0.1 Statistical Mechanics

0.1.1 Maxwell Distribution (Longair p. 258n10.29

We have the identical independent distributions $f(v_x), f(v_y)f(v_z)$. What does it physically mean to say that

$$f(v_x)f(v_y)f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

from which we conclude that $f(v_x) = Ae^{-Bv_x^2}$.
There are many different triplets (v_x, v_y, v_z) corresponding to the same speed. The differences correspond to molecules moving in different directions but at the same speed. The assumption is that the number of molecules at a given speed in one direction is the same as the in any other direction i,e. it is independent of the direction. Thus given a little cuboid with sides du, dv, dw and two velocity vectors $\mathbf{v} = (v_x, v_y, v_z)$ and $\mathbf{v}' = (v_x', v_y', v_z')$ corresponding to the same speed, then

$$f(v_x)f(v_y)f(v_z)dudvdw = f(v_x')f(v_y')f(v_z')dudvdw = \phi(v_x^2 + v_y^2 + v_z^2)dudvdw$$

The existence of ϕ follows from the fact that $f(v_x)f(v_y)f(v_z)$ depends only on the value of $v_x^2+v_y^2+v_z^2$. This equation obviously suggests $f(x) = Ae^{-Bx^2}$.
Mean and Variance of Maxwell Distribution (Longair p 260)
For the mean we need to evaluate $\int_0^\infty x^3e^{-x^2}$ We have, substituting $u = x^2$ and integrating by parts by taking$u = x$ and $v = x^3e^{-x^2}$.

$$\int_0^\infty x^3e^{-x^2} = \frac{1}{2}\int_0^\infty ue^{-u}du = \frac{1}{2}\left[u\int e^{-u}du - \int\left(\int e^{-u}du\right)du\right]_0^\infty$$

which equals

$$\frac{1}{2}\left[-ue^{-u} - \int -e^{-u}du\right]_0^\infty = \frac{1}{2}\left[-ue^{-u} - e^{-u}\right]_0^\infty = \frac{1}{2}$$

as required. For the variance we need to evaluate $\int_0^\infty x^4e^{-x^2}dx$. Taking $u = x$ and $v = x^3e^{-x^2}$ and integrating by parts the integral reduces to $\int_0^\infty x^3e^{-x^2}dx$ which we have already integrated.

0.1.2 Boltzmann Distribution. Kuhm Ch 2 and Thompson Ch1

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Let $f(\mathbf{v},t)d\mathbf{v}$ be, at time t the number of molecules per unit volume (i.e. the number density) whose velocities are within $d\mathbf{v}$ of $\mathbf{v}$. This is assumed to be a large number and the density does not depend on the location of the molecules and is the same everywhere throughout the enclosure. We can thus consider two groups of molecules - those in Group 1 having velocities within $d\mathbf{v}_1$ of $\mathbf{v}_1$ and those in Group 2 having velocities within $d\mathbf{v}_2$ of $\mathbf{v}_2$. The number density of Group1 molecules at a time t is $f(\mathbf{v}_1,t)d\mathbf{v_1}$ and of Group 2 molecules is $f(\mathbf{v}_2,t)d\mathbf{v}_2$. We can now ask about the number of collisions that occur between Group 1 and Group 2 molecules between times t and $t+\delta t$.

Some other quantities and assumptions need to be introduced. First of all we assum only binary collisions. Let the molecules be modelled as spheres of radius σ, For each collision the line from the centre of the Group 1 molecule to the centre of the Group 2 molecule passes through the point of contact. We will restrict the problem to finding the number density of collisions which, as well as ocurring between t and $t+\delta t$, also have the property that the lines from the centre of the Group 1 sphere to the point of contact with the Group 2 sphere all lie within a small solid angle $d\lambda$..

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Consider a Group 1 molecule m_1 and a Group 2 molecule m_2, both of diameter σ, in an inertial frame whch makes m_2 at rest and in which the velociity of $m_1$is thus $\mathbf{g}$ the relative velocity of m_1 w.r.t. m_2. We can now inagine m_1 doubled in radius i.e with diameter 2σ while m_2 is reduced to its central point. Let $\delta\lambda$ be a patch on the surface of the extended sphere around m_1. Let c be the line from the centre of m_1 to the midde of the patch (i.e c is the

axis of a cone). Let θ be the angle between c and the directionof the motion of the centre of m_1 (i.e. the direction of $\mathbf{g}$). $(-\pi/2 \leq \theta \leq \pi/2$ as we are only interested n the hemsphere of m_1 facing m_2.) In a time δt the patch traces out a cylindrical volume $g\delta t$ (the length of the cylinder) $\times$ $\sigma^2 \cos\theta$ (the area of an end-face — a solid angle of 4π represents the whole surface area $4\pi\sigma^2$). If m_2 is in this volume there will be a collision between m_1 and m_2. Therefore the total number of collisions per unit area is

$$f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) \sigma^2 g \cos\theta \delta\lambda \delta\mathbf{v}_1 \delta\mathbf{v}_2 \delta t$$

where $g = |\mathbf{g}|$.

Radiation

When we describe the laminar flow of a river we can do so by specifyng a velocity vector $\mathbf{v}(p)$ at each point p. Alternatively and equivalently we can describe it as a flux by specifying a dua vector $\mathbf{v}^*(p)$ at each point p where $\mathbf{v}^*(d\sigma)$ is the volume of the fluid flowing through the oriented area $d\sigma$ in one second. Radiation is manifest in the flow of energy across surfaces but we cannot describe it as a simple vector field because, unlike in a smoothly flowing river, there is no definite direction of the flow at a point and we have to take the flow in all drections into account.

An area element vector $d\sigma$ is a vector at p perpendicular to a patch of area $d\sigma$ containing p and of magnitude the size of $d\sigma$. An element of solid angle vector, $d\mathbf{\Omega}$, is a vector at p havng the magnitude of a small patch on the surface of the unit spher, $d\Omega$, around the point of intersectiion of $d\mathbf{\Omega}$ (extended) and the surface. Thus $d\mathbf{\Omega}$ identifies a set of directions aroud a given direction.

What we have at each point is a bilinear map at each point p $R_p(\mathbf{u}, \mathbf{v})$ where $R(d\sigma, d\mathbf{\Omega})$ is the rate of energy flow through the surface $d\sigma$ from the directions $d\mathbf{\Omega}$

0.1.3 Loschmidt paradox- Kuhn p 46

This is about reversibiity in mechanics. A trajectory of a mechanical system is determined by the initial positions and momenta - $q_i(t_0), p_i(t_0)$ for $1 \leq i \leq n$. Suppose at $t_1 > t_0$ the positions and momenta are $q_i(t_1), p_i(t_1)$ for $1 \leq i \leq n$. Then the system will follow the same trajectory in reverse for initial conditions $q_i(t_1), -p_i(t_1)$ for $1 \leq i \leq n$. e.g. consider a particle thrown up to a height h when it has velocity 0. Starting at height h with velovity -0 it retraces its trajectory in the opposite direction. In general we can revere a trajectory by reversing the final momenta to become new initial momnts at the final position.
Losscmidt used this to argue that there could be no function of positions and momenta (i.e of the micro state of a system) that increases steadily as time passed because in the reverse direction such a function would decrease. A general issue is therefore to reconcile micro reversibility with macro level irreversibility

0.1.4 Planck p 93 - Complexions and States

Planck considers a continuous random variable f whose domain is the set of N atoms in the gas ,whose codomain is the phase space $\mathbf{R}^3 \times (\mathbf{R}^3)^*$ with $f(x_1, x_2, x_3, p_1, p_2, p_3)dx_1dx_2dx_3dp_1dp_2dp_3$ giving the proportion of the atoms in the volume element. $dx_1dx_2dx_3dp_1dp_2dp_3$ around $(x_1, x_2, x_3, p_1, p_2, p_3)$. Planck now posits that phase space is divided up into P elements of equal volume. Next Planck says that each molecule is equally likely to be in any volume element - this is plausible for the positions, less so for the momenta. Planck models the situation as N dice each dice having P equally likely sides. A **STATE** of the system is a distribution of the N dice among the P elements e.g. $\frac{1}{24}$ in the first volume element, $\frac{1}{35}$ in the second and so on i.e. a state is defned by a sequence of P non negatve numbers adding to 1. Each

throw of the N dice results in a state but many throws will correspond to the same state. Each throw specfies an assignment of the individual molecules to different phase volume elements and is called a **COMPLEXION**.
The Entropy is of a state is tied to its probability. Given that all comlexions are equally likely, it is the proportion of complexions that result in that state.

0.1.5 Blundell & Blundell Chapter 4

The zero'th lawshows the possibility of having thermometers but but offers no concpet of an underlying scale against which dfferent thermometers might be judged.

Micro and Macro States

The exact position, velocity or energy of an atom cannot be specifoed EXACTLY as thse are continuous quantities. So they must be discretiised into cells from 1 to M (for position and momentum) or quanta from 1ϵ to $P\epsilon$ for energy. Once this is done we can specify a microstate by sayng e.g. that Atom n is in Cell nn for each atom $1 \cdots N$. Possible microstates are limitd by facros such as the volume of the box and the total energy .
By contrast a macrostate is just a specification of the number of attoms in each cell or the number having a certan number of quanta of energy without caring about the iidentity of the individual atoms in a given cell or possessing a given number of quanta. Clearly a microstate specification dtermies a macrostate but many microstates will determine the same macrostate.
In regard to discretised energy the assumptions are:

1. The total number of microstates is a function $\Omega(E)$ of the total energy E.

2. The systems internal dynamics (collisions or whatever) cause a continuous changing of its microstate

3. All microstates are equally likely - i.e. the system speds equal amounts of time in each microstate. So at any given time the chance of the system being in a given microstate is simply $1/\Omega$.

4. The macrostate determines the value of the thermodynamic variables - pressure, temperature etc, of the system

5. An isolated system will eveolve so that it will spend most of its time in the most popular macrostate - where **popular** reflects the proportion of microstaes corrsponding to a macro state.

P34-35 consider a new systm created by allowogn two existing ones to interact, The first system has total energy E_1 and number of microstates $\Omega_1(E_1)$ and the second has total energy E_2 and number of microstates $\Omega_2(E_2)$. The combined system has totla energy $E_1 + E_2$ and $\Omega_1(E_1) \times \Omega_2(E_2)$ microstates. Once we have joind the systems together then E_1 and E_2 start to vary but $E_1 + E + 2$ stays constant. The calculation assumes thar E_1 and E_2 will take valus that maximise the number of microstates of the combined system.(Is thos obvious?) This what gves us

$$\frac{dln\Omega_1}{dE_1} = \frac{dln\Omega_2}{dE_2}$$

suggesting a definition of temperature.

0.1.6 Blundell & Blundell Chapter 4 p38-39

We want to formulate the probability distribution as a distribution p_X corresponding to a random variable X. Let S be the the set of all ways if distributing 400 quanta over 400 sites. All such ways are equally likely. Let X be a random variable whose codomain is the set M of all distict macrostates (i.e. distinct sequences $\{x_0 \cdots x_{40}$ where x_i is the number of sites with i quanta so that $\sum_i x_i = 400$). Then $X(s)$ is the macrostate m corresponding

to the microstate s. Then $p_X : M \to [0\ 1]$ is the probability of a macro state m is $p_X(m)$. Then p_X has a sharp peak and the macro state corresponding to this peak is called the Boltzmann distribution.
For the $10^3 \times 10^3$ lattice with 10^6 quanta the Boltzmann macrostate can be described bya graph plotting the log of the number of sites containing n quanta as n along the x axis goes from zero upwards. This shows that the vast majority of sites are empty in the Boltzmann distribution. This graph is of the form $logN = -kn + c$ where $c \approx 5.5$ and $k \approx 1$.
'The temperature corresponds to the number of quanta n play". If we had 800 quanta distributed over 400 sites we would obviously get a different most probable macro state.

0.1.7 Maxwell Theory of Heat pp 220, 223, 224

p220. This is important.
But by estimating the heating effect of a radiation that is entirely absorbed by the heated body, we obtain a true measure of the energy of the radiation. It is found that surfaces coated with lampblack absorb nearly the whole of the radiation falling on them.
p 223
Let the lampblack be B and the substance be S and R_B, A_B be the anount of radiatiion emiitted/absorbed by B and similarly for S Then

$$A_S = \sigma R_B \ \ and \ \ A_B = R_S \Rightarrow \frac{R_S}{R_B} = \sigma = \frac{A_S}{R_B}$$

as noted dby Maxwell as $\sigma < 1$ and R_B is the total radiation falling on S.
p 224
Again when a substance at a certain temperature absorbs certan kinds of radiation and transmits others, it emits at that temperature ONLY those kinds of radiation whch it absorbs.
I don't think this is quite true. Electrons can jump up more than one shell by

absorbing a photon of a certain frequency but then emit photons of different frequency depending on how it de-excites.

0.1.8 Blundell & Blundell Chapter 23 (Photons) p 248

The Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ comes from the Helmholtz free energy expression

$$F = U - TS \Rightarrow dF = dU - TdS - SdT = -p(V,T)dV - S(V,T)dT$$

As $\frac{\partial F}{\partial V} = -p$ and $\frac{\partial F}{\partial T} = -S$ we have $\frac{\partial^2 F}{\partial V \partial T} = -\frac{\partial p}{\partial T} = -\frac{\partial S}{\partial V}$.
From $dU = dQ - pdV$ (the increase in internal energy is the heat supplied less the work done by the gas's expansion) $= TdS - pdV$. Hence $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -p$
With $U = U(S,V)$ and $S = S(V,T)$ implicitly giving $U(V,T)$ we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

as in Equation 23.7.
Equation 23.11 follows as $\left(\frac{\partial u}{\partial V}\right)_T = 0$ and hence $u(V,T) = u(T)$ i.e. $\left(\frac{\partial u}{\partial T}\right)_V = \frac{du}{dT}$.

0.1.8.1 Sections 23.2 and 23.3

Section 23.3 is the argument that the energy density between wavelengths λ and $\lambda + d\lambda$ is $u_\lambda d\lambda$ where u_λ depends only on λ and the temperature$T$ of the cavity. The soot linesd and silver lined spherical cavities were just one example of a general phenomenon.
. Section 23.4 is Kirchoff's law. Equation 23.15 is an immediate consequence of Eq 23.5. In an equilibrium situation Kirchoff's law $e_\lambda/a_\lambda = cu_\lambda/4$ is then immediate.The ratio e_λ/a_λ thus depends only on λ and T as this is also true of u_λ.