ particle separation $\left(\dfrac{V}{N}\right)^{1/3}$

$\Rightarrow$ QM important

Here: only monatomic gases, non-interacting

C.5.1 Bose-Einstein (BE) distribution

Notation: state: $|r\rangle$, # of particles in state $|r\rangle :\ n_r$

particles indistinguishable

$\Rightarrow$ system described by $n_1 \equiv$ # of particles in state $|1\rangle$, n_2, n_3, ...

CE: $Z = \sum\limits_{\{n_r\}} e^{-\beta \sum_r n_r E_r}$; sum over all states $\{n_r\}$ with $\sum\limits_r n_r = N$; Tricky!

GrCE: chem. potential μ, N can fluctuate

any state can be occupied by any # of particles

$$\Rightarrow \mathcal{Z}_r = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = \frac{1}{1 - e^{-\beta(E_r - \mu)}}$$

"$\sum\limits_{\text{states}}$ # particles in state" = "$\sum\limits_{\text{particles}}$ states of particles"

converges only if $E_r - \mu > 0$. We fix $E_0 = 0 \Rightarrow$ BE gas needs $\mu < 0$.

$$\Rightarrow \boxed{\mathcal{Z} = \prod_r \frac{1}{1 - e^{-\beta(E_r - \mu)}}}$$

$$\Rightarrow \quad N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \sum_r \frac{1}{e^{\beta(E_r - \mu)} - 1} =: \sum_r \langle n_r \rangle \; ; \qquad \boxed{\langle n_r \rangle = \frac{1}{e^{\beta(E_r - \mu)} - 1}}$$

BE distribution

TD limit $\Rightarrow$ $n_r \approx \langle n_r \rangle$

cf. photons, phonons which are bosons!

Def.: "fugacity" $\zeta \equiv e^{\beta\mu}$

BE gas: $\mu < 0 \Rightarrow 0 < \zeta < 1$

Ideal BE gas

1 particle: $E = \dfrac{\hbar^2 k^2}{2m}$

Recall: # of states in $[E, E + de)$ for one particle: $g(E)dE = \dfrac{V}{4\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}\, dE$

$$\rightarrow \quad N = \sum_r \langle n_r \rangle = \int g(E)\, \langle n_r \rangle \, dE = \int \frac{g(E)}{\zeta^{-1} e^{\beta E} - 1} dE = N(\mu, T)$$

Comment: in practice N often fixed, e.g. # of He^4 ; GrCE chosen for convenience!

$\Rightarrow$ we often need to invert $N = N(\mu, T)$ to $\mu = \mu(T, N)$;
cf. ideal gas in GrCE

Energy: $E_{\text{tot}} = \displaystyle\int \frac{E\, g(E)}{\zeta^{-1} e^{\beta E} - 1} dE$

pressure: $p = -\frac{\Phi}{V}$

$$\Rightarrow \quad pV = \frac{1}{\beta}\ln \mathcal{Z} = -\frac{1}{\beta}\sum_r \ln\left[1 - \zeta e^{-\beta E_r}\right]$$

$$= -\frac{1}{\beta}\int \underbrace{g(E)}_{u'}\,\underbrace{\ln\left[1-\zeta e^{-\beta E}\right]}_{v}\,dE$$

int. by parts, $g(E) \sim E^{1/2}$

$$\Rightarrow \quad pV = \frac{2}{3}\int \frac{E\,g(E)}{\zeta^{-1}e^{\beta E}-1}dE = \frac{2}{3}E_{\text{tot}}$$

Problem: we still need integrals $\int \frac{g(E)}{\zeta^{-1}e^{\beta E}-1}dE, \quad \int \frac{E\,g(E)}{\zeta^{-1}e^{\beta E}-1}\,dE$

C.5.2 QM gas at high T

Let us first consider the limit $\zeta = e^{\beta\mu} \ll 1$

$$\Rightarrow \frac{N}{V} = \frac{1}{V}\int \frac{g(E)}{\zeta^{-1}e^{\beta E}-1}dE = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{E^{1/2}}{\zeta^{-1}e^{\beta E}-1}dE$$

$$= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\zeta e^{-\beta E}\sqrt{E}}{1-\zeta e^{-\beta E}}dE \qquad \Big| \quad x = \beta E$$

$$= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\zeta}{\beta^{3/2}}\int_0^\infty \sqrt{x}e^{-x}\left(1+\zeta e^{-x}+\ldots\right)dx \qquad \Big| \quad \text{solve integral with } x = u^2$$

$$\Rightarrow \ldots \Rightarrow \frac{N}{V} = \frac{\zeta}{\lambda^3}\left(1 + \frac{\zeta}{2\sqrt{2}} + \ldots\right) \qquad (*)$$

What does $\zeta \ll 1$ mean?

Evidently $\frac{\lambda^3 N}{V} \ll 1 \quad \Rightarrow \quad \lambda \ll$ particle distance $\Rightarrow$ high T expansion

Note: appears surprising: $T \to \infty \quad \Rightarrow \quad \beta \to 0$, so $\zeta = e^{\beta\mu}$ should go to 1?

No! Change T at constant N $\Rightarrow$ μ changes: $\frac{N}{V} = \text{const} \approx \frac{\zeta}{\lambda^3}$

$\Rightarrow \quad \zeta \sim T^{-3/2}, \ \mu \to -\infty$

High T EOS of BE gas

$$\frac{E}{V} = \frac{1}{V}\int_0^\infty \frac{E\,g(E)}{\zeta^{-1}e^{\beta E}-1}dE = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{E^{3/2}}{\zeta^{-1}e^{\beta E}-1}dE \qquad \Bigg| \quad x=\beta E,\ \ \zeta \ll 1$$

$$= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\zeta}{\beta^{5/2}}\int_0^\infty x^{3/2}e^{-x}\left(1+\zeta e^{-x}+\ldots\right)dx$$

$$= \ldots = \frac{3\zeta}{2\lambda^3\beta}\left(1+\frac{\zeta}{4\sqrt{2}}+\ldots\right) \qquad (**)$$

Eliminate ζ in $(*)$ and $(**)$ for $\zeta \ll 1$:

$$(*) \quad \Rightarrow \zeta \approx \frac{\lambda^3 N}{V}\left(1-\frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V}+\ldots\right)$$

$$\Rightarrow \frac{E}{V} = \frac{3}{2}\frac{N}{\beta V}\left(1-\frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V}+\ldots\right)\left(1+\frac{1}{4\sqrt{2}}\frac{\lambda^3 N}{V}+\ldots\right)$$

$$\Rightarrow pV \overset{!}{=} \frac{2}{3}E = Nk_BT\left(1-\underbrace{\frac{\lambda^3 N}{4\sqrt{2}V}}_{=B_2(T)}+\ldots\right)$$

$= 2^{\text{nd}}$ virial term; not from interactions but QM statitstics

BE statistics reduce pressure in the high T limit

C.5.3 Bose Einstein condensation

Def.: Gamma function: $\Gamma(n) \equiv \int_0^\infty u^{n-1}e^{-u}du$; $\Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}$

Def.: polylogarithms: $g_n(z) \equiv \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}}{z^{-1}e^x-1}dx$

$$\Rightarrow g_n(z) = \frac{1}{\Gamma(n)}\int \frac{zx^{n-1}e^{-x}}{1-ze^{-x}}dx = \frac{1}{\Gamma(n)}z\int\left[x^{n-1}e^{-x}\sum_{m=0}^{\infty}z^m e^{-mx}\right]dx$$

$$= \frac{1}{\Gamma(n)}\sum_{m=1}^{\infty}z^m\int x^{n-1}e^{-mx}dx = \frac{1}{\Gamma(n)}\sum_{m=1}^{\infty}\frac{z^m}{m^n}\underbrace{\int u^{n-1}e^{-u}du}_{=\Gamma(n)} \qquad \Bigg| \quad u=mx$$

$\Rightarrow g_n(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^n}$ monotonically increasing with z

Def.: Zeta function $\hat{\zeta}(s) \equiv \sum_{n=1}^{\infty} \frac{1}{n^s}$

$$\Rightarrow \; g_n(1) = \hat{\zeta}(n) \; ; \quad g_{3/2} = \hat{\zeta}\left(\frac{3}{2}\right) \approx 2.612$$

Recall: $\frac{N}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{\zeta^{-1}e^x - 1} dx = \frac{1}{\lambda^3} g_{3/2}(\zeta)$ **(∗)**

For fixed $\frac{N}{V}$: decrease T $\Rightarrow$ λ increases $\Rightarrow$ $g_{3/2}(\zeta)$ must increase $\Rightarrow$ ζ increases

Def.: $T_c \equiv$ temperature where **(∗)** gives $\zeta = 1$:

$$T_c = \left(\frac{2\pi\hbar^2}{k_B m}\right)\left(\frac{1}{g_{3/2}(1)}\frac{N}{V}\right)^{2/3} \; ; \quad \lambda_c \equiv \sqrt{\frac{2\pi\hbar^2}{k_B T_c m}} = \left[g_{3/2}(1)\frac{V}{N}\right]^{1/3}$$

Note: We shall see that **(∗)** is not correct, so we do not have $\zeta = 1$ at $T = T_c$!

Problem: ζ must be < 1. What happens at $T \leq T_c$?

According to **(∗)**: λ increases $\Rightarrow$ N decreases,

but particles don't disappear through cooling!

What's wrong?

Answer: we used $\sum_k \approx \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int \sqrt{E}\, dE$

The ground state $E = 0$ doesn't contribute to $\int$ but should be in $\sum$

$\Rightarrow$ The "missing" particles are in the ground state:

$$\langle n_0 \rangle = \frac{1}{e^{\beta(E_0-\mu)} - 1} = \frac{1}{\zeta^{-1} - 1} = \frac{\zeta}{1-\zeta}$$

For most $\zeta \in (0,1)$, $\langle n_0 \rangle$ is small, but for $\zeta \approx 1 - \frac{1}{N}$, $\langle n_0 \rangle \approx N$

$\Rightarrow$ we must correct **(∗)** : $N = \frac{V}{\lambda^3} g_{3/2}(\zeta) + \frac{\zeta}{1-\zeta}$

$$T < T_c \quad \Rightarrow \quad \zeta \ \text{ close to } 1$$

$$\Rightarrow \quad N \approx \frac{V}{\lambda^3} g_{3/2}(1) + \langle n_0 \rangle$$

$$\Rightarrow \quad \frac{n_0}{N} = 1 - \frac{V}{N\lambda^3} g_{3/2}(1) = 1 - \left(\frac{\lambda_c}{\lambda}\right)^3 = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

$\Rightarrow$ at $T < T_c$ a macroscopic number of particles is in the ground state

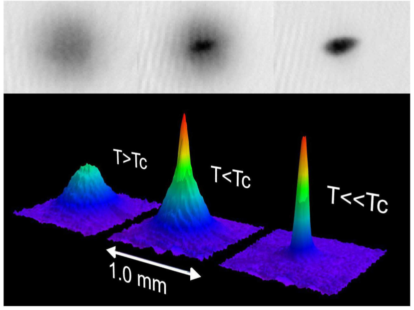
"BE condensation"

First experimental BE cond. in 1995:

Rb, Na, Li, $N \sim 10^4 \ldots 10^7$ atoms, $T_c \sim 10^{-7}\ K$

→ 2001 Nobel Prize

Peak: Ground state in momentum space



EOS: Recall $pV = \frac{2}{3} E_{\text{tot}} = \frac{2}{3} \int \frac{E\, g(E)}{\zeta^{-1} e^{\beta E} - 1} dE = \frac{k_B T V}{\lambda^3} g_{5/2}(\zeta)$

Comment: The ground-state contribution can be shown to be negligible

$$T < T_c \quad \Rightarrow \quad \zeta \approx 1 \quad \Rightarrow \quad p = \frac{k_B T}{\lambda^3} g_{5/2}(1)$$

Note: $p \sim T^{5/2}$ and p independent of particle density $\frac{N}{V}$

C.5.4 Heat capacity: A first look at phase transitions

Let us consider C_V near T_c

Recall: $\frac{E_{\text{tot}}}{V} = \frac{3}{2} p = \frac{3}{2} \frac{k_B T}{\lambda^3} g_{5/2}(\zeta) \sim T^{5/2}$

$$\Rightarrow \frac{C_V}{V} = \frac{1}{V} \frac{\partial E_{\text{tot}}}{\partial T} = \frac{15}{4} \frac{k_B}{\lambda^3} g_{5/2}(\zeta) + \frac{3}{2} \frac{k_B T}{\lambda^3} \frac{d g_{5/2}}{d\zeta} \frac{d\zeta}{dT}$$

Case 1: $T < T_c$

$$\zeta \approx 1 \quad \Rightarrow \quad \frac{d\zeta}{dT} \approx 0 \;\text{ and }\; C_V \approx \frac{15}{4}\frac{Vk_B}{\lambda^3} g_{5/2}(1)$$

Case 2: $T \gtrsim T_c$

$$g_n(\zeta) = \sum_{m=1}^{\infty} \frac{\zeta^m}{m^n} \quad \Rightarrow \quad \frac{dg_n}{d\zeta} = \frac{1}{\zeta} g_{n-1}(\zeta)$$

$$\Rightarrow \quad \frac{dg_{5/2}}{d\zeta} = \zeta^{-1} g_{3/2}(\zeta)\ ; \ \text{ as } \ T \to T_c: \ \frac{dg_{5/2}}{d\zeta} \to g_{3/2}(1)$$

We still need $\dfrac{d\zeta}{dT}$

For $T > T_c$, **(∗)** is still valid: $\dfrac{N\lambda^3}{V} = g_{3/2}(\zeta)$

$$\Big(\text{say } \zeta = 1 - 10^{-6} \quad \Rightarrow \quad n_0 \approx 10^6 \quad \Rightarrow \quad \zeta \approx 1 \quad \wedge \quad \frac{n_0}{N} \approx 0\Big)$$

$$\begin{aligned}
\frac{dg_{3/2}}{d\zeta} &= \frac{1}{\zeta}\, g_{1/2} = \frac{1}{\zeta}\, \frac{1}{\Gamma(1/2)} \int_0^\infty \frac{x^{-1/2}}{\zeta^{-1} e^x - 1} dx \qquad \text{diverges for } \zeta \to 1 \\
&= \frac{1}{\zeta}\, \frac{1}{\Gamma(1/2)} \int_0^\epsilon \frac{x^{-1/2}}{\zeta^{-1}(1+x) - 1} dx + \text{finite} \qquad \Big|\ e^x \approx 1 + x \\
&= \frac{1}{\Gamma(1/2)} \int_0^\epsilon \frac{x^{-1/2}}{(1-\zeta) + x} dx + \ldots \qquad \Big|\ u = \sqrt{\frac{x}{1-\zeta}} \\
&= \frac{2}{\sqrt{1-\zeta}}\, \frac{1}{\Gamma(1/2)} \int_0^\epsilon \frac{1}{1+u^2} du + \ldots
\end{aligned}$$

$$\Rightarrow \quad \text{Series expansion:} \quad g_{3/2}(\zeta) = g_{3/2}(1) + A\sqrt{1-\zeta} + \ldots$$

$$\Rightarrow \quad \frac{N\lambda^3}{V} = g_{3/2}(\zeta) \approx g_{3/2}(1) + A\sqrt{1-\zeta}$$

$$\Rightarrow \quad \zeta \approx 1 - \frac{1}{A^2}\left[g_{3/2}(1) - \frac{N\lambda^3}{V}\right]^2$$

Recall: $T_c = \dfrac{2\pi\hbar^2}{k_B m}\left[\dfrac{1}{g_{3/2}(1)}\,\dfrac{N}{V}\right]^{2/3} \quad \Rightarrow \quad \left(\dfrac{T_c}{T}\right)^{3/2} = \dfrac{\lambda^3 N}{V}\,\dfrac{1}{g_{3/2}(1)}$

$$\Rightarrow \quad \zeta \approx 1 - \frac{[g_{3/2}(1)]^2}{A^2}\left[1 - \left(\frac{T_c}{T}\right)^{3/2}\right]^2 \approx 1 - B\left(\frac{T-T_c}{T_c}\right)^2 \qquad \Big| \; T = T_c(1+\epsilon)$$

So for $T \gtrsim T_c$: $C_V = \frac{15}{4}\frac{k_B V}{\lambda^3} g_{5/2}(\zeta) + \tilde{b}\frac{d\zeta}{dT}$; $\tilde{b}$ finite > 0

$$\Rightarrow \quad \boxed{C_V = \frac{15}{4}\frac{k_B V}{\lambda^3} g_{5/2}(\zeta) - b\frac{T-T_c}{T_c}} \qquad \text{with } b > 0$$

Comments:

- The first term smoothly goes over to the result of Case 1) for $T < T_c$
- The second term goes to zero as $T \to T_c$, but with finite slope

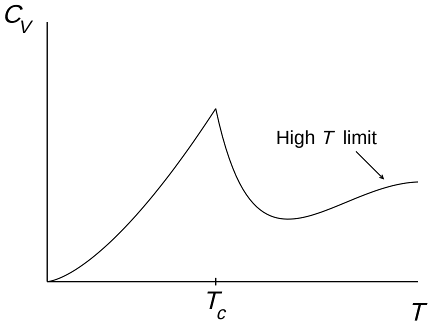
  $\Rightarrow$ C_V has discontinuous deriv.
- Recall: $\langle n_0 \rangle = \frac{\zeta}{1-\zeta}$, for $T < T_c$: $\frac{n_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$

$$\Rightarrow \quad \zeta = \left(1 + \frac{1}{n_0}\right)^{-1} = \left\{1 + \frac{1}{N}\frac{1}{[1-(T/T_c)^{3/2}]}\right\}^{-1} \quad \text{for } T < T_c$$

$$\Rightarrow \quad \frac{d\zeta}{dT} \sim \frac{1}{N} \quad \text{for } T < T_c$$

whereas $\frac{d\zeta}{dT} = \mathcal{O}(1)$ for $T > T_c$

$\Rightarrow$ true discontinuity and phase transition only in TD limit



Superfluid Helium-4

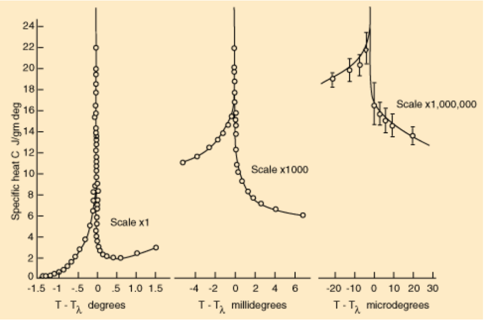
He^4: bosons

superfluid transition at $t = 2.17$ K

"λ transition"

superfluidity results from interaction of particles

not the same, but related to non-interacting BE cond.



C.6 Fermions

non-interacting fermions: e^-, in metals, He^3, white dwarfs, neutron stars, …

fermions: $\left(\text{integer} + \frac{1}{2}\right)$ spin, $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$ $\Rightarrow$ Pauli exclusion

GrCE: $\mathcal{Z}_r = \sum_{n=0,1} e^{-\beta n(E_r-\mu)} = 1 + e^{-\beta(E_r-\mu)}$: state occupied or not

$$\mathcal{Z} = \prod_r \mathcal{Z}_r$$

$$\Rightarrow \quad N = \langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} = \sum_r \frac{1}{e^{\beta(E_r-\mu)}+1} = \sum_r \langle n_r \rangle$$

$$\Rightarrow \quad \boxed{\langle n_r \rangle = \frac{1}{e^{\beta(E_r-\mu)}+1}} \qquad \text{“Fermi-dirac” (FD) disttibution}$$

μ can be positive or negative; unlike BE!

C.6.1 Ideal Fermi gas

$E = \frac{\hbar^2 k^2}{2m}$, one particle

degeneracy for spin s : $g_s = 2s+1$; e.g. e^- : $g_s = 2$

$$\Rightarrow \quad g(E) = \frac{g_s V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$N = \int \frac{g(E)}{\zeta^{-1}e^{\beta E}+1} dE \,, \qquad E_{\text{tot}} = \int \frac{E g(E)}{\zeta^{-1}e^{\beta E}+1} dE \,,$$

$$pV = -\Phi = \frac{1}{\beta}\ln\mathcal{Z} = \frac{1}{\beta}\int g(E)\,\ln\left(1+\zeta e^{-\beta E}\right) dE = \frac{2}{3}E_{\text{tot}} \qquad \Big| \text{ int by parts}$$

$$\text{high } T \quad \Rightarrow \quad \overset{\text{Sec. 5.2}}{\dots} \quad \Rightarrow \quad pv = N k_B T \left(1 + \underbrace{\frac{\lambda^3 N}{4\sqrt{2} g_s V}}_{=B_2(T)} + \dots \right)$$

virial coeff. $B_2(T) > 0$: QM statistics → increase p

C.6.2 Degenerate Fermi gas and the Fermi surface

$T \to 0 \quad \Rightarrow$ FD distr. simple: $\dfrac{1}{e^{\beta(E-\mu)}+1} \quad \to \quad \begin{cases} 1 & \text{for } E < \mu \\ 0 & \text{for } E > \mu \end{cases}$

$\Rightarrow$ Each Fermion falls to the lowest available state

Def.: Fermi energy $E_F \equiv \mu(T=0)$ at fixed N

$= \text{energy limit of occupied states at } T = 0$

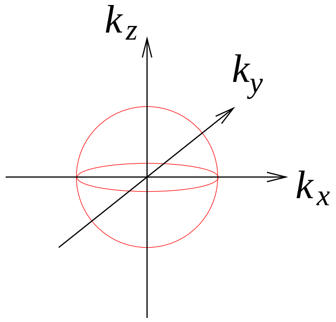
Def.: Fermi temperature $T_F \equiv \dfrac{E_F}{k_B}$

$\sim 10^4$ K for e^- in metal ; $\sim 10^7$ K in white dwarfs

Momentum space: $\hbar k_F = \sqrt{2mE_F}$

All states with $|\vec{k}| \leq k_F$ filled

Fermis "sea" or "sphere" with "surface" $|\vec{k}| = k_F$



What is $E_F(N)$?

$$T \to 0 \quad \Rightarrow \quad N = \int_0^\infty \frac{g(E)}{\zeta^{-1}e^{\beta E}+1} dE = \int_0^{E_F} g(E) dE = \frac{g_s V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$\Rightarrow \quad E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g_s}\frac{N}{V}\right)^{2/3}$$

$$\Rightarrow \quad E = \langle E \rangle = \int_0^{E_F} E\, g(E)\, dE = \frac{3}{5} N E_F$$

$\Rightarrow \quad pV = \dfrac{2}{5} N E_F$ "degeneracy pressure" $\neq 0$ even at $T = 0$

important for compact stars

C.6.3 Fermi gas at low T

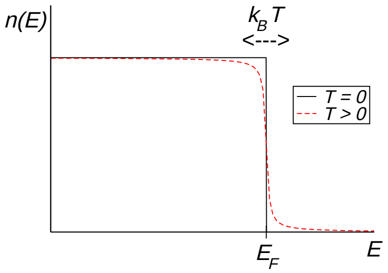
Recall: $N = \int_0^\infty \frac{g(E)}{\zeta^{-1}e^{\beta E}+1}\,dE\,, \quad E_{\text{tot}} = \int_0^\infty \frac{E\,g(E)}{\zeta^{-1}e^{\beta E}+1}\,dE\,, \quad g(E) = \frac{g_s V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{2/3} E^{1/2}$

Rigorous treatment for small T tricky because $n(E)$ discontinuous at $T=0$

Non-rigorous discussion: 1) At small T :

the FD distr. only changes near E_F

2) We assume $\left.\frac{d\mu}{dT}\right|_{T=0} = 0$



Claim: $\frac{dN}{dT} = 0$ at $T=0$ if $\frac{d\mu}{dT} = 0$ at $T=0$.

Proof: $\frac{dN}{dT} = \frac{d}{dT}\int_0^\infty \frac{g(E)}{e^{\beta(E-\mu)}+1}\,dE = \int_0^\infty g(E)\,\frac{d}{dT}\left(\frac{1}{e^{\beta(E-\mu)}+1}\right)dE$

$$\approx g(E_F)\int_0^\infty \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta(E-\mu)}+1}\right)dE$$

1) $\frac{d}{dT}$(FD) ≈ 0 except $E \approx E_F$

2) no inner deriv. of μ ; $\mu = E_F$

$$\Rightarrow \frac{dN}{dT} \approx g(E_F)\int_0^\infty \underbrace{\left(\frac{E-E_F}{k_B T^2}\right)}_{\text{odd in } E-E_F}\ \underbrace{\frac{1}{4\cosh^2\left[\beta(E-E_F)/2\right]}}_{\text{even in } E-E_F}\,dE \approx 0 \qquad \square$$

Heat capacity: $C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \int_0^\infty E\,g(E)\,\frac{\partial}{\partial T}\left[\frac{1}{e^{\beta(E-\mu)}+1}\right]dE$

Taylor: $E\,g(E) \sim E^{3/2} \quad \Rightarrow \quad E\,g(E) \approx E_F\,g(E_F) + \frac{3}{2}g(E_F)\,(E-E_F)$

$$\Rightarrow \quad C_V = \int_0^\infty \left[\underbrace{E_F\,g(E_F)}_{\text{even}} + \underbrace{\frac{3}{2}g(E_F)\,(E-E_F)}_{\text{odd}}\right]\underbrace{\frac{\partial}{\partial T}\left[\frac{1}{e^{\beta(E-E_F)}+1}\right]}_{\substack{\text{odd in } (E-E_F)\\ \text{cf. above}}}$$

$$\Rightarrow \ldots \Rightarrow \quad C_V \approx \frac{3}{2} g(E_F)\, T \int_{-\infty}^{\infty} \frac{x^2}{4\cosh^2 \frac{x}{2}}\, dx \qquad \Bigg| \; x = \beta(E - E_F)$$

Here we extended the integral from $\displaystyle\int_{-\beta E_F}^{\infty} \ldots dx$ to $\displaystyle\int_{-\infty}^{\infty} \ldots dx$ because contributions far from $E = E_F$ are negligible!

$\Rightarrow C_V \sim T\, g(E_F)$

Interpretation: at low T only particles within $\Delta E \approx k_B T$ of E_F take part in the physics

Each of these picks up an energy $\sim k_B T$

There are $\sim g(E_F)\, k_B T$ such particles $\Rightarrow$ $E \approx \text{const} + g(E_F)\, (k_B T)^2$

$\Rightarrow C_V \sim g(E_F)\, T$

Recall: $N \sim E_F^{3/2} \sim E_F\, g(E_F) \sim T_F\, g(E_F)$

$$\Rightarrow C_V \sim N k_B \frac{T}{T_F}$$

Comment: More rigorous treatment: *Sommerfeld expansion* ; cf. Sec. 3.6.4 in D. Tong [2]

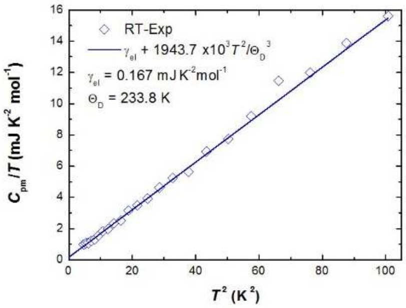
Lengthier calculation $\Rightarrow$ $C_V = N k_B \dfrac{\pi^2}{2} \dfrac{T}{T_F}$

Heat capacity of metals

Recall: phonon contribution at low T : $C_V \sim T^3$

now: FD gas = e^- contribution: $C_V \sim T$

$\Rightarrow C_V = \gamma T + \alpha T^3$



One can show that the 2 contributions are $\approx$ equal for $T^2 \sim \dfrac{T_D^3}{50\; T_F}$

Typically: $T_D \sim 10^2$ K , $T_F \sim 10^4$ K $\Rightarrow$ $\dfrac{T_D^3}{50\; T_F} = \mathcal{O}(1)$ K

Note: Surprising that e^- are well described by ideal FD gas.

Coulomb interaction? Explained by Landau's Fermi-liquid theory ...

C.6.4 White Dwarfs and the Chandrasekhar limit

When stars exhaust their fuel (H, He, ...): $T \to 0$, degeneracy pressure; "White Dwarfs"

constant density approximation $\Rightarrow$ $E_{\text{grav}} = -\frac{3}{5}\frac{GM^2}{R}$; G = Newton's constant

minimize $E_{\text{grav}} + E_{\text{kin}}$ $\Rightarrow$ ... $\Rightarrow$ $R \sim M^{-1/3}$ (example sheet)

Note: WDs shrink when mass is added!

$$\Rightarrow \quad E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g_s}\frac{N}{V}\right)^{2/3} \quad \text{increases}$$

$\Rightarrow$ gas becomes relativistic

ultrarelativistic regime with $g_s = 2$:

$$g(E) = \frac{V}{\pi^2\hbar^3c^3}\left(E^2 - \frac{m^2c^4}{2} + \dots\right) \qquad \bigg| \; E \gg m$$

$$\Rightarrow \quad E_{\text{kin}} = \int_0^{E_F} E\, g(E)\, dE = \frac{V}{\pi^2\hbar^3c^3}\left(\frac{1}{4}E_F^4 - \frac{m^2c^4}{4}E_F^2 + \dots\right)$$

$$N = \int_0^{E_F} g(E)\, dE = \frac{V}{\pi^2\hbar^3c^3}\left(\frac{1}{3}E_F^3 - \frac{m^2c^4}{2}E_F + \dots\right)$$

White Dwarf mass, volume: $M = N\, m_p$, $V = \frac{4}{3}\pi R^3$, m_p = proton mass,

eliminate E_F in E_{kin}, N to leading order

$$\Rightarrow \; \dots \; \Rightarrow \quad E_{\text{grav}} + E_{\text{kin}} = \left[\frac{3\hbar c}{4}\left(\frac{9\pi M^4}{4m_p^4}\right)^{1/3} - \frac{3}{5}GM^2\right]\frac{1}{R} + \mathcal{O}(R)$$

Case 1: leading $\frac{1}{R}$ term > 0

$\Rightarrow$ $\frac{dE_{\text{tot}}}{dR} = 0$ has a solution: $\frac{1}{R}$ term balances R term

$\Rightarrow$ star settles into new equilibrium

Case 2: leading $\frac{1}{R}$ term $r < 0$ $\Rightarrow$ no equilibrium $\Rightarrow$ neutron star or black hole

This happens if $M > M_c \sim \left(\frac{\hbar c}{G}\right)^{3/2}\frac{1}{m_p^2} \approx 1.5\ M_\odot$

C.6.5 Pauli paramagnetism (not lectured)

Consider e^- gas in magnetic field $\vec{B}$

$\Rightarrow$ 2 effects: 1) Coupling of spin to $\vec{B}$

2) Lorentz force $\vec{v} \times \vec{B}$

Here 1)

e^- has "spin up", $s = +1$, or "spin down", $s = -1$

$$\Rightarrow \quad E_{\text{spin}} = -\mu_B \, s \, B \; ; \quad \mu_B \equiv \frac{|e|\hbar}{2mc} \quad \text{"Bohr magneton"}$$

Def.: $f_n(\zeta) \equiv \dfrac{1}{\Gamma(n)} \displaystyle\int_0^\infty \frac{x^{n-1}}{\zeta^{-1}e^x + 1} \overset{!}{=} -g_n(-\zeta)$ cf. Sec. C.5.3

The two spin states now have different energies

$$\Rightarrow \quad \frac{N_\uparrow}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E_{\text{kin}}^{1/2}}{e^{\beta(E_{\text{kin}} - \mu_B B - \mu)} + 1} \, dE_{\text{kin}} = \frac{1}{\lambda^3} f_{3/2}(\zeta e^{+\beta\mu_B B})$$

$$\frac{N_\downarrow}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E_{\text{kin}}^{1/2}}{e^{\beta(E_{\text{kin}} + \mu_B B - \mu)} + 1} \, dE_{\text{kin}} = \frac{1}{\lambda^3} f_{3/2}(\zeta e^{-\beta\mu_B B})$$

Def.: Magnetization $\mathcal{M} \equiv \dfrac{\partial E}{\partial B}$

one e^- : $E_{\text{spin}} = s \, \mu_B \, B$

$$\Rightarrow \quad \mathcal{M} = \mu_B (N_\uparrow - N_\downarrow) = \frac{\mu_B V}{\lambda^3}\left[f_{3/2}\left(\zeta e^{\beta\mu_B B}\right) - f_{3/2}\left(\zeta e^{-\beta\mu_B B}\right)\right]$$

High T limit: One shows (as for bosons in Sec. C.5.2): $\zeta \to 0$

$$\Rightarrow \quad f_n(\zeta) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{\zeta^{-1}e^x + 1} dx \approx \frac{\zeta}{\Gamma(n)} \underbrace{\int_0^\infty \frac{x^{n-1}}{e^x} dx}_{=\Gamma(n)} = \zeta$$

$$\Rightarrow \quad \mathcal{M} \approx \frac{2\mu_B V \zeta}{\lambda^3} \sinh(\beta\mu_B B)$$

likewise: $N \equiv N_\uparrow + N_\downarrow \approx \dfrac{2V\zeta}{\lambda^3} \cosh(\beta\mu_B B)$

$$\Rightarrow \quad \mathcal{M} \approx \mu_B N \tanh(\beta\mu_B B) \;\; = \text{classical result!}$$

Def.: magnetic susceptibility $\chi = \dfrac{\partial \mathcal{M}}{\partial B}$

For small B : $\tanh(\beta\mu_B B) \approx \beta\mu_B B$

$$\Rightarrow \quad \chi(B=0) = \frac{N\mu_B^2}{k_B T} \qquad \text{“Curie's law”}$$

Low T limit: One can show for $\beta\mu \gg 1$: $f_n(\zeta) = \dfrac{(\ln\zeta)^n}{\Gamma(n+1)}$

$$\Rightarrow \quad \mathcal{M} = \mu_B(N_\uparrow - N_\downarrow) = \frac{\mu_B V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[(E_F + \mu_B\, B)^{3/2} - (E_F - \mu_B\, B)^{3/2}\right]$$

$$\mu_B\, B \ll E_F \quad \Rightarrow \quad \mathcal{M} \approx \frac{\mu_B^2 V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{1/2} B$$

density of states: $g(E) = \dfrac{g_s V}{4\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}\,; \qquad g_s = 2$

$$\Rightarrow \quad \mathcal{M} \approx \mu_B^2 g(E_F) B$$

$$\Rightarrow \quad \chi = \frac{\partial \mathcal{M}}{\partial B} = \mu_B^2\, g(E_F) \sim \text{const}$$

Interpretation: The e^- deep below the Fermi surface cannot flip their spin because those states are already occupied. Only e^- at the Fermi surface can flip the state. These e^- have density of states $g(E_F)$.

Note: $\chi > 0$. Such materials are “paramagnetic”

Effect 2) [Lorentz force] $\Rightarrow \ldots \Rightarrow \mathcal{M} = -\dfrac{\mu_B^2}{3} g(E_F) B \overset{!}{<} 0$; “diamagnetism”; cf. [2].

D Classical Thermodynamics

Macroscopic description of systems without regard to microscopic constituents

widely applicable: Black Holes, biological systems, engineering,...

D.1 Temperature and the 0^{th} law

Def.: "insulated system": no influence from outside, enclosed in adiabatic walls

"diathermal system": enclosed in non-moving walls, heat flow possible

"equilibrium": no change in time

defining quantities: for now: pressure p, volume V

(sometimes more, e.g. magnetic field, magnetization, ...)

0^{th} law: If two systems A, B are in equilibrium with a third system C

$\Rightarrow$ A, B are in equilibrium with each other. "transitivity"

Suppose A is in state (p_1, V_1) and C in (p_3, V_3)

A, C in equilibrium $\Rightarrow$ given p_1, V_1, p_3 fixes $V_3 = f_{AC}(p_1, V_1\,; p_3)$

B, C in equilibrium $\Rightarrow$ $V_3 = f_{BC}(p_2, V_2\,; p_3)$

$\Rightarrow$ $f_{AC}(p_1, V_1\,; p_3) = f_{BC}(p_2, V_2\,; p_3)$

Fix p_3 at some value and define $\Theta_A(p_1, V_1) \equiv f_{AC}(p_1, V_1\,; p_3)$

$\Theta_B(p_1, V_1) \equiv f_{BC}(p_2, V_2\,; p_3)$

0^{th} law: A, B are in equilibrium $\Leftrightarrow$ $\Theta_A(p_1, V_1) = \Theta_B(p_2, V_2)$

Def.: Temperature $T \equiv \Theta(p, V)$ "Equation of State"

We could choose temperature $= \sqrt{\Theta(p, V)}$ or so, but $\exists$ canonical choice:

Carnot cycle; cf. below

Reference choice for now: ideal gas $T = \dfrac{pV}{Nk_B}$

D.2 The 1^{st} law

1^{st} law: The amount of work required to change an otherwise isolated system from state 1 to state 2 is independent of how the work is done.

$\Rightarrow$ There exists a function $E(p,V)$, energy, and $\Delta E = W$

Heat: If the system is not otherwise isolated, $\Delta E \neq W$

A change resulting exclusively from T differences is called heat Q

$\Rightarrow \Delta E = Q + W$

Note: We cannot write $E = Q + W$; neither Q, W are functions of state.

$dE = \dfrac{\partial E}{\partial p}dp + \dfrac{\partial E}{\partial V}dV$ is a total derivative.

not possible for Q, W

we write $dE = đQ + đW$

E.g. specific way to do work: “squeeze” $\Rightarrow$ $đW = -pdV$

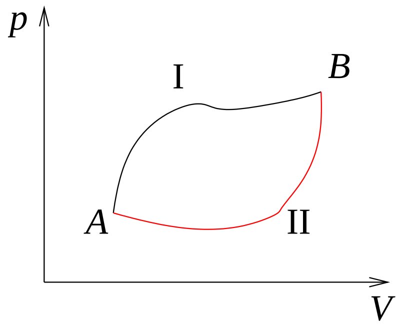
meaning of $đ$: There exists no function $W(p,V)$ such that “$dW = -pdV$”

Def.: Quasistatic process: a process of E transfer where the system is always effectively in equilibrium; view as “slow” change

vary system quasistatically from A to B

$\Rightarrow \quad \int dE = E(p_2,V_2) - E(p_1,V_1)$,

but $W = -\int pdV$ depends on path



D.3 The 2^{nd} law

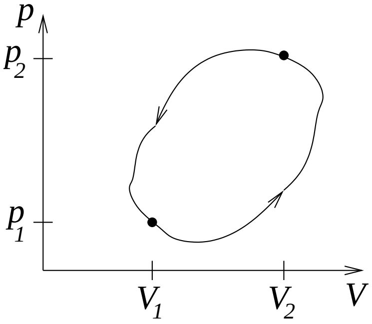
Reverstible processes

Def.: Reversible process ≡ quasi-static process that can be run backwards: "no friction"

For a roundtrip: $\oint dE = 0$

But in general: $\oint p\,dV \neq 0$

1^{st} law ⇒ $\oint đQ = \oint p\,dV$



It would be great to run this circle such that heat is transformed into work...

2^{nd} law: Kelvin: No process is possible whose sole effect is to extract heat from a hot reservoir and convert it entirely into work.

Clausius: No process is possible whose sole effect is the transfer of heat from a colder to a hotter body.

Keywords: "sole effect"! E.g. fridge uses work to cool a colder system.

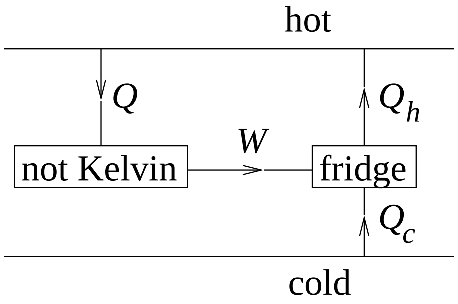
Comment: Kelvin ⇔ Clausius !

Imagine a machine in violation of Kelvin's form.

Use that to drive a fridge.

The compound machine violates Clausius form.

One similarly finds "Kelvin" ⇒ "Clausius"



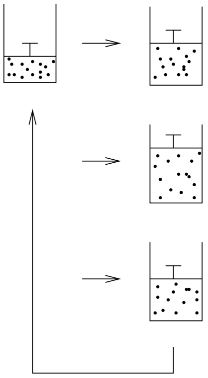
D.3.1 The Carnot cycle

Recall: for a reversible cycle: $\oint đQ = - \oint đW$

Can we use this to contradict Kelvin?

No! It must do something else: deposit heat into a cold reservoir

Consider **Carnot cycle**



A) isothermal expansion $T_H = \text{const}\,,\quad Q_H$ into system

B) adiabatic expansion $Q = 0\,,\quad T,\, p$ decrease

C) isothermal contraction $T_C = \text{const} < T_h\,,\quad Q_C$ out of system

D) adiabatic contraction $Q = 0\,,\quad T,\, p$ increase

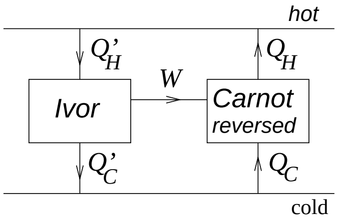
net heat absorbed: $Q_H - Q_C = W$ done by the system

<u>Def.:</u> efficiency $\eta \equiv \dfrac{W}{Q_H} = 1 - \dfrac{Q_C}{Q_H}$

Kelvin forbids $\eta = 1 \quad \Leftrightarrow \quad Q_C = 0$

Carnot's theorem: Of all engines operating between a hot reservoir H and a cold one C, a reversible one is the most efficient.

$\Rightarrow$ all reversible engines have the same $\eta = \eta(T_H, T_C)$



Proof: Consider an irreversible engine "Ivor" and use it to drive a reversed Carnot

$\Rightarrow$ $Q'_H - Q_H$ extracted from H,

$Q'_C - Q_C = Q'_H - Q_H$ deposited to C

Clausius $\Rightarrow Q'_H \geq Q_H$

$$\Rightarrow \eta_{\text{Ivor}} = 1 - \frac{Q'_C}{Q'_H} = \frac{Q'_H - Q'_C}{Q'_H} = \frac{Q_H - Q_C}{Q'_H} \leq \frac{Q_H - Q_C}{Q_H} = \eta_{\text{Carnot}}$$

Suppose Ivor were reversible. Then likewise we'd show $\eta_{\text{Ivor}} \geq \eta_{\text{Carnot}}$

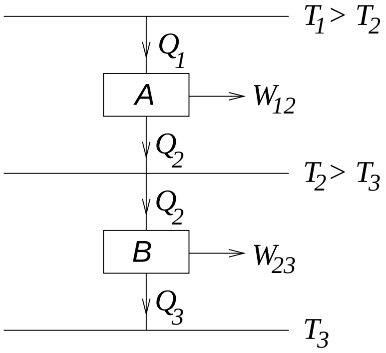
$\Rightarrow$ A reversible Ivor has the same η as Carnot. The only variables are $T_H,\ T_C$

$\Rightarrow \quad \eta = \eta(T_H, T_C)$

D.3.2 Thermodynamic temperature scale and ideal gas

0^{th} Law $\Rightarrow$ $\exists$ a function $\Theta(p, V)$ whose equality implies thermal equilibrium

What shall we choose? Θ, $\sqrt{\Theta}$, $\ldots$?



Consider 2 Carnot engines A, B

$\Rightarrow Q_2 = Q_1 \left[1 - \eta(T_1, T_2)\right]$

$\wedge \ \ Q_3 = Q_2 \left[1 - \eta(T_2, T_3)\right] = Q_1 \left[1 - \eta(T_1, T_2)\right] \left[11 - \eta(T_2, T_3)\right]$

Now regard $AB \equiv A + B$ as a compount Carnot engine

$\Rightarrow Q_3 = Q_1 \left[1 - \eta(T_1, T_3)\right]$

$\Rightarrow 1 - \eta(T_1, T_3) = \left[1 - \eta(T_1, T_2)\right] \left[1 - \eta(T_2, T_3)\right]$

T_2 cancels on rhs. $\Rightarrow$ $1 - \eta(T_1, T_2) = \dfrac{f(T_2)}{f(T_1)}$

Def.: Thermodynamic temperature: Choose T such that $\eta = 1 - \dfrac{T_2}{T_1}$

Carnot cycle for ideal gas

ideal gas: $T = \dfrac{pV}{k_B T}$

energy $E = \dfrac{3}{2} N k_B T$

Note: Without statistical physics (19th century) these are empirical

$A \to B$: isothermal expansion: $dT = 0 \quad \Rightarrow \quad dE = 0 \quad \Rightarrow \quad \text{đ}Q = -dW$

$$\Rightarrow \quad Q_H = \int_A^B \text{đ}Q = \int_A^B -dW = \int_A^B p dV = \int_A^B \frac{N k_B T_H}{V} dV = N k_B T_H \ln \frac{V_B}{V_A}$$

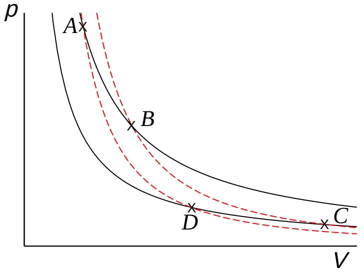
$B \to C$: adiabatic expansion: $\text{đ}Q = 0 \quad \Rightarrow \quad dE = -pdV \overset{!}{=} \dfrac{3}{2} N k_B dT$

$$pV = N k_B T \quad \Rightarrow \quad -\frac{N k_B T}{V} dV = \frac{3}{2} N k_B \, dT \quad \Rightarrow \quad -\frac{dV}{V} = \frac{3}{2} \frac{dT}{T}$$

$$\Rightarrow \quad -\ln V = \frac{3}{2} \ln T + \text{const} \quad \Rightarrow \quad p \sim V^{-5/3}$$

$$\Rightarrow \quad T\, V^{2/3} = \text{const}$$

$$\Rightarrow \quad T_H\, V_B^{2/3} = T_C\, V_C^{2/3} \quad \Rightarrow \quad \frac{T_C}{T_H} = \frac{V_B^{2/3}}{V_C^{2/3}}$$



$C \to D$: isothermal compression: $Q_C = -N k_B T_C \ln \dfrac{V_D}{V_C} = N k_B T_C \ln \dfrac{V_C}{V_D}$

Note: $Q_C > 0$; heat given away by engine

$D \to A$: adiabatic compression: $T_C\, V_D^{2/3} = T_H\, V_A^{2/3} \quad \Rightarrow \quad \dfrac{T_C}{T_H} = \dfrac{V_A^{2/3}}{V_D^{2/3}} \overset{!}{=} \dfrac{V_B^{2/3}}{V_C^{2/3}}$

Balance: $\eta = 1 - \dfrac{Q_C}{Q_H} = 1 - \dfrac{T_C}{T_H} \dfrac{\ln(V_C/V_D)}{\ln(V_B/V_A)} = 1 - \dfrac{T_C}{T_H}$

$\Rightarrow$ Thermodynamic T = ideal gas T

D.3.3 Entropy

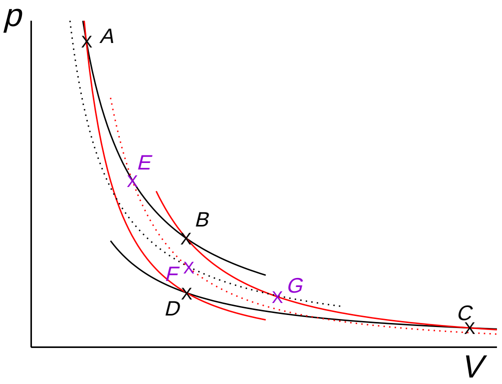
Notation: Count Q as heat absorbed by the system

$Q < 0 \;\Rightarrow\;$ system releases heat

Set $T_1 \equiv T_H, \; T_2 \equiv T_C \;\Rightarrow\; Q_1 = Q_H, \; Q_2 = -Q_C$

Carnot cycle $\Rightarrow \dfrac{Q_C}{Q_H} = \dfrac{T_C}{T_H} \;\Rightarrow$ for any Carnot cycle $\displaystyle\sum_{i=1}^{2} \frac{Q_i}{T_i} = 0$

Subdivide Carnot cycle:



Normal cycle $ABCD$: $\Rightarrow \dfrac{Q_{AB}}{T_H} + \dfrac{Q_{CD}}{T_C} = 0$

Mini cycle $EBGF$: $\Rightarrow \dfrac{Q_{GF}}{T_{FG}} + \dfrac{Q_{EB}}{T_H} = 0$

Bizarre cycle $AEFGCD$: $\Rightarrow Q_{AB} = Q_{AE} + Q_{EB}$

$$Q_{FG} = -Q_{GF}$$

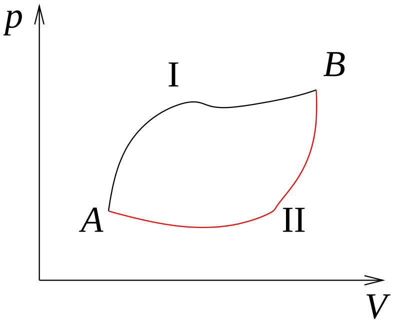
$$\Rightarrow \frac{Q_{AE}}{T_H} + \frac{Q_{FG}}{T_{FG}} + \frac{Q_{CD}}{T_C} = \frac{Q_{AB} - Q_{EB}}{T_H} - \frac{Q_{GF}}{T_{FG}} + \frac{Q_{CD}}{T_C} = 0$$

We can approximate any reversible cycle through such subdivisions!

$\Rightarrow$ for any reversible cycle $\boxed{\displaystyle\oint \frac{\text{đ}Q}{T} = 0}$

$\Rightarrow$ for any two states A, B: $\displaystyle\int_A^B \frac{\text{đ}Q}{T}$ is pathindependent,

as long as the process is reversible



<u>Def.:</u> Fix some reference state $\mathcal{O}$

For any state A with p, V we define the entropy

$S(p,V) \equiv \displaystyle\int_{\mathcal{O}}^{A} \frac{\text{đ}Q}{T}$ as given by a reversible path

Comment: $dS = \frac{đQ}{T} \quad \Rightarrow \quad 1^{\text{st}}$ law $\; dE = T\,dS - p\,dV$

$\Rightarrow$ This entropy is the same as that defined in Sec. A

Irreversibility

$$\eta_{\text{irr}} = 1 - \frac{Q'_C}{Q'_H} \leq \eta_{\text{Car}} = 1 - \frac{Q_C}{Q_H} \quad \Rightarrow \quad \frac{Q'_H - Q'_C}{Q'_H} \leq \frac{Q_H - Q_C}{Q_H}$$

Consider a reversible and an irreversible machine doing the same work:

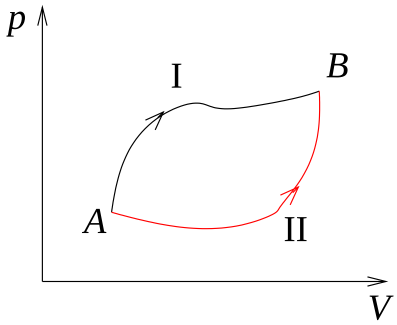
$$W = Q'_H - Q'_C = Q_H - Q_C \quad \Rightarrow \quad \frac{1}{Q'_H} \leq \frac{1}{Q_H}$$

$$\Rightarrow \quad \frac{Q'_H}{T_H} - \frac{Q'_C}{T_C} = \underbrace{\frac{Q_H}{T_H} - \frac{Q_C}{T_C}}_{=0} + (Q'_H - Q_H)\left(\frac{1}{T_H} - \frac{1}{T_C}\right) = \underbrace{(Q'_H - Q_H)}_{\geq 0}\underbrace{\left(\frac{1}{T_H} - \frac{1}{T_C}\right)}_{<0} \leq 0$$

$$\Rightarrow \quad \frac{Q'_1}{T_1} + \frac{Q'_2}{T_2} \leq 0$$

Subdivision of Carnot cycle $\Rightarrow$ $\boxed{\oint \frac{đQ}{T} \leq 0}$ for any path ; “Clausius inequality”

Consider two states A, B, path I irrev., path II rev.



$$\Rightarrow \quad \oint \frac{đQ}{T} = \int_{\text{I}} \frac{đQ}{T} - \int_{\text{II}} \frac{đQ}{T} \leq 0$$

$$\Rightarrow \quad \int_{\text{I}} \frac{đQ}{T} \leq S(B) - S(A) \; ; \quad \frac{đQ}{T} \leq dS \text{ for irrev. process}$$

Suppose, path I is adiabatic $\Rightarrow$ $đQ = 0$ $\Rightarrow$ $S(B) \geq S(A)$

If path I is also rev. $\Rightarrow$ $S(B) = S(A)$

Isolated systems can only evolve to equal or higher entropy → time arrow

D.4 Thermodynamic potentials: Free Energy, Enthalpy

We have many thermodynamic variables: p, V, T, E, S, ...

We can choose any two to describe the system. Which? Depends...

E.g. energy is best expressed as $E(S,V)$: $dE = TdS - pdV$

Free energy

good if $T = \text{const}$

$F = E - TS \quad \Rightarrow \quad dF = -SdT - pdV$ "Legendre trafo"

$$\Rightarrow \quad \left.\frac{\partial F}{\partial T}\right|_V = -S\,, \qquad \left.\frac{\partial F}{\partial V}\right|_T = -p$$

What's "free" about F?

Consider an isothermal process $\Rightarrow \quad dF = -pdV$

$$\Rightarrow \quad F(B) - F(A) = \int_A^B -p\,dV = -\text{"work done by system"}$$

$\Rightarrow F =$ measure of work free to be done at constant T

Gibbs Free Energy

Def.: Gibbs free energy $G \equiv E + pV - TS$

Consider system $\mathcal{S}$ with fixed pressure, and a reservoir $\mathcal{R}$ such that

$V_{\text{tot}} = V_{\mathcal{R}} + V_{\mathcal{S}} = \text{const}$

$$\begin{aligned} \Rightarrow S_{\text{tot}}(E_{\text{tot}}, V_{\text{tot}}) &= S_{\mathcal{R}}\left(E_{\text{tot}} - E_{\mathcal{S}}, V_{\text{tot}} - V_{\mathcal{S}}\right) + S_{\mathcal{S}}(E_{\mathcal{S}\dashv}, V_{\mathcal{S}}) \\ &\approx S_{\mathcal{R}}(E_{\text{tot}}, V_{\text{tot}}) - \frac{\partial S_{\mathcal{R}}}{\partial E_{\text{tot}}} E_{\mathcal{S}} - \frac{\partial S_{\mathcal{R}}}{\partial V_{\text{tot}}} V_{\mathcal{S}} + S_{\mathcal{S}}(E_{\mathcal{S}}, V_{\mathcal{S}}) \qquad \Bigg| \quad \left.\frac{\partial S}{\partial V}\right|_E = \frac{p}{T} \\ &= S_{\mathcal{R}} - \frac{E_{\mathcal{S}} + p\,V_{\mathcal{S}} - T\,S_{\mathcal{S}}}{T} \end{aligned}$$

S_{tot} max if Gibbs free energy $G = E + pV - TS = F + pV$ is min.

$dG = -SdT + Vdp$

with N: $dF = -SdT - pdV + \mu dN, \quad dG = -SdT + Vdp + \mu dN$

Comment: $G = G(T, p, N)$; only N is extensive $\Rightarrow$ $G(p, T, N) = \mu(p, T)\, N$

$$\mu = \frac{\partial G}{\partial N} = \frac{G}{N}$$

Enthalpy

Def.: Enthalpy $H \equiv E + pV \quad \Rightarrow \quad dH = T\, dS + V\, dp$

E, F, G, H are "thermodynamic potentials"

D.4.1 Maxwell's relations

Regard $E = E(S, V)$; 1^{st} law: $dE = T\, dS - p\, dV$

$$\Rightarrow \left.\frac{\partial E}{\partial S}\right|_V = T\,, \qquad \left.\frac{\partial E}{\partial V}\right|_S = -p$$

Second derivatives commute $\Rightarrow \dfrac{\partial^2 E}{\partial S\, \partial V} = \dfrac{\partial^2 E}{\partial V\, \partial S}$

$$\Rightarrow \boxed{-\left.\frac{\partial p}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S} \qquad \text{“Maxwell Relations”}$$

mathematically trivial, physically non-obvious!

Play the same game for F: $dF = -S\, dT - p\, dV$

$$\Rightarrow \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$$

and for G, H: $\left.\dfrac{\partial S}{\partial p}\right|_T = -\left.\dfrac{\partial V}{\partial T}\right|_p \,, \quad \left.\dfrac{\partial T}{\partial p}\right|_S = \left.\dfrac{\partial V}{\partial S}\right|_p \quad \longrightarrow$ 4 Maxwell relations

To remember: cross-multiplication always → TS, pV ; 4 ways to construct Eqs.

keep the conjugate variable constant: $\left.\dfrac{\partial T}{\partial\, .}\right|_S \,, \quad \left.\dfrac{\partial S}{\partial\, .}\right|_T \,, \quad \left.\dfrac{\partial p}{\partial\, .}\right|_V \,, \quad \left.\dfrac{\partial V}{\partial\, .}\right|_p$

minus signs: not obvious . . . , sorry

Heat capacity revisited

Taking further derivatives of the Maxwell eqs. , we can derive

further useful relations → example sheet

These include for $C_V = T \left.\frac{\partial S}{\partial T}\right|_V$, $C_p = T \left.\frac{\partial S}{\partial T}\right|_p$:

$$\left.\frac{\partial C_V}{\partial V}\right|_T = T \left.\frac{\partial^2 p}{\partial T^2}\right|_V , \quad \left.\frac{\partial C_p}{\partial p}\right|_T = -T \left.\frac{\partial^2 V}{\partial T^2}\right|_p$$

$$C_p - C_V = T \left.\frac{\partial V}{\partial T}\right|_p \left.\frac{\partial p}{\partial T}\right|_V$$

For ideal gas: $C_p - C_V = N k_B$

$C_p > C_V$ because more heat needed to increase T at constant pressure; some goes into work

D.5 The 3$^{\text{rd}}$ law

We have only considered changes in entropy so far; no reference S_0

3$^{\text{rd}}$ law: "Nernst's postulate": $\lim_{T\to 0} S(T) = 0$

can be relaxed to: $\frac{S}{N} \to 0$ for $T \to 0\,,\ N \to \infty$

⇒ the ground state entropy must not grow too much with N

Comment: In Sec. A.2.2, we saw: $\Delta S = \int \frac{C_V}{T}\, dT$

integral must converge ⇒ $C_V \sim T^n$ with $n > 0$

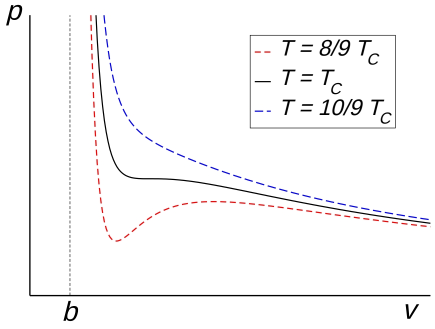
ideal gas: $C_V = \frac{3}{2} N k_B \sim T^0$ violates 3$^{\text{rd}}$ law

⇒ The 3$^{\text{rd}}$ law tells us that the low T world is QM, not classical

E Phase transitions

Abrupt, discontinuous changes in systems; cf. BE condensate

E.1 Liquid-gas transition

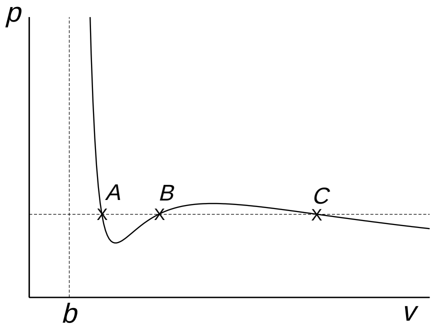


Recall van der Waals EOS: $p = \frac{k_B T}{v-b} - \frac{a}{v^2}$; $v = \frac{V}{N}$

3 shapes: $T > T_C$: $\approx$ ideal gas; ignore $\frac{a}{v^2}$ term

$T = T_C$: $k_B T_C = \frac{8a}{27b}$ $\rightarrow$ inflection point

$T < T_C$: $k_B T \approx \frac{a}{v}$ realized in range $v > b$ $\Rightarrow$ local min, max



At $T < T_C$: for some pressures: > 1 volume possible

V_B: $\left.\frac{dp}{dv}\right|_T > 0$ $\Rightarrow$ unstable

expand system $\rightarrow$ p increases

squeeze system $\rightarrow$ p decreases

V_A : $v \gtrsim b$: atoms are as close as they can be $\rightarrow$ liquid

van der Waals is not supposed to work for

liquids, but let's ignore that for now

V_C : $v \gg b$: gas

E.1.1 Phase equilibrium

What's going on between A and C? Co-existence of gas, liquid

$\rightarrow$ chemical equilibrium $\mu_{\text{liq}} = \mu_{\text{gas}}$

Recall: Gibbs free energy G: $\mu = \frac{G}{N}$

Maxwell construction

Clearly, between A, B, $p(v)$ does not behave like van der Waals

At A) $\mu = \mu_{\text{liq}}$

At C) $\mu = \mu_{\text{gas}}$

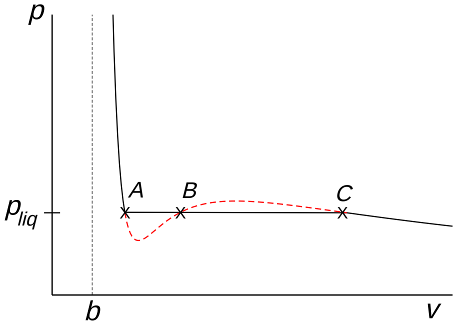
We now assume that $\mu_{\text{liq}} = \mu_{\text{gas}}$ and from A to C, μ does not change.

What does this imply for $p(v)$

along isotherm: $d\mu = \left.\frac{\partial \mu}{\partial p}\right|_T dp$

$$\left.\frac{\partial \mu}{\partial p}\right|_T = \frac{1}{N}\left.\frac{\partial G}{\partial p}\right|_{N,T} = \frac{1}{N}V$$

$$\Rightarrow \mu(p,T) = \mu_{\text{liq}} + \int_{p_{\text{liq}}}^{p} \frac{V(\tilde{p},T)}{N}\, d\tilde{p}$$



from A to C we don't want μ to change. $\frac{V}{N} > 0$

$\Rightarrow$ the only way to avoid a change in μ is $dp = 0$

$\Rightarrow$ horizontal line from A to C in pv diagram

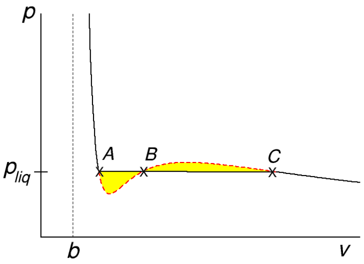
But what is p_{liq} ?

Maxwell: Assume the van der Waals EOS were correct.

$$\Rightarrow \mu(p,T) = \underbrace{\mu_{\text{liq}}}_{=\mu_A} + \int_{p_{\text{liq}}}^{p} \frac{V(\tilde{p},T)}{N}\, d\tilde{p} \overset{!}{=} \underbrace{\mu_{\text{gas}}}_{=\mu_C}$$

$$\Rightarrow \int_A^C V\, dp = \int_A^B V\, dp + \int_B^C V\, dp \overset{!}{=} 0$$

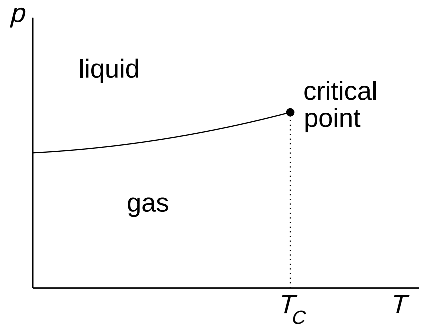
$\Rightarrow$ The shaded areas AB and BC must be equal



$\Rightarrow$ The coexistence isotherm between A and C is $p = \text{const} = p_{\text{liq}}$ such that $A_{AB} = A_{BC}$

As we move from A to C, more and more liquid becomes gas.

E.1.2 The Clausius-Clapeyron Equation



Consider the liquid-gas transition in the $p-T$ plane.

Say, we sit in the gas phase at $T < T_C$ very close to the liquid edge.

Then increase p just a bit.

→ liquid ; V shrinks discontinuously.

→ phase transition

$\mu_{\text{liq}} = \mu_{\text{gas}} \quad \Rightarrow \quad G_{\text{liq}} = G_{\text{gas}}$

how does G change along the line of phase transition?

$$dG_{\text{liq}} = -S_{\text{liq}}dT + V_{\text{liq}}dp \overset{!}{=} dG_{\text{gas}} = -S_{\text{gas}}dT + V_{\text{gas}}dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{S_{\text{gas}} - S_{\text{liq}}}{V_{\text{gas}} - V_{\text{liq}}}$$

Def.: latent heat $L \equiv (S_{\text{gas}} - S_{\text{liq}})\,T$

$$\Rightarrow \text{Clausius-Clapeyron Eq.:} \quad \frac{dp}{dT} = \frac{L}{T(V_{\text{gas}} - V_{\text{liq}})}$$

Def.: For an n^{th} order phase transition, the n^{th} deriv. of the thermodynamic potential (typically F or G) is discontinuous.

Here: $V = \dfrac{\partial G}{\partial p}\,, \quad S = -\dfrac{\partial F}{\partial T}$ discontinuous

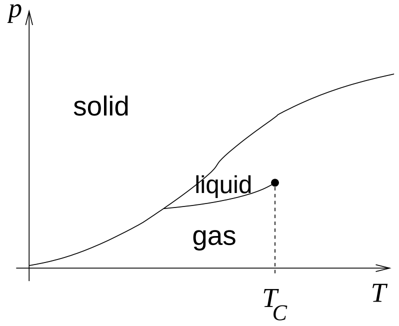
⇒ liquid-gas phase transition is 1^{st} order.

As $T \to T_C$: $V_{\text{liq}} \to V_{\text{gas}}$.

One can show that at T_C we have a 2^{nd} order Ph.Tr.

At $T > T_C$ no distinction between gas, liquid.

In general, phase diagrams also include a solid phase.



E.1.3 The critical point

Critical point: inflection point in $p = p(V)$

$$\Rightarrow \frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0 \quad \Rightarrow \ldots \Rightarrow \quad k_B T_C = \frac{8a}{27b}$$

Now consider vdW EOS: $pv^3 - (pb + k_B T)v^2 + av - ab = 0$

$T < T_C \quad \Rightarrow \;$ 3 roots

$T > T_C \quad \Rightarrow \;$ 1 root

$T = T_C$ all 3 roots coincide

$$\Rightarrow p_C (v - v_C)^3 = 0$$

Compare coeffs. $\Rightarrow \; k_B T_C = \dfrac{8a}{27b}\,, \quad v_C = 3b\,, \quad p_C = \dfrac{a}{27b^2}$

<u>The law of corresponding states</u>

Invert the last relations: $b = \dfrac{v_C}{3}\;; \quad a = \dfrac{27}{64}\dfrac{(k_B T_C)^2}{p_C}$

<u>Def.:</u> reduced variables: $\bar{T} \equiv \dfrac{T}{T_C}\,, \quad \bar{v} \equiv \dfrac{v}{v_C}\,, \quad \bar{p} \equiv \dfrac{p}{p_C}$

$$\Rightarrow \quad \text{vdW:} \;\; \bar{p} = \frac{8}{3}\frac{\bar{T}}{\bar{v} - \frac{1}{3}} - \frac{3}{\bar{v}^2}$$

p_C, T_C, v_C only depend on 2 vars.: a, b

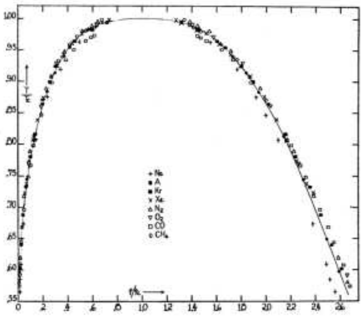
$\Rightarrow$ eliminate a, b

$\Rightarrow$ compressibility ratio $\dfrac{p_C\, v_C}{k_B T_C} = \dfrac{3}{8}$ should hold for all gases

Experiment: $\dfrac{p_C\, v_C}{k_B T_C} = 0.28 \ldots 0.3\,$. OK, given that vdW is not really good for liquids.

Coexistence curve for various gases in reduced variables is nearly universal: Ne, O_2, CO, CH_4,...

Chemical makeup appears irrelevant → "universal" behaviour



Critical exponents

1) How does $v_{\text{gas}} - v_{\text{liq}}$ behave at the critical point?

$$\text{vdW:}\quad \bar{p} = \frac{8}{3}\,\frac{\bar{T}}{\bar{v}-\frac{1}{3}} - \frac{3}{\bar{v}^2} = \frac{8\bar{T}}{3\bar{v}_{\text{liq}}-1} - \frac{3}{\bar{v}_{\text{liq}}^2} = \frac{8\bar{T}}{3\bar{v}_{\text{gas}}-1} - \frac{3}{\bar{v}_{\text{gas}}^2}$$

$$\Rightarrow\quad \bar{T} = \frac{(3\bar{v}_{\text{liq}}-1)\,(3\bar{v}_{\text{gas}}-1)\,(\bar{v}_{\text{liq}}+\bar{v}_{\text{gas}})}{8\bar{v}_{\text{gas}}^2\,\bar{v}_{\text{liq}}^2} \qquad (*)$$

Critical point $\Rightarrow\quad \bar{v}_{\text{gas}}\,,\ \bar{v}_{\text{liq}} \to 1 \quad\Rightarrow\quad \bar{T} \to 1$

Expand $(*)$ in $\epsilon = \bar{v}_{\text{gas}} - \bar{v}_{\text{liq}} \quad\Rightarrow\quad \bar{v}_{\text{gas}} = 1 + \frac{\epsilon}{2}\,,\quad \bar{v}_{\text{liq}} = 1 - \frac{\epsilon}{2}$

$$\Rightarrow \ldots \Rightarrow\quad \bar{T} \approx 1 - \frac{1}{16}\,(\bar{v}_{\text{gas}} - \bar{v}_{\text{liq}})^2$$

$$\Rightarrow v_{\text{gas}} - v_{\text{liq}} \sim (T_C - T)^{1/2}$$

2) How does v change with p along a critical isotherm?

There exists a unique function $p = p(v, T_C)$

Furthermore $\dfrac{\partial p}{\partial v} = \dfrac{\partial^2 p}{\partial v^2} = 0$ at critical point

Taylor expansion $\Rightarrow\quad p - p_C \sim (v - v_C)^3$

3) How does the compressibility $\kappa \equiv -\dfrac{1}{v}\,\dfrac{\partial v}{\partial p}\Big|_T$ change as $T \to T_C$ from $T > T_C$?

At the critical point: $\dfrac{\partial p}{\partial v}\Big|_{T_C} = 0$

$$\text{Taylor expand in } T - T_C \quad\Rightarrow \left.\frac{\partial p}{\partial v}\right|_{T, v=v_C} = -\alpha(T - T_C) + \ldots \qquad \Big|\ \alpha = \text{const}$$

$$\Rightarrow \kappa \sim \frac{1}{T - T_C}$$

How do these agree with experiment? How good is our vdW based model?

Answer: Experimental results do not depend on the type of gas. Good!

But the exact scaling is different: $v_{\text{gas}} - v_{\text{liq}} \sim (T_C - T)^{\approx 0.32}$

$$p - p_C \sim (v - v_C)^{\approx 4.8}$$

$$\kappa \sim \frac{1}{(T - T_C)^{\approx 1.2}}$$

The exponents are called "critical exponents"

Conclusion: The vdW EOS does a good job qualitatively, but is quantitatively inaccurate.

One can show that for $T \to T_C$: $\dfrac{\Delta N^2}{N} \sim \kappa \sim \dfrac{1}{T - T_C}$, i.e. diverges.

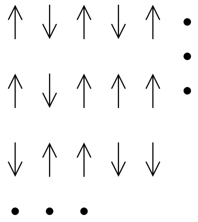
We work with averaged quantities! Becomes inaccurate for large fluctuations

→ New physical areas...

E.2 The Ising model

N sites in a d-dimensional lattice: each has spin up: ↑, $s_i = +1$, or

spin down: ↓, $s_i = -1$



magn. field $B \Rightarrow E_B = -B \sum_{i=1}^{N} s_i$; ↑ has lower energy ⇒ ↑ is "favored"

In contrast to our 2-state spin system from Sec. A.2.3, we use here interaction:

$$E_I \equiv -J \sum_{\langle ij \rangle} s_i \, s_j$$

$\langle ij \rangle$ = summation over "nearest-neighbour pairs"

Number of nearest neighbours: q ; $d = 1 \Rightarrow q = 2$, $d = 2 \Rightarrow q = 4$, $d \Rightarrow q = 2d$

We consider $J > 0$ ⇒ neighbours prefer to be aligned.

CE: $Z = \sum_{\{s_i\}} e^{-\beta E[s_i]} = \sum_{\{s_i\}} \exp\left[\beta\left(J \sum_{\langle ij \rangle} s_i \, s_j + B \sum_i s_i\right)\right]$

<u>Def.:</u> magnetization: $m \equiv \dfrac{1}{N} \sum_i \langle s_i \rangle = \dfrac{1}{N\beta} \dfrac{\partial}{\partial B} \ln Z$

E.2.1 Mean-field theory

m is the average spin per particle

$$\Rightarrow s_i\, s_j = [(s_i - m) + m]\;[(s_j - m) + m]$$
$$= (s_i - m)(s_j - m) + m(s_j - m) + m(s_i - m) + m^2$$

Mean field theory: Fluctuations in the particle spin are small when summed over $\langle ij\rangle$.

This is a weaker assumption than assuming small $\langle (s_i - m)^2\rangle$!

$$\Rightarrow \;\; E = E_B + E_I = -J\sum_{\langle ij\rangle}\left[m(s_i + s_j) - m^2\right] - B\sum_i s_i$$
$$= \underbrace{\frac{1}{2}JNq}_{(1)}\, m^2 - (\underbrace{Jqm}_{(2)} + B)\sum_i s_i$$

(1) Each particle has q nearest neighbours: Nq pairs, but every one is counted twice!

$\Rightarrow$ The sum $\sum_{\langle ij\rangle}$ has $\frac{Nq}{2}$ pairs – try for small N ...

For periodic boundary conditions this is exact.

For non-periodic BCs, a good approximation for large N.

(2) Again, we have $\frac{Nq}{2}$ pairs in the sum.

Particles i and j appear equally in the sum $s_i + s_j$

$\Rightarrow$ one sum over i and the factor $\frac{1}{2}$ cancels the factor 2 from the sum $s_i + s_j$.

Comments:

- The $\frac{1}{2}JNqm^2$ term in E is merely a constant factor in Z

  $\Rightarrow$ no effect on physics

- We now have a non-interacting system with $B_{\text{eff}} = B + Jqm$

$$Z = e^{-\frac{1}{2}\beta JNqm^2}\sum_{s_1}\cdots\sum_{s_N} e^{\beta B_{\text{eff}}\sum_i s_i} = \left(\sum_{s_i=\pm 1} e^{\beta B_{\text{eff}} s_i}\right)^N$$

$$\Rightarrow Z = e^{-\frac{1}{2}\beta JNqm^2}\left(e^{-\beta B_{\text{eff}}} + e^{\beta B_{\text{eff}}}\right)^N = e^{-\frac{1}{2}\beta JNqm^2}\, 2^N \cosh^N \beta B_{\text{eff}}$$

$$\Rightarrow m = \frac{1}{N\beta}\frac{\partial}{\partial B}\ln Z = \tanh(\beta B + \beta Jqm)\ ; \qquad \text{implicit equation for } m$$

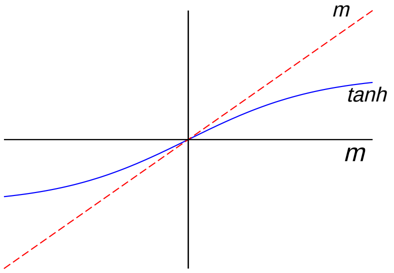
1) $\boldsymbol{B = 0}$: $\Rightarrow m = \tanh(\beta Jqm)$

$\tanh x \approx x - \frac{1}{3}x^3 \Rightarrow$ slope of $\tanh(\beta Jqm)$ at $m = 0$: βJq

a) $\beta Jq < 1 \Rightarrow$ only one solution: $m = 0$

at high T (small β), temperature randomizes

the system $\Rightarrow$ no average magnetization



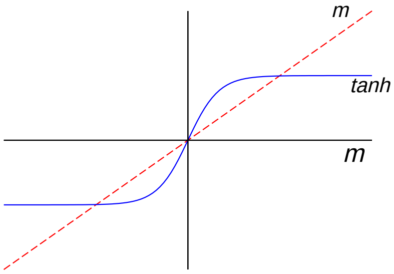
b) $\beta Jq > 1 \Rightarrow$ 3 solutions: $m = 0, \quad \pm m_0$

$m = 0$ can be shown to be unstable.

at low T, interactions win out and align the spins (either up or down)

$T \to 0 : \beta \to \infty \quad \Rightarrow$ tanh becomes Heaviside function

$\Rightarrow \quad m_0 = \pm 1$



The critical T seperating a), b) is: $k_B T_C = Jq$

Note: Magnetization turns off at finite $T = T_C$

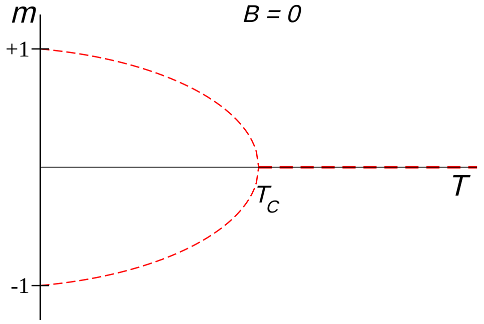
2) $\boldsymbol{B \neq 0}$: a) $\beta \to 0 : m = \tanh\left[\beta(B + Jqm)\right] \approx \beta(B + Jqm)$

$$\Rightarrow m \approx \frac{B}{k_B T}$$

Note: now m smoothly decreases to 0 at infinite T

b) low T: m asymptotes to ± 1 as $T \to 0$, but the sign of B determines the sign of m : $\text{sign}(m) = \text{sign}(B)$;

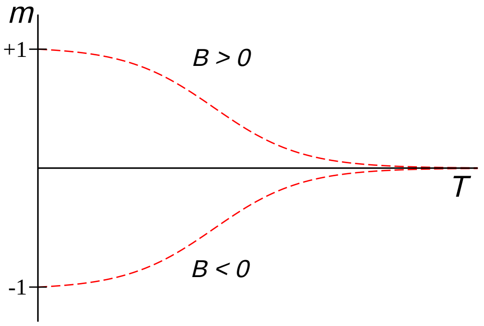
the other solution can be shown to be metastable



Summary

$\boldsymbol{B = 0}$:
- phase transition at $T = T_C$
- can be shown to be of 2nd order

  as we vary T at $B = 0$



$\boldsymbol{B \neq 0}$:
- no phase transition as we vary T
- but if we vary B at fixed $T < T_C$, we have

  a phase transition: m swaps sign
- $m = \frac{1}{N\beta}\frac{\partial}{\partial B}\ln Z = -\frac{1}{N}\frac{\partial}{\partial B}F$

  $\Rightarrow$ 1st order phase transition

E.2.2 Critical exponents

Let's compare the 1st order phase transition of the Ising model with the liquid-gas one.

Ising: Fix $T < T_C$, vary B from positive to negative (or vice versa)

$\Rightarrow$ 1st order transition: magnetization m jumps

liq.-gas: Fix $T < T_C$, vary pressure across the liquidization value

$\Rightarrow$ 1st order transition: v jumps from v_{gas} to v_{liq}

Critical exponents; cf. gas-liquid

1) m at $B=0$ as $T \to T_C$

Recall: $m = \tanh(\beta B + \beta J q m) = \tanh(\beta J q m)$; $\tanh x \approx x - \frac{1}{3}x^3$

$T = T_C \Rightarrow \beta J q = 1$

$T \lesssim T_C \Rightarrow \beta J q = 1 + \epsilon$

$$\Rightarrow m = \tanh\left[(1+\epsilon)m\right] \approx (1+\epsilon)m - \frac{(1+\epsilon)^3}{3}m^3 \approx (1+\epsilon)m - \frac{1+3\epsilon}{3}m^3$$

$$\Rightarrow 1 \approx 1 + \epsilon - \frac{1+3\epsilon}{3}m^2 \quad \Rightarrow \quad \left(\frac{1}{3}+\epsilon\right)m^2 \approx \epsilon \quad \Rightarrow \quad m \approx \pm\sqrt{3\epsilon}$$

$$\epsilon = \frac{Jq}{k_B T} - \frac{Jq}{k_B T_C} = \frac{Jq}{k_B}\frac{1}{T T_C}(T_C - T) \approx \frac{Jq}{k_B T^2}(T_C - T)$$

$$\Rightarrow \boxed{m \sim \pm(T_C - T)^{1/2}}$$

$$\Rightarrow \frac{dm}{dT} \sim (T_C - T)^{-1/2} \to \infty \ \text{ at } \ T_C$$

cf. $v_{\text{gas}} - v_{\text{liq}} \sim (T_C - T)^{1/2}$

2) Fix $T = T_C$, how does m vary as $B \to 0$?

At $T = T_C$: $\beta J q = 1 \quad \Rightarrow \quad m = \tanh\left[\frac{B}{Jq} + m\right]$

Note: For simplicity we assume now that m grows less than linearly with B

We shall see that this is true.

Expand tanh for small B, m

$$\Rightarrow m \approx \frac{B}{Jq} + m - \frac{1}{3}\left(\frac{B}{Jq} + m\right)^3 \approx \frac{B}{Jq} + m - \frac{1}{3}m^3 + \ldots$$

$$\Rightarrow \frac{1}{3}m^3 \approx \frac{B}{Jq} \quad \Rightarrow \quad m \sim B^{1/3}$$

cf. $v_{\text{gas}} - v_{\text{liq}} \sim (p - p_C)^{1/3}$ along isotherm

3) **<u>Def.:</u>** magnetic susceptibility $\chi \equiv N \left.\frac{\partial m}{\partial B}\right|_T$; cf. gas compressibility

Fix $B = 0$; how does χ change as $T \to T_C$ from $T \gtrsim T_C$?

$$m = \tanh(\beta B + \beta\, Jqm) \quad \Rightarrow \quad \chi = \frac{N\beta}{\cosh^2(\beta\, Jqm)}\left(1 + \frac{Jq}{N}\chi\right) \text{ at } B = 0$$

$$T \to T_C \quad \Rightarrow \quad \beta\, Jq \to 1 \text{ and } m \to 0 \quad \Rightarrow \quad \cosh^2(\beta\, Jqm) \to 1$$

$$\Rightarrow \chi = N\beta\left(1 + \frac{Jq}{N}\chi\right) \quad \Rightarrow \quad N\beta \approx \chi(1 - \beta\, Jq) \sim \chi\left(\frac{1}{T_C} - \frac{1}{T}\right)$$

$$\Rightarrow \ldots \Rightarrow \quad \chi \sim (T - T_C)^{-1} \; ; \quad \text{cf. } \kappa \sim \frac{1}{T - T_C} \text{ for gas}$$

How good are our mean-field predictions? Depends on dims. of lattice...

$d = 1$: Wildly wrong: Analytic solution of $d = 1$ Ising model

$\Rightarrow$ no phase transition; cf. Sec. 5.2.4 in [2]

$d = 2$: $m_0 \sim (T_C - T)^\alpha$: $\alpha_{\text{an}} = \frac{1}{8}$ $\alpha_{\text{mf}} = \frac{1}{2}$

$m \sim B^{1/\delta}$: $\delta_{\text{an}} = 15$ $\delta_{\text{mf}} = 3$

$\chi \sim (T - T_C)^{-\gamma}$: $\gamma_{\text{an}} = \frac{7}{4}$ $\gamma_{\text{mf}} = 1$

$d = 3$: Numerics $\Rightarrow$ $\alpha \approx 0.32$, $\delta \approx 0.48$, $\gamma \approx 1.2$

Same as van der Waals! Both are wrong in the same way.

Memory of microphysics has been lost...

$d = \infty$: Mean field theory turns out to be exact.

Explanation: Fluctuations spoil mean-field theory approximation.

small d $\Rightarrow$ few neighbors $\Rightarrow$ high fluctuations

E.3 Landau Theory

Unified way to look at phase transitions: Microphysics arbitrary.

Key variable: Free energy F; we defined it for equilibrium configurations.

Now take its definition for any configs.

e.g.: Ising model: $F = -\frac{1}{\beta} \ln Z = \frac{1}{2} JNqm^2 - \frac{N}{\beta} \ln\left(2 \cosh \beta B_{\text{eff}}\right)$

Note: F is a function of m

Equilibrium: F can be shown to be minimal

$$\Rightarrow \frac{\partial F}{\partial m} = 0 \quad \Rightarrow \quad m = \tanh(\beta B_{\text{eff}}) \; ; \quad \text{cf. Sec. E.2.1}$$

In Landau theory, m is called an order parameter:

$m \neq 0 \;\; \Rightarrow$ order ; $\qquad m = 0 \;\; \Rightarrow$ randomness

E.g. gas-liquid transition: $m = v_{\text{gas}} - v_{\text{liq}}$

E.3.1 Second order phase transitions

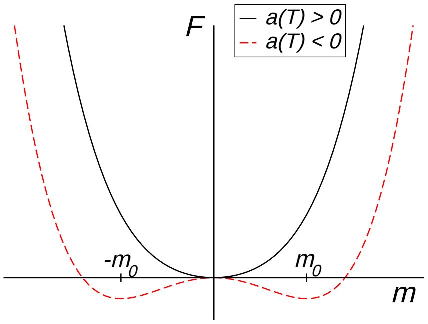
Here we consider systems with symmetry under $m \to -m$

$\Rightarrow$ Expansion of F in m has only even powers: $F(T;m) = F_0(T) + a(T)\, m^2 + b(T)\, m^4 + \ldots$

$B = 0$ Ising model: Use $\cosh x \approx 1 + \frac{1}{2}x^2 + \frac{1}{4!}x^4$, $\quad \ln(1+y) \approx y - \frac{1}{2}y^2$, $\quad$ Taylor in m, B

$$\Rightarrow \ldots \Rightarrow F(T;m) = -Nk_BT \, \ln 2 + \left[\frac{NJq}{2}(1 - Jq\beta)\right] m^2 + \frac{N\beta^3 J^4 q^4}{12} m^4 + \ldots$$

Equilibrium: $\frac{\partial F}{\partial m} = 0\,.$ Solutions depend on signs of $a(T)$, $b(T)$.



We assume $b(T) > 0$; otherwise we'd need m^6 terms.

Consider $F(m)$: $\;a(T) > 0 \;\; \Rightarrow \;\; F$ has only one extremum.

$a(T) < 0 \;\; \Rightarrow \;\; F$ has three extrema.

Ising model: $\;a(T) > 0 \;\; \Leftrightarrow \;\; T > T_C \;\; \Rightarrow$ 1 equilibrium: $m = 0$

$a(T) < 0 \;\; \Leftrightarrow \;\; T < T_C \;\; \Rightarrow$ 2 equilibria: $m = \pm m_0$

If $a(T)$ is smooth $\Rightarrow$ Equilibrium changes smoothly from $m = 0$ to $m \neq 0$ at $T < T_C$.

$\Rightarrow$ 2^{nd} order phase transition at $T = T_C$ where $a(T_C) = 0$

Once we know the equilibrium value m, plug this into $F(T; m)$

$$\to\ F(T)\ \to\ \text{all physical quantities: } S = -\frac{\partial F}{\partial T}\,, \quad C_V = T\left.\frac{\partial S}{\partial T}\right|_V\,, \ \ldots$$

Critical exponents: assume that near T_C: $b(T) \approx b_0\,,\quad a(T) \approx a_0(T - T_C)$

$$\Rightarrow \ldots \Rightarrow \quad m_0 \approx \pm\sqrt{\frac{a_0}{2b_0}}(T_C - T)^{1/2} \quad \text{for} \quad T < T_C$$

Comments: Landau theory predicts $m_0 \sim (T_C - T)^{1/2}$ for all dims. d of the Ising model

At $T < T_C$ the system must choose between m_0, $-m_0$ → symmetry breaking

E.3.2 First order phase transitions

Now consider systems where F also has odd powers of m:

$$F(T; m) = F_0(T) + \alpha(T)m + a(T)m^2 + \gamma(T)m^3 + b(T)m^4 + \ldots$$

Example: $B \neq 0$ Ising model: Taylor expansion in m, B:

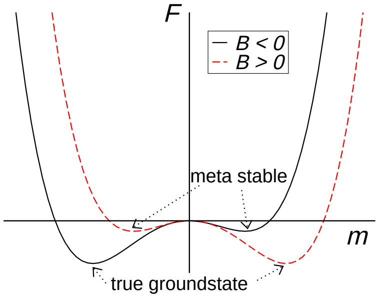
$$F(T; m) = -Nk_BT\,\ln 2 + \frac{JNq}{2}m^2 - \frac{N}{2k_BT}(B + Jqm)^2 + \frac{N}{12(k_BT)^3}(B + Jqm)^4 + \ldots$$

We again assume $b(T) > 0$ for all T

Low T: either one min or two min, one max

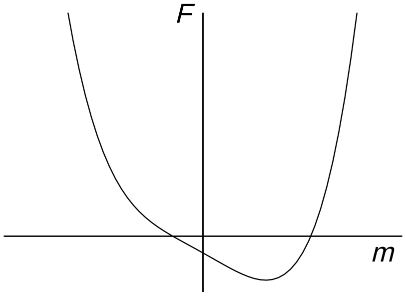
When $\alpha(T)$, $\gamma(T)$ change sign

$\Rightarrow$ true ground state changes from $m < 0$ to $m > 0$



High T: double-well potential is lost

$\Rightarrow$ single min in F shifted from $m = 0$; e.g.:



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