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Books:

Mandl, "Statistical Physics" Bowley &^ Sanchez, "Introductory Statistical Physics" (Adkins, "Equilibrium Thermodynamics" Zemansky & Dittman, "Heat and Thermomechanics")

1. The First Law of Thermodynamics

1.1 Recap of First Law

(Mandel 1.2, B&S 1.5, Adkins 3.1-4, Z. 4.1-6)

There is a property of systems called their internal energy, E. E is a "function of state", i.e. its' value only depends on the current state of the system and not its' history. Pressure, volume, temperature and entropy are all functions of state.

For a non-ferromagnet, the magnetization is a function of state, but for a ferromagnet M depends on history and is not a function of state.

There are two ways of changing E: by transferring heat (random motion of molecules) or by doing work (ordered macroscopic chance e.g. applying a force).

 $\mathsf{D} E = Q + W$

Where Q is the heat added TO the system, and W the work done ON the system. D is the change in the energy, $E_{\text{final}} - E_{\text{initial}}$.

If only the initial and final states are seen, there is no way to tell how the energy was added. Many different combinations of heating and doing work can end in the same change of state. Q and W are not function of state. We can't say that a body has so much heat in it - only energy.

Look at two methods of keeping a gas at the same temp, but doubling the volume. Either an insulated box with a devision in it to start with, removing the devision to double the space. Q = 0, W = 0, hence DE = 0.

Alternatively, have a piston with the gas in contact with a reservoir at constant temperature. Move the piston backwards slowly, doubling the volume. Temperature will remain the same.

But DE = 0 still (function of state). So Q = |W|, Q + W = 0.

1.2 First Law for small changes

(Mandel 1.3, B&S 1.5)

dE = dQ + dW

d is the infinitesimal change in E, while d is the infinitesimal amount of heat and work. Use d to indicate amounts, not changes in functions of state.

Mathematical analogy: if we write $df = 3y^2 dx + 6xydy$ we can ask if a function f^{Ax} , y^{h} exists of which this is the exact (or perfect) differential.

If there is then $3y^{2} = \frac{2f}{2x}$ and $6xy = \frac{2f}{2y}$ $f^{x}, yh = 3xy^{2} + const.$ Check; $\frac{2^{2}f}{2x2y} = \frac{2^{2}f}{2y2x}$ so $\frac{2}{2y}^{3}y^{2}h = \frac{2}{2x}^{6}xyh$ Yes, 6y. On the other hand; df = 2ydx + 5xydy is not an exact differential. $\frac{2}{2v}$ /2yh! $\frac{2}{2x}$ /5xyh $3y^2 dx$ and 6xydy are not perfect differentials, but the sum is. As dE = dQ + dW#dE = DE(finite change of energy). #dQ = Q(finite amount of heat.) 1.3 Cvcles A cycle is a set of changes to a system in which it passes through intermediate, different states, but returns to the original state. All functions of state - V, P, T, E - are the same at the end as at the beginning. If DE = 0, then #dQ + #dW = 0However, dadq! 0 and $\frac{d}{d}W! 0$ cf: heat engine. Q_1 in, Q_2 out: $#dQ = Q_1 - Q_2$ Total work done by the system is; - $\#dW = Q_1 - Q_2$ 1.4 Work (Adkins 3.5, Z. 3, Mandel 1.3, B&S 1.6) 1.4.1 Fluid This is a liquid or a gas. Again consider a container with a piston, containing a gas/liquid at P, V. Force applied is F, the piston moves a distance dx into the container. For compression, *F* \$ *PA* where A is the area of the piston. The work done on the system is dW = Fdx\$ PAdxThis is a decrease in volume, - dv. dW \$ - Pdv This will be greater than zero for compression. The minimum work will require very slow compression and no friction. In that case, F = PA plus an infinitesimal amount. An infinitesimal decrease in F would change the direction from compression to expansion. This is called a reversible process. $dW_{rev} = -PdV$ Processes are normally drawn on a P-V plot, with a starting point, and a path ^{Ap} Vth leading up

to some ending point. The work done is the area under the curve (from V_1 to V_2). The sign depends on the direction of the process.

For instance, an isothermal process for an ideal gas: PV = nRT

$$P = \frac{nRT}{V}$$

 $W =- nRT #_{V_1}^{2} \frac{dV}{V} =- nRT \ln c \frac{V_2}{V_1} m < 0h$ Or: adiabatic (ideal gas). $PV^{\circ} = const.$

 $C = \frac{C_{\rho}}{C_{\nu}}$

 $W = - P_1 V_1 \#_{V_1}^2 \frac{dV}{V^c}$

But note that adiabatic means that Q = 0. So $W = DE = c_v T_2 - T_1 h_1$

(Enough work will show that the two expressions are the same.)

Also, you can go between the start and the end points via a variety of different paths (e.g. constant P, then constant V. Or both changing at the same time. Or ...). In all of these cases, different amounts of heat will have been put in, and different amounts of work will be done. For a given change in state, W can vary but W + Q is constant.

1.4.2 Stretching a wire

If the tension in the wire is denoted by C and the change in length dI, then dW = C dI.

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1.4.3 Stretching a Surface.

F = cL

<sup>C</sup> is the surface tension.

dW = Fdx = cLdx = cdA
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1.4.4 Magnetic Work (Mandel 1.4, B&S appendix A. Different expressions in different books) $dW =- n \circ V\underline{M} \cdot \underline{dB} =- V\underline{M} \cdot \underline{dH}$ for a weak paramagnet. $M << n \circ B$ so $n \circ B \cdot H$

1.5 Temperature

(Mandel 1.2, B&S 1.2, Adkins Ch. 2, Z. Ch. 1)

1.5.1 The Zeroth Law

If two bodies are brought into thermal contact and do not change as a result, they are said to be in thermal equilibrium. There will be no net heat flow between them.

The Zeroth law states: If body A is separately in thermal equilibrium with bodies B and C, then B and C are also in thermal equilibrium.

This allows us to define something measurable called temperature: A, B and C are at the same temperature. If A is something which changes visibly, say a column of mercury or a gas in a balloon, it can be used as a thermoscope.

Bodies can be ordered by their temperature using the thermoscope.

1.5.2 Temperature Scales

Early temperature scales led to the discovery of Boyle's Law: if 2 "flexible" containers with the same amount of gas in them were in thermal equilibrium, the product of their pressure and volume was the same. A possible temperature scale is where T is proportional to PV.

Boyle's Law held best in the low pressure limit, where all gases approach ideal gases.

In 1954, the ideal gas temperature scale was adopted. Inherent is this scale is the idea of absolute zero - a minimum temperature where PV " 0. Therefore to set a scale, only one reference point is needed. This is taken to be the triple point of water. At this point, ice, water and vapour all coexist. The corresponding pressure is ~600*Pa*. The temperature is defined to be 273.16*k*.

 $T = \lim_{P \to 0} \frac{PV}{PV g_{triple point}} x273.16k$

This agrees with the centigrade degree to a 5 figure accuracy. With that definition of the scale; PV = nRT $R = 8.314 J mol^{-1}K^{-1}$ n is the number of moles of gas. For future reference; PV = NkTwhere k is Boltzman's constant. $k = \frac{R}{N_A} = 1.381 \times 10^{-23} \, J K^{-1} = 8.62 \, eV \, K^{-1}$

kT is a measure of the molecular thermal energy. It is approximately $\frac{1}{40}eV$ at room temperature.

2. The Second Law 2.1 Heat Engines and Refrigerators (Adkins 4.8, Z. 6.1-5) The Otto Cycle. e.g. car engine. $1 \rightarrow 2$, Adabatic compression.

 $3 \rightarrow 4$ Adiabatic expansion, at hotter T that the original compression. Q_{μ} is put into the system.

 $2 \rightarrow 3$, the volume stays constant but heat is absorbed.

 $4 \rightarrow 1$ Cooling back to the original temperature with Q_{\circ} discarded.

All useful engines work in cycles, returning to their initial condition. The total useful work done is the area bounded by the curve on the PV plot, d∰PdV

By the first law, work done is Q_{H} - Q_{c} .

The efficiency of the engine is;

$$h = \frac{W}{Q_{H}}$$

This is always less than 1. For an Otto cycle;

h = 1 -
$$c\frac{V_2}{V_1}m$$
 = 1 - $\frac{T_1}{T_2}$
Note that;

 $h < 1 - \frac{T_c}{T_h}$

where T_{c} is the coldest temperature T_{1} , and T_{H} is the hottest temperature, T_{3} .

Because Q_{c} is non-zero, a heat engine running in reverse will pump heat from a cold reservoir to a hot one.

The efficiency of a heat pump is defined as;

$$h_{pump} = \frac{Q_H}{W} > 1$$
 by definition.
 $h_{fidge} = \frac{Q_C}{W} > 1$ usually.

In general;

 $h = \frac{useful output}{\cos tly input}$

A fridge and a heat pump are not dissimilar in idealistic conditions - they are just being used for different things.

A reversible heat engine run in reverse is a heat pump (or fridge). The signs of W, Q_H and Q_c all change, but the magnitudes don't.

 $h_{pump}^{rev} = \frac{Q_H}{W}$ $h^{rev}_{engine} = \frac{W}{Q_c}$ $h^{rev}{}_{pump} = \frac{1}{h^{kv}{}_{engine}}$ Carnot Engine: ideal gas See website for picture. 4 steps: 1) Isothermal compression at $T_c \stackrel{h}{=} T_1 = T_2 h$ 2) Adiabatic compression 3) Isothermal expansion at $T_{H} = T_3 = T_4 h$ 4) Adiabatic expansion pV = nRTAdiabatic stages: $TV^{c-1} = const.$ (Related to $PV^{c} = const.$). During the stage 2-3; $T_2 V_2^{c-1} = T_3 V_3^{c-1}$ $\frac{V_2}{V_3} = c \frac{T_H}{T_c} m^{\frac{1}{c-1}}$ For stages 4-1: $T_4 V_4^{c-1} = T_1 V_1^{c-1}$ $\frac{V_1}{V_4} = c \frac{T_H}{T_c} m^{\frac{1}{c-1}}$ So; $\frac{V_2}{V_3} = \frac{V_1}{V_4}$ $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ 1) Adiabatic $W_1 = - \# P dV$ and $P = \frac{nRT_c}{V}$ Which gives; $W_1 = -nRT_c \ln c \frac{V_2}{V_1} n$ DE = 0 $Q_1 = + nRT_c \ln c \frac{V_2}{V_1} n$ $2) Q_2 = 0$ $W_2 = DE = c_v T_H - T_c h$ 3) $W_3 = -nRT_H \ln c \frac{V_4}{V_3} m = -nRT_H \ln c \frac{V_1}{V_2} n$ $Q_3 = + nRT_H \ln c \frac{V_1}{V_2} m$ $w_4 = c_v T_c - T_H h$ So the work done by the engine is;

Which is equal to;

-
$$W_1$$
- $W_3 = nR \Lambda T_H$ - T_c hln c $\frac{V_1}{V_2}$ m> 0

$$Q_{H} = Q_{3} = nRT_{H} \ln c \frac{V_{1}}{V_{2}} n$$

$$Q_c = -Q_1$$

 $h = \frac{W}{Q_H} = \frac{T_H - T_c}{T_H} = 1 - \frac{T_c}{T_H} < 1$

Note: this only works when T is in Kelvin, not Celsius.

2.2 The Second Law of Thermodynamics

Kelvin-Planck:

It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

Clausius:

It is impossible to construct a refrigerator which, operating in a cycle, will produce no other effect than the transfer of heat from a cooler body to a hotter one.

2.3 Carnot Engines & Cycles

A Carnot cycle is any cycle that satisfies two criteria;

1) Reversible

2) Uses only two reservoirs, and hence exchanges heat with those during two isothermal steps. The other steps must therefore be adiabatic. Note that only heat exchange between bodies at the same temperature is reversible.

The nature of the working fluid - gas, liquid etc - is unimportant. Can even involve magnetic rather than hydrodynamic processes.



In this image, the green engines / pumps are Carnot, and the brown ones are irreversible. A carnot engine is more efficient than an irreversible engine:

1. Carnot point;

 $h_{pump} = \frac{1}{h_{carnot}}$

working alongside an irreversible engine $h_{\mathcal{E}}$.

We need Q_{μ} ' \$ Q_{μ} or we would have net heat flow from the cold reservoir to the hot one, violating Claussius.

From the first law,
$$Q_{H} - Q_{c} = W = Q_{H}' - Q_{c}'$$
. So;

$$\frac{W}{Q_{H}'} = \frac{W}{Q_{H}} \frac{Q_{H}}{Q_{H}}$$

$$\frac{Q_{H}}{Q_{H}} \# 1$$
So $h_{engine} \# h_{carnot}$

2. Carnot engine and irreversible pump h_{pump} .

There we need Q_{H} \$ Q_{H} " to avoid violating Claussius.

Now;

$$\frac{Q_{H}}{W} = \frac{Q_{H}}{W} \frac{Q_{H}}{Q_{H}}$$

$$\frac{Q_{H}}{Q_{H}} \# 1$$

$$\frac{Q_{H}}{Q_{H}} = \frac{1}{2}$$

 $h_{pump} # \frac{1}{h_{carnot}}$

So the Carnot engine is more efficient than an irreversible one either as an engine or as a pump. If we allow the second engine to also be reversible, there can be no net heat transfer in either case. $Q_{H}' = Q_{H} = Q_{H}''$. In this case, the equalities are satisfied.

So all Carnot engines have the same efficiency when working between the same reservoirs. For the ideal gas;

 $h = 1 - \frac{T_c}{T_H}$

This holds for all carnot engines. Note that by definition:

$$h = \frac{W}{Q_{H}} = \frac{Q_{H} - Q_{c}}{Q_{H}} = 1 - \frac{Q_{c}}{Q_{H}}$$

Thus;
$$\frac{T_{c}}{T_{H}} = \frac{Q_{c}}{Q_{H}}$$

or;
$$\frac{Q_{c}}{T_{c}} = \frac{Q_{H}}{T_{H}}$$

Example of a heat engine calculation;

Want to site a power station by a river to use river water as a coolant as the cool reservoir (at 10 degrees C)

Environmental concerns limit Q_c to 1MW. How much power can we extract with unlimited fuel in a furnace at 400 degrees C?

1) $Q_{H} - Q_{c} = W$ (First Law) 2) $\frac{Q_{c}}{T_{c}} = \frac{Q_{H}}{T_{H}}$ (Carnot Engine / 2nd law) 3) $Q_{c} = 1MW$

$$W = Q_{H} - Q_{c} = \frac{T_{H}}{T_{c}}Q_{c} - Q_{c} = c\frac{T_{H}}{T_{c}} - 1mQ_{c} = 1.3MW$$

2.4 Thermodynamic Temperature

Adkins 4.5-5, ZZ 7.5, B&S 2.3

Because all carnot engines have the same efficiency, we can deduce that this depends only on T_{H} and T_{c} (even if we hadn't calculated it). This could form the basis of a new temperature scale.



We can show that if temperatures are denoted by i_{H} and i_{c} (in arbitrary units)

$$h = 1 - \frac{H h_c h}{H h_{H} h}$$

So H can be used as a new scale. Proof (using the above picture);

Define a new function $f \dot{n}_{c}$, $\dot{i}_{H}\dot{h}$ so that $Q_{c} = f \dot{n}_{c}$, $\dot{i}_{H}hQ_{H}$ for any Carnot engine. Look at the right hand side of the above picture.

 $h = 1 - f \wedge c, i_{H}h$ $W = hQ_{H}$

Using the left hand side; First engine: $Q_3 = f \Lambda_{3, i, \mu} h Q_{\mu}$

 $W_{A} = \underline{1} - f \wedge _{3}, i H h Q_{H}$ Second engine; $Q_{c} = f \wedge _{3}, i H h Q_{3} = f \wedge _{3}, i H h Q_{H}$

$$W_B = 1 - f \wedge c$$
, $i_3 h Q_3$

 $W_A + W_B = 1 - f \dot{A}_{c}, i_{3}hf \dot{A}_{3}, i_{H}h Q_H = hQ_H$

But the combined engine is just a complicated carnot engine acting between Q_{H} and Q_{c} , just like the right hand side. So it' efficiency bust be $h = 1 - f h_{c}$, i $_{H}h_{c}$.

Comparing these, we have; $f \land i_c, i_3 h f \land i_3, i_{H} h = f \land i_c, i_{H} h$ This is independent of i_{3} . Therefore;

 $f \land i_{1}, i_{3}h = \frac{H \land i_{1}h}{H \land i_{2}h}$ $h \land c_{1}, i_{H}h = 1 - \frac{H \land i_{2}h}{H \land i_{H}h}$

However if we measure the temperature on the ideal gas scale, we know that;

$$h \wedge c, i_{H}h = 1 - \frac{T_{c}}{T_{H}}$$

So the ideal gas and thermodynamic scales are proportional, and can be taken to be identical.



Clausius's Theorem says that the sum of the heat added to a system during a cycle, weighted by the temperature of which it is added, is equal or greater than 0.

$$\#\frac{dQ}{T} \# 0$$

We can do work W^{sys} and add heat Q^{sys} to the system. The heat is added at an instantaneous temperature T via a Carnot engine which extracts Q^{res} from a heat bath at T_o .

If we add $d^{Q^{sys}}$ to the system, then we extract $d^{Q^{res}}$ from the reservoir.

$$\frac{dQ^{sys}}{dQ^{res}} = \frac{T}{T_o}$$

At the end of a cycle of the system, both the system and the engine are in their original states, so the net energy must be zero.

 $Q^{res} + W^{carnot} + W^{sys} = 0$

Either we put in less work than we get out; $W^{carnot} + W^{sys} < 0$ in which case $Q^{res} > 0$, or we put more work in than we get out. $W^{carnot} + W^{sys} > 0$ and $Q^{res} < 0$.

The first possibility violates Kelvin-Planck, so we must have $Q^{res} # 0$.

$$Q^{res} = \oint dQ^{res} = T_o \oint \frac{dQ^{sys}}{T} \# 0$$

$$T_{\circ} > 0$$
 so $\# \frac{dQ^{sys}}{T} \# 0$

So far we have not specified reversible or irreversible. If we carry out the cycle very slowly with a frictionless piston the cycle will be reversed. Therefore we could run the system in reverse, reversing all energy flows but without changing their magnitude.

 $\# \frac{dQ^{\text{sys}}}{\tau}$ \$ 0

Only compatible with Clausius's theorem if the equality holds.

$$\oint \frac{dQ^{rev}}{T} = 0$$

Consider a cycle consisting of two reversible paths between two points.



$$\frac{dQ^{rev}}{T} = \# \frac{dQ^{rev}}{T} + \# \frac{dQ^{rev}}{T} = 0$$

$$0 = \#_{1}^{2} \cdot \frac{dQ^{rev}}{T} + \#_{2}^{1} \cdot \frac{dQ^{rev}}{T}$$

$$\#_{1}^{2} \cdot \frac{dQ^{rev}}{T} = \#_{1}^{2} \cdot \frac{dQ^{rev}}{T}$$

Therefore it is path independent. There must be a new function of state, S, so that; $#_{1}^{2} \frac{dQ^{rev}}{T} = S_{2} - S_{1}$

Now consider a reversible path followed by an irreversible one.



2.6 Examples of Entropy change

1) Heat flow

Imagine that an amount of heat dQ is transferred from a body at T_1 to another at T_2 .

$$dS^{]0} = \frac{dQ}{T_{1}}$$

$$dS^{]29} \frac{dQ}{T_{2}}$$

$$dS^{]1+29} dQ C \frac{1}{T_{2}} - \frac{1}{T_{1}} n$$

$$dS^{]1+29} 0$$
if $T_{2} \# T_{1}$

We know that spontaneous transfer will only happen if $T_2 \# T_1$ - accompanied by an increase in the overall entropy.

2) 2 blocks, heat capacity C, one at $100^{\circ}C$, the other at $0^{\circ}C$. Bring them together - what will happen?

We know that they will exchange heat till the temperature is equal.

The first saw tells us that since they are identical blocks, the amount of heat gained in one will be equal and opposite to the amount of heat lost by one, so they will both end up at $50^{\circ}C$, Q = 50xC having been exchanged.

What is the entropy change?

Take the blocks one at a time.

The hot block:

$$\mathsf{DS} = \# \frac{d Q^{rev}}{T}$$

While this is not a reversible process, we know the initial and endpoints of the process. As the entropy change only depends on these, we can use a reversible process between these states to get the same results.

$$DS = \#_{T_i}^{T_i} \frac{CdT}{T} = C \ln \frac{T_i}{T_i}$$

$$DS = C \ln \frac{323}{373} < 0$$
For the cold block;
$$DS = C \ln \frac{T_i}{T_i}$$

$$DS = C \ln \frac{323}{273} > 0$$
The total entropy change;
$$DS^{\mathbb{J}_{H+} cg} = C \ln \frac{323^2}{373 \times 273} > = 0.024C > 00$$
The units of entropy are JK^{-1} , and are the

Note that C is the specific heat capacity of the block, while c is per unit mass and thus you would need to know the mass of the block.

same as for the heat capacity.

3) Ideal gas confined to one half of an adiabatic container, then the partition is removed. We know that the gas will expand to fill the entire container. Entropy change?

We can't use $ds = \frac{1}{T}$ directly, as this is an irreversible process. But an isothermal, reversible expansion connects the same two endpoints, so we can use that process instead.

$$W =- \# P dV =- nRT \ln \frac{V_2}{V_1}$$

DE = 0

$$Q =- W = nRT \ln \frac{V_2}{V_1}$$
$$DS = \# \frac{d Q^{rev}}{T} = \frac{1}{T} \# d Q^{rev} = \frac{Q^{rev}}{T} = nR \ln \frac{V_2}{V_1}$$

In each case, the entropy change of the gas is the same for the irreversible process. But for the irreversible case, the system is isolated and there is no other entropy change that takes place.

For the reversible case, heat is removed from the heat bath at the same temperature and $DS^{bath} = -DS^{gas}$. $DS^{universe} = 0$

In all cases, spontaneous changes are associated with entropy increase.

In any system that starts off out of equilibrium, the system will evolve with an increase of entropy until no further increase is possible.

Note that a reversible adiabatic process must happen at constant entropy of the system.

In these contexts, we use the term "universe" to represent the system, and any surroundings that have any influence on the system.

2.7 The Fundamental Thermodynamic Relation

This is a restatement of the first law.

 $dE = d Q + d W = d Q^{rev} + d W^{rev}$

dE = TdS - pdV / fluidh

 $dE = TdS + C dI ^{Stretched stringh}$

dE = TdS - VMdB Magnetic material, also written mdBh

M is the magnetic moment per unit volume, while V is just the amount of matter. Note that dE = TdS - pdV holds for any process, since T, S, P and V are all functions of state.

2.8 Thermodynamic Potentials

(Mandl 4.4, B&S 2.6, Adkins 7.2, Z 10.1)

Define Enthalpy as H = E + PV. From dE = TdS - pdV and $d PVg = ^{dPhV} + ^{dVhP}$, we get; dH = TdS + VdP.

i.e. the natural variables that the system changes with is volume and entropy.

Helmholz Free Energy; F = E - TSdF = -SdT - pdV

Gibbs Free Energy; G = E - TS + PVdG = -Sdt + VdP

Energy vs. Enthalpy;

$$dE = dQ^{rev} - PdV$$

$$dH = dQ^{rev} + VdP$$
Heat capacity;

$$c = \frac{dQ^{rev}}{dT}$$
So;

$$c_v = \frac{dQ^{rev}}{dT} \Big|_v = \frac{2E}{2T} \Big|_v$$

$$c_p = \frac{dQ^{rev}}{dT} \Big|_p = \frac{2H}{2T} \Big|_p$$

The difference between the two is the work done pushing aside the atmosphere.

2.10 Use of Gibbs Free Energy in Phase Transitions

Adkins 10.4-5, Z. 11.3-4, Mandl 8.2-4, B&S 11.4-5

Here we are considering systems with one component (i.e. one substance), but more than one phase (e.g. gas, liquid, solid, ...)

Controlled temperature T_{\circ} and pressure P_{\circ} .

The phases have different entropies, energies and volumes (per unit mass). In general, they will also have different Gibbs Free Energies.

$$a = \frac{a}{a}$$

Let $g = \overline{m}$ (Gibbs Free Energy per unit mass, or the specific Gibbs Free Energy.) The total Gibbs Free Energy is; $G = m_1g_1 + m_2g_2$ (Let liquid water be phase 1, and water vapour be phase 2)

If some of the material changes phase;

If the two phases are in equilibrium, there is no net change of mass. That happens if $g_1 = g_2$. So the phase coexistence line on the PT plot is the line at which the specific Gibbs free energies of the two phases is the same.



We can derive an expression for the slope of these phase coexistence lines. This is called the Clausius-Clapeyron Equation.



where L is the latent heat. Remember that; $DS = \frac{Q}{T}$ for isothermal transitions. So finally; $\frac{dP}{dT} = \frac{L}{TDV}$ This is the Clausius-Clapeyron equation. Hints; L and DV must refer to the same amount of "stuff" $DV ! \frac{m}{Dt}$

 $\mathsf{D} V = \frac{m}{\mathsf{t}_1} - \frac{m}{\mathsf{t}_2}$

2.9 Approach to Equilibrium

Adkins 10.2, Mandl 4.6

Clausius: for an isolated system, equilibrium is the state with maximized entropy.

Consider a system in contact with a heat bath at temperature T_{\circ} , and pressure P_{\circ} .

Suppose that during some spontaneous change heat Q is absorbed by the system, and the volume changes by DV. In this case, for the volume to change work of P_{\circ} DV is done by the system on the surroundings so $W = -P_{\circ}$ DV.

Also by Clauseus;

The entropy change of the system and the surroundings must be greater than, or equal to, 0.

 $DS^{system} - \frac{Q}{T_o} \$ 0$

where Q/T is the entropy decrease of the surroundings. $Q = DE + P_o DV$

$$DS - \frac{1}{T_o} ^{\prime} DE + P_o DVh \$ 0$$

 $-D^{h}E - T_{o}S + P_{o}Vh \$ 0$

So the "availability" $A = AE - T_o S + P_o Vh$

must be minimized. $A \neq 0$.

The system will evolve to minimize its' "availability".

The availability is so-called as it relates to the maximum work out of the system.

Note that if the system starts at the same temperature and pressure as its' surroundings; $T_o = T$, $P_o = P$. A = G. DG # 0.

If in addition the volume is unchanged, DV = 0. A = F. DF # 0. If also the system is isolated, so DE = 0. DS 0 as expected.

2.11 Useful Work

If we have a system out of equilibrium with its surroundings, how much useful work can we extract from it as it equilibriates?



Two reasons why we can't use all of the change in energy DE to do useful work;

1) work is wasted pushing aside the atmosphere at P_{\circ} .

2) Heat must leak to the surroundings to increase their entropy compensating for the entropy decrease of the system.

 $DE = Q + W = Q - P_o DV - W^{useful}$

Work is done by the system.

But the heat exchanged with the surroundings has to be such that;

DS - $\frac{Q}{T_o}$ \$ 0 So;

Q # T.DS So:

 W^{useful} # - $^{A}DE - T_{\circ}DS + P_{\circ}DVh = DA$

So the change in availability is related to the amount of useful work that can be extracted. Example (from Mandl 4.7)

How much work can be extracted from cooling 1 mole of a perfect gas at constant volume from an initial temperature T to a final temperature T_{\circ} the temperature of the surroundings.

 $W^{\text{max}} = -DE + T_{o}DS$ For a perfect (ideal) gas; $DE = c_v DT$

 $DS =- c_v \ln \frac{T}{T_o}$

 $W^{\max} = c_v cT - T_o - T_o c_v \ln \frac{T}{T_o} n$

this is greater than 0 if $T > T_{\circ}$. (Probably an exam guestion on this!)

2.12 Maxwell Relations Adkins 7.3, Mandl 4.1&4.5, B&S 2.6, Z. 10.5 Remember dE = Tds - pdV. If we want to regard E as depending on S and V, then;

$$dE = \frac{2E}{2S} \Big|_{V} + \frac{2E}{2V} \Big|_{S}$$

Thus;

$$T = \frac{2E}{2S} \Big|_{V}$$

$$p = -\frac{2E}{2V} \Big|_{S}$$

$$\frac{2T}{2V} \Big|_{S} = \frac{2^{2}E}{2S2V} = \frac{2^{2}E}{2V2S} = -\frac{2P}{2S} \Big|_{V}$$

$$\frac{2T}{2V} \Big|_{S} = -\frac{2P}{2S} \Big|_{V}$$

From
$$dF = -SdT - pdV$$

 $S = -\frac{2F}{2T}\Big|_{v}$
 $P = -\frac{2F}{2V}\Big|_{\tau}$
 $\frac{2S}{2V}\Big|_{\tau} = \frac{2P}{2T}\Big|_{v}$
 $dH = TdS + VdP$
 $\frac{2T}{2P}\Big|_{s} = \frac{2V}{2S}\Big|_{P}$
 $dG = -SdT + VdP$
 $\frac{2S}{2P}\Big|_{\tau} = -\frac{2V}{2T}\Big|_{P}$

The second and third of these are the most useful.

The main use is to write derivates of S with respect to P and V in terms of measurable or calculable quantities.

2.13 Heat Capacities Mandl 5.3, Adkins 8.1, B&S 2.5, 2.6 Heat capacity; $c = dQ^{rev}$

$$C = \frac{dQ}{dT}$$

C will be used for an extensive quantity, while c will be used fro the specific heat capacity. C = nc or C = mc depending on whether the specific heat capacity is per mole or kg. The heat capacity is not path-independent. There is no such thing as *the* heat capacity. The most useful are:

The most useful alle,

$$c_{v} = \frac{dQ^{rev}}{dT} \Big|_{v} = T \frac{dS}{dT} \Big|_{v}$$

$$c_{p} = \frac{dQ^{rev}}{dT} \Big|_{p} = T \frac{dS}{dT} \Big|_{p}$$

$$c_{p} = \frac{dQ^{rev}}{dT} \Big|_{p} = \frac{2E}{2T} \Big|_{p} + P \frac{2V}{2T} \Big|_{p}$$

$$c_{v} = \frac{2E}{2T} \Big|_{v}$$

$$dE = \frac{2E}{2T} \Big|_{v} dT + \frac{2E}{2V} \Big|_{\tau} dV$$
It is only for an ideal gas that;

$$\frac{2E}{2V} \Big|_{\tau} = 0$$
and $dE = c_{v} dT$.

Relation between c_{p} and c_{V} . Starting with $S \Lambda T$, Vh $dS = \frac{dS}{dT} \Big|_{V} dT + \frac{dS}{dV} \Big|_{T} dV$ $dS = \frac{c_{v}}{T} dT + \frac{dP}{dT} \Big|_{V} dV$ Also from $S \Lambda T$, Ph; $dS = \frac{c_{p}}{T} dT - \frac{2V}{2T} \Big|_{p} dP$ Equating and rearranging; $\Lambda c_{p} - c_{v}hdT = T \frac{d2V}{2T} \Big|_{p} dP + \frac{2P}{2T} \Big|_{V} dV n$ Holding either V or P fixed;

$$c_{p} - c_{v}h = T \frac{2V}{2T} \Big|_{P} \frac{2P}{2T} \Big|_{V}$$

If the equation of state is known, we can calculate this (check that we get nR for an ideal gas) Also;

$$c_{p} - c_{v} = - \frac{T d \frac{2V}{2T} \Big|_{p}}{\frac{2V}{2P} \Big|_{T}}$$

 $\frac{1}{V}\frac{2V}{2T}$

is the isobaric thermal expansivity a.

$$-\frac{1}{V}\frac{2V}{2P}\Big|_{T}$$

is the isothermal compressibility 1 7.

$$c_p - c_v = VT \frac{a^2}{|\tau|} > 0$$

In exam papers;

"By considering the entropy as a function of temperature and length" means; $dS = \frac{2S}{2T} \left| dT + \frac{2S}{2L} \right|_{T} dL$

3. Statistical Theory of Thermodynamics Mandl 2.3, B&S 1.2, Kittel & Kroemer 1.2

What is the basis of Entropy? Why does it increase? Can we derive the equation of state for a system from first principles?

3.1 Microstates and Macrostates

Mandl 2.1-2, B&S 4.1

If we have an isolated system in equilibrium, then we can say everything that is to be known about it by specifying a few bulk quantities. There are a handful of equations that can calculate the rest. And as the system is in equilibrium, these don't change with time.

This is a macrostate, and is what we've known up until now as the state of the system.

If we look at what underlies the system, we know that it is not in fact one completely uniform substance down all sizes, but is made up of atoms etc. that are not in a stationary state. These are not only moving, but constantly interacting. If one were to state what was happening to every particle, not only would the description of the system be very complex but it would be constantly changing.

A microstate is a description of the system an the microscopic level, where the position and momentum (or quantum state) of each particle is specified. This description would be immensely detailed and would change very frequently. Yet all of these changes on the microscopic level are not evident on the macroscopic state. So huge numbers of microstates must all correspond to the same macrostate.

For the checkerboard, a "macrostate" is specified by the total number of green and blue counters; a "microstate" by the colour of counter occupying each numbered square. Even for a 6x6 board, there are as many as 10¹⁰ microstates for each macrostate.

Even though all microstates are equally probable, some macrostates (those with roughly equal numbers of green and blue) are much more likely than others).

The principle of equal apriori (i.e. in the absence of other information) probabilities: all microstates of an isolated system are consistent with the constraints of total energy and volume are equally likely.

If the total number of such microstates is X, then the probability of the ith state;

$$P_i = \frac{1}{X}$$

X /W, E, Vh for a fluid.

We calculate the macroscopic value of an observable by averaging over the value of each microstate.

 $\langle x \rangle = ! p_i X_i$

Where $\langle x \rangle$ is the "ensemble average" macroscopic value, and X_i the value in the ith state. $\langle x \rangle = \frac{1}{X} | X_i$

It is worth pointing out philosophically that this theory is very hard to prove, due to the rapid changes within the system (approximately every 10⁻³⁴ seconds a collision will occur within a system).

3.2 The statistical basis of entropy and the approach to equilibrium

Suppose there is some macroscopic property of the system - a - not determined by E, V, N (the appropriate variables for an isolated system.). The number of microstates is a function of a: X $^{\Lambda}E$, V, N, ah. The most probable macrostate (i.e. value of a) is the one that maximizes the

number of microstates, i.e.;

 $\frac{dX}{da} = 0$

This will happen at a_{\circ} , where X is the largest.

If we start the system at some value of $a^{!} a_{\circ}$, then the random evolution of microstates is more likely to load to an a closer to a_{\circ} (where there are more microstates) than to a further from a_{\circ} (where there are fewer microstates)

Once the system reaches $a - a_{\circ}$ then fluctuations to either side are equally likely and no further evolution takes place. This is equilibrium - the macrostate with the most microstates.

Is X equivalent to entropy?

No: if we double N, E and V then we would expect to double the entropy - it is extensive. However the number of microstates twice the size of the original one is X². Instead, suggest that;

 $S = k_B \ln X$

Constant of proportionality turns out to be k_{B} for correspondence with classical thermodynamics.

3.3 The Spin- $\frac{1}{2}$ Paramagnet (Ideal)

For our purposes, a paramagnet is a collection of small magnets that prefer to align themselves with an external magnetic field. It is a lattice of spin- $\frac{1}{2}$ particles that do not interact.

In the absence of a magnetic field, the energy is independent of the orientation of the spins. Macroscopically, all we measure is the total magnetization.

 $m = n_{1} - n_{0} hn = 2n_{1} - Nhn$

E ! *E*]*m*g

Microscopically we can specify whether the spin at each lattice position is up or down. For 3 spins, the macrostates are m = 3n, n, -n, -3n.

 $3n_{1}//$ $n_{1}//0$ /0/ 0// $-n_{1}00/$ 0/0 /00 $-3n_{1}$ 000

So the most probable are n and -n.

What about N spins with $n_{/}$ up. and $n_{0} = N - n_{/}$? X /W, $n_{/}h = \frac{N!}{n_{/}!/N - n_{/}h!}$

where N! is the number if distinguishable, $n_{/}!$ is swapping up's, and $N - n_{/}h!$ is swapping down. the function

 $\frac{N!}{n/!^{N} - n/h!}$

is a very sharply peaked function of n, centered on

$$n = \frac{N}{2}$$

Magnetization of 0 is overwhelmingly likely if N is large. Useful approximations;

- Sterling's approximation;

 $N! - \sqrt{2r N} N^{N} e^{-N}$ In]N!g - NIn N - N + $\frac{1}{2}$ In /2r Nh

The last term can almost always be ignored.

X /W, *n*h,
$$c \frac{2}{r N} m^{\frac{1}{2}} 2^{N} e^{-\frac{2 \Lambda_{1} - \frac{N}{2} h^{2}}{N}}$$

(See K&K "sharpness of multiplicity function) This is a Gaussian with mean of N/2.

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

So;
$$\frac{V}{n} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

Probability of deviations:
$$1V = 33\%$$

$$2V = 4.6\%$$

$$3V = 0.27\%$$

$$10V = 1.5x10^{-23}$$

$$100V = 10^{-2173}$$

$$\frac{100V}{\overline{n}} = \frac{100}{\sqrt{N}}$$

For $N \sim 10^{24}$;

 $100v = 10^{-10} N$

Even incredibly rare fluctuations of 100v would be unobservable for macroscopic systems. Equilibrium really does appear to be static and unchanging.

3.4 Temperature and Pressure

How can macroscopic properties such as temperature and pressure be derived from a microscopic consideration?

Imagine a single system split in two by a partition that allows heat to flow across it, and can move back and forward depending on the conditions of either side. Isolated system. Energy E, volume V. The system is split such that the first partition has E_1 , V_1 and E_2 , V_2 . E and V are fixed, but each side can vary as heat is passed through the dividing wall, and as the wall moves.

$$dE_2 = - dE_1$$
$$dV_2 = - dV_1$$

The number of microstates of the whole system can be written in terms of the microstates on either side, and hence can be $X = X_1 X_2$

So the entropy is;

$$S^{A}E_{1}, E_{2}, V_{1}, V_{2}h = S_{1}AE_{1}, V_{1}h + S_{2}AE_{2}, V_{2}h$$

$$dS = \frac{2S}{2E_{1}}\Big|_{E_{2}, V_{1}, V_{2}} dE_{1} + \frac{2S}{2E_{2}}\Big|_{E_{1}, V_{1}, V_{2}} dE_{2} + \frac{2S}{2V_{1}}\Big|_{E_{1}, E_{2}, V_{2}} dV_{1} + \frac{2S}{2V_{2}}\Big|_{E_{1}, E_{2}, V_{1}} dV_{2}$$

$$dS = e\frac{2S_{1}}{2E_{1}}\Big|_{E_{2}, V_{1}, V_{2}} - \frac{2S_{2}}{2E_{2}}\Big|_{E_{1}, V_{1}, V_{2}} odE_{1} + e\frac{2S_{1}}{2V_{1}}\Big|_{E_{1}, E_{2}, V_{2}} - \frac{2S_{2}}{2V_{2}}\Big|_{E_{1}, E_{2}, V_{1}} odV_{1}$$

Entopy will increase until further infinitesimal shifts of energy and volume no longer change it; dS = 0 at equilibrium for $dE_1 \stackrel{!}{=} 0$, $dV_1 \stackrel{!}{=} 0$. So: $\frac{2S_1}{2E_1}\Big|_{V_1} = \frac{2S_2}{2E_2}\Big|_{V_2}$

Exchanging heat no longer changes entropy.

 $\frac{2S_1}{2V_1}\Big|_{E_1} = \frac{2S_2}{2V_2}\Big|_{E_2}$

Exchanging volume no longer changes entropy.

So

 $\frac{2S}{2E}$

has something to do with temperature, and

 $\frac{2S}{2V}\Big|_{E}$

has something to do with pressure.

Even without classical thermodynamics and the experience of heat engines, we can establish the existence of things that represent volume and temperature increase.

If we define;

$$\frac{1}{T} = \frac{2S}{2E}\Big|_{v}$$
and

$$\frac{P}{T} = \frac{2S}{2V}\Big|_{E}$$
Then:

$$dS = \frac{dE}{T} + \frac{PdV}{T}$$

Or;

E = Tds - PdV

These are called the statistical definitions of pressure and temperature. They differ from the normal ones in that they can be defined for an isolated system.

If we have a system of fixed E and V, and we can calculate S, we can find P and T.

e.g. first attempt at ideal gas

We can easily deduce the dependance on V. Imagine splitting a finite volume into many tiny cells, each of volume DV. Make sure that it is sufficiently that there will be approximately one molecule per volume.

Take a single atom that can be in any one of the V/DV cells. N atoms: each can be in any one of the cells.

 $X \sim c \frac{V}{DV} m^{N}$

$$S = K \ln X = Nk \ln c \frac{V}{DV} m$$
+ volume independent terms

The non-interacting part is hidden in the first equation.

Also; $\frac{P}{T} = \frac{2S}{2V}\Big|_{E} = \frac{nk}{V}$ pV = nkT(and Nk = nR)

Another example: a spin-^{1/2} paramagnet in a magnetic field

The energy depends on the magnetic field. So n spin-up, and N - n spun-down. $E = -nn \cdot B + n \cdot N - n \cdot hB = n \cdot N - 2n \cdot hB = -mBC$ So if we fix the energy, we fix the number of up states. The number of microstates for a given E (and hence n) is; $X \cdot n \cdot h = \frac{N!}{n \cdot ! \cdot N - n \cdot h!}$

So;

 $S]Eg = k \ln X = k \ln d \frac{N!}{n! N - n! h!} n$ Using Stirling's approximation for a large number of spins, we have; $\ln N! = N \ln N - N$ $S = k N \ln N - N - m \ln n - n h - M - n h \ln N - n h - M - n h j$ $S = k N \ln N - n \ln n_{-} - N - n_{-} \ln N - n_{-} h$ $\frac{1}{T} = \frac{2S}{2E}\Big|_{B}$ $\frac{1}{T} = \frac{2S}{2E} \Big|_{B} = \frac{2S}{2n} \Big|_{N} \frac{2n}{2E} \Big|_{B}$ $n_{-} = \frac{1}{2} dN - \frac{E}{nB} n$ After a few steps; $\frac{1}{T} = \frac{k}{2nB} \ln c \frac{n}{N - n} n$ (See example 13) DE

$$\frac{n_{.}}{n_{-}} = e^{-\frac{2nB}{kT}} = e^{-\frac{2nB}{kT}}$$

Note that 2^{nB} is the amount by which the energy of the down spin is higher than that of the up spin.

Also, from

$$dS = \frac{dE}{T} + \frac{m}{T} dB$$

we see that
 $\frac{m}{T} = \frac{2S}{2B}\Big|_{E} = \frac{2S}{2n}\Big|_{N}\frac{2n}{2B}\Big|_{E,N}$
 $m = -\frac{E}{B}$
(missing a few steps)
or $E = -mB$ as we know.

4. Boltzman Distribution - Non isolated systems.

4.1 System in contact with a heat bath Mandl 2.5, B&S 5.1, K&K 3.

<u>R</u>)		
	$E_R = E_0 - \epsilon$	
		(R)
		E _s =ε

R is the reservoir and S the system.

System + reservoir = single isolated "supersystem" to which we can apply the ideas of the previous section. Total energy E_{\circ} , system energy $f << E_{\circ}$.

What is the probability that the system is in a particular microstate with energy \uparrow ?

(Not what is the probability that the system will have energy \dagger - that depends on how many such microstates there are.)

The number of microstates of the supersystem which have this particular microstate for the system is just;

X_{res}/E_o-fh So the probability is; $P]fg = \frac{X_{res} E_{o} - fh}{X_{total} f_{o}h} (1)$ Write $X_{res} \hbar E_o - fh = e^{\frac{\Lambda_1}{k_B} S_{res} E_o - f \frac{\Lambda_1}{k_B}}$ (2) and using $f << E_{\circ}$; $S_{res} \mathcal{F}_{o} - fh = S_{res} \mathcal{F}_{o}h - f \frac{dS_{res}}{dE}\Big|_{E_{o}} + \frac{f^{2}}{2} \frac{d^{2} S_{res}}{dE^{2}}\Big|_{E_{o}} + \dots$ $\frac{dS_{rev}}{dE}\Big|_{N,V} = \frac{1}{T_{KS}}$ So: $\frac{2^2 S}{2E^2} = \frac{2}{2E} b_T^1 I = \frac{1}{T^2} \frac{2T}{2E} \bigg|_V = -\frac{1}{T^2 C_V}$ Therefore; $\frac{S_{res}}{k_B} \Lambda E_o - fh = \frac{S_{res}}{k_B} \Lambda E_o h - \frac{f}{k_B} - \frac{f^2}{k_B^2 T^2} \frac{k_B}{C_v^{res}}$ (3)

Now $C_v - Nk_B$ when N is the number of atoms of the system, and is large. So;

 $\frac{k_B}{C_V} \sim \frac{1}{N}$

which tends to 0 for a macroscopic reservoir.

Taylor expansion is good and we can drop all but the first two terms.

From (1), (2) and (3);

$$P]fg = \frac{e^{\frac{Ses}{Ks}}e^{-\frac{f}{KsT}}}{X_{total}}e^{-\frac{f}{KsT}}h$$

The first factors of the top and bottom rows are the same for all microstates. All that is important is;

P]fgGe⁻ $\frac{t}{\kappa_{BT}}$

This is the Boltzman distribution.

Since $P_{i} = 1$

i I.

$$P_{i} = \frac{c}{\prod_{i} e^{-\frac{e_{i}}{K_{B}T}}}$$

Although the Boltzman distribution applies to macroscopic systems, for weakly interacting atoms in a gas or paramagnet we can also apply it to individual atoms (with rest acting as the reservoir). So for instance for the paramagnet, a single atom just has two states - where f = -nB and down where $f_{+} = + nB_{+}$

$$P_{-} = \frac{e^{-\frac{\int nB}{k_{B}T}}}{e^{\frac{nB}{K_{B}T}} + e^{-\frac{nB}{K_{B}T}}}$$
$$P_{-} = \frac{e^{\frac{\int nBg}{k_{B}T}}}{e^{-\frac{nB}{K_{B}T}} + e^{\frac{nB}{K_{B}T}}}$$
and

$$\frac{P_{.}}{P_{.}} = e^{-\frac{2nB}{k_BT}} = \left\langle \frac{n_{.}}{n_{.}} \right\rangle$$

for a large system. This is as before. Note that;

 $\frac{P_{\cdot}}{P_{\cdot}} < 1$

always.

hence there are always more particles in the lower energy state (up) than the higher energy state (down). This is counter-intuitive.

 \overline{P} 1

Not to う.



4.2 Partition function Mandl 2.5, B&S 5.2, K&K ch. 3 The denominator in the Boltzman distribution is called the partition function $Z = \begin{bmatrix} e^{-\frac{f_{I}}{Kk_{T}T}} \end{bmatrix}$

this is the sum over all microstates of the system.

"Just" a normalization constant.

However, Z is a function of T and - through \dagger_{i} - of B or V, and all the macroscopic properties of the system can be derived from it (P, S, E, M)

For instance: the energy. <E> is the ensemble average for 0 copies of the system, with $o_i = P_i o$ in each microstates.

$$=\frac{! \quad o_if_i}{o} = ! \quad P_if_i$$

$$=! \quad f_i \frac{e^{-\frac{f_i}{k_BT}}}{! \quad e^{-\frac{f_i}{x_BT}}} = \frac{! \quad f_i e^{-\frac{f_i}{k_BT}}}{! \quad e^{-\frac{f_i}{k_BT}}}$$
Let;
$$b = \frac{1}{kT}$$
So;

$$\langle E \rangle = \frac{ \int_{i}^{i} e^{-f_{i}b} }{ \int_{j}^{i} e^{-f_{j}b} }$$
$$\langle E \rangle = \frac{-\frac{2Z}{2b}}{Z}$$
$$\langle E \rangle = -\frac{2\ln Z}{2b} \Big|_{V,N}$$

We have $P(\varepsilon) = const x e^{-\frac{\varepsilon}{k_B T}}$, the Boltzmann distribution. constant = $\frac{1}{7}$

Z is the partition function $=\sum_{i} e^{-\frac{\varepsilon_{i}}{kT}}$ i.e. the sum over all the microstates.

$$< E >= \sum_{i} \varepsilon_{i} P_{i} = -\frac{\partial \ln Z}{\partial \beta}$$

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

May want the heat capacity.

$$c_{v} = \frac{\partial \langle E \rangle}{\partial T} \bigg|_{v} = k\beta^{2} \frac{\partial^{2} \ln Z}{\partial \beta^{2}}$$
Fluctuations in E;

$$\left(\Delta E\right)^{2} = \left\langle E^{2} \right\rangle - \left\langle E \right\rangle^{2}$$

$$= \frac{1}{Z} \frac{\partial^{2} Z}{\partial \beta^{2}} - \left(-\frac{1}{Z} \frac{\partial Z}{\partial \beta}\right)^{2}$$

$$= \frac{\partial^{2} \ln Z}{\partial \beta^{2}}$$

$$= \frac{c_{v}}{k\beta^{2}} = \left(k_{B}T\right)^{2} \frac{c_{v}}{k_{B}}$$
But $E \sim Nk_{p}T$

So $\frac{\Delta E}{E} = \frac{1}{\sqrt{N}}$. Again, 1 in 10¹².

For practical purposes, $\langle E \rangle = E$

So the energy fluctuations are very little about its' average, and we often write E rather than $\langle E \rangle$.

4.3 Entropy and Helmholtz Free Energy

(Mandl 2.5w B&S 5.3 \rightarrow 6)

Define entropy of a system as entropy of an ensemble of v copies of the system divided by v. As usual, have v_i copies in each microstate, $v_i = P_i v$.

The total number of microstates is the number of ways we can arrange this.

$$\Omega_{v} = \frac{v!}{v_{1}!v_{2}!v_{3}!...}$$

where the bottom line is the number that are identical to each other.

$$\ln \Omega_{v} = v \ln v - v - \left[v_{1} \ln v_{1} - v_{1} + v_{2} \ln v_{2} - v_{2} + ... \right]$$
$$= v \ln v - v - \sum_{i} v_{1} \ln v_{1} + \sum_{i} v_{i} (= v)$$
$$= -\sum_{i} v_{i} \ln \frac{v_{i}}{v}$$
$$= -v \sum_{i} P_{i} \ln P_{i}$$
$$S = \frac{S_{v}}{v} = -k_{b} \sum_{i} P_{i} \ln P_{i}$$

where the final sum is the sum over all microstates.

cf isolated system;
$$P_i = \frac{1}{\Omega}$$

So $S = k_B \ln \Omega$ as before.
So for Boltzmann distribution;
 $P_i = \frac{e^{-\epsilon_i \beta}}{Z}$
 $S = -k_B \sum_i P_i (\epsilon_i \beta - \ln Z)$
 $= k_B \beta \langle E \rangle + k_B \ln Z$
 $= \frac{1}{T} \langle E \rangle + k_B \ln Z$
So $k_B T \ln Z = TS - \langle E \rangle = -\langle F \rangle$
or $\left[\langle F \rangle = -k_B T \ln Z \right]$
From $dF = -SdT - pdV$;
 $S = -\frac{\partial F}{\partial T} \Big|_V$ and $P = -\frac{\partial F}{\partial V} \Big|_T$ (or $m = -\frac{\partial F}{\partial B} \Big|_T$)
Isolated system E, V fixed. $\Omega \to S \to P, T$.
Heat bath T, V fixed. $Z \to F \to S, P$.
(Note that Z depends on V (or β) through ϵ_i .)

4.4 Spin 1/2 paramagnet at temperature T (Mandl ch. 3, B&S 5.7, K&K ch. 3)

N spins in a magnetic field B either up $(E = -\mu B)$ or down $(E = +\mu B)$. For a single spin;

$$Z_{1} = e^{+\mu B} + e^{-\mu B} = 2\cosh\left(\frac{\mu B}{k_{B}T}\right)$$
$$\langle E \rangle = \sum_{i} P_{i}\varepsilon_{i} = \frac{1}{Z}\left(-\mu B e^{+\mu B\beta} + \mu B e^{-\mu B\beta}\right)$$
$$= -\mu B \frac{2\sinh\mu B\beta}{2\cosh\mu B\beta} = -\mu B \tanh\left(\frac{\mu B}{k_{B}T}\right)$$

Alternative method;







Spin-flips happen when $k_{\rm B}T \ll 2\mu B$ so an increase in temperature doesn't significantly change

$$n_{\uparrow}$$
 or n_{\downarrow} . So $\frac{dE}{dT} \sim 0$ (universal).

At high temp, $P_{\downarrow} \approx P_{\uparrow} \approx \frac{1}{2}$ but P_{\downarrow} never rises above $\frac{1}{2}$. Again, it is hard for the system to absorb energy.

$$\frac{dE}{dT} \rightarrow 0$$
 again.

This is not universal as it requires a "highest energy" - if there is not one, then there arealways higher energy levels a particle can be promoted into.

$$c_{v} = \frac{k}{3} \left(\frac{\mu B}{kT}\right)^{2} \text{ (since } \cosh\left(\frac{\mu B}{kT}\right) \rightarrow 1\text{)}$$
$$c_{v} \approx \frac{1}{T^{2}} \text{ (Pierre Curie)}$$

Assume all along that $E_N = NE_1$, $(c_v)_N = N(c_v)_1$ etc.

This is reasonable for non-interacting or weakly-interacting particles. However, suppose we want to work with the partition function of the whole system. We could have started with Z_N , the N-particle particle particle particle number.

e.g. N = 2.4 states.

$$Z_{2} = e^{-(-2\mu B)\beta} + e^{0} + e^{0} + e^{-2\mu B\beta} = e^{2\mu B\beta} + 2 + e^{-2\mu B\beta} = \left(e^{2\mu B\beta} + e^{-2\mu B\beta}\right)^{2} = Z_{1}^{2}$$

In general, $Z_N = (Z_1)^{\prime\prime}$.

This is true for distinguishable particles.

So the energy
$$\langle E_N \rangle = -\frac{\partial \ln Z_N}{\partial \beta} = N \langle E_1 \rangle$$
 as $\ln Z_N = N \ln Z_1$

Helmholtz free energy;

$$F = -kT \ln Z_{N} = -NkT \ln \left(2\cosh\frac{\mu B}{k_{B}T} \right)$$

$$S = -\frac{\partial F}{\partial T}\Big|_{B} = Nk_{B} \ln \left(2\cosh\left(\frac{\mu B}{k_{B}T}\right)\right) + \underbrace{Nk_{B}T\left(-\frac{\mu B}{k_{B}T^{2}}\right)}_{=-\frac{N\mu B}{T}} \underbrace{\frac{\sinh\left(\frac{\mu B}{k_{B}T}\right)}{\cosh\left(\frac{\mu B}{k_{B}T}\right)}}_{\tanh\left(\frac{\mu B}{k_{B}T}\right)}$$

$$\left(= -\frac{F}{T} + \frac{E}{T} \right)$$

$$T \to 0 \left(\beta \to \infty\right)$$
 and $\sinh\left(\frac{\mu B}{k_B T}\right) \to e^{\mu\beta B}$. Therefore $\tanh\left(\frac{\mu B}{k_B T}\right) \to 1$.
 $S \to kN \ln e^{\left(\frac{\mu B}{k_B T}\right)} - \frac{\mu NB}{T} = 0$

Obvious as all the spins are up - no disorder.

$$T \to \infty \left(\beta \to \infty\right) \operatorname{cosh}\left(\frac{\mu B}{k_{B}T}\right) \to 1, \ \operatorname{tanh} \to \mu B\beta$$

 $S \to Nk_{B}\ln 2 + 0\left(\frac{1}{T^{2}}\right)$

As expected because in this case up and down are degenerate and all microstates are equally likely.



For an ideal paramagnet, $S = Nk \ln 2$ for all T but any real one will have a weak force aligning the spins and at low enough T this will cause alignment and $S \rightarrow 0$ as $T \rightarrow 0$. (This is general).

$$M_{m} = -\frac{\partial F}{\partial B}\Big|_{\tau} = +\frac{\partial}{\partial B} \left(NkT \ln\left(2\cosh\mu B\beta\right) \right)$$
$$= N\mu \tanh\frac{\mu B}{kT}$$
$$= -\frac{E}{B}$$

as expected (E = -mB).

4.5 Applications of the Paramagnet - Adiabatic cooling and the third law (Mandl 5.6)



By magnetising and demagnetizing a sample we can cool it.

1) Start at B_1 and increase the magnetic field to B_2 at constant temperature. System has become more ordered. $S \downarrow .$

2) Isolate the system and slowly demagnetize to B_1 . Reversible adiabatic \rightarrow constant S. Temperature decreases.



Entropy unchanged; n_{\downarrow} and n_{\downarrow} unchanged - consistent with Boltzman but at a lower temperature.

Since $S = S\left(\frac{B}{T}\right)$ halving B will halve T.

Could repeat with a fraction of the sample (the rest acting as the heat bath in step one). But soon we gain less and less in each step. Cannot reach T = 0 in a finite number of steps. Since $T \rightarrow 0$ behaviour of entropy curves in universal so is the unattainability of T = 0 - third law of thermodynamics.

4.6.1 Vibrational energy of a diatomic molecule

Vibrational energy levels of a single molecule are $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$ where $\omega = \sqrt{\frac{k}{\mu}}$ (k is the spring

constant).

$$Z_{1} = \sum_{n=0}^{\infty} e^{-E_{n}\beta}$$
$$= e^{-\frac{1}{2}\hbar\omega\beta} + e^{-\frac{3}{2}\hbar\omega\beta} + e^{-\frac{5}{2}\hbar\omega\beta}$$
$$= e^{-\frac{1}{2}\hbar\omega\beta} \left(1 + e^{-\hbar\omega\beta} + e^{-2\hbar\omega\beta} + \dots\right)$$

This is $1 + x + x^2 + x^3 + ...$ where $x = e^{-\hbar\mu\beta}$. This is the same as $\frac{1}{1-x}$.

Hence;

$$Z_{1} = \frac{e^{-\frac{2}{2}\hbar\omega\beta}}{1 - e^{-\hbar\omega\beta}} = \frac{1}{2\sinh\frac{\hbar\omega\beta}{2}}$$
$$\left\langle E_{1} \right\rangle = -\frac{\partial \ln Z_{1}}{\partial\beta} = +\frac{\partial}{\partial\beta}\ln\left(2\sinh\frac{\hbar\omega\beta}{2}\right)$$
$$= \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega\beta}{2}\right)$$
As $T \to 0 \ \beta \to \infty$, $\coth\left(\frac{\hbar\omega\beta}{2}\right) \to 1$, $\left\langle E_{1} \right\rangle \to \frac{1}{2}\hbar\omega$.

At lower temperatures, all molecules are in the ground state.

$$T \to \infty \ \beta \to 0$$
. $\operatorname{coth}\left(\frac{\hbar\omega\beta}{2}\right) \to \frac{2}{\hbar\omega\beta}, \ \langle E_1 \rangle \to k_B T$

(Note $c_v \rightarrow k_B$, not to 0. This is because this system does not have a finite number of levels.)

4.6.1 Rotational energy levels

Here the energy levels are
$$\frac{L(L+1)\hbar^2}{2I}$$

$$\left(\frac{L^2}{2I}=\frac{1}{2}I\omega^2\right)$$

- ε_{o} occurs just once. $(m_{L} = 0)$
- ε_1 occurs 3 times. $(m_1 = \pm 1, 0)$
- ε_2 occurs 5 times $(m_1 = \pm 2, \pm 1, 0)$
- ε_{L} occurs (2L+1) times. (degeneracy)

$$Z_{1} = \sum_{i} e^{-\varepsilon_{i}\beta} = \sum_{L=0}^{\infty} \sum_{m_{L}=-L}^{L} e^{-\varepsilon_{L}\beta} = \sum_{L=0}^{\infty} (2L+1)e^{-\varepsilon_{L}\beta}$$

Note that in general we can write

$$Z = \sum_{i} e^{-\varepsilon_{i}\beta} = \sum_{\varepsilon} g(\varepsilon) e^{-\varepsilon\beta}$$

(sum over states \rightarrow sum over energy)

where $g(\varepsilon)$ is the degeneracy - the number of states with the same energy.

$$Z_{1} = 1 + 3e^{-\frac{\hbar^{2}\beta}{l}} + 5e^{-\frac{3\hbar^{2}\beta}{l}} + \dots$$

If $k_{\rm B}T \sim \frac{\hbar^2}{I}$ we can sum terms until they become very smooth, then neglect the rest.

But if $k_{B}T \gg \frac{\hbar^{2}}{I}$ (this turns out to be a few Kelvin), we can replace the sum over closely spaced states with an integral.

$$Z_{1} = \int_{0}^{\infty} (2L+1) e^{-L(L+1)\frac{\hbar^{2}\beta}{l}} dL$$

Let;
$$L(L+1) = x$$

$$(2L+1) dL = dx$$

$$Z_{1} = \frac{l}{\hbar^{2}\beta}$$

So the energy is;

$$\langle E_1 \rangle = -\frac{1}{Z_1} \frac{\partial Z_1}{\partial \beta} = \frac{1}{\beta} = k_B T$$

4.7 Translational energy of an atom or molecule (Mandl 7.1 \rightarrow 4 + appendix B1&2, B&S 5.92 7.2, K&K ch. 3) Particle in a cuboid box;

$$\Psi = A\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

where in order to satisfy boundary conditions;

$$\begin{aligned} k_x &= \frac{n_x \pi}{L_x}, \ k_y = \frac{n_y \pi}{L_y}, \ k_z = \frac{n_z \pi}{L_z} \text{ where L is the length of the box in that direction.} \end{aligned}$$
Satisfies $\frac{-\hbar^2}{2m} \nabla^2 \Psi = E \Psi$.

$$k^2 &= k_x^2 + k_y^2 + k_z^2$$

$$E &= \frac{\hbar^2}{2m} \left(k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2 k^2}{2m}$$
If $= \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$

If $L_x = L_y = L_z$ the states will be degenerate.

$$Z_{1} = \sum_{n_{x}, n_{y}, n_{z}} e^{-\varepsilon^{\left(n_{x}, n_{y}, n_{z}\right)/kT}}$$

Note that the spacing of the energy levels, $n \sim \frac{\hbar^2 \pi^2}{2mL^2}$ is about $10^{-18} eV$ for $L \sim 1m$. So any achievable value of T satisfies $kT >> \Delta E$ and we can replace the sum \sum_{n_x,n_y,n_z}

integral $\int dn_x$ or by $\frac{L_x}{\pi} \int_0^\infty dk_x$ to avoid issues with n being an integer. So;

$$Z_{1} = \left(\frac{L_{x}}{\pi}\right) \left(\frac{L_{y}}{\pi}\right) \left(\frac{L_{z}}{\pi}\right) \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} e^{-\varepsilon(k_{x},k_{y},k_{z})\beta} dk_{x} dk_{y} dk_{z}$$
$$= \frac{V}{\pi^{3}} \int_{0}^{\infty} \int_{0}^{\frac{\pi}{2}} \int_{0}^{\frac{\pi}{2}} e^{-\varepsilon(k)\beta} k^{2} \sin\theta_{k} dk d\theta_{k} d\phi_{k}$$

where V is 1/8 of a full sphere, the limits are due to the fact that we are integrating over the positive octant of the sphere, and $\varepsilon(k)$ is independent of the angle. θ_k and ϕ_k are the angles the vector k makes.

$$Z_{1} = \frac{4\pi}{8} \frac{V}{\pi^{3}} \int_{0}^{\infty} k^{2} e^{-\varepsilon(k)\beta} dk$$
$$= \int_{0}^{\infty} D(k) e^{-\varepsilon(k)\beta} dk$$

where D(k) is called the "density of state".

$$D(k) = \frac{v}{2\pi^2} k^2$$

So $Z_1 = \frac{V}{2\pi^2} \int_0^\infty k^2 e^{-\frac{\hbar^2 k^2 \beta}{2m}} dk = V \left(\frac{m}{2\hbar^2 \beta \pi}\right)^{3/2}$
using $\int_0^\infty e^{-\alpha k^2} dk = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$ and $\int_0^\infty k^2 e^{-\alpha k^2} dk = -\frac{\partial}{\partial \alpha} \int e^{-\alpha k^2} dk = \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}}$.

For Z_1 to be dimensionless, $\left(\frac{mkT}{2\hbar^2\pi}\right)^{r_2}$ must have dimensions of m^{-3} . This is the same dimensions as a number density. Call it n_q (as it appears less frequently) so that $Z_1 = Vn_q$. This is the "Quantum concentration" or density.

So
$$\langle E_1 \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T$$

4.8 Equipartition

(Mandl 7.9, B&S 5.14)

Last 3 results are examples of equipartition. For each degree of freedom that is quadratic in the energy or momentum, the average energy is $\frac{1}{2}k_{B}T$ and the contibution to the heat capacity c_{v}

is
$$\frac{1}{2}k_{B}$$
.

- Vibration $E = \frac{1}{2}m\dot{r}^{2} + \frac{1}{2}kr^{2}$ 2dof E = kT.
- Rotation $E = \frac{1}{2}I\omega_1^2 + \frac{1}{2}I\omega_2^2$ 2dof E = kT
- Translational $E = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$ 3dof $E = \frac{3}{2}kT$

Classical theorem, and holds only if $kT >> \Delta \varepsilon$ the spacing between quantum energy levels. In all cases we saw that equipartition breaks down for $kT \le \Delta \varepsilon$ and as $T \to 0$, $c_v \to 0$ "frozen out".



Example of a non-quadratic (linear) dof is the translational energy of an ultra-relativistic particle. $E^2 = p^2 c^2 + m^2 c^4$

Aside on "density of states"

From
$$Z_1 = \int_0^\infty e^{-\varepsilon(k)\beta} D(k) dk$$

D(k)dk is the number of states of the system with k between k and k + dk where $dK >> \frac{\pi}{1}$



(B&S 6.5, Mandl 7.1, 7.4 \rightarrow 6, K&K 3) Single particle in a box;

$$Z_1 = Vn_q = V \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

 $0.33n_{\rm Q}=\lambda_{\rm T}^{-3}$

where λ_{τ} is the de Broglie wavelength for a particle with thermal energy $k_{B}T$ and mass m.

Number of states available out to $\frac{3}{2}kT$ is $1.38N_{\rm q}$.

If $n \sim n_{q}$ then quantum (interference) effects will be important. In this section we are only considering the classical regime. Details to follow. N particles in a box.

 $\langle E_1 \rangle = \frac{3}{2}kT$. Clearly $\langle E_N \rangle = \frac{3}{2}NkT$ which presumably we again get from $Z_N = (Z_1)^N$. This is wrong.

Consider Helmholtz free energy.

 $F = -k_B T \ln Z_N = -k_B T N \ln Z_1 = -k_B T N \left[\ln V + \ln n_Q \right]$

But $N \ln V$ is not extensive (n_q is intensive so $N \ln n_q$ is OK). If we double N and V, F doesn't double.

What might be wrong?

 $Z_{N} = (Z_{1})^{N}$ only holds for distinguishable particles. But atoms of the same element in the same internal state are not just practically but fundamentally indistinguishable. In a gas we can't use lattice position (coordinates) to label them.

e.g. 2 particles, 2 energy levels. If they are distinguishable;

Distinguishable; 4 states, energies $0, \varepsilon, \varepsilon, 2\varepsilon$.



Indistinguishable particles

Indistinguishable; $Z_2 = 1 + e^{-\epsilon\beta} + e^{-2\epsilon\beta} \neq Z_1^2$

If all the particles are in different 1-particle states, the expression Z_1^N overcounts the contribution of that N-particle state to the partition function Z_N by N!.

If the number of 1-particle states is much larger than the number of particles, it will be very uncommon for two particles to be in the same state and $Z_N = \frac{(Z_1)^N}{N!}$ will be a good approximation. Remember that n_Q was roughly the number of accessible ($E \le \frac{3}{2}kT$) states in a gas. So the condition above translates into $n << n_Q$ - classical regime.

$$F = -kT \ln Z_{N}$$

= $-kT (N \ln Z_{1} - \ln N!)$
= $-kTN (\ln Z_{1} - \ln N + 1)$
= $-kTN \left(\ln \left(\frac{V}{N} \right) + \ln n_{Q} + 1 \right)$
 $\frac{V}{N} = \frac{1}{n}$ - intensive so $N \ln \frac{V}{N}$ is extensive.

$$F = -kTN\left(\ln\frac{n_{Q}}{n} + 1\right).$$

It works!
$$P = -\frac{\partial F}{\partial V}\Big|_{T} = +\frac{kTN}{V}$$

Or $PV = NkT$ (ideal gas)
$$S = -\frac{\partial F}{\partial T}\Big|_{V} = +kN\left(\ln\frac{n_{Q}}{k} + 1\right) + kTN\frac{\partial\ln n_{Q}}{\partial T}$$
$$= +k_{B}N\left(\ln\frac{n_{Q}}{n} + 1\right) + \frac{3}{2}k_{B}N$$
$$= Nk_{B}\left(\ln\frac{n_{Q}}{n} + \frac{5}{2}\right)$$

>0 for $n \ll n_{\odot}$ (only regime where it is valid)

Sackeur-Tetrode

This contains $Nk_B \left(\ln V - \frac{3}{2} \ln T \right) + ...$ which gives $\Delta S = Nk_B \left(\ln \Delta V - \frac{3}{2} \ln \Delta T \right)$ as required by classical thermodynamics. But now the absolute entropy is predicted. This agrees with measurements.

4.10 Diatomic Gases

$$\begin{split} \varepsilon &= \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} \\ Z_{N} &= \frac{\left(Z_{1}^{trans}\right)^{N} \left(Z_{1}^{rot}\right)^{N} \left(Z_{1}^{vib}\right)^{N}}{N!} \\ &= Z_{N}^{trans} \left(Z_{1}^{rot}\right)^{N} \left(Z_{1}^{vib}\right)^{N} \\ F &= F^{trans} + F^{rot} + F^{vib} \end{split}$$

E and S add too.

4.11 Maxwell-Boltzmann Distribution

(Mandl 4.7, B&S 7.4, K&K chapter 14) What is the distribution of molecular speeds in an ideal gas? Probability of given velocity (v_x, v_y, v_z) is;

$$P(v_x, v_y, v_z) = \frac{e^{-\frac{1}{2}mv^2\beta}}{Z_1}$$

where Z_1 is the translational partition function for 1 particle.

(Provided
$$(v_x, v_y, v_z)$$
 is one of the allowed values $\underline{v} = \frac{\hbar}{m} \underline{k}$, $\underline{k} = \left(\frac{n_x \pi}{L_x} + \frac{n_y \pi}{L_y} + \frac{n_z \pi}{L_z}\right)$)

For speed however (not caring about direction);

$$P(v)dv = P(v \to v + dv) = \frac{D(k)dke^{-\frac{\hbar^{2}k^{2}}{2m}\beta}}{Z_{1}} = \frac{\frac{V}{2\pi^{2}}k^{2}dke^{-\frac{\hbar^{2}k^{2}}{2m}\beta}}{Vn_{Q}} = \underbrace{\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}_{1} 4\pi v^{2}e^{-\frac{1}{2}mv^{2}/kT}dv}_{normalization}$$

where
$$k = \frac{mv}{\hbar}$$
.

The normalization constant can be reconstructed from $\int p(v) dv = 1$.

$$(cf P(r) = r^{2} |\psi|^{2} in 3D QM.)$$
P(v)
$$\int_{T}^{T} \frac{k_{B} T}{m}$$
Most probable speed $\frac{dP}{dv} = 0 \Rightarrow v_{p} = \sqrt{\frac{2kT}{M}}$.
Average speed $\int_{0}^{\infty} vP(v) dp \Rightarrow \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = 1.13v_{p}$
rms $\sqrt{\int_{0}^{\infty} v^{2}P(v) dv} \Rightarrow \sqrt{\langle v^{2} \rangle} = \sqrt{\frac{3kT}{m}} = 1.22v_{p}$
 $\left(\frac{1}{2}m\langle v^{2} \rangle = \frac{3}{2}kT\right)$

2.14 Systems with more than one component (Mandl 8.1, B&S 2.9)

From the considerations of entropy in section 3.4 "from entropy to temperature" we can deduce

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either side. This must correspond to some quantity in thermodynamics which governs particle flow, just as temperature governs heat flow.

$$\frac{\partial S}{\partial N}\Big|_{E,V} = -\frac{u}{T} \qquad \text{c.f.} \left. \frac{\partial S}{\partial V} \right|_{E,N} = +\frac{p}{T}$$

 $\mu\,$ is called the "chemical potential".

$$ds = \frac{dE}{T} + \frac{PdV}{T} - \frac{\mu dN}{T}$$
$$dE = TdS - PdV + \mu dN$$
$$\mu = \frac{\partial E}{\partial N}\Big|_{S,V}$$
$$F = E - TS \Rightarrow dF = -SdT - pdV + \mu dN$$
$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V}$$
$$G = E - TS + PV \Rightarrow dE = -SdT + VdP + \mu dN$$

$$\mu = \frac{\partial \boldsymbol{G}}{\partial \boldsymbol{N}}\Big|_{\boldsymbol{P},\boldsymbol{T}}$$

Note that in $G \equiv G(T, P, N)$, T and P are intensive but G is extensive, as is N.

So the dependence of G on N is linear. G = Ng(P,T) where g(P,T) is a form of specific Gibbs free energy (per molecule).

But $\mu = \frac{\partial G}{\partial N}\Big|_{PT} = g$! So μ is the Gibbs Free Energy per molecule.

If we have more than one particle type present, we can write $dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2 + \dots$ Now with 2 extensive variables N_1 and N_2 we can no longer say that μ_1 is the Gibbs free energy per molecule of type 1.

Why is it called the chemical potential?

Consider simplest chemical reachion $A \rightleftharpoons B$

e.g. $C_5 H_{12}$



pentane

methylbutane

(hydrogens omitted)

At constant T and P, which way will the reaction go? Need to minimize G. $dG = \mu_A dN_A + \mu_B dN_B$ but $dN_A = -dN_B$ so $dG = (\mu_A - \mu_B) dN_A$

 $dG = 0 \rightarrow \mu_{A} = \mu_{B}$

Equilibrium \rightarrow equal chemical potentials.





5. Systems with variable particle number and Quantum Statistics

5.1 The Gibbs Distribution

(Mandl 11.1, B&S 9.7-9.9, K&K 5)

In the Boltzmann distribution, we wanted the probability that the system is in a microstate with energy E_i and particle number N. This is proportional to the number of microstates of the

reservoir with energy $\varepsilon_o - \varepsilon_i$ and particle number $N_o - N_i$. From $S = k \ln \Omega$,

$$\Omega_{res}\left(\varepsilon_{o}-\varepsilon_{i},N_{o}-N_{i}\right)=e^{\left[S_{res}\left(\varepsilon_{o}-\varepsilon_{i},N_{o}-N_{i}\right)/k_{B}\right]}.$$

Expanded;

$$S_{res} = S(\varepsilon_o, N_o) - E_i \underbrace{\frac{\partial S}{\partial E}}_{T} - N_i \underbrace{\frac{\partial S}{\partial N}}_{-\frac{\mu}{T}} + \dots$$

$$\Omega = e^{\frac{S_o}{k}} e^{-\frac{1}{k} \left(\frac{\varepsilon_i - \mu N_i}{T}\right)} = const \cdot e^{-\frac{(\varepsilon_i - \mu N_i)}{k_B T}}$$

$$p_i = \frac{e^{-\frac{(\varepsilon_i - \mu N_i)}{k_B T}}}{\mathbb{Z}}$$

This is the Gibbs distribution, and is the same as the Boltzmann distribution, but has the number of particles also in the exponential.

 \mathbb{Z} is called the grand partition function.

$$\mathbb{Z} = \sum_{i} e^{-\frac{(\varepsilon_{i} - \mu N_{i})}{k_{B}}}$$

The relevant ensemble is a collection of copies which can exchange energy and particles (grand canonical ensemble).

(cf canonical for Boltzmann and microcanonical for isolated system.)

$$\langle x \rangle = \sum_{i} P_{i} X_{i}$$

Some results which follow from the arguments analogous to the Boltzmann section.

$$\langle \mathbf{E} - \mu \mathbf{N} \rangle = -\frac{\partial \ln \mathbb{Z}}{\partial \beta} \langle \mathbf{N} \rangle = \mathbf{k}_{B} T \frac{\partial \ln \mathbb{Z}}{\partial \mu} \langle \mathbf{S} \rangle = -\mathbf{k}_{B} \sum_{i} p_{i} \ln p_{i} = -\mathbf{k}_{B} \sum_{i} p_{i} \left[-\left(\mathbf{E}_{i} - \mu \mathbf{N}_{i}\right) \beta - \ln \mathbb{Z} \right] = -\mathbf{k}_{B} \left(-\langle \mathbf{E} \rangle \beta + \mu \langle \mathbf{N} \rangle \beta - \ln \mathbb{Z} \right) = \frac{1}{T} \left[\langle \mathbf{E} \rangle - \mu \langle \mathbf{N} \rangle + \mathbf{k} T \ln \mathbb{Z} \right] -\mathbf{k} T \ln \mathbb{Z} = \langle \mathbf{E} \rangle - T \langle \mathbf{S} \rangle - \mu \langle \mathbf{N} \rangle = \langle \mathbf{F} \rangle - \mu \langle \mathbf{N} \rangle$$

We denote $-kT \ln \mathbb{Z}$ by $\Phi_{_{G}}$ the "grand potential".

(B&S use Ξ for \mathbb{Z} . Mandl uses Ω for Φ_{c} .)

$$\Phi_{G} = E - TS - \mu N$$

Now we are talking about classical potentials, so fluctuations can be ignored.

 $\begin{aligned} d\Phi_{g} &= dE - TdS - Sdt - \mu dN - Nd\mu \\ \text{But } dE &= TdS - pdV + \mu dN \text{ . So;} \\ d\Phi_{g} &= -SdT - pdV - Nd\mu \\ &\Rightarrow \Phi_{g} \left(T, V, \mu \right). \\ S &= -\frac{\partial \Phi_{g}}{\partial T} \bigg|_{V,\mu}, P = -\frac{\partial \Phi_{g}}{\partial V} \bigg|_{T,\mu}, N = -\frac{\partial \Phi_{g}}{\partial \mu} \bigg|_{T,V}. \\ \Phi_{g} &\equiv \Phi_{g} \left(T, V, \mu \right). \text{ But of these, T and } \mu \text{ are intensive. Only V is extensive. So, } \Phi_{g} = Vf \left(T, \mu \right). \\ \text{But } \frac{\partial \Phi_{g}}{\partial V} \bigg|_{T,V} &= -P = f \end{aligned}$

So
$$\Phi_{G} = -PV!$$

While this isn't new, this doesn't mean it isn't a useful quantity to extract S, P and N from $\mathbb Z$.

System	Isolated	Thermal	Diffusive
Fixed	E, N, V	T, N, V	Τ, μ V
Distribution	$p_i = \frac{1}{\Omega}$	$P_i = \frac{e^{-E_i\beta}}{Z}$	$\boldsymbol{P}_i = \frac{\mathbf{e}^{-(\boldsymbol{E}_i - \mu \boldsymbol{N}_i)}}{\mathbb{Z}}$
Key microscopic function	Number of microstates Ω	Z partition function	\mathbb{Z} grand potential function
Key macroscopic function	$S = k_{_B} \ln \Omega$	$F = -k_{B}T \ln Z$	$\Phi_{_B} = -k_{_B}T\ln\mathbb{Z}$
	$\frac{1}{T} = \frac{\partial S}{\partial E}\Big _{N,V}$	$S = -\frac{\partial F}{\partial T}\Big _{N,V}$	$S = -\frac{\partial \Phi_{G}}{\partial T}\Big _{\mu,V}$
	$\frac{P}{T} = \frac{\partial S}{\partial V}\Big _{E,N}$	$\boldsymbol{P} = -\frac{\partial \boldsymbol{F}}{\partial \boldsymbol{V}}\Big _{\boldsymbol{N},\boldsymbol{T}}$	$\boldsymbol{P} = -\frac{\partial \boldsymbol{\Phi}_{\boldsymbol{G}}}{\partial \boldsymbol{V}}\Big _{\boldsymbol{\mu},\boldsymbol{\tau}}$
	$\left.\frac{\mu}{T} = -\frac{\partial S}{\partial N}\right _{E,V}$	$\mu = \frac{\partial F}{\partial N}\Big _{T,V}$	$N = -\frac{\partial \Phi_{G}}{\partial \mu}\Big _{\tau, \nu}$

A site which can bind a single particle only and which is in contact with a solution or gas of that particle e.g. myoglobin binds O_2 in contact with tissue fluid contaning dissolved O_2 at a given chemical potential μ .

2 states;

- 0 particles bound,
$$E = 0$$
, $N = 0$.
- 1 particle bound. $E = \varepsilon$, $N = 1$.
 $\mathbb{Z} = e^{-(0-0\mu)\beta} + e^{-(\varepsilon-1\mu)\beta} = 1 + e^{-(\varepsilon-\mu)\beta}$
 $P(0) = \frac{1}{\mathbb{Z}}$, $P(1) = \frac{e^{-(\varepsilon-\mu)\beta}}{\mathbb{Z}}$.
 $\langle N \rangle = 0P(0) + 1P(1) = P(1) = \frac{1}{e^{(\varepsilon-\mu)\beta} + 1}$

Second example; A site which can bind many particles, all with the same binding energy. States; 0 particles, E = 0

1 particle,
$$E = \varepsilon$$
.
2 particles, $E = 2\varepsilon$
3 particles, $E = 3\varepsilon$
...
 $\mathbb{Z} = 1 + e^{-(\varepsilon - \mu)\beta} + e^{-2(\varepsilon - \mu)\beta} + e^{-3(\varepsilon - \mu)\beta} + ...$
cf $1 + x + x^{2} + ... = \frac{1}{1 - x}$
 $\Rightarrow \mathbb{Z} = \frac{1}{1 - e^{-(\varepsilon - \mu)\beta}}$
 $\langle N \rangle = +k_{B}T \frac{\partial \ln \mathbb{Z}}{\partial \mu} = -kT \frac{\partial}{\partial \mu} (1 - e^{-(\varepsilon - \mu)\beta}) = -kT \frac{(0 + \beta e^{-(\varepsilon - \mu)\beta})}{1 - e^{-(\varepsilon - \mu)\beta}} = \frac{1}{e^{(\varepsilon - \mu)\beta} - 1}$





Only makes sense for $\varepsilon > \mu$. If energy cost of adding a particle is less than μ infinitely many particles can be bound.

5.3 Bosons and Fermions (Mandl 9.2, B&S 10.2)

All quantum particles have spin which is an integer multiple of $\frac{\hbar}{2}$.

Spin 0; ⁴*He* is ground state, pion, ¹*H* in ground state, Higgs Boson.

Spin 1/2; ³*He* is ground state, quark, electron, neutrino, proton.

Spin 1; Gluon, photon, W and Z bosons, $\,
ho\,$ meson, 1st excited state of $\,{}^4H\!e\,$ $\,{}^1H\!e\,$

Spin 3/2: Δ baryon (excitations of protons and neutrons), ⁵He

Spin 2; graviton, ¹⁶O atom in ground state.

Spin >2; many atoms and nuclei, but no elementary particles.

We classify these depending on whether the spin is integer, or odd half-integer. The first are bosons, the latter fermions.

A collection of elementary particles is a fermion if it contains an odd number of elementary fermions (electrons, quarks). Excitation (e.g. ⁴*He* from ground state to 1st excited state) doesn't change this.

Fermions obey the Pauli exclusion principle - can't have more than one in any quantum state. Bosons don't - can have any number in the same state.

For a single quantum state;

either
$$\mathbb{Z} = 1 + e^{-(\varepsilon - \mu)\beta}$$
 and $n \equiv \langle N \rangle = \frac{1}{e^{(\varepsilon - \mu)\beta} + 1}$ for Fermi-Dirac statistics

or
$$\mathbb{Z} = \frac{1}{1 - e^{-(e-\mu)\beta}}$$
 and $n = \frac{1}{e^{(e-\mu)\beta} - 1}$ for Bose-Einstein statistics.

5.3 Ideal gas without classical approximation

(Mandl 11.2, 11.5, B&S 10.2-3)

The grand partition function allows us to treat the ideal gas without requiring $n \ll n_{o}$.

If the system consists of non-interacting particles, we can enumerate the single-particle states of the system (e.g. by specifying n_x, n_y, n_z in the wave function.)

A microstate of the whole system is described by specifying the number of particles in each single particle state.

$$\mathbb{Z} = \sum_{n_i} e^{-(n_1(\varepsilon_1 - \mu) + n_2(\varepsilon_2 - \mu) + n_3(\varepsilon_3 - \mu) + \dots)\beta}$$

where n_i is the number of particle in each single particle state., and the total energy is $n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3$ and the total particle number is $n_1 + n_2 + n_3 + ...$

$$\mathbb{Z} = \sum_{n_i} \mathbf{e}^{-n_1(\varepsilon_1 - \mu)\beta} \mathbf{e}^{-n_2(\varepsilon_2 - \mu)\beta} \dots = \mathbb{Z}_1 \mathbb{Z}_2 \dots = \Pi_i \mathbb{Z}_i$$

where Π_i is the sum over all single-particle states / energy levels.

Note factorization can only be done because $n_1 + n_2 + n_3 + ...$ has not been fixed in advance - μ has been fixed instead.

$$\ln \mathbb{Z} = \sum_{i} \ln \mathbb{Z}_{i}$$

$$\Phi_{G} = \sum_{i} \Phi_{G,i}$$

$$\langle N \rangle = -\frac{\partial}{\partial \mu} (-kT \ln \mathbb{Z}) = \sum_{i} kT \frac{\partial \ln \mathbb{Z}_{i}}{\partial \mu} = \sum_{i} n_{i}$$

$$\langle E \rangle = \sum_{i} n_{i} \varepsilon_{i}$$

For a gas in 3D, we can replace the sum over levels by an integral weighted by the density of states.

$$N = \int D(k)n(k)dk$$
$$E = \int \varepsilon(k)n(k)D(k)dk$$
$$n(k) = \frac{1}{e^{(\varepsilon(k)-\mu)\beta} \pm 1}$$

(plus for Fermions, minus for bosons). For bosons, we need $\mu < \epsilon_{\min}$ but for fermions μ can be positive or negative.

Continued in PC3151.

5.4 Classical Approximation again

(Mandl 11.4, B&S 10.2-3)

If we have a large system, then we should recover our previous results for the classical limit $n << n_{_{\rm Q}}$.

$$\begin{split} \Phi_{G} &= -kT \ln \mathbb{Z} = -kT \sum_{i} \ln \mathbb{Z}_{i} \\ \mathbb{Z}_{i} &= \frac{1}{e^{-(\varepsilon_{i} - \mu)\beta} - 1} \text{ bosons} \\ \mathbb{Z}_{i} &= 1 + e^{-(\varepsilon_{i} - \mu)\beta} \text{ fermions.} \\ \Phi_{G} &= \mp kT \sum_{i} \ln \left(1 \pm e^{(\mu - \varepsilon_{i})\beta} \right) \end{split}$$

Assume that $e^{\mu\beta} \ll 1$ (μ large and negative). This will turn out to be the same as the classical limit.

Use
$$\ln(1+x) \approx x$$
.
 $\Phi_{G} = -kT \sum_{i} e^{\mu\beta} e^{-\varepsilon_{i}\beta} = -kT e^{\mu\beta} Z_{1}$

This ends with the normal single particle partition function $= vn_{o}$.

$$N = -\frac{\partial \Phi_{g}}{\partial \mu} = e^{\mu\beta} Z_{1}$$
$$\mu = -kT \ln\left(\frac{Z_{1}}{N}\right) = -kT \ln\left(\frac{n_{q}}{n}\right)$$

So $\mu << 0$ is the same as $n_q >> n$

Finally,
$$F = \Phi_G + \mu N = -NkT - NkT \ln\left(\frac{Z_1}{N}\right) = -NkT\left(\ln\left(\frac{Z_1}{N}\right) + 1\right)$$
 as before.

 \rightarrow since F is the same, S, P and E will all be as before.

Exam questions; 2003 Q1.
a)

$$\int -pdV$$

$$W = \Delta E - Q = \Delta E \text{ for adiabatic.}$$
b) THIS WILL PROBABLY BE ON THE EXAM! LEARN IT!

$$\Delta S = c \ln \frac{T_r}{T_i} = c \ln \frac{T_0}{T_1}$$

$$W = -\Delta A = -(\Delta E - T_o \Delta S) = -(c(T_o - T_i) - T_o \Delta S)$$
c)

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$
e)

$$\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{V,N}$$
Q2;
a)
This will be easy when it's exam time... ③

b)

$$dS = \frac{\partial S}{\partial T} \Big|_{P} dT + \frac{\partial S}{\partial P} \Big|_{S} dP$$

$$dS = \frac{1}{T} c_{P} dT + -\frac{\partial V}{\partial T} \Big|_{P} dP$$

c) Reversible adiabatic $\rightarrow \Delta S = 0$.

$$\int_{T_1}^{T_2} \frac{\boldsymbol{c}_p}{T} dT = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T} \Big|_{\boldsymbol{p}} \right) d\boldsymbol{P}$$

Answer will turn out to be in atmospheres * ... Need to multiply by 1.0135×10^5 to get SI units.

3)
a)
$$P_{i} = \frac{e^{-E\beta}}{Z}$$
$$Z = \sum_{i} e^{-\varepsilon_{i}\beta}$$

Sketch derivation done for Boltzmann, revised for Gibbs.

$$P_{i}(E) \propto \Omega_{res} (E_{o} - E)$$
where $\Omega_{res} = e^{\frac{S}{k_{B}}}$
Expand S about $S(E_{o})$
Boltzmann factor comes from $\frac{\partial S}{\partial E}\Big|_{V} = \frac{1}{T}$

$$\Omega_{res} \propto e^{-\frac{E}{k_{B}T}}$$
b)
$$Z_{1} = \sum_{E} g(E)e^{-E\beta}$$
where g is the degeneracy factor.
$$Z_{1} = \sum_{n} (n+1)e^{-ne\beta}$$
Geometric series with $x = e^{-e\beta}$.
 $\rightarrow Z_{1} = \frac{1}{(1 - e^{-e\beta})^{2}}$
c)
 $\langle E \rangle = -\frac{\partial \ln Z_{1}}{\partial \beta} = 2\frac{\partial}{\partial \beta} (\ln(1 - e^{-e\beta})) = \frac{2e}{e^{e\beta} - 1}$
 $T \rightarrow 0, \ \epsilon\beta \rightarrow \infty, \ e^{e\beta} \gg 1.$
 $\langle E \rangle \approx 2ee^{-e\beta} \rightarrow 0$
100% probability of being in the lowest state.

$$T \to \infty$$
, $e^{\varepsilon\beta} \to 1 + \frac{\varepsilon}{kT}$

 $\langle E \rangle \rightarrow 2k_{\rm B}T$. System with 4 degrees of freedom. What you would expect for a 2D harmonic oscillator. d) $c_v = \frac{\partial E}{\partial T}$ Low temp limit. Use $E = 2\varepsilon e^{-\varepsilon\beta}$. $\rightarrow c_v = 7.4 \times 10^{-7} k_B$ 4) $\dot{F} = \gamma L$ $dW = Fdx = \gamma Ldx = \gamma dA$ $dE = TdS + \gamma dA \qquad TdS + \Gamma dL$ TdS – mdB F = E - TS $dF = -SdT + \gamma dA$ $S = -\frac{\partial F}{\partial T} \Big|_{A}$ $\gamma = \frac{\partial F}{\partial A} \bigg|_{T}$ b) Aside: $Z = \int D(k) e^{-\varepsilon(k)\beta} dk \qquad \varepsilon(k) = \frac{\hbar^2 k^2}{2m} \text{ or } \hbar ck$ $D(k) = \frac{A}{\pi} k dk$ in 2D. $\frac{V}{2\pi^2}k^2dk$ in 3D. Question; $F = -kT \ln Z_N$ where $Z_N = \frac{(Z_1)^N}{N!}$ c) Non-relativistic $\gamma = -\frac{NkT}{A}$ $\gamma A = -NkT$ is the equation of state for a 2D gas.

E = NkT 2 degrees of freedom, quadratic.

Relativistic; $\gamma = -\frac{NkT}{A}$ E = 2NkT equipartition doesn't hold as they are not quadratic degrees of freedom.

2002, question 4;

It is not permissible to use $Z_N = \frac{(Z_1)^N}{N!}$ in this question. Just count the states and their energies, and write down the partition function as a sum.