Statistical and Thermal Physics (MP203), *Some notes for review*

Disclaimer: *These notes are a learning aid, but do not represent the full content of the course. Formulas and other information besides what is provided here are likely to be useful in passing this course. Any mistakes in these notes are not an excuse to make the same mistake on the exam (check with the book!).*
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The ideal gas *book section 1.2*

An ideal gas is an idealized model of a real gas, in which the gas is described as a collection of particles that move freely and do not interact with one another. This is usually a good approximation to real gases at low densities.

The **ideal gas law** is

$$pV = NkT = nRT$$

p is the pressure,
V is the volume,
N is the number of particles of gas,
k is Boltzmann's constant, $k \approx 1.34 \times 10^{-23} J/K$
T is the Kelvin temperature,
n is the number of *mol* of gas
R is the gas constant. $R \approx 8.31 J/K$

The ideal gas law is valid when the gas is in equilibrium.
It is a special case of an *equation of state*. This is a name for any relation between the macroscopic variables of a system which holds in equilibrium states.
For example, a more realistic equation of state for many gases is the van der Waals equation, $(p + n^2 a/V^2)(V - nb) = nRT$. This involves the constants a and b, which depend on the actual gas which is being described.

Moles, Avogadros number etc.

One *mol* is a quantity of N_A particles. N_A is Avogadro's number, $N_A \approx 6.0221 \times 10^{23}$.
We must have $Nk = nR$. Since $N = nN_A$ this means $R = N_A k$
The mol is defined so that 1 mol of Hydrogen (H) atoms has a mass of approximately $1\,g$. Similarly, the mass of a mol of any substance is approximately equal to the total number of protons and neutrons (combined) in one molecule of the substance. So 1 mol of Hydrogen gas *molecules* (H_2) has a mass of approximately $2\,g$, One mol of Oxygen (O_2) molecules has a mass of approximately $32\,g$, since an O-atom has 8 protons and 8 neutrons. Water (H_2O) has a molar mass of approximately $18\,g$, etc.

The Equipartition Theorem *book section 1.3*

At temperature T, the average energy U of a classical system with M quadratic degrees of freedom is $U = \frac{MkT}{2}$.

Further explanation: A *degree of freedom* is a parameter that can be used to partially describe the microstate of the system. When we say that a system has M degrees of freedom that means that M independent parameters need to be given to determine a state of the system.
A degree of freedom x is said to be *quadratic* of the energy of the system contains a term of the form cx^2, where c is a constant, and no other terms depending on x.
For example, a single atom has 6 degrees of freedom, its position coordinates (x, y, z) and its velocity components (v_x, v_y, v_z). If the particle is free, its energy is just the kinetic energy $U = \frac{1}{2}m|v|^2 = \frac{1}{2}m(v_x)^2 + \frac{1}{2}m(v_y)^2 + \frac{1}{2}m(v_y)^2$. Here m is the mass of the atom. We see that v_x, v_y and v_z are quadratic degrees of freedom. The position coordinates x, y and z are not, since they don't appear in the energy.
Note: The equipartition theorem can give good results also for a quantum mechanical system, if the spacing between the energy levels of the system is much smaller than kT. This is usually the case at high temperatures, but not at low temperatures, so for real systems, we can think of the theorem as a high temperature approximation. The equipartition theorem can't be used if the energy takes a complicated (non-quadratic) form. This happens for example in liquids.

Energies for gases and solids

The equipartition theorem gives us estimates for the energy U of gases and solids.
In general, for a gas or solid consisting of N particles, we have the estimate

$$U \approx \frac{f}{2}NkT$$

Here, f is a constant which depends on the system. In fact f is the number of quadratic degrees of freedom per particle.
For a **monatomic gas**, $f = 3$.
Monatomic gases have molecules that consist of a single atom.
Examples: Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr)
The 3 quadratic degrees of freedom for each particle are its velocity components v_x, v_y and v_z.
For a **diatomic gas**, $f = 5$.
Diatomic gases have molecules that consist of a two atoms.
Examples: Nitrogen (N_2), Oxygen (O_2), Hydrogen (H_2).
The 5 quadratic degrees of freedom for each molecule are the velocity components v_x, v_y and v_z and two angular velocities describing the velocity of rotation of the atoms in the molecule around their common center of gravity.
For a **solid**, $f = 6$
We can model a solid (naively) as a collection of particles oscillating around quilibrium positions which lie on a lattice. The 6 quadratic degrees of freedom for each particle are its velocity components v_x, v_y and v_z and the components u_x, u_y and u_z of the displacement of the particle from its equilibrium position. The microscopic formula for the energy of the particle is $U = \frac{1}{2}m|v|^2 + \frac{1}{2}C|u|^2$. Here C is a constant, which indicates how strongly the particle is attracted to its equilibrium position.
The estimate for solids does not work equally well for all solids and always fails at low temperatures due to quantum effects.

Work, Heat and Energy – the First Law ***book section 1.4***

Energy can be exchanged in the form of work (W) or heat (Q).
Work is simply macroscopically observable work, the same as in classical mechanics. A system loses internal energy when it performs positive work.
Heat is energy in spontaneous flow. (Basically this is the remaining energy flow which can't be associated with macroscopic work.)
First Law: The change in the internal energy U of a system in any process satisfies the equation

$$\Delta U = Q - W.$$

Here Q is the amount of heat absorbed by the system and W is the amount of work performed by the system. This is the first law of thermodynamics. The energy difference ΔU is the system's energy after the process minus the system's energy before the process.

Work due to volume change (expansion or compression) ***book section 1.5***

Work due to expansion or compression of the system can be expressed in terms of the system's pressure and volume.
The work $đW$ done by the system in an infinitesimal process where the system volume changes by dV is given by

$$đW = p\,dV$$

Here we use the symbol $đ$ for infinitesimal quantities which depend on the infinitesimal process which gets us from the initial to the final state. In general, the work done may depends on the process and it is even possible to have nonzero work in a process with the same initial and final state. We use d for infinitesimal quantities which only depend on the inital and final state of a process. Here, dV is such a quantity since it is just the difference between the final and the initial volume.
For any process where the volume changes from an initial value V_i to a final value V_f we get the total work done by integrating the formula for $đW$

$$W = \int_{process} đW = \int_{V_i}^{V_f} p(V)\,dV.$$

We need to know p as a function of V to calculate this.
Examples:

1. **If p is constant** (independent of V) during the process, then we find

$$W = \int_{V_i}^{V_f} p\,dV = p\int_{V_i}^{V_f} dV = p(V_f - V_i) = p\Delta V$$

2. **If T is constant** during the process and the **system satisfies the ideal gas law**,

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{nRT}{V}\,dV = nRT\int_{V_i}^{V_f} \frac{1}{V}\,dV = nRT\log(\frac{V_f}{V_i}).$$

   We used the ideal gas law in the second equality and the fact that T remains constant in the third equality.

Heat capacity and specific heat ***book section 1.6***

When heat is added to a system, the temperature usually increases (but not always - see latent heat below). The **heat capacity** C of a system is defined as the amount of heat absorbed by the system per unit temperature increase. So,

$$C = \frac{đQ}{dT}$$

The infinitesimal heat $đQ$ absorbed by the system depends on the process and hence the same is true for the heat capacity C. Two important special cases are the heat capacity at constant volume C_V and the heat capacity and at constant pressure C_p.

The **specific heat** c of a substance is the heat capacity of a unit amount of that substance. The unit amount can be a unit of mass (usually the kg) or a mol, or even a unit volume. This gives specific heats per unit mass, per mol (the molar specfic heat) or per unit volume. All of these still depend on the process and we again have the special cases c_V at constant volume and and c_p at constant pressure.

For example, water has a specific heat $c_p \approx 4.2\,\mathrm{kJ/(kg \cdot K)}$ at atmospheric pressure ($p \approx 1.0 \times 10^5\,\mathrm{Pa}$). This means you need to add $4.2\,\mathrm{kJ}$ heat to $1\,\mathrm{kg}$ of water to increase the temperature of the water by $1\,\mathrm{K}$. A quantity of $21\,\mathrm{kg}$ of water will have a heat capacity $C_p = 21\,\mathrm{kg} \times c_p$. If you want to increase the temperature of this amount of water by $15\,\mathrm{K}$ (at atmospheric pressure) you will have to add an amount of heat equal to $15\,\mathrm{K} \times 21\,\mathrm{kg} \times c_p$.

Generally, C and c will be functions of p and T but often they are approximately constant over the range of p and T we are interested in (for example for water the value of c_p only varies in the third decimal place between $0°C$ and $100°C$ at atmospheric pressure).

If heating of a substance takes place in the absence of work ($đW = 0$), then the first law of thermodynamics says that $đQ = dU + đW = dU$. Usually there is no work if the volume remains constant. Hence, we find

$$C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

This also gives us an estimate for C_V for gases and solids, $C_V \approx \frac{f}{2}Nk$.

Phase Transitions and Latent Heat ***book section 1.6, from pg. 32***

A typical simple substance (consisting of only one type of molecule) appears in at least three forms, or ***phases***: solid, liquid and gaseous. More phases are possible, for example there may be different types of solid phase with different crystal structures or different magnetic behavior.

A ***phase transition*** is a process in which a system goes from one phase to another. Examples are melting and solidifying (between liquid and solid), evaporation or condensation (between liquid and gas) and sublimation (between solid and gas).

In phase transitions a substance will often absorb or release heat without any corresponding change in temperature. For example, ice melts at constant temperature ($0°C$), but absorbs heat in the process. This heat is called ***latent heat***, often denoted L.

Latent heat is usually given per unit amount of substance, so $L = Q/m$ for latent heat per unit mass, or $L = Q/n$ for molar latent heat. These are really specific latent heats

For example the latent heat of melting for ice , per unit mass, is $L_{\mathrm{melting\,H_2O}} \approx 334\,\mathrm{kJ/kg}$. To melt $4\,\mathrm{kg}$ of ice (at $T = 0°C$), we need to add $4\,\mathrm{kg} \times 334\,\mathrm{kJ/kg} \approx 1.3 \times 10^3\,\mathrm{kJ}$ of heat.

Types of thermodynamic processes

- **Adiabatic Processes** are processes in which **no heat is absorbed or released** by the system, so $Q = 0$, or $đQ = 0$ for an infinitesimal process.
  Since $đQ = 0$, the first law gives $dU = -đW$ for an adiabatic process. For adiabatic expansion or compression, this gives $dU = -p\,dV$. We can use this to calculate the ***adiabatic curves*** or ***adiabats*** of the system. These are curves in the (p, V) or (p, T) or (V, T) diagram which describe the adiabatic process. To do this we also need to have an equation for U in terms of (p, V, T) and we may also need to use the equation of state relating p, V and T themselves.
  Example: Adiabats for a monatomic ideal gas
  In this case, we have $pV = NkT$ and $U = \frac{3}{2}NkT = \frac{3}{2}pV$.
  For an adiabatic volume change, $dU = -p\,dV$.
  Here, $dU = \frac{3}{2}d(pV) = \frac{3}{2}(p\,dV + V\,dp) = -p\,dV$ so we find $\frac{5}{2}p\,dV = -\frac{3}{2}V\,dp$.
  Dividing by pV, we get $\frac{5}{2}\frac{1}{V}\,dV = -\frac{3}{2}\frac{1}{p}\,dp$.
  Integrating both sides gives $\frac{5}{2}\log(V) = -\frac{3}{2}\log(p) + c$, where c is a constant of integration. Taking the exponential, we find $V^{\frac{5}{2}} = p^{-\frac{3}{2}}C$, where $C = e^c$ and finally we find that $p^{\frac{3}{2}}V^{\frac{5}{2}} = C$, or $pV^{\frac{5}{3}} = D$ (here $D = C^{\frac{2}{3}}$ is still a constant). This describes an adiabatic curve in the (p, V) diagram.
  We have found that the product $pV^{\frac{5}{3}}$ is constant during an adiabatic expansion or compression of a monatomic ideal gas. We can use this to compare initial and final volumes and pressures, since we must have $p_i V_i^{\frac{5}{3}} = p_f V_f^{\frac{5}{3}}$

- **Isothermal Processes** are processes which occur at **constant temperature**.
  For the special case of an ideal gas this means that the energy is also constant (since $U = \frac{f}{2}NkT$). The first law then says that $Q = W$.

- **Isobaric Processes** are processes which occur at **constant pressure**. This gives for the work W due to volume change that $W = p\Delta V$. If there is no other work, the first law then gives $Q = \Delta U + p\Delta V = \Delta H$, where H is the **enthalpy**, defined by $H = U + pV$. So, in isobaric processes where work occurs only through volume change, the heat absorbed is equal to the change in the enthalpy. Many real systems are at **atmospheric pressure**, which is always approximately 1.0×10^5 Pa

- **Isochoric Processes** are processes in which **no work is done**, so $W = 0$ and the first law gives $Q = \Delta U$. These are typically processes at **constant volume** (so $dV = 0$ and hence $đW = p\,dV = 0$).

- **Cyclic processes, or Cycles** are processes for which **the initial state of the system is the same as the final state**. These are very important in describing all sorts of engines and machines. Since the initial and final state are equal, we have $\Delta U = U_f - U_i = U_i - U_i = 0$. The first law then gives $Q = W$, so the heat absorbed in a cycle is equal to the work done by the system in the cycle.

Enthalpy and chemical reactions ***book section 1.6, pg.33 and onward***

The **enthalpy** H is defined by the formula $H = U + pV$.
Here, U is the internal energy, p the pressure and V the volume of the system
For a process **at constant pressure**, the heat absorbed is equal to the change in the enthalpy of the system: $Q = \Delta H$. This makes the enthalpy particularly useful for calculating the heat produced or absorbed in chemical reactions which take place in contact with a reservoir at constant pressure (usually the atmosphere). Enthalpy changes for many processes are tabulated. The **enthalpy of formation**, $\mathbf{\Delta_f H}$ is an important example. The enthalpy of formation of a substance is defined as the change of enthalpy that occurs in the formation of 1 mol of that substance from its constituent elements, assuming that the elements and the substance formed are all in their standard states, usually at $p = 1.01 \times 10^5$ Pa and $T = 298$ K. In any chemical reaction, we can imagine first converting the reactants (input chemicals) into their constituent elements and then forming the products (output chemicals) from those elements. This gives the total amount of heat absorbed or released in the reaction in terms of the formation enthalpies of the reactants and products.
Example: Burning methane (CH_4). Reaction formula: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.
Converting CH_4 into its elements ($CH_4 \rightarrow C + 2H_2$) gives an enthalpy change of $-\Delta_f H(CH_4)$ (negative, because the process is the opposite of the formation of methane).
Oxygen (O_2) is already in elementary form, so no enthalpy change is needed.
We now have $C + 2H_2 + 2O_2$.
Forming a mole of CO_2 changes the enthalpy by $\Delta_f H(CO_2)$.
Forming 2 mol of H_2O changes the enthalpy by $2\Delta_f H(H_2O)$.
The overall enthalpy change in burning 1 mol of CH_4 is then

$$\Delta H(\text{reaction}) = \Delta_f H(CO_2) + 2\Delta_f H(H_2O) - \Delta_f H(CH_4).$$

Notice that this is the enthalpy of formation of the proucts minus the enthalpy of formation of the reactants (with the appropriate coefficients from the reaction formula). This enthalpy change is equal to the amount of heat absorbed by the chemicals in the reaction. In this case, it turns out to be negative (look up values for the formation enthalpies to check this), which means that the reaction releases heat (it"absorbs a negative amount").

Heat Transport ***book section 1.7***

For a system in which the temperature T varies in one direction (say, the x-direction), we can calculate the heat that flows through a surface area of size A (orthogonal to the x-direction) using ***Fourier's law of heat conduction:***.

$$\frac{đQ}{dt} = -\kappa A \frac{dT}{dx}$$

Here, $\frac{đQ}{dt}$ is the rate of heat flow (the amount of heat that flows per second).
κ is the ***thermal conductivity*** of the material through which the heat flows. The unit of κ is W/(K m). If κ is large, the material conducts heat well. Schroeder uses the notation k_t instead of κ.
If the rate of flow does not change during a time Δt then $\frac{đQ}{dt} = \frac{Q}{\Delta t}$, where Q is the amount of heat that flows through the surface in the time Δt. Schroeder uses this to

write Fourier's law as $\frac{Q}{\Delta t} = -k_t A \frac{dT}{dx}$.
Often, we want to think of heat flow through a layer of material of thickness Δx, where there is a constant temperature difference ΔT between the two sides of the layer. In such cases you can replace $\frac{dT}{dx}$ by $\frac{\Delta T}{\Delta x}$.
Example: Copper has a thermal conductivity of $401\,\mathrm{W/(K\,m)}$. If we keep a copper wire of 10 cm length with a cross section of $1\,\mathrm{mm}^2$ at a temperature of 373 K on one end (at $x = 0$) and at a temperature of 273 K on the other end (at $x = 10\,\mathrm{cm}$), then the rate of heat flow through this wire will be $\frac{đQ}{dt} = -\kappa A \frac{\Delta T}{\Delta x}$ with $\kappa = 401\,\mathrm{W/(K\,m)}$, $A = 1\,\mathrm{mm}^2 = 1 \times 10^{-6} m^2$, $\Delta T = 100\,\mathrm{K}$ and $\Delta x = 10\,\mathrm{cm} = 0.1\,\mathrm{m}$. This gives a heat flow rate $\frac{đQ}{dt} = -0.4\,\mathrm{W} = -0.4\,\mathrm{J/s}$ through the wire. Notice that the heat flow is negative. This means that heat flows in the negative x-direction. This happens because the wire has a higher temperature at large x and so the heat flows from large x to small x.

Heat transport in gases ***book section 1.7, p.41 and onward***

For gases, we can get an estimate of the thermal conductivity from a microscopic model of the gas (a model of particles moving around and colliding with each other).
Important concepts in these types of estimates are:

- The **mean free path** ℓ is the average distance a particle travels between collisions. A rough estimate for ℓ in a gas is $\ell \approx \frac{V}{4\pi r^2 N}$ (see book pg. 41 for a derivation). Here V is the volume of the gas, N is the number of particles and r is the radius of a particle (or if the particle is not spherical, another measure of its size - typically we use the van der Waals radius).

- The **root mean square velocity** v_{rms} is the square root of the average of $|v|^2$ over the particles, so by definition $(v_{\mathrm{rms}})^2 = \frac{1}{N}\sum_{i=1}^{N}(v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2)$, where the sum runs over the N particles. v_{rms} gives a good idea of the typical speed of a particle, though it is usually not equal to the average speed. Notice that $(v_{\mathrm{rms}})^2 = \frac{1}{N}\frac{2}{m}U_{kin}$, where U_{kin} is the kinetic energy associated with the (center of mass) motion of the particles and m is the mass of a single particle. Since $U_{kin} = \frac{3}{2}NkT$ we then find

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}}$$

- The **mean free time** τ is the average time a particle travels between successive collisions. A rough estimate for the mean free time is $\tau \approx \frac{\ell}{v_{\mathrm{rms}}}$

One may now derive (see book, pg. 42-43) an **estimate for the thermal conductivity** κ of a dilute (nearly ideal) gas,

$$\kappa \approx \frac{1}{2}\frac{C_V}{V}\ell v_{\mathrm{rms}}$$

Using $C_V = \frac{f}{2}Nk$ and and our formulas for ℓ and v_{rms} above, we find then that

$$\kappa \approx \frac{f\,k}{16\pi r^2}\sqrt{\frac{3kT}{m}}$$

So in a dilute gas, the thermal conductivity is proportional to $\sqrt{T}$.

The Heat Equation

The **heat equation** for a system whose temperature can vary in the x direction in space, as well as over time, is

$$\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial x^2}.$$

Here, $K = \frac{\kappa}{c\rho}$, where κ is the thermal conductivity of the material, ρ is its density (mass per volume) and c is its specific heat per unit mass.
This differential equation can be derived from Fourier's law (see notes). The solutions tend to be such that any maxima or minima of the temperature in space are smoothed out over time. Important special case: If T is constant in time, then $\frac{\partial T}{\partial t} = 0$ and the equation tells us that $\frac{\partial^2 T}{\partial x^2} = 0$. Integrating twice, we find $T(x) = c_1 + c_2 x$, with c_1 and c_2 constants of integration. We see that the only time independent temperature distributions $T(x)$ are linear functions of x.

The Entropy and the Multiplicity

Thermodynamic systems have many components, for example many molecules in a gas or many dipoles in a magnet.
A **microstate** of the system gives a full description of the states of all components, enough information to calculate how the system will evolve in time. For a system of point particles described using classical mechanics, this means a microstate is described by giving the positions and velocities of all the particles.
A **macrostate** of the system is described by a few parameters that we can measure using a macroscopic apparatus. For a gas, these are usually pressure volume and temperature. In an equilibrium state, these quantities can be related by an equation of state (for example the ideal gas law).
For large systems, there are very many microstates that correspond to the same macrostate. The **multiplicity of a macrostate** A is the number of microstates that correspond to this macrostate. This multiplicity is written $\Omega(A)$. If the macrostate is determined by (for example) the volume V and energy U of the system, we can also write $\Omega(V, U)$, etc.
The **entropy** $S(A)$ of a macrostate A is defined as the product of Boltzmann's constant k and the logarithm of the multiplicity of A, so

$$S(A) = k\log(\Omega(A))$$

(This is not how the entropy was originally defined - originally there was a different definition and this formula was a great discovery). S has the same units as k, so J/K.

In a **system with two independent subsystems**, we can describe the macrostate of the full system as a pair (A, B) of macrostates of the two subsystems.
The multiplicity of the full system is the product of the multiplicities of the subsystems, $\Omega(A, B) = \Omega(A)\Omega(B)$, because the microstates of the subsystems which correspond to the macrostates A and B can be chosen independently. As a result,
The entropy of the full systems is the sum of the entropies of the subsystems, $S(A, B) = S(A) + S(B)$.

Paramagnets (entropy and multiplicity) ***book sections 2.1 and 3.3***

A paramagnet is a system which does not behave like a magnet normally, but can become magnetized in the presence of a magnetic field. The system consists of magnetic dipoles (think: particles that behave as microscopic bar magnets) which do not interact with each other. If there is no field, the dipoles point in random directions. If a magnetic field is applied (think: a magnet is brought in proximity to the system), the dipoles align with the magnetic field (and with each other) and the system develops a magnetization M.
To be concrete, a 2-state paramagnet is a system of N dipoles which can each be two states, labeled $\uparrow$ and $\downarrow$, which have magnetic dipole moment $+\mu$ and $-\mu$ along a chosen direction (we will call it the z-direction). The ***magnetization*** M of the system is defined by $M = N_\uparrow\mu - N_\downarrow\mu$, where $N_\uparrow$ is the number of dipoles in the state $\uparrow$ and $N_\downarrow$ is the number of dipoles in the state $\downarrow$. Also, $N = N_\uparrow + N_\downarrow$. In the presence of a magnetic field of strength B in the z direction, the paramagnet has energy $U = -BM$.
A ***microstate of the paramagnet*** is given by an assignment of a state ($\uparrow$ or $\downarrow$) to each dipole. This gives a total of 2^N microstates.
A ***macrostate of the paramagnet*** is determined by the value of the magnetization (or the energy if $B \neq 0$). Both of these are determined by the value of $N_\uparrow$.
The ***multiplicity of a macrostate*** with a given value of $N_\uparrow$ is equal to the number of microstates for which $N_\uparrow$ dipoles are in the state $\uparrow$ (the others are automatically in the state $\downarrow$). There are as many such microstates as there are ways to choose $N_\uparrow$ dipoles out of the total of N dipoles, so $\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!(N-N_\uparrow)!}$.
This also gives the entropy, $S(N_\uparrow) = k\log(\Omega(N_\uparrow)) = k\log(\binom{N}{N_\uparrow})$.
We can also write this in terms of M (or U) by writing $N_\uparrow$ in terms of M (or U).

Entropy for the ideal gas ***book section 2.5***

Classical many particle systems in principle always have infinitely many microstates per macrostates, because the particles' positions and velocities can be varied continuously. To get to a finite counting of microstates, it is necessary to introduce resolutions Δx in position space and Δp in momentum space (or $\Delta v = \frac{\Delta p}{m}$ if you prefer using velocity instead of momentum). Quantum mechanics, specifically the Heisenberg uncertainty principle, dictates that we should take $\Delta x \Delta p = h$, where $h \approx 6.63 \times 10^{-34}$ Js is Planck's constant.
For a gas of N point particles (think: atoms) in a volume V, we now have $\frac{V}{(\Delta x)^3}$ independent choices of position for each particle, which gives $\frac{V^N}{(\Delta x)^{3N}}$ position states in total. The momenta lie on a $3N-1$-dimensional hypersphere in the $3N$-dimensional momentum space, since $\sum_{i=1}^{N}(p_{x,i})^2 + (p_{y,i})^2 + (p_{z,i})^2 = 2mU$ and the energy U is constant. The number of momentum states available to the system is then the "area" of this hypersphere (see appendix B in the book) divided by $(\Delta p)^{3N-1}$. Up to some small factors this gives formula (2.40) in the book,

$$\Omega_N(U,V) \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}(\sqrt{2mU})^{3N}$$

The factor of $N!$ is needed to correct for overcounting which occurs when the gas particles are indistinguishable (of the same type). The V^N comes from the position states, the h^{3N} from the resolutions Δx and Δp and the other factors come from the volume of the hypersphere in momentum space. The entropy of the system is $S_N(U,V) = k\log(\Omega_N(U,V))$.

Stirling's approximation of the factorial ***book section 2.4 and appendix B***

To be able to do calculations involving entropy it is useful to have an approxiumate formula for the logarithm of the factorial.
Stirling's formula says that for large N,

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

If N is large enough, the term $\frac{1}{2}\log(2\pi N)$ is very small compared to the other two terms and it is often omitted to simplify calculations.

Results for the entropy obtained using Stirling's formula

Using Stirling's formula and a fair amount of algebraic manipulation we find the following formula for the **Entropy of a 2-state paramagnet**,

$$S(x) = -Nk\left(x\log(x) + (1-x)\log(1-x)\right), \qquad \text{with } x = \frac{N_\uparrow}{N} = \frac{M}{2\mu N} + \frac{1}{2} = -\frac{U}{2\mu BN} + \frac{1}{2}$$

Similarly, we can find the ***Sackur-Tetrode formula*** **for the entropy of a monatomic ideal gas**,

$$S_N(U,V) = Nk\left(\log\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right)$$

Note that the **entropy is *extensive***. This means that it is proportional to the size of the system (N), if locally observable quantitites like the magnetisation per particle ($\frac{M}{N}$) or the energy per particle and the volume per particle ($\frac{U}{N}$ and $\frac{V}{N}$) are kept fixed.

The three laws of thermodynamics

The First Law:

Total energy is conserved in any thermal process, when heat is taken into account as a form of energy (namely energy in spontaneous flow). For any process, this means that the change in the internal energy U of the system under consideration equals the difference between the amount of heat Q absorbed by the system and the amount of work W performed by the system, $\Delta U = Q - W$.
We may write the first law in infinitesimal form as $dU = đQ - đW$
(Alternatively, we can write $\Delta U = Q + W'$, where $W' = -W$ is the work performed *on* the system, and similarly $dU = đQ + đW'$.)

The Second Law:

The second law can be stated in a number of forms.
Second law in terms of entropy: *In any thermodynamic process, the change in the total entropy S satisfies $\Delta S \geq 0$. For an isolated system, this means the change of the entropy of the system in any process is greater than or equal to zero. The system will tend towards an equilibrium state, which is a state of maximal entropy.*

The second law in this form goes together with the **fundamental assumption of statistical mechanics**: all accessible microstates of a system are equally likely to be observed. This means the macrostate with the highest multiplicity (which is the same as the largest entropy) is most likely to be observed.

Older formulations of the second law are
Clausius Postulate: *If heat flows by conduction from a body A to a body B then there is no process that makes heat flow from B to A without any other effect.*
This basically says you can't bring heat from a system at low temperature to a system at high temperature without doing some amount of work, which leads to additional effects on the total system (It is clearly possible to bring heat from a cold to a warm place if you do allow for work, this is refrigeration).
Kelvin Postulate
There is no process whose only effect is to take heat from a system at constant temperature and turn it into work
If it was possible to violate this postulate, you could build a "perpetuum mobile of the second kind", which is precisely a machine that would take heat from its surroundings and turn it all into work.
The Kelvin and Clausius postulates are equivalent and can be proved from the second law in terms of entropy.

The Third Law:

In any thermodynamic system, the entropy vanishes as the temperature is taken to absolute zero. In other words $\lim_{T \downarrow 0} S(T) = 0$.
This happens because the system will go into its quantum mechanical ground state (lowest energy state) as the temperature is lowered to absolute zero.
The ground state is usually unique so $\Omega(T = 0) = 1$ and $S(T = 0) = k \log(1) = 0$.
Even if the ground state has a small multiplicity (which can happen), S will be at most a few times $k \approx 1.34 \times 10^{-23}\,\mathrm{J/K}$, which is not measurably different from zero.

Connection between Entropy and Heat and Thermodynamic Identity

The relation between the change in the entropy of a system and the heat it absorbs in a process is as follows: ***book sections 3.2,3.4***

$$dS \geq \frac{đQ}{T}, \quad \text{with} \quad dS = \frac{đQ}{T} \quad \text{for quasistatic processes}$$

A quasistatic process is a process which happens slowly enough so that the system is always (approximately) in an equilibrium state. For example for a gas this means that the system has a well defined pressure and temperature at all times during the process.
Using the first law, we can write $đQ = dU + đW = dU + p\,dV$ (assuming all work is due to volume change).
This leads to the **Thermodynamic Identity**, ***book section 3.4***

$$đQ = T\,dS = dU + p\,dV$$

Getting $U(p,T)$ and $V(p,T)$ from the entropy

The thermodynamic identity can also be written in the form $dS = \frac{1}{T}dU + \frac{p}{T}\,dV$
From this equation we can read off that

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}.$$

If we know $S(U,V)$ we can use these equations to calculate U and V in terms of p and T.
Examples:

1. For the **ideal gas**, we find from the Sackur-Tetrode formula on page 10 that $\left(\frac{\partial S}{\partial V}\right)_U = \frac{Nk}{V}$. This means that we must have $\frac{p}{T} = \frac{Nk}{V}$ which is just a way of writing the ideal gas law. In particular we find $V(p,T) = \frac{NkT}{p}$. Similarly, we find $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{3}{2}\frac{Nk}{U}$, which gives the wel known result that $U(T) = \frac{3}{2}NkT$ for a monatomic ideal gas.

2. For the 2**-state paramagnet**, the V and p play no role, but we can still find $U(T)$ using $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$ and the formula for $S(x)$ on page 10. After some algebraic manpulation, this gives $U(T) = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$ and hence $M = -U/B = N\mu \tanh\left(\frac{\mu B}{kT}\right)$. If $\frac{\mu B}{kT} \ll 1$, then $\tanh\left(\frac{\mu B}{kT}\right) \approx \frac{\mu B}{kT}$ and it follows that M is proportional to to B/T. This behavior of the magnetization is called ***Curie's law***. ***book sec. 3.3***

Entropy and heat capacity ***book sections 3.2, 3.4***

. We can calculate the entropy of a system if we know its heat capacity $C(T)$. We have

$$S(T) = S(\text{temp. } T) - S(\text{temp. } 0) = \int_{\text{temp. 0 state}}^{\text{temp. T state}} dS = \int_0^T \frac{1}{T'}\frac{đQ}{dT'}dT' = \int_0^T \frac{C(T')}{T'}dT'$$

We used the third law, giving $S(\text{temp. } 0) = 0$.
Then we introduced $1 = \frac{dT'}{dT'}$ and we used that $dS = \frac{đQ}{T}$ (we assume that the integral is along a quasistatic process, so that temperature is always well defined).
Finally we used the definition of the heat capacity, $C = \frac{đQ}{dT}$.
Vanishing heat capacity at low temperature: From the formula for S in terms of C, we see that we must have $\lim_{T\downarrow 0} C(T) = 0$ for all systems. If this was not the case, the integral which equals $S(T)$ would be infinite.

Calculating entropy differences from macroscopic data

In a process with initial state A and final state B the entropy change can often be calculated directly from macroscopic data (we don't need to know about microstates).
If the temperature is varying during the process, we can write

$$\Delta S_{A\to B} = S(B) - S(A) = \int_{T_A}^{T_B} dS = \int_{T_A}^{T_B} \frac{1}{T'}\frac{đQ}{dT'}dT' = \int_{T_A}^{T_B} \frac{C(T')}{T'}dT'$$

If the temperature is constant during the process, we find

$$\Delta S_{A\to B} = S(B) - S(A) = \int_{A}^{B} dS = \int_{A}^{B} \frac{đQ}{T} = \frac{Q_{A\to B}}{T}.$$

Here $Q_{A\to B}$ is the heat absorbed by the system in the process. Typical constant temperature processes are the phase transitions between the soid liquid and gaseous phases of a simple substance (a simple substance consists of only one type of molecule – think water). In this case the heat absorbed is the latent heat of the transition and the change in entropy is the latent heat divided by the (Kelvin) temperature at the transition point.