Chapter 1 & 2: Multiplicity, Entropy etc.

Multiplicity is defined in Kittel as the number of (quantum) states with very nearly the same energy. However, other authors such as Schroeder prefer to define it as the number of microstates that correspond to any given macrostate.

Binary systems: An example of a system that is simple enough for us to write an expression for the multiplicity are binary systems, for example 1/2-spin particles, whose spin either points upwards ($\uparrow$) or downwards ($\downarrow$). In this case the multiplicity, $g(N, N_\uparrow, N_\downarrow)$, is given by

$$g(N, N_\uparrow, N_\downarrow) = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{\left(\frac{1}{2}N + s\right)!\left(\frac{1}{2}N - s\right)!}$$

where $2s \equiv N_\uparrow - N_\downarrow$. Using **Stirling's Approximation** this allows us to approximate the multiplicity of binary systems as a Gaussian distribution *for large* N:

$$g(N, s) \approx g(N, 0)\exp\left(-\frac{2s^2}{N}\right),$$
$$g(N, 0) \approx \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} 2^N$$

The energy of a **binary spin system** consisting of N spin-1/2 particles is

$$U = -\sum_{i=1}^{N} \boldsymbol{m}_i \cdot \boldsymbol{B} = -mB(N_\uparrow - N_\downarrow) = -2msB$$

where $\boldsymbol{m}$ is the single magnetic moment, and $\boldsymbol{B}$ is the applied magnetic field. We can also define the total magnetic moment $M = 2ms$.

Multiplicity function for N harmonic oscillators: (Einstein solid). Suppose we have n energy quanta, so that the system has total energy $\varepsilon = n\hbar\omega$, then the multiplicity is given as

$$g(N, n) = \frac{(N + n - 1)!}{n!(N-1)!}$$

Averages Let's suppose a physical property, X, has the value $X(s)$ when in the state s, then the average value of X will be:

$$\langle X \rangle = \sum_s X(s)P(s), \quad \sum_s P(s) = 1$$

where $P(s)$ is the probability of finding the system in state s.

Interacting systems:

Given two systems with N_1 and N_2 particles respectively. If their respective multiplicities are given by $g_1(N_1, s_1)$ and $g_2(N_2, s_2)$ and we hold $s = s_1 + s_2$ constant, then the combined multiplicity of the systems is

$$g(N, s) = \sum_{s_1} g_1(N_1, s_1) g_2(N_2, s - s_1)$$

Two spin systems in thermal contact: Once again using the Stirling Approximation we can approximate the multiplicity of two interacting spin-1/2 systems as gaussian in the variables s_1 and s_2:

$$g_1(N_1, s_1) g_2(N_2, s_2) = g_1(0) g_2(0)\exp\left(-\frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}\right)$$
$$= g_1(0) g_2(0)\exp\left(-\frac{2s_1^2}{N_1} - \frac{2(s - s_1)^2}{N_2}\right)$$

where $g_i(0)$ are given by the same expression we had before for independent binary systems. By taking the first and second derivative of this with respect to s_1 we see that the maximum (and thus the most likely state) is achieved when

$$\frac{s_1}{N_1} = \frac{s_2}{N_2}$$

Thermal equilibrium and temperature: If we more generally write g as a function of N and U we will see that at thermal equilibrium (i.e. the state of maximal multiplicity) the following equation holds:

$$\frac{1}{g_1}\left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2}$$

here we see that it is natural to introduce $\ln g(N, U) = \sigma$, because that transforms the equation above into:

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}$$

This leads naturally to the concept of temperature; we define temperature as

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N, \quad \tau = k_B T$$

which agrees with the fact that two systems in thermal equilibrium will have the same temperature. σ is the unitless entropy, and is related to the entropy in Schroeder by the simple relation

$$S = k_B \sigma = k_B \ln g$$

Laws of thermodynamics:

0. If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.

1. Heat is a form of energy transfer.
2. If a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically in successive instants of time.
3. $\lim_{T\to 0} S(T) = 0$.

Chapter 3: Boltzmann Distribution & Helmholtz Free Energy

Partition function:

$$Z \equiv \sum_s \exp\left(-\frac{\varepsilon_s}{\tau}\right)$$

where each individual term is referred to as a Boltzmann factor. The **probability** to find a system in state s is:

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/\tau)}{Z}$$

from here we see that $\sum_s P(\varepsilon_s) = 1$, as expected. With the partition function we can calculate many useful quantities, such as the total energy of the system:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau}$$

Thermodynamic identity:

$$\mathrm{d}U = \tau \mathrm{d}\sigma - p\mathrm{d}V$$

from here we see that U is naturally a function of σ and V. However, using a Legendre Transformation we can transform U into a new function F which is a function of τ and V:

$$F \equiv U - \tau\sigma \rightsquigarrow \mathrm{d}F = -\sigma \mathrm{d}\tau - p\mathrm{d}V$$

F is the **Helmholtz Free Energy** and can be more useful than U, for instance in cases where we know τ and not σ. F is *minimized* at equilibrium for constant volume (because σ is *maximised*).

From our expression for dF we see that

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

Another useful property of F is that it is closely related to the partition function:

$$F = -\tau \ln Z$$

Ideal Gas: An ideal gas is a gas of non-interacting particles confined in a box. Thus each particle has energy

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

In which case

$$Z = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp\left(-\frac{\hbar^2\pi^2(n_x^2+n_y^2+n_z^2)}{2mL^2\tau}\right)$$

which can be approximated with three integrals, giving

$$Z = \frac{\pi^{\frac{3}{2}}}{8}\left(\frac{2mL^2\tau}{\hbar^2\pi^2}\right)^{\frac{3}{2}} = \frac{V}{(2\pi\hbar^2/m\tau)^{\frac{3}{2}}} = n_Q V$$

where we've defined the **quantum concentration:**

$$n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

This is the concentration associated with an atom in a cube with side length equal to the thermal average de Broglie length. From here we can define

Classical Regime: $n \ll n_Q$

where $n = N/V$.

For a **system of N indistinguishable particles** the combined partition function is:

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

where the $N!$ accounts for us being able to interchange particles without affecting the partition function. This interchangeability has been shown to be true experimentally.

From the partition function of N indistinguishable particles we can calculate the energy and entropy of an ideal gas:

$$U = \tau^2\left(\frac{\partial \ln Z_N}{\partial \tau}\right) = \frac{3}{2}N\tau$$

which is just the kinetic part of the equipartition theorem. Additionally using that $F = -\tau \ln Z$ and that $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$ we get the **Sackur-Tetrode Equation:**

$$\sigma = N\left(\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right)$$

Entropy of mixing: A system with N particles of type A and $N-t$ particles of type B has the following multiplicity:

$$g(N,t) = \frac{N!}{(N-t)!t!}$$

as seen previously. The entropy associated with this system is therefore given by

$$\begin{aligned}\sigma &= \ln N! - \ln(N-t)! - \ln t! \\ &\approx -(N-t)\ln(1-t/N) - t\ln(t/N)\end{aligned}$$

where I have used Stirling's Approximation. Letting $x = t/N$ we get

$$\sigma(x) = -N\left((1-x)\ln(1-x) + x\ln x\right)$$

which looks a lot like a concave parabola, reaching its maximum at $x = 1/2$, i.e. where there are exactly as many particles of species A as there are of species B.

Chapter 4: Thermal Radiation

Planck distribution function: Let ε_s denote the energy that is associated with s photons each with (angular) frequency ω, that is

$$\varepsilon_s = s\hbar\omega$$

The partition function for this system is

$$Z = \sum_{s=0}^{\infty} \exp(-\hbar\omega s/\tau) = \frac{1}{1-\exp(-\hbar\omega/\tau)}$$

Thus the probability to find the system in state s is

$$P(s) = \frac{\exp(-\hbar\omega s/\tau)}{Z}$$

The thermal average of s is

$$\begin{aligned}\langle s\rangle = \sum_{s=0}^{\infty} sP(s) = Z^{-1}\sum s\exp(-\hbar\omega s/\tau) \\ = \frac{1}{\exp(\hbar\omega/\tau)-1}\end{aligned}$$

which is known as the **Planck distribution function.** Using this distribution function we can calculate the total energy of the system:

$$U = \sum_{n_x}\sum_{n_y}\sum_{n_z} \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau)-1} \approx \frac{V\pi^2}{15\hbar^3c^3}\tau^4$$

where I have used a method that is described in the appendix to approximate the triple sum as an integral. The result,

$$\frac{U}{V} = \frac{\pi^2}{15\hbar^3c^3}\tau^4$$

is known as the **Stefan-Boltzmann law of radiation.** Additionally the integrand from the expression that is used to calculate the Stefan-Boltzmann law is the spectral density and is given as

$$u_\omega = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{\exp(\hbar\omega/\tau)-1}$$

which is the well known distribution that describes radiation from black bodies, as can be seen in the following figure

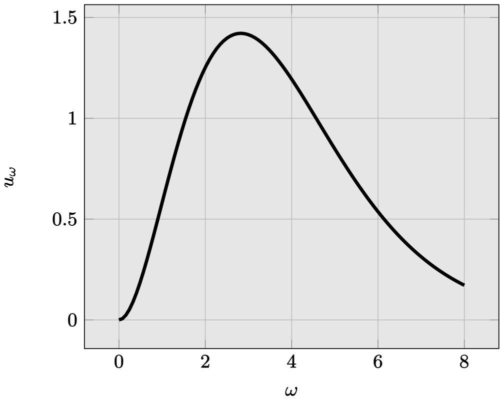

Figure 1: *Planck Distribution Function*

Phonons: For phonons there is a limit to the total number of modes: $3N$. Therefore

$$\frac{3}{8}\int_0^{n_D} 4\pi n^2 \mathrm{d}n = 3N$$

where the 3 on the left side of the equality is because phonons have three polarizations. From there we get

$$n_D = \left(\frac{6N}{\pi}\right)^{\frac{1}{3}}$$

and the total energy of this system is

$$U = \frac{3\pi}{2}\int_0^{n_D} \mathrm{d}n\, n^2 \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau)-1}$$

which in the low temperature limit becomes

$$U \approx \frac{3\pi^4 N k_B T^4}{5\theta^3}, \quad \theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$

where v is the velocity of sound in the medium. This thus leads us to an important result

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{12\pi^4 N}{5}\left(\frac{\tau}{k_B\theta}\right)^3, \tau \ll k_B\theta$$

The τ^3 dependency was observed experimentally, but couldn't be explained theoretically prior to **Debye**.

Chapter 5 & 6: Chemical Potential

Let's imagine two systems $\mathcal{S}_1$ and $\mathcal{S}_2$ that are in thermal contact with each other, and with a reservoir. Additionally the systems can interchange particles. If the systems are in thermal equilibrium and their volumes are constant then

$$\left(\frac{\partial F_1}{\partial N_1}\right)_\tau = \left(\frac{\partial F_2}{\partial N_2}\right)_\tau$$

at chemical equilibrium. From here we define the **chemical potential:**

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

thus $\mu_1 = \mu_2$ at chemical equilibrium. Note that particles will tend to "flow" from high chemical potential to low chemical potential. (Just like energy flows from high temperature to low temperature).

For an ideal gas

$$\mu = \tau \ln\left(\frac{n}{n_Q}\right)$$

which can be found directly from our prior definition of Z for an ideal gas.

Internal and external chemical potential: External potentials will offset the chemical potential of a system:

$$\mu = \mu_{int} + \mu_{ext}$$

For instance **an ideal gas in a gravitational potential**:

$$\mu = \tau \ln\left(\frac{n}{n_Q}\right) + mgh$$

here we can already see that particles will tend to "flow" downwards, where the gravitational potential is lowest. In equilibrium the chemical potential is independent of height, and thus we can get that

$$n(h) = n(0)\exp(-mgh/\tau)$$

which of course is only true close to the surface of Earth.

Another example is **magnetic dipoles in a uniform magnetic field:**

$$\mu_{tot}(\uparrow) = \tau \ln\left(\frac{n_\uparrow}{n_Q}\right) - mB$$
$$\mu_{tot}(\downarrow) = \tau \ln\left(\frac{n_\downarrow}{n_Q}\right) + mB$$

Again using our equilibrium condition that $\mu_{tot}(\uparrow) = \mu_{tot}(\downarrow)$ we get that

$$n(B) = n(0)\cosh(mB/\tau)$$

concentration increases with increasing magnetic field, which you can observe by putting iron dust close to a bar magnet.

Extending the thermodynamic identity:

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

which can be written as

$$\mathrm{d}\sigma = \frac{1}{\tau}\mathrm{d}U + \frac{p}{\tau}\mathrm{d}V - \frac{\mu}{\tau}\mathrm{d}N$$

or, equivalently

$$\mathrm{d}U = \tau\mathrm{d}\sigma - p\mathrm{d}V + \mu\mathrm{d}N$$

Gibbs Factor and Gibbs Sum:

A system that is in thermal and chemical contact with a reservoir can be described using the Gibbs sum (that is to say that the system can interchange *energy* and *particles* with a reservoir). The **Gibbs sum*** or **Grand sum** is defined as

$$\mathcal{Z} = \sum_{N=0}^{\infty}\sum_{s(N)} \exp\left(\frac{N\mu - \varepsilon_{s(N)}}{\tau}\right)$$

which, like with the partition function, allows us to define the probability of finding the system in state N_1, ε_1:

$$P(N_1, \varepsilon_1) = \frac{\exp\left((N_1\mu - \varepsilon_1)/\tau\right)}{\mathcal{Z}}$$

Once again it is clear that $\sum_N \sum_{s(N)} P(N, s(N)) = 1$. Often one defines the **absolute activity:**

$$\lambda = \exp(\mu/\tau)$$

The average number of particles is thus

$$\langle N\rangle = \lambda\frac{\partial \ln \mathcal{Z}}{\partial \lambda} = \tau\frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

and the total energy is

$$U = \langle \varepsilon\rangle = \left(\tau\mu\frac{\partial}{\partial \mu} + \tau^2\frac{\partial}{\partial \tau}\right)\ln \mathcal{Z}$$

An example where Kittel uses the Gibbs sum can be seen on page 141-144.

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* I bogen bruger de et andet skrevet Z men det kunne jeg ikke finde i LaTeX.

Often we use $f(\varepsilon)$ interchangeably with $\langle N\rangle$:

$$f(\varepsilon) = \langle N\rangle$$

Fermi-Dirac distribution:

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

Used to describe *fermions* – particles with half-integer spin that obey the Pauli exclusion principle. We define the Fermi energy as

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

Note that

$$\lim_{\tau\to 0} \frac{1}{\exp((\varepsilon-\mu)/\tau)+1} = \begin{cases} 1 & \text{for } \varepsilon < \varepsilon_F \\ 0 & \text{for } \varepsilon > \varepsilon_F \end{cases}$$

Bose-Einstein Distribution

For particles with integer spin (bosons) the Pauli exclusion principle does not hold, which means that different particles *can* occupy the same state. This implies that as $\tau \to 0$ more and more particles will be in the ground state (at $\tau = 0$ they will *all* be in the ground state). For bosons we use:

$$f(\varepsilon) = \frac{1}{\exp((\varepsilon-\mu)/\tau)-1}$$

Classical limit:

Note that both distribution functions behave identically in the classical limit. The classical limit is defined as

$$\exp\left(\frac{\varepsilon-\mu}{\tau}\right) \gg 1$$

Here both distributions are approximately

$$f(\varepsilon) \approx \lambda \exp\left(-\frac{\varepsilon}{\tau}\right)$$

known as the **classical distribution function**.

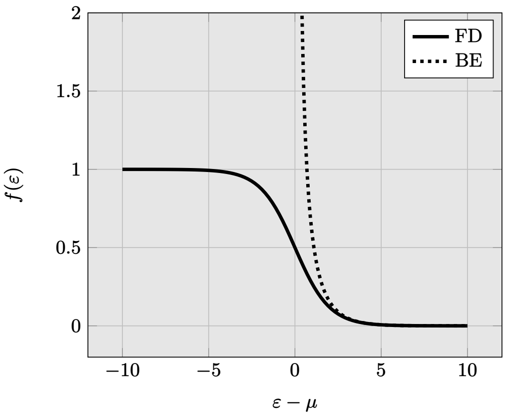

Figure 2: *Fermi-Dirac distribution (solid) and the Bose-Einstein distribution (dotted)*

Ideal Gas:

We previously related Z of an ideal gas to the concentration, from here we can define the chemical potential of an ideal gas as

$$\mu = \tau \ln\left(\frac{n}{n_Q}\right)$$

Internal degrees of freedom

If the energy of an ideal gas can be written as

$$\varepsilon = \varepsilon_n + \varepsilon_{int}$$

where ε_n is the old energy and ε_{int} is some additional internal energy (perhaps due to rotational kinetic energy), then we can make the substitution $\varepsilon_n \rightsquigarrow \varepsilon_n + \varepsilon_{int}$ in all our prior results. This would modify our Gibbs sum to

$$\mathcal{Z} = 1 + \lambda Z_{int} \exp(-\varepsilon_n/\tau),$$
$$Z_{int} = \sum_{int} \exp(-\varepsilon_{int}/\tau)$$

For more on this see page 170-171.

Expansion of ideal gases

	ΔU	$\Delta\sigma$	δW	δQ
RITE	0	$N\ln\frac{V_2}{V_1}$	$-N\tau\ln\frac{V_2}{V_1}$	$N\tau\ln\frac{V_2}{V_1}$
RISE	$-\frac{3}{2}N\tau_1\left(1-\left(\frac{V_1}{V_2}\right)^{\frac{2}{3}}\right)$	0	$-\frac{3}{2}N\tau_1\left(1-\left(\frac{V_1}{V_2}\right)^{\frac{2}{3}}\right)$	0
IE	0	$N\ln\frac{V_2}{V_1}$	0	0

Table I: *RITE: Reversible isothermal expansion, RISE: reversible isentropic expansion, IE: irreversible expansion*

Chapter 7: Fermi & Bose gases

Quantum gas

A quantum gas is defined as a gas in the limit

$$n \geq n_Q \equiv \left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

Or, if we have fixed the concentration, then a gas becomes quantum (or degenerate) when

$$\tau < \tau_Q = \frac{2\pi\hbar^2}{m} n^{\frac{2}{3}}$$

Ground state of Fermi gas (i.e $\tau = 0$) The highest energy level is

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{\pi n_F}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}},$$
$$n_F = \left(\frac{3N}{\pi}\right)^{\frac{1}{3}}$$

The total energy

$$U_0 = 2\sum_n \varepsilon_n = \frac{\pi^3}{2m}\left(\frac{\hbar}{L}\right)^2 \int_0^{n_F} \mathrm{d}n n^4 = \frac{3}{5}N\varepsilon_F$$

Don't confuse n here for N/V. **Density of states** Instead converting the sum into an integral over n it can be useful to integrate over ε. However, the integrand then needs to be weighted according to how many particles have the energy ε:

$$\sum_n(\cdots) \rightsquigarrow \int \mathrm{d}\varepsilon \mathcal{D}(\varepsilon)(\cdots)$$

where $\mathcal{D}(\varepsilon)$ is the **density of states.** We can calculate it using

$$\mathcal{D}(\varepsilon) \equiv \frac{\mathrm{d}N}{\mathrm{d}\varepsilon}$$

For instance a 3D Fermi gas has the following density of states:

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

For 1D and 2D expressions use the length of a line or area of a circle instead of the surface of a sphere when deriving equation 7.6 in the book.

Heat Capacity of electron gas

The energy increase of an electron gas when heated from 0 to τ can be calculated using $\mathcal{D}(\varepsilon)$:

$$\Delta U = \int_{\varepsilon_F}^{\infty} \mathrm{d}\varepsilon\ \varepsilon\mathcal{D}(\varepsilon)f(\varepsilon)$$

and from there we can get the following low-temperature expression for the heat capacity of an electron gas:

$$C_{el} = \frac{1}{3}\pi^2\mathcal{D}(\varepsilon_F)\tau = \frac{1}{2}\pi^2 N\frac{\tau}{\tau_F}, \quad \tau \ll \tau_F$$

Heat Capacity of metals

$$C_V = \gamma\tau + A\tau^3$$

where γ and A are constants characteristic of the material. Note that the linear term is due to the electrons whereas the cubic term is due to lattice vibrations.

For a short note on white dwarf stars and nuclear matter see pages 196-199.

Boson gas and Einstein condensation

When a boson gas reaches very low temperatures a substantial fraction of the total number of particles will occupy the ground state – this phenomenon is known as **Einstein condensation**. The chemical potential for an Einstein condensate is

$$\mu = -\frac{\tau}{N}$$

The chemical potential of a boson system must always be lower in energy than the ground state energy in order for the occupancy of every orbital to be non-negative.

Occupancy of the ground state of a boson gas

We can split the particles into particles that are in the ground state, of which there are N_0, and particles that are excited, of which there are N_e:

$$N = N_0(\tau) + N_e(\tau) = N_0(\tau) + \int_0^{\infty} \mathrm{d}\varepsilon\ \mathcal{D}(\varepsilon)f(\varepsilon,\tau)$$

or

$$N_e = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \tau^{\frac{3}{2}} \int_0^{\infty} \mathrm{d}x\ \frac{x^{\frac{1}{2}}}{\lambda^{-1}e^x - 1}$$

from where we get that

$$\frac{N_e}{N} \approx 2.612\frac{n_Q}{n}$$

Einstein condensation temperature

The temperature where $N = N_e$ is the **Einstein condensation temperature:**

$$\tau_E \equiv \frac{2\pi\hbar^2}{m}\left(\frac{N}{2.612V}\right)^{\frac{2}{3}}$$

This might seem like an odd definition, but as soon as $\tau < \tau_E$ the number of particles in the ground state becomes significant. This allows us to write

$$\frac{N_e}{N} \approx \left(\frac{\tau}{\tau_E}\right)^{\frac{3}{2}}$$

Chapter 9: Gibbs free energy

The Gibbs free energy is defined as

$$G \equiv U - \tau\sigma + pV$$

Note that this is a (double) Legendre transformation, where we have replaced the variables σ and V (which U is a function of) with τ and p, thus

$$\mathrm{d}G = -\sigma \mathrm{d}\tau + V\mathrm{d}p + \mu \mathrm{d}N$$

which implies that

$$\left(\frac{\partial G}{\partial \tau}\right)_{p,N} = -\sigma, \quad \left(\frac{\partial G}{\partial p}\right)_{\tau,N} = V$$
$$\left(\frac{\partial G}{\partial N}\right)_{\tau,p} = \mu$$

Due to the fact that G is a function only of N, p and τ, and that p and τ are *intensive quantities* (see Appendix for a definition of these), we know that G has to be linearly proportional to N, and using the partial derivative above we get that

$$G = N\mu(\tau, p)$$

Equilibrium in (chemical) reactions

Suppose we write a chemical reaction as

$$\sum_i v_i A_i = 0$$

where A_i is just the name of the chemical (this means products have *negative* v_i and reactants have *positive* v_i). Due to the fact that $\mathrm{d}G = 0$ at equilibrium we infer that

$$\sum_i \mu_i v_i = 0$$

Ideal gases For ideal gases we have that

$$\mu_j = \tau(\ln n_j - \ln c_j), \quad c_j \equiv n_{Qj} Z_j^{\text{int}}$$

hence

$$\sum_j v_j \ln n_j = \sum_j v_j \ln c_j \rightsquigarrow \prod_j n_j^{v_j} = K(\tau)$$

which is known as the **law of mass action**, defining

$$K(\tau) \equiv \prod_j c_j^{v_j}$$

Chemists often write for example

$$\frac{[A][B]}{[AB]} = K(\tau)$$

where $[\cdot]$ denotes the concentration. This would be for the reaction

$$A + B \leftrightharpoons AB$$

Chapter 10: Phase transitions

Under particular conditions two (or more) phases of a material can exist. However, if the system is at equilibrium then all the chemical potentials must be equal, for example

$$\mu_\ell(p,\tau) = \mu_g(p,\tau)$$

By expanding this linearly in p and τ we get that

$$\frac{\mathrm{d}p}{\mathrm{d}\tau} = \frac{\left(\frac{\partial \mu_\ell}{\partial \tau}\right)_p - \left(\frac{\partial \mu_g}{\partial \tau}\right)_p}{\left(\frac{\partial \mu_\ell}{\partial p}\right)_\tau - \left(\frac{\partial \mu_g}{\partial p}\right)_\tau} = \frac{s_g - s_\ell}{v_g - v_\ell}$$

note that $v = V/N$! The change in entropy is related to the heat transfer. We define the (additional) heat that is required for the phase transition as the **latent heat:**

$$L \equiv \tau(s_g - s_\ell)$$

Which means

$$\frac{\mathrm{d}p}{\mathrm{d}\tau} = \frac{L}{\tau \Delta v}$$

The **Clausius-Clapeyron equation** (or **vapor pressure equation**).

Van der Waals equation of state

By modifying our expression for F for an ideal gas using the following substitution

$$V \rightsquigarrow V - Nb$$

where Nb accounts for the volume occupied by the particles and by accounting for their interactions using the *mean field method* we obtain

$$F_{\text{vdW}} = -N\tau\left(\ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1\right) - \frac{N^2 a}{V}$$

from which we can calculate the pressure $\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = -p$, and by moving some terms around we obtain a modified ideal gas equation (**van der Waals equation of state**)

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

From here we define the following critical quantities

$$p_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad \tau_c = \frac{8a}{27b}$$

This allows us to write the **law of corresponding states**, which is a modified dimensionless gas equation

$$\hat{p} = \frac{\frac{8}{3}\hat{\tau}}{\hat{V} - \frac{1}{3}} - \frac{3}{\hat{V}^2}$$

where the ^ implies we have divided the respective values by their corresponding critical values. Plotting $\hat{p}(\hat{V})$ yields

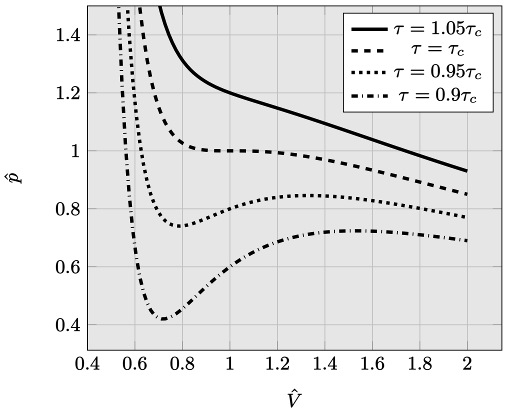

Figure 3: *For $\tau < \tau_c$ the minimum of the function is not a point of inflection. For $\tau \geq \tau_c$ this cannot be said, which implies that there is no difference between the phases*

If $\tau < \tau_c$ we can draw a *coexistence line* as in Figure 10.13 in the book, along which the two phases can coexist. Once we've left the coexistence line there can only be one stable phase.

Nucleation: Our results can be used to predict the critical radius that is required for a droplet of liquid to be stable (droplets that are too small vaporize). Let

$$\Delta\mu = \mu_g - \mu_\ell$$

then

$$R_c = \frac{2\gamma}{n_\ell \Delta\mu}$$

where γ is the surface free energy and n_ℓ is the concentration of the molecules in the liquid. For an example with ferromagnetism see pages 295-298

Landau theory of phase transitions

Suppose a system can be described by a single parameter, ξ, (as well as temperature), and hence we define the **Landau free energy function**

$$F_L(\xi, \tau) \equiv U(\xi, \tau) - \tau\sigma(\xi, \tau)$$

and let ξ_0 be the value of ξ at equilibrium. F_L is minimised at equilibrium, thus $F(\tau) = F_L(\xi_0, \tau) \leq F_L(\xi, \tau)$. Let us write out F_L in a power series

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 + \cdots$$

(we restrict ourselves to systems where F_L is even in ξ). The simplest example of a phase transition is a **second order phase transition**, which occurs if $g_2(\tau)$ changes sign at temperature τ_0, for example

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)\xi^2 + \frac{1}{4}g_4\xi^4$$

We would like to minimise this in ξ, which is achieved at

$$\xi = 0 \vee \sqrt{\frac{\alpha(\tau_0 - \tau)}{g_4}}$$

($\vee$ is or). From this we get an expression for the Helmholtz free energy

$$F(\tau) = g_0(\tau) - \frac{\alpha^2}{4g_4}(\tau - \tau_0)^2$$

First order transitions A first order transition is defined similarly to a second order transition, except that we additionally require that g_4 is negative:

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 - \frac{1}{4}|g_4(\tau)|\xi^4 + \cdots$$

First order phase transitions will have a discontinuity in the first derivative of the free energy, whereas second order transitions have a discontinuity in the second derivative – see pages 300-305.

Appendix:

Stirling's Approximation:

$$N! \approx (2\pi N)^{\frac{1}{2}} N^N \exp\left(-N + \frac{1}{12N} + \cdots\right)$$

which for large N yields

$$\ln N! \approx N \ln N - N + \frac{1}{2}\ln(2\pi N) \approx N \ln N - N$$

Approximating infinite sums as integrals:

The total energy of photons in a $L \times L \times L$ cavity is

$$U = \sum_n \langle \varepsilon_n \rangle = \sum_{n_x}\sum_{n_y}\sum_{n_z} \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau) - 1},$$
$$\omega_n = \frac{n\pi c}{L}$$

However, assuming each term in the sum is small we can approximate this triple sum by an integral

$$U \approx \frac{1}{8}\int_0^\infty \frac{4\pi n^2 \hbar\omega_n}{\exp(\hbar\omega_n/\tau) - 1} \mathrm{d}n$$

The 1/8 is because we are only looking at the positive octant (because n_x, n_y and n_z are positive) and the

$4\pi n^2$ is because we are integrating the shell of a sphere, because the number of possibilities of n_x, n_y and n_z for which $n^2 = n_x^2 + n_y^2 + n_z^2$ goes like n^2.

Fermion or Boson?

Particles with *integer* spin are bosons, whereas particles with *half-integer* spin are fermions, for example

e, p, n	Fermion
H_2	Boson
^3He	Fermion
^4He	Boson

For atoms: in general if the number of neutrons is odd the atom is a fermion, otherwise it's a boson (because each proton is matched by an electron).