

PHAS2228 : Statistical Thermodynamics

Luke Pomfrey

Last L^AT_EXed on: April 1, 2007

Contents

I. Notes	1
1. Basic Thermodynamics : Zeroth and First Laws	2
1.1. Zeroth Law - Temperature and Equilibrium	2
1.2. The Equation of State and Functions of State	3
1.3. Perfect Gas Temperature Scale	4
1.4. Particle Interaction Probability	6
1.4.1. Mean time between collisions for molecules in thermal equilibrium	7
1.4.2. The meanings of τ	7
1.4.3. Collision Mean Free Path	8
1.4.4. Collision Cross Section	8
1.5. Work, Heat and Energy : The First law of Thermodynamics	9
1.5.1. What is E in general?	9
1.5.2. Example	10
1.5.3. Reversibility & Irreversibility	11
1.6. Heat Capacity	12
2. The Second and Third Laws of Thermodynamics	14
2.1. Statements of the Second Law	14
2.1.1. Entropy as a measure of disorder	15
2.2. Macrostates and Microstates	15
2.2.1. Equilibrium of an isolated system.	17
2.2.2. Equilibrium Postulate	17
2.2.3. Entropy	18
2.2.4. Temperature, Pressure and Chemical Potential as derivatives of Entropy	18
2.2.5. Temperature as a derivative of entropy	19
2.2.6. Pressure as a derivative of entropy	20
2.2.7. Chemical potential, μ , as a derivative of entropy	20
2.3. Schottky defects in a crystal	21
2.3.1. How does the number of defects depend on the temperature? . .	21
2.4. Equilibrium of a system in a heat bath	22
2.4.1. Systems of a constant temperature and variation in energy . . .	22
2.4.2. The Boltzmann distribution for a system in a heat bath	23
2.4.3. Discreet probability distribution in energy	25
2.4.4. Mean energy and fluctuations	25

2.4.5.	Continuous probability distribution in energy	26
2.4.6.	Entropy and the Helmholtz free energy	26
2.5.	Infinitesimal Changes : Maxwell Relations and Clausius' Principle . . .	28
2.5.1.	Clausius' principle	31
2.5.2.	Heat Engines	33
2.6.	Third Law of Thermodynamics	34
2.6.1.	Absolute zero is unattainable	34
3.	Energy Distributions of Weakly Interacting Particles	35
3.1.	Thermal energy distributions	35
3.1.1.	The mean number of particles per state, $f(E)$ as a function of T	37
3.1.2.	$f(E)$ for a perfect (quantum) boson gas	38
3.1.3.	$f(E)$ for a perfect (quantum) fermion gas	38
3.1.4.	$f(E)$ for a perfect classical gas	39
3.1.5.	α and the chemical potential, μ	39
3.1.6.	Density of states $g(E)$	39
3.2.	A gas of particles in a box	40
3.3.	Bosons : Black Body Radiation	43
3.3.1.	Radiation : Some basic definitions and units	44
3.3.2.	Various black-body laws and facts	47
3.3.3.	Kirchoff's law	49
3.3.4.	A general body's spectral radiance	49
3.3.5.	Radiation pressure	50
3.4.	Astronomical examples involving black bodies	51
3.4.1.	Stellar temperatures	51
3.4.2.	Planetary temperatures	51
3.4.3.	Cosmic Microwave Background	51
3.5.	A perfect gas of bosons at low temperatures (Bose-Einstein condensation)	51
3.5.1.	The density of states, $g(E)$, for matter waves in a box	51
3.6.	Fermions (Electrons in white dwarf stars and in metals)	55
3.6.1.	Pressure due to a degenerate Fermion gas of electrons	57
3.6.2.	Pressure due to a degenerate electron gas in a white dwarf	59
3.6.3.	Neutron stars	61
4.	Classical gases, liquids and solids	62
4.1.	Definition of a classical gas	62
4.1.1.	Finding the mean number of particles per unit momentum, $n(p)$	62
4.1.2.	The mean number of particles per one particle state, $f(p)$	62
4.1.3.	The density of states, $g(p)$	64
4.2.	The Maxwell speed and velocity distributions and the energy distribution	64
4.2.1.	The energy of a classical gas	67
4.3.	The equipartition of energy and heat capacities	69
4.4.	Isothermal atmospheres	71
4.4.1.	Density vs. height for an isothermal atmosphere	72
4.4.2.	The Boltzmann law	73

4.4.3. Van der Waals equation of state for real gases	74
4.5. Phase changes and the Gibbs free energy	74
4.5.1. The Clausius equation	76

II. Appendix **78**

Part I.

Notes

1. Basic Thermodynamics : Zeroth and First Laws

Overview - Thermal Properties of Matter

- Temperature
- Heat
- Energy
- etc.

In this course we will be mainly concerned with the gas phase. How do we analyse properties of macroscopic systems? Huge number of particles - Avogadro's number $N_A \approx 6 \times 10^{23}$ particles/mol.

It is impossible to get a full microscopic description of the system, we can only measure macroscopic properties (e.g: P , V , T ) Historically there are two approaches:

1. **Thermodynamics** : Laws relating these observable macroscopic properties. Justified by empirical success. (Carnot, Clausius, Kelvin, Joule, etc. ca. 19Th C.) For systems in equilibrium we can define obvious macroscopic properties (e.g: P , V , T ...) and find empirical laws relating them:
 - Temperature equalisation : When hot and cold bodies are placed in thermal contact.
 - Water at standard temperature and pressure always boils at 100 °C.
 - Pressure exerted by a dilute gas on a containing wall is given by the ideal gas laws ($PV = nRT$ etc.)
2. **Statistical Mechanics** : Start from atomic and molecular properties and deduce the laws for macroscopic systems by statistical averaging.

The division is now largely historical and instead we refer to “Statistical Thermodynamics.”

1.1. Zeroth Law - Temperature and Equilibrium

Concept of T is intuitive, based on the concept of “hot” or “cold.” T tends to equalise by the flow of energy.

Zeroth Law

Temperature is defined as a macroscopic property. If two bodies are separately in thermal equilibrium with a third body, then they are in equilibrium with each other. (See *Thermal Physics course*.)

Temperature Scale

A temperature scale is a scale between 2 points, with a number of “degrees” separating them. Temperature scales are thus arbitrary (the Second Law removes this.) Absolute temperature uses absolute zero and one fixed point (the triple point of water; 273.16 K.)

Equilibrium State

Consider an isolated system, and assume it is not in equilibrium, and therefore contains density, P and T variations etc.

The system will change with time and after a “relaxation time” will reach equilibrium (where all the gradients will have disappeared.) After this the system undergoes no observable macroscopic changes.

1.2. The Equation of State and Functions of State

In thermodynamics in general we only consider systems in the equilibrium state. (Just called a “state”, hereafter.) - Determined by a few macroscopic parameters. E.g: for a homogeneous fluid: m, V, P .

These variables determine all the other macroscopic properties, which are functions of state if they depend on the state of the system. e.g:

- T is a function of state.
- Chemistry is not a function of state.
- Work (W) is not a function of state.
- Heat supplied (Q) is not a function of state.

The equation of state is a single relationship that links all of the parameters needed to describe the system:

In the above example, the equation of state is:

$$T = f(P, V, m) \tag{1.1}$$

f is generally found empirically and can be quite complex.

Note: Approach breaks down if some variable depends on the previous history of the system (“hysteresis.”)

1.3. Perfect Gas Temperature Scale

For very low pressures for real gases we find that for one mole of gas:

$$PV = RT \quad (1.2)$$

Where R is the Gas constant. We can define a perfect gas temperature scale:

$$T = \lim_{P \rightarrow 0} \left(\frac{PV}{R} \right) \quad (1.3)$$

The (thermodynamic) gas temperature scale is completely determined if we define R , we do this by defining one point on the scale, this is the triple point of water (T_{tr}). The triple point was chosen so that the size of the “degree” in the gas scale equals as closely as possible the degree Celsius.

Thus:

$$T_{\text{tr}} = 273.16\text{K}$$

and:

$$T = 273.16 \frac{\lim_{P \rightarrow 0} (PV)_T}{\lim_{P \rightarrow 0} (PV)_{T_{\text{tr}}}} \quad (1.4)$$

and:

$$R = 8.31 \times 10^{-23} \text{ J mol}^{-1}\text{K}^{-1}$$

Now, from Avogadro’s number $N_0 = 6.02 \times 10^{23}$ molecules mol^{-1} we can determine the “gas constant per molecule.”

$$\begin{aligned} \frac{R}{N_0} &= k \text{ (Boltzmann’s Constant)} \\ &= 1.38 \times 10^{-23} \text{ J K}^{-1} \end{aligned} \quad (1.5)$$

So the equation of state of a perfect gas is the perfect gas law:

$$PV = NkT \quad (1.6)$$

Where N is the number of molecules in the sample.

kT is physically significant. Classically kT is of the order of each component of the energy of a molecule in a macroscopic body at temperature T .

Kinetic Theory of the Perfect Gas : Pressure

We can derive the perfect gas law from kinetic theory and this gives meaning to pressure and temperature.

Assume we have N particles of gas in a box of volume V with one end terminated by a frictionless piston. We apply a force F to balance the force (the momentum change

per second due to particle impacts) exerted by the gas.
Then pressure on a particle is:

$$P = \frac{F}{A} \quad (1.7)$$

Consider the collision of a particle of mass m and velocity \mathbf{v} . We assume the collision is elastic so energy (and $\therefore \mathbf{v}$) \therefore x component of momentum changes from mv_x to $-mv_x$ \therefore change in momentum and momentum delivered to piston is $2mv_x$. Now the number of particles per unit volume, $n = \frac{N}{V}$

During time interval t the only particles to hit the piston are those with positive v_x and within a distance $v_x t$ of the piston. These are in a volume $v_x t A$ and so therefore there are $nv_x t A$ of them. So the number of particles hitting per second is $nv_x A$. If all the particles have the same v_x then the total force caused by these impacts would be $F = (nv_x A)(2mv_x)$ \therefore $P = 2nv_x^2 m$. But the particle velocities and directions may vary so take an average $\langle v_x^2 \rangle$. But this includes those with -ve v_x , so we take $\frac{\langle v_x^2 \rangle}{2}$ to get just the +ve v_x 's.

$$P = nm \langle v_x^2 \rangle \quad (1.8)$$

By symmetry:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{\langle \mathbf{v}^2 \rangle}{3} \quad (1.9)$$

$$P = \frac{2}{3} n \left\langle \frac{m\mathbf{v}^2}{2} \right\rangle \quad (1.10)$$

Where $\left\langle \frac{m\mathbf{v}^2}{2} \right\rangle$ is the average translational kinetic energy per particle.

Kinetic theory : Temperature

Consider 2 parts of a box with different gases, separated by a movable piston. "Bombardment" must quickly move the piston to equalise the pressure ($P = n \left\langle \frac{m\mathbf{v}^2}{2} \right\rangle$) if the system is to be in equilibrium.

$$n_1 \left\langle \frac{m_1 \mathbf{v}_1^2}{2} \right\rangle = n_2 \left\langle \frac{m_2 \mathbf{v}_2^2}{2} \right\rangle \quad (1.11)$$

Can we have equilibrium with a large value of n and a small value of V on the right hand side and a small n but large V on the left hand side?

No! Because the piston is not static, but is "jiggling" left and right. If an energetic particle on the left collides with and moves the piston to the right, then the particle has lost some energy to the piston. If the piston then hits a particle on the right hand side, that particle gains energy, i.e. energy is transferred between the sides and equilibrium is achieved when the rate of energy transfer through the piston is the same

same in both directions.

The solution is that average kinetic energies of gas particles must be equal:

$$\left\langle \frac{m_1 \mathbf{v}_1^2}{2} \right\rangle = \left\langle \frac{m_2 \mathbf{v}_2^2}{2} \right\rangle \quad (1.12)$$

$$\therefore \left\langle \frac{m \mathbf{v}^2}{2} \right\rangle \propto T$$

So temperature has a physical meaning: For a perfect gas T is a measure of average translational energy of particles. T is a measure of energy associated with molecular (macroscopically unobserved) motion of a system.

Perfect Gas Law From Kinetic Theory

Is this temperature scale the same as we had before?

$$P = \frac{2}{3} n \left\langle \frac{m \mathbf{v}^2}{2} \right\rangle \quad (1.13)$$

$$n = \frac{N}{V} \quad (1.14)$$

$$PV = N \frac{2}{3} \left\langle \frac{m \mathbf{v}^2}{2} \right\rangle \quad (1.15)$$

This is just the perfect gas law:

$$PV = NkT$$

If:

$$\left\langle \frac{m \mathbf{v}^2}{2} \right\rangle = \frac{3}{2} kT \quad (1.16)$$

The total translational kinetic energy of the gas is:

$$E_{\text{tr}} = N \frac{3}{2} kT = \frac{3}{2} PV \quad (1.17)$$

1.4. Particle Interaction Probability

If the gas is near (but not in) equilibrium, we can use kinetic theory to consider molecular collisions.

Note: The averages in this section are assumed to be approximately the same. (We omit small numerical factors.)

1.4.1. Mean time between collisions for molecules in thermal equilibrium

Any one molecule experiences a random series of collisions with other molecules. In a long period of time t it will experience N collisions:

$$N \propto T \quad (1.18)$$

We can write $N = \frac{t}{\tau}$ where τ is the average time between collisions. What is the chance of a collision in time $\delta t \ll \tau$?

Intuitively we know either:

- Fraction colliding in $\delta t = \frac{\left(\frac{N_0 \delta t}{\tau}\right)}{\left(N_0 - \frac{\delta t}{\tau}\right)}$
- Or, the probability of one molecule colliding in δt is $\frac{\delta t}{\tau}$

We also want to know how far a molecule can go without collision (the “mean free path”). So we can also consider the probability of particles not colliding in time δt .

Start off with N_0 molecules. Let $N_0(t)$ not collide between $t = 0$ and time t . So $N(t + \delta t)$ is going to be less than $N(t)$ by the amount that have collided in extra time, δt . Between t and $t + \delta t$, we start with $N(t)$ collision less molecules and end with $N(t + \delta t) = N(t) + \delta N$ of them. But, the fraction colliding in time δt is $\frac{\delta t}{\tau}$ so:

$$\frac{\delta N(t)}{N(t)} = -\frac{\delta t}{\tau} \quad (1.19)$$

$$\therefore N(t) = N_0 e^{-\frac{t}{\tau}} \quad (1.20)$$

To get the probability $P(t)$ that any one molecule has no collision up to time t , which is also the fraction not colliding up to time t .

$$P(t) = e^{-\frac{t}{\tau}} \quad (1.21)$$

The time from $t = 0$ to the next collision for any one particle is on average τ .

Note: $t = 0$ is an arbitrary start time and is not necessarily the previous collision time.

1.4.2. The meanings of τ

1. The average time between collisions.
2. The average time to the next collision from any instance.
3. The average time from the last collision to any instance.

1.4.3. Collision Mean Free Path

If average time between collisions is τ and the particles have average speed $|\mathbf{v}|$, then the average distance between collisions, the mean free path:

$$l = v\tau \quad (1.22)$$

Using the arguments above, the chance that a molecule will have a collision in a distance δx is $\frac{\delta x}{l}$, and the rules for l follow the meanings of τ .

From any start position, the average distance a molecules travels without colliding is l . The probability a molecule will travel x before it's next collisions is $e^{-\frac{x}{l}}$.

1.4.4. Collision Cross Section

Mean free path depends on:

1. Density of particles.
2. How “big” a target each particle represents.

The collision cross section (σ_c) for a particle is just the area within which, an incoming particle must be located if it is to collide.

Classically for spheres of radius r_1 and r_2 colliding we get that $\sigma_c = \pi(r_1 + r_2)^2$. Consider a moving particle which travels a distance δx through a gas, with a density n_0 (i.e. with n_0 “scatterers” per unit volume.) For each unit area perpendicular to the direction of travel we have $n_0 \delta x$ molecules (“scatterers”), covering a total area of $\sigma_c n_0 \delta x$ if each molecule is identical. The chance that the incoming particle will have a collision in δx is just the ratio of the area covered by the targets to the total area (1 as we are using a unit area), so the probability is:

$$\frac{\sigma_c n_0 \delta x}{1}$$

But the probability is also just $\frac{\delta x}{l}$, so:

$$\sigma_c n_0 l = 1 \quad (1.23)$$

This means on average there will be 1 collision when the particle has gone through a distance where the “scatterers” could just cover the area.

Note: In a column of unit area and length l in fact, the “scatterers” would not cover the area completely because some would be hidden by others. So some molecules can travel distances greater than l before colliding and, conversely, others travel less than l . On average, however, particles will travel a distance l before colliding.

1.5. Work, Heat and Energy : The First law of Thermodynamics

The First Law of Thermodynamics concerns the conservation of energy. Consider first a thermally isolated system (i.e. the walls do not transmit heat.) This is an *adiabatic system*.

We can change the state of the system by doing work on it. If we do work on the system the temperature, and the total of the system will rise (changing it's state.) Joule (1840) found that the work done (W) in changing a system from state 1 to state 2 adiabatically is independent of the method used. We can then define a function of state which we shall call E such that for one of these thermally isolated systems, the work done W equals the change in the energy ΔE .

$$W = \Delta E = E_2 - E_1 \quad (1.24)$$

E is called the energy of the system. If we now consider the changes of state in a system that is not thermally isolated:

$$\Delta E = W + Q \quad (1.25)$$

Where Q is the heat energy supplied to the system.

So ΔE is a combination of the work done W and the heat energy supplied Q . This is a statement of the First Law of Thermodynamics - conservation of energy applied to processes involving macroscopic bodies, and recognising that heat and work are separate forms of energy.

Note: ΔE is a function of state, but Q and W are not.

For infinitesimal changes, the First Law is written as:

$$dE = dQ + dW \quad (1.26)$$

Note: d is a reminder that dQ and dW are not changes in functions of state.

1.5.1. What is E in general?

E is the sum of two contributions:

- The energy of the macroscopic mass motion of the system (the kinetic energy of the centre of mass of the system plus and potential energy due to external fields of force.)
- Internal energy of the system: Energy associated with the internal degrees of freedom.

We usually ignore the first of these and consider the energy E as referring to the internal energy. So:

$$E = \text{K.E.}(\text{molecular motion}) + \text{P.E.}(\text{molecular interaction}) \quad (1.27)$$

i.e. E is associated with the random motions of the particles, also known as the thermal energy.

E is a function of state. For a constant mass of fluid:

$$\left. \begin{array}{l} E = E(P, T) \\ E = E(V, T) \end{array} \right\} \begin{array}{l} \text{Depending on independent variables} \\ \text{we choose to specify the state of the system.} \end{array} \quad (1.28)$$

What is E for a perfect gas?

We assume potential energy is negligible.

$$E = \begin{array}{l} \text{kinetic energy} \\ \text{of translation} \end{array} + \begin{array}{l} \text{rotational/vibrational} \\ \text{kinetic energy (in molecules.)} \end{array}$$

$E = E(T)$ only. This was proved by Joule's experiment. If an ideal gas expands from half a box into the whole box: $W - Q = 0 \therefore \Delta E = 0$

Note: For real gases T drops slightly as work is done against the cohesive forces within the gas. So $E = E(T)$ is the second criterion for a perfect gas.

Recall the two criteria for a perfect gas:

- Perfect gas law: $PV = NkT = nRT$
- Internal energy is a function of temperature: $E = E(T)$

Generally W and Q are *not* functions of state. Work and heat are, essentially, different forms of energy transfer.

- **Work:** Energy transfer by macroscopic degrees of freedom of a system.
- **Heat:** Energy transfer by microscopic degrees of freedom of a system.

1.5.2. Example

Work is done during the isothermal compression of a perfect gas, the process is reversible. Consider one mole of an ideal gas compressed by a piston, in contact with a heat bath (a heat bath has a very large heat capacity and a constant temperature.) Work done by the piston moving through a distance δx :

$$\begin{aligned} W &= \text{Force} \times \text{Distance moved} \\ W &= PA \cdot (-\delta x) \end{aligned}$$

Assuming compression is reversible, and occurs at an isotherm; $PV = N_0kT$ applies. The work done on the gas in compressing it from a volume V to a volume $V + \delta V$ is:

$$\#W = -P\delta V$$

Note the -ve, since the change in volume is negative. \therefore for a change from V_1 to V_2 we have:

$$\begin{aligned} W &= - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{N_0kT}{V} dV \\ &= N_0kT \ln \left(\frac{V_1}{V_2} \right) \\ W &= \underline{\underline{RT \ln \left(\frac{V_1}{V_2} \right)}} \end{aligned} \tag{1.29}$$

Note: For a different (non-isothermal) path between states 1 and 2 the work (are under the curve) will be different. In a cyclical process we can have a net work done, whereas in a δE around the cyclical path is 0 (since E is a function of state.)

1.5.3. Reversibility & Irreversibility

To be reversible:

1. The process must be quasi-static.
2. There must be no hysteresis effect.

Quasi-static: When we can define every intermediate state of a process as a succession of equilibrium states. A process is reversible if it's direction can be reversed by an infinitesimal change in the direction - this is an idealisation from reality. A *non*-quasi-static change would be, for example, a sudden compression of a gas at pressure P .

Hysteresis: When the state depends not only on instantaneous values of parameters, but also on the system's previous history.

Note: Reversibility is an ideal, all real processes are irreversible.

Example of non-quasi-static change:

Imagine a clamped piston with two masses on it, with the gas contained in the piston at a pressure P . The piston exerts a pressure P_0 with $P_0 > P$. The clamp is released causing a volume change δV . The work done by the mass on the system is:

$$\#W = -P_0\delta V$$

Since: $P_0 > P$ and $\delta V > 0$. This leads to the statement:

$$\delta W > -PdV \quad (1.30)$$

The same result applies for rapid expansion. An example of this would be the expansion of gas into a vacuum. Here, no work is done on the gas ($-\delta W = 0$) but PdV is positive.

Example of hysteresis:

Compression with friction between the cylinder and piston. For the ideal situation, $\delta W = -PdV$ there must be no frictional forces between the cylinder and the piston. If there is friction between them, then in compressing the gas the applied pressure $P_0 > P$ in order to overcome the frictional forces, and $\delta W > -PdV$.

The dashed curve on the graph shows the gas pressure P and the continuous curve shows the applied pressure P_0 for compression and expansion of the gas. If we carry out a cycle $ABCD$ the applied force has done a net amount of work given by the area of the cycle. Some of the work, however, is lost as heat (and subsequently passed into a heat bath.) $ABCD$ is a hysteresis curve and the process is irreversible. On reversing external conditions the system will not traverse the original path.

Summary:

$$\delta W \geq -PdV$$

$$\delta W \begin{cases} = -PdV & , \text{for reversible changes} \\ > -PdV & , \text{for irreversible changes} \end{cases}$$

1.6. Heat Capacity

Although the work is done in a reversible change is well defined, it does depend on the path. We can join states 1 and 2 by many paths (we chose isothermal compression in an example above). The work done is given by the area under the curve.

For curve A:

$$W_A = - \int_{V_{1A}}^{V_{2A}} PdV \quad (1.31)$$

In a cyclic process the work done is represented by the area inside the loop:

$$\oint PdV = W_A - W_B \neq 0 \quad (1.32)$$

The work around a complete cycle does, therefore, not vanish, but:

$$\Delta E = \oint dE = 0 \quad (1.33)$$

At any point on the path, E has a defined value because it is a function of state.

We had:

$$dE = dQ + dW$$

We also have for reversible changes:

$$dW = -PdV$$

So, therefore the First Law of Thermodynamics for a reversible change is:

$$dQ = dE + PdV \quad (1.34)$$

We define heat capacities as:

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

The rate of heat input per unit increase in T per mole of gas. This is in $\text{W K}^{-1} \text{mol}^{-1}$.

The specific heat, τ , is the same per unit mass.

Since dQ is not a function of state, we find that C depends on the mode of heating.

Heat capacity at constant volume (per mole.)

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{dE}{dT} \right)_V \quad (1.35)$$

Heat capacity at constant pressure (per mole)

$$C_P = \left(\frac{dQ}{dT} \right)_P = \left(\frac{dE}{dT} \right)_P + P \left(\frac{dV}{dT} \right)_P \quad (1.36)$$

For a perfect gas $E = E(T)$, so:

$$\left(\frac{dE}{dT} \right)_V = \left(\frac{dE}{dT} \right)_P \quad (1.37)$$

Using $PV = N_0kT$, this leads to:

$$C_P - C_V = P \left(\frac{dV}{dT} \right)_P = N_0k = R \quad (1.38)$$

Finally in the first law we must allow for all forms of work, (e.g. magnetic etc.)

2. The Second and Third Laws of Thermodynamics

The first law covers energy balance and conservation, the second law governs a processes direction.

“Left to itself a system, not initially in equilibrium, will change in a definite direction towards equilibrium.”

2.1. Statements of the Second Law

Clausius (1850):

“Heat, *by itself*, cannot pass from a colder to a hotter body.”

Kelvin (1851):

“A process whose *only* effect is the complete conversion of heat to work cannot occur.”

What is the efficiency?

Consider a system (a **heat engine**) that absorbs heat Q_1 , converts some to work W , and rejects the remainder as Q_2 .

The first law says: $W = Q_1 - Q_2$ Thermal efficiency, η , is the proportion of heat converted to work:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} < 1 \quad (2.1)$$

The general formulation of the second law was given by Clausius who, in 1854 and 1865, introduced the concept of entropy.

2.1.1. Entropy as a measure of disorder

The macroscopic concept of ‘entropy’ S , is defined by (see later)

$$dS \begin{cases} = \frac{dQ}{T} , \text{ for a reversible change} \\ > \frac{dQ}{T} , \text{ for an irreversible change} \end{cases} \quad (2.2)$$

Note: Entropy, S , is a function of state.

Boltzmann, in the 1870s, related entropy to the microscopic disorder of a system. Given Any given macroscopic state can be in any one of an enormous number of microscopic states. The course macroscopic description cannot distinguish between these.

Our previous example of a gas expanding into a vacuum is an irreversible change. So in the final state we have less knowledge of the system, in that, initially we know all of the molecules are in one half of the container, after the expansion they fill the container.

The final state is a less ordered, more random state.

“For any real process, the entropy of an isolated system always increases to a maximum.”

Since entropy is a measure of the degree of disorder, it is a function of state.

For a change in the system between two definite states, ΔS is independent of how the change occurs.

2.2. Macrostates and Microstates

Consider a real system containing N molecules (of the same type, for simplicity.) The macrostate can be defined depending on the constraints.

Generally, conditions imposed on the system forcing certain variables to be fixed are called constraints. Generally, we assume the system is enclosed and isolated. We can fix E, V, N , which fully determine a macrostate of a system. In a non-equilibrium state other quantities must be specified. Generally, we label the additional variables α ($\alpha_1, \alpha_2 \dots \alpha_n$).

The macrostate is then determined by (E, V, N, α).

Microscopic description is very complicated, in equilibrium all we need to know is how many microstates correspond to a given macrostate. Quantum mechanics helps here as the microstates then form a discrete set and not a continuum. Which is to say, every macrostate of a system comprises a perfectly discrete number of microstates of the system.

The number of microstates that can give the same macrostate, and which have an energy between E and $E + \delta E$ give the statistical weight of the system, Ω .

For our isolated system:

$$\begin{aligned} \Omega(E, V, n) &, \text{ equilibrium state} \\ \Omega(E, V, n, \alpha) &, \text{ non-equilibrium state} \end{aligned}$$

There are several reasons for defining a macrostate as having an imprecise energy lying in δE . Experimentally energy is only defined to some finite accuracy. We choose δE for convenience, if it is large it may contain many microstates. This will mean $\Omega(E, V, n, \alpha)$ will be a smooth changing function of energy. If δE is small, Ω will be wildly fluctuating, being different from zero when E coincides with a microstate.

Example - A paramagnetic solid in a magnetic field

Molecules, each having a magnetic moment, $\bar{\mu}$ (consider them as little bar magnets) are arranged on the lattice sites of a crystal. When a B -field is applied, each molecule (dipole) acquires an interaction energy.

$$-\bar{\mu} \cdot \mathbf{B}$$

This tends to align the dipole along the field, it is opposed by disorganising thermal motion. Classically any orientation is allowed, but in quantum mechanics only certain, specific orientations are.

For the simplest situation consider spin $\frac{1}{2}$ dipoles (with angular momentum: $\frac{\hbar}{2}$), only two orientations can occur:

1. Parallel (spin-up) to the B -field, or...
2. Anti-parallel (spin-down) to the B -field.

So each dipole has two possible 'one particle states'.

Spin up gives an energy of $-\mu B$. Spin-down gives an energy of μB . The energy states differ by $\Delta E = 2\mu B$.

Consider now a system of N dipoles in a B -field. If n are spin up, then $(N - n)$ are spin down. Then the energy of the system is:

$$\begin{aligned} E(B, V, N, n) &\equiv E(n) \\ E(n) &= n(-\mu B) + (N - n)(\mu B) \\ E(n) &= (N - 2n)(\mu B) \end{aligned} \tag{2.3}$$

E , and hence the macrostate, is determined by n . Ω is related to how many ways we can choose n sites to be spin up and $(N - n)$ sites to be spin down.

Example: For $N = 4, n = 2$ there are six possible combinations. We have 2 possible orientations of N sites, i.e. 2^N microstates in total. The number of microstates with energy $E(n)$ is:

$$\Omega(n) = \frac{N!}{n!(N-n)!} \quad (2.4)$$

(See ${}^n C_r$)

We choose δE so that $\delta E < 2\mu B$. The interval δE contains $\ll 1$ energy levels and $\Omega(n)$ is the statistical weight of the macrostate with energy $E(n)$. For $n = N$ all dipoles are aligned parallel. The energy is a minimum, $E(n) = -\mu BN$, this is the ground state. Here $\Omega(N) = 1$ (there is only one microstate.) For $n = \frac{N}{2} \Rightarrow E(\frac{N}{2}) = 0$ this is a state with random orientation, the most disordered state, the state we have if there is no B -field. $\Omega(n)$ attains it's maximum here. Thus, Ω is a measure of the disorder of the system.

2.2.1. Equilibrium of an isolated system.

Postulate of equal a priori probability.

The macrostate is fully specified by E, V and N . There are fluctuations about equilibrium. Additional variables α must be defined, with a statistical weight for each one. Over time a system will pass through all the possible microstates so long as the values E, V and N are fixed.

For each value of α we expect that the corresponding $\Omega(E, V, N, \alpha)$ microstates are equally probable.

This leads to the postulate of equal *a priori* probability:

“For an isolated system all microstates compatible with the given constraints of the system are equally likely to occur.”

Result: The probability that a system is in a particular macrostate (E, V, N, α) is proportional to the number of microstates $\Omega(E, V, N, \alpha)$.

2.2.2. Equilibrium Postulate

“Equilibrium corresponds to that value of α for which our $\Omega(E, V, N, \alpha)$ attains it's maximum value, with (E, V, N) fixed.”

Meaning: The equilibrium state is simply the state of maximum probability, that is with a maximum statistical weight Ω .

2.2.3. Entropy

Entropy (a measure of disorder) is defined by (Boltzmann):

$$S(E, V, N, \alpha) = k \ln \Omega(E, V, N, \alpha) \quad (2.5)$$

Entropy reaches a maximum for the equilibrium macrostate.

Note: This gives us a zero point for the entropy, when $\Omega = 1$ $S = 0$. This is the situation of perfect order.

Clausius:

“Entropy of a real, isolated system always increases. In equilibrium entropy is at a maximum.”

2.2.4. Temperature, Pressure and Chemical Potential as derivatives of Entropy

We use the second law to derive the temperature, pressure and chemical potential (T, P, μ) as functions of energy.

Consider an isolated system, separated into subsystems 1 and 2 by a partition. Where heat can pass through the partition. In equilibrium it's macrostate would be given by:

$$(E, V, N) \text{ with } E = E_1 + E_2, V = V_1 + V_2, N = N_1 + N_2 \quad (2.6)$$

Assume now that the system is not in equilibrium, but with an overall small energy exchange between the subsystems it will be. The number of microsystems for each subsystem is:

Subsystem 1 has: $\Omega_1(E_1, V_1, N_1)$

Subsystem 2 has: $\Omega_2(E_2, V_2, N_2)$

The whole system has:

$$\Omega(E, V, N, E_1, V_1, N_1)$$

E_1, V_1 and N_1 are our α 's.

Note: In equilibrium the number of microstates for the whole system is simply $\Omega(E, V, N)$, E_1, V_1, N_1 become other descriptors, α .

We do not use E_2, V_2, N_2 as these are not independent of E_1, V_1, N_1 .

We can make any whole system microstate by taking a microstate from each of the subsystems and combining them:

$$\Omega = \Omega_1 \Omega_2 \quad (2.7)$$

Thus, for the definition of $S = k \ln \Omega$ we have:

$$S(E, V, N, E_1, V_1, N_1) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \quad (2.8)$$

So entropies add just like E, V, N in (2.6), hence the logarithm. These properties are proportional to the size of the system.

Extensive and Intensive variables.

- Quantities which are proportional to system size are extensive.
- Quantities that are *not* proportional to system size are intensive.

We can convert from extensive to intensive quantities by dividing by the system size.

2.2.5. Temperature as a derivative of entropy

We assume the partition is fixed by a diathermal (permeable to heat) divider.

- V_1, V_2, N_1, N_2 are fixed.
- E_1, E_2 are variable.

So we have one independent variable E .

From the second law we obtain the equilibrium condition by maximum entropy. From (2.8) we have:

$$\left(\frac{dS}{dE_1} \right)_{E_1, V, N, V_1, N_1} = \left(\frac{dS_1}{dE_1} \right)_{V_1, N_1} + \left(\frac{dS_2}{dE_2} \right)_{V_2, N_2} \left(\frac{dE_2}{dE_1} \right) = 0 \quad (2.9)$$

Since $E_1 + E_2 = E$:

$$\Rightarrow \frac{dE_2}{dE_1} = -1$$

So:

$$\left(\frac{dS_1}{dE_1} \right)_{V_1, N_1} = \left(\frac{dS_2}{dE_2} \right)_{V_2, N_2} \quad (2.10)$$

Criterion For Thermal Equilibrium

We can define an absolute temperature scale, T_i for each subsystem.

$$\left(\frac{dS_i}{dE_i} \right)_{V_i, N_i} = \frac{1}{T_i} \quad (2.11)$$

Thus, two systems are in equilibrium with each other when $T_1 = T_2$.

The definition (2.11) is chosen so it is identical with the perfect gas temperature scale.

Is T positive? Yes, as $\Omega(E)$ is a rapidly increasing function of E . $\frac{dS}{dE} > 0 \therefore T > 0$.

Are hot and cold correct? Yes. Consider a system coming to equilibrium:

$$\begin{aligned}\frac{dS}{dt} &= \left(\frac{dS_1}{dE_1}\right) \left(\frac{dE_1}{dt}\right) + \left(\frac{dS_2}{dE_2}\right) \left(\frac{dE_2}{dE_1}\right) \left(\frac{dE_1}{dt}\right) \\ &= \left[\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \frac{dE_1}{dt} > 0\end{aligned}\quad (2.12)$$

If $T_1 < T_2$ then $\frac{dE_1}{dt} > 0$, i.e. heat flows from hot to cold.

2.2.6. Pressure as a derivative of entropy

Now consider a movable, frictionless, diathermal partition:

- N_1, N_2 are fixed.
- E_1, E_2, V_1, V_2 can vary.

In equilibrium pressure and temperature are the same on both sides of the partition. If the entropy S is maximised with respect to energy E and volume V , as independent variables, one again obtains:

$$\left(\frac{dS_1}{dE_1}\right)_{V_1, N_1} = \left(\frac{dS_2}{dE_2}\right)_{V_2, N_2} \quad (2.13)$$

i.e. Equal temperatures.

As a second criterion:

$$\left(\frac{dS_1}{dV_1}\right)_{E_1, N_1} = \left(\frac{dS_2}{dV_2}\right)_{E_2, N_2} \quad (2.14)$$

Which must be interpreted as implying equal pressures in the 2 sub systems. We define the pressure as:

$$P_i = T_i \left(\frac{dS_i}{dV_i}\right)_{E_i, N_i} \quad i = 1, 2, 3, \dots \quad (2.15)$$

This is identical (see later) with the conventional definition: $PV = NkT$.

The Clausius principle ($\frac{dS}{dt} > 0$) applies, so that when not in pressure equilibrium the sub system at higher pressure expands, and the sub system at lower pressure contracts.

2.2.7. Chemical potential, μ , as a derivative of entropy

Now consider using a fixed, porous, diathermal partition.

- V_1, V_2 fixed.
- E_1, E_2, N_1, N_2 can vary.

We again get the first condition:

$$\left(\frac{dS_1}{dE_1}\right)_{V_1, N_1} = \left(\frac{dS_2}{dE_2}\right)_{V_2, N_2} \quad (2.16)$$

Maximising entropy with respect to N_1 leads to a another condition:

$$\left(\frac{dS_1}{dN_1}\right)_{E_1, V_1} = \left(\frac{dS_2}{dN_2}\right)_{E_2, V_2} \quad (2.17)$$

i.e. There is no net transfer of particles.

We define μ by:

$$\mu = -T_i \left(\frac{dS_i}{dN_i}\right)_{E_i, V_i} \quad (2.18)$$

This is useful when subsystems have different phases. In equilibrium the μ values of the phases must be equal.

2.3. Schottky defects in a crystal

- At $T = 0$ the atoms or molecules occur completely regularly in the crystal lattice.
- At $T > 0$ thermal agitation occurs, causing the vibration of particles. This can lead to particles being displaced altogether from lattice sites leaving site vacancies called point defects.
- One type of defect is called a Schottky defect, where the atom or molecule is removed completely and migrates to the surface of the crystal.

2.3.1. How does the number of defects depend on the temperature?

Let ϵ be the energy of formation of a Schottky defect, the binding energy of an atom or molecule at the surface of the crystal relative to interior atoms or molecules (i.e. at surface energy $E = 0$). Take a crystal of N atoms and in a certain macrostate. Say it has n Schottky defects.

The energy of formation of these defects is: $E = n\epsilon$.

(We assume that $n \ll N$, so each point defect is surrounded by a well ordered lattice and therefore ϵ is well defined.)

The number of ways we can remove n atoms from a crystal of N atoms is the statistical weight $\Omega(n)$ of the macrostate.

$$\Omega(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!} = {}^n C_N \quad (2.19)$$

The entropy associated with the disorder is:

$$\begin{aligned} S(n) &= k \ln[\Omega(n)] \\ &= k \ln \left[\frac{N!}{n!(N-n)!} \right] \end{aligned} \quad (2.20)$$

Note: We neglect a surface entropy effect due to the ways of arranging the n atoms on the surface since it is relatively small.

For a crystal in thermal equilibrium:

$$\frac{1}{T} = \frac{dS}{dE} = \frac{dS(n)}{dn} \frac{dn}{dE} = \frac{1}{\epsilon} \frac{dS(n)}{dn} \quad (2.21)$$

Since $E = n\epsilon$.

To calculate $\frac{dS(n)}{dn}$ it is possible to use Stirling's formula for $N \gg 1$:

$$\ln(N!) = N \ln(N) - N \quad (2.22)$$

$$S(n) = k [N \ln(N) - n \ln(n) - (N - n) \ln(N - n)] \quad (2.23)$$

So:

$$\frac{dS(n)}{dn} = k [-\ln(n) + \ln(N - n)] \quad (2.24)$$

And:

$$\frac{1}{T} = \frac{k}{\epsilon} \ln \left(\frac{N - n}{n} \right) \quad (2.25)$$

Taking components and solving for n :

$$\frac{n}{N} = \frac{1}{e^{\frac{\epsilon}{kT}} + 1} \quad (2.26)$$

For $n \ll N$ (i.e. $\epsilon \gg kT$), we get the concentration of defects as:

$$\frac{n}{N} = e^{\frac{-\epsilon}{kT}} \quad (2.27)$$

2.4. Equilibrium of a system in a heat bath

2.4.1. Systems of a constant temperature and variation in energy

What do we mean by a constant temperature? We mean putting a system in a heat bath at temperature T , where T is a constant. The equilibrium macrostate here is specified by (T, V, N) . The state is not specified by energy E now since at a constant temperature there are tiny fluctuations in the energy. For a macroscopic system these fluctuations are negligible but this is not true for a system with a small number of particles. In the above (arbitrary) energy level diagram for an atom, we can see that

the associated average energy \bar{E} for the temperature T of the atom is between two energy levels.

We consider one atom as a system in equilibrium with a “heat bath” of the other atoms. E (and the microstate) fluctuate a lot, but in thermal equilibrium \bar{E} (the time average energy) is constant, as is the temperature T .

We can consider a new system made up of these one particle sub systems and find the probability (as a function of T) that an isothermal system is in a certain macrostate - the Boltzmann distribution.

2.4.2. The Boltzmann distribution for a system in a heat bath

Consider a system in a heat bath with N particles and a volume V . The equilibrium macrostate for the system is specified by (T, V, N) - T is constant and E fluctuates. The system has a discrete set of microstates :

$$i = 1, 2, 3, \dots, r$$

With:

$$E_i = E_1, E_2, E_3, \dots, E_r$$

Note: Many microstates may have the same energy, E_i are not all different. In general the energy of a system is quantised.

Example: A paramagnetic solid, with four particles ($N = 4$).

We choose δE as the minimum spacing between energy levels, δE contains at most one energy level. Using our previous analysis of a system partitioned by a diathermal wall, we have our system being the atom and our heat bath being the other atoms.

Omitting all V and N as constants, we now have:

$$E_{\text{System}} + E_{\text{Heat bath}} = E_0 \quad (\text{Constant})$$

Thus:

$$E_{\text{Heat bath}} = E_0 - E_{\text{System}}$$

The macrostate of the combined system and heat bath is specified by E_0 and E_{System} , and having $\Omega(E_0, E_{\text{System}})$ possible microstates.

We can state:

1. The probability that the system and the heat bath are in the microstate specified by (E_0, E_{System}) is proportional to $\Omega(E_0, E_{\text{System}})$

$$2. \Omega(E_0, E_{\text{System}}) = \Omega_{\text{System}}(E_{\text{System}}) \Omega_{\text{Heat bath}}(E_0 - E_{\text{System}})$$

Let us constrain the system to be in a single microstate r . Then:

$$E_{\text{System}} = E_r$$

And:

$$\Omega_{\text{System}}(E_{\text{System}}) = \Omega_{\text{System}}(E_r) = 1$$

From the second fact we have:

$$\Omega(E_0, E_{\text{System}}) = \Omega_{\text{Heat bath}}(E_0 - E_r)$$

Thus, the probability P_r that our combined system and heat bath is in a macrostate where the system is in a definite macrostate r is given by:

$$P_r \propto \Omega_{\text{Heat bath}}(E_0 - E_r) \quad (2.28)$$

The corrected, normalised probability is (summed over all of the states of the system):

$$P_r = \frac{\Omega_{\text{Heat bath}}(E_0 - E_r)}{\sum_r \Omega_{\text{Heat bath}}(E_0 - E_r)} \quad (2.29)$$

$\Omega_{\text{Heat bath}}(E_0 - E_r)$ is the “partition function.”

We can express this in terms of the entropy of the heat bath (using $S = k \ln \Omega$):

$$P_r = \text{Const.} e^{\frac{S_{\text{Heat bath}}(E_0 - E_r)}{k}} \quad (2.30)$$

So far this is general but the heat bath must have a lot more energy than the system, i.e. $E_0 \gg E_r$, therefore we can expand $\frac{S_{\text{Heat bath}}(E_0 - E_r)}{k}$ as a Taylor series:

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2!}f''(x) + \frac{h^3}{3!}f'''(x) + \dots \quad (2.31)$$

$$\frac{1}{k}S_{\text{Heat bath}}(E_0 - E_r) = \frac{1}{k}S_{\text{Heat bath}}(E_0) - \frac{E_r}{k} \frac{dS_{\text{Heat bath}}(E_0)}{dE_0} \quad (2.32)$$

Since, by definition:

$$\left(\frac{dS_i}{dE_i} \right)_{V_i, N_i} = \frac{1}{T_i} \quad (2.33)$$

We have (since $E_0 \gg E_r$):

$$\frac{dS_{\text{Heat bath}}(E_0)}{dE_0} = \frac{1}{T} \quad (2.34)$$

Where T is the temperature of the heat bath:

$$\frac{1}{k}S_{\text{Heat bath}}(E_0 - E_r) = \frac{S_{\text{Heat bath}}(E_0)}{k} - \frac{E_r}{kT} \quad (2.35)$$

So:

$$P_r \propto e^{\frac{S_{\text{Heat bath}}(E_0)}{k}} e^{-\frac{E_r}{kT}} \quad (2.36)$$

The first term here is the constant of proportionality, obtained by normalisation. From this we get the Boltzmann distribution:

$$P_r = \frac{1}{z} e^{-\beta E_r} \quad (2.37)$$

Where, β is the temperature parameter $\frac{1}{kT}$ and z is the normalising partition function $\sum_r e^{-\beta E_r}$. $e^{-\beta E_r}$ is sometimes called the “Boltzmann factor”.

The Boltzmann distribution tells us the probability that a system at a constant temperature T will be in a state with energy E . It depends on E_r and T .

2.4.3. Discreet probability distribution in energy

The partition function is the sum over all states r . We sometimes define $g'(E_r)$ as the number of states with energy E_r (the degeneracy). Therefore, we can regroup the summed terms in the partition function z as a sum over energies rather than states.

$$z = \sum_{E_r} g'(E_r) e^{-\beta E_r} \quad (2.38)$$

Since there are $g'(E_r)$ states with energy E_r the probability that a system is in a state with energy E_r is:

$$P(E_r) = \frac{1}{z} g'(E_r) e^{-\beta E_r} \quad (2.39)$$

The discreet distribution in energy.

2.4.4. Mean energy and fluctuations

Now consider:

$$\begin{aligned} \left(\frac{d \ln z}{d\beta} \right) &\equiv \left(\frac{d \ln z}{dz} \right) \left(\frac{dz}{d\beta} \right) \\ &= \frac{1}{z} \left(\frac{dz}{d\beta} \right) \\ &= \frac{1}{z} \sum_r [-E_r e^{-\beta E_r}] \\ &= - \sum_r P_r E_r \end{aligned} \quad (2.40)$$

Using the equations for P_r and z this just becomes the mean energy \bar{E} . So for a system in a heat bath the mean energy is:

$$\bar{E} = \sum_r P_r E_r = - \frac{d \ln z}{d\beta} \quad (2.41)$$

It can be shown that for a system of N particles the relative size of energy fluctuations is $\frac{\Delta E}{E} \sim 10^{-11}$, i.e. very small.

2.4.5. Continuous probability distribution in energy

To derive the discrete distribution in energy we made δE a lot less than the energy level spacing.

Generally the number of energy levels in a ‘reasonable’ value of δE is huge. Therefore, we use a continuous energy distribution.

Define $P(E)$ as the probability per unit energy (probability density function), so $P(E)\delta E$ is the probability of the system having energy from E to $E + \delta E$.

We define the density of states $g(E)$ so that $g(E)\delta E$ is the number of states in the interval E to $E + \delta E$.

If $E_r \sim E$ throughout the interval then with p_r being the probability of the system being in a state with energy E , we get the result:

$$P(E) = p_r g(E) \delta E \quad (2.42)$$

Which gives the continuous form:

$$P(E) = \frac{1}{z} g(E) e^{-\beta E} \quad (2.43)$$

And normalising we get:

$$z = \int_E g(E) e^{-\beta E} \delta E \quad (2.44)$$

Note: In some cases $f(E)$ is used in place of $g(E)$.

For a real system $g(E)$ increases rapidly with an increase in E , and $e^{-\beta E}$ decreases rapidly with an increase in E .

2.4.6. Entropy and the Helmholtz free energy

Previously entropy was defined for the special case of an isolated system. We now generalise that and then apply it to a system in a heat bath.

Consider a macroscopic system with microstates $1, 2, 3, \dots, r$ and we let p_r be the probability that the system is in a microstate r . The only constraint is normalisation:

$$\sum_r p_r = 1$$

The general definition of entropy is:

$$S = -k \sum_r p_r \ln(p_r) \quad (2.45)$$

We can show that this reduces to the original definition for an isolated system. For an isolated system with energy E to $E + \delta E$ there are Ω different microstates with energy E_r in their interval. Hence, the probability p_r of finding the system in one of these states is:

$$p_r = \frac{1}{\Omega(E, V, N)}$$

$$\sum_r p_r = 1$$

If there are Ω non-zero terms in (2.45) and $p_r = \frac{1}{\Omega}$ for each of there:

$$S(E, V, N) = k \ln \Omega(E, V, N) \quad (2.46)$$

In agreement with the earlier definition.

To get the entropy of the system in the heat bath at temperature T . We substitute the Boltzmann distribution in:

$$S(T, V, N) = k \ln z + \frac{\bar{E}}{T} \quad (2.47)$$

Note: This is a function of T , not E for an isothermal system.

For a macroscopic system at T we know that $\frac{\Delta E}{E}$ for the bath is negligible, i.e. the energy is well defined.

Hence, the entropy of a body in a heat bath is sharply defined and is equal to the entropy of an isolated body with energy equal to \bar{E} of a system at temperature T .

$$S(T, V, N) = k \ln \Omega(E, V, N) \quad (2.48)$$

Table 2.1 contains a summary of the variables for isolated systems and systems in a

	Isolated system	System in heat bath
Independent vars	(E, V, N)	(T, V, N)
Basic stat. quantity	$\Omega(E, V, N)$	$Z(T, V, N) = \sum_r e^{-\beta E_r}$
Basic t.d. quantity	$S(E, V, N)$	$F(T, V, N)$
Eqm. cond.	S is at a maximum.	F is at a minimum.

Table 2.1.: Variable comparison in isolated systems and systems in a heat bath showing: The independent variables, the basic statistical quantity, the basic thermodynamic quantity and the equilibrium condition for both types of system.

heat bath. In the above table (Table 2.1) F is the ‘‘Helmholtz free energy:’’

$$F(T, V, n) = -kT \ln [z(T, V, N)] \quad (2.49)$$

Eliminating z from (2.47) and (2.49) we obtain:

$$F = E - TS \quad (2.50)$$

We have replaced \bar{E} with E for a well defined system. Equations ((2.48) or (2.49) tell us the choice of independent variables (E, V, N) or (T, V, N) , which leads to using S or F .

Note: Be aware of the conditions for equilibrium in the above table.

2.5. Infinitesimal Changes : Maxwell Relations and Clausius’ Principle

What is the entropy change dS for a change between 2 very close states in an isolated system (with N constant)?

$$V \rightarrow V + dV$$

$$\beta \rightarrow \beta + d\beta \quad \beta = \frac{1}{kT} \quad (\text{The temperature constant.})$$

$$E = \sum_r p_r E_r \quad (2.51)$$

$$\therefore dE = \sum_r E_r dp_r + \sum_r p_r dE_r \quad (2.52)$$

For a system in a heat bath we know that E_r varies with V but not with β . p_r varies with both V and β (Boltzmann distribution) since $p_r = \frac{1}{z} e^{-\beta E_r}$.

So:

$$z p_r = e^{-\beta E_r} \quad (2.53)$$

$$\ln(z) + \ln(p_r) = -\beta E_r \quad (2.54)$$

Consider the terms in (2.52).

First:

$$\begin{aligned} \sum_r E_r dp_r &= \left(\frac{-1}{\beta}\right) \left\{ \sum_r \ln(z) dp_r + \sum_r \ln(p_r) dp_r \right\} \\ &= \left(\frac{-1}{\beta}\right) \left(\sum_r \ln(p_r) dp_r \right) \end{aligned} \quad (2.55)$$

As the sum of all probability changes has to be zero.

Recall:

$$S = -k \sum_r p_r \ln(p_r) \quad (2.56)$$

$$\therefore dS = -k \left\{ \sum_r \ln(p_r) dp_r + \sum_r p_r d(\ln(p_r)) \right\} \quad (2.57)$$

$$dS = -k (E_r \ln(p_r) dp_r) \quad (2.58)$$

$$\therefore \sum_r E_r dp_r = T dS \quad (2.59)$$

Returning to the second term in (2.52):

$$\sum_r p_r dE_r = \sum_r p_r \frac{dE_r}{dV} dV \quad (2.60)$$

Now if the system is in microstate r and stays in that state then a volume change dV implies an energy change.

$$dE_r = \frac{dE_r}{dV} dV = -P_r dV \quad (2.61)$$

So if we have a probability distribution p_r of the system in state r , the total pressure is:

$$P = \sum_r p_r \left(\frac{-dE_r}{dV} \right) \quad (2.62)$$

So:

$$\sum_r p_r dE_r = -P dV$$

This is valid for quasi-static changes.

$$\therefore dE = T dS - P dV \quad (2.63)$$

Compare (2.63) with the first law of thermodynamics:

$$dE = \delta Q + \delta W$$

For infinitesimal, reversible changes:

$$\begin{aligned}dW &= -PdV \\dS &= \frac{dQ}{T}\end{aligned}\tag{2.64}$$

If the system and the heat bath are at the same temperature, and we supply heat dQ reversibly, entropy increases by $\frac{dQ}{T}$.

For an irreversible change this becomes:

$$dW > -PdV$$

In fact both the Kelvin and Clausius statements for the second law follow from this in-equality.

From (2.65) we have two useful relationships:

$$T = \left(\frac{dE}{dS}\right)_V \quad P = -\left(\frac{dE}{dV}\right)_S\tag{2.65}$$

And since:

$$\frac{d^2 E}{dV dS} = \frac{d^2 E}{dS dV}\tag{2.66}$$

$$\left(\frac{dT}{dV}\right)_S = -\left(\frac{dP}{dS}\right)_V\tag{2.67}$$

This is one of the Maxwell relations.

There are three other Maxwell relations that hold for any equilibrium system. We can derive these relationships from the Helmholtz free energy F .

$$F = E - TS \quad dE = TdS - PdV\tag{2.68}$$

$$\Rightarrow dF = -SdT - PdV \quad P = -\left(\frac{dF}{dV}\right)_T\tag{2.69}$$

Since $F = -kT \ln(z)$ we will use this later to derive the pressure of a system in a heat bath from the partition function z .

2.5.1. Clausius' principle

In general going from state 1 to state 2 means:

$$\Delta S = S_2 - S_1 \quad (\text{This is } > 0 \text{ for a real system.})$$

Entropy increases. If the change is reversible $\Delta S = 0$.

Consider a system with a piston (T, P) in a very large heat bath at (T_0, P_0) . For an isolated composite system:

$$\Delta S_{\text{Total}} = \{\Delta S_{\text{System}} + \Delta S_{\text{Heat bath}}\} \geq 0 \quad (2.70)$$

We can transfer heat Q from the heat bath to the system by moving the piston. Since T_0 and P_0 are constant we can reversibly transfer heat to and from the heat bath.

$$\begin{aligned} \Delta S_{\text{Heat bath}} &= \frac{-Q}{T_0} \\ \Delta S_{\text{System}} - \frac{-Q}{T} &\geq 0 \end{aligned} \quad (2.71)$$

We can apply the first law to the system:

$$\Delta E = Q + W$$

If the heat bath does work on the system then:

$$\begin{aligned} W &= -P_0 dV \\ Q &= \Delta E - W \end{aligned}$$

So we get:

$$\Delta S_{\text{System}} - \left\{ \frac{\Delta E + P_0 dV}{T_0} \right\} \geq 0 \quad (2.72)$$

This is the Clausius in-equality, it depends on both the system *and* it's surroundings. It may be written:

$$\Delta A \leq 0 \quad (2.73)$$

Where: $A \equiv E + P_0 V - T_0 S$.

A is the "availability", a property of the system and it's surroundings. If $\Delta A \leq 0$ then the availability of the system in the given environment tends to decrease. In equilibrium ΔA has a minimum value, no further changes are possible.

$$dS = \frac{dQ}{T}$$

Example: Water being heated by heat transfer from a heat bath.

We have a heat bath at 80 °C and 1 litre of water at 20 °C. The specific heat of water is:

$$C = 4.2 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$$

The heat supplied by the heat bath:

$$Q = (-)1000 \times 4.2 \times 60 \text{ J}$$

So the entropy change:

$$\Delta S_{\text{Heat bath}} = \frac{Q}{T}$$

$$T_{\text{Heat bath}} = 353 \text{ K}$$

So:

$$\Delta S_{\text{Heat bath}} = -713.9 \text{ J K}^{-1}$$

Since the temperature of the water is changing:

$$\Delta S_{\text{Water}} = \int_{\text{State 1}}^{\text{State 2}} \frac{dQ}{T}$$

$$dQ = MCdT \tag{2.74}$$

So for:

$$T_1 = 20^\circ\text{C} \quad T_2 = 80^\circ\text{C}$$

$$\Delta S_{\text{Water}} = MC \int_1^2 \frac{dT}{T} = MC \ln \left(\frac{T_1}{T_2} \right)$$

$$= 4200 \ln \left(\frac{353}{293} \right)$$

$$= 782.4 \text{ J K}^{-1}$$

Therefore, the net change in entropy $\Delta S = 68.5 \text{ J K}^{-1}$. This is because the process is irreversible.

Now consider a two stage heating process with the following stages:

1. A heat bath at 50 °C and 1 litre of water at 20 °C.
2. A heat bath at 80 °C and 1 litre of water at 50 °C.

With this we get:

$$\text{Stage 1 entropy change: } \Delta S_{b1} = -390.1 \text{ J K}^{-1}$$

$$\text{Stage 2 entropy change: } \Delta S_{b2} = -356.9 \text{ J K}^{-1}$$

$$\Delta S_{\text{Total}} = -747.0 \text{ J K}^{-1}$$

$$\Delta S_{\text{Water}} = 782.4 \text{ J K}^{-1}$$

$$\Delta S_{\text{Net}} = 35.4 \text{ J K}^{-1}$$

If we increase the number of stages towards ∞ then ΔS tends towards 0 and the process is reversible.

2.5.2. Heat Engines

Consider an engine which obeys the second law (i.e. a real engine). The engine operates in a cycle. Heat Q_1 is extracted from a hot bath at T_1 , work W is done by the engine, and heat Q_2 is rejected to a cold bath at T_2 .

- First law: $Q_2 = Q_1 - W$
- Second law: $\Delta S = \left(-\frac{Q_1}{T_1}\right) + \left(\frac{Q_2}{T_2}\right) \geq 0$

The efficiency of the heat engine:

$$\eta = \frac{W}{Q_1}$$

Since $\Delta S \geq 0$:

$$\begin{aligned} -\frac{Q_1}{T_1} + \frac{Q_1 - W}{T_2} &\geq 0 \\ -\frac{Q_1}{T_1} + \frac{Q_1(1 - \eta)}{T_2} &\geq 0 \end{aligned} \quad (2.75)$$

Therefore:

$$\eta \leq 1 - \frac{T_2}{T_1} \quad (2.76)$$

This maximum value of η is only possible if the process is reversible.

η depends on the temperatures of the heat baths. It is often difficult to reduce T_2 so we increase T_1 to increase η .

Example: In a steam engine:

$$T_1 \approx 800 \text{ K} \quad T_2 \approx 300 \text{ K}$$

So T_2 is above room temperature.

This gives:

$$\eta_{\text{Max}} \approx 0.62$$

In reality we only achieve $\frac{\eta_{\text{Max}}}{2}$.

2.6. Third Law of Thermodynamics

What is the zero point of entropy? (i.e. S of a system cooled to $T \rightarrow 0$ K).
Can we reach $T = 0$?

Consider a system with energy levels $E_1 < E_2 < E_3 < \dots < E_r$, with degeneracy g_r for each energy level.

When T is so low that $kT \ll E_2 - E_1$ then only the lowest level has a significant probability of occupation.

$$p(E_1) \approx 1$$

So, as $S = k \ln(\Omega)$, $\lim_{T \rightarrow 0} S \rightarrow k \ln(g_1)$.

Now the ground state of any system is non-degenerate (i.e. $g_1 = 1$). Therefore as $T \rightarrow 0$, $S \rightarrow 0$.

This leads to the following statement:

“The entropy of a perfect crystal of an element at $T = 0$ is zero.”

This follows from the Nernst-Simon statement of the third law:

“If ΔS is the entropy change during any reversible, isothermal process in a condensed system, then $\Delta S \rightarrow 0$ as $T \rightarrow 0$.”

2.6.1. Absolute zero is unattainable

An alternate statement of the third law:

“It is impossible to reduce the temperature of any system, or part of a system, to absolute zero in a finite number of operations.”

x_1 and x_2 are values of some parameter (i.e. magnetic field strength) which can be varied. In a finite series of isothermal ($\Delta T = 0$) and adiabatic ($\Delta S = 0$) $T = 0$ could be reached but it would violate the third law, since the third law says that as $T \rightarrow 0$, $S \rightarrow 0$. As the third law applies for all values of x the temperature reduction for each adiabatic change gets smaller and smaller, and so you can get arbitrarily close to absolute zero, but you cannot reach it in a finite number of operations.

3. Energy Distributions of Weakly Interacting Particles

This section does not deal with the fundamental force, nor WIMPs, rather it looks at the differences between bosons and fermions.

- **Bosons**

Obey Bose-Einstein statistics

Have an integral spin quantum number.

Spin angular momentum: $0, \hbar, 2\hbar, 3\hbar, \dots$

Examples: Photons, π and k mesons....

No restriction on the occupation numbers (i.e. not restricted by the Pauli Exclusion principle.) $n_r = 0, 1, 2, 3, \dots$

- **Fermions**

Obey Fermi-Dirac statistics and the Pauli Exclusion Principle.

Spin angular momentum: $\frac{\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots$

Examples: Electrons, positrons, protons, neutrons...

Occupation numbers restricted, at most one particle can occupy any one state. $n_r = 0, 1$ (For all r)

3.1. Thermal energy distributions

Consider an isothermal system of N particles.

We want the thermal energy distribution - the partition (arrangement) of particles amongst the energy levels. Since this is rapidly changing, we take a time average. We can use discrete and/or continuous distributions, e.g. in a discrete distribution, the mean fraction of particles at an energy E is just $\frac{n(E)}{N}$.

Note: The mean fraction at energy E is the same as the probability p_E of finding any particle with energy E at any particular time.

For a single particle system at constant temperature and hence a constant average

energy, we have the Boltzmann distribution:

$$\begin{aligned} p(E) &= \frac{1}{z} g'(E) e^{-\beta E} \\ z &= \sum_E g'(E) e^{-\beta E} \end{aligned} \quad (3.1)$$

Does this apply to a particle in a collection? Generally, no.

We tend to use the mean number distribution, so:

$$\begin{aligned} n'(E) &: \text{Discret} \\ n(E) &: \text{Continuous} \end{aligned}$$

Discret energy distributions

So we have:

- $n'(E)$: The mean number of particles with energy E .
- $g'(E)$: The number of quantum mechanical states with energy E (i.e. the degeneracy of the energy level at E .)
- $f(E)$: The mean number of particles per (one particle) state at E .

We have here:

$$n'(E) = g'(E) f(E) \quad (3.2)$$

The total number of particles is N , therefore:

$$N = \sum_E [n'(E)] = \sum_E [g'(E) f(E)] \quad (3.3)$$

The total energy is then:

$$E_{\text{Total}} = \sum_E [n'(E) E] \quad (3.4)$$

And the mean energy of any particle is:

$$\bar{E} = \frac{\sum_E [n'(E) E]}{N} \quad (3.5)$$

The probability of a particle having an energy E is:

$$p(E) = \frac{n'(E)}{N} \quad (3.6)$$

Continuous energy distributions

Where δE is much larger than the spacing between the energy levels, we have:

- $n(E)$: The mean number of particles per unit energy.
- $g(E)$: The number of quantum mechanical states.
- $f(E)$: The mean number of particles per (one particle) state.

We have:

$$n(E) = g(E)f(E) \quad (3.7)$$

$$N = \int_E g(E)f(E)dE \quad (3.8)$$

The total energy is:

$$E_{\text{Total}} = \int_E n(E)EdE \quad (3.9)$$

Average energy is:

$$\langle E \rangle = \frac{(\int_E n(E)EdE)}{N} \quad (3.10)$$

The probability per unit energy at energy E is:

$$p(E) = \frac{n(E)}{N} \quad (3.11)$$

In general we need to find $g'(E)$ or $g(E)$ and $f(E)$ which depend on the type of particle and the constraints on the system.

3.1.1. The mean number of particles per state, $f(E)$ as a function of T

At any T , $f(E)$ is determined by the system and the particle states. $f(E)$ is often referred to as the “statistics” of the system.

$f(E)$ for localised particles (e.g. in a solid) is weakly interacting. Particles are distinguishable by their position in the lattice, but are not individually distinguishable. (Swapping particles with some the same one-particle state does not create a new microstate.)

All possible arrangements are allowed and we can consider the particles independently.

$p(E)$ is as for separate particles. So:

$$n(E) = Np(E)$$

Hence:

$$n'(E) = \frac{N}{z} g'(E) e^{-\beta E} \quad (3.12)$$

But:

$$n'(E) = g'(E)f(E)$$

So:

$$\frac{f(E)}{N} = \frac{e^{-\beta E}}{z} \quad (3.13)$$

Note: The N particles are split into their possible states in the same ratio as z is split into Boltzmann factor terms.

So:

$$f(E) = \frac{N}{z} e^{-\beta E} = A e^{-\beta E} = e^{-(\alpha - \beta E)} \quad (3.14)$$

For localised particles:

$$f(E) = \frac{1}{e^{\alpha + \beta E}} \quad (3.15)$$

Where $A = \frac{N}{z}$ and $\alpha = -\ln\left(\frac{N}{z}\right)$, and they both depend on the system and the number of particles.

They can be found by normalising:

$$\begin{aligned} N &= \sum_E g'(E)f(E) \\ N &= \int_E g(E)f(E) \end{aligned} \quad (3.16)$$

3.1.2. $f(E)$ for a perfect (quantum) boson gas

In a perfect gas, the particles are indistinguishable. Swapping particles does not create a new microstate, it is fully specified by the number of particles in each one-particle state. Particles cannot be considered individually, we have to consider the ground partition function. (This is complex to derive so we just state results.)

For Bosons, we use Bose-Einstein statistics:

$$f_{\text{BE}}(E) = \frac{1}{e^{\alpha - \beta E} - 1} \quad (3.17)$$

Where α is again a constant found by normalising.

3.1.3. $f(E)$ for a perfect (quantum) fermion gas

Again, particles are indistinguishable. The Pauli exclusion principle imposes an additional constraint: $n_r = 0, 1$ (For all r).

For fermions, we use Fermi-Dirac statistics:

$$f_{\text{FD}}(E) = \frac{1}{e^{\alpha+\beta E} + 1} \quad (3.18)$$

Again, α is found by normalisation.

3.1.4. $f(E)$ for a perfect classical gas

Again, all particles are indistinguishable. For a classical gas we assume that there are many more one-particle states available at any energy than there are particles with that energy, i.e. the number of particles $n'(E) \ll g'(E)$ or $f(E) \ll 1$ (this is valid for a dilute gas.) The probability that any state is occupied by more than one particle here is incredibly small.

For a classical gas, we use Maxwell-Boltzmann statistics:

$$f(E) = \frac{N}{z} e^{-\beta E} = \frac{1}{e^{\alpha+\beta E}} \quad (3.19)$$

3.1.5. α and the chemical potential, μ

In all cases:

$$\beta = \frac{1}{kT}$$

It turns out that:

$$\alpha = -\mu\beta = \frac{-\mu}{kT} \quad (3.20)$$

In all cases we can replace the term $e^{\alpha+\beta E}$ with $e^{\beta(E-\mu)}$.

3.1.6. Density of states $g(E)$

For localised particles, e.g. a particle in a solid state lattice, there is generally only one one-particle state corresponding to each energy level. i.e. The degeneracy $g'(E) = 1$. $g(E)$ is the number of particles per unit energy.

Example - A Paramagnetic Solid

The mean magnetic moment:

$$\bar{\mu} = \mu p \uparrow + (-\mu) p \downarrow \quad (3.21)$$

Writing $x \equiv \frac{\mu B}{kT}$, then $z = e^x + e^{-x}$, and:

$$\bar{\mu} = \frac{\mu(e^x - e^{-x})}{z} = -\mu B \tanh(x) \quad (3.22)$$

And then, the mean energy is:

$$\bar{E} = -\mu B p \uparrow + \mu B p \downarrow = -\mu B \tanh(x) \quad (3.23)$$

For a solid of N non-interacting particles, then, we have:

$$E = -N\mu B \tanh(x) \quad (3.24)$$

The magnetisation curve per unit volume is:

$$I = \frac{M}{V}$$

With M the magnetic moment.

$$\begin{aligned} M &= N\mu \tanh(x) \\ I &= \frac{N\mu}{V} \tanh(x) \end{aligned} \quad (3.25)$$

For $x \ll 1$ $\tanh(x) \sim x$ and for $x \gg 1$ $\tanh(x) \sim 1$.
Therefore, for $x \ll 1$:

$$I \sim \frac{N\mu}{V} x = \frac{N\mu^2}{VkT} B \quad (3.26)$$

So magnetisation is linearly proportional to the applied magnetic field (for small B or large T).

$$\begin{aligned} M &= \chi H \\ \text{Where: } H &= \frac{B}{\mu_0} \end{aligned} \quad (3.27)$$

With χ the magnetic susceptibility.
So:

$$\chi = \frac{N\mu^2\mu_0}{kT} \quad (3.28)$$

This gives rise to Curie's law.

$$\chi \propto \frac{1}{T}$$

This relationship can be implemented to make a thermometer.

3.2. A gas of particles in a box

To find $g(E)$ for agases in general we use quantum mechanics and consider the particles as waves - either matter waves (for electrons/atoms/molecules etc.) or electromagnetic waves (for photons etc.).

In quantum mechanics the energy of a particle E is a simple function of it's wave's angular frequency:

$$\omega = 2\pi f$$

First of all find the density of states as a function of the angular frequency:

$$\omega : g(\omega)$$

Assuming that the particle waves are in a closed box of fixed volume V , then the particles will be standing waves.

$g(\omega)$ is the number of states per unit ω at the specified value of ω . This is equivalent to the number of possible standing wave nodes per unit ω at ω . We have the boundary condition that the waves must have nodes at the volume boundaries.

In 1-dimension the permitted wavelengths are:

$$\lambda = \frac{2L}{n}$$

Where n is an integer ≥ 1 . The permitted wavelengths are then:

$$k = \frac{2\pi}{\lambda} = \frac{\pi n}{L}$$

In 3-dimensions the wavenumber vector \underline{k} has components k_x , k_y , and k_z . The box has the dimensions L_x , L_y , and L_z . So the permitted \underline{k} components are:

$$k_x = \frac{\pi n_x}{L_x}, \quad k_y = \frac{\pi n_y}{L_y}, \quad k_z = \frac{\pi n_z}{L_z}$$

By Pythagoras we have that:

$$\begin{aligned} |\underline{k}|^2 &= k_x^2 + k_y^2 + k_z^2 = k^2 \\ &= \frac{\pi^2 n^2}{L^2} \end{aligned} \tag{3.29}$$

Now let $L_x = L_y = L_z = L$, i.e. a cube for convenience.

For each value of the magnitude of the wavenumber k we have a certain value of n (if L is fixed), but a number of different combinations of n_x , n_y , and n_z . Each combination represents a different direction. Only discrete values of k are allowed, and each combination of wavenumber and direction is a mode.

We need to calculate how many possible modes ($g(E)$) there are for a range of k . Consider n_x , n_y and n_z as orthogonal axes. Then the vector \underline{n} , with magnitude n , defines points on the surface of an octant of a sphere. Each unit cube within this octant represents a possible combination of n_x , n_y and n_z . Thus, the number of possible states up to a value of n is just the number of unit cubes, i.e. the volume of

of an octant of a sphere radius n , is $\frac{\pi n^3}{6}$.
The volume per point in \underline{k} -space is:

$$\left(\frac{\pi}{L}\right)^3 \quad \text{Since: } k = \left(\frac{\pi}{L}\right)^n$$

The number of modes of standing waves with wave-vectors whose magnitude lies in the interval $k \rightarrow k + \delta k$ is equal to the number of lattice points in this \underline{k} -space lying between two shells, centred on the origin, of radii k and $k + \delta k$ in the positive octant. The volume of this region is:

$$\frac{\pi k^2}{2}$$

Therefore, the number of standing wave modes with a wave-vector whose magnitude lies in the range $k \rightarrow k + \delta k$ is:

$$\begin{aligned} g(k)dk &= \frac{\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3} \\ &= \frac{V k^2 dk}{2\pi^2} \end{aligned} \quad (3.30)$$

Where $V = L^3$.

Since the waves phase velocity is $v = \frac{\omega}{k}$ the number of modes per unit ω at ω is:

$$g(\omega) = \frac{V\omega^2}{2\pi^2 V^3} \quad (3.31)$$

Notes:

- We did this for a cubic box but the result holds for any shape.
- The particles may have other independent variables (e.g. polarisation, spin, etc.) which could mean more modes are allowed, i.e. for 2 polarisations $g(\omega)$ is doubled etc.

$g(\omega)$ is the density of states as a function of ω , we can convert this to $g(E)$ using the relationship between ω and E (for the particle involved), we use the equality:

$$g(E)dE = g(\omega)d\omega$$

The momentum of a particle \underline{p} is related to its wavevector \underline{k} by the following.

$$\begin{aligned} \underline{p} &= \hbar \underline{k} \\ \therefore \omega &= \frac{2\pi\nu}{h} p \end{aligned} \quad (3.32)$$

So, since:

$$g(p)dp = g(\omega)d\omega$$

$$g(p) = g(\omega)\frac{d\omega}{dp}$$

We have:

$$g(p)dp = \frac{V4\pi p^2}{h^3}dp \quad (3.33)$$

3.3. Bosons : Black Body Radiation

We consider a photon gas in a closed, opaque box. The walls of the box are continuously emitting and absorbing photons and the gas and the walls are in thermal equilibrium at a temperature T .

Instead of using $n(E)$ it is more useful to find:

$$n(\nu) = g(\nu)f(\nu)$$

Where ν is the frequency of the photons.

Finding the mean number of particles per state, $f(\nu)$

- Photons behave in many ways like particles of spin \uparrow .
- Photons are bosons and, hence, obey Bose-Einstein statistics.
- The photons in the photons gas do not interact, i.e. the photons gas is a perfect gas.
- The continual emission and absorption of photons leads to thermal equilibrium, and also means that the number of photons is not constant, but fluctuates around a mean.

We now have:

$$f(E) = f_{\text{BE}}(E) = \frac{1}{e^{(\alpha+\beta E)} - 1} \quad (3.34)$$

Since the number of photons in the box, N , is not fixed it turns out that $\alpha = 0$. So now we have:

$$f_{\text{BE}}(E) = \frac{1}{e^{\beta E} - 1} \quad (3.35)$$

Since $E = h\nu$, we can write this as:

$$f_{\text{BE}}(\nu) = \frac{1}{e^{\beta h\nu} - 1} \quad (3.36)$$

Finding the density of states, $g(\nu)$

Electromagnetic waves have 2 independent polarisations (e.g. left hand and right hand circular). So that means that the number of modes will be twice that calculated before. Hence:

$$g(\omega) = \frac{V\omega^2}{\pi^2 c^2} \quad (3.37)$$

Waves have $\omega = 2\pi\nu$, so $\frac{d\omega}{d\nu} = 2\pi$. But the number of states in the interval $d\omega$ is $g(\omega)d\omega = g(\nu)d\nu$ so:

$$g(\nu) = g(\omega) \frac{d\omega}{d\nu} = \frac{8\pi V\nu^2}{c^3} \quad (3.38)$$

Finding the density of the radiation

The mean number of photons per unit frequency interval is simply:

$$h(\nu) = g(\nu)f(\nu) = \frac{8\pi V\nu^2}{c^3 (e^{\beta h\nu} - 1)} \quad (3.39)$$

Over the frequency interval $\nu \rightarrow \nu + d\nu$. Each photon has an energy of $h\nu$, so the total average energy per unit frequency interval is $n(\nu)h\nu$.

So the energy density of the radiation in the box, per unit frequency interval gives us the energy per unit volume per unit frequency interval:

$$u(\nu) = \frac{n(\nu)h\nu}{V} \quad (3.40)$$

If we use $\beta = \frac{1}{kT}$ we find:

$$u(\nu) = \frac{8\pi h\nu^3}{c^3 \left(e^{\frac{h\nu}{kT}} - 1 \right)} \quad (3.41)$$

Which is the *Planck Radiation Equation*, with units of $\text{J m}^{-1} \text{Hz}^{-1}$. This is the energy density distribution as a function of frequency, ν , and temperature, T .

3.3.1. Radiation : Some basic definitions and units

Table 3.1 contains some basic definitions of terms and their units. All of the quantities can have values per unit wavelength (i.e. for monochromatic light). Isotropic radiation has equal radiation output from any direction. This isotropic irradiance means the radiance from a surface is equal in any direction within 2π steradians.

Converting energy density to radiance or radiant flux density.

Returning to a gas of photons in a box. Consider the photons in any frequency interval $\nu \rightarrow \nu + d\nu$. The energy density of the photons in the box, in that frequency

Quantity etc.	Definition	Units
<i>Radiant Flux</i>	The total radiant power.	W
<i>Radiant Flux Density</i>	The total radiant power intercepted by a unit area of a plane surface.	W m ⁻²
<i>Irradiance</i>	Incident radiant flux density.	W m ⁻²
<i>Emittance</i> (or <i>Exitence</i>)	Outgoing radiant flux density.	W m ⁻²
<i>Radiance</i>	In a particular direction, the radiant flux per unit solid angle, per unit area projected perpendicular to that direction.	W m ⁻² Sr ⁻¹

Table 3.1.: Radiation definitions and units.

interval is $u(\nu)d\nu$, and the radiation is isotropic.

We want to know what fraction of photons in the box are travelling in approximately one dimension, say the z -direction. Let us take a small range of directions represented by an element $d\Omega$ steradians of solid angle, centered on the $+z$ -direction. This fraction of photons is just:

$$\frac{d\Omega}{4\pi}$$

This must also be the fraction of the energy density due to these photons (let us call them z -photons.) So, the energy due to the z -photons is:

$$\frac{u(\nu)d\nu d\Omega}{4\pi} \quad (3.42)$$

Suppose that in the box there is a plane surface of unit area, perpendicular to the z -direction. The energy per unit time (power) per unit area passing through the surface is the average value of the Poynting vector $\langle s \rangle$:

$$\langle s \rangle = \langle u \rangle c$$

Where, $\langle u \rangle$ is the average energy density.

Now if $d\Omega$ is very small, we can conclude that all of the z -photons pass through the surface. Therefore we can replace $\langle u \rangle$ by $\frac{u(\nu)d\nu d\Omega}{4\pi}$. Now we get that the power per unit area crossing the surface is:

$$u(\nu)c \frac{d\Omega}{4\pi} d\nu \quad (3.43)$$

Now we divide by $d\Omega$, to get the radiance, and by $d\nu$, to get the spectral radiance:

$$R_{\text{BB}} = \frac{u(\nu)c}{4\pi} \quad (3.44)$$

So, the spectral radiance as a function of frequency is:

$$R_{\text{BB}\nu} = \frac{2h\nu^3}{c^2 \left(e^{\frac{h\nu}{kT}} - 1 \right)} \quad (3.45)$$

These expressions are independent of the position, direction and nature of the walls of the container holding the photons. They are the *Planck functions* for black-body radiation.

Black-body radiation

“A black-body is a theoretical ideal substance which absorbs all radiation falling on it, $\alpha_{\text{BB}} = 1$ at all wavelengths.”

The absorptivity, α , is a measure of the fraction of incident radiation which is absorbed. So $1 - \alpha$ of the incident radiation is reflected or transmitted. Certain substances have $\alpha \approx 1$ at some wavelengths. (e.g. soot has an $\alpha \approx 0.95$ at visible wavelengths, water has an $\alpha \approx 0.98$ at infra-red wavelengths around $10 \mu\text{m}$.)

The best experimental approximation to a black hole is a large, closed, opaque box, with a small hole in it. Radiation entering the box will be reflected many times off of the walls and only a very small fraction of the radiation will re-emerge through the hole.

If we give the walls of the box a uniform temperature, T , then the hole is also emitting the box's thermal radiation with the same spectral irradiance etc. as the Planck functions. So the irradiance inside a box at temperature, T , is the same as the emittance of a black-body at a temperature, T . So in a uniform temperature box we have black-body radiation.

We can also have Planck functions in terms of the wavelength, λ , of the radiation, $I_{\text{BB}\lambda}$ and $R_{\text{BB}\lambda}$. By equating the emittance in intervals of $d\nu$ and $d\lambda$.

$$I_{\text{BB}\nu} d\nu = I_{\text{BB}\lambda} d\lambda \quad (3.46)$$

We have, $I_{\text{BB}\nu}$, and $\frac{d\nu}{d\lambda} = \frac{c}{\lambda^2}$ (from $\nu = \frac{c}{\lambda}$), so:

$$I_{\text{BB}\lambda} = \frac{2\pi h c^2}{\lambda^5 \left(e^{\frac{hc}{\lambda kT}} - 1 \right)} = \pi R_{\text{BB}\lambda}(\lambda, T) \quad (3.47)$$

Notes:

1. As temperature increases, the peak frequency increases and wavelength decreases.

2. As temperature increases, the curves lie above the lower temperature curves at all frequencies.
3. At any temperature each curve has three parts: an energy tail in the frequency distribution, a peak frequency, and a rapid fall off at higher frequencies.
4. At any temperature, the total radiance is just the integral $\int_{\nu} R_{\nu} d\nu$, i.e. the area under the curve.
5. Two spectral distributions as functions of frequency, ν , and wavelength, λ , have different shapes for the same spectrum, the intensity maxima appear at different wavelengths. As an example, for solar radiation $\lambda(I_{\lambda \text{ max}}) \approx 450 \text{ nm}$ in the green region of the spectrum, but $\lambda(I_{\nu \text{ max}}) \approx 800 \text{ nm}$ in the red region of the spectrum¹.

3.3.2. Various black-body laws and facts

Stefan-Boltzmann law

For any temperature, T , we can integrate the spectral emittance expression for $I_{\text{BB}\nu}$ or $I_{\text{BB}\lambda}$, over all ν or λ , to get the total emittance of a black body, I_{BB} . We have, for spectral emittance in $\text{W m}^{-2} \text{ Hz}^{-1}$:

$$I_{\text{BB}\nu}(\nu, T) = \frac{2\pi h\nu^3}{c^2 \left(e^{\frac{h\nu}{kT}} - 1 \right)} \quad (3.48)$$

$$I_{\text{BB}}(T) = \int_0^{\infty} I_{\text{BB}\nu}(\nu, T) d\nu \quad \text{W m}^{-2} \quad (3.49)$$

If we put $x = \frac{h\nu}{kT}$, then $d\nu = dx \left(\frac{kT}{h} \right)$, giving:

$$I_{\text{BB}}(T) = \int_0^{\infty} \left[\frac{2\pi k^4 T^4}{h^3 c^2} \right] \left[\frac{x^3}{(e^x - 1)} \right] dx \quad (3.50)$$

But:

$$\int_0^{\infty} \frac{x^3}{(e^x - 1)} dx = \frac{\pi^4}{15} \quad (3.51)$$

So:

$$I_{\text{BB}}(T) = \sigma T^4 \quad \text{W m}^{-2} \quad (3.52)$$

Where, $\sigma = \frac{2\pi^5 k^4}{15c^2 h^3} \simeq 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$, the Stefan-Boltzmann constant.

Note: In terms of the energy density we have that:

$$u(T) = aT^4 \quad (3.53)$$

Where, $a = \frac{4\sigma}{c} \simeq 7.56 \times 10^{-16} \text{ W m}^{-3} \text{ K}^{-4}$.

¹The reason for this is that $|d\nu| = \frac{c}{\lambda^2} |d\lambda|$. As wavelength, λ , increases and frequency, ν , decreases, equal intervals in $d\lambda$ correspond to different intervals in $d\nu$ across the spectrum.

Wien's displacement law

The wavelength of maximum spectral emittance for $R_{\text{BB}\lambda}(\lambda, T)$ is:

$$\lambda_{\text{max}} = \frac{b}{T} \quad (3.54)$$

Where, $b = 2900 \text{ } \mu\text{m K}$.

Note: We will not get the same λ_{max} for I_ν , since I_ν and I_λ are different functions. Maximising $R_{\text{BB}\nu}(\nu, T)$ instead, we get:

$$\lambda_{\text{max}}(R_{\text{BB}\nu}(\nu, T)) = \frac{b'}{T} \quad (3.55)$$

Where, $b' = 5100 \text{ } \mu\text{m K}$.

Mean photon energy

The mean photon energy is the total energy divided by the number of photons.

$$\frac{\int_0^\infty R_{\text{BB}\nu} d\nu}{\frac{\int_0^\infty R_{\text{BB}\nu} d\nu}{h\nu}} = h\nu = 2.7012kT \quad (3.56)$$

So the mean photon energy is of the order of kT .

Rayleigh-Jeans Law (Low energy limit)

The Rayleigh-Jeans law is applicable for cases where $h\nu \ll kT$, i.e the tail of the plots.

Assume that for $h\nu \ll kT$:

$$e^x \simeq 1 + x + \frac{x^2}{2!} + \dots$$

So:

$$R_{\text{BB}\nu} = \frac{2h\nu^3}{c^2} \frac{kT}{h\nu} = \frac{2kT\nu^2}{c^2} \quad (3.57)$$

Similarly:

$$R_{\text{BB}\lambda} = \frac{2kTc}{\lambda^4} \quad (3.58)$$

So Planck's functions approximate to linear functions in temperature, T .

Wien's law

For a very high frequency, $h\nu \gg kT$, $R_{BB\nu}$ approximates to the exponential function:

$$R_{BB\nu} = \frac{2h\nu^3}{c^2} e^{-\frac{h\nu}{kT}} \quad (3.59)$$

And:

$$R_{BB\lambda} = \frac{2hc^2}{\lambda^5} e^{-\frac{hc}{\lambda kT}} \quad (3.60)$$

3.3.3. Kirchoff's law

Kirchoff's law covers the emissivity of a general (non-black) body. Let us place inside our black box at a temperature, T , a general non-black body, with an absorbtivity α , and with the same temperature, T .

The total irradiance, I_{BB} , onto this body will be the black body radiation, as before, integrated over all ν or λ . The radiant power absorbed by the body per unit area will be αI_{BB} .

The body is also emitting radiation with a total emittance I_e , but as the body remains at a temperature T , we can see that $I_e = \alpha I_{BB}$.

If $\alpha = 1$ then this proves that radiation is emitted by a black body, but for $\alpha \neq 1$ we have to consider a general body's emissivity.

We define a body's hemispherical emissivity, ϵ , such that its emittance at a temperature T is a fraction, ϵ , of the emittance, I_{BB} , of a black-body at the temperature T . So:

$$I_e = \epsilon I_{BB}$$

Comparing with the above gives Kirchoff's law:

$$\epsilon = \alpha$$

i.e. good absorbers are good emitters, and vice versa.

3.3.4. A general body's spectral radiance

The spectral radiance, $R_{e\nu}$, emitted by a non-black body varies with frequency, ν , and direction, (θ, ϕ) , such that:

$$R_{e\nu} = \epsilon_{\nu, \theta, \phi} R_{BB} \quad (3.61)$$

Example: To reduce it's temperature, part of a spacecraft which is bathed in sunlight may be coated with special white paint with, for example, $\epsilon = 0.1$ in the visible part of the spectrum, i.e. it reflects sunlight. But, with $\epsilon = 0.9$ in the infra-red. This means that it emits most of it's radiation at ~ 290 K.

If one converts $R_{e\nu}$ to temperature, assuming $\epsilon = 1$, the teperature, T_B is called the brightness temperature, i.e. the temperature of a black-body which gives the same spectral emittance at the same value of ν or λ as the general body.

Equally, one can define an effective temperature, T_{eff} , this equates the total radiance, R , per unit area emitted over all ν or λ with an equivalent black-body temperature.

$$R = \sigma T^4 = \sigma T_{\text{eff}}^4 \quad (3.62)$$

for a black body. For a star we have luminosity, L , being:

$$L = 4\pi r^2 \sigma T_{\text{eff}}^4$$

3.3.5. Radiation pressure

Kinetic theory gives the gas pressure of a monatomic gas as:

$$P = \frac{1}{3} \frac{N}{V} \langle mv^2 \rangle \quad (3.63)$$

Or:

$$P = \frac{1}{3} \frac{N}{V} \langle pv \rangle \quad (3.64)$$

Where p is momentum.

The same result is applicable to a gas of photons, but:

$$\langle pv \rangle = \langle pc \rangle = \langle h\nu \rangle \quad (3.65)$$

So we have:

$$\frac{N}{V} \langle pv \rangle = U(T) \quad (3.66)$$

Where $U(T)$ is the total energy density at a temperature T .

And we also have:

$$U(T) = \int U(\nu) d\nu = \left(\frac{4\sigma}{c} \right) T^4 \quad (3.67)$$

So the black-body radiation pressure is:

$$P_{\text{rad}} = \frac{U(T)}{3} = \left(\frac{4\sigma}{3c} \right) T^4 \quad (3.68)$$

Note: This can also be derived using:

$$P = - \left(\frac{dF}{dV} \right)_T$$

Which we derived earlier. With the Helmholtz free energy, $F = -kT \ln(z)$.

3.4. Astronomical examples involving black bodies

3.4.1. Stellar temperatures

- A star's emergent radiation approximates that of a black-body whose temperature is the brightness temperature of the outer layers of the star.
- We can also define a star's colour temperature, T_c , by measuring the emergent intensities in two or more spectral bands (at specific wavelengths, λ_i) and using the ratio between the two intensities to give the temperature of a black body.
- As noted before we can define an effective temperature, T_{eff} , for a star to be the temperature of a black-body which gives the same observed total emergent intensity from the star integrated over all wavelengths, λ .

$$L_{\star} = 4\pi R_{\star}^2 \sigma T_{\text{eff}}^4$$

3.4.2. Planetary temperatures

A planet's equilibrium temperature, T_e , is such that absorbed radiation from the sun is balanced by the emission of thermal radiation.

3.4.3. Cosmic Microwave Background

Precision measurements of the cosmic microwave background radiation² show that it is well fitted with a temperature $T_{\text{BB}} = 2.735\dots$ K with a typical deviation of $\frac{\Delta T}{T} \lesssim 10^{-6}$.

3.5. A perfect gas of bosons at low temperatures (Bose-Einstein condensation)

3.5.1. The density of states, $g(E)$, for matter waves in a box

First of all, we rewrite $g(E)$ in a form that is applicable not to energy waves, but to matter waves. Consider a closed box of a volume, V , in thermal equilibrium and containing a gas of weakly interacting bosons.

²With COBE, WMAP, *et al.*

The solution of Schrödinger's time-independent wave equation for particle matter waves in a box gives solutions which are standing waves with nodes at the walls of the box. Each possible wavenumber, k , represents an energy level:

$$E = \frac{h^2}{8\pi^2 m} k^2 \quad (3.69)$$

And a momentum:

$$p = \sqrt{2mE} = \frac{h}{2\pi} k \quad (3.70)$$

Note: $p \propto k$ For each wavenumber, k , particles may have many different possible directions.

The general analysis of the mode of waves in a box (which was described earlier) is still valid. Therefore, the density of states is:

$$g(\omega)d\omega = \frac{V\omega^2}{2\pi^2 v^2} d\omega \quad (3.71)$$

Where v is the particle velocity and ω the angular frequency.

Now the waves have $k = \frac{2\pi}{\lambda} = \frac{\omega}{v}$, so we have:

$$E = \frac{\omega^2 h^2}{8\pi^2 m v^2} \quad (3.72)$$

$$\omega^2 = \frac{4\pi^2 2m v^2 E}{h^2} \quad (3.73)$$

$$\omega = \frac{2\pi \sqrt{2m v} \sqrt{E}}{h} \quad (3.74)$$

$$\frac{d\omega}{dE} = \frac{\pi \sqrt{2m v}}{\sqrt{E} h} \quad (3.75)$$

And the number of states in the interval dE is $g(E)dE \equiv g(\omega)d\omega$ so:

$$g(E) = g(\omega) \frac{d\omega}{dE} = \frac{V}{2\pi^2 v^3} \omega^2 \frac{d\omega}{dE} \quad (3.76)$$

We shall use this result again for electrons in a box.

Note: $g(E) \propto E^{\frac{1}{2}}$ and also $g(E) \propto V$ so we get more states per unit energy in larger boxes.

The mean number of particles per state, $f_{\text{BE}}(E)$

Using Bose-Einstein statistics:

$$f_{\text{BE}}(E) = \frac{1}{e^{\beta(E-\mu)} - 1} \quad (3.77)$$

If there are N particles (with $m \neq 0$):

$$N = \sum_i \frac{1}{e^{\beta(E-\mu)} - 1} \quad (3.78)$$

Now, if N is the total number of particles in the box:

$$N = \int n(E)dE \quad (3.79)$$

Where $n(E) = f(E)g(E)$.

So:

$$\begin{aligned} N &= \int f(E)g(E)dE \\ \therefore N &= \left(\frac{V}{4\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{e^{\beta(E-\mu)} - 1} dE \end{aligned} \quad (3.80)$$

For a Bose-Einstein gas³ $\mu < 0$. If we keep N and V constant and vary T , we get that:

$$\frac{N}{V} = \left(\frac{1}{4\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{e^{\frac{(E-\mu)}{kT}} - 1} dE \quad (3.81)$$

The integral is a function of $\frac{\mu}{kT}$ so $|\mu|$ must decrease as the temperature, T , decreases for this equation to be valid. At some minimum temperature, $T = T_c$, we have $\mu = 0$.

$$\frac{N}{V} = \left(\frac{1}{4\pi^2}\right) \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{e^{\frac{E}{kT_c}} - 1} dE \quad (3.82)$$

Now perform a change of variable:

$$\begin{aligned} z &= \frac{E}{kT_c} & dz &= \frac{1}{kT_c} dE \\ \int_0^\infty \frac{z^{\frac{1}{2}}}{e^z - 1} dz & & & \end{aligned} \quad (3.83)$$

$$\frac{N}{V} = (2.61) \left(\frac{2\pi mkT_c}{\hbar^2}\right)^{\frac{3}{2}} \quad (3.84)$$

³This is necessary for the series to converge in the grand partition function (see the extra notes on the course web site for more information).

This implies that the Bose-Einstein gas cannot be cooled at a constant density below the temperature T_c . What has gone wrong? The problem is in going from the sum to the integral.

$$g(E) \propto E^{\frac{1}{2}}$$

So $g(0) = 0$, but as the temperature is lowered the Bose-Einstein gas has a larger and larger occupation of the ground state. This is completely neglected in the integral. So, we write:

$$N = \left(\frac{1}{e^{-\beta E} - 1} \right) \left(\frac{V}{4\pi^2} \right) \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{e^{\beta(E-\mu)} - 1} dE \quad (3.85)$$

Where the $\frac{1}{e^{-\beta E} - 1}$ term is the number of particles with an energy $E = 0$ and the other term is the number of particles with an energy $E > 0$.

For $T > T_c$:

- The number of particles in the ground state $E = 0$ is ~ 0 .
- The chemical potential can be determined from the integral.

For $T < T_c$:

- $\mu \sim 0$ (Although it must be slightly more than 0 for convergence.)
- The number of particles with energy $E > 0$ is:

$$\left(\frac{V}{4\pi} \right) \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{e^{\beta E} - 1} dE \quad (3.86)$$

Integrating gives the number of particles in states with $E > 0$:

$$N_{E>0} = N \left(\frac{T}{T_c} \right)^{\frac{3}{2}} \quad (3.87)$$

So the number of particles in the $E = 0$ state is:

$$N_{E=0} = N \left[1 - \left(\frac{T}{T_c} \right)^{\frac{3}{2}} \right] \quad (3.88)$$

This is *Bose-Einstein condensation* of particles in the zero energy ground state, below T_c . The particles with $E = 0$ and $p = 0$ have no viscosity⁴. Does this really happen? Yes, in ⁴He, the nuclei are bosons. ⁴He stays in the liquid state down to $T \simeq 0$ at normal pressures, becoming a superfluid with very high thermal conductivity.

⁴Since this is due to the transport of momentum.

3.6. Fermions (Electrons in white dwarf stars and in metals)

Remember that fermions obey the Pauli exclusion principle and Fermi-Dirac statistics, i.e. the occupation numbers, n_r , are restricted to $n_r = 0, 1$ only for all r .

Electrons in a box

These conditions are approximated by electrons in a white dwarf star and electrons in a metal⁵.

As before, we have:

$$n(E) = g(E)f(E)$$

We can find $f_{\text{FD}}(E)$, the number of particles per state for fermions, to be:

$$f_{\text{FD}}(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \quad (3.89)$$

Where, at $T = 0$, $\mu = E_f$, the *Fermi energy*.

Finding the density of states $g(E)$

Note that the electrons have two possible spin states, $\pm \frac{\hbar}{2}$, so the number of modes will be twice that calculated before in the general case. Hence:

$$g(\omega)d\omega = \frac{V\omega^2}{\pi^2v^3} \quad (3.90)$$

And:

$$g(E) = \left(\frac{4\pi V}{h^3}\right) (2m)^{\frac{3}{2}} E^{\frac{1}{2}} \quad (3.91)$$

So the number of particles per unit energy at an energy E is:

$$\begin{aligned} n(E) &= f(E)g(E) \\ n(E) &= \left(\frac{4\pi V}{h^3}\right) (2m)^{\frac{3}{2}} E^{\frac{1}{2}} \left(\frac{1}{e^{\beta(E-\mu)} + 1}\right) \end{aligned} \quad (3.92)$$

Normalisation and the Fermi energy

We normalise the distribution of energy, $n(E)$, so that:

$$\int_0^\infty n(E)dE = N$$

⁵The “free” conduction electrons.

Where N is the total number of electrons.

This will define the constant μ , the chemical potential, as.

$$N = \frac{4\pi V}{h^3} (2m)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}} dE}{e^{\beta(E-\mu)} + 1} \quad (3.93)$$

Where at a given temperature $T = \frac{1}{\beta k}$, $\mu = \mu(T, V, N)$.

First of all we normalise at $T = 0$. This is easier since we know that:

$$f_{\text{FD}}(E) = 1 \quad \text{for} \quad E < E_f$$

The Fermi energy, E_f is defined as the value of μ for $T = 0$, so E_f is the maximum electron energy at a temperature of absolute zero. We then define the Fermi temperature by:

$$E_f = kT_f \quad (3.94)$$

And the equivalent velocity and momentum:

$$v_f = \left(\frac{2E_f}{m} \right)^{\frac{1}{2}} \quad (3.95a)$$

$$p_f = (2mE_f)^{\frac{1}{2}} \quad (3.95b)$$

We have:

$$N = \int_0^{E_f} g(E) dE = \frac{8\pi V}{3h^3} (2m)^{\frac{3}{2}} E_f^{\frac{3}{2}}$$

$$E_f = \left(\frac{h^2}{2m} \right) \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}} \quad (3.96)$$

Note: The Fermi energy depends on the number density, $\frac{N}{V}$, and the particle mass, m .

Degenerate Fermi gases

A Fermi gas at a temperature $T = 0$ is called completely degenerate since all states in each energy level are full. At $T \ll T_f$ the distribution is not very different from the $T = 0$ case, and the gas is called extremely degenerate. This is the case with metals at all usual temperatures.

The chemical potential, μ

So μ varies with temperature, but in extremely degenerate cases the variation is weak.

$$\mu(T) \sim E_f \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_f} \right)^2 \right] \quad (3.97)$$

For $\frac{T}{T_f} = 0.1$, the change in μ is only $\sim 1\%$.

Therefore we have high electron energies even at low temperatures. Electron energies can be quite high even at $T = 0$ due to the Pauli uncertainty principle forcing electrons up into higher energy levels.

At $T = 0$ then the system is in a state of lowest energy, but not all electrons can crowd into the lowest energy levels - we can only have one particle per state. Hence, the first N lowest single particle states are filled, the states above these are empty. The Fermi energy is, therefore, the energy of the top most occupied level at $T = 0$.

The properties of metals

The theory of free electrons in metals is very powerful (it explains the conduction of heat, electrical conduction etc.). For electrons in a metal $\frac{N}{V}$ is given by the atomic spacing, typically $\frac{N}{V} \sim 5 \times 10^{28} \text{ m}^{-3}$. With one conduction electron per atom this gives that $E_f \sim 5 \text{ eV}$, $T_f \sim 5 \times 10^4 \text{ K}$ and $v_f \sim 10^6 \text{ m s}^{-1}$.

3.6.1. Pressure due to a degenerate Fermion gas of electrons

Remember, from the kinetic theory of a perfect gas, that:

$$\begin{aligned} P &= \frac{1}{3} \frac{N}{V} \langle mv^2 \rangle \\ &= \frac{2}{3} \frac{N}{V} \left\langle \frac{mv^2}{2} \right\rangle \end{aligned} \quad (3.98)$$

Or:

$$P = \frac{1}{3} \frac{N}{V} \langle pv \rangle \quad (3.99)$$

For a completely degenerate gas we know that $f(E) = 1$ and the number of particles per unit energy at an energy E is:

$$n(E) = \frac{4\pi V}{h^3} (2m)^{\frac{3}{2}} E^{\frac{1}{2}} \quad (3.100)$$

For $0 \leq E \leq E_f$.

But the momentum p is:

$$p = (2mE)^{\frac{1}{2}}$$

So:

$$E = \frac{p^2}{2m} \quad (3.101a)$$

$$\frac{dE}{dp} = \frac{p}{m} \quad (3.101b)$$

So the number of particles from $E \rightarrow E + dE$ is:

$$n(E)dE = n(p)dp \quad (3.102a)$$

$$n(p) = n(E)\frac{dE}{dp}$$

$$n(p) = \frac{8\pi V p^2}{h^3} \quad (3.102b)$$

Where $0 \leq p \leq p_f$.

Now:

$$\langle pv \rangle = \frac{1}{N} \int_0^{p_f} n(p) p v dp \quad (3.103)$$

Manipulating the above gives the electron pressure:

$$P_e = \frac{1}{3} \int_0^{p_f} \frac{8\pi p^2}{h^3} p v dp \quad (3.104)$$

For the non-relativistic case:

$$v = \frac{p}{m} \quad (3.105)$$

So:

$$P_e = \left(\frac{8\pi}{15mh^3} \right) p_f^5 \quad (3.106)$$

For the relativistic case, $v \sim c$ so:

$$P_e = \frac{2\pi c}{3h^3} p_f^4 \quad (3.107)$$

This holds for other fermions as well as electrons.

Electron pressure in white dwarf stars

In the centre of stars we have gravitational compression so $\frac{N}{V}$ is very high. Therefore, E_f and T_f are very high. So even at high temperatures, $T \ll T_f$, and degenerate conditions exist.

For white dwarf stars most of the star is degenerate. So for protons with $m \sim 2000m_e$, for the same values of $\frac{N}{V}$, E_f and P_f (in the non-relativistic case) are both proportional to $\frac{1}{m}$ and are about 2000 times smaller.

So, in a compact star many more electrons have high velocities compared to neutrons and protons and hence the electron pressure is a lot higher. So the majority of gas pressure in the star is due to the electrons.

So the more compact the star, the higher the electron Fermi energy, and also the higher the electron pressure. So we can get a very compact yet stable star where the high gravitational pressure is balanced by the equally high degenerate electron pressure.

White dwarfs have a radius $r \sim 10^4$ km and are the end states of with an initial main sequence mass of ≤ 7 solar masses. They are essentially the exposed inert core of the star supported by the degenerate electron pressure, with an effective temperature $T_{\text{eff}} \sim 10^5$ K. The radiation of heat means that by energy loss they turn into a black dwarf after a period of $\sim 10^9$ years.

3.6.2. Pressure due to a degenerate electron gas in a white dwarf

From the Fermi energy and the electron pressure:

$$\left(\frac{h^2}{2m}\right) \left(\frac{3N}{8mV}\right)^{\frac{2}{3}} \quad (3.108)$$

Where the Fermi momentum $p_f = (2mE_f)^{\frac{1}{2}}$, therefore:

$$\begin{aligned} P_e &= \left(\frac{8\pi}{15mh^3}\right) h^5 \left(\frac{3}{8\pi}\right)^{\frac{5}{3}} \left(\frac{N}{V}\right)^{\frac{5}{3}} \\ &= \left(\frac{h^2}{20m}\right) \left(\frac{3}{\pi}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\frac{5}{3}} \end{aligned} \quad (3.109)$$

But $\frac{N}{V} \equiv \frac{p}{m}$, for this type of gas, so:

$$\frac{N_e}{V} = \frac{p}{m_p \mu_e} \quad (3.110)$$

With $\mu_e = \frac{A}{Z} = \frac{\text{atomic mass}}{\text{atomic number}}$, the mean molecular weight.

With $\mu_e = 2$:

$$p_e = \left(\frac{h^2}{20m} \right) \left(\frac{3}{\pi} \right)^{\frac{2}{3}} \left(\frac{1}{2m_p} \right) P^{\frac{5}{3}} \quad (3.111)$$

In a stable white dwarf the pressure is balanced by the inward gravitational force so the system is in hydrostatic equilibrium. The hydrostatic equilibrium relationship is:⁶

$$\frac{dP}{dr} = -\frac{GM(r)}{r^2} \rho(r) \quad (3.112)$$

Using approximate expressions for the mean density and pressure:

$$\bar{\rho} \simeq \frac{3M}{4\pi R^3} \quad (3.113)$$

And:

$$\begin{aligned} \bar{P} &\simeq \frac{GM\rho}{R} \\ &\simeq \frac{3GM^2}{4\pi R^4} \end{aligned} \quad (3.114)$$

Now:

$$\frac{M^2}{R^4} \propto \left(\frac{M}{V} \right)^{\frac{5}{3}} \propto \left(\frac{M}{R^3} \right)^{\frac{5}{3}} \quad (3.115)$$

So:

$$M^{\frac{1}{3}} \propto \frac{1}{R} \quad (3.116)$$

So the more massive the white dwarf the smaller it is (i.e. it has a higher density), with the limit that P_e increases as M increases until moving to the region where the relativistic degeneracy is important.

$$P_e \propto \bar{e}^{\frac{4}{3}} \quad (3.117)$$

Or:

$$\frac{M^2}{R^4} \propto \left(\frac{M}{R^3} \right)^{\frac{4}{3}} \quad (3.118)$$

i.e. $M^{\frac{2}{3}}$ is constant $\sim \frac{5.80M_{\odot}}{\mu_e^2} \sim 1.45M_{\odot}$. M is independent of R .

This is known as the characteristic mass limit for a stable white dwarf star. A typical white dwarf has the following characteristics:

⁶Usually in the normal state the gravitational pressure is balanced by the gas pressure and the radial pressure.

$$\begin{aligned}
M &\sim 0.7M_{\odot} \\
T_{\text{eff}} &\sim 3 \times 10^4 \text{ K} \\
R &\sim 1 \times 10^{-2}R_{\odot} \\
\bar{\rho} &\sim 10^9 \text{ kg m}^{-3}
\end{aligned}$$

A white dwarf can have a very thin, non-degenerate atmosphere with a thickness of $\sim 5 \times 10^3$ m.

White dwarfs in binary systems - novae

Note that the electron pressure is independent of the temperature. A white dwarf in a binary system with a red giant companion draws material from the red giant, so there is a mass outflow from the red giant. This material is accreted by the white dwarf in a very high gravitational potential. The hydrogen rich accreting gas is heated so that nuclear burning can occur. Note that at the surface of the white dwarf the conditions are still degenerate. At $T \sim 10^7$ K the CNO cycle of H-burning has a rate proportional to T^{17} . As burning occurs the temperature increases, as does the rate of burning along with it. The pressure throughout this stays constant. This causes a thermonuclear runaway, which is halted at $T \gg T_f$, the degeneracy is therefore lifted, this leads to a nova with $\sim 10^{-5}M_{\odot}$ ejected at a velocity $\sim 3 - 4 \times 10^5$ m s $^{-1}$.

3.6.3. Neutron stars

Neutron stars have a mass of $\sim 7 - 10M_{\odot}$ and a final mass of $\sim 1.4M_{\odot}$. The degenerate electron pressure cannot hold off the gravitation pressure and the core collapses, leading to very high densities. Inverse beta-decay occurs:



i.e. a degenerate fermion gas of neutrinos is formed. The neutron star has the following typical characteristics:

$$\begin{aligned}
M &\sim 1.5M_{\odot} \\
R &\sim 10^4 \text{ m} \\
\rho &\sim 10^{18} \text{ kg m}^{-3} \\
v_{\text{escape}} &\sim 0.8c
\end{aligned}$$

The structure of the neutron star is further complicated by two effects:

- The equation of state needed for matter at and above nuclear density must have the strong interaction included in it.
- The high gravitational field means relativity is important.

No simple equation of state exists. As an estimate $P \sim 7 \times 10^{33}$ N m $^{-2}$, and again $M^{\frac{1}{3}} \propto R^{-1}$ in non-relativistic terms. The upper limit of the mass of a neutron star is unclear, but $\leq 2.9M_{\odot}$.

4. Classical gases, liquids and solids

The “perfect gas” is an idealisation in which the potential energy of the interaction between the atoms or molecules of the gas is negligible compared to their kinetic energy of motion.

4.1. Definition of a classical gas

A classical gas is a quantal gas with the time averaged number of particles per one particle state $\ll 1$.

$$f(E) = \frac{n(E)}{g(E)} \ll 1$$

i.e. there are more states available than there are particles to fill, this occurs for a dilute gas (e.g. the Earth’s atmosphere).

4.1.1. Finding the mean number of particles per unit momentum,

$$n(p)$$

Let us consider only the translational states (we ignore the internal motions of atoms and molecules and only consider the translational kinetic energy of the motion of particles, E_{tr}).

$$n(p) = g(p)f(p) \quad (4.1)$$

With $E_{\text{tr}} = \frac{p^2}{2m}$.

4.1.2. The mean number of particles per one particle state, $f(p)$

We assume that the statistics, $f_{\text{BE}}(E) \ll 1$ or $f_{\text{FD}}(E) \ll 1$, so:

$$\frac{1}{e^{\frac{(E-\mu)}{kT}} \pm 1} \ll 1 \quad (4.2)$$

In which case:

$$\frac{1}{e^{\frac{(E-\mu)}{kT}} \pm 1} \simeq \frac{1}{e^{\frac{(E-\mu)}{kT}}} = f_{\text{MB}}(E) \quad (4.3)$$

So, we use the Maxwell-Boltzmann statistics:

$$f_{\text{MB}}(E_{\text{tr}}) = \frac{N}{z_{\text{tr}}} e^{\frac{(E-\mu)}{kT}} \quad (4.4)$$

Or, with respect to the momentum, p :

$$f_{\text{MB}}(p) = \frac{N}{z_{\text{tr}}} e^{-\frac{p^2}{2mkT}} \quad (4.5)$$

Where z_{tr} is the partition function for translational states.

A classical gas as a dilute quantal gas

According to quantum mechanics a particle of momentum p has associated with it a quantum mechanical wavelength (the deBroglie wavelength).

$$\lambda_{\text{dB}} = \frac{h}{p} = \frac{h}{(2mE_{\text{tr}})^{\frac{1}{2}}} \quad (4.6)$$

Where $E_{\text{tr}} = \frac{p^2}{2m}$, also $E_{\text{tr}} = \frac{3}{2}kT$.

So:

$$\lambda_{\text{dB}} = \frac{h}{(3mkT)^{\frac{1}{2}}} = \left(\frac{2\pi}{3}\right)^{\frac{1}{2}} \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}} \quad (4.7)$$

Now, to be in the classical regime:

$$f_{\text{MB}}(E_{\text{tr}}) \ll 1$$

So, using the above:

$$\frac{N}{z_{\text{tr}}} e^{-\frac{E_{\text{tr}}}{kT}} = \frac{N}{V} \left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}} e^{-\frac{E_{\text{tr}}}{kT}} \quad (4.8)$$

Which will be true if $\frac{N}{V} \left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}} \ll 1$. Now, substituting for λ_{dB} :

$$\left(\frac{3}{2\pi}\right)^{\frac{3}{2}} \left(\frac{N}{V}\right) \lambda_{\text{dB}}^3 \ll 1$$

Now, the mean particle separation is $d = \left(\frac{N}{V}\right)^{\frac{1}{3}}$, so we get:

$$\lambda_{\text{dB}}^3 \ll d^3 \quad \text{or} \quad \lambda_{\text{dB}} \ll d \quad (4.9)$$

i.e. the deBroglie wavelength is a lot less than the particle separation, in which case the wave nature of particles is not important. The particle spacing is too large for quantum mechanical interference effects to be significant.

4.1.3. The density of states, $g(p)$

In general we are considering particles of mass m in a box of volume V . We can use the quantum mechanical analysis we had earlier for electrons, but ignoring the factor of 2 for the spin states. So $g(p)$ is just the same as for electrons before but divided by 2. So:

$$g(p)dp = \frac{4\pi V p^2}{h^3} dp \quad (4.10)$$

Also, the translational partition function, z_{tr} , is just:

$$z_{\text{tr}} = \sum_E g'(E) e^{-\beta E_{\text{tr}}} \quad (4.11)$$

Where E_{tr} is the translational kinetic energy. Note that it is possible to sum or integrate of all energies or momenta.

$g(p)dp$ gives the number of states in the range $p \rightarrow p + dp$, or as an integral with respect to the momentum, p :

$$z_{\text{tr}} = \int_0^\infty \frac{4\pi V p^2}{h^3} e^{-\frac{\beta p^2}{2m}} dp \quad (4.12)$$

So, using $I_2(a)$ and $a = \frac{\beta}{2m} = \frac{1}{2mkT}$ (see kinetic theory integrals in the appendix):

$$z_{\text{tr}} = V \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \quad (4.13)$$

Substituting this into the expression $f_{\text{MB}}(p)$ we get:

$$f_{\text{MB}}(p) = \left(\frac{N}{V} \right) \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}} e^{-\frac{p^2}{2mkT}} \quad (4.14)$$

Now, $n(p) = g(p)f_{\text{MB}}(p)$, so:

$$n(p) = \left[\frac{4\pi N p^2}{(2\pi mkT)^{\frac{3}{2}}} \right] e^{-\frac{p^2}{2mkT}} \quad (4.15)$$

Where $n(p)dp$ is the number of particles possessing a momentum of magnitude p in the range $p \rightarrow p + dp$. This is the *Maxwell-Boltzmann distribution*.

4.2. The Maxwell speed and velocity distributions and the energy distribution

Now we have the probability that particles possess momentum in the range $p \rightarrow p + dp$.

$$F(p)dp = \frac{n(p)}{N} dp = \left[\frac{4\pi p^2}{(2\pi mkT)^{\frac{3}{2}}} \right] e^{-\frac{p^2}{2mkT}} dp \quad (4.16)$$

Note that this is correctly normalised, $\int_0^\infty F(p)dp = 1$.

If we substitute for the momentum that $p = mv$ then we obtain the *Maxwell speed distribution*, i.e. the probability that a molecule will have speed v in the interval $v \rightarrow v + dv$.

$$\begin{aligned} F(v)dv &= 4\pi v^2 dv \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} \\ &= \frac{4u^2 du}{\sqrt{\pi}} e^{-u^2} \equiv F_1(u)du \end{aligned} \quad (4.17)$$

Where $u = \frac{v}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}}$, i.e. u is the speed measured in units of $\left(\frac{2kT}{m}\right)^{\frac{1}{2}}$. The maximum of the distribution occurs at $u = 1$, i.e. at a speed:

$$v_{\max} = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \quad (4.18)$$

The mean value involves integrals of the type $I_n(a) = \int_0^\infty x^n e^{-ax^2} dx$ (see appendix) which allow us to find the mean speed, \bar{v} , and the rms speed, v_{rms} .

$$\bar{v} = \int_0^\infty vF(v)dv = \frac{2}{\sqrt{\pi}}v_{\max} \quad (4.19)$$

$$v_{\text{rms}} = \sqrt{\int_0^\infty v^2 F(v)dv} = \sqrt{\frac{3}{2}}v_{\max} \quad (4.20)$$

So v_{\max} , \bar{v} and v_{rms} have nearly the same values.

We can obtain the probability distribution that a molecule should have a translational kinetic energy in the range $E_{\text{tr}} \rightarrow E_{\text{tr}} + dE_{\text{tr}}$ using:

$$E_{\text{tr}} = \frac{p^2}{2m}$$

With:

$$F(E) = F(p) \frac{dp}{dE} \quad (4.21)$$

$$F(E_{\text{tr}})dE_{\text{tr}} = \frac{2\sqrt{E_{\text{tr}}}}{\sqrt{\pi}(kT)^{\frac{3}{2}}} dE_{\text{tr}} e^{-\frac{E_{\text{tr}}}{kT}} \quad (4.22)$$

$$F(E_{\text{tr}})dE_{\text{tr}} = \frac{2}{\sqrt{\pi}} \sqrt{\epsilon} d\epsilon e^{-\epsilon} \equiv F_2(\epsilon)d\epsilon \quad (4.23)$$

Where $\epsilon = \frac{E_{\text{tr}}}{kT}$, the energy in units of kT .

The mean kinetic energy per molecule, $\overline{E_{\text{tr}}}$, is:

$$\overline{E_{\text{tr}}} = \frac{3}{2}kT = \frac{1}{2} \langle v_{\text{rms}} \rangle^2 \quad (4.24)$$

Two factors make up the energy distribution:

1. The Boltzmann factor, $e^{-\epsilon}$.
2. The normalised density of states, $g(E) \propto \epsilon^{\frac{1}{2}}$.

We can next consider the Maxwell velocity distribution, i.e. the probability that a molecule possesses a velocity within the range $\underline{v} \rightarrow \underline{v} + d\underline{v}$, i.e. within the velocity space volume element $d^3\underline{v}$ which is situated at the velocity \underline{v} . Given that the velocity distribution must be isotropic, we can infer the velocity distribution from the speed distribution earlier. We have that:

$$F(\underline{v})d^3\underline{v} = d^3\underline{v} \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m\underline{v}^2}{2kT}} \quad (4.25)$$

By integrating this over all directions of \underline{v} but keeping its magnitude in the range $v \rightarrow v + dv$ we recover the previous form $F(v)dv$.

The probability distribution for each cartesian component of the vector \underline{v} can be obtained by noting that the above equation factorises into 3 identical distributions for each component. By writing:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

And noting that:

$$d^3\underline{v} = dv_x dv_y dv_z$$

Then we get, for say the x -component:

$$F(v_x)dv_x \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}} \quad (4.26)$$

We can also write:

$$F(v_x)dx = \frac{1}{\sqrt{2\pi}} dw e^{-\frac{w^2}{2}} \equiv F_3(w)dw \quad (4.27)$$

Where $w = \frac{v_x}{\left(\frac{kT}{m}\right)^{\frac{1}{2}}}$, the velocity component in terms of $\left(\frac{kT}{m}\right)^{\frac{1}{2}}$.

The rms value of v_x is given by:

$$(v_x)_{\text{rms}} = \left(\frac{kT}{m} \right)^{\frac{1}{2}} \quad (4.28)$$

Which agrees with the rms speed since:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2} \quad (4.29)$$

4.2.1. The energy of a classical gas

The thermal energy E of a gas can be considered to have two components:

$$E = E_{\text{tr}} + E_{\text{int}} \quad (4.30)$$

With E_{tr} the translational energy, and E_{int} the molecules internal energy (rotational, vibrational etc. etc.).

The perfect gas law or equation of state

$$PV = nRT = NkT \quad (4.31)$$

Can we derive this from our statistical definitions of the classical gas?

Remember that pressure:

$$P = - \left(\frac{df}{dV} \right)_{T,N} \quad (4.32)$$

With f , the Helmholtz free energy.

$$f = -kT \ln(z)$$

We had for one particle that:

$$z(T, V, N = 1) = \sum_r e^{-\beta E_r} \quad (4.33)$$

Now, since we have that:

$$E = E_{\text{tr}} + E_{\text{int}}$$

We find:

$$z(T, V, N = 1) = z_{\text{tr}} z_{\text{int}} \quad (4.34)$$

Note that z_{tr} does not depend on the internal structure of the molecule and, therefore, is the same for any perfect classical gas. z_{int} , however, applies to one molecule and hence is independant of volume.

Now, since:

$$f_{\text{MB}}(p) \ll 1$$

In a classical gas, then most single particle states are empty, and:

$$z(T, V, N) = \frac{1}{N!} [z(T, V, N = 1)]^N \quad (4.35)$$

Therefore:

$$z(T, V, N) = \frac{1}{N!} V^N \left(\frac{2\pi mkT}{h^2} \right)^{\frac{N}{2}} z_{\text{int}}(T)^N \quad (4.36)$$

Using Stirling's formula for large N :

$$\begin{aligned}\ln(N!) &= N \ln(N) - N = N [\ln(N) - 1] \\ &= N [\ln(N) - \ln(e)] \\ &= N \left[\ln \left(\frac{N}{e} \right) \right]\end{aligned}\tag{4.37}$$

The Helmholtz free energy is then:

$$\begin{aligned}f &= -kT \ln(z) \\ &= -kT \left\{ -\ln(N!) + N \ln(v) + N \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right] + N \ln(z_{\text{int}}(T)) \right\}\end{aligned}\tag{4.38}$$

So:

$$f = -NkT \ln \left[\left(\frac{eV}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} z_{\text{int}}(T) \right]\tag{4.39}$$

Note that $f \propto N$ and depends on the density, $\frac{N}{V}$. The Helmholtz free energy, f , divides into two contributions from the translational and internal degrees of freedom:

$$f = f_{\text{tr}} + f_{\text{int}}\tag{4.40}$$

Where:

$$f_{\text{tr}}(T, V, N) = -NkT \ln \left[\left(\frac{eV}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right]\tag{4.41}$$

$$f_{\text{int}} = -NkT \ln [z_{\text{int}}(T)]\tag{4.42}$$

The equation of state is:

$$P = - \left(\frac{df}{dV} \right)_{T,N}$$

So, therefore:

$$f_{\text{tr}}(T, V, N) = -NkT \left\{ \ln(V) + \ln \left[\left(\frac{e}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right] \right\}\tag{4.43}$$

f_{int} is independent of volume so:

$$\left(\frac{df_{\text{int}}}{dV} \right)_{T,N} = 0$$

So:

$$\left(\frac{df}{dV} \right)_{T,N} = \left(\frac{df_{\text{tr}}}{dV} \right)_{T,N} = \frac{-NkT}{V}\tag{4.44}$$

So:

$$PV = NkT \quad \square\tag{4.45}$$

Note that this doesn't depend on the internal molecular structure and so the thermodynamic and the perfect gas temperature scales are identical.

Energy is only a function of temperature, $E(T)$

This is the other characteristic of a perfect gas. Energy, E , is not dependant on pressure or volume, but only on the temperature. (From the first law of thermodynamics.)

Now:

$$E = - \left(\frac{\delta \ln(z)}{\delta \beta} \right)_{V,N}$$

With $\beta = \frac{1}{kT}$, and $\ln(z) = \frac{-f}{kT}$, so:

$$\ln(z) = N \ln \left[\left(\frac{eV}{N} \right) \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} \beta^{-\frac{3}{2}} \right] + N \ln [z_{\text{int}}(T)] \quad (4.46)$$

$$E = - \left(\frac{\delta \ln(z)}{\delta \beta} \right)_{V,N} = \frac{3N}{2\beta} - N \frac{\delta \{\ln[z_{\text{int}}(T)]\}}{\delta \beta} \quad (4.47)$$

Or:

$$E = E_{\text{tr}} + E_{\text{int}}$$

Where:

$$E_{\text{tr}} = \left(\frac{3}{2} kT \right) N \quad (4.48a)$$

$$E_{\text{int}} = -N \frac{\delta \{\ln[z_{\text{int}}(T)]\}}{\delta \beta} \quad (4.48b)$$

Note that both E_{tr} and E_{int} are functions of temperature alone. So therefore, the total energy is only a function of the temperature, as required.

4.3. The equipartition of energy and heat capacities

The translational kinetic energy per particle is:

$$E_{\text{tr}} = \left\{ \frac{mv^2}{2} \right\} = \frac{3}{2} kT \quad (4.49)$$

So the total translational energy for N particles is:

$$E_{\text{tr}} = N \left(\frac{3}{2} kT \right) = \frac{3}{2} PV$$

For monatomic gases¹:

$$E_{\text{int}} = 0$$

¹This is not strictly true but is a good approximation

So:

$$E = E_{\text{tr}} = \frac{3}{2}PV$$

For molecular gases:

$$PV = NkT$$

Since the pressure is only caused by translational motion of particles but:

$$E_{\text{int}} \neq 0$$

So although:

$$E_{\text{tr}} = \frac{3}{2}PV$$

$$E \neq \frac{3}{2}PV$$

In general:

$$E = \frac{PV}{(\gamma - 1)}$$

Where $\gamma = \frac{c_p}{c_v}$, the ratio of heat capacities.

Classically each internal degree of freedom of a gas molecule is associated with a certain average thermal energy.

- $\frac{1}{2}kT$ for each translational component, (i.e. $E_{\text{tr}} = N(\frac{3}{2}kT)$).
- $\frac{1}{2}kT$ for each allowed rotational axis, (2 rotational axes means that $E_{\text{int}_r} = N(kT)$, for 3 rotational axes $E_{\text{int}_r} = N(\frac{3}{2}kT)$).
- kT for each allowed vibrational axis, ($\frac{1}{2}kT$ for kinetic energy, $\frac{1}{2}kT$ for potential energy).

Classically all of these contribute to the total energy and the heat capacity. In quantum mechanics some do not since not all of these states are excited.

Now the heat capacity per mole at a constant volume, for a perfect gas is:

$$c_V = \left(\frac{dE}{dT} \right)_V = \left(\frac{dE_{\text{tr}}}{dT} \right)_V + \left(\frac{dE_{\text{int}}}{dT} \right)_V \quad (4.50)$$

$$= c_{V_{\text{tr}}} + c_{V_{\text{int}}}$$

So:

$$c_{V_{\text{tr}}} = \left(\frac{dE_{\text{tr}}}{dT} \right)_V = \frac{3}{2}kN_0 = \frac{3}{2}R \quad (4.51)$$

i.e. independent of the temperature.

For a monatomic gas

Experimentally $c_P = \frac{5}{2}R$, but for a perfect gas:

$$c_P = c_V + R$$

Hence:

$$\frac{c_V}{R} = \frac{1}{\gamma - 1} \quad \gamma = \frac{c_P}{c_V}$$

So:

$$c_V = \frac{3}{2}R = c_{V_{tr}}$$

Therefore:

$$c_{V_{int}} = 0$$

Which implies that:

$$E_{int} = 0$$

And:

$$\gamma = \frac{5}{3}$$

As expected there is no rotational energy, no vibrational energy, and no electronic excitation (at normal temperatures, there is of course at high temperatures), so:

$$E_{int} = E_{int_r} + E_{int_v} + E_{int_{el}} = 0 \quad (4.52)$$

For a molecular gas

The rotational states are generally fully excited for a molecular gas (at normal temperatures), so they give a full classical contribution to the heat capacity, c_V .

- For a linear molecule there are 2 rotational axes, therefore there are 2 degrees of freedom, so $c_{V_{int_r}} = R$
- Non-linear molecules have 3 rotational axes so $c_{V_{int_r}} = \frac{3}{2}R$

Vibrational states are not fully excited (at normal temperatures), the contribution depends on the molecule and the temperature. At low temperatures we can ignore the vibrational contribution to energy, $c_{V_{int_v}} = 0$ and $c_{V_{int_{el}}} = 0$.

$$c_V = c_{V_{tr}} + c_{V_{int_r}} \quad (4.53)$$

4.4. Isothermal atmospheres

Molecules in a gas have a distribution of velocities, therefore, some can reach greater heights than other and density decreases with altitude.

Escape velocity

Consider a molecule of mass m , at a distance r from the centre of a planet with mass M . It moves in a gravitational field with an energy $E = E_{\text{kinetic}} + E_{\text{potential}}$.

$$E = \frac{1}{2}mv^2 + \left(-\frac{GmM}{r}\right) \quad (4.54)$$

With G being the gravitational constant.

The molecule can just escape when $E = 0$ and $v = v_{\text{esc}}$, the escape velocity.

$$v_{\text{esc}} = \sqrt{\frac{2GM}{r}} \quad (4.55)$$

$v_{\text{esc}} \simeq 11300 \text{ m s}^{-1}$ for Earth.

The rms velocity is (from the Maxwell distribution):

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

For the Earth, with $T = 300 \text{ K}$ we have, for Hydrogen $v_{\text{rms}}(\text{H}_2) \simeq 2000 \text{ m s}^{-1}$ and for Nitrogen $v_{\text{rms}}(\text{N}_2) \simeq 500 \text{ m s}^{-1}$. This is less than escape velocity so most gases don't escape much, however some molecules will have velocities greater than the escape velocity due to the shape of the Maxwell distribution.

If g is constant (i.e. the atmosphere thickness is a lot less than the radius of the planet) the molecules maximum height h is given by:

$$\frac{mv^2}{2} = mgh \quad (4.56)$$

Most of the Earth's atmosphere is below $\sim 13 \text{ km}$.

4.4.1. Density vs. height for an isothermal atmosphere

We will derive the density as a function of height for an isothermal atmosphere²

For a perfect gas:

$$PV = NkT \quad P = nkT$$

With $n = \frac{N}{V}$.

So $P \propto n$, the number density. Pressure is the result of bombardment by molecules,

²This is an idealisation, atmosphere's are not isothermal.

so therefore pressure, P , and density, n , fall with height.

Consider the forces on a unit area, i.e. the pressure, at altitudes h and $h + dh$. We have a pressure P at h and a pressure $P + dP$ at $h + dh$. Note that the pressures upwards and downwards are equal at all altitudes. We now make the assumption that the ndh molecules in the height increment dh produce a net downward force on the lower area, which is their weight $mg(ndh)$. This is equal to the increment dP which occurs in the atmospheric pressure, so:

$$dP = -mg(ndh) \frac{dP}{dh} = -mgn$$

$$P = nkT \quad \frac{dP}{dn} = kT$$

Therefore:

$$\frac{dn}{dh} = \frac{-mgn}{kT} \quad (4.57a)$$

$$\frac{dn}{n} = \frac{-mg}{kT} dh \quad (4.57b)$$

$$n = n_0 e^{\frac{-mgh}{kT}} \quad (4.58)$$

With n_0 being the density at $h = 0$.

This means that:

$$P = P_0 e^{\frac{-mgh}{kT}} \quad (4.59)$$

And the scale height is defined as:

$$H = \frac{kT}{mg} \quad (4.60)$$

This is the height interval for which n or P are reduced by a factor of e ($\sim 37\%$). This gives:

$$n = n_0 e^{\frac{-h}{H}} \quad (4.61a)$$

$$P = P_0 e^{\frac{-h}{H}} \quad (4.61b)$$

For the Earth, if the Earth's atmosphere was isothermal at a temperature $T = 290$ K, the scale height would be $H \sim 8.5$ km.

4.4.2. The Boltzmann law

In general:

$$P(E_p) \propto e^{\frac{-E_p}{kT}} \quad (4.62)$$

Where E_p is the potential energy per atom, and $P(E_p)$ is the probability density.

4.4.3. Van der Waals equation of state for real gases

$$\left[P + \left(\frac{N^2 a}{V^2} \right) \right] (V - Nb) = NkT \quad (4.63)$$

Where the $\frac{N^2 a}{V^2}$ term allows for the real interactions between particles (causing an increase in pressure), and the Nb term allows for the finite size of the particles (causing a decrease in volume).

Looking at P - V isotherms we see that for:

- $T \ll T_c$ this is similar to a real gas.
- $T > T_c$ this is similar to a real gas, but with a slight inflection.
- $T = T_c$ this is defined by the gradient $\left(\frac{dP}{dN} \right)_T = 0$ and $\left(\frac{d^2 P}{dV^2} \right)_T = 0$.
- $T < T_c$ the gas condenses into a liquid.

4.5. Phase changes and the Gibbs free energy

Consider an isolated system containing one substance with two phases (e.g. ice and water, water and steam etc. etc.) as before.

$$\left. \begin{aligned} E &= E_1 + E_2 \\ V &= V_1 + V_2 \\ N &= N_1 + N_2 \end{aligned} \right\} E, V, N \text{ are fixed}$$

So the entropy:

$$S(E, V, N, E_1, V_1, N_1) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \quad (4.64)$$

Entropy is at a maximum at equilibrium. So now, with E_1, V_1, N_1 as independent variables:

$$dS = \left[\left(\frac{dS_1}{dE_1} \right)_{V_1, N_1} + \left(\frac{dS_2}{dE_2} \right)_{V_2, N_2} \left(\frac{dE_2}{dE_1} \right) \right] dE_1 \quad (4.65)$$

With similar terms for dV_1 , and dN_1 . We can also use the result:

$$\frac{dE_2}{dE_1} = -1$$

Now, we had:

$$dE = TdS - PdV \quad (4.66)$$

For a system in which the number of particles was fixed (i.e. a one component system). How is this modified if N is variable? Consider now $S = S(E, V, N)$:

$$dS = \left(\frac{dS}{dE} \right)_{V, N} dE + \left(\frac{dS}{dV} \right)_{E, N} dV + \left(\frac{dS}{dN} \right)_{E, V} dN$$

$$dS = \frac{dE}{T} + \frac{PdV}{T} - \frac{\mu dN}{T} \quad (4.67)$$

So:

$$dE = TdS - PdV + \mu dN \quad (4.68)$$

The Helmholtz free energy is defined as:

$$f = E - TS$$

And the Gibbs free energy as:

$$G = E + PV - TS \quad (4.69)$$

So:

$$df = -SdT - PdV + \mu dN \quad (4.70a)$$

$$dG = -SdT + VdP + \mu dN \quad (4.70b)$$

So μ can be found from:

$$\mu = \left(\frac{df}{dN} \right)_{T,V} \quad (4.71a)$$

$$\mu = \left(\frac{dG}{dN} \right)_{P,V} \quad (4.71b)$$

dS is given by:

$$\begin{aligned} dS = & \left[\left(\frac{dS_1}{dE_1} \right)_{V_1, N_1} - \left(\frac{dS_2}{dE_2} \right)_{V_2, N_2} \right] dE_1 \\ & + \left[\left(\frac{dS_1}{dV_1} \right)_{E_1, N_1} - \left(\frac{dS_2}{dV_2} \right)_{E_2, N_2} \right] dV_1 \\ & + \left[\left(\frac{dS_1}{dN_1} \right)_{E_1, V_1} - \left(\frac{dS_2}{dN_2} \right)_{E_2, V_2} \right] dN_1 \end{aligned} \quad (4.72)$$

With $dS = 0$ at a maximum.

Since E_1, V_1, N_1 are all independent, then each square bracket term must be zero, so two phases have equal temperatures and:

$$\left(\frac{dS_1}{dE_1} \right)_{V_1, N_1} = \left(\frac{dS_2}{dE_2} \right)_{V_2, N_2} \quad (4.73)$$

Equal pressures and:

$$\left(\frac{dS_1}{dV_1} \right)_{E_1, N_1} = \left(\frac{dS_2}{dV_2} \right)_{E_2, N_2} \quad (4.74)$$

Equal μ and:

$$\left(\frac{dS_1}{dN_1} \right)_{E_1, V_1} = \left(\frac{dS_2}{dN_2} \right)_{E_2, V_2} \quad (4.75)$$

For a single one component phase:

$$\mu = \left(\frac{dG}{dN} \right)_{T,P}$$

So therefore, μ is the increase of the Gibbs free energy caused by the addition of a particle (i.e. the Gibbs free energy per particle), so:

$$G(T, P, N) \propto N$$

Which means that:

$$G(T, P, N) = Ng(T, P) \quad (4.76)$$

Where $g(T, P)$ is the Gibbs free energy per particle, so:

$$\mu = g(T, P) \quad (4.77)$$

Note that this is generally not valid, it is only for a one component phase. If the system consists of one component in two phases the equilibrium condition then is that $\mu_1 = \mu_2$, which becomes $g_1(T, P) = g_2(T, P)$.

The equilibrium line is where $g_1 = g_2$ and on this line there is only one free variable, i.e. for a given temperature the pressure is defined etc. This leads to the 3-phase diagram. If three phases of a one component system are in equilibrium this defines the triple point in the T - P phase diagram.

4.5.1. The Clausius equation

The points A and B are on the equilibrium curve so at A :

$$g_1(T, P) = g_2(T, P)$$

And at B :

$$g_1(T + dT, P + dP) = g_2(T + dT, P + dP)$$

Now:

$$g_1(T + dT, P + dP) = g_1(T, P) + \left(\frac{dg_1}{dT} \right)_P dT + \left(\frac{dg_1}{dP} \right)_T dP \quad (4.78)$$

And similar for g_2 . So, by subtraction:

$$\left(\frac{dg_1}{dT} \right)_P dT + \left(\frac{dg_1}{dP} \right)_T dP = \left(\frac{dg_2}{dT} \right)_P dT + \left(\frac{dg_2}{dP} \right)_T dP \quad (4.79)$$

Therefore:

$$\frac{dP}{dT} = - \frac{\left[\left(\frac{dg_1}{dT} \right)_P - \left(\frac{dg_2}{dT} \right)_P \right]}{\left[\left(\frac{dg_1}{dP} \right)_T - \left(\frac{dg_2}{dP} \right)_T \right]} \quad (4.80)$$

Now recall that:

$$dg_1 = -S_i dT + V_i dP + \mu_i dN \quad [i = 1, 2]$$

And for a one component phase:

$$g_i = N_i G_i \quad [N_i \text{ fixed}]$$

So:

$$N_i dg_i = -S_i dT + V_i dP \quad (4.81)$$

$$\left(\frac{dg_i}{dT}\right)_P = \frac{-S_i}{N_i} \quad (4.82a)$$

$$\left(\frac{dg_i}{dP}\right)_T = \frac{V_i}{N_i} \quad (4.82b)$$

So the phase equilibrium curve is:

$$\frac{dT}{dP} = \frac{\left[\frac{S_2}{N_2} - \frac{S_1}{N_1}\right]}{\left[\frac{V_2}{N_2} - \frac{V_1}{N_1}\right]} = \frac{\Delta S}{\Delta V} \quad (4.83)$$

The Latent heat, $L = T\Delta S$, so:

$$\frac{dT}{dP} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V} \quad (4.84)$$

This is the *Clausius equation*.

The phase diagram for water is unusual because ice contracts on melting. $\Delta V < 0$, but $\Delta S > 0$ so $\frac{dP}{dT}$ is negative. Increasing the pressure reduces the melting point.

Transitions with $\Delta S, \Delta V \neq 0$ are first order. All solid/liquid/gas transitions are first order but there are some transitions with $\Delta S, \Delta V = 0$ which are second or third order.

END

Part II.
Appendix

Mathematical Formulae For PHAS2228

Combinations and Stirling's formula

The number of ways of choosing n items out of a total of N is:

$$\Omega(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!} \quad (0.1)$$

Stirling's Formula for the factorial function for $n \gg 1$:

$$\ln(n!) = n \ln(n) - n \quad (0.2)$$

Revision note on partial derivatives

If f is a function of variable u , and u is a function of variable x then (chain rule):

$$\frac{df}{dx} = \frac{df}{du} \frac{du}{dx} \quad (0.3)$$

Supposing $f = f(u)$ and $u = u(x, y)$ then from definition of partial derivatives:

$$\left(\frac{\delta f}{\delta x} \right)_y = \frac{df}{du} \left(\frac{\delta u}{\delta x} \right)_y \quad \text{and} \quad \left(\frac{\delta f}{\delta y} \right)_x = \frac{df}{du} \left(\frac{\delta u}{\delta y} \right)_x \quad (0.4)$$

Taylor series

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2!} f''(x) + \frac{h^3}{3!} f'''(x) + \dots \quad (0.5)$$

The 3-D wave equation

$$\nabla^2 \phi(\underline{r}) + k^2 \phi(\underline{r}) = 0 \quad (0.6)$$

Where *wave number* $k = \frac{2\pi}{\lambda}$.

Phase velocity, v , frequency, ν , and wavelength, λ , are all related by: $v = \lambda\nu$.

Angular frequency $\omega = 2\pi\nu$.

So, $v = \frac{\omega}{k}$.

Kinetic theory integrals

In kinetic theory we often have integrals of the form:

$$I_n(a) = \int_0^\infty x^n e^{-ax^2} dx \quad (0.7)$$

With $a > 0$. We can get a recurrence relation:

$$-I_{n+2}(a) = \frac{dI_n(a)}{da} = \int_0^\infty x^n (-x^2) e^{-ax^2} dx \quad (0.8)$$

And we find:

$$I_0(a) = \frac{1}{2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}} \quad I_2(a) = \frac{1}{4a} \left(\frac{\pi}{a}\right)^{\frac{1}{2}} \quad I_4(a) = \frac{3}{8a^2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}} \quad (0.9)$$

$$I_1(a) = \frac{1}{2a} \quad I_3(a) = \frac{1}{2a^2} \quad I_5(a) = \frac{1}{a^3} \quad (0.10)$$