Physics 3P41 Statistical Physics

<u>Instructor</u>: E. Sternin B206, ext. 3414
H 208, ext. 4457
edik@brocku.ca

<u>Lectures</u>: MWTh 08:00-09:00 MC J404

<u>Tutorials</u>: TBA [2hrs every other week]

<u>Prerequisite</u>: PHYS 2P50

<u>Marks</u>:
- – homework assigned, not marked
- 65% – 3 tutorial tests, 2hrs each
- 35% – seminar + report (no exam)

<u>Text</u>: Kittel & Kroemer, "Thermal Physics", 2nd ed
W.H. Freeman & Co., 1980

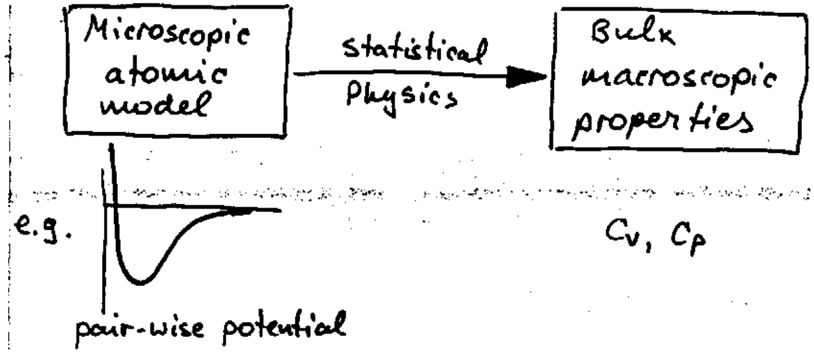
<u>Calendar</u>: "Introduction to probability distribution function, accessible states, entropy, temperature, partition function, and relation to thermodynamic functions"

<u>Other references</u>:
F. Reif, "Statistical Physics", 1965
M. Zemansky, "Heat and thermodynamics", 1981

Thermal Physics = Thermodynamics + Statistical Physics

<u>Thermodynamics</u>: bulk properties such as volume, pressure, specific heat – classical physics, <u>macro</u>scopic

<u>Statistical physics</u>: atomic viewpoint, a <u>micro</u>scopic model describing a limited number of particles or states <u>scaled up</u> to give thermodynamic (<u>macro</u>scopic) laws



Statistical physics is the study of special properties arising when a very large # of microscopic subsystems come together, a "science of large numbers"

Developments in physics may improve our microscopic model, but methods of scaling up are well-established.

Basic problem: must explain experimental facts

For a system of particles, e.g. a gas

- there exists a distribution of kinetic energy among particles, some have more some less
- total energy is related to temperature
- never see all "cold" particles go left, all "hot" ones go right

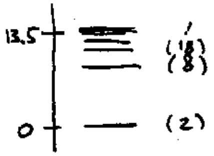
Basic approach: relating statistics to Physics

1. define states of the system
2. postulate probability for each state
3. determine the "actual" state of the system in the probabilistic sense
4. relate the state of the system to macroscopic physical quantities: entropy, temperature, free energy (and pressure, chemical potential, etc. derived from these)

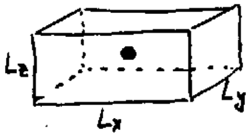
States of the system are quantum states

Ex a real system, Hydrogen atom

$$U_n = 13.5\,\text{eV}\left(1 - \frac{1}{n^2}\right)$$



Ex a real system, a particle in a box



- classical mechanics $U = \frac{m}{2}\left[v_x^2 + v_y^2 + v_z^2\right]$

  E is a continuous function

  ⇒ a continuum of states

- Q.M. $U = \frac{\pi^2\hbar^2}{2m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$ = a discrete function

  ⇒ discrete states (n_x, n_y, n_z)

[follows from the quantization of momentum]

There are advantages in dealing with discrete states:

- it is correct! – because of the underlying Q.M. nature of the laws governing atomic particles
- it is easier to model – tossing of a coin, a set of ideal spins, an ideal gas of particles in a box

Yet the rules developed for scaling up a discrete model system should have universal applicability

Advice to the Student

Learning is an active process. Simply reading or memorizing accomplishes practically nothing. Treat the subject matter of the book as though you were trying to discover it yourself, using the text merely as a guide that you should leave behind. The task of science is to learn ways of thinking which are effective in describing and predicting the behavior of the observed world. The only method of learning new ways of thinking is to practice thinking. Try to strive for insight, to find new relationships and simplicity where before you saw none. Above all, do not simply memorize formulas; learn modes of reasoning. The *only* relations worth remembering deliberately are the few Important Relations listed explicitly at the end of each chapter. If these are not sufficient to allow you to reconstruct in your head any other significant formula in about twenty seconds or less, you have not understood the subject matter.

Finally, it is much more important to master a few fundamental concepts than to acquire a vast store of miscellaneous facts and formulas. If in the text I have seemed to belabor excessively some simple examples, such as the system of spins or the ideal gas, this has been deliberate. It is particularly true in the study of statistical physics and thermodynamics that some apparently innocent statements are found to lead to remarkable conclusions of unexpected generality. Conversely, it is also found that many problems can easily lead one into conceptual paradoxes or seemingly hopeless calculational tasks; here again, a consideration of simple examples can often resolve the conceptual difficulties and suggest new calculational procedures or approximations. Hence my last advice is that you try to understand simple basic ideas well and that you then proceed to work many problems, both those given in the book and those resulting from questions you may pose yourself. Only in this way will you test your understanding and learn how to become an independent thinker in your own right.

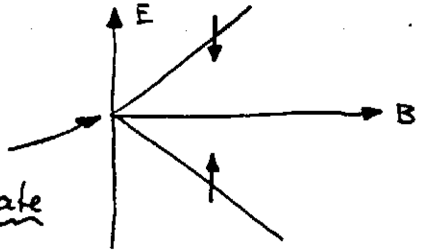
from F. Reif, Statistical Physics
McGraw-Hill, 1965

Ex a model system, a single spin

states $\uparrow$ or $\downarrow$ relative to $\uparrow \vec{B}$

energy levels $U = -\vec{m} \cdot \vec{B}$ $-mB$ $+mB$ $\Rightarrow$ levels "split"

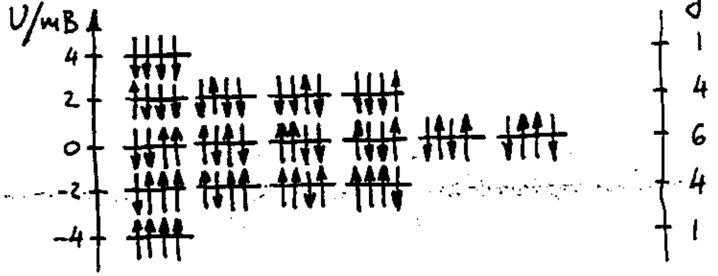
Energy diagram



@ $B = \emptyset$
$U_\uparrow = U_\downarrow = \emptyset$
levels degenerate

Ex a model system of four spins

Energy diagram



g = degeneracy function or multiplicity function

A model system of N spins, in some detail

$\uparrow_1 \downarrow_2 \uparrow_3 \uparrow_4 \uparrow_5 \ldots\ldots \downarrow_{N-1} \uparrow_N$

- each of N spins is either $\uparrow$ or $\downarrow$, independent of others

$\Rightarrow$ total # of possible configurations $= 2^N$

- $\uparrow$ has magnetic moment $+m$
  $\downarrow$ — " — — " — — $-m$

$\Rightarrow$ total magnetic moment $M = (N_\uparrow - N_\downarrow)\,m$

M varies from $+mN$ ($N_\uparrow = 0$, $N_\downarrow = N$, all down)
to $-mN$ ($N_\uparrow = N$, $N_\downarrow = 0$, all up)

- flipping one spin changes M by $\pm 2m$

$\Rightarrow$ M varies in steps of $2m$, $N+1$ states of M
[U varies in steps of $2mB$]

- convenient notation (N = even, without loss of generality)

$$\left.\begin{aligned} N_\uparrow &= \tfrac{1}{2}N + s \\ N_\downarrow &= \tfrac{1}{2}N - s \end{aligned}\right\} \quad N_\uparrow - N_\downarrow = 2s = \underline{\text{spin excess}}$$

$$M = 2sm \quad \text{or} \quad 2s = \frac{M}{m} \quad \Rightarrow U_{total} = -2smB$$

- a symbolic way to list all states of the model system:

$$(\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2) \dots (\uparrow_N + \downarrow_N) =$$
$$= \underbrace{\uparrow_1\uparrow_2 \dots \uparrow_N + \dots\dots + \downarrow_1\downarrow_2 \dots \downarrow_N}_{2^N \text{ terms}}$$

macroscopic parameter M depends on how many are up, not which ones, hence can drop site subscripts:

$$(\uparrow + \downarrow)^N = \uparrow^N + N\uparrow^{N-1}\downarrow + \dots + \downarrow^N = \sum_{N_\uparrow = 0}^{N} \frac{N!}{N_\uparrow!\,N_\downarrow!}\,\uparrow^{N_\uparrow}\downarrow^{N_\downarrow}$$

cf. binomial coefficients $C_N(k) = \binom{N}{k} = \dfrac{N!}{(N-k)!\,k!}$

- rewrite using $\begin{cases} N_\uparrow = \frac{1}{2}N + s \\ N_\downarrow = \frac{1}{2}N - s \end{cases} \Rightarrow s = -\frac{1}{2}N + N_\uparrow$

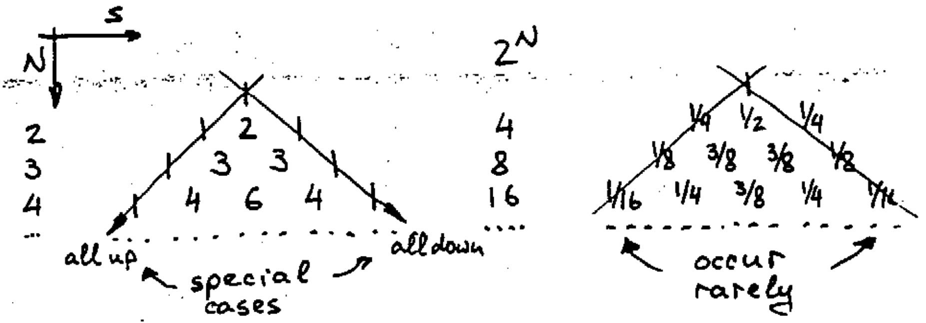
$\Rightarrow \quad 0 \le N_\uparrow \le N \longleftrightarrow -\frac{1}{2}N \le s \le +\frac{1}{2}N$

$$\Rightarrow \boxed{(\uparrow + \downarrow)^N = \sum_{s=-\frac{1}{2}N}^{+\frac{1}{2}N} \underbrace{\frac{N!}{(\frac{1}{2}N - s)!\,(\frac{1}{2}N + s)!}}_{g(N,s)} \uparrow^{\frac{1}{2}N+s}\downarrow^{\frac{1}{2}N-s}}$$

$g(N,s)$ = degeneracy of the state of N spins with exactly $\frac{1}{2}N+s$ up and $\frac{1}{2}N-s$ down

- normalization $\displaystyle\sum_{k=0}^{N} C_N(k) = 2^N = \sum_{s=-\frac{1}{2}N}^{+\frac{1}{2}N} g(N,s)$

- Pascal's triangle



- Probability $= \dfrac{\#\text{ of favourable outcomes}}{\text{total }\#\text{ of possible outcomes}}$

$$P_N(s) = \frac{g(N,s)}{2^N}$$

For $s = \pm\frac{1}{2}N$, $g(N, \pm\frac{1}{2}N) = 1 \Rightarrow P_N(\pm\frac{1}{2}N) = \frac{1}{2^N}$

For large N, very rarely

(8a)

$$\text{Probability} = \frac{\#\text{ of favourable outcomes}}{\text{total }\#\text{ of possible outcomes}}$$

For a small system, count directly

Ex 2 dice

$7 = 1+6 = 2+5 = 3+4 = 4+3 = 5+2 = 6+1$: 6 outcomes

total # $= 6^2 = 36$

$P(7) = \frac{1}{6}$

$P(2) = P(12) = \frac{1}{36}$

Ex particles in a box. P(all particles in LHS) = ?

a) 1 particle

total # $= 2^1 = 2$

$P(1 \text{ in LHS}) = \frac{1}{2}$

b) 2 particles:

total # $= 2^2 = 4$

$P(2 \text{ in LHS}) = \frac{1}{2^2} = \frac{1}{4}$

c) 1 cm³ contains 2.5×10^{19} molecules at 1 atm

All molecules move to one side <u>once</u> out of

$2^{2.5\times10^{19}} \simeq 10^{7.5\times10^{18}} = 10^{7500000000000000000}$ configurations

It is not that all molecules <u>never</u> move to one side of a room all at once; it just happens <u>very rarely</u>

Age of the Universe $\sim 10^{18}$ sec

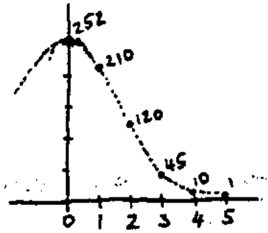
⑨

Features of $g(N,s) = \frac{N!}{(\frac{1}{2}N-s)!\,(\frac{1}{2}N+s)!}$

- Gaussian approximation

$$g(N,s) \simeq g(N,0)\, e^{-2s^2/N} \qquad N \gg 1,\ |s| \ll N$$

Ex $g(10,s)$



$g(100,s)$ KK Fig 1.9

$g(100,0) = 1.01\times10^{29}$

$g(100,10) = 1.37\times10^{28}$

$g(100,20) = 2.94\times10^{25}$

- normalization $\displaystyle\sum_{s=-\frac{1}{2}N}^{+\frac{1}{2}N} g(N,s) = 2^N$

- exact $g(N,0) = \frac{N!}{(\frac{1}{2}N)!(\frac{1}{2}N)!}$

N	4	10	20	100
$g(N,0)$	6	252	184,756	10^{29}
2^N	16	1024	1,048,576	1.3×10^{30}

- Stirling's approximation to $g(N,0)$

$$g(N,0) \simeq \left(\frac{2}{\pi N}\right)^{1/2} 2^N$$

maintains the normalization:

$$\sum_s g(N,s) \underset{\substack{\uparrow\\ \text{for large } N}}{\simeq} \int_{-\infty}^{+\infty} ds \left(\frac{2}{\pi N}\right)^{1/2} 2^N e^{-2s^2/N} = 2^N$$

EFTS verify by direct integration $\int_{-\infty}^{\infty} ds\, g = 2^N$
when using the above approximations
Hint: use an integral from KK App.A

- associated probability distribution

$$P_N(s) = \frac{g(N,s)}{2^N}$$

is, therefore, properly normalized:

$$\int_{-\infty}^{+\infty} P_N(s)\, ds = 1$$

in words: "the system is in *some* state for sure"

Once $P(s)$ is known, can calculate **average values**:

$$\langle f \rangle = \sum_s f(s)\, P(s) = \int_{-\infty}^{\infty} f(s)\, P(s)\, ds$$

f = odd function of s $\Rightarrow$ $\langle f \rangle = 0$ since $P \sim e^{-2s^2/N}$ - even

$f = s^2$: $\langle s^2 \rangle = \ldots = \frac{1}{4} N$

or $\langle (2s)^2 \rangle = N$ = mean squared spin excess

$[\langle (2s)^2 \rangle]^{1/2} = \sqrt{N}$ = r.m.s. spin excess

EFTS Use Gauss' integral $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$
to verify $\langle (2s)^2 \rangle = N$.
Hint: evaluate $\int_{-\infty}^{\infty} dx\, e^{-\alpha x^2}$ and take $-\frac{d}{d\alpha}$ of result

2. Fundamental concepts of Thermal Physics

Closed system: constrain the macroscopic parameters of the system, i.e. fix N, U_{total}, volume...

This may disallow certain states

Ex model spin system with $N=10$ & $U_{total} = -8mB$
i.e. with spin excess $2s = 8$

Instead of $2^{10} = 1024$ states, only those with $s=4$ satisfy the energy constraint, there are

$$\frac{N!}{(\frac{1}{2}N-s)!\,(\frac{1}{2}N+s)!} = \frac{10!}{(5-4)!\,(5+4)!} = 10 \text{ such states}$$

K.K. Fig 2.2

Accessible states are the ones compatible with the external constraints (specifications) of the system

Since we specify constraints *macro*scopically, we have no reason to prefer one *micro*scopic state over another $\Rightarrow$ fundamental **assumption** that

> A closed system is equally likely to be in any of its accessible states

see
J.W.Gibbs
(handout)

PREFACE.

THE usual point of view in the study of mechanics is that where the attention is mainly directed to the changes which take place in the course of time in a given system. The principal problem is the determination of the condition of the system with respect to configuration and velocities at any required time, when its condition in these respects has been given for some one time, and the fundamental equations are those which express the changes continually taking place in the system. Inquiries of this kind are often simplified by taking into consideration conditions of the system other than those through which it actually passes or is supposed to pass, but our attention is not usually carried beyond conditions differing infinitesimally from those which are regarded as actual.

For some purposes, however, it is desirable to take a broader view of the subject. We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time. The fundamental equation for this inquiry is that which gives the rate of change of the number of systems which fall within any infinitesimal limits of configuration and velocity.

Such inquiries have been called by Maxwell *statistical.* They belong to a branch of mechanics which owes its origin to the desire to explain the laws of thermodynamics on mechanical principles, and of which Clausius, Maxwell, and Boltzmann are to be regarded as the principal founders. The first inquiries in this field were indeed somewhat narrower in their scope than that which has been mentioned, being applied to the particles of a system, rather than to independent systems. Statistical inquiries were next directed to the phases (or conditions with respect to configuration and velocity) which succeed one another in a given system in the course of time. The explicit consideration of a great number of systems and their distribution in phase, and of the permanence or alteration of this distribution in the course of time is perhaps first found in Boltzmann's paper on the "Zusammenhang zwischen den Sätzen über das Verhalten mehratomiger Gasmoleküle mit Jacobi's Princip des letzten Multiplicators" (1871).

But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics. Moreover, the separate study of this branch of mechanics seems to afford the best foundation for the study of rational thermodynamics and molecular mechanics.

The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results. The laws of statistical mechanics apply to conservative systems of any number of degrees of freedom, and are exact.

Ensemble is a group of identical systems, one in each of the accessible states. Each member of an ensemble satisfies all external constraints

Probability (any inaccessible state) = 0

⇒ for macroscopic averages, **ensemble average** suffices

Probability (any accessible state) = $\frac{1}{g}$, where g = # of accessible states, since all are equally likely

$$\Rightarrow \quad \langle X \rangle = \sum_{s\in\{\text{ensemble}\}} \frac{X(s)}{g}$$

Ex in Fig. 2.2 what is $\langle U_1 \rangle = ?$

configuration a) : $\downarrow_1$

configurations b)-j) : $\uparrow_1$

$$\Rightarrow \langle U_1 \rangle = \frac{1}{10}(+mB) + \frac{9}{10}(-mB) = -\frac{8}{10}mB$$

Note: same for other spins!

$$\Rightarrow \langle U_{total} \rangle = 10 \times \left(-\frac{8}{10}mB\right) = -8mB$$

as required

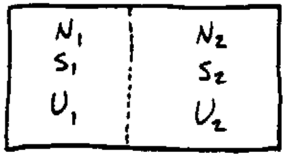
Systems in thermal contact

Two systems :

$N_1 \quad s_1 \quad U_1 = -2s_1 mB$

$N_2 \quad s_2 \quad U_2 = -2s_2 mB$

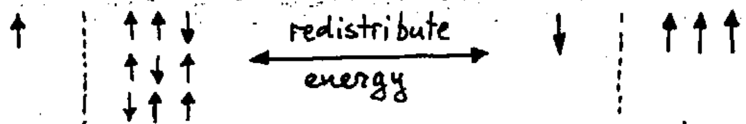
are allowed to exchange energy, but taken together form a closed system :



$U = U_1 + U_2 = const$

$[\text{i.e. } s_1 + s_2 = const]$

Ex



$U_1 = -mB \quad U_2 = -mB \qquad U_1 = +mB \quad U_2 = -3mB$

$U = U_1 + U_2 = -2mB \qquad U = U_1 + U_2 = -2mB$

Total # of accessible states = 4 = 1×3 + 1×1 for the combined system, of which 3 correspond to the subsystem 1 having $U_1 = -mB$ and one – to $U_1 = +mB$

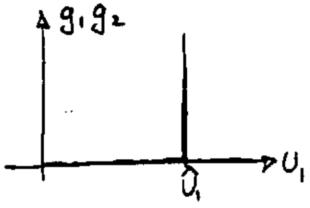
$$\Rightarrow \langle U_1 \rangle = \frac{3}{4}(-mB) + \frac{1}{4}(+mB) = -\frac{1}{2}mB \neq 0$$

When subsystems were isolated, the total # of accessible states was 3 (< 4!!) and U_1 was fixed @ $-mB$

In general,

$$g(N,U) = \sum_{U_1} g_1(N_1,U_1)\, g_2(N_2,U-U_1)$$

The product $g_1 g_2$ is a very sharply varying function of U_1 for large N



Ex $N_1 = N_2 = 10^{22}$, $\frac{U_1-\hat{U}_1}{2mBN_1} = 10^{-10}$

$$\Rightarrow \quad g_1(U_1)\, g_2(U-U_1) = e^{-400} \times g_1(\hat{U}_1)\, g_2(U-\hat{U}_1)$$

⇒ the entire sum is well approximated by a single contribution:

$$g = \sum_{U_1} g_1 g_2 \simeq g_1(\hat{U}_1)\, g_2(U-\hat{U}_1) = (g_1 g_2)_{max}$$

EFTS review p. 37-39 in the text and verify that for the model spin system

$$\frac{\partial}{\partial U_1}[g_1 g_2] = 0 \quad \text{and} \quad \frac{\partial^2}{\partial U_1^2}[g_1 g_2] < 0$$

⇒ $g_1 g_2$ is at a maximum when

$$\frac{U_1}{N_1} = \frac{U_2}{N_2}$$

i.e. energy per spin is the same in both subsystems

This is the point of thermal equilibrium

For a general system, this maximum occurs when the differential

$$dg = 0 = \frac{\partial g}{\partial U_1} dU_1 + \frac{\partial g}{\partial U_2} dU_2$$

$$= \frac{\partial g_1}{\partial U_1} g_2\, dU_1 + g_1 \frac{\partial g_2}{\partial U_2} dU_2$$

Also: $U = U_1 + U_2 = \text{const} \Rightarrow U_2 = U - U_1 \Rightarrow dU_2 = -dU_1$

$$\Rightarrow \quad \frac{\partial g_1}{\partial U_1} g_2 = g_1 \frac{\partial g_2}{\partial U_2} \quad \text{or} \quad \frac{1}{g_1}\frac{\partial g_1}{\partial U_1} = \frac{1}{g_2}\frac{\partial g_2}{\partial U_2}$$

$$\Rightarrow \quad \left(\frac{\partial \log g_1}{\partial U_1}\right)_{\underset{\uparrow}{N_1}} = \left(\frac{\partial \log g_2}{\partial U_2}\right)_{\underset{\uparrow}{N_2}}$$

| note: $\frac{d}{dx}\log y = \frac{1}{y}\frac{dy}{dx}$

added to remind ourselves that N_1, N_2 are held constant

Define $\sigma(N,U) \equiv \log g(N,U)$ = entropy

$$\Rightarrow \quad \boxed{\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}}$$ at thermal equilibrium

Note: σ = log of # of accessible state, a number

Define $\frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N$, τ = temperature, $[\tau] = [U]$

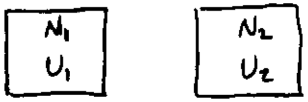
and then the condition for thermal eq^m is $\tau_1 = \tau_2$ as usual.

These are fundamental (statistical) τ & σ

Thermodynamic $T = \frac{1}{k_B}\tau$ & $S = k_B \sigma$

Second Law of Thermodynamics

Initially, two closed systems separated:

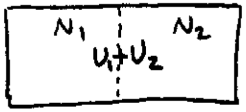


Two constraints:
$U_1 = \text{const}$ & $U_2 = \text{const}$

Total # of configurations $g(U_1;U_2) = g_1(U_1)\,g_2(U_2)$

$\Rightarrow \sigma_{init} = \log g = \log g_1 + \log g_2 = \sigma_1 + \sigma_2$

Bring the systems into thermal contact:



One constraint only:
$U = U_1 + U_2 = \text{const}$

$$g(U) = \sum_{U_1'} g_1(U_1')\,g_2(U-U_1') = \quad \Big|\; U' = \text{running index}$$

$$= g_1(U_1)\,g_2(U_2) + \text{many other terms}$$

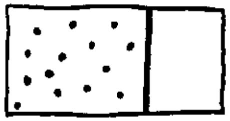
$$\Rightarrow \sigma_{final} = \log g \simeq \log(g_1 g_2)_{max} \geq \sigma_{initial} = \log(g_1 g_2)_{init}$$

⇒ **Entropy of a closed system tends to remain constant or to increase when a constraint internal to the system is removed** 2LT

Examples

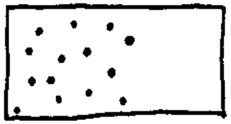
Ex volume expansion

So far, whenever we used "N" we could have said "N, V, and other independent variables"
e.g. thermal eq-m when $\left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1,V_1,\dots} = \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2,V_2,\dots}$



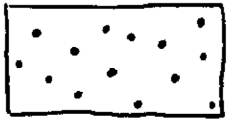
- system is in one of accessible configurations (states)
- g and $\sigma = \log g$ at max

Constraint is removed suddenly:



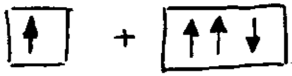
- there are many other states available; in fact <u>this</u> one is a special, rare case
- g and σ are far from max

In time, system equilibrates:



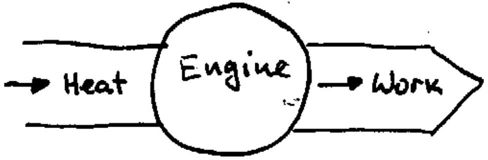
- g & σ <u>increase</u> to a new max

Ex the model systems considered previously



Initial $g = 1\times 3 = 3$
Final $g = 1\times 3 + 1\times 1 = 4$

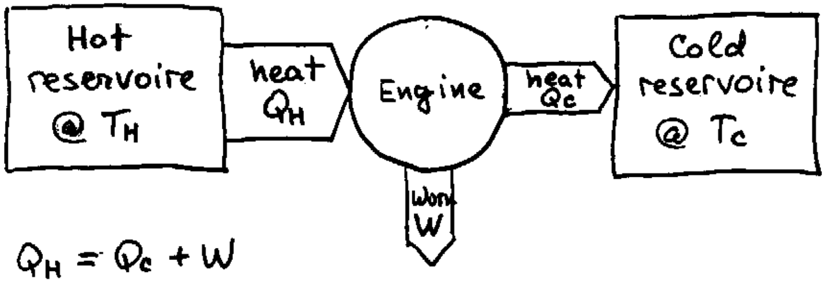
Ex perpetuum motion of second kind



<u>not allowed</u>

This is a form of 2LT

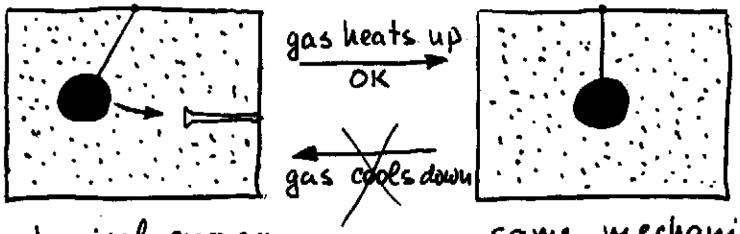
All thermal engines work like this:



$$Q_H = Q_c + W$$

$$\text{Efficiency} = \frac{W}{Q_H} = 1 - \frac{Q_c}{Q_H} \leq 1 - \frac{T_c}{T_H} \quad \text{at best}$$

Why?



• mechanical energy of pendulum	• <u>same</u> mechanical energy distributed among
• carried by <u>one</u> "particle"	• <u>many</u> gas particles
• can use to do work	• cannot "extract" this same energy to do work

The ability to do work by cooling something down would correspond to a spontaneous decrease in total entropy - not very likely!

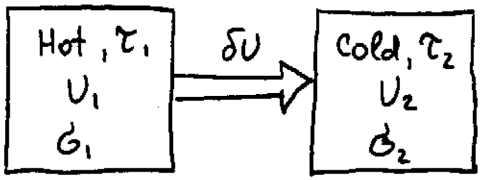
Ex. Direction of heat flow

Q: Is ours a sensible definition of temperature?

Let $\beta \equiv \frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N$

Then at thermal eq-m, $\beta_1 = \beta_2$ as well.

Thermodynamic temperature defined so that heat (energy) flows from hot to cold, from high T to low T



$$\Delta \sigma_{total} = \left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} (-\delta U) + \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2} (+\delta U)$$

$$= \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2}\right) \delta U$$

For $\Delta \sigma$ to be positive:

$$-\frac{1}{\tau_1} + \frac{1}{\tau_2} > 0 \Rightarrow \frac{1}{\tau_1} < \frac{1}{\tau_2} \Rightarrow \underset{\text{Hot}}{\tau_1} > \underset{\text{cold}}{\tau_2} \quad \checkmark$$

⇒ 2LT defines the direction of the heat flow

⇒ "Heat never flows spontaneously from a colder body to a warmer body" is another form of 2LT

Ex paramagnetism KK Pr. 2-2

N spins.

m = magnetic moment of one spin

B = applied external magnetic field

τ = temperature

M = ?

Entropy $\sigma = \log g(N,s) \simeq \log\left[g(N,0)\, e^{-2s^2/N}\right]$

valid for $|s| \ll N$

$$\Rightarrow \quad \sigma = \sigma_0 - \frac{2s^2}{N}, \quad \sigma_0 = \log g(N,0)$$

Energy $U = -2smB \Rightarrow 2s^2 = \dfrac{U^2}{2m^2B^2}$

$$\Rightarrow \quad \sigma = \sigma_0 - \frac{U^2}{2m^2B^2N}$$

Temperature $\dfrac{1}{\tau} = \left(\dfrac{\partial\sigma}{\partial U}\right)_N = -\dfrac{U}{m^2B^2N}$

$$\Rightarrow \quad \boxed{U = -\frac{m^2B^2N}{\tau}} \quad \text{and} \quad \boxed{\sigma = \sigma_0 - \frac{m^2B^2N}{2\tau^2}}$$

On the other hand,

$$\langle U(\tau)\rangle = -2\langle s\rangle mB = -\frac{m^2B^2N}{\tau}$$

$$\Rightarrow \quad 2\langle s\rangle = \frac{mBN}{\tau}$$

$$\Rightarrow \quad \boxed{M(\tau) = 2\langle s\rangle m = \frac{m^2BN}{\tau}}$$

Magnetic susceptibility $\chi = \dfrac{dM}{dB} = \dfrac{m^2N}{\tau}$ ← Curie's Law

Note:

- U & σ increase with τ
- σ (disorder) decreases as B^2
- our approximation was valid for $|s| \ll N$

i.e. $2\langle s\rangle = \dfrac{mBN}{\tau} \Rightarrow \dfrac{2\langle s\rangle}{N} = \dfrac{mB}{\tau}$

$\Rightarrow$ for $mB \ll \tau$

Ex Isentropic magnetic cooling

If we can arrange a process in which B is changed, but σ = const :

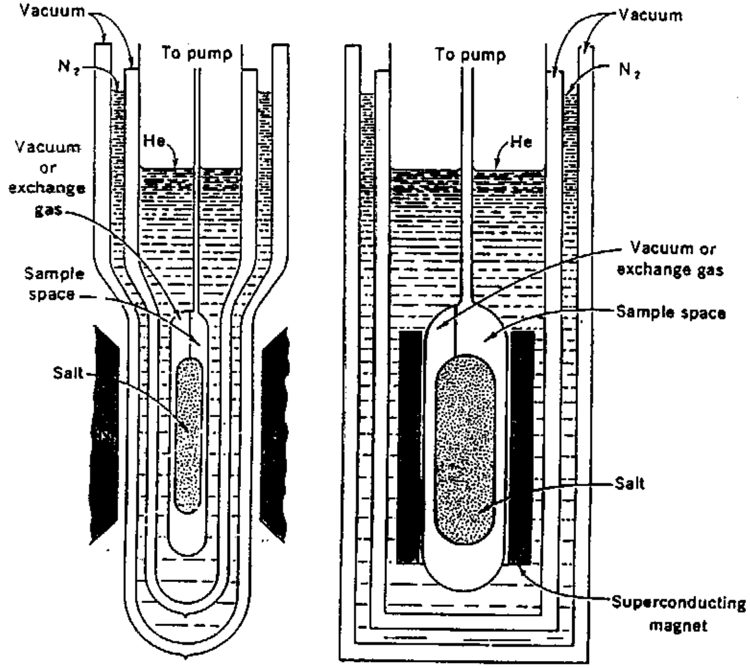
$$\sigma_0 - \frac{m^2B_i^2N}{2\tau_i^2} = \sigma_0 - \frac{m^2B_f^2N}{2\tau_f^2}$$

$$\Rightarrow \quad \boxed{\frac{B_f}{B_i} = \frac{\tau_f}{\tau_i}}$$

[Later we shall see that this occurs when the system is thermally isolated, i.e. no heat flows in or out]

Note: cannot reach $\tau_f = 0$ because when external field B approaches zero, there are still local magnetic fields from the neighboring spins.

From M.W. Zemansky & R.H. Dittman
"Heat and thermodynamics"
6th ed, McGraw-Hill, 1981



With conventional magnet With superconducting magnet

Figure 18-9 Adiabatic reduction of magnetic field experiments are carried out more readily with a superconducting magnet.

Table 18-3 Pioneer results in the magnetic production of low temperatures

Experimenters	Date	Paramagnetic salt	Initial field, 10^6 A/m	Initial temp., K	Final magnetic temp., T^*
Giauque and MacDougall	1933	Gadolinium sulfate	0.64	1.5	0.25
De Haas, Wiersma, and Kramers	1933	Cerium fluoride	2.20	1.35	0.13
		Dysprosium ethyl sulfate	1.55	1.35	0.12
		Cerium ethyl sulfate	2.20	1.35	0.085
De Haas and Wiersma	1934	Chromium potassium alum	1.96	1.16	0.031
	1935	Iron ammonium alum	1.92	1.20	0.018
		Alum mixture	1.92	1.29	0.0044
		Cesium titanium alum	1.92	1.31	0.0055
Kurti and Simon	1935	Gadolinium sulfate	0.43	1.15	0.35
		Manganese ammonium sulfate	0.64	1.23	0.09
		Iron ammonium alum	1.12	1.23	0.038
		Iron ammonium alum	0.66	1.23	0.072
		Iron ammonium alum	0.39	1.23	0.114

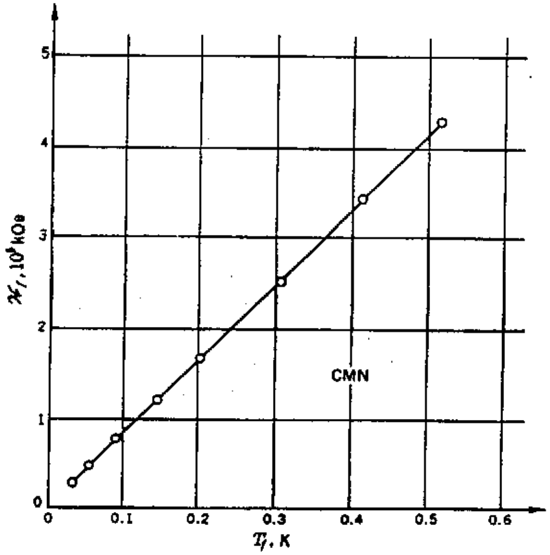
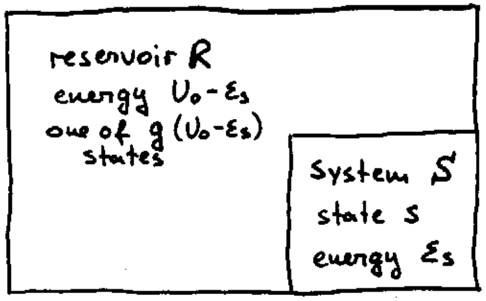


Figure 18-11 Constancy of the ratio $\mathscr{H}_f/T_f$ during adiabatic reduction of the magnetic field of CMN from $\mathscr{H}_i$, T_i (always the same) to $\mathscr{H}_f$, T_f. (*J. S. Hill and J. H. Milner, 1957.*)

3. Boltzmann distribution



# of states accessible to the combined $(R+S)$ together:

$$g_R \times g_S^{=1} = g_R$$

Consider two states s.t. $N_1=N_2$, $V_1=V_2$, etc.

$$\Rightarrow \frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{g_R(U_0-\varepsilon_1)}{g_R(U_0-\varepsilon_2)} = \frac{e^{\sigma_R(U_0-\varepsilon_1)}}{e^{\sigma_R(U_0-\varepsilon_2)}}$$

or $$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = e^{\Delta\sigma_R}$$

Expand $\Delta\sigma_R$ about U_0:

$$\Delta\sigma_R = \sigma_R(U_0) - \left(\frac{\partial\sigma_R}{\partial U}\right)_{\substack{N,V\\U=U_0}}\varepsilon_1 + \dots$$
$$- \left[\sigma_R(U_0) - \left(\frac{\partial\sigma_R}{\partial U}\right)_{\substack{N,V\\U=U_0}}\varepsilon_2 + \dots\right] \simeq -\frac{\varepsilon_1-\varepsilon_2}{\tau}$$

Hence, the ratio of probabilities of two states

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = e^{-\varepsilon_1/\tau + \varepsilon_2/\tau} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}}$$

or $P(\varepsilon) \propto e^{-\varepsilon/\tau}$ = Boltzmann factor

$P(\varepsilon)$ can be fully determined using the normalization condition:

$$\sum_s P(\varepsilon_s) = 1 \Rightarrow P(\varepsilon_s) = \frac{e^{-\varepsilon_s/\tau}}{\sum_s e^{-\varepsilon_s/\tau}}$$

or $$P(\varepsilon) = \frac{e^{-\varepsilon/\tau}}{Z}, \quad Z = \sum P(\varepsilon)$$

Z = partition function (Zusandsumme)

Canonical ensemble: where systems, all in contact with a heat reservoir at τ, are distributed according to $P \propto e^{-\varepsilon/\tau} = e^{-\beta\varepsilon}$

Ex paramagnetism revisited

$\vec{B}$

$\uparrow \quad \varepsilon_\uparrow = -mB \qquad P_\uparrow = C e^{-\beta\varepsilon_\uparrow} = C e^{\beta mB}$

$\downarrow \quad \varepsilon_\downarrow = +mB \qquad P_\downarrow = C e^{-\beta\varepsilon_\downarrow} = C e^{-\beta mB}$

Determine C = const from normalization:

$$P_\uparrow + P_\downarrow = 1 \Rightarrow C = \frac{1}{e^{\beta mB} + e^{-\beta mB}}$$

Average magnetic moment:

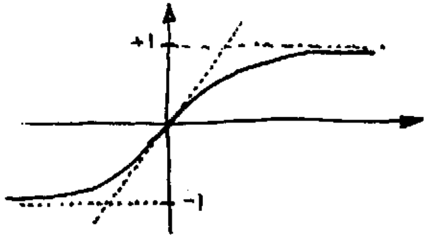
$$\langle M\rangle = (+m)P_\uparrow + (-m)P_\downarrow = m\frac{e^{\beta mB} - e^{-\beta mB}}{e^{\beta mB} + e^{-\beta mB}}$$

$\Rightarrow \langle M_1\rangle = m\tanh(\beta mB)$ for 1 spin

$\langle M\rangle = Nm\tanh(\beta mB)$ for N non-interacting spins

<u>Note</u>: obtained this result <u>without</u> first calculating $g(N,U)$! – an alternative way to count accessible states.

— Aside —



$\tanh x \simeq x$, $|x| \ll 1$

$\tanh x \to +1$, $x \gg 1$

$\tanh x \to -1$, $x \ll -1$

EFTS

$$\langle M \rangle = Nm \tanh \frac{mB}{\tau}$$

- strong field, low temperature : $\frac{mB}{\tau} \gg 1$

  $\Rightarrow \langle M \rangle \simeq Nm$ (all up)

- weak field, high temperature : $\frac{mB}{\tau} \ll 1$

  $\Rightarrow \langle M \rangle \simeq Nm \frac{mB}{\tau} = \frac{m^2 B N}{\tau}$

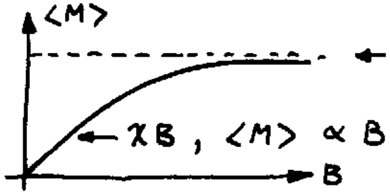
  $\chi = \frac{d\langle M \rangle}{dB} = \frac{m^2 N}{\tau}$ ← recover Curie's Law

  as before.

- also, $\langle M \rangle \propto \frac{1}{\tau} \to 0$ as $\tau \to \infty$

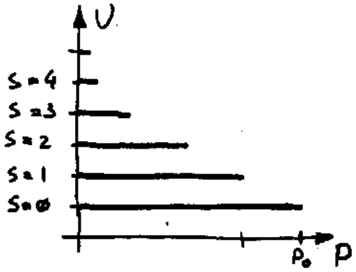
  $\Rightarrow$ high-temperature demagnetization

-



← Nm = saturation limit, no more spins to flip

Ex. harmonic oscillator $U_s = s\hbar\omega$, $s = 0, 1, 2.$



$$P_s = P_0 \, e^{-s\hbar\omega/\tau}$$

How to read this graph: of a large ensemble of N non-interacting h.o.'s ,

$P_0 N$ are in state $s=0$

$P_1 N = P_0 N e^{-\hbar\omega/\tau}$ are in state $s=1$

etc.

Ex verify for a small N by direct counting

- 4 H.O.'s , each has energies $0, \varepsilon, 2\varepsilon, 3\varepsilon, \ldots$ where $\varepsilon = \hbar\omega$.
- constraint : total energy 4ε
- possible distributions of energy among H.O.'s

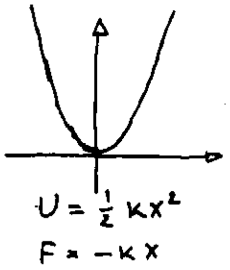
U=	0	ε	2ε	3ε	4ε	5ε	…	# permutation
occupation numbers	0	4	0	0	0	0	0	$C_4(4) = 1$
	2	0	2	0	0	0	0	$C_4(2) \times C_2(2) = 6$
						0	0	
						0	0	
						0	0	
average: 1.71								total 35

$\frac{1}{35}(0 \times 1 + 2 \times 6 + \ldots \quad) = \frac{60}{35} \simeq \underset{\text{occup.\#}}{1.71} \longleftrightarrow \frac{1.71}{4} = 0.43 = P_0$

EFTS complete table; convert to $P(U)$; compare to exp

Helmholtz free energy

Define $\boxed{F \equiv U - \tau\sigma}$



Mechanics : eq-m ⟷ min of U

recall : Force $= -\frac{dU}{dx}$

σ does not enter, since there are no internal changes of states

Thermal physics : eq-m ⟷ min of $F = U - \tau\sigma$

takes into account both min U and max σ

- Relate F and Z :

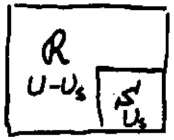
$F \equiv U - \tau\sigma \quad \Rightarrow \left(\frac{\partial F}{\partial \tau}\right)_{N,V} = -\sigma$

$\Rightarrow \; F = U + \tau\left(\frac{\partial F}{\partial \tau}\right)_{N,V}$

$\Rightarrow \; U = F - \tau\left(\frac{\partial F}{\partial \tau}\right)_{N,V} = -\tau^2\frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right)_{N,V}$

But : $U = +\tau^2\frac{\partial}{\partial \tau}(\log Z)$

$\Rightarrow \quad \log Z = -\frac{F}{\tau} \quad \Rightarrow \quad \boxed{F = -\tau \log Z}$

- 

$$\begin{aligned}\sigma_{total} = \sigma_R + \sigma_S &= \sigma_R(U-U_s) + \sigma_S(U_s) \\ &\cong \sigma_R(U) - U_s\left(\frac{\partial \sigma_R}{\partial U}\right)_{N,V} + \sigma_S(U_s) \\ &= \sigma_R(U) - U_s\frac{1}{\tau} + \sigma_S(U_s) \\ &= \sigma_R(U) - \frac{1}{\tau}\Big(\underbrace{U_s - \tau\sigma_S(U_s)}_{F}\Big)\end{aligned}$$

$$\Rightarrow \quad \sigma_{total} = \sigma_R(U) - \frac{F}{\tau}$$

At eq-m, σ_{total} is at a max w.r.to U_s, while $\sigma_R(U)$ does not depend on U_s

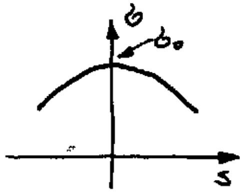
$\Rightarrow$ eq-m is a <u>min</u> of F w.r.to U_s

Ex model spin system: $\left(\frac{N}{2}+s\right)$ spins ↑, $\left(\frac{N}{2}-s\right)$ spins ↓

$$\sigma(s) = \log g(s) = \log \frac{N!}{\left(\frac{N}{2}+s\right)!\left(\frac{N}{2}-s\right)!}$$

In the limit $|s| \ll N$:

$$\sigma(s) \approx \sigma_0 - \frac{2s^2}{N} = N\log 2 - \frac{2s^2}{N}$$



The most likely state is at the peak

- Now bring the system into a thermal contact with a reservoir @ temperature τ, i.e. establish a temperature τ for the model system.

$U(s) = -2smB$

$\Rightarrow F(s) = -2smB - \tau\left(N\log 2 - \frac{2s^2}{N}\right)$

Minimum of F : $\frac{\partial F}{\partial s} = 0 = -2mB + \frac{4\tau s}{N}$

$\Rightarrow$ the equilibrium value of $2s = \frac{mBN}{\tau}$

$\Rightarrow \; M_{eq\text{-}m} = 2sm = \frac{m^2BN}{\tau}$ cf $\langle M \rangle = \frac{m^2BN}{\tau}$ on p.24

EFTS repeat in general, not just $|s| \ll N$. Hint: see KK

Partition function Z is very useful

$$Z = \sum_s e^{-\varepsilon_s/\tau} = \sum_s e^{-\beta\varepsilon_s} \qquad \boxed{\beta \equiv \frac{1}{\tau}}$$

$$P(\varepsilon_s) = \frac{e^{-\beta\varepsilon_s}}{Z}$$

$$U = \langle U \rangle = \sum_s \varepsilon_s P(\varepsilon_s) = \frac{1}{Z}\sum_s \varepsilon_s e^{-\beta\varepsilon_s} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$$

$$\boxed{U = -\frac{\partial}{\partial\beta}(\log Z) = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}}$$

Note: $\frac{\partial\beta}{\partial\tau} = -\frac{1}{\tau^2} \Rightarrow \frac{\partial}{\partial\tau} = \frac{\partial\beta}{\partial\tau}\frac{\partial}{\partial\beta} = -\frac{1}{\tau^2}\frac{\partial}{\partial\beta}$

$$\Rightarrow \boxed{U = \tau^2 \frac{\partial}{\partial\tau}(\log Z)} \quad (*) \qquad \text{cf. KK 3.12}$$

Also, for entropy:

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_{N,V} \Rightarrow \sigma(U) = \int \frac{dU}{\tau}$$

$$\underline{\sigma(U)} = \frac{U}{\tau} + \int d\tau \frac{U}{\tau^2} = \quad \leftarrow \text{use } (*)$$

$$= \tau\frac{\partial}{\partial\tau}(\log Z) + \int d\tau \frac{\partial}{\partial\tau}(\log Z)$$

$$= \tau\frac{\partial}{\partial\tau}(\log Z) + \log Z = \underline{\frac{\partial}{\partial\tau}(\tau\log Z)}$$

[Here we cheated a bit, ignoring $Z(\tau \to 0)$.
We will justify the result later]

$$\boxed{\sigma = \frac{U}{\tau} + \log Z = \frac{\partial}{\partial\tau}(\tau\log Z)}$$

Ex a two-level system

one particle, energy levels 0 & ε

- $Z = \sum_s e^{-\varepsilon_s/\tau} = 1 + e^{-\varepsilon/\tau}$
- $U = \langle U \rangle = \sum_s \varepsilon_s \frac{e^{-\varepsilon_s/\tau}}{Z} = 0 + \frac{\varepsilon e^{-\varepsilon/\tau}}{1 + e^{-\varepsilon/\tau}}$

or
$$U = \tau^2\frac{\partial}{\partial\tau}\log Z = \frac{\tau^2}{Z}\frac{\partial Z}{\partial\tau} = \frac{\cancel{\tau^2}}{1+e^{-\varepsilon/\tau}} e^{-\varepsilon/\tau}(-\varepsilon)\left(-\frac{1}{\cancel{\tau^2}}\right)$$

$$= \frac{\varepsilon e^{-\varepsilon/\tau}}{1+e^{-\varepsilon/\tau}} \quad \checkmark$$

N independent particles, energies 0 & ε each

- $U = N\frac{\varepsilon e^{-\varepsilon/\tau}}{1+e^{-\varepsilon/\tau}} = N\varepsilon \frac{1}{e^{\varepsilon/\tau}+1}$
- Heat capacity $C_V \equiv \left(\frac{\partial U}{\partial\tau}\right)_{N,V} = N\varepsilon\frac{\partial}{\partial\tau}\left(\frac{1}{e^{\varepsilon/\tau}+1}\right)$

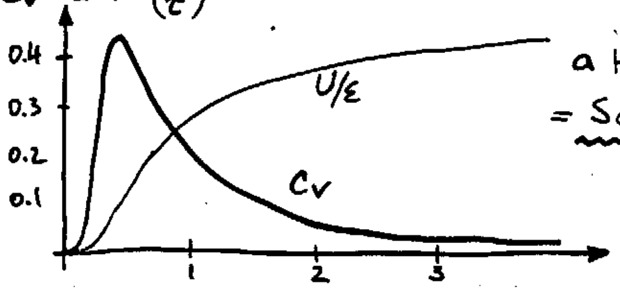
$$\Rightarrow C_V = N\left(\frac{\varepsilon}{\tau}\right)^2 \frac{e^{\varepsilon/\tau}}{(e^{\varepsilon/\tau}+1)^2}$$

high-temperature limit : $\tau \gg \varepsilon$

$$C_V \simeq \frac{1}{4}N\left(\frac{\varepsilon}{\tau}\right)^2$$

low-temperature limit : $\tau \ll \varepsilon$

$$C_V \simeq N\left(\frac{\varepsilon}{\tau}\right)^2 e^{-\varepsilon/\tau} \to 0 \text{ as } \tau \to 0$$



a Hump in C_V
= Schottky anomaly

Free energy and Boltzmann distribution

$$F = -\tau \log Z \quad \Leftrightarrow \quad Z = e^{-F/\tau}$$

$$\Rightarrow \quad \underline{P(\varepsilon_s)} = \frac{e^{-\varepsilon_s/\tau}}{Z} = \underline{e^{-(F-\varepsilon_s)/\tau}}$$

Reversibility

Landau & Lifshitz, V.5

- a process is <u>quasistatic</u>, if it is carried out so slowly that at all times the system remain in the equilibrium configuration
  - thermal eq-m: τ the same for all parts of the system
  - mechanical eq-m: no unbalanced forces, no accelerations (e.g. turbulence)
- if a quasistatic process is isentropic, it is <u>reversible</u>: 2LT will not be violated if we reverse the direction of the process
- quasistatic process applied to a thermally isolated system (no energy exchanged with the surroundings) is <u>adiabatic process</u>
- adiabatic processes are isentropic

  consider an external condition (force) parametrized by $\lambda = \lambda(t)$

$\frac{d\sigma}{dt}$ is then some function of $\frac{d\lambda}{dt}$

For a quasistatic process $\frac{d\lambda}{dt}$ is small

$\Rightarrow$ expand: $\frac{d\sigma}{dt} = A + B\frac{d\lambda}{dt} + C\left(\frac{d\lambda}{dt}\right)^2 + \ldots$

1) When external conditions are constant, i.e. when $\frac{d\lambda}{dt} = 0$, the system is in thermal eq-m and its entropy is not changing, $\frac{d\sigma}{dt} = 0$ $\Rightarrow A = 0$.

2) $\frac{d\lambda}{dt}$ can be +ve or -ve, yet $\frac{d\sigma}{dt}$ can only be +ve (2LT) $\Rightarrow B = 0$

$\Rightarrow \frac{d\sigma}{dt} = C\left(\frac{d\lambda}{dt}\right)^2 + \ldots$ i.e. start with the quadratic term

$$\frac{d\sigma}{dt} = \frac{d\sigma}{d\lambda}\frac{d\lambda}{dt} \simeq C\left(\frac{d\lambda}{dt}\right)^2 \quad \Rightarrow \quad \frac{d\sigma}{d\lambda} = C\frac{d\lambda}{dt}$$

As $\frac{d\lambda}{dt} \to 0$ for a quasi-static process, so does $\frac{d\sigma}{d\lambda} \to 0$ i.e. entropy is not changing with a change in λ

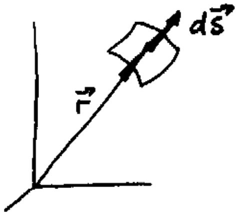
$\Rightarrow$ the adiabatic process is isentropic and, hence, reversible

- the converse is <u>not</u> true, i.e. not all reversible processes are adiabatic

Ex pressure $\lambda = \vec{r}$ of a surface element

From mechanics:

force $\vec{f} = -\dfrac{\partial U}{\partial \vec{r}}$



Ensemble average:

$$\langle \vec{f} \rangle = -\left(\frac{\partial U}{\partial \vec{r}}\right)_{\sigma,N}$$

$$= -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N} \frac{\partial V}{\partial \vec{r}}$$

slow expansion: $\sigma, N = \text{const}$ as required

$\dfrac{\partial V}{\partial \vec{r}} = d\vec{s}$ = surface element (area ds, normal dir)

$$\Rightarrow \quad \langle \vec{f} \rangle = -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N} d\vec{s}$$

or:

$$\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N}}$$

i.e. average force exerted by the gas on the wall of the container is
- normal to the wall
- prop. to area of the wall

Thermodynamic identity

$$\tau = \left(\frac{\partial U}{\partial \sigma}\right)_{V,N}$$

recall: $\dfrac{1}{\tau} = \left(\dfrac{\partial \sigma}{\partial U}\right)_{V,N}$

$$\Rightarrow \quad dU = \left(\frac{\partial U}{\partial \sigma}\right)_{V,N} d\sigma + \left(\frac{\partial U}{\partial V}\right)_{\sigma,N} dV$$

$$\Rightarrow \quad \boxed{dU = \tau d\sigma - p dV}$$

EFTS cf KK p64-68

Free energy and pressure, entropy

$$F = U - \tau\sigma \quad \Rightarrow \quad dF = \underbrace{dU - \tau d\sigma}_{-pdV} - \sigma d\tau$$

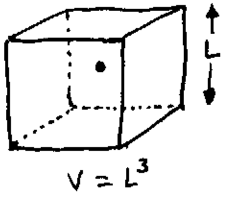
$$\Rightarrow \quad dF = -\sigma d\tau - pdV$$

$$\Rightarrow \quad \boxed{\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma} \quad \text{and} \quad \boxed{\left(\frac{\partial F}{\partial V}\right)_\tau = -p}$$

Also: $$\frac{\partial^2 F}{\partial \tau \partial V} = \frac{\partial^2 F}{\partial V \partial \tau} \quad \Rightarrow \quad \boxed{\left(\frac{\partial \sigma}{\partial V}\right)_\tau = \left(\frac{\partial p}{\partial \tau}\right)_V}$$

a Maxwell relation

Ex a particle in a box



$V = L^3$

S.E.: $-\dfrac{\hbar}{2M}\nabla^2\psi = \varepsilon\psi$

B.C: $\psi = 0$ at boundaries

$\Rightarrow \quad \varepsilon = \dfrac{\hbar^2}{2M}\left(\dfrac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$

where n_α = integers

- partition function

$$Z = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\varepsilon/\tau} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\alpha^2(n_x^2+n_y^2+n_z^2)}$$

$\alpha = \dfrac{\hbar^2\pi^2}{2ML^2\tau}$ and for small α (small step) $\Sigma \to \int$

$$\Rightarrow \quad Z = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \, e^{-\alpha^2 n_x^2} e^{-\alpha^2 n_y^2} e^{-\alpha^2 n_y^2}$$

$$= \left[\int_0^\infty dn_x \, e^{-\alpha^2 n_x^2}\right]^3 = \left[\frac{\sqrt{\pi}}{2\alpha}\right]^3 = \frac{\pi^{3/2}}{8\alpha^3}$$

For a single particle:

$$Z_1 = \frac{\pi^{3/2}}{8\left(\frac{\hbar^2\pi^2}{2ML^2\tau}\right)^{3/2}} = \underbrace{\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}}_{n_Q}\underbrace{L^3}_{V} = n_Q V = \frac{n_Q}{n}$$

n_Q = <u>quantum concentration</u> = one atom per cube of $L = \lambda$ = de Broglie wavelength

recall: $\lambda \simeq \frac{\hbar}{M\langle v\rangle} \sim \frac{\hbar}{(M\tau)^{1/2}}$; λ^3 = the "smallest" possible V

$n = \frac{1}{V}$ = concentration

He @ 1atm & 300K : $Z_1 = \frac{n_Q}{n} \simeq 3\times10^{-6} \ll 1$

$\Rightarrow$ in a <u>classical regime</u>

<u>Ideal gas</u> = non-interacting particles in the classical regime

$$U = \frac{\sum_s \varepsilon_s e^{-\varepsilon_s/\tau}}{Z_1} = \tau^2 \frac{\partial}{\partial\tau}(\log Z_1) = \tau^2\frac{\partial}{\partial\tau}\log(A\tau^{3/2})$$

$$= \tau^2\frac{\partial}{\partial\tau}\left[\log A + \frac{3}{2}\log\tau\right] = \tau^2\,\frac{3}{2}\,\frac{1}{\tau} = \frac{3}{2}\tau$$

Ideal gas of one atom : $\boxed{U = \frac{3}{2}\tau} = \frac{3}{2}k_BT$

For N non-interacting atoms: $U = \frac{3}{2}N\tau$
(i.e. low-density gas, in the classical regime)

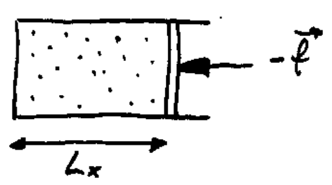
NB ‖ average energy of the gas is a function of temperature only, and is independent of the dimensions of the container

In general, $L_x \neq L_y \neq L_z$:

$$\varepsilon_s = \frac{\hbar^2\pi^2}{2M}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

for state $s = (n_x, n_y, n_z)$

Consider the case of expansion in 1D only:



$\vec{f}$ = force exerted by gas on the piston

$\varepsilon_s = \varepsilon_s(L_x) \Rightarrow f_s = -\frac{\partial\varepsilon_s}{\partial L_x}$

Note: $\frac{\partial}{\partial L_x}\left(e^{-\varepsilon_s/\tau}\right) = -\frac{1}{\tau}e^{-\varepsilon_s/\tau}\frac{\partial\varepsilon_s}{\partial L_x}$

$\Rightarrow$ for one particle,

$$\langle f_1\rangle = \frac{1}{Z_1}\sum_s e^{-\varepsilon_s/\tau} f_s = \frac{1}{Z_1}\sum_s \underbrace{e^{-\varepsilon_s/\tau}\left(-\frac{\partial\varepsilon_s}{\partial L_x}\right)}_{\tau\frac{\partial}{\partial L_x}\left(e^{-\varepsilon_s/\tau}\right)}$$

$$= \frac{\tau}{Z_1}\sum_s \frac{\partial}{\partial L_x}\left(e^{-\varepsilon_s/\tau}\right)$$

$$\Rightarrow \langle f_1\rangle = \tau\,\frac{1}{Z_1}\,\frac{\partial Z_1}{\partial L_x} = \tau\frac{\partial}{\partial L_x}\log Z_1$$

since $\log Z_1 = \log(n_Q V) = \text{const} + \log(L_xL_yL_z)$

$$\Rightarrow \langle f_1\rangle = \tau\frac{\partial}{\partial L_x}\log(L_xL_yL_z) = \tau\frac{1}{L_x}$$

Entropy

KK Pr. 6-5

- $\tau\, d\sigma = dU + p\, dV$

$$\Rightarrow \quad d\sigma = \frac{1}{\tau}\left(\frac{\partial U}{\partial \tau}\right)_V d\tau + \frac{1}{\tau}\left(\frac{\partial U}{\partial V}\right)_\tau dV + \frac{1}{\tau}\, p\, dV$$

- $pV = N\tau \Rightarrow \frac{1}{\tau} p = \frac{N}{V}$
- $U = \frac{3}{2} N\tau = U(\tau)$ only $\Rightarrow \left(\frac{\partial U}{\partial V}\right)_\tau = 0$
- $\left(\frac{\partial U}{\partial \tau}\right)_V \equiv C_V$
- $\Rightarrow d\sigma = C_V \frac{d\tau}{\tau} + N \frac{dV}{V}$
- Integrate:

$$\sigma(\tau) - \sigma(\tau_0) = C_V \log\tau - C_V \log\tau_0 + N\log V - N \log V_0$$

$$\Rightarrow \quad \boxed{\sigma(\tau) = C_V \log\tau + N \log V + \text{const.}}$$

Free energy

For N *distinct* particles: $Z_N = Z_1^N$

For N *interchangeable* particles: $Z_N = \frac{1}{N!} Z_1^N$

$Z_1 = n_Q V$

$$\Rightarrow F = -\tau \log Z_N = -\tau N\left(\log n_Q + \log V\right) + \tau \log(N!)$$

$$\Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \frac{\tau N}{V} \quad \Rightarrow \quad \boxed{pV = N\tau}$$ as before

For N non-interacting particles:

$$\langle f_N \rangle = \frac{N\tau}{L_x}$$

pressure $$p = \frac{\langle f_N\rangle}{\underbrace{L_y L_z}_{\text{Area}}} = \frac{N\tau}{L_x L_y L_z} = \frac{N\tau}{V}$$

$$\Rightarrow \quad \boxed{pV = N\tau = N k_B T}$$ *ideal gas law*

Heat capacity: C_V and C_p

- $U = \frac{3}{2} N\tau \Rightarrow C_V \equiv \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{3}{2} N \;\Big|\; = \frac{3}{2} N k_B$
- on the other hand, from $dU = \tau d\sigma - p dV$

  $C_V \equiv \left(\frac{\partial U}{\partial \tau}\right)_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V$
- similarly, from $\tau\, d\sigma = dU + p dV$

  $C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p$
- $U = U(\tau)$ *only*! $\Rightarrow \left(\frac{\partial U}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{\partial U}{\partial \tau} = C_V$
- ideal gas law: $pV = N\tau \Rightarrow V = \frac{N\tau}{p}$

  $\Rightarrow p\left(\frac{\partial V}{\partial \tau}\right)_p = p\frac{N}{p} = N$
- $\Rightarrow \boxed{C_p = C_V + N} = \frac{3}{2}N + N = \boxed{\frac{5}{2}N}$
- in thermodynamic units:

  $C_p = C_V + N k_B = \frac{5}{2} N k_B$

For N non-interacting particles:

$$\langle f_N \rangle = \frac{N\tau}{L_x}$$

pressure $$p = \frac{\langle f_N \rangle}{\underbrace{L_y L_z}_{\text{Area}}} = \frac{N\tau}{L_x L_y L_z} = \frac{N\tau}{V}$$

$$\Rightarrow \quad \boxed{pV = N\tau = N k_B T}$$ ideal gas law

Heat capacity: C_V and C_p

- $U = \frac{3}{2}N\tau \Rightarrow C_V \equiv \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{3}{2}N$ | $= \frac{3}{2}N k_B$
- on the other hand, from $dU = \tau d\sigma - p dV$
  $C_V \equiv \left(\frac{\partial U}{\partial \tau}\right)_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V$
- similarly, from $\tau d\sigma = dU + p dV$
  $C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p$
- $U = U(\tau)$ only! $\Rightarrow \left(\frac{\partial U}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{\partial U}{\partial \tau} = C_V$
- ideal gas law: $pV = N\tau \Rightarrow V = \frac{N\tau}{p}$
  $\Rightarrow p\left(\frac{\partial V}{\partial \tau}\right)_p = p\frac{N}{p} = N$
- $\Rightarrow \boxed{C_p = C_V + N} = \frac{3}{2}N + N = \boxed{\frac{5}{2}N}$
- in thermodynamic units:
  $C_p = C_V + N k_B = \frac{5}{2} N k_B$

Entropy

KK Pr. 6-5

- $\tau d\sigma = dU + p dV$

$\Rightarrow d\sigma = \frac{1}{\tau}\left(\frac{\partial U}{\partial \tau}\right)_V d\tau + \frac{1}{\tau}\left(\frac{\partial U}{\partial V}\right)_\tau dV + \frac{1}{\tau} p dV$

- $pV = N\tau \Rightarrow \frac{1}{\tau}p = \frac{N}{V}$
- $U = \frac{3}{2}N\tau = U(\tau)$ only $\Rightarrow \left(\frac{\partial U}{\partial V}\right)_\tau = 0$
- $\left(\frac{\partial U}{\partial \tau}\right)_V \equiv C_V$
- $\Rightarrow d\sigma = C_V \frac{d\tau}{\tau} + N\frac{dV}{V}$
- Integrate:
  $\sigma(\tau) - \sigma(\tau_0) = C_V \log\tau - C_V \log\tau_0 + N\log V - N\log V_0$
  $\Rightarrow \boxed{\sigma(\tau) = C_V \log\tau + N\log V + \text{const.}}$

Free energy

For N *distinct* particles: $Z_N = Z_1^N$

For N *interchangeable* particles: $Z_N = \frac{1}{N!}Z_1^N$

$Z_1 = n_Q V$

$\Rightarrow F = -\tau\log Z_N = -\tau N(\log n_Q + \log V) + \tau\log(N!)$

$\Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \frac{\tau N}{V} \Rightarrow \boxed{pV = N\tau}$ as before

From p. 34 : $n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} = A\,\tau^{3/2}$

$$\Rightarrow \quad F = -\tau N\left(\log A + \tfrac{3}{2}\log\tau + \log V\right) + \tau\log N!$$

$$\Rightarrow \quad \sigma = -\left(\frac{\partial F}{\partial\tau}\right)_V = N\log(n_Q V) + \cancel{\tau}N\frac{3}{2}\frac{1}{\cancel{\tau}} - \log N!$$

Stirling approximation: $\log N! \simeq N\log N - N$

$$\Rightarrow \quad \sigma \simeq N\log\frac{n_Q V}{N} + \tfrac{3}{2}N + N$$

$$\Rightarrow \quad \boxed{\sigma = N\left(\log\frac{n_Q}{n} + \frac{5}{2}\right)}$$

Sackur-Tetrode equation

Note how using F allowed us to determine the previously unknown integration constant!

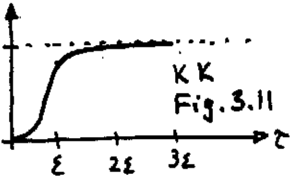
EFTS Verify $U = F + \tau\sigma = \frac{3}{2}N\tau$

Ex a two-level system: $Z = 1 + e^{-\varepsilon/\tau}$ KK Pr 3-1

$$F = -\tau\log Z = -\tau\log\left(1 + e^{-\varepsilon/\tau}\right)$$

$$\sigma = -\left(\frac{\partial F}{\partial\tau}\right)_V = \log\left(1+e^{-\varepsilon/\tau}\right) + \tau\frac{1}{1+e^{-\varepsilon/\tau}}\frac{\varepsilon}{\tau^2}e^{-\varepsilon/\tau}$$

$$= \log\left(1+e^{-\varepsilon/\tau}\right) + \frac{\varepsilon/\tau}{e^{\varepsilon/\tau}+1}$$



KK Fig. 3.11

High-temperature limit:

$$\sigma \to \log\left(1 + e^{0}\right) + \frac{1/\infty}{e^0+1} = \ln 2$$

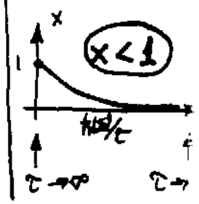
Also: $U = F + \tau\sigma = \ldots = \underline{\dfrac{\varepsilon}{e^{\varepsilon/\tau}+1}}$ as on p. 27

EFTS: use a computer to generate Fig 3.11

Ex a harmonic oscillator: $\varepsilon_s = s\hbar\omega$

$$Z = \sum_s e^{-s\hbar\omega/\tau} = \sum_s x^s, \quad x \equiv e^{-\hbar\omega/\tau}$$

$$= 1 + x + x^2 + \ldots = \frac{1}{1-x} = \frac{1}{1-e^{-\hbar\omega/\tau}}$$



$$\Rightarrow F = -\tau\log Z = -\tau\log\left(\frac{1}{1-e^{-\hbar\omega/\tau}}\right)$$

$$\Rightarrow \underline{F = \tau\log\left(1 - e^{-\hbar\omega/\tau}\right)}$$

see KK Pr. 3-3

High-temperature approximation: $\frac{\hbar\omega}{\tau} \ll 1$

$$\Rightarrow e^{-\hbar\omega/\tau} = 1 - \frac{\hbar\omega}{\tau} + \frac{1}{2!}\left(\frac{\hbar\omega}{\tau}\right)^2 - \ldots \simeq 1 - \frac{\hbar\omega}{\tau}$$

$$\Rightarrow \underline{F \simeq \tau\log\frac{\hbar\omega}{\tau}}$$

Entropy $\sigma = -\left(\frac{\partial F}{\partial\tau}\right)_V =$

$$= -\log\left(1-e^{-\hbar\omega/\tau}\right) - \tau\frac{1}{1-e^{-\hbar\omega/\tau}}\left(-e^{-\hbar\omega/\tau}\right)\left(-\frac{-\hbar\omega}{\tau^2}\right)$$

$$\Rightarrow \sigma_{HO} = \frac{\hbar\omega/\tau}{e^{\hbar\omega/\tau}-1} - \log\left(1-e^{-\hbar\omega/\tau}\right)$$

Fig 3.1.

$$= \frac{\varepsilon/\tau}{e^{\varepsilon/\tau}-1} - \log\left(1 - e^{-\varepsilon/\tau}\right), \quad \varepsilon = \hbar\omega$$

Compare with

$$\sigma_{0,\varepsilon} = \frac{\varepsilon/\tau}{e^{\varepsilon/\tau}+1} + \log\left(1+e^{-\varepsilon/\tau}\right) \leftarrow$$ a 2-level system p.3 Fig3.1

$$\sigma_{\varepsilon,0,\varepsilon} = \frac{2\varepsilon/\tau}{e^{\varepsilon/\tau}+2} + \log\left(1+2e^{-\varepsilon/\tau}\right) \leftarrow$$ a 3-level system Tut. #2

EFTS use a computer to generate Fig 3.13 and to compare with the other two.

4. Planck distribution

"Temperature is a measure of energy"

Q. what is the temperature of em radiation?

e.g. - spectrum of radiation emitted by a hot body photons
- energy spectrum of lattice vibrations in a crystal phonons
- energy inside a cavity with conducting walls

QM description of a particle in a box

SE : $i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)$

separation of variables: $\psi(\vec{r},t) = \phi(\vec{r})\,\xi(t)$

time evolution: $\xi(t) = e^{-i\varepsilon_n t/\hbar}$

spatial part: ϕ_n solution of $\mathcal{H}\phi_n = \varepsilon_n\phi_n$

where $\mathcal{H}$ = Hamiltonian, the energy operator $= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ in 1D

$\phi_n(\vec{r})$ = wavefunction (orbital) in coordinate representation

ε_n = eigenvalue of energy (a number)

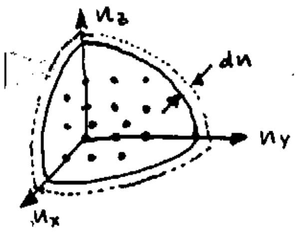
Eigenvalues fixed by the boundary conditions:

ϕ must vanish at boundary ⇒ standing waves

$\Rightarrow \varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$ & $\phi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi n x}{L}$ in 1D

$n^2 = n_x^2 + n_y^2 + n_z^2$ & $\phi_n(\vec{r}) \propto \sin\frac{\pi n_x x}{L_x} \times \sin\frac{\pi n_y y}{L_y} \dots$

Density of states



in n-space: $n^2 = n_x^2 + n_y^2 + n_z^2$

$\varepsilon_n \propto n^2$

- # of states in the interval $(n, n+dn)$ $= \mathcal{D}(n)\,dn$
  e.g. in 1D it is dn itself
  $\Rightarrow \mathcal{D}(n) = \frac{dn}{dn} = 1$
- in 3D consider a thin spherical shell of inner radius n and outer radius n+dn
  ⇒ there are $4\pi n^2\,dn$ states
- n's are +ve integers, do not distinguish $\pm n$, since n^2
  $\Rightarrow \frac{1}{8}4\pi n^2\,dn$
- spin adds multiplicity $\gamma = 2I+1$ to each state
  $\Rightarrow \mathcal{D}(n)\,dn = \frac{\pi n^2 \gamma}{2}\,dn$
- e.g. electron spin $I = \frac{1}{2}$ ⇒ $\gamma = 2$
  $\Rightarrow \mathcal{D}(n) = \pi n^2$
- also possible:

$$\mathcal{D}(\omega) = \underbrace{\frac{\pi n^2}{2}}_{\text{geometry}} \cdot \underbrace{\gamma\frac{dn}{d\omega}}_{\text{type of particle}}$$

EM radiation (photons)

- Wave equation: $\frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2} = \nabla^2\vec{E}$ | cf $i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi$

subject to : $\text{div}\,\vec{E} = 0$ (no sources)

and BC : $E = 0$ @ boundary

time dependence : $e^{-i\varepsilon_n t/\hbar} = e^{-i\omega_n t}$; $\omega_n = \frac{\varepsilon_n}{\hbar}$

ω_n values fixed by BC:

$$\omega_n^2 = c^2\left(\frac{\pi n}{L}\right)^2 \quad \Big| \text{ cf } \varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

$$\Rightarrow \boxed{\omega_n = \frac{c\pi n}{L}}$$

details see EM
e.g. Jackson

- Rewrite : $n = \frac{L\omega_n}{\pi c} \Rightarrow \frac{dn}{d\omega} = \frac{L}{\pi c}$

$$\Rightarrow \mathcal{D}(\omega) = \frac{\pi n^2}{2}\gamma\frac{dn}{d\omega} = \frac{\pi}{2}\left(\frac{L\omega_n}{\pi c}\right)^2\gamma\frac{L}{\pi c} = \frac{\gamma}{2}\frac{\overset{=L^3}{V}}{\pi^2 c^3}\omega_n^2$$

Photons : $I = 1$ so γ should be $= 3$; but $\text{div}\,\vec{E} = 0$ requires that only 2 components of $\vec{E}$ are independent $\Rightarrow \gamma = 2$. E.P. Wigner, Reviews of Modern Physics 29: 255, 1957

$\Rightarrow$ Density of photon modes

$$\boxed{\mathcal{D}(\omega) = \frac{V}{\pi^2 c^3}\omega^2}$$

- occupation # of each mode is determined by the Boltzmann factor:

$$P(s) = \frac{1}{Z}e^{-\hbar\omega_n s/\tau}$$

! completely equivalent to a H.O. problem

$$\Rightarrow \langle s\rangle = \sum_{s=0}^{\infty} s\, e^{-\frac{\hbar\omega_n}{\tau}s} = \ldots \text{EFTS} \ldots = \frac{1}{e^{\hbar\omega_n/\tau} - 1}$$

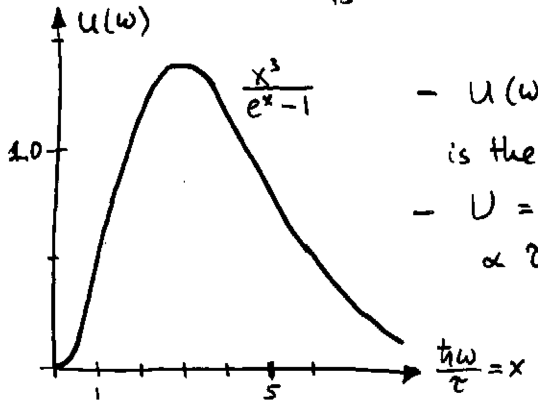
- $u(\omega_n) = \langle s\rangle\hbar\omega_n\mathcal{D}(\omega_n) = \frac{V\hbar}{\pi^2 c^3}\frac{\omega_n^3}{e^{\hbar\omega_n/\tau} - 1}$

$$U = \sum_n u(\omega_n) \simeq \int_0^\infty d\omega\, u(\omega) = \frac{V\hbar}{\pi^2 c^3}\int_0^\infty d\omega\frac{\omega^3}{e^{\hbar\omega/\tau} - 1}$$

$x = \frac{\hbar\omega}{\tau} \Rightarrow \omega^3 = \left(\frac{\tau}{\hbar}\right)^3 x^3$, $d\omega = \frac{\tau}{\hbar}dx$

$$\Rightarrow \boxed{U = \frac{V\hbar}{\pi^2 c^3}\left(\frac{\tau}{\hbar}\right)^4 \underbrace{\int_0^\infty dx\frac{x^3}{e^x - 1}}_{=\frac{\pi^4}{15}\text{, from tables}} = \frac{\pi^2 V}{15\hbar^3 c^3}\tau^4}$$

Stefan - Boltzmann law of radiation

- 

  - $u(\omega) \propto \frac{x^3}{e^x - 1}$, $x = \frac{\hbar\omega}{\tau}$ is the Planck radiation law
  - U = area under the curve $\propto \tau^4$ (Stefan-Boltzmann)

- max of energy : $\frac{d}{dx}\left(\frac{x^3}{e^x - 1}\right) = 0 = \frac{3x^2}{e^x - 1} - \frac{x^3 e^x}{(e^x - 1)^2}$

$\Rightarrow 3e^x - 3 - xe^x = 0 \Rightarrow 3 - 3e^{-x} = x$ solve numerically

$\Rightarrow x \simeq 2.82 \Rightarrow \underline{u}(\omega) = \max$ near $\frac{\hbar\omega}{\tau} = 2.82$

Ex. surface temperature of a star

$$\frac{\hbar\omega}{\tau} = \frac{\hbar\omega}{k_B T} = 2.82 \quad \Leftrightarrow \quad \lambda = \frac{2\pi\hbar c}{2.82\, k_B T} \simeq \frac{0.51}{T} \text{ cm}$$

Sun: $u(\omega)$ = max near $\lambda \simeq 0.8 \times 10^{-4}$ cm

⇒ $T \approx 6000$ K @ Sun's surface

Ex cosmic background radiation peaks out @ $\lambda \simeq 0.16$ cm ⇒ $T \simeq 2.9$ K | one of the term projects

EFTS surface temperature of Earth due to re-radiation of Sun's energy KK Pr. 4-5

Elastic waves (phonons)

Very similar to photons, but:

- multiplicity $\gamma = 3$ (two transverse waves and one longitudinal wave possible)

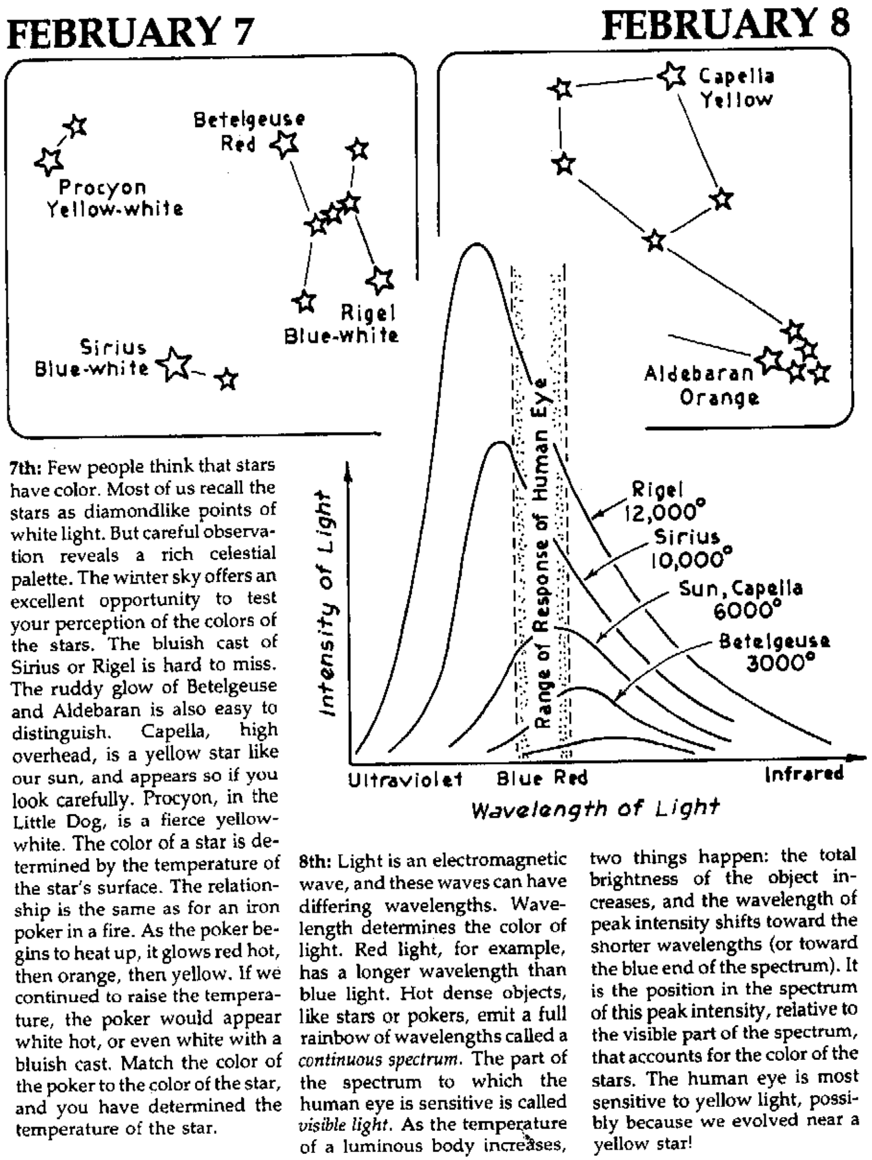
  ⇒ $\mathcal{D}(n) = \frac{3}{2}\pi n^2$

- assuming all modes propagate with the same velocity, $v = v_{sound}$, i.e. no dispersion

  ⇒ $\mathcal{D}(\omega) = \frac{3}{2}\frac{V}{\pi^2 v^3}\omega^2$

- the above only valid up to a maximum $\omega = \omega_D$, after which $\mathcal{D}(\omega > \omega_D) = \emptyset$. $\omega_D = \omega_{Debye}$

"... every solid of finite dimensions contains a finite number of atoms and therefore has a finite number of free vibrations..."



FEBRUARY 7

FEBRUARY 8

7th: Few people think that stars have color. Most of us recall the stars as diamondlike points of white light. But careful observation reveals a rich celestial palette. The winter sky offers an excellent opportunity to test your perception of the colors of the stars. The bluish cast of Sirius or Rigel is hard to miss. The ruddy glow of Betelgeuse and Aldebaran is also easy to distinguish. Capella, high overhead, is a yellow star like our sun, and appears so if you look carefully. Procyon, in the Little Dog, is a fierce yellow-white. The color of a star is determined by the temperature of the star's surface. The relationship is the same as for an iron poker in a fire. As the poker begins to heat up, it glows red hot, then orange, then yellow. If we continued to raise the temperature, the poker would appear white hot, or even white with a bluish cast. Match the color of the poker to the color of the star, and you have determined the temperature of the star.

8th: Light is an electromagnetic wave, and these waves can have differing wavelengths. Wavelength determines the color of light. Red light, for example, has a longer wavelength than blue light. Hot dense objects, like stars or pokers, emit a full rainbow of wavelengths called a *continuous spectrum*. The part of the spectrum to which the human eye is sensitive is called *visible light*. As the temperature of a luminous body increases, two things happen: the total brightness of the object increases, and the wavelength of peak intensity shifts toward the shorter wavelengths (or toward the blue end of the spectrum). It is the position in the spectrum of this peak intensity, relative to the visible part of the spectrum, that accounts for the color of the stars. The human eye is most sensitive to yellow light, possibly because we evolved near a yellow star!

Actual page from 365 Starry Nights

- find ω_D from normalization:

$$\int_0^\infty d\omega\, \mathcal{D}(\omega) \rightarrow \int_0^{\omega_D} d\omega\, \mathcal{D}(\omega) = 3N$$

since total # of elastic modes = # of degrees of freedom = 3N

$$\Rightarrow \int_0^{\omega_D} d\omega \frac{3}{2}\frac{V}{\pi^2 v^3}\omega^2 = \frac{V}{2\pi^2 v^3}\omega_D^3$$

$$\Rightarrow \underline{\omega_D = \left(\frac{6\pi^2 N v^3}{V}\right)^{1/3}}$$

- $$U = \int_0^{\omega_D} d\omega\, \mathcal{D}(\omega) \langle s\rangle \hbar\omega = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/\tau}-1}$$

$$x = \frac{\hbar\omega}{\tau} \Rightarrow \omega = \frac{\tau}{\hbar}x \text{ and } d\omega = \frac{\tau}{\hbar}dx$$

$$\Rightarrow \boxed{U = \frac{9N\tau^4}{(\hbar\omega_D)^3}\int_0^{x_D} dx \frac{x^3}{e^x-1}}$$

where $x_D = \frac{\hbar\omega_D}{\tau} = \frac{\hbar\omega_D}{k_B}\frac{1}{T} = \frac{\Theta}{T}$

with $\Theta = \frac{\hbar\omega_D}{k_B}$ = Debye temperature

- In particular, at low temperatures: $T \ll \Theta$

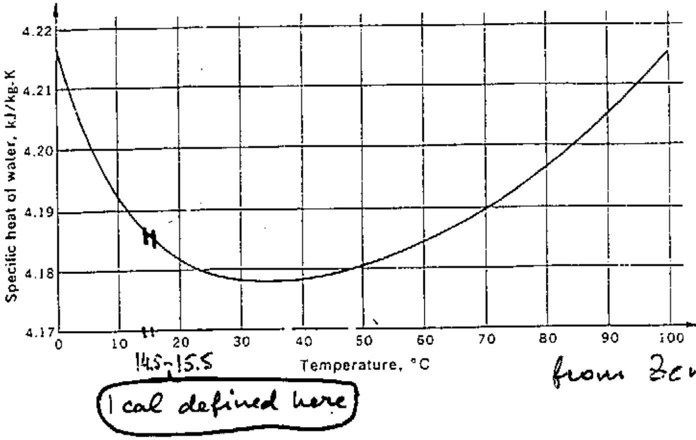
$\Rightarrow x_D \gg 1 \Rightarrow$ approximate $\int_0^{x_D}$ by $\int_0^\infty$

$$\Rightarrow U(T \ll \Theta) \simeq \frac{9N\tau^4}{(\hbar\omega_D)^3}\underbrace{\int_0^\infty dx \frac{x^3}{e^x-1}}_{=\frac{\pi^4}{15}} = \frac{3\pi^4 N k_B}{5\Theta^3}T^4$$

$$\Rightarrow \boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{12\pi^4 N k_B}{5\Theta^3}T^3 = \underbrace{\frac{12\pi^4 N k_B}{5}\left(\frac{T}{\Theta}\right)^3}_{\text{Debye } T^3 \text{ law}}}$$

see Fig. 4.10

EFTS examine $T \gg \Theta$ (Pr. 4-11)



H_2O a fluid

from Zemansky

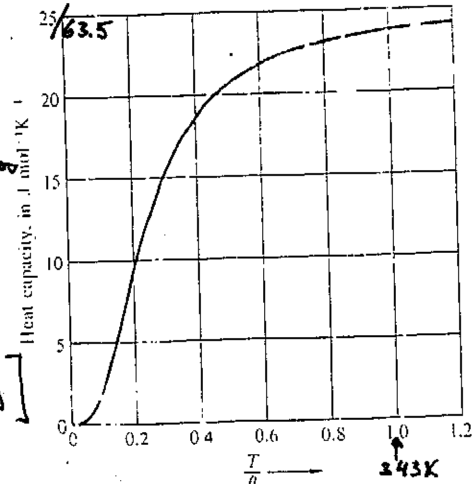


Figure 4.1. Heat capacity C_V of a solid according to the Debye approximation. The vertical scale is in J mol^{-1} K^{-1}. The horizontal scale is the temperature normalized to the Debye temperature θ. The region of the T^3 law is below 0.1θ. The asymptotic value at high values of T/θ is 24.943 J mol^{-1} K^{-1}.

[phonons only, ignoring C_V of electrons]

$\Theta_{Cu} = 343K$

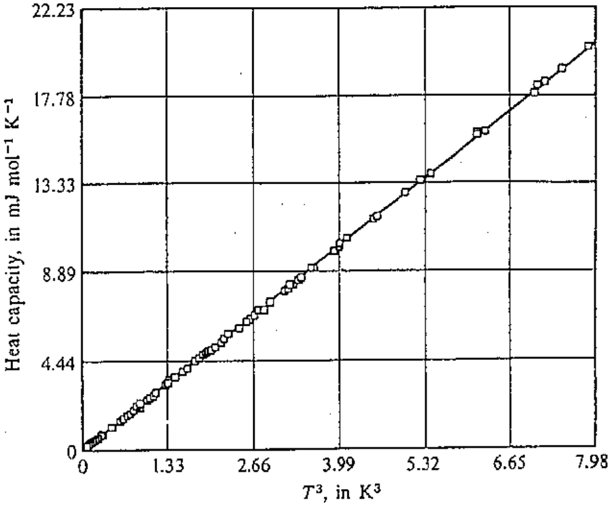


Figure 4.10 Low temperature heat capacity of solid argon, plotted against T^3 to show the excellent agreement with the Debye T^3 law. The value of θ from these data is 92 K. Courtesy of L. Finegold and N. E. Phillips.

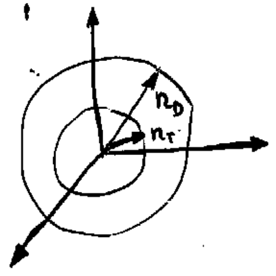
Table 4.1 Debye temperature θ_0 in K

Li 344	Be 1440											B	C 2230	N	O	F	Ne 75
Na 158	Mg 400											Al 428	Si 645	P	S	Cl	Ar 92
K 91	Ca 230	Sc 360	Ti 420	V 380	Cr 630	Mn 410	Fe 470	Co 445	Ni 450	Cu 343	Zn 327	Ga 320	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56	Sr 147	Y 280	Zr 291	Nb 275	Mo 450	Tc	Ru 600	Rh 480	Pd 274	Ag 225	Cd 209	In 108	Sn *w* 200	Sb 211	Te 153	I	Xe 64
Cs 38	Ba 110	Laβ 142	Hf 252	Ta 240	W 400	Re 430	Os 500	Ir 420	Pt 240	Au 165	Hg 71.9	Tl 78.5	Pb 105	Bi 119	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd 200	Tb	Dy 210	Ho	Er	Tm	Yb 120	Lu 210	
			Th 163	Pa	U 207	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

NOTE: The subscript zero on the θ denotes the low temperature limit of the experimental values.

Debye T^3 law : an intuitive argument

- traveling wave modes $e^{-i(\vec{n}\cdot\vec{r}-\omega t)}$
- no modes for $|\vec{n}| > n_D$
- at temperature $\tau = k_B T$, all modes below n_T have energy $\varepsilon = \tau = k_B T$ and above n_T (but below n_D) modes are not excited.
- total # of modes $= 3N$
- in n-space : 2 spheres



$$\frac{\text{total \# of excited modes}}{\text{total \# of modes} \approx 3N} = \Big(\underset{\overset{\uparrow}{n \propto T}}{\frac{n_T}{n_D}}\Big)^3 = \Big(\frac{T}{\theta}\Big)^3$$

- $U = k_B T \times 3N \times \left(\frac{T}{\theta}\right)^3 = 3N k_B \frac{T^4}{\theta^3}$

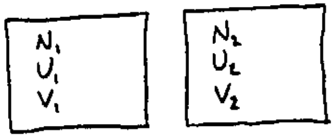
$$\Rightarrow \quad C_V = 12 N k_B \left(\frac{T}{\theta}\right)^3$$

We used $\langle n \rangle = \frac{1}{e^{\hbar\omega/\tau}-1} \simeq \frac{1}{1+\frac{\hbar\omega}{\tau}+\ldots-1} \simeq \frac{\tau}{\hbar\omega}$

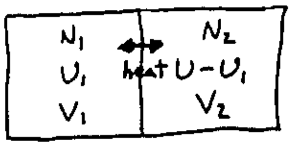
$$\Rightarrow \underline{\underline{\langle n \rangle \propto T}}$$

5. Gibbs distribution

Systems in diffusive contact

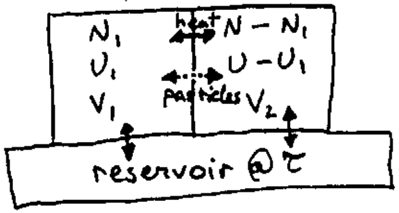


Bring the two systems into thermal contact



- one fewer constraints
- $\frac{1}{\tau_1} \equiv \left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1,V_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2,V_2} = \frac{1}{\tau_2}$ at equilibrium
- Heat flows from the system with higher τ to the one with lower τ; $\tau_1 = \tau_2$ @ eq-m.
- at eq-m, $F = U - \tau\sigma$ is at a minimum w.r. to the partitioning of energy $U_1 / U - U_1$ i.e. subject to constraint $U_1 + U_2 = U = \text{const}$.

Bring the systems into diffusive contact as well



- for simplicity, maintain $\tau = \text{const}$ by placing both systems into thermal contact with a reservoir @ τ
- diffusive eq-m ⇔ F is at a minimum w.r. to the partitioning of particles $N_1 / N - N_1$, i.e. subject to constraint $N = N_1 + N_2 = \text{const}$

At a minimum:

$$dF = 0 = \left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2} dN_2$$

Also: $N_1 + N_2 = N = \text{const} \Rightarrow dN_1 + dN_2 = dN = 0$

$\Rightarrow dN_1 = -dN_2$

$$\Rightarrow dF = \left[\left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} - \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2}\right] dN_1 = 0$$

$$\Rightarrow \underline{\left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} = \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2}} \quad \text{at diffusive eq-m}$$

$$\mu = \mu(\tau, V, N) \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \text{chemical potential}$$

$$\Rightarrow \boxed{\mu_1 = \mu_2} \quad \text{at diffusive eq-m}$$

Direction of particle flow

Assume particle flow from $S_1 \to S_2$

$\Rightarrow dN_1 < 0$, $dN_2 > 0$

The combined system is moving towards eq-m i.e. a minimum of F if $dF < 0$

$$\Rightarrow \left[\left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} - \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2}\right] > 0$$

$\Rightarrow \mu_1 - \mu_2 > 0 \Rightarrow \underline{\mu_1 > \mu_2}$

⇒ To bring the system to diffusive eq-m particles flow from regions of high μ to regions of low μ

Ex <u>ideal gas</u>

Strictly speaking, the smallest $dN = 1$ particle

$$\Rightarrow \quad \mu(\tau, V, N) = F(\tau, V, N) - F(\tau, V, N-1)$$

In the derivation of ideal gas law on p.37 we had:

$$F = -\tau N(\log n_Q + \log V) + \tau \log(N!)$$

$$\Rightarrow \mu = F(N) - F(N-1)$$
$$= -\tau(\log n_Q + \log V) + \tau\big[\underbrace{\log N! - \log(N-1)!}_{\log\frac{N!}{(N-1)!} = \log N}\big]$$

$$\Rightarrow \boxed{\mu = \tau \log \frac{N}{n_Q V} = \tau \log \frac{n}{n_Q}}$$

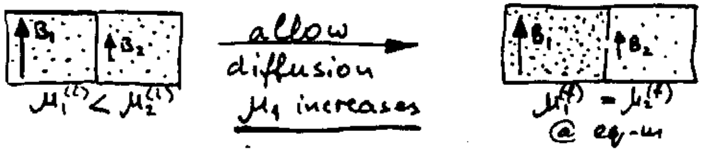
where $n = \frac{N}{V}$ = concentration of particles

Note: μ increases with concentration
$\Rightarrow$ to reach diffusive eq-m particles flow from regions of higher concentration to regions of lower concentration.

Ex paramagnetism

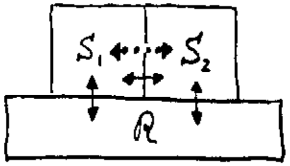
$$F = U - \tau\sigma = -\frac{m^2B^2N}{\tau} - \tau\left(\sigma_0 - \frac{m^2B^2N}{\tau^2}\right) \quad \text{see p.20}$$

$$\Rightarrow \mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = -\frac{m^2B^2}{2\tau}$$



! magnetic particles concentrate in region of high B

Entropy and chemical potential



$$\sigma = \sigma(U, V, N)$$

$$d\sigma = \left(\frac{\partial\sigma}{\partial U}\right)_{V,N} dU + \cancel{\left(\frac{d\sigma}{\partial V}\right)_{U,N} dV}^{\,\phi} + \left(\frac{d\sigma}{\partial N}\right)_{U,V}$$

- In this case – when we break the membrane separating S_1 and S_2 – total V = const $\Rightarrow dV =$
- Because of the reservoir, τ = const. This imposes a constraint on dU, dV, dN, i.e. dU, dV, dN cannot be varied independently, only in a certain way, to keep τ = const.

  Notation: $d\sigma \to (\delta\sigma)_\tau$, $dU \to (\delta U)_\tau$, $dN \to (\delta N)$
- $$(\delta\sigma)_\tau = \left(\frac{\partial\sigma}{\partial U}\right)_{V,N} (\delta U)_\tau + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} (\delta N)_\tau$$

$$\Rightarrow \underset{\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V}}{\overset{\parallel}{\frac{(\delta\sigma)_\tau}{(\delta N)_\tau}}} = \underset{\frac{1}{\tau}}{\overset{\parallel}{\left(\frac{\partial\sigma}{\partial U}\right)_{V,N}}} \underset{\left(\frac{\partial U}{\partial N}\right)_{\tau,V}}{\overset{\parallel}{\frac{(\delta U)_\tau}{(\delta N)_\tau}}} + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V}$$

$$\Rightarrow \tau\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,V} \qquad (*)$$

- $F = U - \tau\sigma$ and since τ = const:

$$\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} - \tau\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V} \qquad (**)$$

- Now subtract $(**)$ from $(*)$

$$\Rightarrow \cancel{\tau\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V}} - \mu = \tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,V} + \cancel{\tau\left(\frac{\partial\sigma}{\partial N}\right)_{\tau,V}}$$

$$\Rightarrow \boxed{\mu = -\tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,V}} \quad \text{or} \quad \boxed{-\frac{\mu}{\tau} = \left(\frac{\partial\sigma}{\partial N}\right)_{U,V}}$$

cf. $\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_{N,V}$

- Note that the <u>same</u> physical relationship between σ, U, V, N can be looked upon as

$\sigma = \sigma(U,V,N)$ or $U = U(\sigma,V,N)$ or $F = F(\tau,V,N)$

<u>Summary</u>

KK Table 5-1

	$\sigma(U,V,N)$	$U(\sigma,V,N)$	$F(\tau,V,N)$
temperature τ	$\frac{1}{\tau} \equiv \left(\frac{\partial\sigma}{\partial U}\right)_{V,N}$ notes p.15	$\tau = \left(\frac{\partial U}{\partial\sigma}\right)_{V,N}$ KK p.42 *	τ itself a variable
pressure p	$\frac{p}{\tau} = \left(\frac{\partial\sigma}{\partial V}\right)_{U,N}$ KK p.66-67 *	$-p = \left(\frac{\partial U}{\partial V}\right)_{\sigma,N}$ notes p.32	$-p = \left(\frac{\partial F}{\partial V}\right)_{\tau,N}$ notes p.33
chemical potential μ	$-\frac{\mu}{\tau} = \left(\frac{\partial\sigma}{\partial N}\right)_{U,V}$ notes p.50	$\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$ KK Pr. 5-11 *	$\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$ notes p.47

EFTS review KK p.42; pp.66-67; do Pr. 5-11

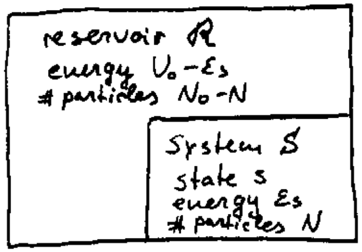
Ex thermodynamic identity

was: $\boxed{d\sigma = \frac{1}{\tau}dU + \frac{p}{\tau}dV}$ or $\boxed{dU = \tau d\sigma - p dV}$

generalize: $d\sigma = \left(\frac{\partial\sigma}{\partial V}\right)_{V,N} dU + \left(\frac{\partial\sigma}{\partial V}\right)_{U,N} dV + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} dN$

$$\Rightarrow \boxed{d\sigma = \frac{1}{\tau}dU + \frac{p}{\tau}dV - \frac{\mu}{\tau}dN} \quad \text{or} \quad \boxed{dU = \tau d\sigma - p dV + \mu dN}$$

<u>The grand partition function</u>



repeat the derivation of Boltzmann factor on p.22 <u>but</u> now allow $\mathcal{R}$ and $\mathcal{S}$ to be in thermal <u>and</u> diffusive eq-m.

Highlights:

- $g(\mathcal{R}+\mathcal{S}) = g_{\mathcal{R}} \times \overset{=1}{g_{\mathcal{S}}} = g_{\mathcal{R}}$
- compare 2 states: $U_0 - \varepsilon_1,\ N_0 - N_1$
  $U_0 - \varepsilon_2,\ N_0 - N_2$

$$\Rightarrow \frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{g(N_0-N_1,\,U_0-\varepsilon_1)}{g(N_0-N_2,\,U_0-\varepsilon_2)} = e^{\Delta\sigma_R}$$

- $\sigma(N_0-N,\,U_0-\varepsilon) = \sigma(N_0,U_0) - N\left(\frac{\partial\sigma}{\partial N}\right)_{N_0,U_0} - \varepsilon\left(\frac{\partial\sigma}{\partial U}\right)_{N_0,U_0} + \dots$

$\Rightarrow$ to first order in (N_1-N_2) and $(\varepsilon_1-\varepsilon_2)$:

$$\Delta\sigma = \sigma(N_0-N_1,\,U_0-\varepsilon_1) - \sigma(N_0-N_2,\,U_0-\varepsilon_2) \simeq$$

$$= -(N_1-N_2)\underbrace{\left(\frac{\partial\sigma}{\partial N}\right)_{N_0,U_0}}_{\equiv -\frac{\mu}{\tau}} - (\varepsilon_1-\varepsilon_2)\underbrace{\left(\frac{\partial\sigma}{\partial U}\right)_{N_0,U_0}}_{\equiv \frac{1}{\tau}}$$

$$= \frac{(N_1-N_2)\mu}{\tau} - \frac{\varepsilon_1-\varepsilon_2}{\tau}$$

was: just $-\frac{\varepsilon_1-\varepsilon_2}{\tau}$

- $\Rightarrow \boxed{\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{e^{(N_1\mu-\varepsilon_1)/\tau}}{e^{(N_2\mu-\varepsilon_2)/\tau}}}$

or $P(N,\varepsilon) \propto e^{(N\mu-\varepsilon)/\tau}$ = <u>Gibbs factor</u>

- normalization:

$$\mathcal{Z}(\mu,\tau) = \sum_{\underset{\uparrow}{N_s=0}}^{\infty} \sum_{\underset{\uparrow}{S(N)}} e^{(N_s\mu-\varepsilon_s)/\tau} = \sum_{ASN} e^{(N_s\mu-\varepsilon_s)/\tau}$$

sum over # particles; sum over all states, for a given # particles

$\mathcal{Z}(\mu,\tau)$ = grand partition function — grand sum, Gibbs sum

and then

$$P(N,\varepsilon) = \frac{1}{\mathcal{Z}} e^{(N\mu-\varepsilon)/\tau}$$

is properly normalized: $\sum_{ASN} P(N,\varepsilon) = \frac{\mathcal{Z}}{\mathcal{Z}} = 1$

- the grand canonical ensemble

Ex $\langle N_s\rangle = \frac{1}{\mathcal{Z}} \sum_{ASN} N_s e^{(N_s\mu-\varepsilon)/\tau}$ by def-n.

Noting that $\frac{\partial \mathcal{Z}}{\partial\mu} = \frac{1}{\tau}\sum_{ASN} N e^{(N\mu-\varepsilon)/\tau}$

$$N = \langle N_s\rangle = \frac{\tau}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu} = \tau\frac{\partial}{\partial\mu}(\log\mathcal{Z})$$

- $\boxed{\lambda \equiv e^{\mu/\tau}}$ = absolute activity | cf $\beta \equiv \frac{1}{\tau}$

$$\Rightarrow \mathcal{Z} = \sum_{ASN} \lambda^N e^{-\varepsilon_s/\tau}$$

and since $\frac{\partial\mathcal{Z}}{\partial\mu} = \frac{\partial\mathcal{Z}}{\partial\lambda}\frac{\partial\lambda}{\partial\mu} = \frac{\partial\mathcal{Z}}{\partial\lambda}\frac{1}{\tau}\lambda$

$$\Rightarrow N = \frac{\lambda}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\lambda} = \lambda\frac{\partial}{\partial\lambda}(\log\mathcal{Z})$$

| cf $U = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$

Ex $U = \langle\varepsilon_s\rangle = \frac{1}{\mathcal{Z}}\sum_{ASN}\varepsilon_s e^{\beta(N_s\mu-\varepsilon_s)}$

Note: $\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\beta} = \frac{1}{\mathcal{Z}}\sum_{ASN}(N_s\mu-\varepsilon_s)e^{\beta(N_s\mu-\varepsilon_s)} = \langle N_s\mu-\varepsilon_s\rangle$

$$= \langle N_s\rangle\mu - \langle\varepsilon_s\rangle = N\mu - U$$

$$\Rightarrow \boxed{U} = N\mu - \frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\beta} = \tau\mu\frac{\partial}{\partial\mu}(\log\mathcal{Z}) - \frac{\partial}{\partial\beta}(\log\mathcal{Z})$$

$$\boxed{= \left[\frac{\mu}{\beta}\frac{\partial}{\partial\mu} - \frac{\partial}{\partial\beta}\right](\log\mathcal{Z})} = \left[\mu\tau\frac{\partial}{\partial\mu} - \tau^2\frac{\partial}{\partial\tau}\right](\log\mathcal{Z})$$

- Again, for small systems:
  1. calculate $\mathcal{Z}$ by explicit summation
  2. obtain thermodynamic quantities from $\mathcal{Z}$

Ex a two-level system KK Pr 5-6

two states:
- occupied, N , $\varepsilon_s = 0$ or ε
- unoccupied, $N = 0$, $\varepsilon_s = 0$

a) $\mathcal{Z} = \sum_{N_s}\sum_{s} e^{(N_s\mu-\varepsilon_s)/\tau} = \sum_{N_s}\sum_{s}\lambda^{N_s}e^{-\varepsilon_s/\tau} = \lambda^0 e^0 + \lambda^1 e^0 + \lambda^1 e^{-\varepsilon/\tau}$

$$= 1 + \lambda + \lambda e^{-\varepsilon/\tau}$$

b) $N = \langle N_s\rangle = \sum_{ASN}\frac{N\lambda^N e^{-\varepsilon_s/\tau}}{\mathcal{Z}} = \frac{0\lambda^0e^0 + 1\lambda^1e^0 + 1\lambda^1e^{-\varepsilon/\tau}}{\mathcal{Z}}$

$$= \frac{\lambda + \lambda e^{-\varepsilon/\tau}}{\mathcal{Z}}$$

c) $$\langle N_\varepsilon \rangle = \sum_{\substack{N_\varepsilon, \\ \varepsilon_s = \varepsilon}} \frac{N_\varepsilon \lambda^N e^{-\varepsilon/\tau}}{\mathcal{Z}} = \frac{1\lambda^1 e^{-\varepsilon/\tau}}{\mathcal{Z}} = \frac{\lambda e^{-\varepsilon/\tau}}{\mathcal{Z}}$$

d) $$\langle \varepsilon_s \rangle = \sum_{ASN} \frac{\varepsilon_s \lambda^N e^{-\varepsilon_s/\tau}}{\mathcal{Z}} = \frac{0\lambda^0 e^0 + 0\lambda^1 e^0 + \varepsilon\lambda^1 e^{-\varepsilon/\tau}}{\mathcal{Z}}$$

$$= \frac{\varepsilon \lambda e^{-\varepsilon/\tau}}{\mathcal{Z}}$$

e) $$\mathcal{Z} = \sum_{ASN} \lambda^N e^{-\varepsilon_s/\tau} = \underset{N=0}{\lambda^0 e^0} + \underset{\substack{N=1\\ \varepsilon_1=0}}{\lambda^1 e^0} + \underset{\substack{N_1\\ \varepsilon_1=\varepsilon}}{\lambda^1 e^{-\varepsilon/\tau}} + \underset{\substack{N=2\\ \varepsilon_1=0,\, \varepsilon_2=\varepsilon}}{\lambda^2 e^{-\varepsilon/\tau}}$$

$$= \left(1+\lambda + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-\varepsilon/\tau}\right) = (1+\lambda)\left(1+\lambda e^{-\varepsilon/\tau}\right)$$

Note: $\mathcal{Z} = \mathcal{Z}_1 \mathcal{Z}_2$ where

$\mathcal{Z}_1$: states of $\varepsilon_s = 0$: occupied $\underset{\lambda}{}$ and unoccupied $\underset{1}{}$

$\mathcal{Z}_2$: states of $\varepsilon_s = \varepsilon$: occupied $\underset{\lambda e^{-\varepsilon/\tau}}{}$ and unoccupied $\underset{\underline{\underline{1}}}{}$!

Effectively, two separate independent systems

Ex O_2 carried by myoglobin KK Ex. pp. 140-2

$\underset{\substack{N=0\\ \varepsilon_s=0}}{\square}$ or $\underset{\substack{N=1\\ \varepsilon_s=\varepsilon}}{\boxed{O_2}}$ $\Rightarrow \mathcal{Z} = 1 + \lambda e^{-\varepsilon/\tau}$

$$\Rightarrow P(\text{occupied}) = \frac{\lambda e^{-\varepsilon/\tau}}{1+\lambda e^{-\varepsilon/\tau}} = \frac{1}{\frac{1}{\lambda}e^{\varepsilon/\tau}+1}$$

ideal gas : $\mu = \tau \log \frac{n}{n_Q} = \tau \log \frac{p}{\tau n_Q}$ see p. 48

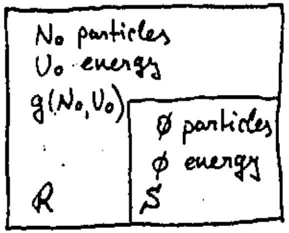
$$\Rightarrow P(\text{occ.}) = \frac{p}{n_Q e^{\varepsilon/\tau} + p} = \frac{p}{p_0 + p}$$ Langmuir isotherm KK Fig 5-11

Other distribution functions

- **Fermions** : particles of $\frac{1}{2}$-integer spin $(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots)$

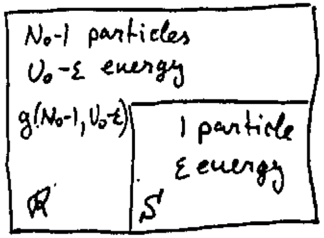
e.g. $\bar{e}, n, p$ have $I = \frac{1}{2}$; ^3He has $2\bar{e}, 2p, 1n \rightarrow$ half-integer

QM : Pauli exclusion principle requires that only one particle per state is allowed :



vacant state
[occupancy = 0]

and



occupied state
[occupancy = 1]

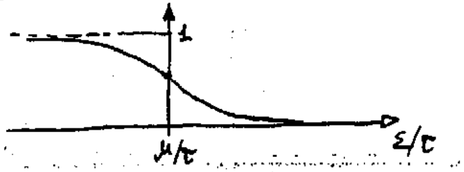
$$\mathcal{Z} = \lambda^0 e^0 + \lambda^1 e^{-\varepsilon/\tau} = 1 + \lambda e^{-\varepsilon/\tau}$$

$$N = \langle N_s \rangle = \frac{0\lambda^0 e^0 + 1\lambda^1 e^{-\varepsilon/\tau}}{\mathcal{Z}} = \frac{\lambda e^{-\varepsilon/\tau}}{1+\lambda e^{-\varepsilon/\tau}} = \frac{1}{\frac{1}{\lambda}e^{\varepsilon/\tau}+1}$$

Recall: $\lambda \equiv e^{\mu/\tau} \Rightarrow N = \frac{1}{e^{(\varepsilon-\mu)/\tau}+1}$

N = average occupancy of the orbital of energy ε

Denote: $$\boxed{f(\varepsilon) = N_\varepsilon = \frac{1}{e^{(\varepsilon-\mu)/\tau}+1}}$$ Fermi-Dirac distribution



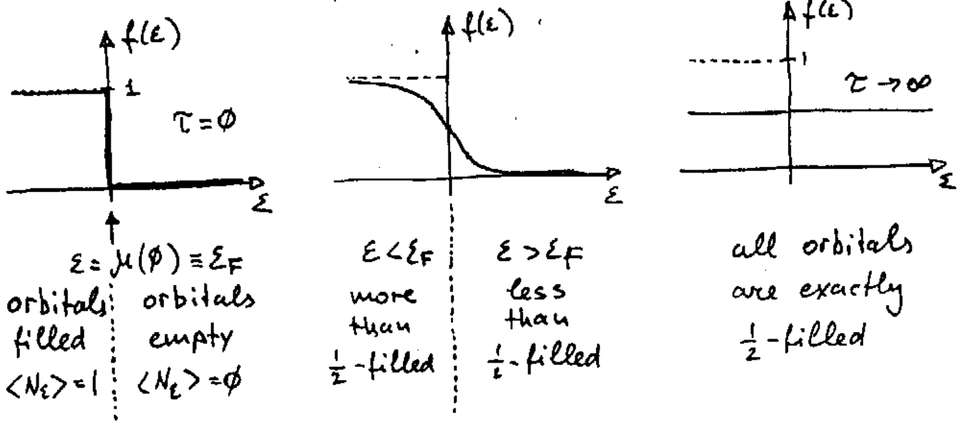
Note: the horizontal axis is in units of τ!

Hence the temperature dependence of $f(\varepsilon)$.

In particular, KK Pr. 6-1

$$\frac{\partial f}{\partial \varepsilon} = \frac{\frac{1}{\tau}\, e^{(\varepsilon-\mu)/\tau}}{\left(e^{(\varepsilon-\mu)/\tau}+1\right)^2} \xrightarrow[\varepsilon=\mu]{} \frac{1}{4\tau}$$

, i.e. slope of the curve is steeper at low temperatures:



Actually, at high temperatures is slightly more complicated. $f(\varepsilon=\mu) = \frac{1}{2}$ always, but $\mu(\tau) \neq \mu(0)$

See KK Fig 7-5.

In the classical regime, i.e. far away from the quantum limit of $\varepsilon \sim \tau = k_B T$, have

$$\varepsilon - \mu \gg \tau$$

$\Rightarrow$ occupancy of all orbitals is very small, $f(\varepsilon) \ll 1$ for all ε

- Bosons: particles of integer spin $(0, 1, 2 \ldots)$

e.g. ^{4}He has $2\bar{e}, 2p, 2n$ → integer spin ; photons, phonons (in some contexts)

Q.M.: arbitrary number of particles can be in any given state.

Choose one state (one q.m. orbital) as the system $\mathcal{S}$; all others are in $\mathcal{R}$

$N_{\varepsilon_s} = 0, 1, 2 \ldots$ are all possible

$$\Rightarrow \mathcal{Z} = \sum_{N=0}^{\infty} \lambda^N e^{-N\varepsilon/\tau} = \sum_{N=0}^{\infty}\left[\lambda e^{-\varepsilon/\tau}\right]^N = \frac{1}{1-\lambda e^{-\varepsilon/\tau}}$$

for N non-interacting bosons

Note: $\frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots = \sum_{N=0}^{\infty} x^N$ only if $x < 1$

$$\Rightarrow \lambda e^{-\varepsilon/\tau} < 1 \Rightarrow e^{(\mu-\varepsilon)/\tau} < 1 \Rightarrow \mu - \varepsilon < 0$$

$$\Rightarrow \mathcal{Z} = \frac{1}{1-\lambda e^{-\varepsilon/\tau}} = \frac{1}{1-e^{(\mu-\varepsilon)/\tau}} \quad \text{for } \varepsilon > \mu$$

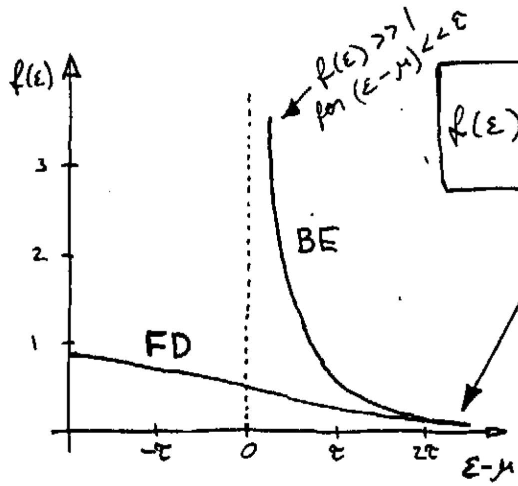
$$\overset{\text{see p.52}}{\Rightarrow} N = \lambda \frac{\partial}{\partial\lambda}(\log \mathcal{Z}) = \lambda \frac{\partial}{\partial\lambda}\left[-\log\left(1-\lambda e^{-\varepsilon/\tau}\right)\right]$$

$$= -\lambda \frac{-e^{-\varepsilon/\tau}}{1-\lambda e^{-\varepsilon/\tau}} = \frac{1}{\frac{1}{\lambda}e^{\varepsilon/\tau} - 1}$$

$$\Rightarrow \boxed{f(\varepsilon) = N_\varepsilon = \frac{1}{e^{(\varepsilon-\mu)/\tau} - 1}}$$

Bose-Einstein distribution

Note: only works for $\varepsilon > \mu$, else N = # of bosons diverges



$$\boxed{f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau} \pm 1}}$$

<u>classical regime</u>:

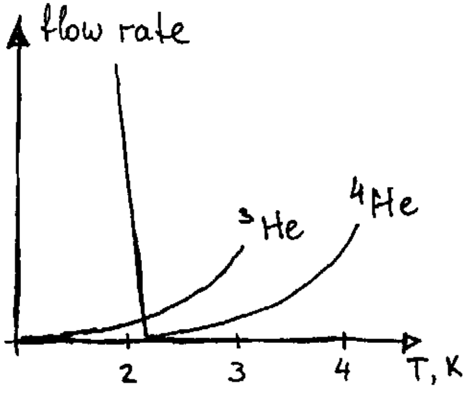
$(\varepsilon - \mu) \gg \tau$

$\Rightarrow e^{(\varepsilon-\mu)/\tau} \gg 1$

$$\Rightarrow f_{FD}(\varepsilon) \approx f_{BE}(\varepsilon) \approx \underbrace{\lambda e^{-\varepsilon/\tau}}_{\text{classical distribution function}}$$

In the classical regime the occupancy of <u>both</u> fermion and boson systems is very small.

- Experimentally, the change in sign has dramatic consequences: ^{4}He superfluidity



As seen by Kapitsa in 1949:
ratio of flow viscosities above and below 2.17 K of 10^7!

Ex <u>ideal gas (revisited)</u>

- <u>Reminder</u>: SE for N particles in a box is being solved only <u>approximately</u> when we distribute our N particles among "orbitals"

  orbital = solution of SE for <u>one</u> particle

  This is only valid for non-interacting particles
- in the classical regime, $f(\varepsilon_s) \simeq \lambda e^{-\varepsilon/\tau} \ll 1$
- $N = \langle N_\varepsilon \rangle = \sum_s f(\varepsilon_s)$ ← now summing over orbitals s, of energy ε_s

$$= \lambda \underbrace{\sum_s e^{-\varepsilon_s/\tau}}_{= Z_1 = \text{partition function for 1 particle}} = \lambda Z_1$$

As before:

$Z_1 = n_Q V \quad , \quad n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$ see p. 34

$\Rightarrow \lambda = \frac{N}{Z_1} = \frac{N}{n_Q V} = \frac{n}{n_Q}$ with $n \equiv \frac{N}{V}$

By def'n: $\lambda \equiv e^{\mu/\tau} = \frac{n}{n_Q}$

$\Rightarrow \underline{\mu = \tau \log\left(\frac{n}{n_Q}\right)}$ cf. p. 48

or $\underline{\mu = \tau \left[\log N - \log V - \frac{3}{2}\log\tau + \frac{3}{2}\log\frac{2\pi\hbar^2}{M}\right]}$

- free energy

At constant τ & V : $\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$

$$\Rightarrow \quad F = \int_0^N dN\, \mu(N;\tau,V) = \int_0^N dN\, \tau \log\frac{n}{n_Q}$$

$$= \tau \int_0^N dN \left[\underbrace{\log N} - \log V - \tfrac{3}{2}\log\tau + \tfrac{3}{2}\log(\dots)\right]$$

From integral tables: $\int dN \log N = N\log N - N$

$$\Rightarrow \quad F = \tau\left[N\log N - N - N\log V - N\tfrac{3}{2}\log\tau + N\tfrac{3}{2}\log(\dots)\right]$$

$$= \tau N\left[\log N \enclose{circle}{-1} - \log V - \tfrac{3}{2}\log\tau + \tfrac{3}{2}\log(\dots)\right]$$

$$\Rightarrow \boxed{F = \tau N\left[\log\frac{n}{n_Q} - 1\right]}$$

- pressure

At constant τ & N : $p \equiv -\left(\frac{\partial F}{\partial V}\right)_{\tau,N}$

$$\Rightarrow \quad p = -N\tau\frac{\partial}{\partial V}\left[\log N - 1 \underbrace{-\log V} - \tfrac{3}{2}\log\tau + \tfrac{3}{2}\log(\dots)\right] = \frac{N\tau}{V}$$

$$\Rightarrow \quad \boxed{pV = N\tau = Nk_BT}$$

- entropy

At constant V & N : $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N}$

$$\Rightarrow \quad \sigma = -N\left[\log\frac{n}{n_Q} - 1\right] - N\tau\frac{\partial}{\partial\tau}\left[\dots - \tfrac{3}{2}\log\tau + \dots\right]$$

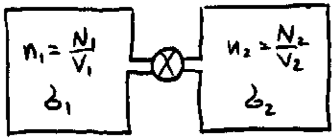
$$= -N\left[\log\frac{n}{n_Q} - 1 - \tfrac{3}{2}\right] = N\left[\log\frac{n_Q}{n} + \tfrac{5}{2}\right]$$

$$\boxed{\sigma = N\left[\log\frac{n_Q}{n} + \frac{5}{2}\right]}$$

Sackur-Tetrode equ.

FITS DATA! – read KK pp. 167-8

Ex



$n_1 = n_2 = n$

i.e. same concentration

$$\sigma_{\text{total}} = \sigma_1 + \sigma_2 = (N_1+N_2)\left[\log\frac{n_Q}{n} + \frac{5}{2}\right]$$

Open valve: $n' = \frac{N_1+N_2}{V_1+V_2} = \frac{n_1V_1 + n_2V_2}{V_1+V_2} = \frac{n(V_1+V_2)}{V_1+V_2} = n$

$$\sigma' = N'\left[\log\frac{n_Q}{n'} + \frac{5}{2}\right] = (N_1+N_2)\left[\log\frac{n_Q}{n} + \frac{5}{2}\right]$$

$\Rightarrow$ entropy unchanged

EFTS If the gases are not of identical particles, there is a change of entropy, called the entropy of mixing [$= 2N\log 2$ for $N_1 = N_2 = N$

This Gibbs paradox is discussed in every book on thermal physics ... except KK

KK Pr. 6-6

- energy $F = U - \tau\sigma \Rightarrow U = F + \tau\sigma$

$$\Rightarrow \quad U = N\tau\left[\log\frac{n}{n_Q} - 1\right] + N\tau\left[\log\frac{n_Q}{n} + \frac{5}{2}\right]$$

$$\Rightarrow \quad \boxed{U = \tfrac{3}{2}N\tau = \tfrac{3}{2}Nk_BT}$$

Review the logical chain that leads to $\frac{3}{2}$:

$$\varepsilon_n \sim (n_x^2 + n_y^2 + n_z^2) \longrightarrow \left[\int_0^\infty dx\, e^{-x^2}\right]^3$$

$$\longrightarrow n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} \longrightarrow U = \tfrac{3}{2}N\tau$$

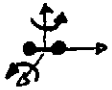
Thus, $\frac{3}{2}$ is valid in 3D space

Generalize : $U = \frac{1}{2} N\tau = \frac{1}{2} N k_B T$ per degree of freedom

Ex. diatomic molecule

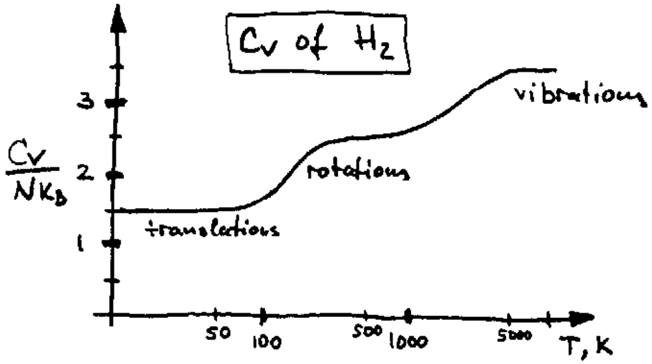
The energy is distributed among:


3 translations of C.o.M.


2 rotations
( does not count)


1 kinetic
1 potential } of vibrations

} terms in the energy operator, the Hamiltonian



KK Fig 3.9

$C_V = \frac{\partial U}{\partial T} = \frac{3}{2} N k_B$ for 3D translations only

or directly :

$$C_V = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_{V,N} = \tau \frac{\partial}{\partial \tau}\left(N\left[\ldots + \frac{3}{2}\log\tau + \ldots\right]\right) = \frac{3}{2} N$$

Also, repeating the arguments on p. 36 :

$$C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_{p,N} = C_V + N \quad = \frac{5}{2} N + C_{internal}$$

EFTS read KK pp. 169-171; Pr. 6-9

Chemical potential as potential energy

- μ depends on concentration :

  $\mu = \tau \log \frac{n}{n_Q}$

as two systems are brought into diffusive contact, the particles flow until $\mu_{1,fin} = \mu_{2,fin}$

Strictly speaking, this is $\mu_{internal}$

- when particles move in an *external* applied field, their motion is accompanied by a change in their potential energy :

$$\mu_{total} = \mu_{internal} + \mu_{external}$$

$= \tau \log \frac{n}{n_Q} + Mgh$ – for transport in a gravitational field

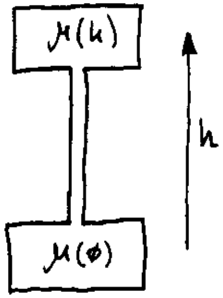
$= \tau \log \frac{n}{n_Q} + qV$ – for transport of charged particles across voltage V

- transport can be stopped by an application of an external potential step : adjust Δh or ΔV until $\mu_{1,total} = \mu_{2,total}$ and thus there is no net particle flow.

$\Rightarrow$ a way to measure μ directly

- only differences in chemical potential have physical meaning ; zero of μ_{total} is arbitrary

Ex isothermal atmosphere



- at eq-m: $\mu(0) = \mu(h) = \text{const}$

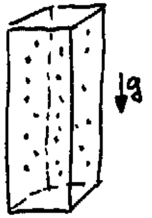
$$\Rightarrow \tau \log \frac{n(h)}{n_Q} + Mgh = \tau \log \frac{n(0)}{n_Q}$$

$$\Rightarrow n(h) = n(0)\, e^{-Mgh/\tau}$$

- since $p = \frac{N}{V}\tau = n\tau$ & $\tau = \text{const}$

$$\Rightarrow \boxed{p(h) = p(0)\, e^{-Mgh/\tau}}$$ see KK Fig 5-5

Ex KK Pr 5-3



Consider a column of atoms of mass M

- total # of atoms in the column:

$$N = \int_0^\infty n(h)\, dh = \int_0^\infty n(0)\, e^{-Mgh/\tau} dh = n(0) \frac{\tau}{Mg}$$

- total potential energy

$$U_{\text{total}} = \int_0^\infty Mgh\; n(h)\, dh = n(0) \frac{\tau^2}{Mg} \underbrace{\int_0^\infty x e^{-x} dx}_{(-xe^{-x} - e^{-x})_0^\infty = 1} = n(0) \frac{\tau^2}{Mg} = N\tau$$

- average potential energy per atom $= \frac{U_{\text{total}}}{N} = \tau$
- average kinetic energy per atom $= \frac{3}{2}\tau$, as usual

$\Rightarrow$ average total energy per atom $= \frac{5}{2}\tau$

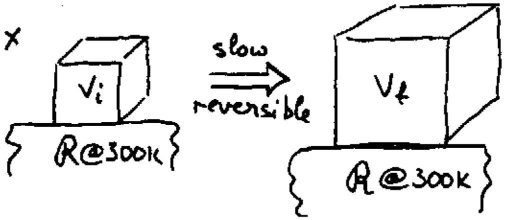
heat capacity per atom $= \frac{5}{2}$ or $= \frac{5}{2} k_B$

- $p(0) = \frac{\text{weight}}{\text{area}} = \text{const}$, i.e. does not depend on τ!

$\Rightarrow$ C is really $C_p = \frac{5}{2}$

chemical potential and work

Ex



$N = 1 \times 10^{22}$ atoms of ^{4}He
$V_i = 1 \times 10^3 \text{ cm}^3$
$V_f = 2 \times 10^3 \text{ cm}^3$
$T = 300\text{K} = \text{const}$

i.e. reversible isothermal expansion

- $pV = N\tau \Rightarrow p_f = \frac{1}{2} p_i$
- $\sigma = N\left[\log \frac{n_Q}{n} + \frac{5}{2}\right] = N \log V + \text{terms indep. of } V$

$$\Rightarrow \sigma_f - \sigma_i = \Delta\sigma = N \log \frac{V_f}{V_i} = N \log 2 = 0.693 \times 10^{22}$$

note: $\Delta\sigma > 0$ as required by 2LT

- work done on gas $= \int_{V_i}^{V_f} p\, dV = N\tau \int_{V_i}^{V_f} \frac{dV}{V}$

$$= N\tau \log \frac{V_f}{V_i} = N\tau \log 2 = 10^{22} \times 1.381 \times 10^{-23} \text{ J/K} \times 300\text{K} \times 0.693$$

$$= 28.7 \text{ J}$$

- $U = \frac{3}{2} N\tau = \text{const}$

$\Rightarrow$ there was some heat coming in to balance out the work done:

$$\left.\begin{array}{l} -\text{ work done } \underline{\text{by}} \text{ gas}, \quad W = -27\text{ J} \\ -\text{ heat added to gas}, \quad Q = +27\text{ J} \end{array}\right\} W + Q = 0$$

Ex. reversible isentropic process

same expansion, but now isolate the system undergoing the expansion

$\Rightarrow$ $Q = 0$ and τ must change

- $\sigma = N\left[\ldots + \frac{3}{2}\log\tau + \log V + \ldots\right] = \text{const}$

if $\frac{3}{2}\log\tau + \log V = \text{const}$

or $\tau^{3/2} V = \text{const}$ $\Rightarrow$ $\boxed{\tau_i^{3/2} V_i = \tau_f^{3/2} V_f}$

$\Rightarrow$ $T_f = T_i\left(\frac{V_i}{V_f}\right)^{2/3} = 300\,\text{K}\left(\frac{1}{2}\right)^{2/3} = 189\,\text{K}$ ← cooling!

- $U_f - U_i = \Delta U = \frac{3}{2} N k_B (T_f - T_i) =$

$= \frac{3}{2} \times 10^{22} \times 1.381 \times 10^{-23}\,\text{J/K} \times (189\,\text{K} - 300\,\text{K}) = -23\,\text{J}$

i.e. energy of the gas is <u>de</u>creased

$\Rightarrow$ gas does 23 J of work in the expansion

- other forms:

$V = \frac{N\tau}{p}$ $\Rightarrow$ $\boxed{\frac{\tau_i^{5/2}}{p_i} = \frac{\tau_f^{5/2}}{p_f}}$

$\tau = \frac{pV}{N}$ $\Rightarrow$ $p_i^{3/2} V_i^{5/2} = p_f^{3/2} V_f^{5/2}$ $\Rightarrow$ $\boxed{p_i V_i^{5/3} = p_f V_f^{5/3}}$

Note: all 3 forms for monatomic ideal gas only

EFTS KK Pr. 6-10 ← generalize for $\frac{C_P}{C_V} \equiv \gamma \neq \frac{5}{3}$

Ex of an irreversible process: expansion into vacuum

- no piston $\Rightarrow$ no work done, $W = 0$
- system isolated, expansion rapid $\Rightarrow$ no heat, $Q = 0$
- $\Delta U = U_f - U_i = 0 = W + Q$
- $U = \text{const}$ $\Rightarrow$ $\tau = \text{const}$ since $U \propto \tau$
- $\Delta\sigma = \sigma_f - \sigma_i = N\log\frac{V_f}{V_i}$, as before

  $\Delta\sigma = 0.693 \times 10^{22}$ if the volume doubles
- during expansion, different parts of the system are at different concentrations $\Rightarrow$ not eq-m

  $\Rightarrow$ process irreversible

<u>Summary</u>

		ΔU	$\Delta\sigma$	W	Q
REVERSIBLE EXPANSION	ISOTHERMAL $\tau_i = \tau_f$	0	$N\log\frac{V_f}{V_i}$	$-N\tau\log\frac{V_f}{V_i}$	$-W$
	ISENTROPIC $\tau_i^{2/3} V_i = \tau_f^{2/3} V_f$	$\frac{3}{2}N(\tau_f - \tau_i)$	0	$\frac{3}{2}N(\tau_f - \tau_i)$	0
IRREVERSIBLE EXPANSION		0	$N\log\frac{V_f}{V_i}$	0	0

KK Table 6.3

Experimental tests of Sackur-Tetrode equation

$$\boxed{\sigma = N\left[\log\frac{n_Q}{n}+\frac{5}{2}\right]}$$

If $n=\frac{N}{V}$ = const, the entropy is proportional to N

$\|$ entropy scales with the size of the system

Ex Ne gas K. Clusius, 1936

- solid below 24.55 K (m.p.)
- liquid below 27.2 K (b.p.)

1. $S = k_B\sigma = 0$ at absolute 0K 3LT
2. S increase on heating from 0K to the m.p
   - measure heat capacity betw. 12.3K & 24.55K
   - extrapolate to 0K, using Debye T^3 law
   - integrate $\int dT\,\frac{C_p}{T}$ to get the entropy: $14.29\,\frac{J}{mol\,K}$
3. S increase in solid → liquid transformation
   - measure: at 24.55K, need 335 J/mol to melt

   $\Rightarrow \quad \Delta S_{melting} = \frac{335\ J/mol}{24.55K} = 13.64\,\frac{J}{mol\,K}$
4. S increase on heating the liquid from m.p. to b.p.
   - measure: b.p. @ 27.2K, @ 1atm: $3.85\,\frac{J}{mol\,K}$
5. S increase in liquid → gas transformation
   - measure: @ 27.2K need 1761 J/mol to vaporize

   $\Rightarrow \quad \Delta S_{vaporization} = \frac{1761\ J/mol}{27.2\,K} = 64.62\,\frac{J}{mol\,K}$

Total: $14.29 + 13.64 + 3.85 + 64.62 = 96.40\,\frac{J}{mol\,K}$

Calculated from ST eq-n: $96.45\,\frac{J}{mol\,K}$ @ 27.2K

!

Other noble gases:

	measured	ST eq-n
Ar	129.75	129.24
Kr	144.56	145.06

Fluctuations in an ideal gas

Ex concentration fluctuations KK Pr 5-10

$$\langle N\rangle = \sum_{ASN} N\,\frac{\lambda e^{-\varepsilon/\tau}}{\mathfrak{Z}} = \dots = \frac{\tau}{\mathfrak{Z}}\left(\frac{\partial \mathfrak{Z}}{\partial\mu}\right)_{\tau,V} \quad \text{p.52}$$

where we used the fact that $\frac{\partial}{\partial\mu}\left(e^{N\mu/\tau}\right) = \frac{N}{\tau}\,e^{N\mu/}$

Take the derivative twice:

$$\Rightarrow \frac{\partial^2\mathfrak{Z}}{\partial\mu^2} = \frac{1}{\tau^2}\sum_{ASN} N^2\lambda e^{-\varepsilon/\tau}$$

$$\Rightarrow \langle N^2\rangle = \sum_{ASN} N^2\,\frac{\lambda e^{-\varepsilon/\tau}}{\mathfrak{Z}} = \frac{\tau^2}{\mathfrak{Z}}\,\frac{\partial^2\mathfrak{Z}}{\partial\mu^2}$$

mean-squared deviation $= \langle\Delta N^2\rangle$

$$\langle\Delta N^2\rangle = \langle(N-\langle N\rangle)^2\rangle = \langle N^2 - 2N\langle N\rangle + \langle N\rangle^2\rangle$$

$$= \langle N^2\rangle - 2\langle N\rangle\underset{\overset{\parallel}{\langle N\rangle}}{\langle\langle N\rangle\rangle} + \langle N\rangle^2$$

$$= \langle N^2\rangle - \langle N\rangle^2$$

$$= \tau^2\left[\frac{1}{\mathfrak{Z}}\,\frac{\partial^2\mathfrak{Z}}{\partial\mu^2} - \frac{1}{\mathfrak{Z}^2}\left(\frac{\partial\mathfrak{Z}}{\partial\mu}\right)^2\right]$$

On the other hand,

$$\frac{\partial}{\partial\mu}\langle N\rangle = \frac{\partial}{\partial\mu}\left[\frac{\tau}{\mathcal{Z}}\,\frac{\partial\mathcal{Z}}{\partial\mu}\right] = \frac{\tau}{\mathcal{Z}}\,\frac{\partial^2\mathcal{Z}}{\partial\mu^2} - \frac{\tau}{\mathcal{Z}^2}\left(\frac{\partial\mathcal{Z}}{\partial\mu}\right)^2$$

$$\Rightarrow \underline{\frac{\partial}{\partial\mu}\langle N\rangle = \frac{1}{\tau}\langle\Delta N^2\rangle}$$

For an ideal gas: $\mu = \tau\log\frac{n}{n_Q}$

$$\Rightarrow \frac{\langle N\rangle}{V} = n_Q\,e^{\mu/\tau} \quad \Rightarrow \underline{\langle N\rangle = V n_Q\,e^{\mu/\tau}}$$

$$\Rightarrow \langle\Delta N^2\rangle = \tau\frac{\partial}{\partial\mu}\left[V n_Q\,e^{\mu/\tau}\right] = \cancel{\tau}\,\frac{1}{\cancel{\tau}}\,\underbrace{V n_Q\,e^{\mu/\tau}}_{=\langle N\rangle}$$

⇒ fractional fluctuations:

$$\frac{\langle\Delta N^2\rangle}{\langle N\rangle^2} = \frac{\langle N\rangle}{\langle N\rangle^2} = \frac{1}{\langle N\rangle} \leftarrow$$ extremely small for a macroscopic # of particles

For $N\sim10^{20}$, root-mean-square fluctuations

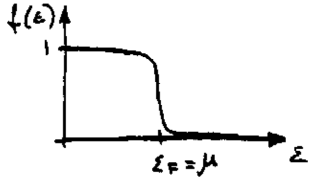
$$\left[\frac{\langle\Delta N^2\rangle}{\langle N\rangle^2}\right]^{1/2} = \frac{1}{\langle N\rangle^{1/2}} \sim 10^{-10}$$

⇒ with an accuracy of one part per 10^{10}, a macroscopic system in diffusive contact with a reservoir (at chemical potential μ) is a system with a fixed # of particles

Fermi and Bose gases

Summary

- FD ($\frac{1}{2}$-integer spin) distribution $f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau}+1}$
  - Pauli exclusion principle ⇒ individual orbitals have occupancy 0 or 1
  - low $\tau \ll \varepsilon_F$:

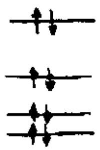


$\varepsilon<\varepsilon_F \Rightarrow f\simeq 1$, almost fully occupied

$\varepsilon>\varepsilon_F \Rightarrow f\simeq 0$, essentially vacant

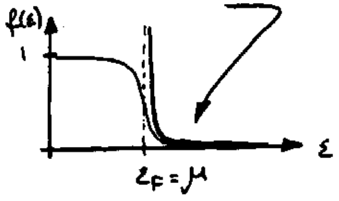
this limit is called the degenerate Fermi gas

  - a characteristic feature: high kinetic energy, even in the ground state



- BE (integer spin) distribution $f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau}-1}$
  - high concentration of particles in the ground orbital, low concentration at higher ε
  As $\tau\to0$, all particles condense to the ground state

- classical regime : $n \ll n_Q \equiv \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$



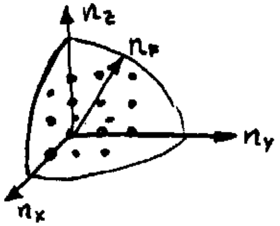
$\Rightarrow$ ideal gas

Degenerate Fermi gas in 3D

| i.e. $\tau \ll \varepsilon_F$

$$\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{2M}\left(\frac{\pi n}{L}\right)^2$$

For the system to hold N particles (electrons) in the lowest energy states, need to fill a $\frac{1}{8}$-sphere of radius n_F in n-space :



$$N = \underset{\substack{\text{2 electrons}\\ \text{per orbital,}\\ \text{spin} \uparrow \text{or} \downarrow}}{2} \times \underset{\substack{\text{do not}\\ \text{distinguish}\\ (\pm n_\alpha)^2 = n_\alpha^2\\ \alpha = x, y, z}}{\frac{1}{8}} \times \frac{4}{3}\pi n_F^3 = \frac{\pi}{3} n_F^3$$

$$\Rightarrow \quad n_F = \left(\frac{3N}{\pi}\right)^{1/3}$$

$$\Rightarrow \boxed{\varepsilon_F = \frac{\hbar^2}{2M}\left(\frac{\pi n_F}{\underset{V^{1/3}}{\overset{\parallel}{L}}}\right)^2 = \frac{\hbar^2}{2M}\left(\frac{\pi\,(3N)^{1/3}}{V^{1/3}\,\pi^{1/3}}\right)^2 = \frac{\hbar^2}{2M}\left(\frac{3\pi^2 N}{V}\right)^{2/3}}$$

Recall : $n \equiv \frac{N}{V}$ = concentration

$\Rightarrow \quad \varepsilon_F = \frac{\hbar^2}{2M}(3\pi^2 n)^{2/3}$ $\quad$ | $= \tau_F$, Fermi temperature

- total energy in the ground state

$$U_0 = \int_0^{n_F} \underbrace{2 \times \frac{1}{8} \times 4\pi n^2 dn}_{\substack{\text{thin shell @ } n\text{, of}\\ \text{thickness } dn}} \times \varepsilon_n$$

$$= \frac{\hbar^2}{2M}\frac{\pi^3}{L^2}\int_0^{n_F} n^4 dn = \frac{\hbar^2}{10M}\frac{\pi^3}{L^2} n_F^5$$

$$= \frac{\hbar^2}{10M}\frac{\pi^2 n_F^2}{L^2}\underbrace{\frac{\pi n_F^3}{}}_{=3N} = \frac{3}{5}N\underbrace{\frac{\hbar^2}{2M}\left(\frac{\pi n_F}{L}\right)^2}_{=\varepsilon_F}$$

$\Rightarrow \quad U_0 = \frac{3}{5}N\varepsilon_F$; per particle : $\boxed{\frac{U_0}{N} = \frac{3}{5}\varepsilon_F}$

If N = const, $\varepsilon_F \propto V^{-2/3}$ $\Rightarrow$ increases with decreasing volume $\Rightarrow$ resists compression $\Rightarrow$ a <u>repulsive</u> interaction

- density of orbitals

– # of states in the interval $(n, n+dn) = \mathcal{D}(n)\,dn$

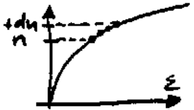
$$\mathcal{D}(n) = \underbrace{\frac{\pi n^2}{2}}_{\text{geometry}}\gamma$$

see p.41

– # of states in the interval $(\varepsilon, \varepsilon + d\varepsilon) = \mathcal{D}(\varepsilon)\,d\varepsilon$

$$\mathcal{D}(\varepsilon) = \frac{\pi n^2}{2}\gamma\frac{dn}{d\varepsilon}$$

– $\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{\pi n}{L}\right)^2$



$$\Rightarrow n = \left(\frac{2M\varepsilon L^2}{\hbar^2\pi^2}\right)^{1/2} \quad \Rightarrow \quad \frac{dn}{d\varepsilon} = \left(\frac{ML^2}{2\hbar^2\pi^2\varepsilon}\right)^{1/2}$$

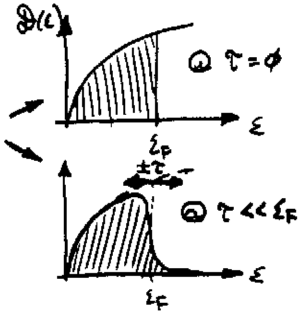
$$\Rightarrow \mathcal{D}(\varepsilon) = \frac{\cancel{\pi}\gamma}{2}\,\frac{2M\varepsilon L^2}{\hbar^2\pi^2}\left(\frac{ML^2}{2\hbar^2\cancel{\pi}^2\varepsilon}\right)^{1/2} = \frac{\gamma \overset{=L^3}{V}}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}$$

For electrons, $\gamma = 2$ $\Rightarrow$ $\boxed{\mathcal{D}(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}}$

density of orbitals for free electrons in volume V

- These orbitals are occupied according to the FD distribution function, $f(\varepsilon)$

$\Rightarrow$ density of <u>occupied</u> orbitals $= \mathcal{D}(\varepsilon) f(\varepsilon)$



- calculate average values as usual, e.g.

$$N = \int_0^\infty d\varepsilon\ \mathcal{D}(\varepsilon) f(\varepsilon) \quad \& \quad U = \int_0^\infty d\varepsilon\ \varepsilon\ \mathcal{D}(\varepsilon) f(\varepsilon)$$

- in the ground state, orbitals are filled up to ε_F

$$N = \int_0^{\varepsilon_F} d\varepsilon\ \mathcal{D}(\varepsilon) \qquad \& \quad U_0 = \int_0^\infty d\varepsilon\ \mathcal{D}(\varepsilon)$$

since $f(\varepsilon) = \begin{cases} 1, & \varepsilon \leq \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases}$

Ex $\varepsilon_F = \frac{\hbar^2}{2M}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \Rightarrow N = \frac{V}{3\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\varepsilon_F^{3/2}$

$\Rightarrow \log N = \frac{3}{2}\log \varepsilon_F + \text{const}$

$\Rightarrow \frac{dN}{N} = \frac{3}{2}\frac{d\varepsilon}{\varepsilon_F} \Rightarrow \underline{\mathcal{D}(\varepsilon = \varepsilon_F) = \left(\frac{dN}{d\varepsilon}\right)_{\varepsilon_F} = \frac{3N}{2\varepsilon_F}}$

EFTS KK Pr. 7-1 $\mathcal{D}(\varepsilon)$ in 1D and 2D

[recall: in 1D $\mathcal{D}(n) = \frac{dn}{dn} = 1$, see p.41]

- heat capacity of a degenerate Fermi gas
  - measured heat capacity of electrons in metals is $\ll \frac{3}{2}N$, as for an ideal gas (classical regime of both FD and BE distributions)

$\Rightarrow$ need corrections

- As we heat a gas of N Fermi particles from 0 to a finite temperature τ:

$$\Delta U = U(\tau) - U(0) = U(\tau) - U_0$$
$$= \int_0^\infty d\varepsilon\ \varepsilon\,\mathcal{D}(\varepsilon) f(\varepsilon) - \int_0^{\varepsilon_F} d\varepsilon\ \varepsilon\,\mathcal{D}(\varepsilon)$$
$$= \int_0^{\varepsilon_F} d\varepsilon\,\varepsilon\,\mathcal{D}(\varepsilon)\left[f(\varepsilon) - 1\right] + \int_{\varepsilon_F}^\infty d\varepsilon\ \varepsilon\,\mathcal{D}(\varepsilon) f(\varepsilon) \quad (*)$$

- At both temperatures, N is the same:

$$\int_0^\infty d\varepsilon\ \mathcal{D}(\varepsilon) f(\varepsilon) = N = \int_0^{\varepsilon_F} d\varepsilon\ \mathcal{D}(\varepsilon)$$

multiply by ε_F (= const):

$$0 = \int_0^\infty d\varepsilon\ \varepsilon_F\,\mathcal{D}(\varepsilon) f(\varepsilon) - \int_0^{\varepsilon_F} d\varepsilon\ \varepsilon_F\,\mathcal{D}(\varepsilon)$$
$$= \int_0^{\varepsilon_F} d\varepsilon\ \varepsilon_F\,\mathcal{D}(\varepsilon)\left[f(\varepsilon) - 1\right] + \int_{\varepsilon_F}^\infty d\varepsilon\ \varepsilon_F\,\mathcal{D}(\varepsilon) f(\varepsilon)$$

and subtract from (*)

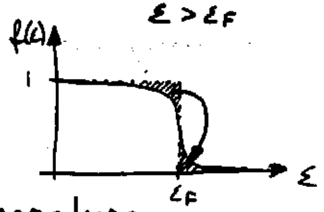
$$\boxed{\Delta U = \underbrace{\int_0^{\varepsilon_F}}_{0<\varepsilon<\varepsilon_F} d\varepsilon\,(\varepsilon - \varepsilon_F)\,\mathcal{D}(\varepsilon)\left[f(\varepsilon) - 1\right] + \underbrace{\int_{\varepsilon_F}^\infty}_{\varepsilon>\varepsilon_F} d\varepsilon\,(\varepsilon - \varepsilon_F)\,\mathcal{D}(\varepsilon) f(\varepsilon)}$$

see KK Fig 7-4

To interpret, rewrite as

$$\Delta U = \underbrace{\int_0^{\varepsilon_F} d\varepsilon\, (\varepsilon_F - \varepsilon)\, \mathcal{D}(\varepsilon) \left[1 - f(\varepsilon)\right]}_{\text{raising } \bar{e} \text{ from } \varepsilon < \varepsilon_F \text{ to } \varepsilon_F} + \underbrace{\int_{\varepsilon_F}^{\infty} d\varepsilon\, (\varepsilon - \varepsilon_F)\, \mathcal{D}(\varepsilon) f(\varepsilon)}_{\text{raising } \bar{e} \text{ from } \varepsilon_F \text{ to } \varepsilon > \varepsilon_F}$$

Note: both contributions +ve!



– in the above expressions, temperature dependence is only in $f(\varepsilon, \tau)$, i.e.

$$\underline{C_{\bar{e}}} = \frac{dU}{d\tau} = \int_0^{\varepsilon_F} d\varepsilon\, (\varepsilon - \varepsilon_F)\, \mathcal{D}(\varepsilon) \frac{df}{d\tau} + \int_{\varepsilon_F}^{\infty} d\varepsilon\, (\varepsilon - \varepsilon_F)\, \mathcal{D}(\varepsilon) \frac{df}{d\tau}$$

$$\underline{= \int_0^{\infty} d\varepsilon\, (\varepsilon - \varepsilon_F)\, \mathcal{D}(\varepsilon) \frac{df}{d\tau}}$$

Can calculate numerically, inserting

$$f = \frac{1}{e^{(\varepsilon-\mu)/\tau} + 1}, \quad \varepsilon_F = \frac{\hbar^2}{2M} \left(\frac{3\pi^2 N}{V} \right)^{2/3}, \text{ and}$$

$$\mathcal{D}(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2M}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

EFTS in preparation for a numerical integration, reduce $C_{\bar{e}}$ to a dimensionless form by choosing appropriate units, e.g. $\tau' = \tau/\varepsilon_F$ etc.

Ex in metals, $\varepsilon_F = k_B \times 50{,}000\,\text{K}$ or so

⇒ under normal circumstances, $\tau < 0.01\, \varepsilon_F$

⇒ can make several approximations

- approximations $\quad C_{\bar{e}} = \int_0^{\infty} d\varepsilon\, (\varepsilon - \varepsilon_F)\, \mathcal{D}(\varepsilon) \frac{df}{d\tau}$

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau} + 1}$$

– $\frac{df}{d\tau}$ is large only in the vicinity of $\varepsilon \approx \mu$

recall: $\displaystyle \frac{df}{d\varepsilon} = \frac{1}{\tau} \frac{e^{(\varepsilon-\mu)/\tau}}{\left(e^{(\varepsilon-\mu)/\tau} + 1\right)^2} \longrightarrow \frac{1}{4\tau}$ near $\varepsilon = \mu$

cf. p.56/KK.Pr6-
p.77a

$$\Rightarrow C_{\bar{e}} \simeq \mathcal{D}(\varepsilon_F) \int_0^{\infty} d\varepsilon\, (\varepsilon - \varepsilon_F) \frac{df}{d\tau}$$

– if μ is independent of τ : $\mu(\tau) = \mu_0 = \varepsilon_F$

$$\Rightarrow (\varepsilon - \varepsilon_F) \frac{df}{d\tau} = (\varepsilon - \varepsilon_F) \frac{e^{(\varepsilon-\varepsilon_F)/\tau}}{\left(e^{(\varepsilon-\varepsilon_F)/\tau} + 1\right)^2} \frac{\varepsilon - \varepsilon_F}{\tau^2} = x^2 \frac{e^x}{(e^x+1)^2}$$

where $x = \frac{\varepsilon - \varepsilon_F}{\tau}$; $\tau dx = d\varepsilon$; $\varepsilon\Big|_0^{\infty} \longleftrightarrow x\Big|_{-\varepsilon_F/\tau}^{\infty}$

$$\Rightarrow C_{\bar{e}} = \mathcal{D}(\varepsilon_F)\, \tau \int_{-\varepsilon_F/\tau}^{\infty} x^2 \frac{e^x}{(e^x+1)^2}\, dx$$

– degenerate Fermi gas, $\tau \ll \varepsilon_F$

⇒ $-\varepsilon_F/\tau$ is a large –ve number

$$\Rightarrow \int_{-\varepsilon_F/\tau}^{\infty} \approx \int_{-\infty}^{\infty} \quad \text{and} \quad \int_{-\infty}^{\infty} dx\, x^2 \frac{e^x}{(e^x+1)^2} = \frac{\pi^2}{3}$$

from tables

$$\Rightarrow \underline{C_{\bar{e}}} = \frac{\pi^2}{3} \underbrace{\mathcal{D}(\varepsilon_F)}_{= \frac{3}{2} \frac{N}{\varepsilon_F},\ \text{p.74}} \tau = \underline{\frac{\pi^2}{2} N \frac{\tau}{\varepsilon_F}} \quad \Bigg| = \frac{\pi^2}{2} N \frac{\tau}{\tau_F}$$

$$\text{or} \quad \boxed{C_{\bar{e}} = \frac{\pi^2}{2} N k_B \frac{T}{\varepsilon_F}}$$

- in fact, can show [PHYS 4P41]

$$\mu = \mu(\tau) = \mu_0 \left[1 - \frac{\pi^2}{12}\left(\frac{\tau}{\mu_0}\right)^2 - \frac{\pi^4}{80}\left(\frac{\tau}{\mu_0}\right)^4 + \dots \right]$$

with $\mu_0 = \varepsilon_F = \frac{\hbar^2}{2M}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$ p.72

Then $f(\varepsilon)$ changes [p.78a] and eventually:

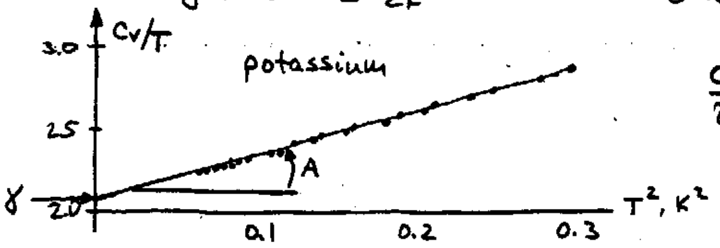
$$\Delta U = \frac{3}{5} N \mu_0 \left[1 + \frac{5\pi^2}{12}\left(\frac{\tau}{\mu_0}\right)^2 - \frac{\pi^4}{16}\left(\frac{\tau}{\mu_0}\right)^4 + \dots \right]$$

EFTS verify that to 1st order $C_{\bar{e}} = \frac{\pi^2}{2} N k_B \frac{T}{\varepsilon_F}$ still, and calculate the leading correction term

Ex heat capacity in metals

$$C_V = \underbrace{\gamma\tau}_{\text{electrons}} + \underbrace{A\tau^3}_{\text{lattice}} \qquad \gamma, A = \text{constants}$$

namely, $\gamma = \frac{\pi^2}{2}\frac{N}{\varepsilon_F}$ and $A = \frac{12\pi^4 N}{5 k_B^3 \theta^3}$ Debye τ^3-law p.45



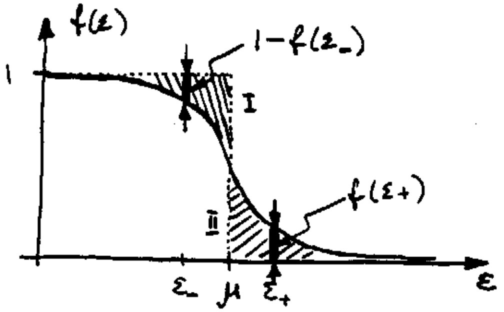
$\frac{C_V}{\tau} = \gamma + A\tau^2$ is a straight line (at low temperatures)

Ex white dwarf stars } EFTS KK pp. 196-199
Ex nuclear matter }

Ex liquid ^{3}He as a Fermi gas EFTS KK Pr. 7-5

Also attempt Pr. 7-4*; will be solved in class

- temperature dependence of μ, a "back-of-an-envelope" calculation KK Pr 7.4



$$\begin{cases} \varepsilon_+ = \mu + \delta \\ \varepsilon_- = \mu - \delta \end{cases}$$

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau} + 1}$$

- Interpret:

$f(\varepsilon_+)$ = probability that an orbital @ ε_+ is occupied

$f(\varepsilon_-)$ = ——"——"—— @ ε_- is occupied

$1 - f(\varepsilon_-)$ = ——"——"—— @ ε_- is vacant
a hole

KK Pr 6-2: $f(\varepsilon_+) = 1 - f(\varepsilon_-)$

i.e. Area I ▨ = Area II ▨

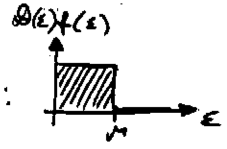
- in 3D: $\mathcal{D}(\varepsilon) \propto \varepsilon^{1/2}$, increases with ε

Density of occupied orbitals $= \mathcal{D}(\varepsilon) f(\varepsilon)$

⇒ there are more occupied orbitals @ ε_+ than holes @ ε_-

⇒ Area II > Area I

⇒ as we increase τ from $\tau = 0$:



to a finite $\tau > 0$:

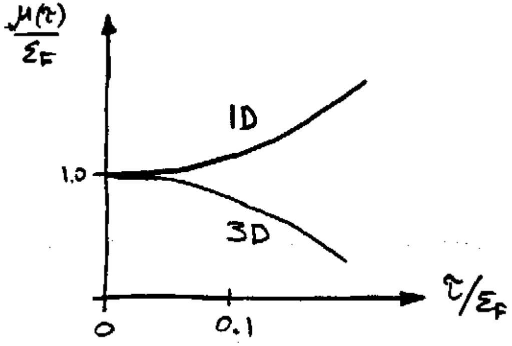
there is a net increase in area under curve

But! $N = \int_0^\infty \mathcal{D}(\varepsilon) f(\varepsilon)\, d\varepsilon$ = area under the curve

- must be independent of temperature

$\Rightarrow$ μ must decrease with temperature

- in 1D: $\mathcal{D}(\varepsilon) \propto \varepsilon^{-1/2}$ $\Rightarrow$ μ must increase



$\mu(\tau = 0) = \mu_0 = \varepsilon_F$

- to quantify the increase/decrease in μ, consider

$N_+ = \int_0^\infty d\delta\ \mathcal{D}(\mu+\delta) f(\mu+\delta)$ = # of occupied orbitals above μ

$N_- = \int_0^\infty d\delta\ \mathcal{D}(\mu-\delta) \underbrace{[1 - f(\mu-\delta)]}_{= f(\mu+\delta)}$ = # of holes below μ Pr. 6-2

$$\Rightarrow N_+ - N_- = \int_0^\infty [\mathcal{D}(\mu+\delta) - \mathcal{D}(\mu-\delta)]\, f(\mu+\delta)\, d\delta$$

For $\tau \ll \mu$ use a linear approximation:

$$\mathcal{D}(\mu+\delta) - \mathcal{D}(\mu-\delta) \simeq 2 \left(\frac{d\mathcal{D}}{d\varepsilon}\right)_{\varepsilon=\mu} \delta$$

$$\Rightarrow N_+ - N_- = 2\left(\frac{d\mathcal{D}}{d\varepsilon}\right)_{\varepsilon=\mu} \int_0^\infty f(\mu+\delta)\, \delta\, d\delta$$

$$f(\mu+\delta) = \frac{1}{e^{[(\mu+\delta)-\mu]/\tau} + 1} = \frac{1}{e^{\delta/\tau} + 1} = \frac{1}{e^x + 1}$$

$$x \equiv \frac{\delta}{\tau}, \quad dx = \frac{d\delta}{\tau}$$

$$\Rightarrow N_+ - N_- = 2\left(\frac{d\mathcal{D}}{d\varepsilon}\right)_{\varepsilon=\mu} \tau^2 \underbrace{\int_0^\infty \frac{x\, dx}{e^x + 1}}_{= \pi^2/12} = \frac{\pi^2}{6}\left(\frac{d\mathcal{D}}{d\varepsilon}\right)_{\varepsilon=\mu} \tau^2$$

N remains constant as we raise τ:

$$N = \underbrace{\int_0^\mu \mathcal{D}(\varepsilon)\, d\varepsilon}_{@\ \tau = 0} + N_+ - N_- = \text{const}$$

$$\Rightarrow \frac{dN}{d\tau} = 0 = \mathcal{D}(\mu)\frac{d\mu}{d\tau} + \frac{\pi^2}{3}\left(\frac{d\mathcal{D}}{d\varepsilon}\right)_{\varepsilon=\mu} \tau$$

$$\Rightarrow \frac{d\mu}{d\tau} = -\frac{\pi^2 \tau}{3} \underbrace{\frac{1}{\mathcal{D}(\varepsilon=\mu)}\left(\frac{d\mathcal{D}}{d\varepsilon}\right)_{\varepsilon=\mu}}_{= \frac{d}{d\varepsilon}(\log \mathcal{D})_{\varepsilon=\mu}}$$

3D: $\mathcal{D}(\varepsilon) \propto \varepsilon^{1/2}$ $\Rightarrow$ $\frac{d}{d\varepsilon}(\log \mathcal{D}) = \frac{1}{2}\frac{1}{\varepsilon} > 0$

$\Rightarrow \frac{d\mu}{d\tau} < 0$

1D: $\mathcal{D}(\varepsilon) \propto \varepsilon^{-1/2}$ $\Rightarrow$ $\frac{d\mu}{d\tau} > 0$

Boson gas

$$f_{BE}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/\tau} \underset{\nearrow\nwarrow}{-} 1}$$

At low temperatures, $\tau \to 0$:
- occupancy of the ground state $\to N$
- occupancy of higher states $\to 0$

Arrange energy scale so that $\varepsilon_{g.s.} = 0$:

$$\lim_{\tau\to 0} f(\varepsilon=0, \tau) = N = \lim_{\substack{\tau\to 0 \\ \text{i.e.} \\ \tau \ll \mu}} \frac{1}{e^{-\mu/\tau} - 1} \simeq \frac{1}{\cancel{1} - \frac{\mu}{\tau} - \cancel{1}} = -\frac{\tau}{\mu}$$

$$\Rightarrow \boxed{\mu = -\frac{\tau}{N}} \quad \text{at low } \tau$$

Ex $N = 10^{22}$, $T = 1\text{K}$ $\Rightarrow \mu \simeq -\frac{1 \times 1.38 \cdot 10^{-23}}{10^{22}} = -1.38 \times 10^{-45}\,\text{J}$

Note: $\mu < 0$, i.e. <u>below</u> the ground state, $\varepsilon_{g.s.} = 0$

For comparison, the next-highest energy level is:

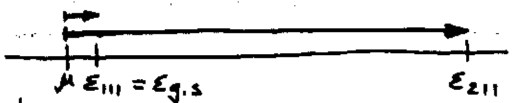
$$\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

$$\Delta\varepsilon = \varepsilon_{211} - \varepsilon_{111} = 3\,\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2$$

KK. p.201

For $1\,\text{cm}^3$ of ^4He: $\Delta\varepsilon \simeq 2.48 \cdot 10^{-37}\,\text{J}$

$\Rightarrow |\mu| \ll \Delta\varepsilon$



$$\Rightarrow \frac{f(\varepsilon_{211})}{f(\varepsilon_{111})} = \frac{e^{(\mu-\varepsilon_{111})/\tau} - 1}{e^{(\mu-\varepsilon_{211})/\tau} - 1} \simeq \frac{\mu - \varepsilon_{111}}{\mu - \varepsilon_{211}} \ll 1$$

$\Rightarrow$ most particles are in the ground state

<u>Bose-Einstein condensation</u>

3D: $\mathcal{D}(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}$ p.76

$\mathcal{D}(\varepsilon) \to 0$ as $\varepsilon \to 0$, while $f(\varepsilon) \to \infty$

$\Rightarrow$ calculate the occupancy of the ground state separately:

$$N = N_0 + \int_{0^+}^{\infty} d\varepsilon\, \mathcal{D}(\varepsilon) f(\varepsilon)$$

- for the [single] ground orbital @ $\varepsilon_{g.s.} = 0$:

$$N_0 = \frac{1}{e^{-\mu/\tau} - 1} = \frac{1}{\frac{1}{\lambda} - 1} \quad \text{with } \lambda \equiv e^{\mu/\tau}$$

At low τ, N_0 is very large $\Rightarrow \lambda \approx 1$

- for all other [excited] orbitals:

$$N_{exc.}(\tau) = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2} \int_{0^+}^{\infty} d\varepsilon\, \frac{\varepsilon^{1/2}}{\underbrace{\frac{1}{\lambda}}_{\approx 1} e^{\varepsilon/\tau} - 1}$$

again, use $x \equiv \frac{\varepsilon}{\tau} \Rightarrow d\varepsilon = \tau\, dx$, $\varepsilon^{1/2} = \tau^{1/2} x^{1/2}$

$$\Rightarrow N_{exc}(\tau) = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2} \tau^{3/2} \underbrace{\int_{0^+}^{\infty} dx\, \frac{x^{1/2}}{e^x - 1}}_{= 1.306\sqrt{\pi}}$$

$$\Rightarrow N_{exc}(\tau) = \frac{1.306\,V}{4\,\pi^{3/2}}\left(\frac{2M}{\hbar^2}\right)^{3/2} \tau^{3/2} = 2.612\,V\,n_Q$$

where $n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$

<u>All</u> atoms are in excited states, above $\varepsilon_{g.s.}$ when $N_{exc}(\tau) = N$, i.e. when temperature is

$$\boxed{\tau_E = \frac{2\pi\hbar^2}{M}\left(\frac{N}{2.612\,V}\right)^{2/3} = \frac{2\pi\hbar^2}{M}\left(\frac{n}{2.612}\right)^{2/3}}$$

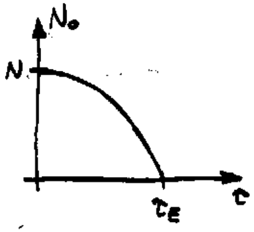
BE condensati temperature

EFTS K.K. Pr. 7-9

Now: $N_{exc}(\tau) = 2.612\, V\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} = (\dots)\, \tau^{3/2}$

@ $\tau = \tau_E$: $N_{exc}(\tau_E) = N = (\dots)\, \tau_E^{3/2}$

$\Rightarrow \frac{N_{exc}(\tau)}{N_{exc}(\tau_E)} = \frac{N_{exc}(\tau)}{N} = \left(\frac{\tau}{\tau_E}\right)^{3/2}$



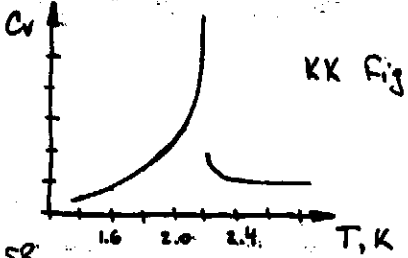
and $N_0 = N - N_{exc} = N\left[1 - \left(\frac{\tau}{\tau_E}\right)^{3/2}\right]$

$N \sim 10^{22} \Rightarrow N_0 >> 1$ as soon as $\tau < \tau_E$

$\Rightarrow$ A significant number of atoms condenses into the ground orbital immediately below τ_E

Ex ^{4}He

calculated $\tau_E = 3.1\,K$
measured $\tau_E = 2.17\,K$



a "λ-transition"

KK Fig 7.12

Below τ_E : superfluidity p.58

A body moving through a boson gas in a condensed state can only be slowed down if it loses its kinetic energy to the gas, and excites some atoms out of the condensate. If body's velocity is too low: $\frac{MV^2}{2} < \Delta\varepsilon$, transitions cannot be induced.

In ^{4}He, $V_{critical} \simeq 50\,m/s$. Below that, there is no resistance to the motion.

Ex Heat capacity of the degenerate boson gas

KK Pr. 7-8

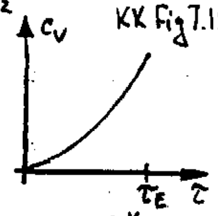
- energy: only atoms in the excited state(s) contribute to U

$N_{exc}(\tau) = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\tau^{3/2}\int_0^\infty dx\, \frac{x^{1/2}}{e^x - 1}$, $\varepsilon = x\tau$ p.83

$\Rightarrow U(\tau) = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\tau^{\textcircled{5/2}}\underbrace{\int_0^\infty dx\, \frac{x^{\textcircled{3/2}}}{e^x - 1}}_{0.7702 \times 1.306\sqrt{\pi}}$

$\Rightarrow U(\tau) = 0.77 \times N_{exc}(\tau) \times \tau = 0.77\, N\, \frac{\tau^{5/2}}{\tau_E^{3/2}}$

$\Rightarrow C_V = \left(\frac{\partial U}{\partial \tau}\right)_{V,N} = \frac{5}{2} \times 0.77\, N\left(\frac{\tau}{\tau_E}\right)^{3/2}$ for $\tau < \tau_E$



KK Fig 7.15

not quite a "λ-transition", but qualitatively similar

Also: $C_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_{V,N} \Rightarrow \left(\frac{\partial \sigma}{\partial \tau}\right)_{V,N} = \frac{C_V}{\tau} = \frac{5}{2} \times 0.77\, N\, \frac{\tau^{1/2}}{\tau_E^{3/2}}$

$\Rightarrow \sigma(\tau) = \frac{5}{3} \times 0.77\, N\left(\frac{\tau}{\tau_E}\right)^{3/2} + \underbrace{\sigma(0)}_{= 0,\ 3LT}$

Fluctuations in Fermi and Bose gases

KK Pr 7-11
7-12

$\langle(\Delta N)^2\rangle = \langle(N - \langle N\rangle)^2\rangle = \langle N^2\rangle - \langle N\rangle^2$

- Fermions: $N = 0$ or 1 $\Rightarrow N^2 = 0$ or 1

$\Rightarrow \langle N^2\rangle = \langle N\rangle$

$\Rightarrow \langle(\Delta N)^2\rangle = \langle N\rangle - \langle N\rangle^2 = \langle N\rangle[1 - \langle N\rangle]$

- **bosons** : can't use the same trick

⇒ "go to Plan B":

$$\frac{\partial}{\partial\mu}\langle N\rangle = \frac{1}{\tau}\langle(\Delta N)^2\rangle \qquad \text{p.70}$$

$$\Rightarrow \langle(\Delta N)^2\rangle = \tau\frac{\partial}{\partial\mu}\langle N\rangle = \tau\frac{\partial}{\partial\mu}f(\varepsilon)$$

bosons: $f_{BE}(\varepsilon) = \dfrac{1}{e^{(\varepsilon-\mu)/\tau}-1}$

$$\Rightarrow \langle(\Delta N)^2\rangle = \tau\times\left\{-\frac{-\frac{1}{\tau}e^{(\varepsilon-\mu)/\tau}}{[e^{(\varepsilon-\mu)/\tau}-1]^2}\right\} = \frac{e^{(\varepsilon-\mu)/\tau}}{[e^{(\varepsilon-\mu)/\tau}-1]^2}$$

On the other hand:

$$\langle N\rangle(1+\langle N\rangle) = \frac{1}{e^{(\varepsilon-\mu)/\tau}-1}\times\left(1+\frac{1}{e^{(\varepsilon-\mu)/\tau}-1}\right)$$

$$= \frac{e^{(\varepsilon-\mu)/\tau}\cancel{-1}\cancel{+1}}{[e^{(\varepsilon-\mu)/\tau}-1]^2} \qquad ✓$$

Clearly, this approach ("plan B") would also work for fermions (EFTS)

Ex two-orbital boson system

- $f(\varepsilon) = \dfrac{1}{e^{(\varepsilon-\mu)/\tau}-1}$ ⇒ $\dfrac{1}{f(\varepsilon)}+1 = e^{(\varepsilon-\mu)/\tau}$
- Put $\varepsilon = 0$ in the ground orbital:
- we are told : $\langle N_0\rangle = 2\langle N_\varepsilon\rangle$

$$\Rightarrow \begin{cases} \langle N_0\rangle = f(0) = \frac{2}{3}N \\ \langle N_\varepsilon\rangle = f(\varepsilon) = \frac{1}{3}N \end{cases} \qquad N = \text{total \# of atoms}$$

$$\Rightarrow \begin{cases} \dfrac{1}{\frac{2}{3}N}+1 = e^{-\mu/\tau} \\ \dfrac{1}{\frac{1}{3}N}+1 = e^{(\varepsilon-\mu)/\tau} \end{cases}$$

Divide one equation by the other:

$$e^{\varepsilon/\tau} = \frac{1+3\frac{1}{N}}{1+\frac{3}{2}\frac{1}{N}} = \left(1+3\frac{1}{N}\right)\left(1-\frac{3}{2}\frac{1}{N}+\dots\right)$$

$$= 1+3\frac{1}{N}-\frac{3}{2}\frac{1}{N}+\mathcal{O}\left(\frac{1}{N^2}\right) \approx 1+\frac{3}{2}\frac{1}{N} \quad \text{for } \frac{1}{N}\ll 1 \quad [N\gg 1]$$

$$\Rightarrow \frac{\varepsilon}{\tau} = \log\left(1+\frac{3}{2}\frac{1}{N}\right) \simeq \frac{3}{2}\frac{1}{N}, \quad \frac{1}{N}\ll 1 \qquad \Big| \ \log x = x-\frac{x^2}{2}+\frac{x^3}{3}-\dots$$

$$\Rightarrow \boxed{\tau \simeq \frac{2}{3}N\varepsilon}$$

- Note: Boltzmann factor $\dfrac{e^{-\varepsilon/\tau}}{e^{0}} = \dfrac{1}{2}$ ⇒ $\varepsilon = 0.693\tau$

⇒ $\tau \sim \varepsilon$

Here $\tau \sim N\varepsilon \gg \varepsilon$ since $N \gg 1$

⇒ Bose condensation occurs at temperatures much higher than the energy separation between the ground and the lowest excited state would suggest   KK pp. 201-202

EFTS KK Pr. 7-7

Thermodynamic potentials

Helmholtz Free energy $F \equiv U - \tau\sigma$

> F is at a minimum for a system in thermal contact with a reservoir, if the volume is const.

i.e. @ $\underline{\tau = \text{const}, \ V = \text{const}}$ p.28

A purist's point-of-view: F is only *defined* at eq-m, it is the equilibrium free energy

Generalize: $\tilde{F} \equiv U - \tau\sigma$ = Landau free energy function defined for both eq-m and non-eq-m situations — important in the description of phase transitions KK Ch.10

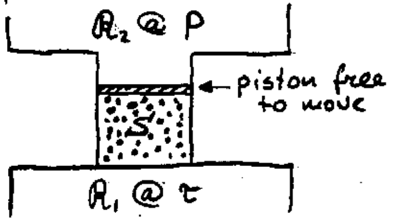
$\tilde{F}$ reduces to F at eq-m.

Gibbs free energy $G \equiv U - \tau\sigma + pV$

a.k.a. *thermodynamic potential*

Useful @ $\underline{\tau = \text{const}, \ p = \text{const}}$:

> G is at a minimum for a system in thermal contact with a reservoir, if the pressure is constant



$$dG = dU - \tau d\sigma - \cancelto{0}{\sigma d\tau} + p dV + \cancelto{0}{V dp}$$

for τ = const & p = const

- In a reversible process,

$$dU = \tau d\sigma - p dV + \mu dN \qquad \text{thermodynamic identity, p.50}$$

$$\Rightarrow dU - \tau d\sigma + p dV = \mu dN$$

$$\Rightarrow dG = \mu \cancelto{0}{dN} = 0 \quad \Rightarrow \text{G is at an } \underline{\text{extremum}}$$

- R_2 is thermally insulated ⇒ its entropy = const

⇒ need to consider only σ_S and σ_{R_1}:

$$d\sigma_S + d\sigma_{R_1} = 0 \quad \text{at eq-m (extremum)}$$

and $\underbrace{\Delta\sigma_S + \Delta\sigma_{R_1}}_{\text{finite changes}} \leq 0$ if extremum is a maximum

$\Rightarrow \Delta G \geq 0 \Rightarrow$ G is at a $\underline{\text{minimum}}$ at eq-m.

- in general, as a function of τ and p:

$$dG = \mu dN - \sigma d\tau + V dp$$

and
$$dG(N,\tau,p) = \underbrace{\left(\frac{\partial G}{\partial N}\right)_{\tau,p}}_{\mu} dN + \underbrace{\left(\frac{\partial G}{\partial \tau}\right)_{N,p}}_{-\sigma} d\tau + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{\tau,N}}_{V} dp$$

EFTS KK Pr. 9-1 Obtain Maxwell's relations by calculating second-order cross-derivatives, i.e. by using the fact that $\frac{\partial^2 G}{\partial\alpha\,\partial\beta} = \frac{\partial^2 G}{\partial\beta\,\partial\alpha}$

- at constant τ and p : $dG = \mu\, dN$

Integrate : $\boxed{G = \mu N}$, G scales with the size of the system

---

Aside

intensive variables are independent of the size of the system: p, τ, μ $\quad \boxed{\mu} + \boxed{\mu} \rightarrow \boxed{\mu}$

extensive variables scale with the size of the system: V, σ, U, G, H, N $\quad \boxed{N} + \boxed{N} \rightarrow \boxed{2N}$

- for a multi-component system,

$$G = \sum_j \mu_j N_j$$ ← important for chemical reactions

Enthalpy

$$H \equiv U + pV$$

Useful @ $p = \text{const}$

- Ex. no effective work being done , $d(pV) = 0$

$\Rightarrow$ ΔH = heat transferred to the system

e.g. the latent heat of vapourization

- in a reversible process

$$dH = dU + p\,dV + V\,dp = \underbrace{\tau\, d\sigma - \cancel{p\,dV} + \mu\, dN}_{dU} + \cancel{p\,dV} + V\,dp$$

$$= \tau\, d\sigma + \mu\, dN + V\, dp$$

and $$dH = \underset{\substack{\| \\ \tau}}{\left(\frac{\partial H}{\partial \sigma}\right)_{N,p}} d\sigma + \underset{\substack{\| \\ \mu}}{\left(\frac{\partial H}{\partial N}\right)_{\sigma,p}} dN + \underset{\substack{\| \\ V}}{\left(\frac{\partial H}{\partial p}\right)_{N,\sigma}} dp$$

- at constant N and p $\quad (dN = dp = 0)$

$$dH = \tau\, d\sigma$$

$$\Rightarrow \left(\frac{\partial H}{\partial \tau}\right)_{p,N} = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_{p,N} \equiv C_p$$

or $$\boxed{C_p \equiv T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \left(\frac{\partial H}{\partial T}\right)_{p,N}}$$

measured experimentally
e.g. in chemical reactions
@ constant p

Ex. a general relation between C_V and C_p

"a triumf of manipulation of thermodynamic relations"

- Recall : ideal gas was $C_p = C_V + R$

- $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$ $\quad$ | work in thermal units

- Consider $$\underset{\substack{\| \\ \frac{1}{T}C_V}}{\left(\frac{\partial S}{\partial T}\right)_V} = \underset{\substack{\| \\ \frac{1}{T}C_p}}{\left(\frac{\partial S}{\partial T}\right)_p} + \underset{\substack{\| \\ -\left(\frac{\partial V}{\partial T}\right)_p}}{\left(\frac{\partial S}{\partial p}\right)_T} \left(\frac{\partial p}{\partial T}\right)_V$$ ← see homework , Pr. 9-1

$$\Rightarrow \quad C_V = C_p - T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V$$

- on the other hand, at constant volume:

$$dV = 0 = \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$\Rightarrow C_V = C_p + T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T = C_p - \frac{TV\alpha^2}{K_T} \rightarrow C_p \text{ as } T \to 0$$

where $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ = thermal expansivity

$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ = isothermal compressibility

Ex equilibrium in chemical reactions

At constant τ & p: $d\tau = dp = 0$

$$\Rightarrow \quad dG = \sum_j \mu_j \, dN_j \quad \leftarrow \text{non-interacting species}$$

Chemical reaction relates different dN_j's:

$$\nu_1 A_1 + \nu_2 A_2 + \dots \rightleftarrows \nu_3 A_3 + \nu_4 A_4 + \dots$$

ν_j = coefficients, A_j = reactants/products of reaction

Each time the reaction occurs, N_j changes by ν_j

If the reaction takes place $d\hat{N}$ times: $dN_j = \nu_j d\hat{N}$

$$\Rightarrow \quad dG = \left[\sum_j \mu_j \nu_j\right] d\hat{N}$$

At equilibrium, $dG = 0 \Rightarrow \boxed{\sum_j \mu_j \nu_j = 0}$

- for ideal gases, $\mu = \tau \log \frac{n}{n_Q}$

$$\Rightarrow \quad \mu_j = \tau \log n_j - \underbrace{\tau \log n_{Q_j}}_{\text{indep. of } n_j = \text{concentrations}}$$

$$\Rightarrow \quad \sum_j \mu_j \nu_j = 0 = \tau \left[\sum_j \nu_j \log n_j - \sum_j \nu_j \log n_{Q_j} \right]$$

$$\Rightarrow \quad \sum_j \log n_j^{\nu_j} = \sum_j \nu_j \log n_{Q_j} \equiv \log K(\tau) \Big| \begin{array}{l} = \text{function of } \tau, \\ \text{but indep. of } n_j\text{'s} \end{array}$$

$$\Rightarrow \quad \log \prod_j n_j^{\nu_j} = \log K(\tau)$$

$$\Rightarrow \quad \boxed{\prod n_j^{\nu_j} = K(\tau)} \quad \underline{\text{Law of Mass Action}}$$

c.f. $\overset{\nu=1}{H_2O} \rightleftarrows \overset{\nu=-1}{H^+} + \overset{\nu=-1}{OH^-}$

$$K(\tau) = \frac{[H_2O]}{[H^+][OH^-]}$$

$K(\tau)$ = <u>equilibrium constant</u>

- include the <u>internal degrees of freedom</u>

$$Z \rightarrow Z \times Z^{int}$$

$$\Rightarrow \quad \mu = \tau \left[\log \frac{n}{n_Q} - \log Z^{int} \right] = \tau \log n - \tau \log (n_Q Z^{int})$$

KK pp. 169-170

clearly, Z^{int} is independent of n

$\Rightarrow$ can retain $\prod_j n_j^{\nu_j} = K(\tau)$ if we re-define

$$\log K(\tau) \equiv \log \prod_j \left(n_{Q_j} Z_j^{int}\right)^{\nu_j}$$

$$\Rightarrow \quad K(\tau) = \prod_j n_{Q_j}^{\nu_j} e^{-\nu_j F_j^{int}/\tau}$$

where $F_j^{int} = -\tau \log Z_j^{int}$ = internal free energy

Ex KK Pr. 9-2a thermal ionization of atomic hydrogen

$$\underset{\nu=1}{\bar{e}} + \underset{\nu=1}{H^+} \rightleftarrows \underset{\nu=-1}{H}$$

- neglecting the spin, $\bar{e}$ and H^+ have <u>no</u> internal free energy, $F^{int}(\bar{e}) = F^{int}(H^+) = 0$

$$\Rightarrow \quad K(\tau) = \frac{n_Q(\bar{e}) \, \cancel{n_Q(H^+)}}{\cancel{n_Q(H)} \, e^{-F^{int}(H)/\tau}}$$

- $m_p \gg m_e \Rightarrow n_Q(H^+) \simeq n_Q(H)$
- I = energy required to ionize atomic hydrogen

$$= \Delta F^{int}(H \longrightarrow H^+ + \bar{e}) = \left[\underset{0}{\cancel{F^{int}(H^+)}} + \underset{0}{\cancel{F^{int}(\bar{e})}}\right] - F^{int}(H)$$

$$\Rightarrow \quad F^{int}(H) = -I$$

$\Rightarrow$ $\underline{K(\tau) = n_Q(\bar{e})\, e^{-I/\tau}}$ Saha eq-n

- even if we include the spin, the above result holds!

e.g. $\bar{e}$ has spin $\frac{1}{2}$:

$z^{int} \to 2 \times z^{int}$ $\quad F^{int} \to F^{int} - \tau \log 2$

and this is true when $\bar{e}$ is by itself (LHS) and when it is a part of a hydrogen atom (RHS)

Also: $\nu(\bar{e}) = -\nu(H)$

$\Rightarrow$ have the same contribution to both sides of the reaction equation $\Rightarrow$ cancels out

$\Rightarrow$ $K(\tau)$ unaffected

[Similarly for the spin of the proton]

EFTS KK Pr. 9-5

Imperfect gases

- Ideal gases consist of non-interacting particles:

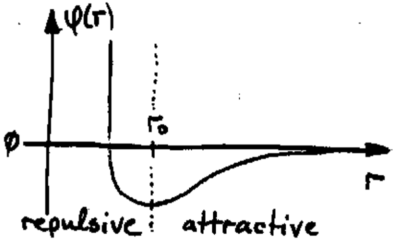
$$pV = N\tau \qquad U = \tfrac{3}{2} N\tau$$

$$\Rightarrow p = \frac{N\tau}{V} = \frac{\frac{2}{3}U}{V}$$

- add interactions between particles:

$$\tfrac{2}{3}U \to \tfrac{2}{3}U + \varphi(r)$$

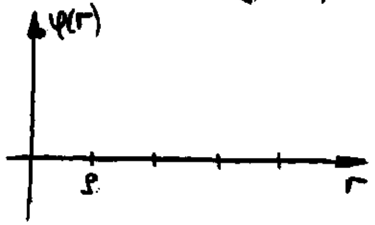
where $\varphi(r)$ = interaction potential between particles a distance r apart



- strongly repulsive at short distances
- attractive at longer distances ($r > r_0$)
- $\varphi(r) \to 0$ as $r \to \infty$

Recall: force $f = -\frac{\partial \varphi}{\partial r}$

Ex "hard-core" potential is the simplest form of a strong repulsive interaction:



incompressible billiard balls colliding

- an order-of-magnitude estimate, to be refined later:

$$p = \frac{\frac{2}{3}U + \varphi}{V} = \frac{\frac{2}{3}U}{V} + \frac{\varphi}{V} = \frac{N\tau}{V} - a\frac{N\varepsilon}{V} = n\tau - an\varepsilon$$

where $-\varepsilon$ = interaction energy per particle (average)
a = a proportionality constant

$\varphi = -aN\varepsilon$ emphasizes the <u>attractive</u> part of the interaction

- net interaction energy increases with the frequency of collisions, i.e. with density n

$$\varepsilon \propto n = \frac{N}{V}$$

$$\Rightarrow \quad p = n\tau - an^2$$

mutual attraction of gas particles <u>reduces</u> the effective pressure on the walls of the container

$$\Rightarrow \quad p + an^2 = n\tau$$

$$\Rightarrow \quad \left(p + a\frac{N^2}{V^2}\right)V = N\tau \qquad \Big| \text{ cf } \quad pV = N\tau$$

- in its simplest form, the hard-core repulsion reduces the effective volume available:

$$V \rightarrow V - bN$$

where $b \propto \rho^3$ = volume forbidden to other molecules by the presence of a molecule in the middle

- finally,

$$\boxed{\left(p + \frac{aN^2}{V^2}\right)(V - bN) = N\tau}$$

van der Waals equation of state

- reduce to dimensionless form:

- define $\quad p_c \equiv \frac{a}{27b^2} \quad V_c \equiv 3Nb \quad \tau_c \equiv \frac{8a}{27b}$
- convert to $\quad \hat{p} \equiv \frac{p}{p_c} \quad \hat{V} = \frac{V}{V_c} \quad \hat{\tau} \equiv \frac{\tau}{\tau_c}$

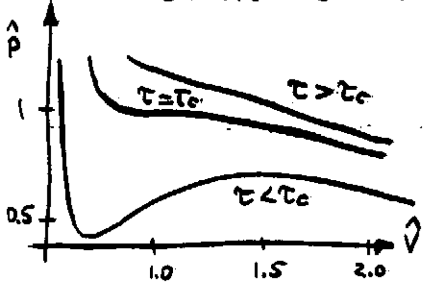
$$\Rightarrow \left(\hat{p}p_c + \frac{aN^2}{\hat{V}^2V_c^2}\right)(\hat{V}V_c - bN) = N\hat{\tau}\tau_c$$

$$\left(\frac{\hat{p}a}{27\cancel{b^2}} + \frac{a\cancel{N^2}}{\hat{V}^2 9\cancel{N^2}\cancel{b^2}}\right)(\hat{V}3\cancel{N}\cancel{b} - \cancel{b}\cancel{N}) = \cancel{N}\hat{\tau}\frac{8a}{27\cancel{b}}$$

$$\Rightarrow \boxed{\left(\hat{p} + \frac{3}{\hat{V}^2}\right)(3\hat{V} - 1) = 8\hat{\tau}}$$

law of correspondin states

- dimensionless (computer-ready)
- universal, all gases look the same
- describes well: Ar, Xe, ... not so well: O_2, CO_2, ...
- can rewrite as an eq-n of state (isothermal)



KK Fig. 10.10

$$\hat{p}_\tau(\hat{V}) = \frac{8/3\,\hat{\tau}}{\hat{V} - 1/3} - \frac{3}{\hat{V}^2}$$

EFTS prove that the inflection point, $\left(\frac{\partial \hat{p}}{\partial \hat{V}}\right)_{\hat{\tau}} = 0$ and $\left(\frac{\partial^2 \hat{p}}{\partial \hat{V}^2}\right)_{\hat{\tau}} = 0$ occurs when $\hat{p} = 1$, $\hat{V} = 1$, $\hat{\tau} = 1$ i.e. at the <u>critical point</u>: $p = p_c$, $V = V_c$, $\tau = \tau_c$

Free energy

Apply the same method:

$$\frac{2}{3}U \longrightarrow \frac{2}{3}U - \underbrace{aN\frac{N}{V}}_{*} \qquad V \longrightarrow V - bN$$

- **Helmholtz**: $F = -N\tau\left[\log \frac{n_Q}{\underset{\underset{N/V}{\|}}{n}} + 1\right]$

$$\Rightarrow \quad F = -N\tau\left[\log\frac{n_Q(V-bN)}{N} + 1\right] - a\frac{N^2}{V}$$

Check: $p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = \frac{N\tau}{V-bN} - \underbrace{\frac{aN^2}{V^2}}_{*}$

$$\Rightarrow \left(p + a\frac{N^2}{V^2}\right)(V-bN) = N\tau \quad ✓ \quad \text{v.d.W.}$$

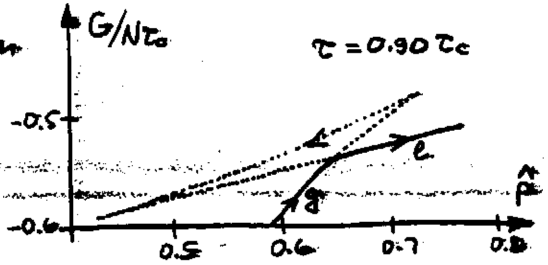
- **Gibbs**: $G = F + pV$

$$\Rightarrow G = -N\tau\left[\log\frac{n_Q(V-bN)}{N} + 1\right] + \frac{N\tau V}{V-bN} \overset{\overset{*}{\downarrow}}{-2}\frac{aN^2}{V}$$

$\tau \geq \tau_c$: G is a single-valued function of p

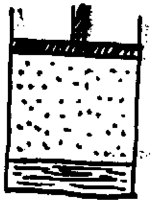
$\tau < \tau_c$: there is a region of p values where G has 3 values →

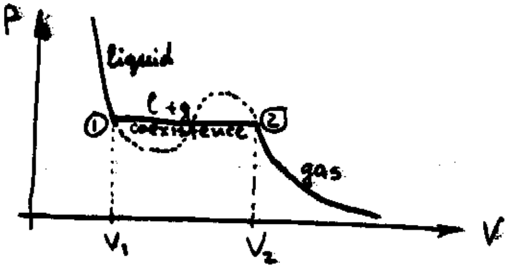
The lowest branch is the stable one



V = parametic value, increasing along blue arrows.

Phase equilibria





v.d.W equation remains valid, but there is a region (only if $\tau < \tau_c$) where free energy is minimized by adjusting N_g/N_ℓ, subject to $N_g + N_\ell = N = \text{const}$

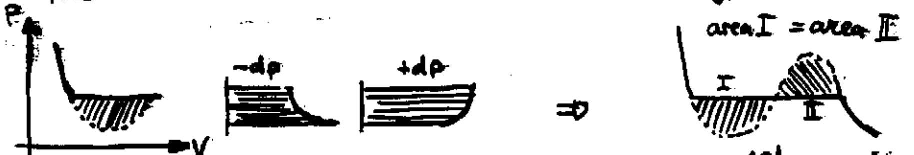
- along an isotherm of a vdW gas, $d\tau = \emptyset$

$$\Rightarrow dG = -\cancelto{\emptyset}{\sigma d\tau} + Vdp + \cancelto{\emptyset}{\mu \underset{\underset{\text{const}}{\|}}{dN}} = Vdp$$

$$\Rightarrow \int_{V_1}^{V_2} dG = G_2 - G_1 = \int_{①}^{②} V dp$$ where the integral is calculated along the dotted line

- along the [straight] coexistence line, the two phases are in equilibrium: $\mu_\ell = \mu_g$

This is satisfied if $\int_{①}^{②} Vdp = \emptyset$ i.e. when the areas above and below the straight line are equal



and similarly for the other one

Maxwell's construction

van der Waals formula as an interpolation

- ideal gas = non-interacting particles
  - ⇒ ideal gas law
  - ⇒ *all* ideal gases behave the same way
- liquid = condensed phase, particles interact strongly
  - ⇒ properties of a liquid depend on the nature of the interaction
  - ⇒ all liquids are different.
- there is no universal formula that can describe *both* ideal gases & liquids, over the entire range rarefied gas ⟶ condensed liquid
- interpolation formulas which give the correct limiting behaviour *are* possible; must give
  - low $n = \frac{N}{V}$ ⟶ ideal gas
  - high n ⟶ incompressibility of liquids
- v.d.W. equation is *one* such formula, by no means *the only* one!

A proper derivation of v.d.W. equation

Landau & Lifshitz, V.5

- *Mechanics*: the state of the system is specified by a set of coordinates $(q_1, q_2, \ldots)$ and momenta $(p_1, p_2, \ldots)$ associated with the particles and dimensions of the system

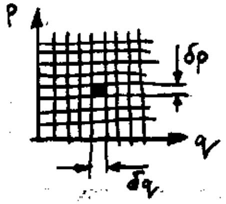
Ex 1 particle in 3D : $x, y, z; p_x, p_y, p_z$

Ex 3 particles in 1D : $x_1, x_2, x_3; p_1, p_2, p_3$

A full description of the system is a vector in $(N_q + N_p)$-dimensional phase space

Solving the equation of motion ⟺ finding a trajectory in phase space

- *Q.M.*: there is a limit of precision, a "unit volume" of phase space



$$\boxed{\delta q \, \delta p \gtrsim 2\pi\hbar}$$

Heisenberg uncertainty principle

In a r-dimensional space, denote an element of phase space $d\Gamma = \frac{\delta p \, \delta q}{(2\pi\hbar)^r}$

- *Stat. mech*: $F = -\tau \log Z = -\tau \log \sum_s e^{-\varepsilon_s/\tau}$

approximate: $F \simeq -\tau \log \int_s e^{-\varepsilon_s/\tau} d\Gamma$

where index s involves all coordinates in phase spa.

For N identical particles

$$\int_s d\Gamma = \int_p \times \int_q d\Gamma = \int_p \times \frac{1}{N!} \int \ldots \int dV_1 \ldots dV_N$$

- factor $\frac{1}{N!}$ because of the symmetry w.r. to particle interchange (identical particles)
- $\int dV_i = \iiint dx_i\, dy_i\, dz_i$ = integral over the entire gas volume but for <u>one</u> particle only
- $\varepsilon_s(p, q) = \underbrace{\sum_{i=1}^{N} \frac{p_i^2}{2m}}_{\text{kinetic}} + \underbrace{\varphi(q)}_{\text{potential}}$

The difference between ideal and non-ideal gases only arises in the potential energy term

ideal gas: $\varphi = \emptyset \Rightarrow \int \ldots \int e^{-\varphi/\tau} dV_1 \ldots dV_N = V^N$

monatomic non-ideal gas: $\varphi = \varphi_{ij} \neq \emptyset$

$$\Rightarrow F = F_{i.g.} - \tau \log \frac{1}{V^N} \int \ldots \int e^{-\varphi/\tau} dV_1 \ldots dV_N$$

$$= F_{i.g.} - \tau \log \Big[\frac{1}{V^N} \int \ldots \int \underbrace{(e^{-\varphi/\tau} - 1) dV_1 \ldots dV_N + 1}_{\text{add \& subtract}} \Big]$$

- Assume that collisions are relatively rare, so only <u>one</u> two-particle collision can happen at any one time; i.e. only one φ_{ij} makes a significant contribution to the integral at one time.

- select two particles (say, #1 & #2) in any one of $\frac{1}{2}N(N-1)$ ways; since the particles are identical & interchangeable:

$$F = F_{i.g.} - \tau \log \Big[\frac{1}{V^N} \frac{N(N-1)}{2} \int \ldots \int (e^{-\varphi_{12}/\tau} - 1) dV_1 \ldots dV_N + 1 \Big]$$

$$= F_{i.g.} - \tau \log \Big[\frac{N(N-1)}{2V^N} \iint (e^{-\varphi_{12}/\tau} - 1) dV_1 dV_2 \times \underbrace{\int \ldots \int dV_3 \ldots dV_N}_{V^{N-2}} + 1 \Big]$$

approximate: $\frac{1}{2}N(N-1) \simeq \frac{1}{2}N^2$, for $N \gg 1$

$\log(1+x) \simeq x, \quad x \ll 1$

$$\Rightarrow \underline{F = F_{i.g.} - \tau \frac{N^2}{V^2} \iint (e^{-\varphi_{12}/\tau} - 1)\, dV_1\, dV_2}$$

- change variables: $\begin{cases} r_1 \\ r_2 \end{cases} \rightarrow \begin{cases} r_{c.o.m.} = \frac{1}{2}(r_1 + r_2) \\ r_{12} = r_1 - r_2 \end{cases}$

$\varphi_{12} = \varphi(r_{12})$ is independent of $r_{c.o.m.}$

$\Rightarrow$ integrate w.r. to $r_{c.o.m.}$: $\int dV_{c.o.m.} = V$

$$\Rightarrow \underline{B(\tau) = \frac{1}{2} \int \left(1 - e^{-\varphi(r_{12})/\tau}\right) dV_{12}}$$

and $\underline{F = F_{i.g.} + \frac{\tau N^2}{V} B(\tau)}$

$$\Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_{\tau, N} = p_{i.g.} + \frac{N^2}{V^2} \tau B(\tau) \quad \Big| \text{ cf } p \rightarrow p + a\frac{N^2}{V^2}$$

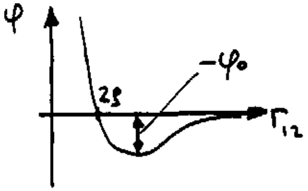
Aside

$p_{i.g.} = \frac{N\tau}{V}$ (ideal gas law)

$$\Rightarrow p = \frac{N\tau}{V} \Big[\underbrace{1}_{i.g.} + \underbrace{\frac{N}{V} B(\tau)}_{\text{2-particle}} + \underbrace{\frac{N^2}{V^2} C(\tau)}_{\text{3-particle}} + \ldots \Big]$$

$B(\tau), C(\tau), \ldots$ are <u>virial coefficients</u>

- truncate at $B(\tau)$ when concentration is relatively low, i.e. ignore 3-particle & higher collisions.



$$B(\tau) = 2\pi\int_0^{2\rho}\left(1-e^{-\varphi_{12}/\tau}\right)r^2dr + 2\pi\int_{2\rho}^{\infty}\left(1-e^{-\varphi_{12}/\tau}\right)r^2dr$$

since $dV = 4\pi r^2 dr$

$0<r<2\rho$, φ is large $\Rightarrow e^{-\varphi/\tau} \ll 1$

$\Rightarrow$ the first integral is $\underline{b \simeq 16\pi\frac{\rho^3}{3}}$

$2\rho < r$, $|\varphi| \leq \varphi_0$, and $\varphi_0/\tau \ll 1$ | recall: $\varepsilon \ll \tau$

$\Rightarrow e^{-\varphi/\tau} \simeq 1 - \frac{\varphi}{\tau}$

$\Rightarrow$ the second integral is $-\frac{2\pi}{\tau}\int_{2\rho}^{\infty}\varphi_0 r^2 dr \underline{= -\frac{a}{\tau}}$ ← const > 0

$\Rightarrow \boxed{B(\tau) = b - \frac{a}{\tau}}$

- put it all together:

$$F = F_{i.g.} + \frac{N^2}{V}(b\tau - a) = -N\tau\left[\log\frac{n_Q}{n}+1\right] + \frac{N^2}{V}(b\tau-a)$$

$$= -N\tau\log\frac{n_Q}{n} - N\tau \underbrace{- N\tau\log V + \frac{N^2}{V}b\tau}_{-N\tau\left[\log V - \frac{Nb}{V}\right]} - \frac{aN^2}{V}$$

$b = 16\pi\frac{\rho^3}{3} \Rightarrow$ at low concentration $Nb \ll V$

$\Rightarrow \frac{Nb}{V} \ll 1$ $\qquad\log(1-x) \simeq -x,\ x \ll 1$

$\Rightarrow \log(V-Nb) = \log V + \log\left(1-\frac{Nb}{V}\right) \approx \log V - \frac{Nb}{V}$

$$\Rightarrow F = -N\tau\log\frac{n_Q}{N} - N\tau - N\tau\log(V-Nb) - \frac{aN^2}{V}$$

--- Aside

$$\underbrace{-N\tau\log V}\qquad\underbrace{+N\tau\log V}$$

$$= F_{i.g.} \qquad - N\tau\log\left(1-\frac{Nb}{V}\right) - \frac{aN^2}{V}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = \frac{N\tau}{V-Nb} - \frac{aN^2}{V^2}$$

$\Rightarrow \boxed{\left(p + a\frac{N^2}{V^2}\right)(V-bN) = N\tau}$ ✓ v.d.W.

where a & b are fully determined by $\varphi(r)$

- a compact empirical form of $\varphi(r)$ which provides good agreement with "real-life" potentials is

$$\varphi(r) = 4\varphi_0\left[\left(\frac{\rho}{r}\right)^{12} - \left(\frac{\rho}{r}\right)^{6}\right]$$

Lennard-Jones or 6-12 potential

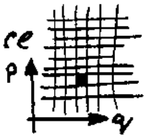
EFTS determine $B(\tau)$ for a repulsive $\propto r^{-n}$ potential $(n>3)$

Hint: express the answer in terms of a Γ-function KK App. A

EFTS KK Pr. 10-1

Kinetic theory

Phase space: cell of the grid in phase space = state of the system



Mechanics: grid is arbitrarily fine

Q.M.: spacing has the lower bound

Statistical mechanics: probability $P_s \propto e^{-\varepsilon_s/\tau}$

Probability density: (in r-dimensional space)

$$\rho(q_1 \dots q_r; p_1 \dots p_r)\, dq_1 \dots dq_r\, dp_1 \dots dp_r =$$
$$= \text{const} \times e^{-\varepsilon_s(q_1 \dots q_r; p_1 \dots p_r)/\tau} dq_1 \dots dq_r\, dp_1 \dots dp_r$$

with const determined from normalization

Maxwell velocity distribution   Mvd

Ex a particle in a 3D box

- ignoring interactions between particles,

$$\varepsilon = \text{kinetic only} = \frac{Mv^2}{2} = \frac{p^2}{2M}$$

$$\Rightarrow \rho(\vec{r}, \vec{q})\, d^3\vec{r}\, d^3\vec{p} \propto e^{-p^2/2M\tau} \underbrace{d^3\vec{r}}_{dx\,dy\,dz} \underbrace{d^3\vec{p}}_{dp_x dp_y dp_z}$$

- fraction of N particles which have velocity between $\vec{v}$ and $\vec{v}+d\vec{v}$:

$$f(\vec{v})\, d^3\vec{v} \propto N e^{-Mv^2/2\tau} d^3\vec{v}$$

! only magnitude $|\vec{v}| = v$ matters

find proportionality constant from normalization $\Rightarrow$ Mvd

Ex ideal gas

The same problem of "a particle in a 3D box", but a different approach: use what we know about ideal gases:

- $f(\varepsilon_n) = \lambda e^{-\varepsilon_n/\tau}$, $\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{\pi n}{L}\right)^2$
- interpred ε_n as kinetic energy (non-interacting particles)

$$\Rightarrow \varepsilon_n = \frac{Mv^2}{2}$$

$$\Rightarrow v^2 = \frac{\hbar^2 \pi^2 n^2}{M^2 L^2} \quad \Rightarrow \quad \underline{v = \frac{\hbar \pi}{ML} n}$$

- in 3D:

$$f(n)\, dn = \frac{1}{8} \times 4\pi n^2 \times dn \times \lambda e^{-\varepsilon_n/\tau} = \frac{1}{2}\pi n^2 dn\, \lambda e^{-\varepsilon_n/\tau}$$

$$- n = \frac{ML}{\hbar\pi} v \quad \& \quad dn = \frac{ML}{\hbar\pi} dv$$

$$- \lambda = \frac{n}{n_Q} = \frac{N}{\underbrace{V}_{=L^3}}\left(\frac{2\pi\hbar^2}{M\tau}\right)^{3/2} = N\left(\frac{2\pi\hbar^2}{ML^2\tau}\right)^{3/2}$$

$$\Rightarrow \boxed{f(v)\, dv} = \frac{1}{2}\pi\left(\frac{ML}{\hbar\pi}\right)^2 v^2 \frac{ML}{\hbar\pi} dv\, N\left(\frac{2\pi\hbar^2}{ML^2\tau}\right)^{3/2} e^{-Mv^2/2\tau}$$
$$\boxed{= 4\pi N\left(\frac{M}{2\pi\tau}\right)^{3/2} v^2 e^{-Mv^2/2\tau} dv}$$

Maxwell velocity distrib.

$f(v)\, dv =$ fraction of N particles

$\Rightarrow$ probability of velocity between v and $v+dv$

$$P(v) = \frac{f(v)dv}{N} = 4\pi\left(\frac{M}{2\pi\tau}\right)^{3/2} v^2 e^{-Mv^2/2\tau} dv$$

from :

4.4.4 *Maxwell's derivation of the velocity distribution in a gas*

The velocity distribution derived above makes use of the Boltzmann distribution. It is interesting to see how Maxwell derived the velocity distribution before the more general ideas of Boltzmann had been developed. The following is based on Maxwell's paper published in 1860.

Let n be the total number of molecules, and let u, v, w, be the components of the velocity of each molecule in three rectangular directions. Then if the number of molecules for which velocity component u lies between u and $u+\mathrm{d}u$ is $nf(u)\,\mathrm{d}u$, where $f(u)$ is the function to be determined, the number of molecules for which v lies between v and $v+\mathrm{d}v$ will be $nf(v)\,\mathrm{d}v$ and similarly for w, where f always stands for the same function since there is no preferred direction in the gas.

Now the existence of the velocity u does not in any way affect that of the velocities v and w since these are all at right angles to each other and independent. Consequently the number of molecules whose velocity components lie simultaneously between u and $u+\mathrm{d}u$, between v and $v+\mathrm{d}v$ and between w and $w+\mathrm{d}w$ is

$$\mathrm{d}n = nf(u)f(v)f(w)\,\mathrm{d}u\,\mathrm{d}v\,\mathrm{d}w. \tag{4.57}$$

Let this now refer to all those molecules which have a resultant velocity c, where

$$c^2 = u^2 + v^2 + w^2. \tag{4.58}$$

We now consider the condition under which the components u, v, w, can vary whilst c remains constant. This is found by differentiating equation (4.58) and putting $\mathrm{d}c = 0$; we obtain

$$u\,\mathrm{d}u + v\,\mathrm{d}v + w\,\mathrm{d}w = 0. \tag{4.59}$$

Since no direction is preferred over any other, it follows that $\mathrm{d}n$ in equation (4.57) must remain constant whatever the individual values of u, v and w, provided these satisfy equation (4.59). This implies that

$$\frac{\mathrm{d}}{\mathrm{d}u}(\mathrm{d}n)\,\mathrm{d}u + \frac{\mathrm{d}}{\mathrm{d}v}(\mathrm{d}n)\,\mathrm{d}v + \frac{\mathrm{d}}{\mathrm{d}w}(\mathrm{d}n)\,\mathrm{d}w = 0. \tag{4.60}$$

From equation (4.57) this gives

$$f'(u)\,\mathrm{d}u\,f(v)f(w) + f'(v)\,\mathrm{d}v\,f(u)f(w) + f'(w)\,\mathrm{d}w\,f(u)f(v) = 0,$$

where $f'(u)$ is the differential of $f(u)$ with respect to u, etc. Dividing throughout by $f(u)\,f(v)\,f(w)$ we obtain

$$\frac{f'(u)}{f(u)}\,\mathrm{d}u + \frac{f'(v)}{f(v)}\,\mathrm{d}v + \frac{f'(w)}{f(w)}\,\mathrm{d}w = 0. \tag{4.61}$$

In order to solve equations (4.59) and (4.61), we multiply equation (4.59) by an arbitrary constant λ and add it to equation (4.61). The result is

$$\left(\frac{f'(u)}{f(u)} + \lambda u\right)\mathrm{d}u + \left(\frac{f'(v)}{f(v)} + \lambda v\right)\mathrm{d}v + \left(\frac{f'(w)}{f(w)} + \lambda w\right)\mathrm{d}w = 0.$$

Each term must identically be equal to zero, and since $\mathrm{d}u, \mathrm{d}v, \mathrm{d}w$, although very small are not themselves zero, the quantities in the brackets must be zero. Hence

$$\frac{f'(u)}{f(u)} + \lambda u = 0 \quad \text{or} \quad \frac{f'(u)}{f(u)} = -\lambda u.$$

Integrating this relation we have

$$\ln f(u) = -\frac{\lambda u^2}{2} + A,$$

where A is an integration constant. This may be written in the form

$$f(u) = B\exp\left(-\frac{\lambda u^2}{2}\right).$$

As Maxwell remarks, if λ were negative, the number of molecules would be infinite, so consequently, λ must be positive. The number of molecules with velocities between u and $u+\mathrm{d}u$ then becomes

$$\mathrm{d}n = nf(u)\,\mathrm{d}u = nB\exp\left(-\frac{\lambda u^2}{2}\right).$$

There is no way of establishing the value of λ except by calculating the mean square velocity $\overline{c^2}$ and making use of the gas equation: $\frac{1}{3}m\overline{c^2} = kT$. It is then found that λ has the value m/kT. The result is

$$\mathrm{d}n = nB\exp\left(-\frac{mu^2}{2kT}\right)\mathrm{d}u,$$

which is identical with equation (4.42).

4.4.5 *Experimental determination of velocity distribution*

In most of the earlier experimental studies of the velocity distribution, a furnace was used to produce a vapour of metal atoms, which behave like a monatomic gas, at the temperature of the enclosure. They were allowed to condense on a cold surface and, by the ingenious use of moving shutters, atoms with different velocities were caught at different points on the surface. The intensity of condensed atoms provides then a measure of the relative number of atoms within that velocity range. One method due to I. F. Zartman (1931) and C. C. Ko (1934) is illustrated in figure 32(*a*). Atoms of bismuth are produced by a furnace and the vapour is collimated by a series of slits, S_1, S_2, S_3; the vapour beam reaches a drum rotating at a speed of 6000 rev. per min. and can only enter the drum at the slit S. The atoms then strike the plate P where they condense; the fastest ones reaching A, and slower ones B and the slowest C.

A more elegant and refined experiment by I. Esterman, O. C. Simpson and O. Stern (1947) gave results shown in figure 32(*b*). The agreement with the Boltzmann distribution is surprisingly good.

Figure 32. (*a*) Method due to Zartman and Ko for determining the velocity distribution of bismuth atoms: the atoms are evaporated, collimated by the slits S_1, S_2, S_3 and enter the rotating drum. They fall on the cold plate P where they condense. (*b*) Results obtained in a later experiment by Esterman, Simpson and Stern.

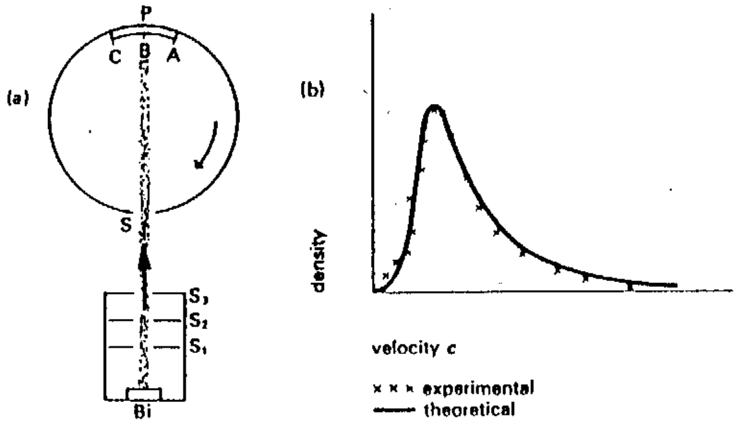
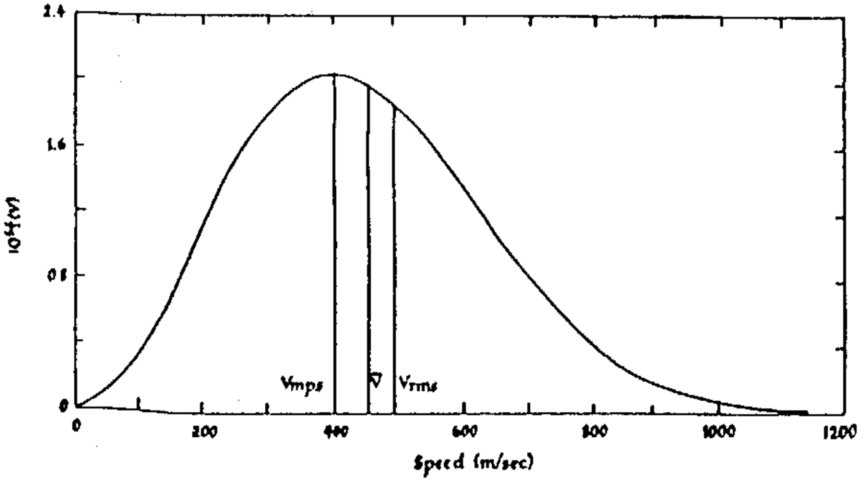


Figure 11.4. Maxwellian distribution of speeds for nitrogen at 0°C. Most probable speed v_{mps} = 401 m/sec; average speed $\bar{v}$ = 453 m/sec; root-mean-square speed v_{rms} = 492 m/sec.



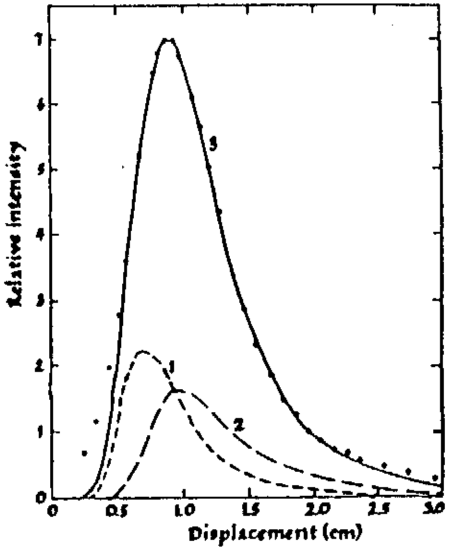


Figure 11.6. Velocity distribution for bismuth vapor at 1148°K. [Adapted from C. C. Ko, "The Heat of Dissociation of Bi Determined by the Method of Molecular Beams," *J. Franklin Inst.* 217, 173, 1934.]

from: Zemansky & Dittman
Heat & thermodynamics
McGraw-Hill, 1981

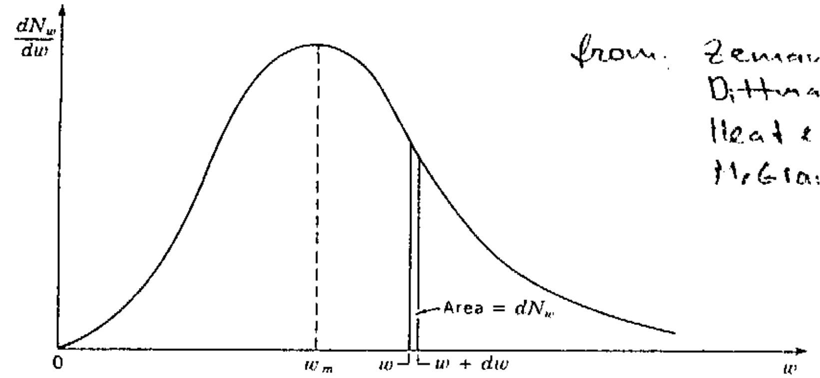


Figure 11-5 Graph of Maxwell speed-distribution function.

If the speed of a molecule is w, then

$$\epsilon = \tfrac{1}{2}mw^2,$$

and substituting dg_ϵ/Z and ϵ into Eq. (11-33), we get

$$dN_w = \frac{2N}{\pi^{1/2}(kT)^{3/2}}\,(\tfrac{1}{2}mw^2)^{1/2}mw\;d(we^{-(1/2)mw^2/kT}),$$

and finally

$$\boxed{\frac{dN_w}{dw} = \frac{2N}{\sqrt{2\pi}}\left(\frac{m}{kT}\right)^{3/2} w^2 e^{-(1/2)mw^2/kT}.} \tag{11-34}$$

The expression on the right is the famous *Maxwell speed-distribution* function, and is plotted in Fig. 11-5. Figure 11-6 shows the function for three different temperatures. The higher the temperature, the wider is the spread of values of the speed.

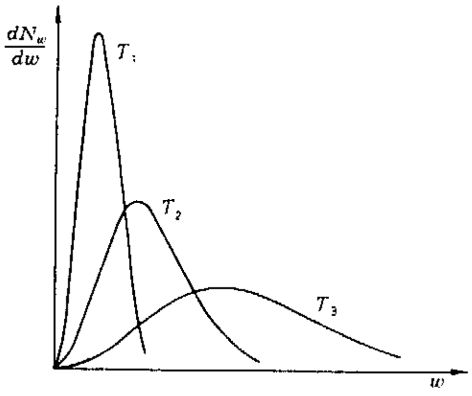


Figure 11-6 Maxwellian speed distribution at various temperatures. $T_3 > T_2 > T_1$.

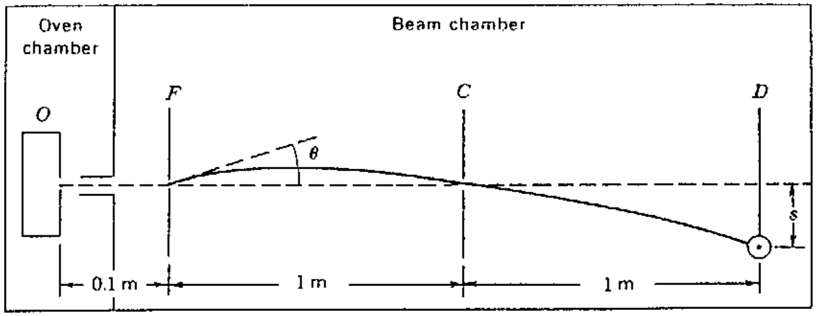


Figure 11-7 Apparatus of Estermann, Simpson, and Stern for the deflection of a molecular beam by gravity. O, oven; F and C, slits; D, detector.

Maxwell's equation for the distribution of molecular speeds has been experimentally verified directly as well as indirectly. One of the most convincing experiments was performed by Estermann, Simpson, and Stern in 1947, making use of the apparatus depicted schematically in Fig. 11-7, in which atoms are deflected *by gravity only*. Cesium atoms issue from a minute slit in an oven O at the left of a long, highly evacuated chamber. Most of these atoms are stopped by the diaphragm F, and those which go through the slit constitute a narrow, almost horizontal beam. The slit C, called the *collimating slit*, is halfway between F and the detector D. The atoms are detected by the method of surface ionization, in which nearly every cesium atom striking a hot tungsten wire leaves the wire as a positive ion and is collected by a negatively charged plate. The plate current is then a measure of the number of cesium atoms striking the detector wire per unit of time.

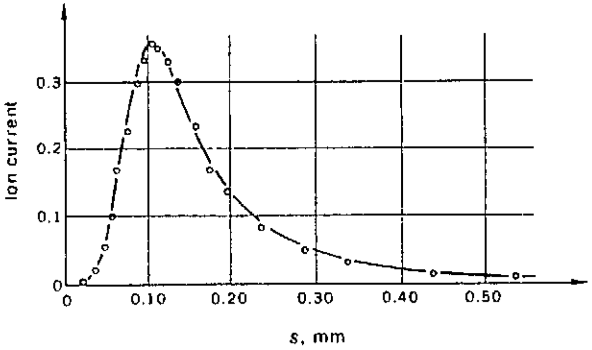
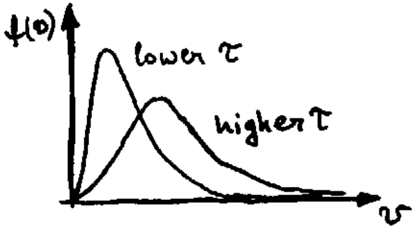


Figure 11-8 Distribution of speeds of cesium atoms in atomic beam deflected by gravity. *(Estermann, Simpson, and Stern.)*

A simple analysis of the parabolic paths of the atoms that pass through F and C provides a relation between the deflection s and the speed w. The departure angle θ is practically zero. The experimental results are shown in Fig. 11-8, where the smooth curve is a plot of Maxwell's function and the dots are experimental points.

- because of the v^2 factor, the distribution is not a symmetric Gaussian of $e^{-Mv^2/2\tau}$



max @ $\frac{df}{dv} = 0$

$$\Rightarrow -\frac{Mv}{\tau} \times v^2 + 2v = 0$$

$$\Rightarrow \underbrace{v_{mp}}_{\text{most probable velocity}} = \sqrt{\frac{2\tau}{M}} = \sqrt{\frac{2kT}{M}}$$

Note: $v_{mp} \neq v_{rms} \equiv \langle v^2 \rangle^{1/2}$ for an asymmetric distribution.

EFTS relate v_{rms} and v_{mp} for a Maxwellian distribution. Hint: $\int_0^\infty x^{2a} e^{-r^2x^2} dx = \frac{1 \cdot 3 \ldots (2a-1)}{2^{a+1} r^{2a+1}} \sqrt{\pi}$ for $r > 0$, $a = 1, 2, \ldots$

- $v_{mp} \sim 10^2 \frac{m}{s}$ for gases at room T, $\approx v_{sound}$ KK Table 14.1
$\Rightarrow$ relativistic effects do not contribute to M.v.d.
- $q^3 \sim \frac{V}{N} \Rightarrow q \sim n^{-1/3} \underbrace{\simeq 33\text{Å}}_{\gg \text{ size of molecules}}$ for He @ room T

$p \sim Mv_{mp} = \sqrt{2MkT}$

$\Rightarrow pq \sim n^{-1/3}\sqrt{2MkT} \gg \hbar$

as long as:
- dilute gas
- high T
- M not small

$\Rightarrow$ quantum effects can be neglected as well

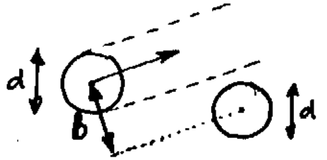
- experimental determination of M.v.d. – handout

Transport processes : predictions of stat. mech.

- Mean free path.

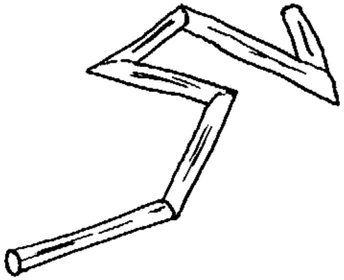
Dilute gas :
- time between collisions >> time of each collision
- most collisions involve 2 molecules
- mean distance between molecules >> de Broglie (Q.M.) wavelength of molecules, i.e. can treat molecules as classical particles.

ℓ = mean free path ≡ the distance a molecule travels between collisions, on average.



Collisions occur only when $b \leq d$

Ex: $d \simeq 2.2\text{Å}$ for He
$\simeq 3.6\text{Å}$ for Ar



A molecule of diameter d will "sweep out" a volume $\pi d^2 L$ (i.e. collide with all molecules whose center is within this volume)

If $n = \frac{N}{V}$ = concentration of molecules, the average # of molecules within the swept volume — and thus the # of collisions — is:

$$n \pi d^2 L$$

$\Rightarrow$ Travelling a distance L, the molecule experiences $n\pi d^2 L$ collisions

$$\Rightarrow \quad \underline{\ell} = \frac{L}{n\pi d^2 L} = \underline{\frac{1}{n\pi d^2}} = \text{the average distance between collisions}$$

Ex. He at 0°C and 1atm:

$$\ell = \frac{1}{n\pi d^2} = \frac{1}{3.14 \times (2.2 \times 10^{-10})^2 m^2 \times \underbrace{2.69 \cdot 10^{25}\ mol./m^3}_{\text{Loschmidt number}}} = 2.5 \cdot 10^{-7} m$$

Note 1: $\ell \simeq 1000 \times d$

Previously, we determined $v_{rms} \simeq 10^2\ m/s$

$$\Rightarrow \quad \frac{v_{rms}}{\ell} = \frac{10^2\ m/s}{10^{-7} m} \simeq 10^9 \text{ collisions/sec.} \leftarrow \text{dilute!}$$

Note 2: $\ell \ll$ size of experimental apparatus, @ 1atm

But at 10^{-6} atm ℓ becomes 0.25m, $\simeq$ comparable to the size of container. Hence, collisions with the walls of the apparatus will contribute significantly!

Note 3: The other molecules do not hold still $\Rightarrow$ what matters is the relative velocity of the two molecules:

$$\vec{v} = \vec{v}_1 - \vec{v}_2 \quad \Rightarrow \quad \vec{v}^2 = \vec{v} \cdot \vec{v} = \vec{v}_1^{\,2} + \vec{v}_2^{\,2} - 2\vec{v}_1 \cdot$$

taking the average:

$$\langle \vec{v}^2 \rangle = \langle \vec{v}_1^{\,2} \rangle + \langle \vec{v}_2^{\,2} \rangle - 2 \cancelto{0}{\langle \vec{v}_1 \cdot \vec{v}_2 \rangle}$$

to the extent that $v_{rms} \simeq \langle v \rangle \simeq v_{mp}$:

$$\langle \vec{v}^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle = 2 \langle v^2 \rangle \quad \text{for identical molecules}$$

This factor of 2 introduces a correction into our calculation of the mean free path:

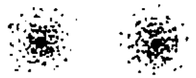
$$\boxed{\ell \simeq \frac{1}{\sqrt{2}\, n\pi d^2}}$$

πd^2 = cross-sectio
$= \sigma$

Note 4: Also need corrections for:

- overlap, counting the volume more than once in $(\pi d^2) \times L$; more important at higher rates of collisions

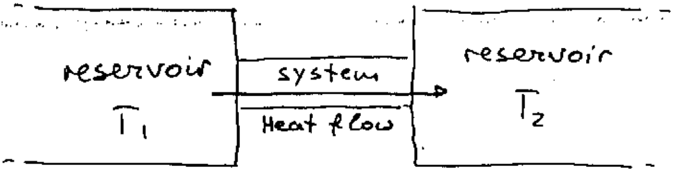
- "fuzziness" of molecules $\Rightarrow$ collisions are not like those of billiard balls



Transport processes in general

We deal here with non-equilibrium, steady-state processes.

E.g.



Here, the temperature difference is the driving force for the process:

ΔQ = energy $\propto \frac{\Delta T}{\Delta z}$ = temperature difference per unit length

or

Heat flux = rate of energy transport $\propto$ temperature gradient

Phenomenological Transport Laws

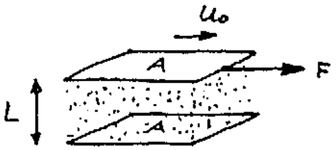
Effect	Flux of	Law	Coefficient
Diffusion	number	$\vec{J}_n = -D \,\mathrm{grad}\, n$	Diffusivity $D = \frac{1}{3}\bar{v}\ell$
Heat conduction	energy	$\vec{J}_E = -K \cdot \mathrm{grad}\, T$	Thermal conductivity $K = \frac{1}{3} C_V \bar{v}\ell$
Viscosity	transverse momentum	$\frac{F_x}{A} = J_p^{(x)} = -\eta \frac{d v_x}{dz}$	Viscosity $\eta = \frac{1}{3}\rho\bar{v}\ell$
Electrical conduction	charge	$\vec{J}_Q = \sigma \vec{E}$	Conductivity $\sigma = \frac{n Q^2 \ell}{M \bar{v}}$

In general, flux of A:

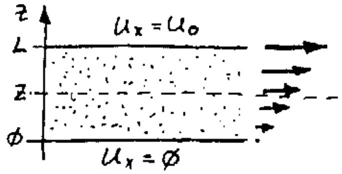
$\vec{J}_A \equiv$ net amount of A across unit area in unit time

Derivation of a transport equation: viscosity

Reif 8.



A force F is required to move a plate of area A with velocity u_0 relative to another plate, a distance L away.

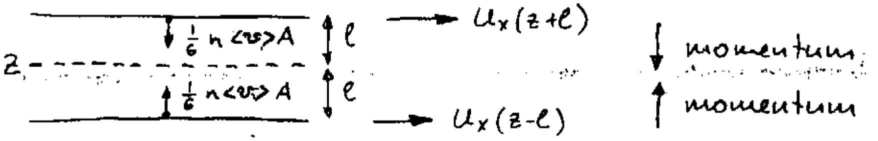


The boundary conditions are

$u_x = 0$ at $z = 0$

$u_x = u_0$ at $z = L$

Consider some surface parallel to the plate. The average momentum carried across this surface is associated with molecules having their last collision a distance ℓ from the plane:



Molecules moving in z-direction will carry excess momentum in and out of the plane:

- momentum brought up from $z-\ell$: $M\, u_x(z-\ell)$ per mol.
- momentum brought down from $z+\ell$: $M\, u_x(z+\ell)$ per mol.

All directions being equally probable $(\pm x, \pm y, \pm z)$, $\frac{1}{6}$ of molecules is moving up (and $\frac{1}{6}$ down), on average.

There will be $\frac{1}{6} n \langle v \rangle A$ molecules that count, per unit time.

Finally, the net transfer of momentum through the plane, per unit time, is:

$$\frac{1}{6} n \langle v \rangle A \left[M u_x(z-\ell) - M u_x(z+\ell) \right]$$

Note:
+ve direction is up.

$$\approx \frac{1}{6} n \langle v \rangle A \; M \left[u_x(z) - \frac{\partial u_x}{\partial z}\ell - \left(u_x(z) + \frac{\partial u_x}{\partial z}\ell \right) \right]$$

$$= \frac{1}{6} n \langle v \rangle A M \left(-2 \frac{\partial u_x}{\partial z} \ell \right)$$

On the other hand, rate of change of momentum = force, i.e.

$$\boxed{F = -\eta A \frac{\partial u_x}{\partial z}} \quad \text{with} \quad \boxed{\eta = \frac{1}{3} n \langle v \rangle M \ell}$$

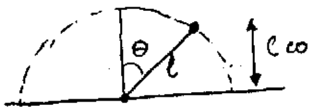
or force per unit area = stress:

$$P_z = \frac{F}{A} = -\eta \frac{\partial u_x}{\partial z}$$

c.f. R. p.327

Note 1: $\eta \propto \langle v \rangle$ i.e. $\eta \propto T^{1/2}$

Note 2: $\textcircled{\frac{1}{6}}$ factor (Joule's classification) is slightly wrong! — need to do proper integration:



- molecules coming from θ are a distance ℓ cos θ away from the plane
- there are $\frac{1}{2}\sin\theta\, d\theta$ within $d\theta$ of θ

$$\Rightarrow \int_0^{\pi/2} \frac{1}{2} \sin\theta\, d\theta\, n \langle v \rangle \cos\theta = \textcircled{\frac{1}{4}} n \langle v \rangle, \text{ per unit area}$$

each brings momentum $M \frac{\partial u_x}{\partial z} \ell \cos\theta$,

But: since the total momentum transfer is unchanged $\Rightarrow \eta = \frac{1}{3} n \langle v \rangle M \ell$ as before.

A startling experimental prediction

$$\left.\begin{aligned} \ell &= \frac{1}{\sqrt{2}\, \textcircled{n}\, \pi d^2} \\ \eta &= \frac{1}{3} M \textcircled{n} \langle v \rangle \ell \end{aligned}\right\} \quad \boxed{\eta = \frac{M \langle v \rangle}{3\sqrt{2}\, \pi d^2}} = \frac{M \langle v \rangle}{3\sqrt{2}\, \sigma}$$

! η is independent of $n = \frac{N}{V}$ = density of gas

Robert Boyle, 1660

"Experiment 26. .... We observ'd also that when the Receiver was full of Air, the included Pendulum continu'd its Recursions about fifteen minutes (or a quarter of an hour) before it left off swinging; and that after the exclusion of the Air, the Vibration of the same Pendulum (being fresh put into motion) appear'd not (by a minutes Watch) to last sensibly longer. So that the event of this Experiment being other than we expected, scarce afforded us any other satisfaction, than that of our not having omitted to try it."

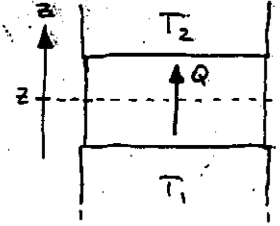
Explained by Maxwell (1866)

Corrections:

- at very high pressures, when molecules are almost always in contact
- at very low pressures, when the mean free path ℓ becomes longer than the dimensions of the apparatus

Transport of Energy

Reif 8.3



$$\boxed{J_U = -K \frac{\partial T}{\partial z}}$$

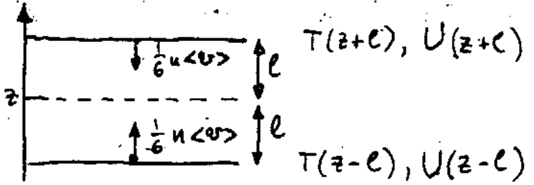
As in the case of momentum transport, except:

$$J_p = \frac{F}{A} \longrightarrow J_U = \frac{Q}{A}$$

$$\frac{\partial v}{\partial z} \longrightarrow \frac{\partial T}{\partial z}$$

$$\eta = \frac{1}{3} M n \langle v \rangle \ell \longrightarrow \mathcal{K} = ?$$

The derivation is completely analogous to the case of the transport of momentum:



The net flux of energy through the plane at z is:

$$J_U = \frac{1}{6} n\langle v \rangle \left[U(z-\ell) - U(z+\ell) \right]$$

$\uparrow +$, +ve direction is up

$$= \frac{1}{6} n \langle v \rangle \left[-2 \frac{\partial U}{\partial z} \ell \right]$$

$$= -\frac{1}{3} n \langle v \rangle \ell \frac{\partial U}{\partial T} \frac{\partial T}{\partial z}$$

$\frac{\partial U}{\partial T} \equiv c$ = heat capacity per molecule

$$\Rightarrow \boxed{J_U = -\frac{1}{3} n \langle v \rangle \ell c \frac{\partial T}{\partial z} = -\mathcal{K} \frac{\partial T}{\partial z}}, \quad \boxed{\mathcal{K} = \frac{1}{3} n \langle v \rangle \ell c}$$

Note 1: Again, $\frac{1}{6}$ may need adjusting

Note 2: Again, $\mathcal{K} = \frac{c \langle v \rangle}{3\sqrt{2}\,\sigma}$ = independent of n !

Note 3: For a monatomic gas, $U = \frac{3}{2} k_B T \Rightarrow c = \frac{3}{2} k_B$

Numerical estimates

- N_2 gas at room temperature: $T \simeq 300°K$

$$\left.\begin{aligned} M &= \frac{\text{m.w.}}{N_A} = \frac{28}{6 \cdot 10^{23}} = 4.7 \cdot 10^{-23}\,g \\ M\langle v \rangle &\simeq \sqrt{3 M k_B T} = 2.4 \cdot 10^{-18}\,g\,cm\,s^{-1} \\ \sigma &\simeq \pi d^2 \simeq 1.2 \cdot 10^{-15}\,cm^2 \end{aligned}\right\} \quad \eta = \frac{M \langle v \rangle}{3\sqrt{2}\,\sigma} \approx 5 \cdot 10^{-4}\,g\,cm^{-1}$$

[measured value: $1.78 \times 10^{-4}\,g\,cm^{-1}s^{-1}$]

- Ar (monatomic, i.e. $c \simeq \frac{3}{2} k_B$) at 300°K

$$\left.\begin{aligned} &\sigma \simeq \pi d^2 \simeq 1.3 \cdot 10^{-15}\,cm^2 = 1.3 \cdot 10^{-19}\,m^2 \\ &\langle v \rangle \simeq 400\,m/s \qquad k_B = 1.38 \times 10^{-23}\,J\,deg^{-1} \end{aligned}\right\} \quad \mathcal{K} = \frac{c\langle v \rangle}{3\sqrt{2}\,\sigma} = \frac{k_B \langle v \rangle}{2\sqrt{2}\,\sigma}$$

$$\mathcal{K} \sim 1.5 \cdot 10^{-2}\,W\,m^{-1}deg^{-1}$$

[measured value: $1.65 \times 10^{-2}\,W\,m^{-1}\,deg^{-1}$]

- The ratio: $\frac{\mathcal{K}}{\eta} = \frac{\frac{c\langle v \rangle}{3\sqrt{2}\sigma}}{\frac{M\langle v \rangle}{3\sqrt{2}\sigma}} = \frac{c}{M} \frac{\times N_A}{\times N_A} = \frac{C_V}{\text{m.w.}}$

$\Rightarrow$ expect $\frac{\mathcal{K}\,\text{M.W.}}{\eta\, C_V} \simeq 1$

	$\mathcal{K}$, cal $cm^{-1}s^{-1}deg^{-1}$	η, $g\,cm^{-1}s^{-1}$	$\frac{\mathcal{K}\,\text{m.w.}}{\eta\, C_V}$
He	3.36×10^{-4}	1.88×10^{-4}	2.40
Ar	0.389×10^{-4}	2.10×10^{-4}	2.49
H_2	3.97×10^{-4}	0.857×10^{-4}	1.91
N_2	0.54×10^{-4}	1.67×10^{-4}	1.91
O_2	0.57×10^{-4}	1.92×10^{-4}	1.90

Transport of number: diffusion

R.8.4

Context: label all molecules in a small volume in some way (radioactivity, fluorescence) and watch them spread out.

J_p : transport of momentum

J_U : transport of energy

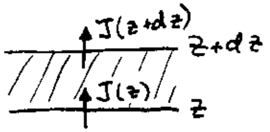
J_n : transport of the number of particles

As before: $J_n = -D \frac{\partial n}{\partial z}$, D = diffusivity

— Aside —

The "standard" form of a diffusion equation:

$$n_t - D n_{zz} = 0 \qquad n_t = \frac{\partial n}{\partial t}, \quad n_{zz} = \frac{\partial^2 n}{\partial z^2}$$



Consider the molecules inside the volume between z and z+dz:

There are: $(A\,dz)\cdot n$ of them.

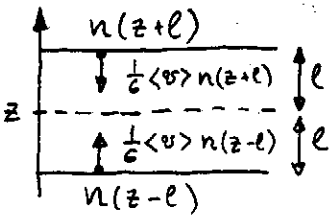
Their number is changing in time: $\frac{\partial}{\partial t}[A\,dz\,n]$

Due to the net flux at the boundaries:

$$\frac{\partial}{\partial t}[A\,dz\,n] = +A\,J(z) - A\,J(z+dz)$$

$$\Rightarrow \cancel{A\,dz}\,\frac{\partial n}{\partial t} = -\cancel{A}\,\frac{\partial J}{\partial z}\,\cancel{dz}$$

$$\Rightarrow \frac{\partial n}{\partial t} = -\frac{\partial J}{\partial z} = D\,\frac{\partial^2 n}{\partial z^2}$$



$$J_n = \frac{1}{6}\langle v\rangle n(z-\ell) - \frac{1}{6}\langle v\rangle n(z+\ell)$$

$$= \frac{1}{6}\langle v\rangle\left[-2\,\frac{\partial n}{\partial z}\,\ell\right]$$

$$\Rightarrow \boxed{J_n = -D\,\frac{\partial n}{\partial z}} \qquad \boxed{D = \frac{1}{3}\langle v\rangle \ell}$$

With: $\langle v\rangle = \sqrt{\frac{3kT}{M}}$ $\qquad \ell = \frac{1}{\sqrt{2}\,n\sigma} = \frac{1}{\sqrt{2}\,\sigma}\left(\frac{kT}{p}\right)$ Ideal gas Law; pressure

$$\Rightarrow D = \frac{1}{\sqrt{6}\,p\sigma}\,\frac{(kT)^{3/2}}{M^{1/2}}$$

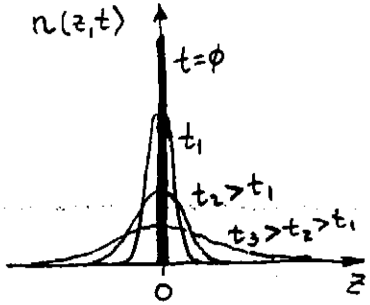
$\sim T^{3/2}$ at $p = $ const, $\sigma = $ const.

$\sim \frac{1}{p}$ at T = const

Numerically, $D = \frac{1}{3}\langle v\rangle\ell \simeq \frac{1}{3}\,400\,\text{m/s}\cdot 2.5\cdot 10^{-7}\,\text{m}$

$\Rightarrow D \simeq 3\times 10^{-5}\,\text{m}^2\,\text{s}^{-1}$ [experimentally: $1.85\cdot 10^{-5}$ for N_2 at 0°C

Solving the diffusion equation



ℓ = mean free path

$\tau = \frac{\ell}{\langle v\rangle}$ = mean time between collisions

$N = \frac{t}{\tau}$ = "steps" of random walk taken in time t; each of length ℓ_z

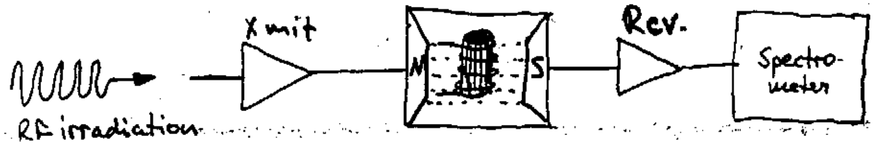
$$\Rightarrow \langle z^2\rangle = N\ell_z^2 = \frac{t}{\tau}\left(\tau\langle v_z\rangle\right)^2$$

But $\langle v_z\rangle^2 \approx \langle v_z^2\rangle \approx \frac{1}{3}\langle v^2\rangle \simeq \frac{1}{3}\langle v\rangle^2$

$$\Rightarrow \underline{\langle z^2\rangle} = \frac{1}{3}\tau\langle v\rangle^2 t = \frac{1}{3}\ell\langle v\rangle\, t \;\underline{= Dt}$$

D determines the width

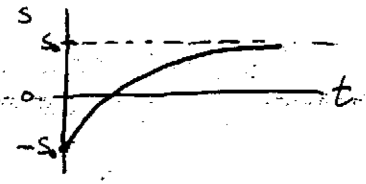
Ex. pore size determination by NMR



Signal S in the spectrometer as a function of time is a measure of how the system returns to equilibrium after being perturbed by the RF irradiation:

$$S(t) \propto S_0\left(1-2e^{-t/T_1}\right)\Big| = \begin{cases} -S_0, & t=0 \\ +S_0, & t=\infty \end{cases}$$

"T_1 relaxation"



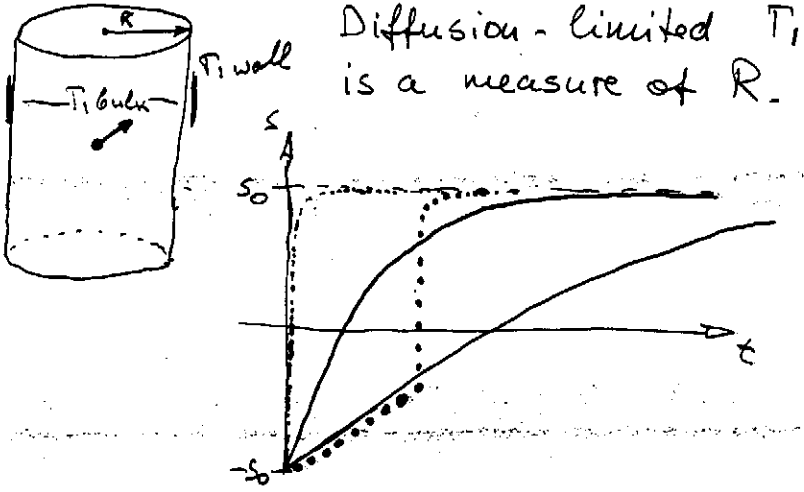
measured by the <u>inversion recovery</u> method, i.e. flip all spins 180° @ $t=0$.

Bulk water: $T_1 \propto$ a <u>few seconds</u>

water in wood: $T_1 \propto$ <u>100 ms</u> ?

Know: other, fast, T_1 <u>relaxation mechanisms</u> exist at the walls, T_1 <u>$\propto 3$ ms.</u>

Diffusion-limited T_1 is a measure of R.



Real wood has a distribution of R's.

Courtesy of Cyndy Araujo.
Presented at the Xth World Biophysical Congress, Aug. '9

Introduction

A sample of wood consists of long cylindrical cells (1 – 5 mm) called tracheids that run vertically along a tree. A sample of wood contains a broad distribution of these cells from the latewood trachieds to the larger earlywood trachieds. Wood also contains ray cells that run radially from the center of the tree outwards. The cell lumens have radii of the order of 10 μm and the distribution and sizes vary for different species and types of wood.

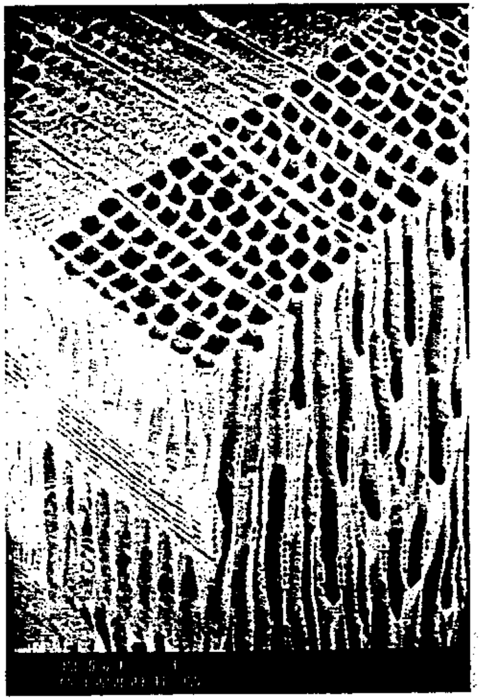
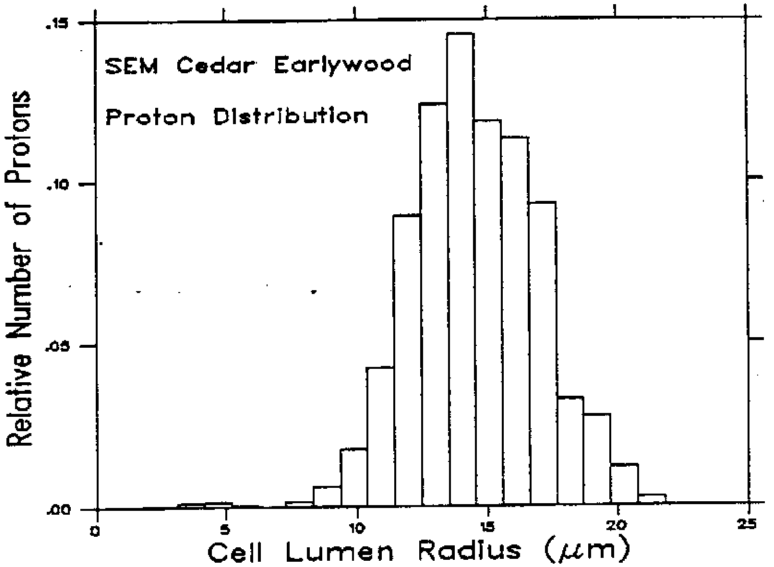
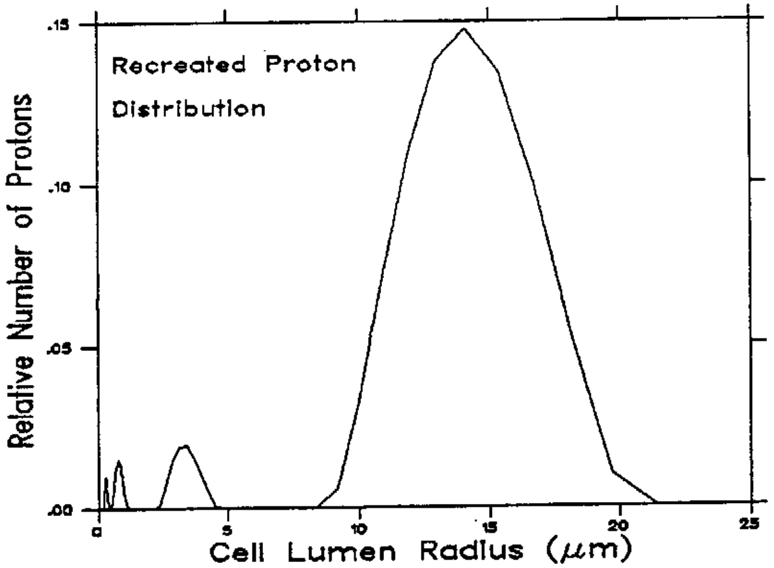


Figure 1: Scanning Electron Microscope image of Douglas fir sapwood, a typical softwood sample.





Introduction to interacting systems

Statistical mechanics: the QM perspective

- assume that QM determines the behaviour of the system
- wavefunction $\Psi(\{\vec{r}_i\},t)$ contains all of the information about the system; here
  $\vec{r}_i$, $i=1\ldots N$ = coordinates of the particles
- Ψ obeys the time-dependent Schrödinger equation
  $$\mathcal{H}\Psi = -i\hbar\frac{\partial\Psi}{\partial t}$$
- if $\mathcal{H}$ is time-independent, can separate spatial and time coordinates:
  $$\Psi(\{\vec{r}_i\},t) = \sum_n a_n\,\varphi_n(\{\vec{r}_i\})\,e^{-i\varepsilon_n t/\hbar}$$
  where
  a_n = constants (complex) determined by the initial conditions
  φ_n = stationary states, eigenfunction of the time-independent SE, $\mathcal{H}\varphi_n = \varepsilon_n\varphi_n$
- system prepared in a stationary state φ_n will remain in this state with a simple oscillatory time dependence, $e^{i\varepsilon_n t/\hbar}$

- for systems confined to finite volumes, the spectrum of ε_n is discrete and bounded from below $\Rightarrow$ there is the lowest (ground) state, s.t.
  $\varepsilon_0 \leq \varepsilon_n$, $\forall n$
- every physical, observable, quantity is represented by an operator $\mathcal{O}$ and the result of a measurement of that quantity is the expectation value
  $$\langle\mathcal{O}(t)\rangle = \int d\{\vec{r}_i\}\,\Psi^*(\{\vec{r}_i\},t)\,\mathcal{O}\,\Psi(\{\vec{r}_i\},t)$$
  $$= \sum_{m,n} a_m^*\,a_n\,\mathcal{O}_{mn}\,e^{-i(\varepsilon_n-\varepsilon_m)t/\hbar}$$
  where
  $$\mathcal{O}_{mn} \equiv \int d\{\vec{r}_i\}\,\varphi_m^*\,\mathcal{O}\,\varphi_n \quad \Big| = \text{an } (m\times n) \text{ matrix of numbers}$$
- thus, in principle, once we know $\{\varphi_n,\varepsilon_n\}$ and $\{a_n\}$ we can get the exact value of any observable

However, in practice:

- impractical for more than a few particles
- much information obtained in this way is not of interest
- the time-dependence $e^{-i(\varepsilon_n-\varepsilon_m)t/\hbar}$ is a rapid oscillation for $m\neq n$, and we want a time average, over the time it takes to perform a given measurement

- additional complication: weak residual time-dependent fields couple φ_n's and cause transitions between "stationary states"

$\Rightarrow \quad a_n \to a_n(t)$ in both amplitude & phase

Thus what we really want is the time average of the expectation value with respect to fluctuations in wave functions:

$$\overline{\langle \mathcal{O} \rangle}_{fl.} \xleftarrow{} \text{time} \qquad = \frac{1}{T}\int_0^T \langle \mathcal{O}(t) \rangle_{fl.}\, dt \qquad \text{where}$$

$$\langle \mathcal{O}(t) \rangle_{fl.} = \sum_{nm} a_m^*(t)\, a_n(t)\, \mathcal{O}_{nm}\, e^{-(\varepsilon_n-\varepsilon_m)t/\hbar}$$

Note: fluctuating time dependence arises not from $\mathcal{O}_{nm} = \mathcal{O}_{nm}(t)$ but from $a_m^*(t), a_n(t)$ being complex random variables.

- $a_n^* a_n = |a_n|^2$ = probability (statistical weight) associated with a stationary state φ_n. Hence, the normalization $\sum_n |a_n(t)|^2 = 1$ simply means that the system is always in some state.
- if ~~$a_m^*(t)$ and $a_n(t)$~~ have independently fluctuating, completely random phases; the time average

$$\overline{a_m^*(t)\, a_n(t)\, e^{-i(\varepsilon_n-\varepsilon_m)t/\hbar}} = \rho_{nn}\,\delta_{mn}$$

i.e. only terms with $m=n$ survive

Here ρ_{nn} = a diagonal matrix, representing operator ρ in the energy representation.

ρ = density matrix operator

Note: $\sum_n \rho_{nn} \equiv \mathrm{Tr}(\rho) = \sum_n a_n^* a_n = \sum_n |a_n|^2 = 1$

$$\boxed{\mathrm{Tr}(\rho) = 1}$$

- in the energy representation,

$$\boxed{\overline{\langle \mathcal{O} \rangle}} = \sum_{mn} \overline{a_m^*(t)\, a_n(t)\, e^{-i(\varepsilon_n-\varepsilon_m)t/\hbar}}\ \mathcal{O}_{mn}$$

$$= \sum_{mn} \rho_{nn}\,\delta_{mn}\,\mathcal{O}_{mn} = \sum_n \rho_{nn}\mathcal{O}_{nn}\ \boxed{= \mathrm{Tr}(\rho\mathcal{O})}$$

- properties of Tr:
  - $\mathrm{Tr}\, A \equiv \sum_n A_{nn}$
  - $\mathrm{Tr}\,(\underleftarrow{AB}) = \sum_{m,n} A_{mn} B_{nm} = \sum_{n,m} B_{nm} A_{mn} = \mathrm{Tr}\,(BA)$

  $\Rightarrow \mathrm{Tr}\,(\underleftarrow{AB\ldots CD}) = \mathrm{Tr}\,(DAB\ldots C)$ = invariant under cyclic permutation
  - if S is a unitary transformation, $SS^{-1} = 1$

  $\mathrm{Tr}\,(S^{-1}\mathcal{O}S) = \mathrm{Tr}\,(\underbrace{SS^{-1}}_{=1}\mathcal{O}) = \mathrm{Tr}\,\mathcal{O}$
- on the other hand, we know

$|a_n|^2 = \rho_{nn} \propto e^{-\varepsilon_n/\tau} = e^{-\beta\varepsilon_n}$ | Boltzmann recall $\beta \equiv \frac{1}{\tau}$

using normalization

$$\rho_{nn} = \frac{e^{-\beta\varepsilon_n}}{\sum_n e^{-\beta\varepsilon_n}} = \frac{1}{Z}\, e^{-\beta\varepsilon_n}$$

- $\mathcal{H}\varphi_n = \varepsilon_n \varphi_n \Rightarrow$ for any function $f(\mathcal{H})$:

$f(\mathcal{H})\,\varphi_n = f(\varepsilon_n)\,\varphi_n$

Prove by expanding f in powers of $\mathcal{H}$.

Ex $\underbrace{\left[e^{-\beta\mathcal{H}}\right]}_{\text{operator}}\varphi_n = \left[1-\beta\mathcal{H}+\beta^2\mathcal{H}^2-\dots\right]\varphi_n$

$$= \left[1-\beta\varepsilon_n+\beta^2\varepsilon_n^2-\dots\right]\varphi_n = e^{-\beta\varepsilon_n}\varphi_n$$

Thus, in the operator form:

$$\boxed{\rho = \frac{1}{Z}\,e^{-\beta\mathcal{H}}} \quad \text{where} \quad \boxed{Z = \mathrm{Tr}\left(e^{-\beta\mathcal{H}}\right)}$$

since $\underbrace{\left(e^{-\beta\mathcal{H}}\right)_{nn}}_{\text{matrix element}} = \int \varphi_n^* \underbrace{\left[e^{-\beta\mathcal{H}}\right]}_{\text{operator}}\varphi_n = \underbrace{e^{-\beta\varepsilon_n}}_{\text{number}}\underbrace{\int \varphi_n^*\varphi_n}_{=1} = e^{-\beta\varepsilon_n}$

Non-interacting spin system $\quad N \times \bigcirc\!\!\!\!\!\uparrow$

$\mathcal{H} = \sum_i \mathcal{H}_i \qquad \mathcal{H}_i$ = single-particle Hamiltonian

$$\rho = \frac{e^{-\beta\sum_i\mathcal{H}_i}}{\mathrm{Tr}\ e^{-\beta\sum_i\mathcal{H}_i}} = \frac{\prod_i e^{-\beta\mathcal{H}_i}}{\prod_i Z_i} = \prod_i \rho_i$$

Ex N spins in an external magnetic field $\qquad$ notes p. 6

$\mathcal{H} = -mB\sum_i s_i \quad , s_i = \pm 1$

As a matrix : $s_i = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \Rightarrow \mathcal{H}_i = \begin{pmatrix}-mB & 0\\ 0 & mB\end{pmatrix}$

$\Rightarrow e^{-\beta\mathcal{H}_i} = \begin{pmatrix}e^{\beta mB} & 0\\ 0 & e^{-\beta mB}\end{pmatrix}$

$\Rightarrow Z_i = \mathrm{Tr}\left(e^{-\beta\mathcal{H}_i}\right) = e^{\beta mB} + e^{-\beta mB} = 2\cosh(\beta mB)$

$$U_i = \langle\mathcal{H}_i\rangle = \frac{\mathrm{Tr}\left(\mathcal{H}_i e^{-\beta\mathcal{H}_i}\right)}{\mathrm{Tr}\left(e^{-\beta\mathcal{H}_i}\right)} \qquad \mathcal{H} = \text{energy operator}$$

$$= \frac{\mathrm{Tr}\begin{pmatrix}-mB\,e^{\beta mB} & 0\\ 0 & mB\,e^{-\beta mB}\end{pmatrix}}{\mathrm{Tr}\begin{pmatrix}e^{\beta mB} & 0\\ 0 & e^{-\beta mB}\end{pmatrix}} = -mB\,\frac{e^{\beta mB}-e^{-\beta mB}}{e^{\beta mB}+e^{-\beta mB}}$$

$$= -mB\,\frac{2\sinh(\beta mB)}{2\cosh(\beta mB)} = -mB\tanh(\beta mB)$$

$\Rightarrow \underline{U_i = -mB\tanh\frac{mB}{\tau}}$

Thermal average is the derivative of the free energy

$Z = \mathrm{Tr}\left(e^{-\beta\mathcal{H}}\right) \Rightarrow F = -\tau\log Z = -\tau\log\left[\mathrm{Tr}\left(e^{-\beta\mathcal{H}}\right)\right]$

Write down the Hamiltonian as

$\mathcal{H} = -\sum_\alpha h_\alpha\mathcal{O}^\alpha$

h_α = a generalized field

$\mathcal{O}^\alpha$ = operator conjugate to field

e.g. $\mathcal{H}_i = -\underbrace{mB}_{h}\underbrace{s_i}_{\mathcal{O}}$

$$\frac{\partial F}{\partial h_\alpha} = -\tau\frac{\partial}{\partial h_\alpha}\log\left[\mathrm{Tr}\left(e^{-\beta\mathcal{H}}\right)\right] = \beta\tau\,\frac{\mathrm{Tr}\left(e^{-\beta\mathcal{H}}\frac{\partial\mathcal{H}}{\partial h_\alpha}\right)}{\mathrm{Tr}\left(e^{-\beta\mathcal{H}}\right)}$$

but $\frac{\partial\mathcal{H}}{\partial h_\alpha} = -\mathcal{O}^\alpha \Rightarrow \frac{\partial F}{\partial h_\alpha} = -\frac{\mathrm{Tr}\left(\mathcal{O}^\alpha e^{-\beta\mathcal{H}}\right)}{\mathrm{Tr}\left(e^{-\beta\mathcal{H}}\right)} = -\langle\mathcal{O}^\alpha\rangle$

$\Rightarrow$ the expectation value (thermal ensemble average) of the operator is = − derivative of free energy with respect to its conjugate field

$$\boxed{\langle O^{\alpha}\rangle = -\frac{\partial F}{\partial h_{\alpha}}}$$

(Ex net magnetisation of a non-interacting spin system

$$F_i = -\tau\log Z_i = -\tau\log 2 - \tau\log[\cosh(\beta m B)]$$

$$M_i = m\langle s_i\rangle = -m\frac{\partial F_i}{\partial(mB)} = \tau\beta\, m\,\frac{\sinh(\beta m B)}{\cosh(\beta m B)}$$

$$\Rightarrow M = N\times M_i = Nm\tanh(\beta m B)$$

or $\underline{M = Nm\tanh\frac{mB}{\tau}}$ cf. notes p.24

- susceptibility $\chi = \frac{\partial M}{\partial B} = Nm\times(\beta m)\times\operatorname{sech}^2(\beta m B)$

$$\Rightarrow \chi = \frac{m^2N}{\tau}\operatorname{sech}^2\left(\frac{mB}{\tau}\right)$$

or $\tau\to\infty$ low-field, $B\to0$: $\chi = \frac{m^2N}{\tau}$ ← recover Curie's law

$\tau\to0$ high-field, $B\to\infty$: $\chi = 0$ ← all spins already lined up, no more to flip

- $F_i = U_i - \tau\sigma_i$

$\Rightarrow \sigma_i = \beta(U_i - F_i)$ = entropy per spin

$$= -\beta m B\tanh(\beta m B) + \log[\cosh(\beta m B)] + \log 2$$

$\tau\to\infty$ $B\to0$: $\sigma_i = \ln 2$ ← fully disordered

$\tau\to0$ $B\to\infty$: $\tanh(\beta m B)\to1$, $\cosh(\beta m B)\to\frac{1}{2}e^{\beta m B}$

$\Rightarrow \log[\cosh(\beta m B)]\to\beta m B - \log 2$

$\Rightarrow \sigma_i = -\beta m B + \beta m B - \log 2 + \log 2 = 0$ ← fully ordered

The Ising model of a ferromagnet

$$\mathcal{H} = \underbrace{-\frac{1}{2}J\sum_{i,\delta}s_i s_{i+\delta}}_{\text{spin-spin interactions}}\quad\underbrace{-h\sum_i s_i}_{\text{non-interacting spins in an external field } h\ (=mB)}$$

i is summed over N sites

δ is summed over y nearest neighbours of site i

$y\times N$ = total # of terms in the sum $\sum_{i,\delta}$

Ex ferromagnetism

- all sites are equivalent
- at high τ, spins mainly disordered, randomly up or down $\Rightarrow\langle s_i\rangle = 0$
- at low τ, all spins are mainly up or mainly dow

$\Rightarrow$ write $s_i = \underbrace{\langle s\rangle}_{\text{the same for all sites}} + \delta s_i$

δs_i = <u>fluctuation</u> of s_i from the average value

- <u>Mean-field approximation</u> (MFA)

$$\mathcal{H} = -\frac{1}{2}J\sum_{i,\delta}\left[\langle s\rangle^2 + \langle s\rangle(\delta s_i + \delta s_{i+\delta}) + \overset{0}{\cancel{\delta s_i\,\delta s_{i+\delta}}}\right] - h\sum_i s_i$$

> MFA is to neglect the second-order terms in the fluctuations

Rewrite: $\delta s_i = s_i - \langle s \rangle$

$\delta s_{i+\delta} = s_{i+\delta} - \langle s \rangle$

$$\Rightarrow \langle s \rangle (\delta s_i + \delta s_{i+\delta}) = \langle s \rangle (s_i + s_{i+\delta}) - 2\langle s \rangle^2$$

$$\Rightarrow \mathcal{H} = \frac{JNy}{2}\langle s \rangle^2 - \sum_i \left(Jy\langle s \rangle + h\right) s_i$$

$$= \text{const} - h_{eff} \sum_i s_i$$

with $\underline{h_{eff} = Jy\langle s \rangle + h}$

And the problem reduces to the case of noninteracting spins in an effective external field h_{eff}

$\Rightarrow$ MFA (neglecting second-order terms in fluctuations) leads to an approximate (truncated) Hamiltonian in which each spin sees the <u>same</u> effective field.

- so far, $\langle s \rangle$ has not been determined.

  But! – we have solved the problem of non-interacting spins, there

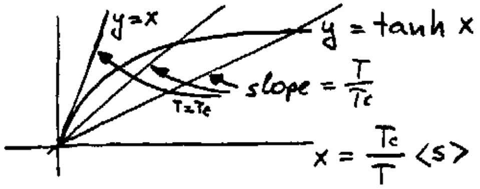
$$\langle s_i \rangle = \frac{\mathrm{Tr}(s_i e^{-\beta \mathcal{H}})}{\mathrm{Tr}(e^{-\beta \mathcal{H}})} = \frac{\mathrm{Tr}(s_i e^{\beta h s_i})}{\mathrm{Tr}(e^{\beta h s_i})} = \tanh(\beta h)$$

Thus, now:

$$\boxed{\underset{\uparrow}{\langle s \rangle} = \tanh(\beta h_{eff}) = \tanh \beta (Jy \underset{\uparrow}{\langle s \rangle} + h)}$$ self-consistency relation

Solving the self-consistency relation yields $\langle s \rangle$, and thus all of the thermodynamic properties of the system.

Ex. a graphical solution for $h = 0$



$\left.\begin{array}{l} y = x \\ y = \tanh x \end{array}\right\}$ for slopes ≥ 1 the only sol'n is $x = 0$.

EFTS Calculate numerically and plot $\langle s \rangle$ vs. T for $h = 0$ and $h = 0.5\, T_c$ in the region $0 < T < 3T_c$

<u>Approximations</u>:

- at high temperature:
  - system is disordered $\Rightarrow \langle s \rangle \ll 1$
  - $\beta \ll 1 \Rightarrow \beta(Jy\langle s \rangle + h) \ll 1$, and $\tanh x \simeq x$, $x \ll 1$

$$\Rightarrow \langle s \rangle \simeq \beta (Jy\langle s \rangle + h)$$

$$\Rightarrow (\tau - Jy)\langle s \rangle = h$$

$$\Rightarrow \langle s \rangle = \frac{h}{\tau - Jy} = \frac{h}{k_B(T - T_c)}, \quad \boxed{T_c \equiv \frac{Jy}{k_B}}$$

$\chi \propto \frac{\partial \langle s \rangle}{\partial h} = \frac{1}{T - T_c}$ Curie-Weiss Law

In the absence of interaction, $J = 0 \Rightarrow T_c = 0$

$\chi \propto \frac{1}{T}$ Curie's Law

$$\boxed{\text{MFT prediction:} \quad \chi \propto (T-T_c)^{-\gamma}, \quad \gamma = 1}$$

- $T \lesssim T_c$, just below the ordering temperature

First, assume $\underline{h=0}$ (i.e. $B=0$)

In the absence of field, usually expect $\langle s\rangle = 0$

However, when a ferromagnetic ordering spontaneously occurs below T_c, let's assume $\langle s\rangle$ begins to grow continuosly from zero. Choose T so that $\langle s\rangle$ is small ($\beta J\langle s\rangle \ll 1$) but not zero, and expand $\tanh x = x - \frac{x^3}{3} + \dots$

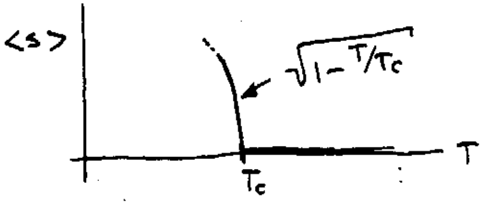
$$\langle s\rangle = \beta J y\langle s\rangle - \frac{1}{3}(\beta J y\langle s\rangle)^3 + \dots$$

$$\frac{1}{3}(\beta J y)^3\langle s\rangle^2 = \beta J y - 1$$

$$\frac{T_c^3}{3T^3}\langle s\rangle^2 = \frac{T_c}{T} - 1 = \frac{T_c - T}{T}$$

$$\Rightarrow \quad \langle s\rangle = \sqrt{3}\,\frac{T}{T_c}\sqrt{\frac{T_c - T}{T_c}} = \sqrt{3}\,\frac{T}{T_c}\sqrt{1 - T/T_c}$$

$$\boxed{\text{MFT prediction:} \quad \text{for } T \lesssim T_c, \ \langle s\rangle = \sqrt{3}\left(1 - \frac{T}{T_c}\right)^{\beta} \quad \beta = \tfrac{1}{2}}$$



- $T = T_c$ and $h \neq 0$, but small $\left|\frac{h}{T_c}\right| \ll 1$

$$\Rightarrow \langle s\rangle = \tanh\left(\langle s\rangle + \frac{h}{T_c}\right) \approx \langle s\rangle + \frac{h}{T_c} - \frac{1}{3}\left(\langle s\rangle + \frac{h}{T_c}\right)^3$$

$$\frac{h}{T_c} = \frac{1}{3}\left(\langle s\rangle + \frac{h}{T_c}\right)^3$$

Assume $\frac{h}{T_c} \ll \langle s\rangle$ (to be verified later). Then

$$\frac{h}{T_c} \simeq \frac{1}{3}\langle s\rangle^3 \quad \Rightarrow \quad \langle s\rangle = \left(\frac{3h}{T_c}\right)^{1/3}$$

This does, indeed, give $\frac{h}{T_c} \ll \langle s\rangle$ for $\left|\frac{h}{T_c}\right| \ll 1$

$$\boxed{\text{MFT prediction:} \quad \langle s\rangle \propto h^{1/\delta}, \quad \delta = 3 \ \text{at } T = T_c}$$

- heat capacity

$$U = \frac{1}{N}\langle \mathcal{H}\rangle = \frac{1}{2}Jy\langle s\rangle^2 - (Jy\langle s\rangle + h)\langle s\rangle$$ see p.132

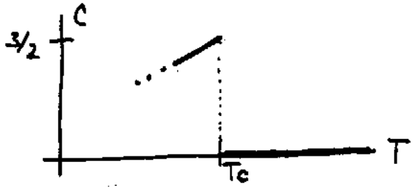
$$= -\frac{1}{2}Jy\langle s\rangle^2 - h\langle s\rangle$$

– for $h=0$, $T \leq T_c$, $\langle s\rangle = \sqrt{3}\,\frac{T}{T_c}\sqrt{1 - T/T_c}$

$\Rightarrow U = \dots$ EFTS

$$\Rightarrow C = \frac{\partial U}{\partial T} = \frac{3}{2}\,\frac{T}{T_c}\,\frac{3T - 2T_c}{T_c} = \frac{3}{2} \ \text{at } T = T_c$$

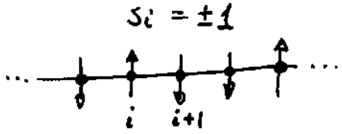
– for $T > T_c$, $\langle s\rangle = 0 \Rightarrow U = 0 \Rightarrow C = 0$



a discontinuity!

- <u>density matrix treatment of a 1D ferromagnet</u>

$$\mathcal{H} = -\frac{J}{2}\sum_{i,\delta=\pm1} s_i s_{i+\delta} - h\sum_i s_i$$



$$= -J\sum_i s_i s_{i+1} - h\sum_i s_i$$

For <u>N spins, $h = 0$</u> :

$$Z_N = \mathrm{Tr}\, e^{-\beta\mathcal{H}} = \underbrace{\sum_{s_1=\pm1}\cdots\sum_{s_N=\pm1} e^{\beta J\sum_{i=1}^{N-1} s_i s_{i+1}}}$$

Sum over $s_N = \pm 1$ only : $\displaystyle\sum_{s_N=\pm1} e^{\beta J s_{N-1} s_N} = e^{\beta J} + e^{-\beta J}$

$$= \boxed{2\cosh\beta J}$$

similarly for others.

continue until left with the last two spins:

$$Z_N = \boxed{2\cosh\beta J}\sum_{s_1=\pm1}\cdots\sum_{s_{N-1}=\pm1} e^{\beta J\sum_{i=1}^{N-2} s_i s_{i+1}} =$$

$$= (2\cosh\beta J)^{N-2}\underbrace{\sum_{s_1=\pm1}\sum_{s_2=\pm2} e^{\beta J s_1 s_2}}_{4\cosh\beta J} =$$

$$\boxed{Z_N = 2\,(2\cosh\beta J)^{N-1}}$$

Free energy per spin : $f = \dfrac{F}{N} = -\dfrac{\tau}{N}\log Z_N$

$$\Rightarrow f = -\cancelto{0,\,N\gg1}{\frac{\tau}{N}}\ln 2 - \tau\cancelto{1,\,N\gg1}{\frac{N-1}{N}}\log(2\cosh\beta J)$$

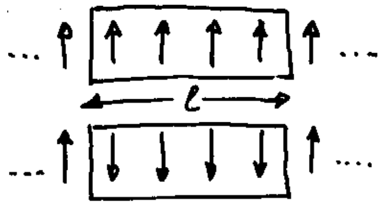
$$\approx -\tau\log(2\cosh\beta J) \quad \text{for } N \gg 1$$

!? This is a perfectly analytic function of τ

$\Rightarrow$ no phase transitions

$\Rightarrow$ there is no spontaneous ferromagnetic ordering in 1D

<u>Why is 1D special</u>: the energy required to flip a block of spins is independent of the size of the block!



Energy cost : $4J$

$\downarrow$ no matter what is ℓ

In general, in a d-dimensional space, reversing a "cube" of spins of linear dimension ℓ affects $n \sim \ell^d$ spins $\Rightarrow$ $\ell \sim n^{1/d}$

Of those, $\ell^{d-1} \sim n^{1-1/d}$ spins are at the surface

$\Rightarrow$ the energy cost of flipping the entire block at once is $\sim J n^{1-1/d}$

$d = 1$: the energy is independent of n, the size of the block

$d \geq 2$: the energy diverges as $n \to \infty$

- **density matrix formalism for MFT of a ferromagnet.**

For non-interacting particles, $\mathcal{H}_N = \sum_{i=1}^{N} \mathcal{H}_i$

$\Rightarrow \ \rho_N = \prod_{i=1}^{N} \rho_i$, where ρ_i = single-spin density function

[Clearly, ρ_i is Hermitian, $\mathrm{Tr}(\rho_i) = 1$]

Strategy: use this $\rho_N = \prod_i \rho_i$ as a trial density matrix and minimize the free energy functional

$$F = \mathrm{Tr}(\mathcal{H}\rho_N) + \tau\, \mathrm{Tr}(\rho_N \log \rho_N)$$

with respect to all the matrix elements of all the ρ_i's.

— Aside : verify —

$$\mathrm{Tr}(\rho\mathcal{H}) + \tau\, \mathrm{Tr}(\rho\log\rho) = \mathrm{Tr}(\rho\mathcal{H}) + \tau\, \mathrm{Tr}\left(\rho \log \frac{e^{-\beta\mathcal{H}}}{Z}\right)$$

$$= \mathrm{Tr}(\rho\mathcal{H}) + \tau\, \mathrm{Tr}\left[-\rho\beta\mathcal{H} - \rho\log Z\right]$$

$$= \cancel{\mathrm{Tr}(\rho\mathcal{H})} - \cancel{\tau}\beta\, \cancel{\mathrm{Tr}(\rho\mathcal{H})} - \tau \log Z\, \overset{\nearrow 1}{\mathrm{Tr}(\rho)} = -\tau\log Z \equiv F$$

The minimization gives the best approximation to the N-particle density function which is of the product form. It is not the most general form of ρ and so the free energy so calculated is only an upper bound to the exact free energy.

Ex: spin-$\frac{1}{2}$ ferromagnet

For simplicity, assume that all spins have the same $\rho_i = \begin{pmatrix} x_i & a_i \\ a_i^* & 1-x_i \end{pmatrix}$

$$S_i = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \Rightarrow S_i\rho_i = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} x & a \\ a^* & 1-x \end{pmatrix} = \begin{pmatrix} x & a \\ -a^* & x-1 \end{pmatrix}$$

$$\langle S_i \rangle = \mathrm{Tr}(\rho_i S_i) = 2x - 1$$

$$\Rightarrow \rho_i = \begin{pmatrix} \frac{1}{2}(1+\langle S_i\rangle) & a \\ a^* & \frac{1}{2}(1-\langle S_i\rangle) \end{pmatrix}$$

$$\left\langle \sum_{i,\delta} S_i S_{i+\delta} \right\rangle = \mathrm{Tr}\left(\rho_N \sum_{i,\delta} S_i S_{i+\delta}\right) = \sum_{i,\delta} \mathrm{Tr}\left(\prod_j \rho_j\, S_i S_{i+\delta}\right)$$

$$= \sum_{i,\delta} \underbrace{\prod_{\substack{j\neq i \\ j\neq i+\delta}} \mathrm{Tr}(\rho_j)}_{1^{N-2}}\ \underbrace{\mathrm{Tr}(\rho_i S_i)}_{\substack{\langle S_i\rangle \\ \parallel \\ \langle S\rangle}}\ \underbrace{\mathrm{Tr}(\rho_{i+\delta} S_{i+\delta})}_{\substack{\langle S_{i+\delta}\rangle \\ \parallel \\ \langle S\rangle}}$$

$$= Ny\langle S\rangle^2$$

$$\Rightarrow \quad \langle \mathcal{H} \rangle = -\frac{1}{2} J N y \langle S\rangle^2 - hN\langle S\rangle$$

Entropy: $\mathrm{Tr}(\rho_N \log\rho_N) = \mathrm{Tr}\left(\prod^{N} \rho_i \log \prod_j \rho_j\right)$

$$= \sum_j \mathrm{Tr}\left(\prod_{i\neq j} \rho_i\right) \mathrm{Tr}(\rho_j \log \rho_j)$$

$= N\, \mathrm{Tr}(\rho_j \log \rho_j)$ since all ρ_j's are the same.

Assume $a = 0$ [actually, one can show $a = 0$]

$\Rightarrow$ ρ_i's are diagonal

$$\Rightarrow \mathrm{Tr}(\rho_j \log \rho_j) = \frac{1+\langle s\rangle}{2} \log \frac{1+\langle s\rangle}{2} + \frac{1-\langle s\rangle}{2} \log \frac{1-\langle s\rangle}{2}$$

$$\Rightarrow f = \frac{F}{N} = -\frac{1}{2} J y \langle s\rangle^2 - h\langle s\rangle + \tau \times$$
$$\times \left[\frac{1+\langle s\rangle}{2} \log \frac{1+\langle s\rangle}{2} + \frac{1-\langle s\rangle}{2} \log \frac{1-\langle s\rangle}{2} \right]$$

To determine free energy, minimize w.r.to $\langle s\rangle$:

$$\frac{\partial f}{\partial \langle s\rangle} = \ldots \text{EFTS} \ldots = -Jy\langle s\rangle - h + \frac{1}{2}\tau \log \frac{1+\langle s\rangle}{1-\langle s\rangle} = 0$$

$$\Rightarrow \beta(Jy\langle s\rangle + h) = \underbrace{\frac{1}{2} \log \frac{1+\langle s\rangle}{1-\langle s\rangle} \equiv x}$$

$$\frac{1+\langle s\rangle}{1-\langle s\rangle} = e^{2x} \quad \Rightarrow \quad 1+\langle s\rangle = e^{2x} - \langle s\rangle e^{2x}$$

$$\Rightarrow \langle s\rangle (1+e^{2x}) = e^{2x} - 1$$

$$\Rightarrow \langle s\rangle = \frac{e^{2x}-1}{e^{2x}+1} = \frac{e^{x}-e^{-x}}{e^{x}+e^{-x}} = \tanh x$$

$$\Rightarrow \boxed{\langle s\rangle = \tanh\left[\beta(Jy\langle s\rangle + h)\right]} \qquad \text{cf. p. 132}$$

just as in the "old-fashioned" MFT

All other thermodynamic consequences follow.

- **Antiferromagnetism** (an outline)

$$\mathcal{H} = \underset{\uparrow}{+} \frac{1}{2} J \sum_{i,\delta} s_i s_{i+\delta} - h \sum_i s_i$$

On a square lattice:

A B A B A
B A B A B
A B—A—B A
B A B A B
A B A B A

Two interpenetrating lattices
$\frac{N}{2}$ A sites + $\frac{N}{2}$ B sites

Average magnetization,
$$M \propto \frac{1}{2}(\langle s_A\rangle + \langle s_B\rangle)$$

Staggered magnetization,
$$m_s \propto \frac{1}{2}(\langle s_A\rangle - \langle s_B\rangle)$$

Can show that M & m_s are subject to:

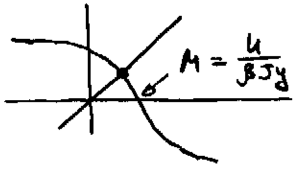
$$\begin{cases} JyM - h + \frac{1}{4} T \log \left[\frac{(1+M+m_s)(1+M-m_s)}{(1-M+m_s)(1-M-m_s)} \right] = 0 \\ -Jy m_s + \frac{1}{4} T \log \left[\frac{(1+M+m_s)(1-M+m_s)}{(1-M-m_s)(1+M-m_s)} \right] = 0 \end{cases}$$

Can solve numerically

- for $m_s = 0$, the second eq-n is satisfied trivially, and the first one reduces to:

$$M = \tanh \beta(h - JyM)$$

$\Rightarrow$ always only 1 solution



At high temperature

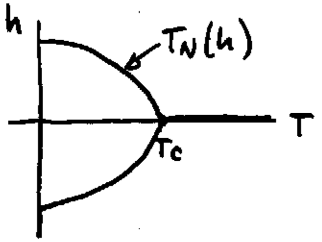
$$M \approx \beta(h - \underbrace{Jy}_{T_c} M) \Rightarrow (T+T_c)M = h$$

$$\Rightarrow M = \frac{h}{T+T_c} \Rightarrow \chi = \frac{1}{T+T_c}$$

$\Rightarrow$ no divergence (for $T > 0$)

- m_s deviates from zero (antiferromagnetic ordering) at the so-called Neel temperature

$$T_N = T_N(h)$$



- Ising models

2D, $h=0$: exact solution by L.Onsager (1944)

2D, $h \neq 0$: } ? approximate solutions
3D, $\forall h$: }

- renormalization group methods
- numerical methods, e.g. Monte Carlo

The Monte Carlo method

Ref: C.Garrod Stat. Mech & Thermodynamics Oxford 1995
D.P.Landau AJP 41:394, 1973
N.Metropolis et al JCP 21:1087, 1953

MC is an efficient algorithm for constructing a sampling sequence with a probability distribution that is the canonical probability density,

$$P(C) \to P_\beta(C) \equiv \frac{e^{-\beta E(C)}}{Z(\beta)} \qquad \beta = \frac{1}{T}$$

where

C = a Configuration (state) of the system
$E(C)$ = energy of the system in state C
$P(C) = \lim_{N\to\infty} \frac{1}{N}$ (# times C happens in a sequence $C_1 C_2 \ldots C_N$)

For any observable $A = A(C)$, the canonical average is

$$\langle A \rangle = \sum_C P_\beta(C)\, A(C)$$

Our objective is to calculate $\langle A \rangle$ by averaging over a long but finite section of the sequence:

$$\underbrace{\langle A \rangle_N}_{\text{MC average}} = \frac{1}{N}\sum_{n=1}^{N} A(C_n) \to \underbrace{\langle A \rangle}_{\text{canonical average}} \text{ for large } N$$

A direct calculation even for a small system is impractical, e.g. a $10\times10\times10$ lattice of spin-$\frac{1}{2}$ (2 states each) would involve 2^{1000} possible states. Summing over those states would take years:

$$2^{1000} = (10^{0.3})^{1000} = 10^{301} = \underbrace{10^{8}}_{100\,\text{MFLOPs}} \times \underbrace{10^{293}\,\text{sec.}}$$

• MC algorithm

Start with an arbitrary state and generate a sequence of states as follows. For each spin in turn:

① calculate ΔE to flip this one spin

② if $\Delta E < 0$, the spin is flipped

③ if $\Delta E > 0$, calculate a random # $0 \le x \le 1$

  a) if $x < e^{-\beta\Delta E}$, the spin is flipped

  b) else spin remains unchanged

As the sequence of states is generated, a certain # of steps will retain the "memory" of the initial state (which was arbitrary). Wait until this memory is lost, i.e. a steady-state regime is reached, and start calculating the averages directly, as

$$\langle s\rangle \approx \langle s\rangle_N, \quad \langle U\rangle \approx \langle U\rangle_N, \quad \text{etc.}$$

Direct numerical differentiation of quantities that contain random fluctuations produces large errors, hence calculate the heat capacity & susceptibility from the fluctuations in the averages:

$$(\Delta A)^2 \equiv \langle (A-\langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2$$

$$\Rightarrow \quad C = \frac{\partial U}{\partial T} = \frac{N^2}{kT^2}(\Delta U)^2$$

$$\chi = \frac{\partial M}{\partial h} = \frac{N^2 m^2}{kT}(\Delta s)^2$$

• why is MC a good algorithm?

Consider a collection of spin-$\frac{1}{2}$: two states, $|1\rangle$ and $|2\rangle$ with energies $E_1 < E_2$

The MC prescription is summarized by the following transition probability matrix:

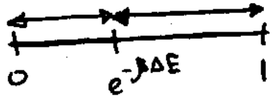
$$T = \begin{array}{c|cc} & |1\rangle & |2\rangle \\ \hline |1\rangle & 1-e^{-\beta\Delta E} & 1 \\ |2\rangle & e^{-\beta\Delta E} & 0 \end{array}$$

i.e.

$|2\rangle \rightarrow |1\rangle$ always, $\Delta E < 0$

$|1\rangle \rightarrow |2\rangle$ in $\boxed{e^{-\beta\Delta E}/1}$ fraction of cases

$|1\rangle \rightarrow |1\rangle$ in $\boxed{1-e^{-\beta\Delta E}}/1$ fraction of cases



An arbitrary state $\psi = \alpha|1\rangle + (1-\alpha)|2\rangle$
$= \begin{pmatrix}\alpha \\ 1-\alpha\end{pmatrix}$

After a single MC step (each one of N spins considered once) what is $T\psi$?

To answer this, find the eigenstates of T:

– eigenvalues: $|T - \lambda \mathbb{1}| = 0$

$$\Rightarrow -\lambda(1-e^{-\beta\Delta E}-\lambda) - e^{-\beta\Delta E} = 0$$

$$\lambda^2 - \lambda(1-e^{-\beta\Delta E}) - e^{-\beta\Delta E} = 0$$

$$\lambda = \frac{1}{2}\left[(1-e^{-\beta\Delta E}) \pm \sqrt{(1-e^{-\beta\Delta E})^2 + 4e^{-\beta\Delta E}}\right]$$

$$= \frac{1}{2}\left[(1-e^{-\beta\Delta E}) \pm (1+e^{-\beta\Delta E})\right]$$

$$= 1 \quad \text{or} \quad -e^{-\beta\Delta E}$$

– $\lambda = 1$ eigenstate : $T\psi = 1\psi = \psi$

$$\Rightarrow \begin{cases} (1-e^{-\beta\Delta E})\alpha_1 + \alpha_2 = \alpha_1 \\ e^{-\beta\Delta E}\alpha_1 = \alpha_2 \end{cases} \quad \text{same!}$$

$$\Rightarrow \frac{\alpha_1}{\alpha_2} = e^{-\beta\Delta E} = \frac{e^{-\beta E_1}}{e^{-\beta E_2}} \quad \& \quad \alpha_1 + \alpha_2 = 1$$

$$\Rightarrow \psi = \begin{pmatrix} \frac{1}{Z} e^{-\beta E_1} \\ \frac{1}{Z} e^{-\beta E_2} \end{pmatrix}, \quad Z = e^{-\beta E_1} + e^{-\beta E_2}$$

Note : $T\psi = \psi \Rightarrow \psi$ = stationary state = $\psi_{eq\text{-}m}$

– $\lambda = -e^{-\beta\Delta E}$ eigenstate

$$\begin{cases} (1-e^{-\beta\Delta E})\alpha_1 + \alpha_2 = -e^{-\beta\Delta E}\alpha_1 \\ e^{-\beta\Delta E}\alpha_1 = e^{-\beta\Delta E}\alpha_2 \end{cases}$$

$$\Rightarrow \begin{cases} \alpha_1 + \alpha_2 = 0 \\ \alpha_1 = -\alpha_2 \end{cases} \quad \text{same}$$

$$\Rightarrow \psi_\delta = \begin{pmatrix} \delta \\ -\delta \end{pmatrix}$$

Note : $T^N \psi_\delta = (-1)^N e^{-N\beta\Delta E}\psi_\delta \to 0$ as $N \to \infty$

An arbitrary state ψ can be expressed as a linear combination of $\psi_{eq\text{-}m}$ and ψ_δ, and

$$\left.\begin{array}{l} T^N \psi_{eq\text{-}m} \to \psi_{eq\text{-}m} \\ T^N \psi_\delta \to 0 \end{array}\right\} \quad T^N \psi \to \psi_{eq\text{-}m}, \ \forall \psi$$

i.e. starting from any ψ, in a sufficiently large # of steps we will approach the eq-m state, i.e. the state with a canonical probability distribution.