
Statistical Physics

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Lent 1998

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Revision: 2.1

Date: 2004/08/23 07:30:03

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Introduction

These notes are based on the course “Statistical Physics” given by Dr. A. J. Macfarlane in Cambridge in the Lent Term 1998. These typeset notes are totally unconnected with Dr. Macfarlane. The recommended books for this course are discussed in the bibliography.

Other sets of notes are available for different courses. At the time of typing these courses were:

Probability	Discrete Mathematics
Analysis	Further Analysis
Methods	Quantum Mechanics
Fluid Dynamics 1	Quadratic Mathematics
Geometry	Dynamics of D.E.'s
Foundations of QM	Electrodynamics
Methods of Math. Phys	Fluid Dynamics 2
Waves (etc.)	Statistical Physics
General Relativity	Dynamical Systems
Combinatorics	Bifurcations in Nonlinear Convection

They may be downloaded from

<http://www.istari.ucam.org/maths/>.

Chapter 1

Quantum Statistical Mechanics

1.1 Introduction to Quantum Statistical Mechanics

Statistical mechanics deals with macroscopic systems of many particles. Consider an isolated system \mathcal{S} of gas in a vessel whose walls neither let heat in or out and is subject to no mechanical action. No matter how it is prepared, it is an experimental fact that \mathcal{S} reaches a steady state (a state of thermodynamic equilibrium) in which a set Σ of (rather few) thermodynamic variables are constant. Σ includes the pressure P , volume V , temperature T , total energy E and entropy S .

Any state of \mathcal{S} (before or after thermodynamic equilibrium is reached) contains particles with positions and momenta changing in time. We cannot possibly analyse this in detail — even if we knew the forces and initial conditions, and could solve the resulting system there is no hope that we could organise usefully the vast amount of data.

At best, we aim to treat the possible states of motion of \mathcal{S} by some averaging or statistical procedure that allows us to predict values of the variables in Σ that are constant in states of thermodynamic equilibrium of \mathcal{S} .

We use quantum mechanical ideas to approach the subject. Consider

- *microstates* of \mathcal{S} , the stationary quantum states $|i\rangle$.
- *macrostates*, which correspond to states of thermodynamic equilibrium.

The latter are not states in the quantum mechanical sense, but do involve the vast numbers of microstates.

The *ergodic hypothesis* (which is provable for some systems) is that \mathcal{S} passes in time through all its possible states compatible with its state of thermodynamic equilibrium. This allows us to replace time averages for a single system \mathcal{S} with averages at a fixed time over a suitable ensemble \mathcal{E} of systems, each identical to \mathcal{S} in its macroscopic properties. The most probable state of \mathcal{E} reveals which microstates of \mathcal{S} contribute to its macroscopic states of thermodynamic equilibrium and yield excellent approximations to the values of its thermodynamic variables.

Let E, N be the total energy and total number of particles of \mathcal{S} respectively. One meets three types of ensemble.

- *microcanonical* : each member of \mathcal{E} has the same values of E and N .

- *canonical* : each member of \mathcal{E} has N particles but E is not fixed, although the average total energy is time independent.
- *grand* : neither E nor N is fixed, although the averages are.

For the latter two, fluctuations about the average values are found to be very small and all three types of ensemble give the same thermal physics. This course studies mainly canonical ensembles. We will do systems with identical bosons/fermions via the grand ensemble for technical simplicity.

The fact that averaging procedures give reliable estimates of values of physical variables and apparently different procedures yield equivalent results is due to the effect of the very large number of particles involved. For instance, consider the probability p_m of obtaining $N/2 + m$ heads from N coin tosses.

$$p_m = 2^{-N} \binom{N}{\frac{N}{2} + m} \sim \sqrt{\frac{2}{\pi N}} e^{-\frac{2m^2}{N}},$$

using Stirling's formula¹ for $N \gg m \gg 0$. If $N = 10^{23}$ and $m = 10^{17}$ then the exponential term $e^{-10^{11}}$ is effectively zero.

1.2 Canonical ensemble

We study a system \mathcal{S} of N particles in a volume V with N and V fixed. The microstates of \mathcal{S} are the (complete orthogonal) set $|i\rangle$ with energy eigenvalues E_i . We assume the spectrum is discrete but with possible degeneracy.

We associate with \mathcal{S} a *canonical ensemble* \mathcal{E} . This is a very large number A of distinguishable replicas of \mathcal{S} , $\mathcal{S}_1, \dots, \mathcal{S}_A$. Suppose that in a possible state of \mathcal{E} there are a_i members of \mathcal{E} in the microstate $|i\rangle$. Then

$$\sum_i a_i = A \quad \text{and} \quad \sum_i a_i E_i = AE. \quad (1.1)$$

The average energy of the members of \mathcal{E} is thus the fixed value E .

Given a set $\{a_i\}$ (a *configuration* of \mathcal{E}) there are $W(\mathbf{a}) = \frac{A!}{\prod_i a_i!}$ ways of realising it.

Proof. We can distribute a_1 systems in the microstate $|1\rangle$ over \mathcal{E} in $\binom{A}{a_1}$ ways. Then we can distribute the a_2 states in $|2\rangle$ in $\binom{A-a_1}{a_2}$ ways (and so on). Thus

$$W(\mathbf{a}) = \binom{A}{a_1} \binom{A-a_1}{a_2} \dots = \frac{A!}{\prod_i a_i!}.$$

□

We assign equal *a priori* probability to each way of realising each possible configuration of \mathcal{E} and thus there is a probability proportional to $W(\mathbf{a})$ of realising the configuration $\{a_i\}$.

We will associate the state of thermodynamic equilibrium of \mathcal{S} (for the fixed values N, V, E) with the configuration of \mathcal{E} that is most probable in the presence of the constraints (1.1).

¹ $\log n! \sim n \log n - n + \frac{1}{2} \log 2\pi n$

To compute this suppose $A \gg 0$ such that $a_i \gg 0$ (negligible probability attaches to configurations where this fails). For large n , Stirling's formula allows $\log n! \sim n(\log n - 1)$ and so

$$\log W \sim A \log A - A - \sum_i a_i (\log a_i - 1) = A \log A - \sum_i a_i \log a_i.$$

We seek to maximise this subject to the constraints (1.1). We use two Lagrange multipliers α and β and solve

$$0 = \frac{\partial}{\partial a_j} \left(\log W - \alpha \sum_i a_i - \beta \sum_i a_i E_i \right)$$

and so $\log a_j + 1 + \alpha + \beta E_j = 0$. Thus

$$a_j = e^{-1-\alpha-\beta E_j}. \quad (1.2)$$

We eliminate α via $A = \sum_i a_i = e^{-1-\alpha} Z$, defining the canonical partition function

$$Z = \sum_i e^{-\beta E_i} \equiv \sum_{E_j} \Omega(E_j) e^{-\beta E_j}, \quad (1.3)$$

where $\Omega(E_j)$ is the degeneracy of the energy level E_j .

The fraction of members of \mathcal{E} in the microstate $|i\rangle$ in the macrostate of thermodynamic equilibrium is

$$\rho_i = \frac{a_i}{A} = \frac{1}{Z} e^{-\beta E_i}. \quad (1.4)$$

This is the *Boltzmann distribution*, and may be thought of as the probability of finding $|i\rangle$ in the state of thermodynamic equilibrium.

We define the average $\langle X \rangle$ of a physical variable X taking the value X_i in the state $|i\rangle$ by

$$\langle X \rangle = \sum_i \rho_i X_i. \quad (1.5)$$

For instance $\langle E \rangle = \frac{1}{A} \sum_i a_i E_i = E$ (reassuringly).

Z is very important. It leads directly from quantum mechanical data to calculation of the thermodynamic variables for \mathcal{S} in thermodynamic equilibrium. For instance,

$$E = -\frac{\partial \log Z}{\partial \beta}. \quad (1.6)$$

Here, holding V fixed corresponds to keeping all the E_i fixed.

For A large (as in all cases of interest) the most probable state is overwhelmingly so. It gives in effect the average over all possible states of the ensemble. The idea of associating average values with actual physical predictions depends on the possible variances being negligible.

We can calculate the variance in the energy in a similar way. Note that $E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$ and so

$$\frac{\partial E}{\partial \beta} = -\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 = -\langle E^2 \rangle + \langle E \rangle^2 = -(\Delta E)^2.$$

For typical large systems $E \propto N$, and as E depends smoothly on β we expect $\frac{\partial E}{\partial \beta} \propto N$ as well. Thus

$$\frac{|\Delta E|}{E} \propto \frac{\sqrt{N}}{N} = N^{-\frac{1}{2}},$$

which is very small for very large N .

1.3 Temperature

Given two systems \mathcal{S}_a and \mathcal{S}_b with fixed volumes V_a, V_b and numbers of particles N_a, N_b respectively we place them in contact to form a composite system \mathcal{S}_{ab} such that energy can pass from one to the other and a state of thermodynamic equilibrium is reached. We make a canonical ensemble \mathcal{E}_{ab} for \mathcal{S}_{ab} by distributing A replicas of \mathcal{S}_a and A replicas of \mathcal{S}_b independently across the A members of \mathcal{E}_{ab} so that each member of \mathcal{E}_{ab} has a component of type \mathcal{S}_{ab} .

Suppose that \mathcal{S}_a has microstates $|i\rangle$ of energy E_{ai} , \mathcal{S}_b has microstates $|\sigma\rangle$ of energy $E_{b\sigma}$ and \mathcal{S}_{ab} has microstates $|i, \sigma\rangle$ of energy $E_{ai} + E_{b\sigma}$.²

Suppose the $|i\rangle$ occurs a_i times, $|\sigma\rangle$ occurs b_σ times and $|i, \sigma\rangle$ occurs $c_{i\sigma}$ times in \mathcal{E}_{ab} . Then we have

$$\sum_i a_i = A \quad \sum_\sigma b_\sigma = A \quad (1.7)$$

$$a_i = \sum_\sigma c_{i\sigma} \quad b_\sigma = \sum_i c_{i\sigma} \quad \sum_{i\sigma} c_{i\sigma} = A \quad (1.8)$$

We demand that the average energy or \mathcal{E}_{ab} be fixed at

$$AE = \sum_i a_i E_{ai} + \sum_\sigma b_\sigma E_{b\sigma} \quad (1.9)$$

$$AE = \sum_{i\sigma} c_{i\sigma} (E_{ai} + E_{b\sigma}). \quad (1.10)$$

Now the configuration $\{c_{i\sigma}\}$ arises in

$$W(\mathbf{c}) \propto \frac{A!}{\prod_{i\sigma} c_{i\sigma}!} \quad (1.11)$$

ways and the configuration $\{a_i\}\{b_\sigma\}$ arises in

$$W(\mathbf{a})W(\mathbf{b}) \propto \frac{A!}{\prod_i a_i!} \frac{A!}{\prod_\sigma b_\sigma!} \quad (1.12)$$

ways. We can calculate the most probable distribution of $\{c_{i\sigma}\}$ by maximising (1.11) subject to (1.8) and (1.10). We get

²If the interaction of particles of \mathcal{S}_a with those of \mathcal{S}_b is negligible, except insofar as necessary to allow a state of thermal equilibrium to be reached.

$$c_{i\sigma} = e^{-1-\alpha_{ab}-\beta(E_{ai}+E_{b\sigma})} \quad \rho_{i\sigma} = \frac{c_{i\sigma}}{A}.$$

We can also maximise (1.12) subject to (1.7) and (1.9) to get

$$\begin{aligned} a_i &= e^{-1-\alpha_a-\beta E_{ai}} & \rho_i &= \frac{a_i}{A} \\ b_\sigma &= e^{-1-\alpha_b-\beta E_{b\sigma}} & \rho_\sigma &= \frac{b_\sigma}{A}. \end{aligned}$$

Defining

$$Z_{ab}(\beta) = \sum_{i\sigma} e^{-\beta(E_{ai}+E_{b\sigma})} \quad Z_a(\beta) = \sum_i e^{-\beta E_{ai}} \quad Z_b(\beta) = \sum_\sigma e^{-\beta E_{b\sigma}}$$

we see that $Z_{ab}(\beta) = Z_a(\beta)Z_b(\beta)$ and $\rho_{i\sigma} = \rho_i\rho_\sigma$. A common value for β characterises the state of thermal equilibrium of \mathcal{S}_{ab} and it is natural to assume that β is some function of temperature T and that the average energy (*the energy*) of a system is a function of N , V and T .

We define T by $\beta = \frac{1}{kT}$ where k is a constant.

As this argument applies to any two systems, k should be a universal constant (Boltzmann's constant) the same for all systems when a universal definition of T is used. We will define T for a standard system (a thermometer) and for other systems by putting them into a state of thermal equilibrium with our standard system.

Recall the ideal gas law, $PV = NkT$ for a sample of N molecules.³ k is the same because equal volumes of all gases at fixed temperature and pressure are observed to have the same number of molecules. T is in degrees Kelvin.

1.4 Towards thermodynamic variables

Recall that in quantum mechanics, spinless particles in a cube of side L have energies $E_{\mathbf{n}} = \frac{\hbar^2}{2mL^2} |\mathbf{n}|^2$, where $\mathbf{n} \in \mathbb{N}^3$. Note that $E \propto V^{-\frac{2}{3}}$ and we generalise this to $E_i = E_i(V)$. Consider \mathcal{S}_{gas} in thermodynamic equilibrium in a container of volume V and change V by a small amount by slowly moving one of its walls.

The E_i will change according to $E_i \mapsto E_i + \frac{\partial E_i}{\partial V} \delta V$ and changes in which the ρ_i do not change will be examined first.

The change in energy is supplied by the work done on \mathcal{S} by a piston applied to the right hand wall. For slow motion the system passes through successive positions of thermal equilibrium and then the applied force just balances the pressure force PA .

³This applies to all gases at sufficiently low density.

Thus the work done to the system is $-PA\delta l = -P\delta V$. $\delta E = \delta W = -P\delta V$. Now $E = \sum_i \rho_i E_i$ and so

$$P = - \sum_i \rho_i \frac{\partial E_i}{\partial V} = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z. \quad (1.13)$$

Consider next changes in which the ρ_i are allowed to vary. Then $\delta E = -P\delta V + \sum_i E_i \delta \rho_i$, and note that $\sum_i \delta \rho_i = 0$.

Define the entropy

$$\begin{aligned} S &= \frac{k}{A} \log W_{\max} \quad \text{that is, } W \text{ at thermal equilibrium} \\ &= \frac{k}{A} \left(A \log A - \sum_i a_i \log a_i \right) \\ &= \frac{k}{A} \left(A \log A - \sum_i a_i \log \rho_i - \log A \sum_i a_i \right) \\ &= -k \sum_i \rho_i \log \rho_i \quad \text{at thermal equilibrium.} \end{aligned} \quad (1.14)$$

We see that

$$\begin{aligned} \delta S &= -k \sum \delta \rho_i \left(\log \rho_i + \rho_i \frac{1}{\rho_i} \log \rho_i \right) \\ &= -k \sum \delta \rho_i (-\beta E_i - \log Z + 1) \\ &= \frac{1}{T} \sum_i E_i \delta \rho_i \end{aligned}$$

and thus $\sum_i E_i \delta \rho_i = T \delta S$. We have defined S such that

$$\begin{aligned} \delta E &= T \delta S - P \delta V \text{ or in terms of exact differentials,} \\ dE &= T dS - P dV. \end{aligned} \quad (1.15)$$

We might regard this as arising from the comparison of ensembles with infinitesimally different states of thermal equilibrium. (1.15) states the *First Law of Thermodynamics*⁴, written in the form

$$dE = \delta Q + \delta W, \quad (1.16)$$

where δQ is the heat supplied to S and δW is the work done on S .

(1.15) also shows that $T = \frac{\partial E}{\partial S}$ and $P = -\frac{\partial E}{\partial V}$.

For a gas of spinless particles, $E = \sum_i E_i \rho_i \propto V^{-\frac{2}{3}}$ and so $P = \frac{2}{3} \frac{E}{V}$, giving $PV = \frac{2}{3} E$. Combined with the result for a perfect gas, $E = \frac{3}{2} NkT$ (see later), we have Boyle's law $PV = NkT$.

We want to be able to calculate S from the partition function. Now, at thermal equilibrium,

⁴You can't win...

$$\begin{aligned}
S &= -k \sum_i \rho_i \log \rho_i \\
&= -k \sum_i \rho_i (-\beta E_i - \log Z) \\
&= \frac{1}{T} E + k \log Z.
\end{aligned}$$

Define the *free energy* $F = E - TS$, then

$$F = -\frac{1}{\beta} \log Z. \quad (1.17)$$

Also,

$$S = -\frac{1}{T} \frac{\partial \log Z}{\partial \beta} + k \log Z = \frac{\partial}{\partial T} (kT \log Z) = -\frac{\partial F}{\partial T}. \quad (1.18)$$

We have a very tangible definition of S , as proportional to $\log W_{\max}$, where W_{\max} is the number of microstates of S contributing to the state of thermal equilibrium.

Given the partition function (1.3), we can calculate the thermodynamic variables in a state of thermal equilibrium, P (by (1.13)), E (by (1.6)), F (by (1.17)) and S (by (1.18)).

1.5 Towards applications

1.5.1 N particle partition function

Consider a composite system with Hamiltonian $H = H_1 + H_2$ and H_1 and H_2 independent (they commute). Let $H_1|a\rangle = E_{1a}|a\rangle$ and $H_2|\alpha\rangle = E_{2\alpha}|\alpha\rangle$. Then as H_1 and H_2 commute, $H|a, \alpha\rangle = E_{a\alpha}|a, \alpha\rangle$, where $E_{a\alpha} = E_{1a} + E_{2\alpha}$. Then the 2 particle partition function is

$$Z = \sum_{a, \alpha} e^{-\beta E_{a\alpha}} = \sum_a e^{-\beta E_{1a}} \sum_{\alpha} e^{-\beta E_{2\alpha}} = Z_1 Z_2.$$

Let $Z \equiv Z_N$ describe the sum over states of a gas of N very weakly interacting particles. If these are supposed independent (distinguishable) then $Z = z^N$, where z is the ‘‘one particle partition function’’. This allows easy calculations, but fails for systems of identical (indistinguishable) bosons or fermions. For the latter it seems best to use grand ensemble methods.

Later we will consider a gas of diatomic molecules, $H = H_T + H_{\text{rot}} + H_{\text{vib}}$, where H_T describes the centre of mass motion, H_{rot} describes rotation about the centre of mass and H_{vib} describes vibration along the axis. We see that the one particle partition function is $z = z_T z_{\text{rot}} z_{\text{vib}}$.

1.5.2 Extensive and intensive variables

Extensive variables are proportional to the amount of matter in a system at fixed temperature, whereas intensive variables are independent of the amount of matter.

In general, N , V , S and E are extensive and T and P are intensive.

Think initially of a system made up of two independent subsystems. Then $V = V_1 + V_2$. In a state of thermal equilibrium the systems have the same β (and hence same T), and so T is intensive. In a state of equilibrium there is mechanical equilibrium and so the systems have the same pressure, and so P is intensive.

As $Z = Z_1 Z_2$ we see that $E = E_1 + E_2$, $S = S_1 + S_2$ and so on. A logical extension of this argument gives that V , E and S are proportional to N and so extensive. This can fail if volume energies do not swamp surface energies or if intermolecular forces are neither weak nor short range.

1.5.3 Density of states

Consider a spinless particle in a box of side L . Instead of using solutions ψ of the Schrödinger equation such that $\psi = 0$ on the walls we use periodic boundary conditions, $\psi(\mathbf{x} + L\mathbf{i}) = \psi(\mathbf{x})$ (and so on). Thus we can use $\psi_{\mathbf{k}} \propto e^{i\mathbf{k}\cdot\mathbf{x}}$ with $\epsilon = \frac{\hbar^2 k^2}{2m}$.

The periodicity gives that $\frac{L\mathbf{k}}{2\pi} \in \mathbb{Z}^3$. There is one such state per unit volume in n -space and in the continuum limit, there are d^3n states with \mathbf{n} in the range $\mathbf{n} \rightarrow \mathbf{n} + d\mathbf{n}$. There are thus d^3n states with \mathbf{k} in the range $\mathbf{k} \rightarrow \mathbf{k} + d\mathbf{k}$ and hence $\left(\frac{L}{2\pi}\right)^3 d^3k$ states with \mathbf{k} in the range $\mathbf{k} \rightarrow \mathbf{k} + d\mathbf{k}$.

We see that

$$\begin{aligned} \sum_i &\rightarrow \int \left(\frac{L}{2\pi}\right)^3 d^3k & (1.19) \\ &= \frac{V}{(2\pi)^3} \int 4\pi k^2 dk \\ &= \frac{V}{(2\pi)^3} 4\pi \int \left(\frac{2m\epsilon}{\hbar^2}\right)^{\frac{1}{2}} \frac{2m d\epsilon}{2\hbar^2} \\ &= 2\pi V \left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \int \epsilon^{\frac{1}{2}} d\epsilon & (1.20) \\ &= \int d\epsilon g(\epsilon). \end{aligned}$$

We insert a factor $g_S = (2S + 1)$ to cope with massive particles of spin S , and

$$g(\epsilon) = g_S 2\pi V \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}$$

gives the density of states. We use (1.20) in isotropic contexts, but (1.19) is needed in kinetic theory.

In two dimensions we consider a square of side L and $A = L^2$ enters in the rôle of V . We find that $g(\epsilon) = \left(\frac{2m}{\hbar^2}\right) g_S 2\pi A$ is independent of ϵ .

For relativistic particles of rest mass m we have $\epsilon = (m^2 c^4 + \hbar k^2 c^2)^{\frac{1}{2}}$ and use (1.19) to get

$$\int d^3k = \int 4\pi k^2 dk = \frac{4\pi}{(\hbar c)^3} \int_{mc^2}^{\infty} \epsilon d\epsilon (\epsilon^2 - m^2 c^4)^{\frac{1}{2}}. \quad (1.21)$$

We also supply a factor $g_S = 2S + 1$ for a particle of spin S with nonzero rest mass. For photons, $m = 0$, $g_S = 2$ and so

$$\sum_i \rightarrow 2 \frac{V}{(2\pi)^3} \left(\frac{4\pi}{\hbar c} \right)^3 \int_0^\infty \epsilon^2 d\epsilon = \frac{8\pi V}{c^3} \int_0^\infty \nu^2 d\nu. \quad (1.22)$$

1.5.4 Gas of spinless particles

Consider N spinless particles in a cube of side length $L = V^{1/3}$. Then the single particle partition function

$$z = \sum_i e^{-\beta\epsilon_i} \rightarrow \int_0^\infty d\epsilon g(\epsilon) e^{-\beta\epsilon},$$

where $g(\epsilon) = DV\epsilon^{1/2}$ and $D = 4\pi \left(\frac{2m}{\hbar^2} \right)^{3/2}$. Setting $y = \beta\epsilon$ we get

$$z = DV (kT)^{3/2} \int_0^\infty dy y^{1/2} e^{-y} = V \left(\frac{2m\pi kT}{h^2} \right)^{3/2}. \quad (1.23)$$

Now $Z = z^N$ and so $\log Z = N \log z$. Thus

$$E = -N \frac{\partial}{\partial \beta} \left(-\frac{3}{2} \log \beta \right) = \frac{3}{2} NkT.$$

This is *the* classical result: there is an energy $\frac{1}{2}kT$ associated with each degree of freedom of each particle. Combining with $PV = \frac{2}{3}E$ we get $PV = NkT$.

1.5.5 Entropy and the Gibbs paradox

Using $Z = z^N$, (1.23) and (1.18) we have

$$S = Nk \log V + \frac{3}{2} Nk \log \left(\frac{2m\pi kT}{h^2} \right) + \frac{3}{2} Nk,$$

which is not extensive, as $V \propto N$. This is Gibbs' paradox.

If instead we use $Z = \frac{z^N}{N!}$, (1.23), (1.18) and Stirling's formula we have

$$S = Nk \log \frac{V}{N} + \frac{3}{2} Nk \log \left(\frac{2m\pi kT}{h^2} \right) + \frac{3}{2} Nk$$

and we see that S is extensive.

Often an additive constant in S does not matter and (1.23) gives all thermodynamics otherwise correctly. It reflects a normal classical view of how to treat indistinguishable particles. Taking $Z = \frac{z^N}{N!}$ cures this but has *no* foundation in classical statistical physics.

1.6 Harmonic oscillator model

Model a crystal by placing one atom at each point of some regular lattice with N sites. In 1D, simplify by taking a simple harmonic oscillator of frequency ω_r instead of the r^{th} atom.

Now $Z_N = \prod_r z(\omega_r)$, and using $E_n = \hbar\omega(n + \frac{1}{2})$ for the simple harmonic oscillator with frequency ω we get

$$z(\omega) = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}}.$$

Even if $\omega_r = \omega$ for all r , the “atoms” are distinguishable as there exists one at each lattice site. This is a one dimensional version of the *Einstein solid*. We find that

$$\frac{E}{N} = -\frac{\partial \log z}{\partial \beta} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

If $\hbar\omega \ll kT$ this gives the classical result $\frac{E}{N} - \frac{1}{2}\hbar\omega = kT$, with energy $\frac{1}{2}kT$ per degree of freedom per “atom”.

If $\hbar\omega \gg kT$ then $\beta\hbar\omega \gg 1$ and $\frac{E}{N} - \frac{1}{2}\hbar\omega \approx \hbar\omega e^{-\beta\hbar\omega}$, which tends to zero as $T \rightarrow 0$.

Quantum statistical mechanics “knows” when to count the full classical $\frac{1}{2}kT$ value per degree of freedom: do it only when T is large on some scale set by the problem. In this case the critical temperature $T_c = \frac{\hbar\omega}{k}$.

Chapter 2

Thermodynamics

2.1 Introduction

Consider a volume V of gas with a fixed number N of particles. The state of thermal equilibrium of this gas is characterised by T and V .

Our work with quantum statistical mechanics has produced some concepts naturally:

- E : the total energy of the system, which arose as the average energy and has negligible fluctuations.
- S : the entropy. This has a clear significance as the number of microstates contributing to the macrostate of thermal equilibrium.
- equations of state: for instance $PV = NkT$.
- $dE = TdS - PdV$, which is true for any thermodynamic change between two infinitesimally close states of thermodynamic equilibrium.

All thermodynamic variables for the sample of gas we are talking about can be regarded as a function of two suitably chosen independent variables. In the case of the energy, E arises as $E(S, V)$.

We also found that $dE = \delta Q + \delta W$, where δQ is the heat supplied *to* the system and δW is the work done *on* the system.

For finite changes from the initial to the final state conservation of energy gives $\Delta E = \Delta Q + \Delta W$. This is the first law of thermodynamics, equivalent to the conservation of energy.

Suppose we change from a state with $E_1(S_1, V_2)$ to $E_2(S_2, V_2)$. In general, we expect

$$\Delta W \geq - \int_{V_1}^{V_2} PdV$$

because of wasted effort (against friction or in producing convection or turbulence). This gives us

$$\Delta Q \leq \int_{S_1}^{S_2} TdS.$$

These inequalities hold as equalities for *reversible* changes, that is changes which are *quasi-static* and non-dissipative.

Quasi-static changes are changes which are done so slowly as to pass through states arbitrarily close to a state of thermodynamic equilibrium, so that all thermodynamic variables are well-defined throughout the change.

Some (obvious) irreversible processes are fast piston movement, free expansion of a gas into a vacuum and the mixing of samples of different gases.

In induced/allowed changes in real life with $\delta Q = 0$, $\delta S > 0$ and so the entropy increases.

2.2 Applications of $dE = TdS - PdV$

2.2.1 Integrability conditions

The internal energy E is seen as $E(S, V)$ within

$$dE = TdS - PdV = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

Thus $T = \left(\frac{\partial E}{\partial S}\right)_V$ and $P = -\left(\frac{\partial E}{\partial V}\right)_S$. dE is an exact differential, so $\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S}$ and

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

This is a *Maxwell relation*.

The free energy $F = E - TS$ is a natural function of T and V , as

$$dF = dE - TdS - SdT = -SdT - PdV.$$

Thus $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $P = -\left(\frac{\partial F}{\partial V}\right)_T$. This gives the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

$H = E + PV$ defines the *enthalpy* $H(S, P)$ and $G = E - TS + PV$ defines the Gibbs function $G(T, P)$.

These give four Maxwell relations, but they are interdependent.

E , F , H and G are all extensive. If (exceptionally) $G = 0$ (true for a gas of photons) then $G = N\mu$ and so the chemical potential μ can vanish for arbitrary finite N .

We need some rules for shunting partial derivatives around. Consider $z = z(x, y)$. Then

$$\delta z = \left(\frac{\partial z}{\partial x}\right)_y \delta x + \left(\frac{\partial z}{\partial y}\right)_x \delta y \quad \text{and hence}$$

$$1 = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and}$$

$$0 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x.$$

This can be rewritten in a slightly different form:

$$\begin{aligned} \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y &= 1 \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y &= -1. \end{aligned} \quad (2.1)$$

When we wrote down E , F , H and G we wrote them in terms of the mathematically natural independent variables in each case. In practice, we would like E as a function of T and V . Recall $TdS = dE + PdV$, so that

$$\begin{aligned} TdS &= \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV \quad \text{and so} \\ T \left(\frac{\partial S}{\partial T}\right)_V &= \left(\frac{\partial E}{\partial T}\right)_V \quad \text{and} \\ T \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial E}{\partial V}\right)_T + P. \end{aligned}$$

Also, we know that $\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T}$ and so

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P.$$

For a perfect gas, $PV = NkT$ and so $\left(\frac{\partial E}{\partial V}\right)_T = 0$. Thus E is a function of T only.

Given the laws of thermodynamics we need two inputs from experiment to specify all thermodynamic variables completely. For instance, for a perfect gas we need the equation of state and $E = CT$.

2.2.2 Specific heats

An amount of gas with N_A (Avogadro's number) of molecules is called a *mole*. The ideal gas law tells us that at fixed temperature and pressure, a mole of *any* ideal gas occupies the same volume. Written in terms of moles, the ideal gas law for n moles of gas is

$$PV = nN_A kT = nRT. \quad (2.2)$$

R is called the *gas constant* and is the same for all ideal gases. In fact, all gases are essentially ideal at sufficiently low density.

For a sample of 1 mole of ideal gas we define the *specific heat* (or heat capacity per mole) using $\delta Q = TdS$ under suitable conditions.

Define $C_V = T \left(\frac{\partial S}{\partial T}\right)_V$, the *specific heat at constant volume* and $C_P = T \left(\frac{\partial S}{\partial T}\right)_P$, the *specific heat at constant pressure*. Now

$$TdS = dE + PdV = dH - VdP$$

and so

$$\begin{aligned} C_V &= T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \\ C_P &= \left(\frac{\partial H}{\partial T}\right)_P. \end{aligned} \quad (2.3)$$

For one mole of ideal gas we know that $E = CT$ and so $C = C_V$. To find C_P we need to use P and T as the independent variables.

Now

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right). \end{aligned}$$

Thus $\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$ and so

$$C_P = C_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = C_V + T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \quad (2.4)$$

This allows the calculation of $C_P - C_V$ from the equation of state: for an ideal gas $C_P - C_V = R$. Define the ratio of specific heats $\gamma = \frac{C_P}{C_V}$. Note that $\gamma = \frac{C_V + R}{C_V} > 1$ for an ideal gas.

Statistical mechanics gives $C_V = \frac{3}{2}R, \frac{5}{2}R, \dots$ (for monatomic, diatomic (etc) gases). Thus $\gamma = \frac{5}{3}, \frac{7}{5}, \dots$

2.2.3 Adiabatic changes

These are (defined as) changes which are reversible and satisfy $\delta Q = 0$. We refer to n moles of ideal gas using $E = nC_V T$ and $PV = nRT$. Now

$$\begin{aligned} 0 &= RdE + RPdV \\ &= RnC_V dT + RPdV \\ &= C_V (PdV + VdP) + RPdV \\ &= C_P PdV + C_V VdP. \end{aligned}$$

Thus $0 = \gamma \frac{dV}{V} + \frac{dP}{P}$ and so PV^γ is constant on adiabatics.

Note that adiabatics PV^γ constant are steeper than isothermals PV constant.

2.2.4 Entropy of n moles of ideal gas

We start (as usual) from

$$\begin{aligned} TdS &= dE + PdV \\ &= nC_V dT + nRT \frac{dV}{V}. \end{aligned}$$

Thus $dS = nC_V \frac{dT}{T} + nR \frac{dV}{V}$,

and so $S = nC_V \log T + nR \log V + c_1$. Thermodynamics cannot determine the constant c_1 , and does not care that S is not explicitly extensive. $S = nC_V \log PV^\gamma + c'$ and so (as expected), S is constant on adiabatics (isentropics).

2.2.5 van der Waal's equation

We get a better agreement with experiment by replacing the perfect gas law with

$$\left(P + \frac{n^2 A}{V^2}\right)(V - nB) = nRT, \quad (2.5)$$

where A , B and R are strictly positive constants.

- Molecules are not treated as point particles, and as $P \rightarrow \infty$ at constant T , $V \rightarrow nB$, which is the residual volume of all the molecules.
- $P + \frac{n^2 A}{V^2}$ reduces the real gas pressure by an amount $\frac{n^2 A}{V^2}$, due to intermolecular attractive forces. If these are short range then the smaller V is the more important these become.

2.2.6 The Joule effect

Consider the apparatus shown, with adiabatic walls and containing n moles of gas at volume V_1 , pressure P_1 and temperature T_1 . Pull back the partition and allow the gas to expand (irreversibly) into the total volume V_2 , and then to reach a state of thermal equilibrium specified by P_2 , V_2 and T_2 .

As $\delta Q = 0$ (adiabatic) and $\delta W = 0$ (no work is done), $dE = 0$ and so for a perfect gas

$$T_2 = T_1 \quad \text{and} \quad S_2 - S_1 = nR \log \frac{V_2}{V_1} > 0 \text{ for } V_2 > V_1.$$

For a van der Waal's gas we still have $dE = 0$ (which is true in general) and so E stays constant. Now

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_E &= -\frac{\left(\frac{\partial E}{\partial V}\right)_T}{\left(\frac{\partial E}{\partial T}\right)_V} \\ &= \frac{P - T\left(\frac{\partial P}{\partial T}\right)_V}{nC_V} \\ &= -\frac{n^2 A}{V^2} \frac{1}{nC_V} \quad \text{for van der Waal's gas} \\ &< 0. \end{aligned}$$

We can show that C_V is independent of V for a van der Waal's gas and we suppose that C_V is also approximately independent of T . We can now integrate this equation to get

$$T_2 - T_1 = \frac{nA}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1}\right) < 0.$$

T decreases because some of the molecular kinetic energy is lost in the expansion against attractive intermolecular forces.

2.3 Some thermodynamics

Suppose a sample \mathcal{S} of n moles of perfect gas is put in thermal contact with a heat bath \mathcal{B} and compressed reversibly from volume V_1 to volume V_2 . If the gas is perfect then $E = E(T) = nC_V T$ and so E stays the same. Now

$$\Delta Q + \Delta W = 0 \quad \Rightarrow \quad \Delta Q = -\Delta W = \int_{V_1}^{V_2} P dV = nRT \log \frac{V_2}{V_1}.$$

Thus $\Delta W > 0$ for compression ($V_2 < V_1$) and $\Delta Q < 0$. Heat is given out to \mathcal{B} by \mathcal{S} . Now $\Delta S = nR \log \frac{V_2}{V_1}$ and so the entropy of \mathcal{S} decreases. However, because the isolated universe of \mathcal{S} and \mathcal{B} has $\Delta S = 0$ the entropy of \mathcal{B} must increase.

2.3.1 The second law

(*Kelvin*) No process can continuously (by going round a cycle) extract heat from a heat bath and perform an equal amount of work.

(*Clausius*) No process can continuously transfer heat from a colder to a hotter body.¹

Take a sample \mathcal{S} of perfect gas around a closed Carnot cycle by means of adiabatics and isothermals ($T_2 > T_1$). On AB the heat bath at T_2 supplies heat $\Delta Q_2 > 0$ to \mathcal{S} at temperature T_2 . On CD the heat bath at T_1 supplies heat $\Delta Q_1 < 0$ to \mathcal{S} at temperature T_1 .

$E = E(T)$ is unchanged over one complete cycle so that the work done in a cycle by \mathcal{S} is $-W = \Delta Q_1 + \Delta Q_2$ by the first law (as $\delta Q = 0$ on adiabatics).

This agrees with the Kelvin statement of the second law, $(-\Delta Q_1) > 0$ of heat is wasted at the low temperature heat bath. The efficiency η is defined

$$\eta = \frac{-W}{\Delta Q_2} = 1 + \frac{\Delta Q_1}{\Delta Q_2} < 1.$$

On adiabatics $TV^{\gamma-1}$ is constant and so

$$T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1} \quad \text{and} \quad T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1}.$$

Thus $\frac{V_A}{V_B} = \frac{V_D}{V_C}$. We know that

$$\Delta Q_2 = nRT_2 \log \frac{V_B}{V_A} > 0 \quad \text{and} \quad \Delta Q_1 = nRT_1 \log \frac{V_D}{V_C} = -nRT_1 \log \frac{V_B}{V_A}.$$

Thus $\eta = \frac{T_2 - T_1}{T_2}$, and clearly $0 < \eta < 1$. This can be generalised to other cycles.

¹You can't break even either... (see footnote on page 6)

2.4 Heat flow

Let \mathcal{S}_1 be a sample of n_1 moles of ideal gas at temperature T_1 in a fixed volume V_1 . Then $E_1(T_1) = n_1 C_{V_1} T_1 = x_1 T_1$. Similarly for \mathcal{S}_2 . Put \mathcal{S}_1 and \mathcal{S}_2 in thermal contact allowing no change in $V_1 + V_2$. Suppose the state of thermal equilibrium is reached at a temperature T . Then (by conservation of energy),

$$x_1(T_1 - T) + x_2(T_2 - T) = 0$$

and we can solve for T . As for the entropy, $\Delta S_{1,2} = x_{1,2} \log \frac{T}{T_{1,2}}$ and $\Delta S_1 + \Delta S_2 \geq 0$.

Chapter 3

Grand ensemble methods

3.1 The formalism

Our approach is a direct extension of the approach we adopted earlier for the canonical ensemble. Given a system \mathcal{S} of fixed volume we construct a grand (canonical) ensemble \mathcal{G} with a large number A of distinguishable replicas of \mathcal{S} in microstates $|i\rangle$ of \mathcal{S} with N_i particles and energies E_i . Suppose that a_i members of \mathcal{G} are in the microstate $|i\rangle$ so that

$$\sum_i a_i = A \quad \sum_i a_i E_i = AE \quad \sum_i a_i N_i = AN.$$

We have thus fixed the average energy and number of particles of members of the ensemble. Each configuration $\{a_i\}$ of \mathcal{G} defines a state of the ensemble and we assign to each configuration equal *a priori* probability. We associate the state of thermodynamic equilibrium of \mathcal{S} with the most probable configuration of \mathcal{G} in the presence of our constraints. We find this by maximising the same $\log W$ as before to get

$$0 = \frac{\partial}{\partial a_i} \left(\log W - \alpha \sum_i a_i - \beta \sum_i a_i E_i - \gamma \sum_i a_i N_i \right).$$

This gives us that

$$a_i = e^{-(1+\alpha)} e^{-\beta(E_i - \mu N_i)},$$

where we have defined the *chemical potential* μ by $\beta\mu = -\gamma$. We now define the grand partition function

$$\mathcal{Z} = \sum_i e^{-\beta(E_i - \mu N_i)}. \quad (3.1)$$

The fraction of members of \mathcal{G} in the microstate $|i\rangle$ is

$$\rho_i = \frac{a_i}{A} = \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}}.$$

The grand ensemble average is

$$\bar{O} = \sum_i \rho_i O_i$$

and $\bar{E} = E$ and $\bar{N} = N$ (which is, on the whole, a good thing). As before we can use \mathcal{Z} to calculate thermodynamic variables:

$$N = \frac{1}{\beta} \left(\frac{\partial \log \mathcal{Z}}{\partial \mu} \right)_{\beta, V}, \quad (3.2)$$

$$E - \mu N = - \left(\frac{\partial \log \mathcal{Z}}{\partial \beta} \right)_{\mu, V}. \quad (3.3)$$

As before, from consideration of changes at constant ρ_i we find that $\delta E = -P\delta V$ and

$$P = - \sum_i \rho_i \frac{\partial E_i}{\partial V} = \frac{1}{\beta} \left(\frac{\partial \log \mathcal{Z}}{\partial V} \right)_{\beta, \mu}. \quad (3.4)$$

More general changes in which $\delta \rho_i \neq 0$ obey

$$\sum_i \delta \rho_i = 0 \quad \sum_i N_i \delta \rho_i = \delta N \quad \delta E = -P\delta V + \sum_i E_i \delta \rho_i.$$

Defining the entropy

$$S = -\frac{k}{A} \log W_{\max} = -k \sum_i \rho_i \log \rho_i$$

gives that

$$\begin{aligned} \delta S &= -k \sum_i \delta \rho_i \log \rho_i - \sum_i \rho_i \frac{1}{\rho_i} \delta \rho_i \\ &= -k \sum_i \delta \rho_i (-\beta(E_i - \mu N_i) - \log \mathcal{Z}). \end{aligned}$$

This gives the fundamental thermodynamic relation

$$T\delta S = \delta E + P\delta V - \mu\delta N, \quad (3.5)$$

yielding the first law $dE = \delta Q + \delta W_{\text{mech}} + \delta W_{\text{chem}}$, where $\delta W_{\text{chem}} = \mu\delta N$ is the work done in adding δN particles to the system \mathcal{S} . The chemical potential is therefore given by

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S, V}. \quad (3.6)$$

Returning to the entropy S we see that

$$S = k\beta(E - \mu N) + k \log \mathcal{Z} \quad (3.7)$$

which can be put in the same form as (1.18), namely

$$S = \left(\frac{\partial kT \log \mathcal{Z}}{\partial T} \right)_{\mu, V}. \quad (3.8)$$

A similar argument to that used to define temperature in 1.3 gives that two systems placed in thermal and “diffusive” contact will reach a thermodynamic equilibrium characterised by common values of $\beta = \frac{1}{kT}$ and μ .

We keep the idea that at fixed N_A, N_B energy flows from the system with the higher temperature to that with the lower temperature until thermodynamic equilibrium is reached. We add that if the contact allows the diffusion of particles then in the state of thermodynamic equilibrium with constant μ there is (on average) no diffusion.

We return to the first law, $dE = TdS - PdV + \mu dN$. We can view E as a function of S, V and N , and when (as for many large systems), E, S and V are extensive we get

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

and so

$$\begin{aligned} E &= S \left(\frac{\partial E}{\partial S} \right)_{V,N} + V \left(\frac{\partial E}{\partial V} \right)_{S,N} + N \left(\frac{\partial E}{\partial N} \right)_{S,V} \\ &= TS - PV + \mu N. \end{aligned}$$

We define the *grand potential* Ω for a state of thermodynamic equilibrium by

$$\begin{aligned} \Omega &= E - TS - \mu N \\ &= E - \mu N - (E - \mu N + kT \log \mathcal{Z}) \\ &= -kT \log \mathcal{Z}. \end{aligned}$$

Thus $\mathcal{Z} = e^{-\beta\Omega}$. Now Ω also equals $-PV$ and so

$$PV = kT \log \mathcal{Z} \quad (3.9)$$

allows the calculation of the equation of state from the grand partition function.

The state of thermodynamic equilibrium corresponds to the most probable state in \mathcal{G} . Some thermodynamic variables arise from averages over microstates weighted by the probability of finding them in the state of thermodynamic equilibrium. The averages are effectively averages over all possible states of the ensemble because the macrostate of thermodynamic equilibrium dominates overwhelmingly. They are also very sharp (for the same reason).

3.2 Systems of non-interacting identical particles

3.2.1 A little quantum mechanics

We will treat such systems with only one type of particle. When interactions are neglected then the wavefunction of each stationary state of the system $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots)$ is obtained by either symmetrization (for bosons) or antisymmetrization (fermions) of the product $\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\dots$ of one particle wavefunctions.

Consider spin 0 bosons in a cube of side L . Then the one particle wavefunctions are

$$\psi_{\mathbf{n}}(\mathbf{x}) = \left(\frac{2}{L} \right)^{\frac{3}{2}} \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \sin \frac{n_3 \pi z}{L}$$

with corresponding energies

$$E_{\mathbf{n}} = \frac{\hbar^2}{2mL^2} |\mathbf{n}|^2.$$

For identical bosons we cannot use wavefunctions $\phi_1(\mathbf{x}_1)\phi_1(\mathbf{x}_2)\phi_2(\mathbf{x}_3)$ which correspond to particles 1 and 2 in state 1 $\equiv \mathbf{n}_1$ and particle 3 in state 2 $\equiv \mathbf{n}_2$, but we must use instead the symmetrized wavefunction

$$\Psi = \sqrt{\frac{1}{3!}} (\phi_1(\mathbf{x}_1)\phi_1(\mathbf{x}_2)\phi_2(\mathbf{x}_3) + \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\phi_1(\mathbf{x}_3) + \phi_2(\mathbf{x}_1)\phi_1(\mathbf{x}_2)\phi_1(\mathbf{x}_3)).$$

All we can say about this is that there are two particles in state $|1\rangle$ and one particle in state $|2\rangle$. Ψ is fully determined by the fact that ϕ_1 is used twice and ϕ_2 used once.

For spin $\frac{1}{2}$ fermions we have

$$\phi(\mathbf{x}) \rightarrow \psi_{\mathbf{n}}(\mathbf{x})\alpha \text{ or } \psi_{\mathbf{n}}(\mathbf{x})\beta,$$

where α is “spin up” \uparrow and β is spin down \downarrow with H and $E_{\mathbf{n}}$ independent of α and β . We can use determinants to build the antisymmetric wavefunctions.

For instance, given $\psi_1(\mathbf{x}, \mu)$ and $\psi_2(\mathbf{x}, \mu)$ (where 1 $\equiv \mathbf{n}_1$, 2 $\equiv \mathbf{n}_2$ and $\mu = \alpha$ or β) we get the antisymmetrized version

$$\Psi(\mathbf{x}_1, \mu_2, \mathbf{x}_2, \mu_2) = \sqrt{\frac{1}{2!}} \begin{vmatrix} \psi_1(\mathbf{x}_1, \mu_1) & \psi_1(\mathbf{x}_2, \mu_2) \\ \psi_2(\mathbf{x}_1, \mu_1) & \psi_2(\mathbf{x}_2, \mu_2) \end{vmatrix}.$$

Similarly for three particles,

$$\Psi = \sqrt{\frac{1}{3!}} \begin{vmatrix} \psi_1(\mathbf{x}_1, \mu_1) & \psi_1(\mathbf{x}_2, \mu_2) & \psi_1(\mathbf{x}_3, \mu_3) \\ \psi_2(\mathbf{x}_1, \mu_1) & \psi_2(\mathbf{x}_2, \mu_2) & \psi_2(\mathbf{x}_3, \mu_3) \\ \psi_3(\mathbf{x}_1, \mu_1) & \psi_3(\mathbf{x}_2, \mu_2) & \psi_3(\mathbf{x}_3, \mu_3) \end{vmatrix}.$$

Ψ reflects the *Pauli exclusion principle* which forbids any two of the ψ_i or any two sets (\mathbf{x}, μ) from being the same.

Each Ψ is determined fully by the number of times each one particle wavefunction is used in the product term that we (anti)symmetrize.

3.2.2 The partition functions

Let the one particle wavefunctions of the particles of \mathcal{S} be $\psi_r(\mathbf{x})$ with energy ϵ_r . Suppose that in the microstate $|i\rangle$, n_r of the particles have wavefunction $\phi_r(\mathbf{x})$.

Then

$$N_i = \sum_r n_r \quad \text{and} \quad E_i = \sum_r \epsilon_r n_r.$$

We see that the microstate $|i\rangle$ of \mathcal{S} is fully determined by $i \equiv \{n_r\}$. We obtain the full set of microstates of \mathcal{S} by letting the n_r vary without restriction over their allowed range of values. (Thus N_i and E_i cannot themselves be restricted — this is why we use the grand ensemble method.)

We can now write down the grand partition function

$$\begin{aligned} \mathcal{Z} &= \sum_i e^{-\beta(E_i - \mu N_i)} \\ &= \sum_{n_1, n_2, \dots} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots - \mu n_1 - \mu n_2 - \dots)} \\ &= \prod_r \sum_{n_r} e^{-\beta n_r (\epsilon_r - \mu)}. \end{aligned}$$

For fermions we have that n_r can only be zero or one, so that

$$\mathcal{Z} = \prod_r \left(1 + e^{-\beta(\epsilon_r - \mu)} \right). \quad (3.10)$$

We use this to find

$$N = \frac{1}{\beta} \left(\frac{\partial \log \mathcal{Z}}{\partial \mu} \right)_{\beta, V} = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1}.$$

Now

$$\begin{aligned} \bar{n}_r &= \sum_{n_1, n_2, \dots} \frac{n_r e^{-\beta(\epsilon_r - \mu)}}{\mathcal{Z}} \\ &= -\frac{1}{\beta} \left(\frac{\partial \log \mathcal{Z}}{\partial \epsilon_r} \right)_{\beta, \mu, \epsilon_s} \quad s \neq r \\ &= \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1}. \end{aligned}$$

We see that $N = \sum_r \bar{n}_r$. \bar{n}_r is the *average occupation number* of the r^{th} one particle state at thermal equilibrium. This is the *Fermi-Dirac* distribution.

For bosons, $0 \leq n_r < \infty$ and

$$\mathcal{Z} = \prod_r \frac{1}{1 - e^{-\beta(\epsilon_r - \mu)}}.$$

This gives that

$$\bar{n}_r = \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1}. \quad (3.11)$$

This is the Bose-Einstein distribution.

If there are g_r one particle states of energy ϵ_r we can write the average number of particles with energy ϵ_r as

$$\bar{n}(\epsilon_r) = \frac{g_r}{e^{\beta(\epsilon_r - \mu)} \mp 1}.$$

for N large we pass to the continuum limit,

$$\sum_r \rightarrow \int d\epsilon g(\epsilon),$$

where $g(\epsilon)$ is the density of states factor, $DV\epsilon^{\frac{1}{2}}$ as in section 1.5.3, where $D = 2\pi \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} g_S$ and $g_S = 2S + 1$ is the spin degeneracy.

The average number of particles with energy in the range $\epsilon \rightarrow \epsilon + d\epsilon$ is

$$n(\epsilon)d\epsilon = \frac{g(\epsilon)d\epsilon}{e^{\beta(\epsilon - \mu)} \mp 1}.$$

Thus in the continuum limit, the grand partition function \mathcal{Z} is given by

$$\log \mathcal{Z} = \mp \int_0^\infty g(\epsilon) \log(1 \mp e^{-\beta(\epsilon - \mu)}) d\epsilon.$$

We can now use the results of section 3.1 to find things like N and E ,

$$N = \int_0^\infty \frac{g(\epsilon) d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1} \quad E = \int_0^\infty \frac{\epsilon g(\epsilon) d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1}.$$

In three dimensions, $g(\epsilon) = DV\epsilon^{\frac{1}{2}}$ and so (integrating by parts) we see that

$$\begin{aligned} \log \mathcal{Z} &= DV \int_0^\infty \frac{2}{3} \frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)} \mp 1} \\ &= \frac{2}{3} \beta \epsilon. \end{aligned}$$

Combining this with (3.9) we find that $PV = \frac{2}{3}E$. The $\frac{2}{3}$ comes from the $\epsilon^{\frac{1}{2}}$ factor in $g(\epsilon)$.

3.2.3 Classical limit

For a volume V of N particles with energy E , we use $g(\epsilon) = DV\epsilon^{\frac{1}{2}}$ and so

$$N = DV \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1} \quad \text{and} \quad E = DV \int_0^\infty \frac{\epsilon^{\frac{3}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} \mp 1}.$$

Putting $z = \beta\epsilon$ we find $N = DV(kT)^{\frac{3}{2}} I_{\frac{1}{2}}(-\beta\mu)$ and $E = DV(kT)^{\frac{5}{2}} I_{\frac{3}{2}}(-\beta\mu)$, with

$$I_n(y) = \int_0^\infty \frac{z^n dz}{e^{z+y} \mp 1}.$$

If $e^y \gg 1$ we can neglect the 1 in the denominator and find that $n(\epsilon) \propto e^{-\beta\epsilon} g(\epsilon)$. We can approximate the integrals (expand the integrand) to get

$$E \sim \frac{3}{2} NkT \left(1 \mp \frac{e^{\beta\mu}}{4\sqrt{2}} + \dots \right).$$

In the lowest approximation $E = \frac{3}{2} NkT$ and $N = DV(kT)^{\frac{3}{2}} \frac{\sqrt{\pi}}{2}$. The condition $e^{-\beta\mu} \gg 1$ is thus

$$\left(\frac{2m\pi kT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \gg 1 \quad \text{if } g_S = 1.$$

This is a classical limit — it holds when h is very small on a scale defined by m and the mean energy per particle $\frac{3}{2}kT$. This condition is satisfied at low density $\frac{V}{N}$ and at high temperature.

It is true for all real gases except helium at very low temperature and very high density. Most real gases liquefy before quantum mechanical effects set in.

It fails to hold for electrons in solids due to the fact that their effective mass inside the solid is much less than the free electron mass.

We can use our formulae for E and N to get the lowest order quantum correction to the equation of state — recall that $PV = \frac{2}{3}E$, so

$$PV = NkT \mp \frac{NP}{(kT)^{\frac{3}{2}} D\sqrt{8\pi}}.$$

3.3 Black body radiation

Consider a cubic cavity of side $L = V^{\frac{1}{3}}$ inside a perfectly black body, the walls of which are maintained at a fixed temperature T . The atoms of the perfectly black body absorb all photons incident on them and independently emit photons such that even in thermodynamic equilibrium the number of photons varies significantly. Thus the total number of photons is not conserved and so no constraint can be applied to them. Therefore $\mu = 0$.

The number of photons depends on the temperature. We must consider a gas of photons in a volume V at a temperature T . These quanta of the electromagnetic field are relativistic bosons of rest mass 0.

Our previous work applies, setting $\mu = 0$. Thus

$$\bar{n}_r = \frac{1}{e^{\beta\epsilon_r} - 1} \quad \text{and} \quad E = \sum_r \frac{\epsilon_r}{e^{\beta\epsilon_r} - 1}.$$

We pass to the continuum limit using (1.22) to get

$$N = \frac{8\pi V}{c^3} \int_0^\infty \frac{\nu^2 d\nu}{e^{\beta h\nu} - 1} \quad \text{and} \quad E = \frac{8\pi V}{c^3} \int_0^\infty \frac{h\nu^3 d\nu}{e^{\beta h\nu} - 1},$$

where $\epsilon = h\nu$. This is Planck's law. We expect classical behaviour at high T or low ν , where $e^{\frac{h\nu}{kT}} - 1 \approx \frac{h\nu}{kT}$ and

$$dE = \frac{8\pi V}{c^3} \nu^2 d\nu kT = kT g(\nu) dV,$$

which agrees with the classical result of energy kT per normal mode of radiation. This is the classical equipartition of energy. Using this result, $\frac{dE}{d\nu} \propto \nu^2$ gives a divergent energy, which is called the *ultraviolet catastrophe*.

Using the full formula for the energy we find that

$$e = \frac{E}{V} = \frac{8\pi}{(hc)^3} (kT)^4 \int_0^\infty \frac{z^3 dz}{e^z - 1} = \sigma T^4.$$

This is *Stefan's law*, and $\sigma = \frac{8\pi^5 k^4}{15h^3 c^3}$ is *Stefan's constant*. We see that the energy density is a function of T only.

Using (3.7) with $\mu = 0$ we see that

$$S = k \log \mathcal{Z} + \frac{E}{T}$$

and we can evaluate $k \log \mathcal{Z} = \frac{4E}{3T}$. The entropy density $\frac{S}{V} = \frac{4}{3}\sigma T^3 \rightarrow 0$ as $T \rightarrow 0$. The energy

$$E = V\sigma T^4 = \left(\frac{3S}{4}\right)^{\frac{4}{3}} \frac{1}{(V\sigma)^{\frac{1}{3}}} \propto V^{-\frac{1}{3}} \text{ at constant entropy.}$$

The pressure P can now be calculated from $P = -\left(\frac{\partial E}{\partial V}\right)_S = \frac{1}{3}\frac{E}{V} = \frac{1}{3}\sigma T^4$. Finally the density of photons, $n = \frac{N}{V} \propto T^3$ (see example sheet 3).

3.4 Degenerate Fermi gas

This is the extreme quantum limit. It occurs for

- electrons in solids,
- electrons in white dwarf stars,
- neutrons in neutron stars and
- nucleons in nuclear matter.

For N electrons in a volume V at a temperature T we have

$$N = \int_0^\infty g(\epsilon)F(\epsilon) d\epsilon \quad \text{and} \quad E = \int_0^\infty g(\epsilon)\epsilon F(\epsilon) d\epsilon,$$

where $g(\epsilon) = DV\sqrt{\epsilon}$, $D = 4\pi \left(\frac{2m}{h^3}\right)^{\frac{3}{2}}$ and

$$F(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}.$$

The range $0 \leq e^{-\beta\mu} < \infty$ is allowed without blowup of F . The region $e^{-\beta\mu} \gg 1$ is the classical realm and we expect that quantum mechanical effects will be most pronounced at low temperature, $e^{\beta\mu} \gg 1$.

We assume that μ is finite and positive and $\mu = E_F = kT_F$ is constant at $T = 0$. We further assume that $\mu = E_F + \mathcal{O}(kT)$ for small T . It can be shown that $\mu = E_F + \mathcal{O}(kT)^2$.

Now

$$\lim_{T \rightarrow 0} e^{\beta(\epsilon-\mu)} = \begin{cases} 0 & \epsilon < E_F \\ \infty & \epsilon > E_F, \end{cases}$$

so that

$$\lim_{T \rightarrow 0} F(\epsilon) = \begin{cases} 1 & \epsilon < E_F \\ 0 & \epsilon > E_F. \end{cases}$$

Thus at $T = 0$ $F(\epsilon) = \theta(\epsilon - E_F)$. At $T = 0$ it is energetically most favourable for electrons to fill up the one particle energy eigenstates (two electrons at a time, one spin up and one spin down) with increasing energy according to the Pauli principle, until the Fermi energy is reached. E_F is the highest energy occupied at $T = 0$.

We can now perform the integrals for N and E to get

$$N = DV \frac{2}{3} E_F^{\frac{3}{2}} \tag{3.12}$$

$$E = DV \frac{2}{3} E_F^{\frac{5}{2}} = \frac{3}{5} N E_F. \tag{3.13}$$

We can solve (3.12) for E_F to get

$$E_F = \left(\frac{3N}{2DV} \right)^{\frac{2}{3}} \propto V^{-\frac{2}{3}}.$$

The equation of state $PV = \frac{2}{3}E$ becomes $PV^{\frac{5}{3}} = \text{const}$. Classical kinetic theory gives $P \rightarrow 0$ as $T \rightarrow 0$. The Pauli principle requires particles to have non-zero momentum and so there is pressure even at $T = 0$.

In fact

$$P = \frac{2}{3} 3^{\frac{2}{3}} \left(\frac{N}{V} \right)^{\frac{5}{3}} \frac{h^2}{2m} \propto m^{-1}$$

and so at $T = 0$ the pressure is much bigger for lighter particles.

3.4.1 Heat capacity at low temperature

We have

$$N = \int_0^{\infty} g(\epsilon) F(\epsilon) d\epsilon \text{ and}$$

$$E = \int_0^{\infty} \epsilon g(\epsilon) F(\epsilon) d\epsilon.$$

We want to find $C = \left(\frac{\partial E}{\partial T} \right)_V$ (which is proportional to the usual C_V). We take $\frac{\partial}{\partial T}$ of both of the above to find

$$C = \int_0^{\infty} g(\epsilon) \frac{\partial F}{\partial T} (\epsilon - E_F) d\epsilon.$$

At low temperature $\frac{\partial F}{\partial T}$ is very like a delta function and so the region $\epsilon \approx E_F$ dominates the integral.

We approximate $g(\epsilon) \approx g(E_F)$ and $\mu \approx E_F$. This gives us

$$C \sim \frac{g(E_F)}{kT^2} \int_0^{\infty} d\epsilon (\epsilon - E_F) \frac{e^{\beta(\epsilon - E_F)}}{(e^{\beta(\epsilon - E_F)} + 1)^2} (\epsilon - E_F)^2$$

$$= g(E_F) k^2 T \int_{-\beta E_F}^{\infty} \frac{z^2 e^z dz}{(e^z + 1)^2}.$$

We know that E_F is finite and positive, so that $-\beta E_F \rightarrow -\infty$ as $T \rightarrow 0$. We therefore approximate the lower limit of the integral by $-\infty$.

$$C \sim g(E_F) k^2 T \int_{-\infty}^{\infty} \frac{z^2 e^z dz}{(e^z + 1)^2}.$$

This leaves a convergent integral whose value is $\frac{\pi^2}{3}$, so that

$$C \sim \frac{\pi^2}{2} N k \frac{T}{T_F},$$

where T_F (the *Fermi temperature*) is defined by $E_F = kT_F$. This approximation is expected to be good for $T \ll T_F$.

3.5 Bose-Einstein condensation

Recall the result

$$N = DV \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1} = DV(kT)^{\frac{3}{2}} \int_0^\infty \frac{z^{\frac{1}{2}} dz}{e^{z-\beta\mu} - 1} = DV(kT)^{\frac{3}{2}} \frac{\sqrt{\pi}}{2} f(-\beta\mu),$$

where

$$f(-\beta\mu) = \sum_{n=1}^{\infty} \frac{e^{n\beta\mu}}{n^{\frac{3}{2}}}.$$

$f(-\beta\mu)$ is convergent iff $\beta\mu \leq 0$. Assuming this, the Bose-Einstein denominator does not vanish for any point in the range of integration.

It is easy to see that f has a maximum value (of 2.612) at $\beta\mu = 0$ and decreases monotonically as $\beta\mu$ decreases through negative values from $\beta\mu = 0$.

Now suppose that $\frac{N}{V}$ is fixed. Our equation for N is OK as T decreases since $f(-\beta\mu)$ can increase by $\beta\mu$ getting less negative. When $\beta\mu$ reaches 0 problems occur as f cannot increase any more. This will be at $T = T_B$, given by

$$\frac{N}{V} = \hat{D}(kT_B)^{\frac{3}{2}} \quad \hat{D} = \frac{D\sqrt{\pi}f(0)}{2}.$$

Our equation for N appears to fail beyond this. Why?

More care is called for in the passage to the continuum limit. The $\epsilon^{\frac{1}{2}}$ factor in $g(\epsilon)$ assigns 0 weight to the particles in the $\epsilon = 0$ state. This would be no problem for fermions (which have the Pauli principle), but no law stops bosons from *condensing* into the $\epsilon = 0$ state if need be. We write $N = N_0 + N_C$, where N_0 is the number of particles in the $\epsilon = 0$ state and N_C is the number of particles in $\epsilon > 0$ states. Then for $T > T_B$

$$\frac{N}{V} = D \frac{\sqrt{\pi}}{2} f(-\beta\mu).$$

For $T = T_B$, $\frac{N}{V} = \hat{D}(kT_B)^{\frac{3}{2}}$, defining T_B . For $T < T_B$ then

$$\frac{N_C}{V} = \hat{D}(kT)^{\frac{3}{2}}, \quad \text{giving} \quad \frac{N_C}{N} = \left(\frac{T}{T_B}\right)^{\frac{3}{2}}.$$

3.6 White dwarf stars

White dwarfs are abnormally faint: they are stars in which the hydrogen supply has run out so that they are composed mainly of helium.

Typically,

$$\begin{aligned} T &\approx T_{\text{sun}} = 10^7 \text{K} \\ M &\approx M_{\text{sun}}, \text{ and} \\ \rho &\approx 10^7 \rho_{\text{sun}}. \end{aligned}$$

We regard them as being a mass of helium at $T \approx 10^7 \text{K}$ and under extreme compression. For $T \approx 10^7 \text{K}$, $kT \approx 10^3 \text{eV}$ is much greater than the binding energy of electrons to helium, so that thermal collisions completely ionize all the atoms, producing an electron gas.

To a good approximation this may be viewed as a Fermi gas in the degenerate (negligible T) limit. This may be seen by computing T_F , the natural temperature scale of the problem (the Fermi temperature). Now

$$kT_F = E_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}} \approx 2 \times 10^6 \text{eV}.$$

Since $\frac{N}{V}$ is so large $T_F \approx 10^{11} \text{K} \gg T$.

The helium nuclei neutralise the charge of the star and produce the gravitational attraction which counteracts the extreme zero-point pressure of the electron gas (which dominates the zero-point pressure from the nuclei).

We can calculate the total energy $E = E_{\text{elec}}(R) + E_{\text{grav}}(R)$ and find the radius R_0 of the star by minimising this.

Treating the electrons relativistically we have

$$\frac{N}{V} = \frac{8\pi}{\hbar^3 c^3} \int_{mc^2}^{E_F} \epsilon d\epsilon (\epsilon^2 - m^2 c^4)^{\frac{1}{2}}.$$

Let $\sqrt{\epsilon^2 - m^2 c^4} = mc^2 x$, so that the integral for $\frac{N}{V}$ can be done to get

$$\frac{N}{V} = \frac{8\pi}{\hbar^3 c^3} (mc^2)^3 \frac{x_F^3}{3}.$$

The integral for the energy density is

$$\frac{E}{V} = \frac{8\pi}{\hbar^3 c^3} (mc^2)^4 \int_0^{x_F} x^2 dx \sqrt{1+x^2}$$

and so $\frac{E}{N} = \frac{3}{4} mc^2 \left(x_F + \frac{1}{x_F} + \mathcal{O}(x_F^{-2}) \right)$. We know that $V \propto R^3$ and so $x_F \propto R^{-1}$. Hence

$$E = \frac{a}{R} + bR - \frac{\gamma}{R},$$

where a , b and γ are positive constants. This only has a minimum if $\gamma \geq a$, which leads to the Chandrasekhar upper limit on the mass of a white dwarf.

Chapter 4

Classical statistical mechanics

4.1 Introduction

Recall the result $Z = z^N$ for a system of distinguishable non-interacting particles. It can be shown that in the classical limit

$$z = \sum_r e^{-\beta \epsilon_r} = \sum_r \langle r | e^{-\beta \hat{H}} | r \rangle$$

gives

$$z = h^{-3} \int d^3p d^3q e^{-\beta H(p,q)}, \quad (4.1)$$

where $\hat{H}(\hat{p}, \hat{q})$ is the quantum mechanical Hamiltonian and $H(p, q)$ is the classical Hamiltonian as a function of classical variables p and q .

The average for the system of a physical variable $f(\mathbf{p}, \mathbf{q})$ is

$$\langle f(\mathbf{p}, \mathbf{q}) \rangle = \frac{\int d^3p d^3q f(\mathbf{p}, \mathbf{q}) e^{-\beta H(p,q)}}{\int d^3p d^3q e^{-\beta H(p,q)}}.$$

We can see that $\langle H(\mathbf{p}, \mathbf{q}) \rangle = - \left(\frac{\partial \log z}{\partial \beta} \right)_V$ agrees with the result

$$E = - \left(\frac{\partial \log Z}{\partial \beta} \right)_V = -N \left(\frac{\partial \log z}{\partial \beta} \right)_V.$$

Now

$$Z = \int \prod_{i=1}^N \left(\frac{d^3p d^3q}{h^3} \right) e^{-\beta \sum_{i=1}^N H(p_i, q_i)},$$

where $\sum_{i=1}^N H(p_i, q_i)$ is the Hamiltonian of the N -particle system.

For a monatomic gas with $H = \frac{p^2}{2m}$ we have

$$z = \frac{V}{h^3} \left(\int dp e^{-\frac{\beta p^2}{2m}} \right)^3 = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}}.$$

This result shows that $E = \frac{3}{2} NkT$, which is the common classical result of energy $\frac{1}{2}kT$ per degree of freedom per particle.

4.2 Diatomic gases

We will study the *rigid dumbbell model* as shown.

We want to write down the partition function $Z = z^N$. To apply (4.1) we need the Hamiltonian H . To find the Hamiltonian we first write down the Lagrangian

$$\mathcal{L} = \frac{1}{2}m\dot{\mathbf{x}}^2 + \frac{1}{2}I\left(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2\right).$$

($V \equiv 0$ in this rigid case.) Note that the Lagrangian splits neatly into translational motion of G and rotational motion about the centre of mass.

We define the generalised momenta $p_\alpha = \frac{\partial\mathcal{L}}{\partial\dot{q}_\alpha}$:

$$p_i = m\dot{x}_i, \quad p_\theta = I\dot{\theta} \quad \text{and} \quad p_\phi = I\sin^2\theta\dot{\phi}.$$

Now

$$H = \sum_\alpha \dot{q}_\alpha p_\alpha - \mathcal{L} = \frac{\mathbf{p}^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta},$$

and

$$z = \frac{1}{h^5} \int d^2p d^3q dp_\phi d\phi dp_\theta d\theta e^{-\beta H} = z_t z_r,$$

where

$$z_t = \frac{1}{h^3} \int d^3p d^3q e^{-\frac{1}{2}m\beta\mathbf{p}^2} = V \left(\frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}}$$

and

$$z_r = \frac{1}{h^2} \int dp_\phi d\phi dp_\theta d\theta e^{-\frac{\beta}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} \right)} = \frac{8\pi^2 I k T}{h^2}.$$

We evaluate the above integral by first doing the p_θ , p_ϕ and ϕ integrals and then doing the θ integral.

Thus $z = z_t z_r = V \left(\frac{2m\pi k T}{h^2} \right)^{\frac{3}{2}} \frac{8\pi^2 I k T}{h^2}$. This gives $E = \frac{5}{2} N k T$.¹

4.3 Paramagnetism

Each molecule of an N molecule solid acts as a little magnet fixed at its own lattice site and free only to rotate about it. Each molecule has a dipole moment \mathbf{m} and gives a contribution $-\mathbf{m} \cdot \mathbf{B}$ to the energy when in an applied magnetic field $\mathbf{B} = (0, 0, B)$.

Now

$$H = \frac{\mathbf{p}^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta} - mB \cos\theta$$

and so

$$z = \frac{2\pi I}{h^2 \beta} 2\pi \frac{2 \sinh y}{y}$$

¹Which ought to be expected!

where $y = m\beta B$. We can calculate the magnetisation of the solid:

$$\mathbf{M} = (0, 0, M) = N\langle M \rangle.$$

Only the third component $\langle m \cos \theta \rangle$ is non-zero:

$$\langle m \cos \theta \rangle = \beta^{-1} \left(\frac{\partial \log z}{\partial B} \right)_{\beta} = m (\coth y - y^{-1}).$$

For small y (high T) we thus have Curie's law, $M = \frac{1}{3} N m y = \frac{N m^2 B}{3 k T}$.

4.4 Specific heats

The result $E = \frac{5}{2} N k T$ for a diatomic gas is found to be accurate at sufficiently high temperatures. E is found to be $\frac{3}{2} N k T$ at lower temperatures. It is as if the rotational degrees of freedom are *frozen out*. This is explained by quantum mechanics.

We have $Z = z^N$ and $z = z_r z_t$. We will look at z_r , using $H_r = \frac{1}{2I} \mathbf{L}^2$ (the quantum mechanical angular momentum operator). Now

$$H_r |l m\rangle = \frac{l(l+1)\hbar^2}{2I} |l m\rangle$$

for $m = -l, -l+1, \dots, l-1, l$ for each of $l = 0, 1, 2, \dots$. Thus

$$z_r = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{l(l+1)T_r}{T}} \quad (4.2)$$

with $T_r = \frac{\hbar^2}{2Ik}$. T_r is typically about 50K and is experimentally accessible.

For $T_r \ll T$ (most gases at normal temperatures) we can turn this sum into an integral to get

$$z_r = \frac{T}{T_r} = \left(\frac{8\pi^2}{h^2} \right) kT$$

as before. For $T_r \gg T$ all of the terms with $l \neq 0$ in (4.2) are exponentially small and we take only the $l = 0$ term to get $z_r \approx 1$ — there is no rotational contribution to the energy (or heat capacity). The contribution to the energy from rotational motion is therefore NkT if $T \gg T_r$ or 0 if $T \ll T_r$.

For high temperatures, E rises to $\frac{7}{2} N k T$ due to vibrational motion along the axis of the dumbbell. There is an extra term in the Hamiltonian

$$H_v = \frac{1}{m} P^2 + \frac{m\omega^2 Q^2}{4}$$

and an extra factor z_v in the one particle partition function.

4.5 Weak interparticle forces

Consider a classical gas of N molecules with Hamiltonian

$$H = \sum_{r=1}^N \frac{\mathbf{p}_r^2}{2m} + \sum_{r<s} \phi(R_{rs}),$$

where $R_{rs} = |\mathbf{q}_r - \mathbf{q}_s|$. We use

$$\begin{aligned} Z &= \int \prod_{r=1}^N \frac{d^3 p_r d^3 q_r}{h^3} e^{-\beta H} \\ &= \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3N}{2}} V^N K \\ &= Z_0 K, \end{aligned}$$

where $Z_0 = z_0^N$ and z_0 is the partition function for one molecule of a spinless gas of N non-interacting molecules and

$$K = V^{-N} \int \prod_r d^3 q_r e^{-\beta \sum_{r<s} \phi(R_{rs})}.$$

We suppose that $\lambda_{rs} = e^{-\beta \phi(R_{rs})} - 1$ is small (weak interaction) and we treat our results to lowest non-trivial order.

Then

$$\begin{aligned} K &= V^{-N} \int \prod_r d^3 q_r \left(1 + \sum_{r<s} \phi(R_{rs}) \right) \\ &= 1 + \frac{N(N-1)}{2V^2} \int d^3 q_a d^3 q_b \lambda_{ab} \quad (\text{no summation}). \end{aligned}$$

This integral can be evaluated using the change of variables $\mathbf{x} = \frac{\mathbf{q}_a + \mathbf{q}_b}{2}$ and $\mathbf{y} = \mathbf{q}_a - \mathbf{q}_b$, so that

$$\int d^3 q_a d^3 q_b \lambda_{ab} = V \int d^3 y \left(e^{-\beta \phi(y)} - 1 \right) \equiv V f(T),$$

defining $f(T)$. Then $K = 1 + \frac{N^2 f(T)}{2V}$ (as $N-1 \sim N$) and

$$\log Z = N \log V + \frac{N^2 f(T)}{V} + \text{stuff which does not depend on } V.$$

Using $\beta P = \left(\frac{\partial \log Z}{\partial V} \right)_\beta$ we get

$$PV = NkT \left(1 - \frac{Nf(T)}{2V} \right) \quad \text{with} \quad f(T) = \int_0^\infty 4\pi y^2 dy \left(e^{-\beta \phi(y)} - 1 \right). \quad (4.3)$$

If we take a specific ϕ we can recover the van der Waals' equation of state (see page 15).

Consider the ϕ shown.

Then the contribution to $f(T)$ from region 1 where ϕ is infinite is

$$\int_0^d 4\pi y^2 dy = -2b.$$

For large T and weak attractive forces the contribution from region 2 is

$$\int_d^\infty 4\pi y^2 dy (-\beta\phi(y)) = 2\beta a.$$

a and b are positive constants. Now $f(T) = -2(b - \beta a)$ and (4.3) becomes

$$\left(P + \frac{N^2 a}{V^2}\right) V = NkT \left(1 + \frac{Nb}{V}\right).$$

For $\frac{Nb}{V}$ small we can (approximately) take $1 + \frac{Nb}{V}$ to the left hand side of the equation to get

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

and the correspondence with (2.5) is completed by setting $A = N^2 a$ and $B = Nb$. Note that B is the volume of all the molecules.

4.6 The Maxwell distribution

Consider a gas with (one particle) Hamiltonian $\frac{\mathbf{p}^2}{2m}$.

The number of molecules in the region $\mathbf{p} \rightarrow \mathbf{p} + d\mathbf{p}$ is

$$n(\mathbf{p}) d^3 p = \frac{N e^{-\beta H}}{\int e^{-\beta H} d^3 p} = C e^{-\frac{\beta \mathbf{p}^2}{2m}}.$$

Now

$$N = \int n(\mathbf{p}) d^3 p = m^3 C \int 4\pi v^2 dv e^{-\frac{1}{2}\beta m v^2} = N \int f(v) dv,$$

which defines the *Maxwell distribution of speeds*,

$$f(v) = \text{const} \times v^2 e^{-\frac{1}{2}\beta m v^2}.$$

$f(v)$ is the probability of finding a particle with speed in $v \rightarrow v + dv$. The constant is (of course) chosen to make $\int_0^\infty f(v) dv = 1$. We can define averages in the obvious way, that is

$$\langle g(v) \rangle = \int_0^\infty f(v) g(v) dv.$$

Approximations

Stirling's formula

We derive the approximation for Stirling's formula from the Γ function using Laplace's method.

Recall that

$$\Gamma(z) = \int_0^{\infty} t^{z-1} e^{-t} dt$$

and $\Gamma(n+1) = n!$. Then

$$n! = \int_0^{\infty} t^n e^{-t} dt = \int_0^{\infty} e^{n \log t - t} dt.$$

Let $v = \frac{t}{n}$, so that

$$n! = n^{n+1} \int_0^{\infty} e^{n(\log v - v)} dv.$$

Now for large n , $e^{n(\log v - v)} \sim e^{n\left(-1 - \frac{(v-1)^2}{2}\right)}$, so

$$n! \sim n^{n+1} e^{-n} \int_{-\infty}^{\infty} e^{-\frac{nu^2}{2}} du = \sqrt{2\pi n} e^{-n} n^n.$$

This is Stirling's formula.