

Part II Thermal & Statistical Physics

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Relevant websites:

<http://www-teach.phy.cam.ac.uk/teaching/webpages.php>

<http://www.bss.phy.cam.ac.uk/~emt1000/statphys.html>

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Part II Thermal & Statistical

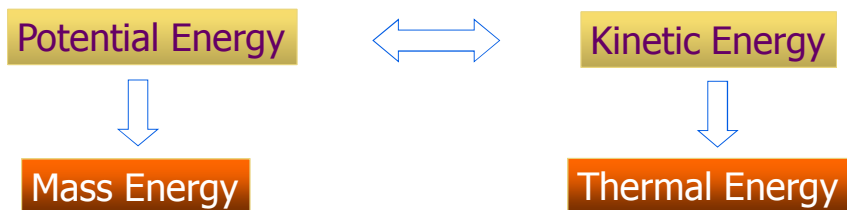
Energy

Over-arching concept ...

Often-misused concept ...

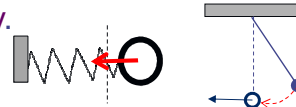
Physical “definition”: there exists a certain scalar quantity that does not change in all the possible transformations that Nature undergoes.

This is essentially an abstract mathematical constraint, but we really can't tell what energy “is”...



Dissipation of energy

In most areas of physics we only consider the situations where the total energy of a given system was conserved. The forces may have done some **work**, but it was possible to convert it back into **potential energy**.



In many situations, however, some of the work will be “lost”. Where would the energy go, if there is a universal Law of conservation of energy?

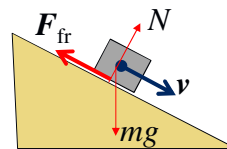
We say it converts into “heat”. One often thinks that “heat” is just the form of **kinetic energy** of many particles – but since there are so many of them (10^{23} in a spoon of water) we have no hope of harvesting this energy back... so it is considered “lost”.

Dissipation of energy

This loss of energy into heat is called “energy dissipation”.

It is a result of **wet friction** (or “dissipative friction”), which in most cases is a force proportional, and opposite in direction to the velocity:

$$\mathbf{F}_{\text{friction}} = -\gamma \mathbf{v}$$



Compare this with the **dry friction** (resistance), which is $\mathbf{F}_{\text{friction}} = -\mu \mathbf{N}$

The force of friction is directly proportional to the applied load. (Amontons 1st Law)

The force of friction is independent of the area of contact. (Amontons 2nd Law)

The force of friction is independent of the sliding velocity. (Coulomb's Law)

Rate of dissipation

Let us calculate the power loss in an oscillator (an example):



$$m \ddot{x} = -k x - \gamma v + F(t)_{\text{external}}$$

$$P = F(t) \frac{dx}{dt} = \left(m \frac{d^2 x}{dt^2} + k x + \gamma \frac{dx}{dt} \right) \frac{dx}{dt}$$

$$P = F_{\text{ext}} \cdot v = \frac{d}{dt} \left[\frac{m v^2}{2} + \frac{k x^2}{2} \right] + \gamma \left(\frac{dx}{dt} \right)^2$$

Which means: you have to spend some external power to make a particle moving against friction! If you don't ($P=0$)

– then the rate of energy loss is: $\frac{d}{dt} [\text{Total Energy}] = -F_{\text{fric.}} \cdot v$

“loss of energy”

heat

Work and Heat

The First Law of thermodynamics states:

“Energy is conserved when heat is taken into account”

In more quantitative terms, we claim that any change of **internal energy** of any system (which we now call U) is converted into **work** and the rest is released as **heat**:

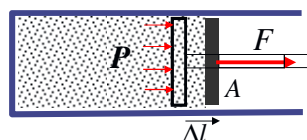
$$\Delta U = \Delta W + \Delta Q$$

If you remember, the work (interpreted as the change of P.E. to be specific) was determined as $\Delta W = -F \cdot \Delta x$

It is common to start the subject of **thermodynamics** with the analysis of gases, so the force is what acts on the piston of area A :

$$\Delta W = -F \cdot \Delta x$$

$$\text{So: } \Delta U = \Delta Q - PdV$$

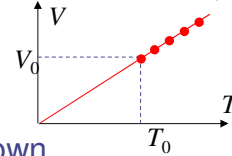


Ideal gas: equation of state

Boyle (1662): at fixed temperature $PV = \text{constant}$

Charles (1787): at fixed mass of gas $V = V_0 + \text{constant} \cdot (T - T_0)$

Extrapolating this linear relation, scientists very early have determined a “zero temperature” at which $V=0$, which in today’s Celsius scale is at $T = -273\text{C}$.



A similar linear P - T relationship was also known

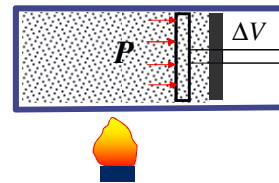
(Amontons 1702) and so, this required $PV = \text{constant} \cdot T$

Finally, Avogadro (1811→1860) determined the constant, which had to be proportional to the amount of gas. He introduced a mol:

A *mol* is the mass in grams of a substance which is equal to its molecular weight. Each *mol* contains exactly the same number of particles, $N_A = 6 \cdot 10^{23}$!

$$PV = nR \cdot T$$

Total amount of particles is: $N = nN_A$



Heat capacity

One of the basic properties of all forms of matter in response to heat is that of **heat capacity**.

The heat capacity describes the change in temperature of a substance when it is supplied with a given amount of heat.

$$\Delta Q = C \cdot \Delta T$$

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

But most materials (especially gas) can also expand on heating. So we must specify in what conditions the heat capacity is measured, e.g. at constant volume or at constant pressure

$$C_v = \left(\frac{dQ}{dT} \right)_V \quad C_p = \left(\frac{dQ}{dT} \right)_P$$

The difference between them is the work ($-PdV$) on expanding the body:

$$V=\text{constant: } dQ = dU = C_v dT$$

$$P=\text{constant: } dQ = dU + PdV = C_v dT + nR dT = (C_v + nR) dT$$

Temperature and Entropy

Entropy (Clausius 1850, Gibbs, Boltzmann) is a measure of the unavailability of a system's energy to do work (see 1st law $\Delta U = \Delta W + \Delta Q$). In simple terms, the entropy S is the “heat per unit temperature”:

$$\Delta S = \frac{\Delta Q}{T} \quad \text{or} \quad dQ = T \cdot dS$$

However, the modern (primary) definition of entropy is from statistical principles. This is often called “Boltzmann entropy” and is defined as $S = k_B \ln \Omega$

where Ω is the number of states the system can explore

The Second Law of thermodynamics states that the entropy of an isolated system can only increase with time ($\Delta S > 0$) and approaches its maximal value in equilibrium.

→ *Heat cannot spontaneously flow from a material at lower temperature to a material at higher temperature.*

Variable particle number

Consider a gas in a box – change particle number ($N \rightarrow N + dN$) while keeping the volume constant ($dV = 0$). If this addition was done **reversible**, that is, not creating heat ($dQ = TdS = 0$), then the increase in the energy of this gas:

$$\Delta U = \mu \Delta N$$

This defines the **chemical potential** $\mu = \left(\frac{\partial U}{\partial N} \right)_{v,s}$

In summary, for an arbitrary process capable of changing the volume of gas (i.e. do mechanical work), converting some of the energy into heat, and also exchanging particles – we have the energy increment:

$$dU = TdS - pdV + \mu dN$$

Other sources of energy

“Paramagnetic Salt” is a model system where each atom is fixed on a lattice and carries a magnetic moment (spin=1/2), independently of its neighbours.

Without an external field the up-down spin energy levels are the same, but the magnetic field splits the degeneracy: $U = -M \cdot B = (N_{\uparrow} - N_{\downarrow})mB$

$$\begin{aligned} \epsilon_{\uparrow} = \epsilon_{\downarrow} = 0 & \begin{cases} \epsilon_{\uparrow} = mB \\ \epsilon_{\downarrow} = -mB \end{cases} \end{aligned}$$

$$dU = TdS - M \cdot dB$$



Please watch the dimensionality... People (and textbooks) are often flippant about the difference between “energy” and “energy density” - and in this case: the “magnetic moment” and “magnetisation”...

Other sources of energy

“Simple Harmonic Oscillator” is a workhorse of physics (this is because any potential energy is quadratic near equilibrium).

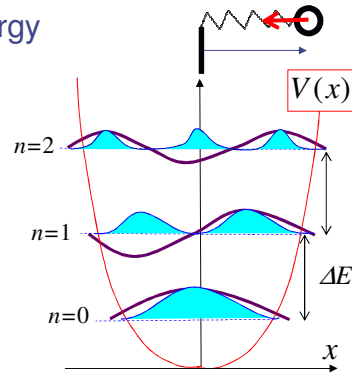
For the potential $V(x) = \frac{1}{2} a x^2$ the n^{th} energy level of the excited oscillation has the value:

$$\epsilon_n = \hbar\omega(n + \frac{1}{2})$$

where the natural frequency $\omega = \sqrt{a/m}$

Total energy of an assembly of such oscillators is then

$$U = \sum_i \hbar\omega(n_i + \frac{1}{2})$$

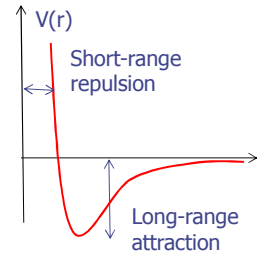


Other sources of energy

Van der Waals gas is an empirical model system that takes into account the pair interactions between particles of gas.

$$\left(p + \frac{N^2 a}{V^2} \right) (V - Nb) = N k_B T$$

$$\text{or } p = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}$$



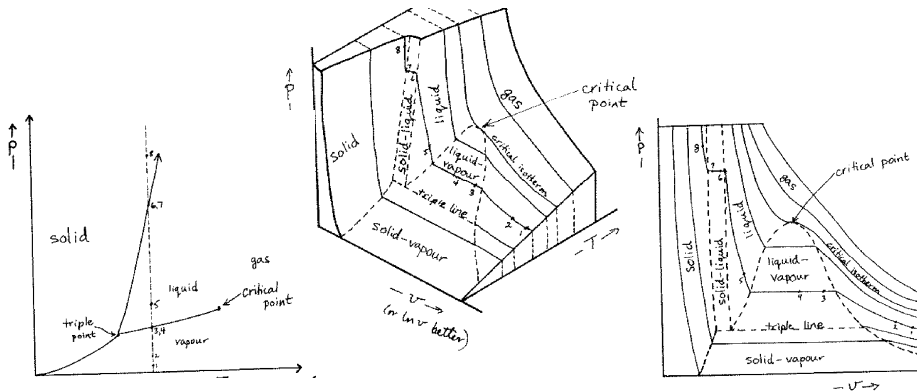
We shall use this model in several contexts in this course. Here let's just note that with a potential like this, the energy can be stored as kinetic or potential form – and one can convert kinetic ↔ potential energy, for example, by Joule expansion.

Equation of state

The equation of state is a relationship between (p, V, T) – for instance:

$$pV = N k_B T \quad \text{or} \quad p = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2} \quad \text{but not} \quad pV^\gamma = \text{const}$$

Such a relationship describes a surface in a 3D (p, V, T) space!



Thermodynamic variables

Thermodynamic variables are observable properties of any system. They fall into two categories, **intensive** and **extensive**:

<u>System</u>	<u>Intensive</u>	<u>Extensive</u>
Linear spring	F force	x displacement
Gas	p pressure	V volume
Particle exchange	μ chemical potential	N number
Surface film	γ surface tension	A area
Electrostatic	V potential	q charge
Magnetic	B "magnetic field"	M "magnetic moment"
...any...	T temperature	S entropy

Intensive and extensive variables form conjugate pairs, whose product has the dimensionality of (and therefore represents) energy,

$$\text{e.g. } \Delta U = \Delta Q + \Delta W = T \cdot \Delta S - P \cdot \Delta V$$

Other forms of work:

$$\Delta W = -F \cdot \Delta x \quad \Delta W = \gamma \cdot \Delta A \quad \text{etc.}$$

Thermodynamic potentials

We have just seen, for the mean internal energy of the system: $\Delta U = T \cdot \Delta S - p \cdot \Delta V$ or $dU = T \cdot dS - p \cdot dV$

This means that (S, V) are the **natural variables** of $U(S, V)$ which means that to determine the value of U we must measure S and V (or "keep them under control").

But in some situations (e.g. in an open container) it may be hard to control/measure the volume, instead the pressure P would be a more natural variable?

Introduce **enthalpy**: $H = U + pV$

$$\text{then } dH = dU + d(pV) = TdS - pdV + pdV + Vdp = TdS + Vdp$$

We conclude that the function $H = H(S, p)$, with the conjugate pair (p, V) "switched" – that is, now V plays the role of a "force" while P the "displacement"

Thermodynamic potentials

What we have just seen: $U(S,V) \rightarrow H(S,p)$ is one example of a general “Legendre transformation” switching between the “force” and “displacement” within pairs of thermodynamic variables.

In many situations it may be hard to control/measure the entropy, instead the temperature T would be a more natural variable?

Introduce **free energy**: $F = U - TS$

$$\text{then } dF = dU - d(TS) = TdS - pdV - TdS - SdT = -SdT - pdV$$

We conclude that the function $F = F(T,V)$. In the similar way we may introduce the **Gibbs free energy**: $G = H - TS = F + pV$

$$dG = dF + d(pV) = -TdS - pdV + pdV + Vdp = -SdT + Vdp$$

Thermodynamic derivatives

Thermodynamic potentials are different forms of energy, expressed in appropriate “natural variables”. We have just seen four: $U(S,V) \rightarrow H(S,p) \rightarrow G(T,p) \rightarrow F(T,V)$.

$$\begin{aligned} dU &= TdS - pdV & dH &= TdS + Vdp \\ dG &= -SdT + Vdp & dF &= -SdT - pdV \end{aligned}$$

This means that we can have partial derivatives, in each case determining the corresponding thermodynamic force:

$$\text{e.g. } T = \left(\frac{dU}{dS} \right)_{V=\text{const}} = \left(\frac{dH}{dS} \right)_{p=\text{const}} \quad p = - \left(\frac{dU}{dV} \right)_{S=\text{const}} = - \left(\frac{dF}{dV} \right)_{T=\text{const}}$$

What will happen if we take a derivative with respect to a “wrong” variable?

$$\begin{aligned} \text{e.g. } \left(\frac{dH}{dV} \right)_{S=\text{const}} &= \frac{TdS + Vdp}{dV} \quad \text{so} \quad \left(\frac{dH}{dV} \right)_{S=\text{const}} = V \left(\frac{dp}{dV} \right)_{S=\text{const}} \\ \left(\frac{dU}{dT} \right)_{V=\text{const}} &= T \left(\frac{dS}{dT} \right)_{V=\text{const}} = C_V \quad \text{so} \quad dS = \frac{C}{T} dT \end{aligned}$$

Maxwell relations

Thermodynamic potentials are different forms of energy, expressed in appropriate “natural variables”. We have seen four: $U(S, V) \rightarrow H(S, p) \rightarrow G(T, P) \rightarrow F(T, V)$.

$$\begin{aligned} dU &= TdS - pdV & dH &= TdS + Vdp \\ dG &= -SdT + Vdp & dF &= -SdT - pdV \end{aligned}$$

One can evaluate a second derivative in two ways:

e.g. $\left(\frac{d^2U}{dS dV}\right) = \left(\frac{dT}{dV}\right)_S = -\left(\frac{dp}{dS}\right)_V$ One of Maxwell relations

$$\left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P \quad \left(\frac{dS}{dV}\right)_T = \left(\frac{dp}{dT}\right)_V \quad \left(\frac{dT}{dP}\right)_S = \left(\frac{dV}{dS}\right)_P$$

Do you notice the pattern?

1) Which two variables \rightarrow 2) Which potential \rightarrow 3) What sign?

Analytic Methods

Chain rule: $\left(\frac{dx}{dy}\right)_z = \left(\frac{dx}{du}\right)_z \left(\frac{du}{dy}\right)_z$ Maxwell rel: $\Pi = \Pi(x, y): \left(\frac{dX}{dy}\right)_x = \pm \left(\frac{dY}{dx}\right)_y$

Reciprocity theorem: $\left(\frac{dx}{dy}\right)_z = -\left(\frac{dx}{dz}\right)_y \left(\frac{dz}{dy}\right)_x$

Entropy of an ideal gas

Suppose $S=S(p, T)$ $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_p dp = C_p \frac{dT}{T} - Nk_B \frac{dp}{p}$$

Now integrate:

$$S = C_p \ln T - Nk_B \ln p + \text{const}$$

$$S = Ns_0 + Nk_B \left[\ln T^{5/2} - \ln \frac{Nk_B T}{V} \right] = Nk_B \ln \left(\text{const} \cdot \frac{VT^{3/2}}{N} \right)$$

C_p and C_v once again...

Let us use this as another example of calculation:

For any function, such as S(T,V): $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

Now evaluate

$$C_p = T \left(\frac{dS}{dT}\right)_p = T \left(\frac{dS}{dT}\right)_V + T \left(\frac{dS}{dV}\right)_T \left(\frac{dV}{dT}\right)_p$$

$$C_p = C_v + T \left(\frac{dp}{dT}\right)_V \left(\frac{dV}{dT}\right)_p$$

We **stop** as soon as the combination (P,V,T) is reached

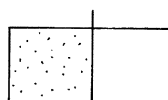
If ideal gas, then: $\left(\frac{dp}{dT}\right)_V = \frac{Nk_B}{V}$; $\left(\frac{dV}{dT}\right)_p = \frac{Nk_B}{p}$

$$\text{so } C_p = C_v + Nk_B$$

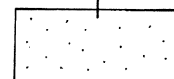
Joule expansion

Isolated system, so $\Delta U=0$. During the expansion $V_1 \rightarrow V_2$

$$T_2 - T_1 = \int_{V_1}^{V_2} \left(\frac{\partial T}{\partial V}\right)_U dV$$



initial



final

$$\left(\frac{dT}{dV}\right)_U = - \left(\frac{dT}{dU}\right)_V \left(\frac{dU}{dV}\right)_T = - \frac{1}{C_v} \left. \frac{TdS - pdV}{dV} \right|_T = - \frac{1}{C_v} \left[T \left(\frac{dp}{dT}\right)_V - p \right]$$

We **stop** as soon as the combination (P,V,T) is reached

If ideal gas, then: $T \left(\frac{dp}{dT}\right)_V = \frac{Nk_B T}{V} = p$; so $\Delta T = 0$

Try to evaluate this for a non-ideal gas, e.g. $p = \frac{Nk_B T}{V-b} - \frac{N^2 a}{V^2}$

Summary so far.....

The 2nd Law of thermodynamics:

“Entropy of a closed system increases to a maximum in equilibrium”

$$dQ = TdS \quad S = k_B \ln \Omega$$

Thermodynamic variables come in *conjugate pairs* of “force”–“variable”. A given set defines the corresponding thermodynamic potential:

“Enthalpies”

“Free energies”

$$U, H, \dots = TdS + \{ Ydx \} \quad F, G, \dots = -SdT + \{ Ydx \}$$

Mean energy $U(S, V, N)$ is the only potential that depends on all the extensive variables! Hence $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$

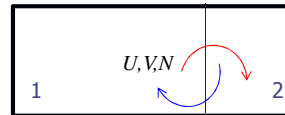
Tools of analytical thermodynamics:

Maxwell relations – Reciprocity – Chain rule → stop at (P, V, T)

Internal equilibrium

Let us consider a closed system, fully isolated from outside. The 2nd Law demands that the change of entropy of this system can only be positive, $\Delta S > 0$, and it should be maximum in equilibrium.

Let's divide the system into two parts: they can exchange U, V and N



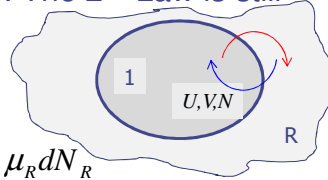
$$\begin{aligned} dS_{\text{tot}} = dS_1 + dS_2 &= \frac{dU_1 + p_1 dV_1 - \mu_1 dN_1}{T_1} + \frac{dU_2 + p_2 dV_2 - \mu_2 dN_2}{T_2} \\ &= \frac{dU_1 + p_1 dV_1 - \mu_1 dN_1}{T_1} + \frac{-dU_1 - p_2 dV_1 + \mu_2 dN_1}{T_2} \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 \end{aligned}$$

Between any two parts inside closed system:

$$T_1 = T_2; \quad p_1 = p_2; \quad \mu_1 = \mu_2$$

Equilibrium in open systems

A much more relevant problem is about a system interacting with a **reservoir** (the rest of the Universe). The 2nd Law is still in action, only it applies to the whole: as before, the two parts of the (closed) Universe can exchange U , V and N



$$dS_{\text{tot}} = \frac{dU_1 + p_1 dV_1 - \mu_1 dN_1}{T_1} + \frac{dU_R + p_R dV_R - \mu_R dN_R}{T_R}$$

$$= \frac{dU_1 + p_1 dV_1 - \mu_1 dN_1}{T_1} + \frac{-dU_1 - p_R dV_1 + \mu_R dN_1}{T_R}$$

$$= dS + \frac{-dU - p_R dV + \mu_R dN}{T_R} = \frac{1}{T_R} (T_R dS - dU - p_R dV + \mu_R dN)$$

since:
 $\Delta X_1 = -\Delta X_2$

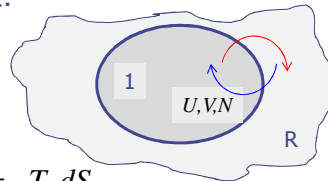
So far, no assumptions were made, but surely the “reservoir” is very big...

Availability

Now assuming the **reservoir** is so big that it “doesn’t notice” any changes that our system inflicts on it:

$$dT_R = dp_R = d\mu_R = 0$$

$$\text{So: } p_R dV = d(p_R V); \text{ etc.}$$



We can now define a new object for our system, called the **availability** A , as: $dA = -T_R dS_{\text{tot}}$

$$dS_{\text{tot}} = \frac{1}{T_R} (T_R dS - dU - p_R dV + \mu_R dN)$$

$$\text{Meaning that: } dA = -T_R dS + dU + p_R dV - \mu_R dN$$

$$dA = (T - T_R) dS - (p - p_R) dV + (\mu - \mu_R) dN$$

- Availability is the function of system variables (U, S, V, N)
- Since R-variables are constant: $A = U - T_R S + p_R V - \mu_R N$
- In equilibrium, availability is at its minimum: $dA \leq 0$

Availability

$$dA \equiv -T_R dS_{\text{total}} = dU - T_R dS + p_R dV - \mu_R dN$$

A particularly important aspect of the 2nd Law in the form of the **availability reaching its minimum** when the system is at equilibrium with the (big) reservoir is that – for any variable X that characterises our system – the **probability** is:

$$P(X) \propto \exp\left(-\frac{A(X)}{k_B T}\right)$$

Now consider our system at constant T, V and N . Then:

$$\begin{aligned} dA &= dU - T_R dS + p_R dV - \mu_R dN \Big|_{T,V,N} \\ &= dU - T dS = d(U - TS) \end{aligned}$$

$$= dF(T, V, N) \quad \dots \text{the Helmholtz free energy, which has } T, V \text{ and } N \text{ as its proper variables.}$$

Check yourself: $dA \Big|_{T,p,N}$; $dA \Big|_{S,p,N}$; or $dA \Big|_{S,V,N}$

Phase equilibrium

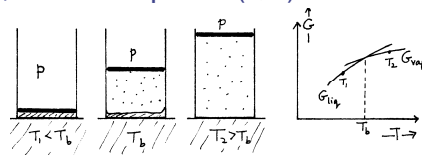
If we are looking at an open system, then it has to be under the (p, T) control, and so has to be described by $G(T, p, N)$, e.g., in contrast to a fixed-volume vessel, which requires (V, T) - and F .

When the two phases coexist, the full potential is $G = G_l + G_v$

In equilibrium: $dA = dG \Big|_{T,p} = 0$

$$dG_l = -S_l dT + V_l dp + \mu_l dN_l \quad = -dG_v = S_v dT - V_v dp - \mu_v dN_v$$

Now, $dT=dp=0$ and $dN_l = -dN_v$, so $\mu_l = \mu_v$

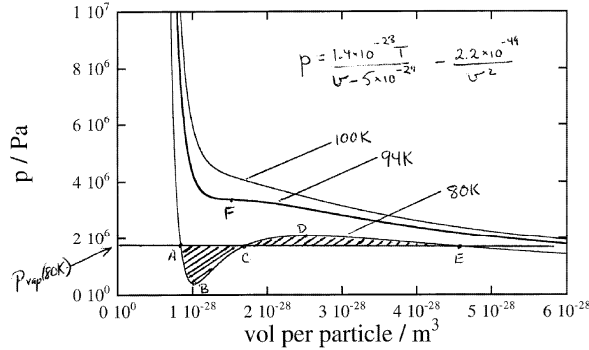


This is a part of our earlier equilibrium condition set for the two parts of a system. Every time when there is a particle exchange, we find μ matching between the subsystems.

Phase equilibrium

Look at the familiar example of VdW isotherms and the resulting gas-liquid transition. On the (p, V) plane we have:

And at a temperature below the critical point F there is a region of coexistence. How can we find the pressure at which this occurs, for a given T ?



$$\mu_l(A) = \mu_v(E)$$

$$\begin{aligned} \mu_v(E) &= \mu_l(A) + \int_A^E \left(\frac{\partial \mu}{\partial p} \right)_T dp \\ &= \mu_l(A) + \int_A^E v dp = 0 \end{aligned}$$

The Gibbs-Duhem equation:

$$d\mu = -s dT + v dp$$

The equal area rule gives the vapour pressure $p_v(T)$

Summary so far.....

Availability – the energy function that reflects the balance between the system and the reservoir:

$$\begin{aligned} dA &= dU - T_R dS + p_R dV - \mu_R dN \\ &= (T - T_R) dS - (p - p_R) dV + (\mu - \mu_R) dN \end{aligned}$$

The system interacting with a reservoir has a probability to have the value of its variable X given by $P(X) \propto \exp\left(-\frac{A(X)}{k_B T}\right)$

When you control a certain set of variables of your system, e.g. (X, Y) , then a small increment in availability is equal to the increment of the corresponding T.D. potential $\Pi(X, Y)$

$$\text{e.g. } dA \Big|_{T, V, N} = dF(T, V, N)$$

Microstates and Macrostate

Microstate is a particular configuration (*realisation*) of the system with certain values of microscopic parameters, e.g.

- set of solutions of a Schrödinger equation with an energy E_i
- positions and velocities of particles in a classical gas
- an arrangement of spins in a paramagnetic lattice

Macrostate is a set of all microstates which has a certain mean energy U and is subject to any other constraint: V, N , etc.

For an isolated system, all microstates compatible with the given constraints are equally likely to occur

Statistical mechanics is all about finding
the number microstates: $\Omega(U, V, N)$

$$\frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial U} \right)$$

The Boltzmann entropy: $S = k_B \ln \Omega$

Statistical entropy

The entropy (*heat per unit temperature*) is the measure of irreversibility, of chaos, of disorder – quantitatively measured as “number of configurations”: $S = k_B \ln \Omega$

Examples: 1) Identical particles in a box: $\Omega = N!$

$$S = k_B \ln(N!) \approx (N \ln N - N) \quad \text{using Stirling approximation:}$$

$$N! \approx N^N e^{-N}$$

2) Several populations ($N_1 + N_2 + N_3 + \dots = N$): $\Omega = \frac{N!}{N_1! N_2! N_3! \dots}$

$$S = k_B \ln \Omega \approx k_B \left(N \ln N - N - \sum_{i=1,2,3,\dots} [N_i \ln N_i - N_i] \right)$$

$$= k_B \left(\sum_{i=1,2,3,\dots} N_i [\ln N - \ln N_i] \right) = -N k_B \sum_{i=1,2,3,\dots} \frac{N_i}{N} \ln \frac{N_i}{N}$$

“Gibbs entropy”: $S = -N k_B \sum_i P(i) \ln P(i)$

Canonical ensemble

Microcanonical ensemble is just a collection of thermally isolated systems, all with the same energy – and hence the same probability of occurrence.

Canonical (or standard) ensemble is a collection of systems all connected to a reservoir (and possibly to each other) so that they can exchange energy. So the mean energy of this ensemble U fluctuates. We have a definite number: N .

There will also be a **grand canonical ensemble** (for the lack of a better name), in which the systems are also allowed to exchange particles, so that both U and N fluctuate (while the intensive variables T and μ are fixed).

Gibbs derives the probability that a chosen subsystem (i) to be found in a microstate E_i :

$$P(i) = \frac{1}{Z} e^{-E_i/k_B T}$$

Partition function

The Boltzmann factor determines the probability for a system to be found in a state with energy E_i

$$P(i) = \frac{1}{Z} \cdot e^{-E_i/k_B T} \quad \text{where the normalization factor} \quad Z = \sum_{\text{all states } \{i\}} \exp\left(-\frac{E_i}{k_B T}\right)$$

This is not just a mere normalization, but a very important object in statistical physics, called the partition function.

It encodes the statistical properties of the whole system.

Its significance is mainly in its role in defining the **free energy**, a most important form of **thermodynamic potential energy**,

expressed as $F = -k_B T \ln Z$ or $Z = e^{-F/k_B T}$

We can find the average energy of the system

$$U = \langle E \rangle = \sum_i E_i P(i) = \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z \quad \text{with } \beta = 1/k_B T$$

Maximum probability

It is now quite obvious that the maximum probability $P(i)$ has the microstate with: [1] the lowest energy (E_i), and [2] the largest “degeneracy” (N_i), i.e. the number of states with the same energy:

$$\begin{aligned} Z &= \sum_{\text{all states}} e^{-E_i/k_B T} = \sum_{\text{microstates } \{E_i\}} e^{-E_i/k_B T} \cdot (N_i!) = \sum_{\{E_i\}} e^{-E_i/k_B T} \cdot e^{\ln \Omega_i} \\ &= \sum_{\{E_i\}} e^{-\frac{1}{k_B T}(E_i - k_B T \ln \Omega_i)} = \sum_{\text{microstates}} e^{-\frac{1}{k_B T}(E_i - TS_i)} = \sum_{\text{microstates}} Z_i \end{aligned}$$

Maximization of the partition function, or (equivalently!) minimization of the free energy $F = U - TS$ is the main driving force in all Nature.

Average (potential) energy $U \rightarrow$ **minimum?** } In balance...
 Average entropy $S \rightarrow$ **maximum?**

Summary so far.....

The maximum probability $P(i)$ is for the microstate with: [1] the lowest energy (E_i), and [2] the largest “degeneracy” (i.e. the number of states with the same energy)

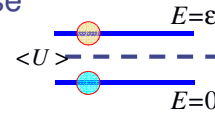
$$\begin{aligned} Z &= \sum_{\text{all states}} e^{-E_i/k_B T} = \sum_{\text{microstates } \{E_i\}} e^{-\frac{1}{k_B T}(E_i - k_B T \ln \Omega_i)} = \sum_{\text{microstates}} Z_i \\ P[i] &= \frac{1}{Z} e^{-\frac{1}{k_B T}(E_i - TS_i)} \end{aligned}$$

Maximization of the partition function, or (equivalently!) minimization of the free energy $F_i = E_i - TS_i$ is the main driving force in all natural processes

Average energy $U \rightarrow$ **minimum** } In balance...
 Average entropy $S \rightarrow$ **maximum**

Two-level system

As one simplest example of a real physical case that we can analyze within proper statistical mechanics, let's consider a 2-level system:



The object (e.g. electron in an atom, or a spin) can exist on either of the two levels:

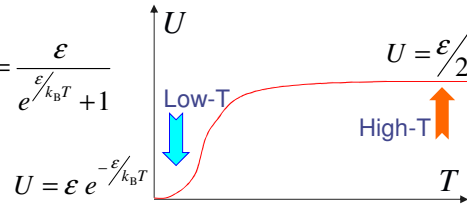
$$Z = \sum_{\text{all states}} e^{-E_i/k_B T} = 1 + e^{-\epsilon/k_B T}$$

Once the partition function is found, you know everything about the system!

Route 1: mean energy $U = -\frac{\partial}{\partial \beta} \ln Z$ where $\beta = 1/k_B T$

Here we have

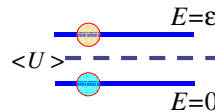
$$U = \frac{1}{1 + e^{-\beta \epsilon}} \left(-\frac{\partial}{\partial \beta} e^{-\beta \epsilon} \right) = \frac{\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} = \frac{\epsilon}{e^{\epsilon/k_B T} + 1}$$



Two-level system

Partition function $Z = 1 + e^{-\epsilon/k_B T}$

Once the partition function is found, you know everything about the system!



Route 2: free energy $F = -k_B T \ln Z = -k_B T \ln(1 + e^{-\epsilon/k_B T})$

Recall thermodynamic potential properties: $dF = -SdT - PdV$

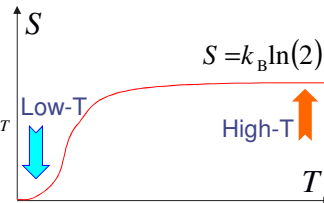
$$S = -\left(\frac{dF}{dT}\right)_V = k_B \ln(1 + e^{-\epsilon/k_B T}) + \frac{k_B T}{1 + e^{-\epsilon/k_B T}} \frac{d}{dT} e^{-\epsilon/k_B T}$$

$$= k_B \ln(1 + e^{-\epsilon/k_B T}) + \frac{\epsilon}{T} \frac{1}{e^{\epsilon/k_B T} + 1}$$

At low temperature $U \rightarrow \text{min}$ "wins"; entropy "loses out"...

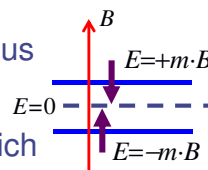
$$S = \frac{\epsilon}{T} e^{-\epsilon/k_B T}$$

At high temperature $S \rightarrow \text{max}$ "wins"; energy follows...



Paramagnetism

Paramagnetism, in its simplest form is analogous to the 2-level system:



Consider a system (e.g. crystalline solid) in which each atom has a magnetic moment [spin]: $m = \mu_M s$. Assume the spins do not interact (each on its own).

Quantum mechanics (selection rules for a spin $s = 1/2$) allows only in 2 states for spins: “up” and “down” with the same energy. But if an external magnetic field B is imposed, the “up” and “down” states have different energy!

$$Z_1 = \sum_{\text{all states}} e^{-E_i/k_B T} = e^{mB/k_B T} + e^{-mB/k_B T} = 2 \cosh\left(\frac{mB}{k_B T}\right)$$

But there are N such atoms in the system, all independent: $Z = Z_1^N$

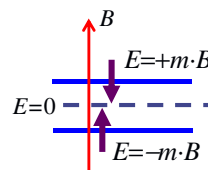
Once the partition function is found, you know everything about the system!

Paramagnetism

Partition function $Z = \left(e^{mB/k_B T} + e^{-mB/k_B T} \right)^N$

Route 2: free energy

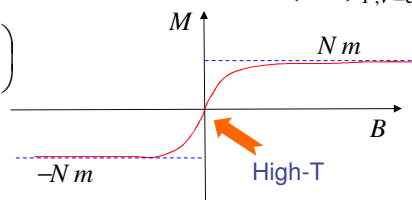
$$F = -N k_B T \ln\left(e^{mB/k_B T} + e^{-mB/k_B T} \right)$$



Magnetization M (exactly like dielectric polarization P) should be defined as the sum of all m -dipoles *per 1 volume*. It is an extensive thermodynamic variable, forming a conjugate pair with the (intensive) B -field (same with PdE): $dF = -SdT - PdV + MdB$ which sign?

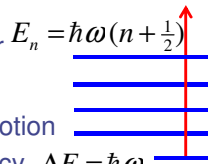
Average magnetization induced by an external B will be $M = (?) \left(\frac{dF}{dB} \right)_{T,V=\text{const}}$ determined by the appropriate thermodynamic derivative:

$$M = N k_B T \frac{d}{dB} \ln\left(e^{mB/k_B T} + e^{-mB/k_B T} \right) = N m \cdot \tanh\left(\frac{mB}{k_B T}\right)$$



Quantum oscillator

Oscillator (e.g. a vibrating molecular bond) has ∞ number of states (labeled by n) separated by equal energy gaps.



Whether we can “see” this discrete nature of oscillator motion depends on our equipment: if it is sensitive to the accuracy $\Delta E = \hbar \omega$

So, from statistical point of view, we look for the partition function:

$$Z = \sum_{n=0}^{\infty} e^{-\frac{\hbar \omega (n+1/2)}{k_B T}}$$

Geometric progression $\rightarrow Z = e^{-\frac{\hbar \omega}{2k_B T}} \sum_{n=0}^{\infty} a^n = \frac{e^{-\frac{\hbar \omega}{2k_B T}}}{1 - e^{-\frac{\hbar \omega}{k_B T}}} = \frac{1}{e^{\frac{\hbar \omega}{2k_B T}} - e^{-\frac{\hbar \omega}{2k_B T}}}$

Low-temperature limit:

$$Z \approx e^{-\frac{\hbar \omega}{2k_B T}}$$

Mean energy: $U = -\frac{\partial}{\partial \beta} \ln Z$

“Zero-temperature oscillations” $\approx \frac{\partial}{\partial \beta} \left(\frac{\hbar \omega}{2} \beta \right) = \frac{1}{2} \hbar \omega$

High-temperature limit:

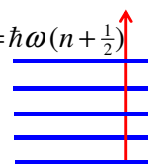
$$Z \approx k_B T / \hbar \omega$$

$$U \approx \frac{\partial}{\partial \beta} \ln(\hbar \omega \beta) = \frac{1}{\beta} = k_B T$$

“Classical limit”, $C_V = k_B$

Quantum oscillator

Oscillator (e.g. a vibrating molecular bond) has ∞ number of states (labeled by n) separated by equal energy gaps.

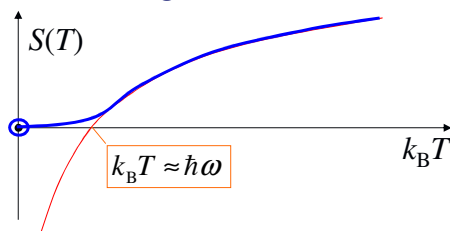


Once we know the partition function, we know all properties of our system...

Low-temperature limit: $Z \approx e^{-\frac{\hbar \omega}{2k_B T}}$

Free energy: $F = -k_B T \ln Z \approx \frac{1}{2} \hbar \omega$

Entropy is zero in the “ground state”: $F=U$



High-temperature limit: $Z \approx k_B T / \hbar \omega$

$$F \approx -k_B T \ln \left(\frac{k_B T}{\hbar \omega} \right)$$

Find entropy in this classical limit

$$S = -\frac{\partial F}{\partial T} = k_B \ln \left(\frac{k_B T}{\hbar \omega} \right) + k_B T \left(\frac{1}{T} \right) = k_B \ln \left(e \cdot \frac{k_B T}{\hbar \omega} \right)$$

Take a deep breath.

... Stretch.

... We move forward

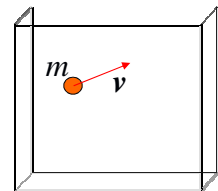
Continuous systems

So far we have seen how to handle physical systems in which we can enumerate different **microstates** (E_i and N_i) – and find the partition function, which in turn makes accurate predictions about average (most probable) state of such systems.

But the simplest(?) and most common object to study in thermodynamics is the **ideal gas**: $PV=Nk_B T$. Let's look at it:

Actually, N particles is far too many:
let's start with just one particle in a box!

$$Z = \sum_{\text{all states}} e^{-\frac{E_i}{k_B T}}$$



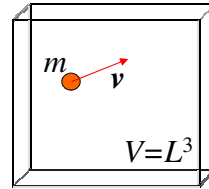
Volume $V=L^3$

We have two (related) difficulties:

(a) what is E , when the particle doesn't interact with anything,
and (b) how to count the "states"...

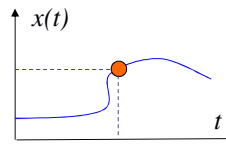
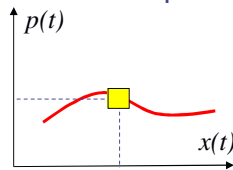
Phase space

Normally, by E we would want to mean the potential energy $W(x)$, which would have a “minimum” and the higher Boltzmann factor. But here there is no P.E. (only *kinetic energy*)



Normally, you would describe your system (here – just 1 particle) by assigning it a position, say, $x(t)$ if we look only on 1 dimension. But this is clearly not a full description!

Need velocity?...

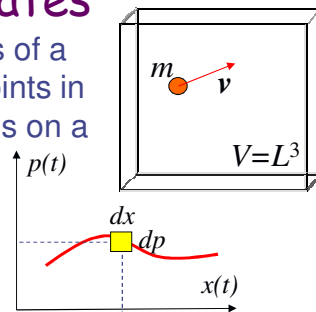


Introduce the “**phase space**”, the coordinate and the momentum along this axis, $x(t)$ and $p=mv$. An element of phase space, at a time t , gives a full predictive description of where it will be at $t+dt$

Continuous states

So we account for all the possible states of a particle by summing over all possible points in its phase space. Consider how to do this on a 1-dimensional example (along x -axis):

$$\sum_{\text{all states}} = \sum_{p_i, x_i} \rightarrow \int \frac{dx dp}{\Delta x \Delta p}$$



But note that the *sum* was non-dimensional, while the *integral* has dimensionality of $[\text{kg}\cdot\text{m}^2/\text{s}]$? The formal conversion of a sum into an integral requires dividing by the elementary “step of discretisation”. Here it is $\Delta x \Delta p$.

What is the smallest possible value $\Delta p \Delta x$ can take?

This result is worth remembering:
“the world is discrete in phase space”

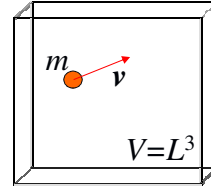
$$\sum_{\text{all states}} = \int \frac{dx dp}{(2\pi \hbar)} = \int dx \frac{dk}{2\pi}$$

$$2\pi \hbar$$

One particle in a box

We can now make progress: the single particle of mass m and momentum p has its statistical partition function:

$$Z_1 = \sum_{\text{all states}} e^{-E/k_B T} = \int \frac{d^3 x d^3 p}{(2\pi \hbar)^3} e^{-\frac{p^2}{2m k_B T}}$$



First of all notice that nothing under the integral depends on x , i.e. there is no potential energy $V(x)$: this is ideal gas!

$$Z_1 = V \cdot \int \frac{d^3 p}{(2\pi \hbar)^3} e^{-\frac{p^2}{2m k_B T}} = V \cdot \left(\int \frac{dp_x}{(2\pi \hbar)} e^{-\frac{p_x^2}{2m k_B T}} \right)^3 = V / \lambda^3$$

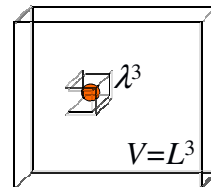
Secondly, instead of doing complicated 3-dimensional integrals, note that $p^2 = p_x^2 + p_y^2 + p_z^2$ and $d^3 p = dp_x dp_y dp_z$

This is a very important expression, and let's call it $1/\lambda$

One particle in a box

The particle of mass m and momentum p has its partition function:

$$Z_1 = \int \frac{d^3 x d^3 p}{(2\pi \hbar)^3} e^{-\frac{p^2}{2m k_B T}} = \frac{V}{\lambda^3}$$



This is how many ways you can "pack" the particle into this box! So what is this length scale λ ?

$$\frac{1}{\lambda} = \int_{-\infty}^{+\infty} \frac{dp}{2\pi \hbar} e^{-\frac{p^2}{2m k_B T}} = \frac{1}{2\pi \hbar} \sqrt{2\pi m k_B T} \quad \text{so} \quad \lambda = \sqrt{\frac{2\pi \hbar^2}{m k_B T}}$$

Recall the de Broglie wave length of a wave representation of a particle. Also recall the mean thermal velocity from the Maxwell distribution.

$$\lambda = \frac{2\pi \hbar}{p} = \frac{2\pi \hbar}{\langle mv \rangle} = \frac{2\pi \hbar}{m \cdot \sqrt{k_B T / m}} = \sqrt{\frac{(2\pi \hbar)^2}{m k_B T}}$$

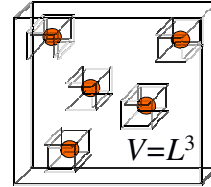
So we managed to "count" the possible states a free classical particle can have in the box – and the result is just: $Z=V/\lambda^3$

Classical ideal gas

One particle of mass m has its partition function:

What if we have N such particles, all independent of each other?

$$Z_1 = \frac{V}{\lambda^3} = V \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2}$$



$$Z_N = \frac{1}{N!} Z_1^N$$

But if all particles are exactly the same (indistinguishable) – we could not tell the difference between many configurations!

We now know everything about ideal gas

Route 1: Mean energy $U = -\frac{\partial}{\partial \beta} \ln Z_N = -\frac{\partial}{\partial \beta} [N \ln Z_1 - \ln(N!)]$

Using factorizing property of logarithms!

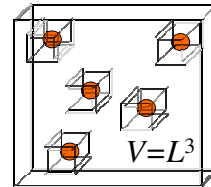
$$U = -N \frac{\partial}{\partial \beta} \ln \left[V \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \right] = -N \frac{\partial}{\partial \beta} \ln \left[\frac{1}{\beta^{3/2}} \right]$$

$$U = \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T \quad \text{-- This is actually correct!}$$

Classical ideal gas

The ideal gas of particles of mass m has

$$Z_N = \frac{Z_1^N}{N!} \quad \text{where} \quad Z_1 = \frac{V}{\lambda^3} = V \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2}$$



Route 2: Free energy

$$F = -k_B T \ln Z_N = -k_B T [N \ln Z_1 - N \ln N + N]$$

Using factorizing property of logarithms!

$$F = N k_B T \left[\ln \left(\frac{N \lambda^3}{V} \right) - 1 \right] = N k_B T \ln \frac{N \lambda^3}{V e}$$

Let's find the pressure: $P = -\left(\frac{dF}{dV} \right)_{T=\text{const}} = \frac{N k_B T}{V}$

Note: we could not find the ideal gas law from the mean energy U , which was in the "wrong variables" T, V !

Entropy is a bit of work: $S = -\left(\frac{dF}{dT} \right)_V = -N k_B \ln \frac{N \lambda^3}{V e} + \frac{3}{2} N k_B$

Grand partition function

In the same way, for a grand canonical ensemble, the probability for a given system to have energy E_i and a number of particles N_i (in contact with reservoir that maintains T, μ) is:

$$P(i) = \frac{1}{\Xi} \cdot \exp\left[-\frac{E_i - \mu N_i}{k_B T}\right] \quad \text{with the grand partition function}$$

$$\Xi = \sum_{N_i=0}^{TOTAL} \left\{ \sum_{\text{all states } \{i\}} \exp\left(-\frac{E_i - \mu N_i}{k_B T}\right) \right\}$$

There is a corresponding thermodynamic potential that needs to be minimised in equilibrium. It is called the **grand potential**:

$$\Phi = -k_B T \ln \Xi \quad \text{or} \quad \Xi = e^{-\Phi/k_B T}$$

Note that its natural variables are (T, V, μ) and it is obtained from $F(T, V, N)$ by the Legendre transformation: $\Phi = F - \mu N$

Grand potential

In the same way as we have analysed the canonical p.f. Z , by identifying a **free energy of a microstate** $E_i - TS_i$, let us re-order the grand-canonical summation and arrange the exponent:

$$\Xi = \sum_{N=0}^{TOTAL} \left\{ e^{\frac{\mu N}{k_B T}} \sum_{\text{all states } \{i\}} e^{-\frac{E_i}{k_B T}} \right\} = \sum_{\text{microstates } E_i} \left\{ \sum_{N_i} e^{-\frac{1}{k_B T} (E_i - k_B T \ln \Omega_i - \mu N_i)} \right\} = \sum_{\{E_i\}} e^{-\frac{1}{k_B T} \Phi_i}$$

The first observation is that one can have a “grand partition function” and a grand potential for a given microstate, if it can exchange particles with other microstates.

Secondly, as in the canonical ensemble, the minimum of Φ_i is the most probable microstate, and at sufficiently low T it can be treated as the average, i.e. thermodynamic $\Phi(T, V, \mu) = F - \mu N$.

$$\text{Probability } P(E_i, N_i) = \frac{1}{\Xi} \exp\left(-\frac{E_i - k_B T \ln \Omega_i - \mu N_i}{k_B T}\right)$$

Grand potential

You will have noticed: $\Xi = \sum_{N=0}^{TOTAL} Z(N) e^{\mu N / k_B T}$

For instance, for a classical ideal gas we know what $Z(N)$ is, so

$$\Xi = \sum_{N=0}^{TOTAL} e^{\mu N / k_B T} \frac{Z_1(T, V)^N}{N!} = \sum_{N=0}^{TOTAL} \frac{(Z_1 e^{\mu / k_B T})^N}{N!} = \exp(Z_1 e^{\mu / k_B T})$$

So if this ideal gas is in contact, and can exchange particles, with a (big) reservoir which maintains a chemical potential μ :

$$\Phi = -k_B T \ln \Xi = -k_B T \left(\frac{V}{\lambda^3} \right) e^{\mu / k_B T}$$

We have the pressure:

$$p = - \left. \frac{\partial \Phi}{\partial V} \right|_{T, \mu} = \frac{k_B T}{\lambda^3} e^{\beta \mu}$$

Mean number of particles:

$$\langle N \rangle = - \left. \frac{\partial \Phi}{\partial \mu} \right|_{T, V} = \frac{V}{\lambda^3} e^{\mu / k_B T}$$

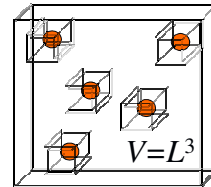
so $\Phi = -k_B T \langle N \rangle$; $\Xi = e^{\langle N \rangle}$

Probability $P(N) = \frac{1}{\Xi} \cdot \frac{(e^{\beta \mu} Z_1)^N}{N!} = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}$

Summary so far.....

Partition function of classical ideal gas

$$Z_1 = \frac{V}{\lambda^3} = V \left(\sqrt{\frac{mk_B T}{2\pi \hbar^2}} \right)^3 \quad Z_N = \frac{Z_1^N}{N!}$$



Systems open to particle exchange:
grand partition function

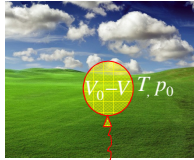
$$\Xi = \sum_{N_i=0}^{TOTAL} \left\{ \sum_{\text{all states } \{i\}} \exp\left(-\frac{E_i - \mu N_i}{k_B T}\right) \right\}$$

Classical ideal gas:

$$\Xi = \exp(Z_1 e^{\mu / k_B T})$$

$$\Phi = -k_B T \ln \Xi = (F - \mu N) = -k_B T \left(\frac{V}{\lambda^3} \right) e^{\mu / k_B T} = -k_B T \langle N \rangle$$

p-T and p-T-μ ensembles



By analogy with constructing the grand partition function in an ensemble when we had particle exchange, under controlled μ , we should build a corresponding statistical sum:

$$\Psi = \sum_{V=0}^{\infty} \left\{ e^{-\frac{p_0 V}{k_B T}} Z(T, V, N) \right\} = \sum_{\text{microstates } E_i} \left\{ \int dV_i e^{-\frac{1}{k_B T}(E_i - k_B T \ln \Omega_i + p_0 V_i)} \right\} = \sum_{\{E_i\}} e^{-\frac{1}{k_B T} G_i(T, p_0, N)}$$

The corresponding thermodynamic potential is $G(T, p, N) = F + pV$.



If now in addition we also open the system to exchange particles (at μ imposed by the reservoir), then the corresponding thermodynamic potential would be $Y(T, p, \mu) = G - \mu N = F + pV - \mu N = \Phi + pV$

In fact, in such an ensemble there is no proper (extensive) thermodynamic potential of the system, that is, $dY = 0$.

Chemical potential of ideal gas

Many different ways to obtain this, but the properly systematic is to obtain the canonical $Z(N)$, then its $F(T, N)$ and then μ :

$$F = Nk_B T \ln \frac{N\lambda^3}{V_e}; \quad \mu = k_B T \left(\ln \frac{N\lambda^3}{V_e} + 1 \right) = k_B T \ln \frac{N\lambda^3}{V}$$

Some additional factors may contribute to the single-particle Z_1 . For instance, a constant (adsorption) potential ϕ , or an internal (e.g. vibrational) degree of freedom: $Z_{\text{vib}} = k_B T / \hbar \omega$

$$F = Nk_B T \ln \left(\frac{N\lambda^3}{V_e \cdot e^{-\beta\phi} Z_{\text{vib}}} \right); \quad \mu = k_B T \ln \left(\frac{N\lambda^3 e^{\beta\phi}}{V Z_{\text{vib}}} \right)$$

Alternatively, from

$$\langle N \rangle = - \frac{\partial \Phi}{\partial \mu} \Big|_{T, V} = \frac{V}{\lambda^3} e^{\mu/k_B T}$$

Extras...
Let us examine what this factor implies

Mixtures

Let us consider the p - T controlled ensemble (natural on the laboratory benchtop) where the gas has several species, that is, $N = \sum_i N_i$. The partial (osmotic) pressure law gives

$$p = \sum_i p_i = \sum_i N_i k_B T / V$$

and similarly for the entropy:

$$S = \sum_i S_i = \sum_i N_i k_B \ln \left(\text{const} \frac{T^{5/2}}{p_i} \right) = \frac{5}{2} N k_B \ln \left(\frac{T}{T_0} \right) - \sum_i N_i k_B \ln \left(\frac{p_i}{p_0} \right)$$

So the change in entropy is: $\Delta S = -k_B \sum_i N_i \ln(c_i)$

In the same way, using the general form for the chemical potential of ideal gas, we have for each species:

$$\mu_i = k_B T \ln \frac{N_i \lambda_i^3}{V} = k_B T \ln \frac{N \lambda_i^3}{V} + k_B T \ln(c_i) = \mu_i(p, T) + k_B T \ln(c_i)$$

Pure gas of i -species
at current p, T

Addition due to
current $c_i = N_i/N$

Chemical reactions

Consider a generic chemical reaction, say, $A + 2B = 2C$.

Remaining in the p - T ensemble, we must work with the Gibbs potential $G(p, T, N) = \sum_i G_i$. In equilibrium: $dG=0$, so we obtain

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C = 0$$

$$\text{but } dN_A = \frac{1}{2} dN_B = -\frac{1}{2} dN_C$$

For an arbitrary reaction in equilibrium: $\Rightarrow \mu_A + 2\mu_B - 2\mu_C = 0$

$$\sum_i \nu_i \mu_i = 0 = \sum_i \nu_i \mu_i(p, T) + k_B T \ln \left(\prod_i (c_i)^{\nu_i} \right)$$

Define the chemical equilibrium constant

$$K_c(p, T) = \prod_i (c_i)^{\nu_i} \quad \Rightarrow \quad K_c = \frac{c_A c_B^2}{c_C^2}$$

$$\ln K_c = -\frac{1}{k_B T} \sum_i \nu_i \mu_i(p, T)$$

Chemical reactions

Consider a fully general chemical reaction, $\sum_i \nu_i A_i = 0$

Remaining in the p - T ensemble, with $dG = \sum_i \mu_i dN_i = 0$

Let us recall what we know about μ_i :

$$\mu_i = k_B T \ln \left(\frac{N_i \lambda_i^3}{V} e^{-\beta\phi} \right)$$

hence $\sum_i \nu_i \mu_i = k_B T \sum_i \nu_i (\ln N_i - \ln Z_{1(i)}) = 0$

Define an alternative chemical equilibrium constant

$$K_N(p, T) = \prod_i (N_i)^{\nu_i}$$

Then its value is given by: $K_N = \prod_i (Z_{1(i)})^{\nu_i}$

For instance, for $A + 2B = 2C$, we might get Potential gain $-\phi$

$$K_N = \frac{(V/\lambda_A^3)(V/\lambda_B^3)^2}{(V/\lambda_C^3)^2} \gg 1 \quad \text{but} \quad K_N = \frac{(V/\lambda_A^3)(V/\lambda_B^3)^2}{(V/\lambda_C^3)^2} e^{-\beta\phi} \ll 1$$

Summary so far.....

A generic chemical reaction, $\sum_i \nu_i A_i = 0$ (e.g. $2H + O = H_2O$)

A "chemical" (empirical) version of chemical equilibrium constant

$$K_c(p, T) = \prod_i (c_i)^{\nu_i}$$

A "statistical" version of chemical equilibrium constant

$$K_N(p, T) = \prod_i (N_i)^{\nu_i} = \prod_i (Z_i)^{\nu_i}$$

This is how you calculate it...

For instance, for $2H + O = H_2O$, we get

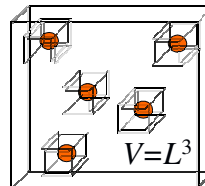
$$K_N = \frac{(V/\lambda_O^3)(V/\lambda_H^3)^2}{(V/\lambda_{H_2O}^3)} \gg 1 \quad \text{but} \quad K_N = \frac{(V/\lambda_O^3)(V/\lambda_H^3)^2}{(V/\lambda_{H_2O}^3)} e^{-\phi/k_B T} \ll 1$$

Bonding potential energy $-\phi$

Classical vs. Quantum

The ideal gas of particles of mass m has

$$Z_N = \frac{Z_1^N}{N!} \quad \text{or} \quad F = N k_B T \ln \frac{N \lambda^3}{V e}$$

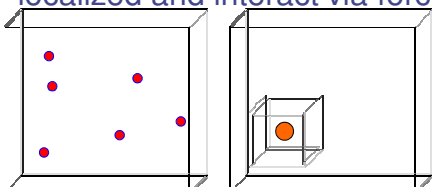


Note how this factor turns up under the logarithm!

What is the meaning of $\frac{N \lambda^3}{V} = \frac{N}{V} \left(\frac{2\pi \hbar^2}{m k_B T} \right)^{3/2}$

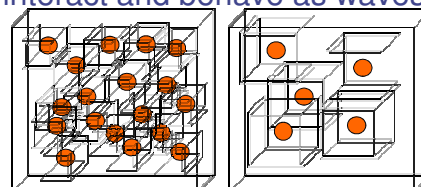
$$1 \gg \frac{N \lambda^3}{V}$$

Classical physics, particles are localized and interact via forces



$$\frac{N \lambda^3}{V} \gg 1$$

Quantum physics, particles interact and behave as waves



Classical vs. Quantum

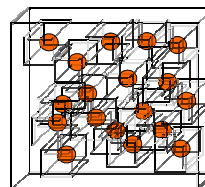
We established an important operation, of changing the order of summation (in different ensembles), to end up summing over the microstates E_i . In the grand canonical ensemble:

$$\Xi = \sum_{N=0}^{TOTAL} \left\{ e^{\frac{\mu N}{k_B T}} Z(N) \right\} = \sum_{\text{microstates } E_i} \left\{ \sum_{N_i} e^{\frac{1}{k_B T} (E_i - k_B T \ln \Omega_i - \mu N_i)} \right\} = \sum_{\{E_i\}} e^{\frac{1}{k_B T} \Phi_i(T, V, \mu)}$$

In this way we identified the grand partition function of a given microstate, and the corresponding potential:

$$\Xi_k = \sum_{n=0}^{TOTAL} \left\{ e^{\frac{1}{k_B T} [\epsilon_k(n) - \mu n]} \right\}; \quad \Phi_k = -k_B T \ln \Xi_k$$

In the quantum regime, when the separate particles cannot be properly distinguished and the statistical sum over microstates could be very difficult, we have an interesting way forward, if it happens so that: $\epsilon_k(n) = n \cdot \epsilon_k$



Classical vs. Quantum

When the energy of a microstate E_k factorises with the number of particles in this state, $E_k(n) = n_k \cdot \epsilon_k$ (and remember, the entropy is always extensive too), then

$$\Xi = \sum_{n_1, n_2, n_3, \dots} e^{-\frac{1}{k_B T}(\epsilon_1 - \mu)n_1} e^{-\frac{1}{k_B T}(\epsilon_2 - \mu)n_2} e^{-\frac{1}{k_B T}(\epsilon_3 - \mu)n_3} \dots = \prod_k \left\{ \sum_{n_k=0}^{TOTAL} e^{-\frac{1}{k_B T}(\epsilon_k - \mu)n_k} \right\} = \prod_k \Xi_k$$

The corresponding full grand potential is just the sum over each energy state:

$$\Phi(T, \mu) = -k_B T \sum_k \ln \Xi_k = \sum_k \Phi_k$$

However, to find any average (e.g. the mean energy U), we need to use the probability:

$$U(N) = \sum_{\text{microstates } \{k\}} \epsilon_k P(\epsilon_k, N)$$

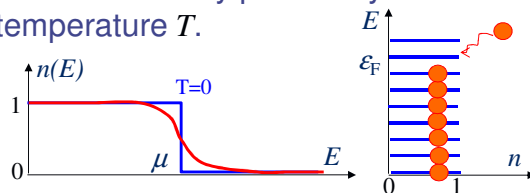
Fermi statistics

The Pauli exclusion principle prohibits more than one Fermi particle to occupy a given energy level ϵ_k :

$$\Xi_k = \sum_{n=0,1} \left(e^{-\frac{1}{k_B T}[\epsilon_k - \mu]} \right)^n = 1 + e^{-\frac{\epsilon_k - \mu}{k_B T}} \rightarrow \Phi_k = -k_B T \ln \left(1 + e^{-\frac{\epsilon_k - \mu}{k_B T}} \right)$$

$$n(\epsilon_k) = -\frac{d\Phi_k}{d\mu} = k_B T \frac{\frac{1}{k_B T} e^{-\frac{\epsilon_k - \mu}{k_B T}}}{1 + e^{-\frac{\epsilon_k - \mu}{k_B T}}} = \frac{1}{e^{\beta[\epsilon_k - \mu]} + 1}$$

This is the famous expression of the **Fermi occupation number**: it tells how many particles you can find having the energy E , at temperature T .



This picture makes it clear that μ at low temperature is the “Fermi energy” – the highest level particles have to pack to.

Fermi energy

Fermi energy is the chemical potential of Fermi particles at very low temperatures, when the density of states is sharp:

$$n(E) = \frac{1}{e^{\frac{E-\varepsilon_F}{k_B T}} + 1} \quad \rightarrow \quad \begin{array}{c} \uparrow n(E) \\ 1 \\ \hline 0 \\ \varepsilon_F \\ \hline E \end{array} \quad T \rightarrow 0$$

If we have the total of N particles, then the sum of all $n(\varepsilon_k)$ has to $= N$

$$N = \sum_{\text{microstates } \{\varepsilon_k\}} n(\varepsilon_k) = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \cdot n(E) \quad \text{This is actually very easy, if you recall that } E=p^2/2m$$

$$N = V \int_0^\infty \frac{4\pi p^2 dp}{(2\pi\hbar)^3} \cdot n(E) = V \int_0^\infty \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \sqrt{E} dE \cdot n(E)$$

$$\frac{N}{V} = \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^{\varepsilon_F} \sqrt{E} dE = \frac{\sqrt{2} m^{3/2}}{3\pi^2\hbar^3} (\varepsilon_F)^{3/2} \quad \rightarrow \quad \varepsilon_F \approx 7.4 \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{2/3}$$

Note how Fermi energy depends on the particle density (or pressure), i.e. it is increasingly hard to add more particles to the system.

Bose statistics

If particles do not have half-integer spin, they are not subject to the Pauli exclusion principle, and can all occupy the same level of energy. These are called **Bose particles**.

$$\Xi(\varepsilon_k) = \sum_{n=0}^{\infty} \left(e^{-1/k_B T [\varepsilon_k - \mu]} \right)^n = \frac{1}{1 - e^{-\frac{\varepsilon_k - \mu}{k_B T}}} \quad \rightarrow \quad \Phi_k = k_B T \ln \left(1 - e^{-\frac{\varepsilon_k - \mu}{k_B T}} \right)$$

As before, we evaluate the mean number of particles with energy E :

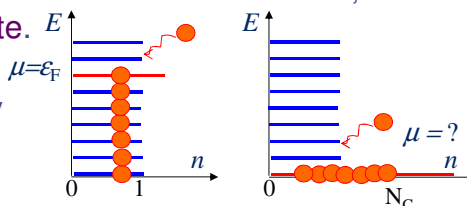
$$n(\varepsilon_k) = -\frac{d\Phi_k}{d\mu} = k_B T \frac{\frac{1}{k_B T} e^{-\frac{\varepsilon_k - \mu}{k_B T}}}{1 - e^{-\frac{\varepsilon_k - \mu}{k_B T}}} = \frac{1}{e^{\beta[\varepsilon_k - \mu]} - 1}$$

This is the famous expression of the **Bose occupation number**: note that $n(E)$ can easily be >1 . But we really need to know what is the value of chemical potential μ in this case!

Bose condensate

Fermi particles, due to the exclusion principle, must occupy increasingly high levels of energy. Bose particles do not! So, at very low temperatures they can all sit at the level $E=0$, which is called **Bose condensate**.

The picture for Bose particles already suggests the answer for $\mu = ?$



A more sophisticated argument says: we have some number of particles (N_C) in the $E=0$ condensate, and some number ($N-N_C$) excited. If the two subsystems are in equilibrium, then their **chemical potentials** are equal (particles can exchange). How to find the optimal number N_C ? It is achieved when the corresponding free energy is minimized, that is, when

$$\frac{dF_C}{dN_C} = 0 \dots \text{which conveniently happens to be the definition of } \mu_C=0.$$

Conclusion: as soon as the **Bose condensate** appears, $\mu \approx 0$.

Bose condensate

The total (fixed) number of particles is determined by the familiar constraint:

$$N = \sum_{\text{microstates } \{\epsilon_k\}} n(\epsilon_k) = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \cdot n(E)$$

In 3D, we have for bosons:

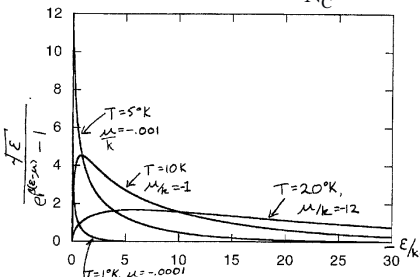
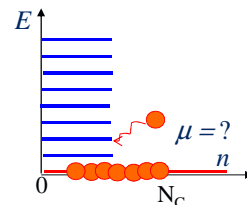
$$N = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{E}}{e^{\beta(E-\mu)} - 1} dE$$

The area under each curve should be equal to N , but at $T \rightarrow 0$ the area can't be preserved...

All particles in the ground state:

$$n(E) = N \text{ for } E = 0, \text{ hence } \frac{1}{e^{-\beta\mu} - 1} = N$$

$$e^{-\beta\mu} = 1 + \frac{1}{N}, \text{ so: } -\beta\mu \approx \frac{1}{N}, \mu = -\frac{k_B T}{N} \rightarrow 0$$



Summary so far.....

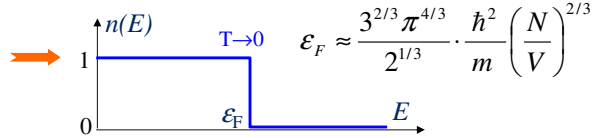
Quantum vs. classical

$$\frac{N\lambda^3}{V} = \frac{N}{V} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \ll 1$$

$$\gg 1$$

Fermi particles:

$$n(E) = \frac{1}{e^{(E-\epsilon_F)/k_B T} + 1}$$



Bose particles:

$$n(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1}$$

Condensate from $\frac{N}{V} \left(\frac{2\pi\hbar^2}{mk_B T_c} \right)^{3/2} \approx 1$

$\mu \approx 0$ { in fact $\mu \approx -\frac{k_B T}{N}$ }

Chemical potential, again

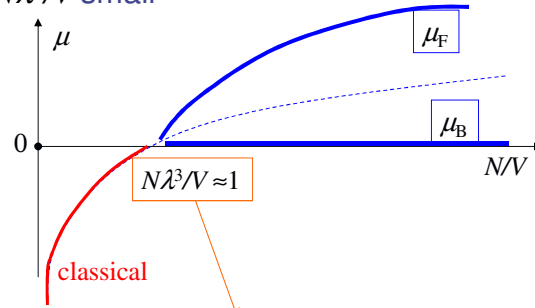
In the classical regime: the ideal gas of N particles

$$\mu = k_B T \ln \left(\frac{N\lambda^3}{V} \right) \quad \text{at } N\lambda^3/V \text{ small}$$

At $N\lambda^3/V$ large, we are in the quantum regime, so Fermi and Bose systems are different:

$$\mu_F = \epsilon_F \approx 7.4 \frac{\hbar^2}{m} \left(\frac{N}{V} \right)^{2/3}$$

$\mu_B \approx 0$ Due to the Bose-condensation in the state with $E=0$



This defines the condensation temperature

$$k_B T_C = \frac{2\pi\hbar^2}{m} \left(\frac{N}{V} \right)^{2/3}$$

Can you estimate number of particles in the condensate, N_C , at any given $T < T_C$?

Ideal Fermi gas at low-T

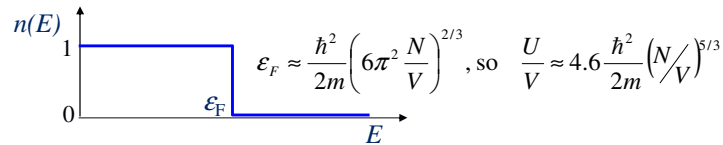
By doing the “grand partition function” trick (for additive $\mathcal{E}(n)=n\epsilon_k$) we got the probability to occupy a level ϵ_k : $n(\epsilon_k) = \frac{1}{e^{\beta[\epsilon_k - \mu]} + 1}$

This is essentially the probability $P(\mathcal{E}, N)$, to be used in place of our earlier forms of statistical probability, which was normalised by the corresponding partition function.

Now we can find the averages, e.g.

$$U = \sum_{\text{microstates } \{k\}} \epsilon_k n(\epsilon_k) = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \frac{E}{e^{\beta[E - \epsilon_F]} + 1} \quad \text{in 3D}$$

$$T=0: \quad U = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\epsilon_F} \frac{E^{3/2}}{e^{\beta[E - \mu]} + 1} dE = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\epsilon_F} E^{3/2} dE = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \left(\frac{2}{5} \epsilon_F^{5/2} \right)$$



Ideal Fermi gas at low-T

At low, but nonzero temperature the problem is much more complicated

$$U = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} \frac{E^{3/2}}{e^{\beta[E - \mu]} + 1} dE$$

Low-T series expansion of “Fermi integrals”

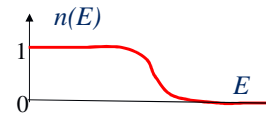
$$\int_0^{\infty} \frac{f(E)}{e^{\beta[E - \mu]} + 1} dE \approx \int_0^{\epsilon_F} f(E) dE + \frac{\pi^2}{6} (k_B T)^2 f'(\epsilon_F) + \dots$$

Note that this works the same way for any $g(\epsilon)$, i.e. in any dimension

For the mean internal energy, in 3-dimensions:

$$f = \frac{V}{4\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2}, \quad \text{so} \quad U = U_0 + \frac{V}{16} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon_F^{1/2} (k_B T)^2 \equiv U_0 + \frac{\pi^2}{4} g(\epsilon_F) \cdot (k_B T)^2$$

$$\text{This is } U(T, V, N), \text{ so: } C_V = \left. \frac{\partial U}{\partial T} \right|_{V, N} = \frac{\pi^2}{2} g(\epsilon_F) k_B^2 T$$



Ideal Fermi gas at low-T

But what if we need any other thermodynamic quantity, not just C_V , which is all we can get from $U(T, V, N)$?

The full grand partition function is $\Xi = \prod_{\text{microstates } \{k\}} \Xi_k$ this is $g(E)$

Therefore the grand potential:

$$\Phi = \sum_{\{k\}} \Phi_k = \int \Phi(\epsilon_k) \frac{d^3x d^3p}{(2\pi\hbar)^3} = -k_B T \int_0^\infty \ln(1 + e^{-\beta(E-\mu)}) \left[\frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \right] dE$$

$$\text{Integration by parts} \rightarrow = -\frac{2}{3} \cdot \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{E^{3/2}}{e^{\beta(E-\mu)} + 1} dE \equiv -\frac{2}{3} U$$

Now we can legitimately differentiate the proper thermodynamic potential $\Phi(T, V, \mu)$:

$$\text{Pressure } p = -\frac{\partial \Phi}{\partial V} = p_F(\tau=0) + \text{const} \cdot \left(\frac{2m}{\hbar^2} \right)^2 \left(\frac{V}{N} \right)^{1/3} (k_B T)^2$$

$$\text{Entropy } S = -\frac{\partial \Phi}{\partial T} = \text{const} \cdot \left(\frac{2m}{\hbar^2} \right)^{3/2} k_B^2 T$$

Bose gas at low-T

The principle is exactly the same: we either find the average energy $U(T, N)$ from which the heat capacity follows – or go for the full grand potential $\Phi(T, \mu)$ and the rest of thermodynamics.

The good (or bad) news is that $\mu=0$.

$$U = \sum_{\text{microstates } \{k\}} \epsilon_k n(\epsilon_k) = \int \frac{E}{e^{\beta E} - 1} \left[\frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \right] dE \quad \text{in 3D}$$

$$\text{Non-dimensional substitution} \rightarrow = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} (k_B T)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx = \text{const} \cdot T^{5/2}$$

$$\Phi = \sum_{\{k\}} \Phi_k = k_B T \int_0^\infty \ln(1 - e^{-\beta(E-\mu)}) \left[\frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \right] dE$$

$$\text{Integrate by parts} \rightarrow = \frac{2}{3} \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{E^{3/2}}{e^{\beta E} - 1} dE \equiv \frac{2}{3} U$$

Be fluent at.....

Quantum regime

$$\frac{N\lambda^3}{V} = \frac{N}{V} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \gg 1$$

Fermi particles at low (non-zero) temperature:

$$n(E) = \frac{1}{e^{(E-\epsilon_F)/k_B T} + 1}$$

How to “do” Fermi integrals...
(mean energy, Φ , pressure)

Bose particles at low temperature:

$$n(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1}$$

How to “do” Bose integrals ($\mu=0$)
(mean energy, etc)

Photons

Photons ($E=\hbar\omega$) are Bose particles of a special type. Since their mass=0, their “number of particles” is not fixed, but varies with temperature. E.g. $E=0$ condensate has no particles at all.

$$n(E) = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Can we find the mean number of photons, of the selected “color” given by the fixed ω ?

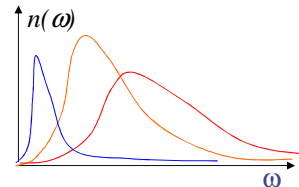
$$N = \sum_{\text{microstates } \{\epsilon_k\}} n(\epsilon_k) = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \cdot n(\hbar\omega)$$

Instead of $E=p^2/2m$ now there is a different relation between energy and momentum:

$$p = \hbar k = \hbar \omega / c$$

$$N = V \int \frac{4\pi^2 \omega^2 d\omega}{(2\pi)^3 c^3} \cdot \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Spectral density $n(\omega)$ is the number of particles at a given ω . $N = \int n(\omega) d\omega$



Stefan-Boltzmann law

Photons in thermal equilibrium (emitted by a hot body) have a very characteristic power spectrum, which has originally led Planck to suggest $E = \hbar\omega$. Now we can understand why!

$$n(E) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \quad \text{Let us find the mean energy of photons.} \quad p = \hbar k = \hbar\omega/c$$

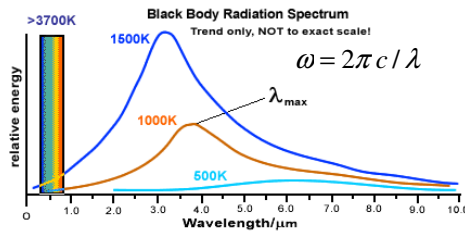
$$U = V \int \frac{4\pi^2 \omega^2 d\omega}{(2\pi)^3 c^3} \cdot \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} = V \int u(\omega) d\omega$$

The spectral density of energy is: $u(\omega) = \frac{1}{2\pi^2 c^3} \cdot \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1}$

The full energy emitted:

$$\frac{U}{V} = \frac{1}{2\pi^2 c^3 \hbar^3} \cdot (k_B T)^4$$

Stefan-Boltzmann law: $U = \sigma T^4$

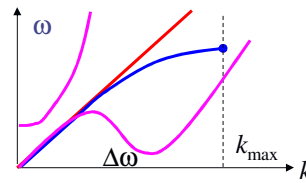


Other excitations

All elementary excitations are Bose particles with $\mu = 0$, zero rest mass (so $E = \hbar\omega$) and a dispersion relation between the energy and the momentum $\omega = \omega(k)$.

$$n(E) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$N = \sum_{\text{microstates } \{k\}} n(\epsilon_k) = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \cdot n(\hbar\omega)$$



In each case there is a need to find the right form of density of states $g(E) dE$, which is now $g(\omega) d\omega$

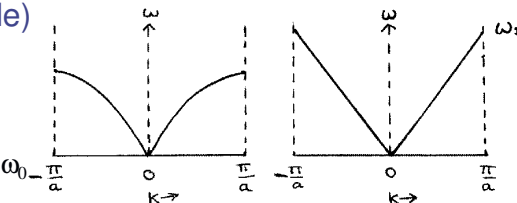
$$U = \sum_k \epsilon_k n(\epsilon_k) = V \int \frac{4\pi^2 k^2 dk}{(2\pi\hbar)^3} \cdot \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Phonons and Debye model

Normal modes of vibrations in a lattice follow the dispersion relation (lowest energy mode)

$$\omega = 2\omega_0 \left| \sin\left(\frac{1}{2}ka\right) \right|$$

where a is the lattice spacing and ω_0 the frequency of each bond.



The Debye model preserves the cutoff, but ignores the slowing of the wave

$$3 \text{ modes per atom : } 3N = \sum_{\text{all states}} 1 = \int_0^{\omega_D} \frac{3V}{2\pi^2 c^3} \omega^2 d\omega \Rightarrow \frac{V}{2\pi^2 c^3} \omega_D^3$$

$$\text{low } -T : U = \frac{3V}{2\pi^2 c^3} \int_0^\infty \frac{\hbar \omega^3 d\omega}{e^{\beta \hbar \omega} - 1} = \frac{3V \hbar}{2\pi^2 c^3} \left(\frac{k_B T}{\hbar} \right)^4 \cdot \int_0^\infty \frac{y^3 dy}{e^y - 1} \Rightarrow C_V \propto T^3$$

$$\text{high } -T : U = \frac{3V}{2\pi^2 c^3} \int_0^{\omega_D} \frac{\hbar \omega^3 d\omega}{e^{\beta \hbar \omega} - 1} \approx \frac{3V}{2\pi^2 c^3} \int_0^{\omega_D} \frac{\hbar \omega^3 d\omega}{(\beta \hbar \omega + \dots)} = \frac{V}{2\pi^2 c^3} \omega_D^3 \cdot k_B T$$

Phonons and Debye model

At high-T one can re-express the integral via the $3N$ constraint, giving the result:

$$\text{high } -T : U \approx 3Nk_B T$$

This is the energy of $3N$ simple harmonic oscillators (see lecture 5).

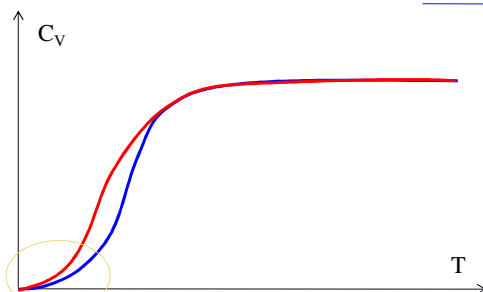
There we had:

$$Z = \frac{1}{2 \sinh\left(\frac{1}{2} \beta \hbar \omega_0\right)}$$

$$U = \frac{1}{2} \hbar \omega_0 \tanh\left(\frac{1}{2} \beta \hbar \omega_0\right)$$

$$C_V = \frac{(\hbar \omega_0)^2}{4k_B T^2} \frac{1}{\sinh^2\left(\frac{1}{2} \beta \hbar \omega_0\right)}$$

Low-T limit (quantum oscillator) is very different...



"photon gas" $\Rightarrow C_V \propto T^3$

"energy gap" $\Rightarrow C_V \propto e^{-\hbar \omega_0 / k_B T}$

So at high-T phonons behave exactly the same as classical oscillators, but at low-T the major difference is due to the continuous phonon spectrum (no gaps!)