

Statistical Mechanics

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Chapter 1

Basic Thermodynamics

We will begin by discussing systems with variable particle number. In order to talk as system where the number of particles N varies, we must consider its *chemical potential*, which is defined in terms of the Gibbs free energy,

$$\mu = \left. \frac{\partial G}{\partial N} \right|_{T,P}. \quad (1.1)$$

We can find a simpler expression for the chemical potential by considering,

$$G = G(N, \underbrace{P, T}_{\text{intensive}}). \quad (1.2)$$

We know that the Gibbs free energy is an extensive variable, and so is the number of particles N . Thus, we can write,

$$G = Nf(P, T) \quad (1.3)$$

where f is some function. We actually ind that $f(P, T) = \mu$, so we can write,

$$\mu = \frac{G}{N} \quad (1.4)$$

from which we can also conclude that μ is a function of P and T . Let us now attempt to generalise this to more than one species of gas. This means that there is more than one extensive variable. For now, let us state without proof,

$$G = \sum_i \mu_i N_i \quad (1.5)$$

where N_i is the number of particles of a particularly species and μ_i is its chemical potential. We can then write,

$$\mu_i = \mu_i \left(T, P, \left\{ \frac{N_j}{N}, \forall j \in \mathbb{N} \right\} \right). \quad (1.6)$$

However, if we consider an ideal gas, we can ignore interactions due to other species of gas so we can simply consider, $\mu_i = \mu_i(T, P, N_i/N)$. However,

$$P = \frac{1}{V} N k_B T = \sum_i P_i \quad N = \sum_i N_i \quad (1.7)$$

$$P_i = \frac{N_i}{V} k_B T \rightarrow \text{Partial pressure} \quad (1.8)$$

$$\Rightarrow \quad \mu_i = \mu_i(T, P_i). \quad (1.9)$$

Let us return to considering a single species, and recall,

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad dE = C_V dT \quad V = \frac{N k_B T}{P} \quad (1.10)$$

from which we can show,

$$-\Delta S = C_P \ln \frac{T}{T_0} - N k_B \ln \frac{P}{P_0} \quad (1.11)$$

1.1 Constant Temperature

At constant temperature, the Gibbs free energy is,

$$\Delta G = -T\Delta S = Nk_B T \ln \frac{P}{P_0} \quad (1.12)$$

$$\implies \Delta\mu = k_B T_0 \ln \frac{P}{P_0}. \quad (1.13)$$

1.1.1 Chemical Reactions

If we consider two gasses separated by a membrane, the chemical potential will govern the diffusion of the gasses, and the partial pressures will tend to equalise. Let us consider a reaction between two substances, $A \rightleftharpoons B$. The Gibbs free energy is,

$$dG = \mu_A dN_A + \mu_B dN_B \quad (1.14)$$

however $dN_B = dN_A$, so,

$$dG = (\mu_A - \mu_B) dN_A. \quad (1.15)$$

We have equilibrium when a small change in N_A leaves G unchanged, so $\mu_A = \mu_B$.

Let us now consider a reaction with double the reactants and products, $aA + bB \rightleftharpoons xX + yY$, where $a, b, x, y \in \mathbb{Z}$. The number of molecules change by,

$$dN_B = \frac{b}{a} dN_A \quad \quad \quad dN_X = -\frac{x}{a} dN_A \quad (1.16)$$

Let us write the Gibbs free energy,

$$\begin{aligned} dG &= \mu_A dN_A + \mu_B dN_B - \mu_X dN_X - \mu_Y dN_Y \\ &= \underbrace{\left(\mu_A + \frac{b}{a}\mu_B - \frac{x}{a}\mu_X - \frac{y}{a}\mu_Y \right)}_{0 \text{ at equilibrium}} dN_A \\ &\implies \mu_A + b\mu_B = x\mu_X + y\mu_Y \end{aligned} \quad (1.17)$$

We wish to work in terms of moles, so let us write the molar Gibbs free energy,

$$g^r = xg_X + yg_Y - ag_A - bg_B \quad (1.18)$$

which will be 0 at equilibrium. If we know the $g_0^r \equiv g_r(T_0, P_0)$ at some reference temperature and partial pressure for all reactants and products, then we can find the molar Gibbs free energy at other partial pressures but the same temperature. Applying our ideal gas assumptions,

$$\begin{aligned} g_r(\{P_i\}, T_0) &= g_r(P_0, T_0) + N_A k_B T_0 \left(x \ln \frac{P_X}{P_0} + y \ln \frac{P_Y}{P_0} - a \ln \frac{P_A}{P_0} - b \ln \frac{P_B}{P_0} \right) \\ &= g_r(P_0, T_0) + \ln \left(\left(\frac{P_X}{P_0} \right)^x \left(\frac{P_Y}{P_0} \right)^y \left(\frac{P_0}{P_A} \right)^a \left(\frac{P_0}{P_B} \right)^b \right). \end{aligned} \quad (1.19)$$

At equilibrium $g_r = 0$, so,

$$\underbrace{\left(\frac{P_X}{P_0} \right)^x \left(\frac{P_Y}{P_0} \right)^y \left(\frac{P_0}{P_A} \right)^a \left(\frac{P_0}{P_B} \right)^b}_Q = \underbrace{\exp \left(-\frac{g_0^r}{RT_0} \right)}_{K_P(T_0)}. \quad (1.20)$$

We can write more generally, an equation for N reactants and N' products,

$$g_r = \sum_{i=1}^{N'} x_i g_{X_i} - \sum_{j=1}^N a_j g_{A_j} \quad (1.21)$$

and at equilibrium,

$$\prod_{i=1}^{N'} \left(\frac{P_{X_i}}{P_0} \right)^{x_i} \sum_{j=1}^N \left(\frac{P_0}{P_{A_j}} \right)^{a_j} = \exp \left(-\frac{g_0^r}{RT_0} \right) \quad (1.22)$$

Chapter 2

Statistical Physics

Before jumping into statistical physics, we must define a few terms,

Definition 1: Macrostate

State of a sufficiently large system in equilibrium specified by a few measurable quantities, i.e., P , T , etc.

Definition 2: Microstate

A description of a system consisting of the position and momentum (or quantum states) of every molecule present in the system.

We wish to relate the macrostate to the microstate and predict macroscopic properties from first principles. For each macrostate, there exist many microstates. In order to formulate statistical mechanics, we must assume that a system can access all available microstates, so we can average over all microstates to predict the macrostate.

2.1 Microcanonical Ensemble

Definition 3: Ensemble

Collection of objects, which are copies of the system at each point in time.

We use the ensemble to avoid taking time averages. The ensemble average is given by,

$$\langle x \rangle = \sum_i P_i X_i \quad (2.1)$$

where P_i is the probability of the i th microstate, and X_i is the value of X in the i th microstate. Let us now say that we have ν objects in the ensemble, with ν_i objects in the i th microstate, and we denote each object in the ensemble with λ , we can write,

$$\langle x \rangle = \frac{1}{\nu} \sum_{\lambda} X_{\lambda} = \frac{1}{\nu} \sum_i \nu_i X_i = \sum_i P_i X_i \quad (2.2)$$

from which we find,

$$P_i = \frac{\nu_i}{\nu}. \quad (2.3)$$

However, for a system in isolation, we can postulate the following,

Postulate 1: Postulate of Equal a priori Probabilities

All microstates are equally likely.

Thus, if our total number of microstates is Ω , the probability of the i th microstate is,

$$P_i = \frac{1}{\Omega}, \quad \forall i. \quad (2.4)$$

For a system with N particles which each can be in one of two states, such that there are n and $N - n$ states respectively, then the total number of microstates is given by,

$$\frac{N!}{n!(N-n)!} = {}^N C_n. \quad (2.5)$$

2.2 Statistical Basis of Entropy

The number of microstates Ω for a number of particles N in the system and a set of particles of size n in one state, m in a second state, etc., is given by,

$$\Omega(n) = \frac{N!}{n!m!\dots!}. \quad (2.6)$$

For a system with just N total particles and two sets of particles of size n , $N - n$ this is,

$$\Omega(n) = \frac{N!}{n!(N-n)!}. \quad (2.7)$$

For large systems, Ω rises dramatically. For two possible states, we can write the distribution of microstates as a binomial distribution,

$$\bar{n} = \frac{N}{2} \quad \sigma_n = \frac{\sqrt{N}}{2} \quad \frac{\sigma_n}{\bar{n}} \approx \frac{1}{\sqrt{N}}. \quad (2.8)$$

For large N , we find that the ensemble average $\langle X \rangle$ is entirely dominated by microstates with the most probable X_i , denoted X_{Prob} . Thus,

$$\langle X \rangle = \sum_i P_i X_i \approx X_{\text{Prob}} \quad (2.9)$$

which is true within a few σ of the most probable value.

As the microstate changes, the vast majority of new states have similar (or essential equal) $X_i \approx X_{\text{Prob}}$ so nothing changes at equilibrium.

If our system begins out of equilibrium, i.e., $n < N/2$, the time evolution must in principle increase or decrease n , but there are vastly more states with greater n and so evolution is overwhelmingly likely to lead to $n \uparrow$ until $n \approx N/2$.

Furthermore, for large N , $\Omega(n)$ tends to an exponential,

$$\Omega(n) = \exp \left(\frac{\left(n - \frac{N}{2}\right)^2}{\frac{N}{2}} \right) \quad (2.10)$$

with mean $N/2$, $\sigma = \sqrt{N}/2$.

We might then think that $\Omega \propto S$, but this is not the case. This is because entropy is extensive, whereas we combine microstates by multiplying them together. Instead, the following relation holds,

$$S = k_B \ln \Omega. \quad (2.11)$$

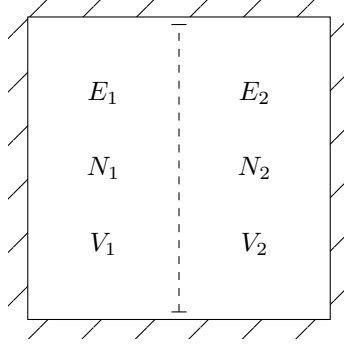


Figure 2.1

2.3 Spin-Half Paramagnet

An atom or molecule of a spin- $\frac{1}{2}$ paramagnet has $s = \frac{1}{2}$, $|\mathbf{S}| = \frac{\sqrt{3}}{2}\hbar$, $S_z = \pm\frac{1}{2}\hbar$. Each molecule has a magnetic moment $\boldsymbol{\mu}$ such that $\mu_z = \pm\mu$. The total magnetisation of the sample is then given by,

$$\begin{aligned} m &= n_{\uparrow} + n_{\downarrow}(-\mu) & n_{\downarrow} &= N - n_{\uparrow} \\ &= (2n_{\uparrow} - N)\mu \end{aligned} \quad (2.12)$$

If there is a magnetic field, the energy is given by,

$$U = -\mathbf{m} \cdot \mathbf{B} \quad (2.13)$$

with each atom having energy $\mp\mu B$ for spin \uparrow, \downarrow , as the atoms align to lower energy. The total energy is then,

$$U = n_{\uparrow}(-\mu B) + n_{\downarrow}(\mu B) = (N - 2n_{\uparrow})\mu B = mB. \quad (2.14)$$

The microstates are then specified by specifying the spin of each atom. For N atoms there are 2^N microstates. If there is no external magnetic field, the atoms have equal probability of being \uparrow or \downarrow , thus equilibrium will be reached at $m = 0$.

2.3.1 Energy to Temperature

Let us consider an isolated system separated by a permeable membrane, as in figure 2.1, such that,

$$E_1 + E_2 = E \quad N_1 + N_2 = N \quad V_1 + V_2 = V \quad (2.15)$$

are fixed. We further have,

$$\Omega = \Omega_1 + \Omega_2 \quad S = k_B \ln \Omega_1 + k_B \ln \Omega_2 = S_1 + S_2. \quad (2.16)$$

Let us consider the heat flow in the system only, keeping V_1, V_2 and N_1, N_2 constant. We have,

$$dS = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 \quad (2.17)$$

however, $dE_1 = -dE_2$, so,

$$dS = \left(\left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \right) dE_1 \quad (2.18)$$

and equilibrium is reached when,

$$\left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} = \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \quad (2.19)$$

this equation thus governs heat transfer. If $dE > 0$, then $dS > 0$ and,

$$\left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} > \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \quad (2.20)$$

so heat flows from high $\left(\frac{\partial S}{\partial E}\right)_{V,N}$ to low $\left(\frac{\partial S}{\partial E}\right)_{V,N}$, so we require T to decrease with $\left(\frac{\partial S}{\partial E}\right)_{V,N}$. Furthermore, $\left(\frac{\partial S}{\partial E}\right)_{V,N} > 0$ for almost all systems, so an appropriate guess would be to say,

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}. \quad (2.21)$$

Repeating similar process, but only allowing V_1, V_2 to vary, we find that $\left(\frac{\partial S}{\partial V}\right)_{E,N}$ governs how the partition moves. If $\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1, N_1} > \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2, N_2}$, we have that V_1 increases and V_2 decreases, like pressure. Thus, we can link this to classical thermodynamics,

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}. \quad (2.22)$$

Considering variable particle number, we obtain,

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = \frac{\mu}{T} \quad (2.23)$$

and thus, we can obtain the fundamental thermodynamic relation,

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN. \quad (2.24)$$

2.3.2 Isolated spin- $\frac{1}{2}$ paramagnet in the presence of a magnetic field

Let us return to the ideal paramagnet. The total energy is given by,

$$E = \mu B (N - 2n_{\uparrow}) = \mu B (2n_{\downarrow} - N). \quad (2.25)$$

The reversible work done is,

$$dW^{\text{rev}} = -m dB \implies \frac{m}{T} = \left(\frac{\partial S}{\partial B}\right)_{E,N}. \quad (2.26)$$

The entropy of the paramagnet is,

$$\begin{aligned} S &= k_B \ln \Omega(E, B) \\ &= k_B \ln \left(\frac{N!}{n_{\uparrow}! (N - n_{\uparrow})!} \right). \end{aligned} \quad (2.27)$$

where Ω is a function of E, B as n_{\uparrow} and E co-vary as,

$$n_{\uparrow} = \frac{1}{2} \left(N - \frac{E}{\mu B} \right). \quad (2.28)$$

We will use Stirling approximation,

$$\ln(x!) = x \ln x - x \quad (2.29)$$

which holds for large x . By writing out,

$$S = k_B [\ln(N!) - \ln(n_{\uparrow}!) - \ln((N - n_{\uparrow})!)] \quad (2.30)$$

and using equation (2.29),

$$S = k_B [N \ln(N) - n_{\uparrow} \ln(n_{\uparrow}) - (N - n_{\uparrow}) \ln(N - n_{\uparrow})] \quad (2.31)$$

While in equilibrium, $n_{\uparrow} = n_{\downarrow} = \frac{N}{2}$, in which case,

$$S = k_B \ln(2^N) \quad (2.32)$$

which indicates that essentially all microstates are at equilibrium. Applying the chain rule to equation (2.21), we find,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial n_{\uparrow}}\right)_N \left(\frac{\partial n_{\uparrow}}{\partial E}\right)_B. \quad (2.33)$$

We then find,

$$\left(\frac{\partial S}{\partial n_{\uparrow}}\right)_B = k_B \ln \frac{N - n_{\uparrow}}{n_{\uparrow}} \quad (2.34)$$

and,

$$\left(\frac{\partial n_{\uparrow}}{\partial E}\right)_B = -\frac{1}{2\mu B} \quad (2.35)$$

thus,

$$\frac{1}{T} = \frac{k_B}{2\mu B} \ln \left(\frac{n_{\downarrow}}{n_{\uparrow}}\right). \quad (2.36)$$

For the magnetic field,

$$\frac{m}{T} = \left(\frac{\partial S}{\partial B}\right)_{E,N} = \frac{k_B E}{2\mu B^2} \ln \left(\frac{n_{\downarrow}}{n_{\uparrow}}\right) \implies m = -\frac{E}{B}. \quad (2.37)$$

For a varied magnetic field, we can write the ratio of spin-down to spin up electrons as,

$$\frac{n_{\downarrow}}{n_{\uparrow}} = \exp \left(-\frac{2\mu B}{k_B T}\right). \quad (2.38)$$

2.4 The Ideal Gas

We can derive the equation for a classical, ideal gas. Let us consider a volume divided into small cells, such that we can treat position microstates as discrete, of volume ΔV . There are $V/\Delta V$ cells, and $(V/\Delta V)^N$ microstates. Thus, the entropy is,

$$S = Nk_B \ln \frac{V}{\Delta V}. \quad (2.39)$$

We then find,

$$\begin{aligned} \frac{P}{T} &= \left(\frac{\partial S}{\partial V}\right)_{E,N} = Nk_B \frac{1}{V} \\ &\implies PV = Nk_B T. \end{aligned} \quad (2.40)$$

Chapter 3

Statistical Physics of Non-Isolated Systems

In order to find the physics of non-isolated systems, we must fix T and E . $\langle E \rangle$ depends on T , although there will be microscopic fluctuations. These fluctuations are of an order,

$$\frac{\Delta E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}. \quad (3.1)$$

3.1 Boltzmann Distribution

Consider an isolated system as in figure 3.1. The total energy of this system is fixed, such that $E = E_R + \varepsilon$. We wish to know, for the i th microstate of S , what is the probability p_i of finding it in that microstate, with an associated energy ε_i . This probability is directly proportional to the total number of microstates,

$$\begin{aligned} p_i &\propto \Omega_{S+R} = \Omega_S \Omega_R \\ &\propto \Omega_R(E - \varepsilon_i) = e^{\frac{1}{k_B T} S_R(E - \varepsilon_i)}. \end{aligned} \quad (3.2)$$

Given $E \ll \varepsilon_i$, we can perform a Taylor expansion up to the first order,

$$S_R(E - \varepsilon_i) = S_R(E) - \varepsilon_i \underbrace{\left. \frac{\partial S_R}{\partial E} \right|_{E_R=E}}_{\frac{1}{T}}. \quad (3.3)$$

Thus, we have,

$$p_i \propto e^{\frac{1}{k_B} S_R(E)} e^{-\frac{\varepsilon_i}{k_B T}} \quad (3.4)$$

which we can write as,

$$p_i = \frac{1}{Z} e^{-\frac{\varepsilon_i}{k_B T}} \quad Z = \sum_j e^{-\frac{\varepsilon_j}{k_B T}} \quad (3.5)$$

which is the Boltzmann distribution, with normalisation Z .

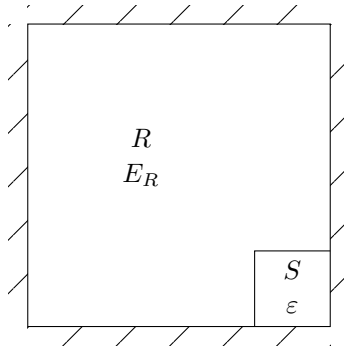


Figure 3.1: Isolated system consisting of large reservoir R and small system S such that $S \ll R$.

3.1.1 Paramagnet

Let us consider a paramagnet consisting of a single atom. There are 2 states, $\uparrow E = -\mu B$ and $\downarrow E = \mu B$. Therefore, the normalisation is,

$$Z = e^{\frac{\mu B}{k_B T}} + e^{-\frac{\mu B}{k_B T}} \quad (3.6)$$

and the probability of spin up and spin down are,

$$P(\uparrow) = \frac{e^{\frac{\mu B}{k_B T}}}{Z} \quad P(\downarrow) = \frac{e^{-\frac{\mu B}{k_B T}}}{Z} \quad (3.7)$$

whose ratio is,

$$\frac{P(\downarrow)}{P(\uparrow)} = e^{-\frac{2\mu B}{k_B T}} \quad (3.8)$$

which is identical to eq. (2.38).

3.2 Partition Function

The normalisation factor Z in equation eq. (3.5) is also known as the *partition function*. It is useful to us, as we are able to extract useful information about different macroscopic properties of a system. If we define $\beta = 1/k_B T$, we have,

$$\langle E \rangle = \frac{\sum_i \varepsilon_i e^{\varepsilon_i \beta}}{\sum_j e^{-\varepsilon_j \beta}} = -\frac{\partial \ln(Z)}{\partial \beta} \quad (3.9)$$

$$\langle C_V \rangle = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial^2 \ln(Z)}{\partial \beta^2} \quad (3.10)$$

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (3.11)$$

$$\Delta E^2 = (k_B T)^2 \frac{C_V}{k_B}. \quad (3.12)$$

3.3 Helmholtz Free Energy and Entropy

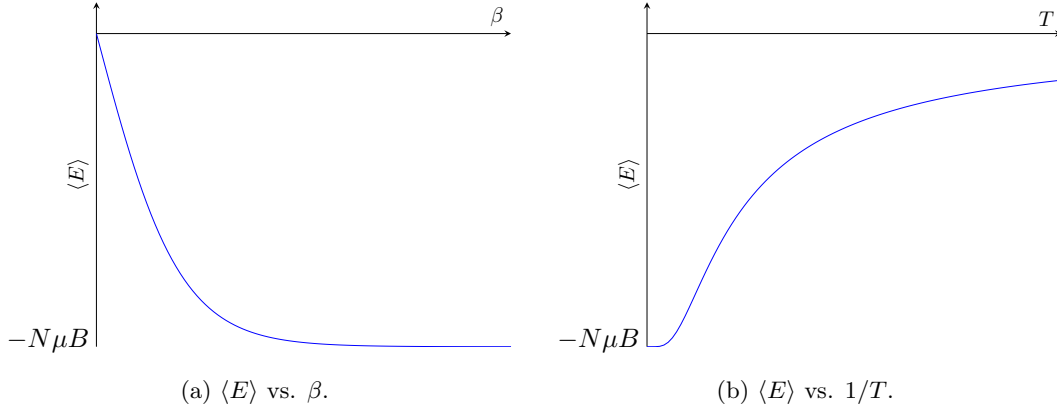
We wish to consider a system larger than S . Let us consider ν copies of the system, all in thermal contact. This can be considered a canonical ensemble because, together, they are large enough to have a well defined T . Then, for any individual S , the rest of the system is the reservoir, whose probabilities follow the Boltzmann distribution.

The ensemble has ν_i copies in the i th microstate, with $p_i = \nu_i/\nu$. The total number of microstates is,

$$\Omega_\nu = \frac{\nu!}{\nu_1! \nu_2! \nu_3! \dots}, \quad (3.13)$$

and by Stirling's approximation,

$$\begin{aligned} \ln \Omega_\nu &= \nu \ln \nu - \nu - \left(\sum_i \nu_i \ln \nu_i - \underbrace{\sum_j \nu_j}_\nu \right) \\ &= \nu \ln \nu - \sum_i \nu_i \ln \nu_i \\ &= \sum_i \nu_i (\ln \nu - \ln \nu_i) \\ &= \sum_i \nu_i \ln \frac{\nu}{\nu_i} \\ &= -\sum_i \nu_i \ln p_i \\ &= -\nu \sum_i p_i \ln p_i \end{aligned} \quad (3.14)$$

Figure 3.2: Function of average energy against β and $1/T$.

and by extensivity,

$$\begin{aligned} \langle S \rangle &= \frac{1}{\nu} \langle S_\nu \rangle \\ &= -k_B \sum_i p_i \ln p_i \end{aligned} \quad (3.15)$$

which is known as the *Gibbs entropy*. Let us check if this works for the macrocanonical ensemble, i.e., $p_i = \frac{1}{\Omega}$. We have,

$$\begin{aligned} \langle S \rangle &= k_B \sum_i \frac{1}{\Omega} \ln \Omega \\ &= k_B \ln \Omega \end{aligned} \quad (3.16)$$

which is what we expect. Furthermore, the Gibbs expression is more general and can be applied to any probability distribution. Let us now apply this to the canonical ensemble, with $p_i = e^{-\varepsilon_i \beta} / Z$,

$$\begin{aligned} \langle S \rangle &= -k_B \sum_i p_i [\ln(e^{-\varepsilon_i \beta}) - \ln Z] \\ &= -k_B \sum_i p_i (\varepsilon_i \beta - \ln Z) \\ &= k_B \left(\frac{1}{k_B T} \langle E \rangle - \ln Z \right) \\ &= -k_B \frac{1}{k_B T} \frac{\partial \ln Z}{\partial \beta} + \ln Z \end{aligned} \quad (3.17)$$

so we can find $\langle S \rangle$ from Z . However, we can rewrite this as,

$$-k_B T \ln Z = \langle E \rangle + T \langle S \rangle = \langle F \rangle \quad (3.18)$$

so we find that Z directly gives us $F(T, V)$ or $F(T, B)$, or the Helmholtz free energy. The Helmholtz free energy is the natural potential for a system at fixed energy. Let us then recall the Maxwell relations,

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V(\text{or } B), N} \quad P = - \left(\frac{\partial F}{\partial V} \right)_{T, N} \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{V, T} \quad (3.19)$$

3.3.1 The paramagnet at fixed temperature

We had first considered a paramagnet consisting of a single atom, with a single spin, whose partition function is,

$$Z_1 = e^{\mu B \beta} + e^{-\mu B \beta} = 2 \cosh(\mu B \beta) \quad (3.20)$$

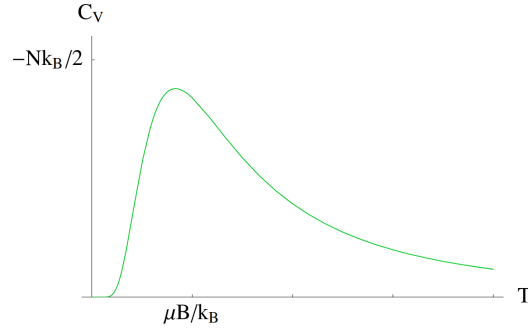


Figure 3.3

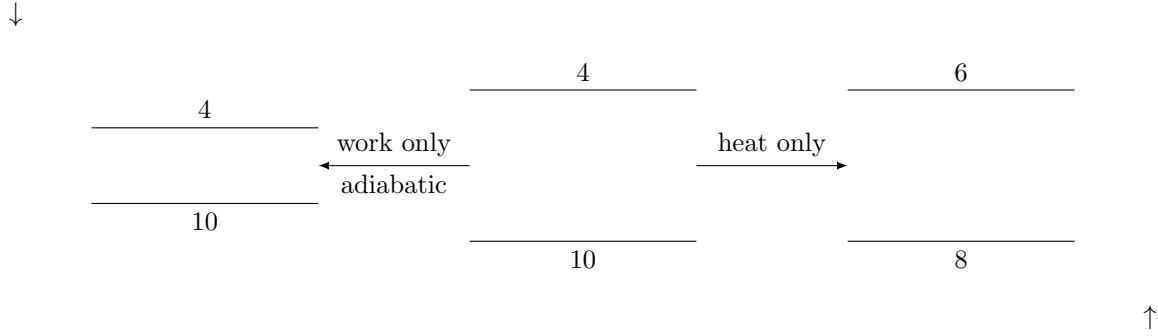


Figure 3.4

and average energy,

$$\langle E_1 \rangle = -\mu B \frac{2 \sinh(\mu B \beta)}{2 \cosh(\mu B \beta)} = -\mu B \tanh(\mu B \beta). \quad (3.21)$$

We can see how this energy varies in figure 3.2. We can also look at the heat capacity of the paramagnet,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,B} = N k_B (\mu B \beta)^2 \operatorname{sech}^2(\mu B \beta) \quad (3.22)$$

which we visualise in figure 3.3.

For N non-interacting spins, we can see that the energy will be $\langle E \rangle = N \langle \varepsilon_1 \rangle$. However, this does not hold for entropy. In order to progress to a paramagnet with N spins, we require the partition function of the entire system, let us call this Z_N . This is given by,

$$Z_N = (Z_1)^N. \quad (3.23)$$

So,

$$Z_N = (e^{\mu B \beta} + e^{-\mu B \beta})^N \quad (3.24)$$

and the Helmholtz free energy is,

$$F = -N k_B T \ln(Z_1) \quad (3.25)$$

the entropy is,

$$\langle S \rangle = N k_B (\ln(2 \cosh(\mu B \beta)) - \mu B \beta \tanh(\mu B \beta)) \quad (3.26)$$

and the average magnetic dipole is,

$$\langle m \rangle = - \langle E \rangle / B. \quad (3.27)$$

3.4 Adiabatic Demagnetisation

Let us consider a system initially at a particular energy, we want to know its behaviour as we change temperature, energy, and/or heat. The energy is given by,

$$dE = -m dB - B dm. \quad (3.28)$$

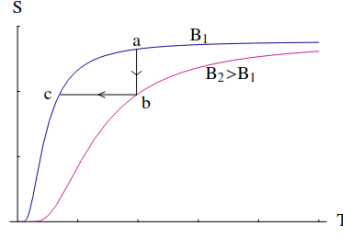


Figure 3.5

where $m dB$ indicates work and $B dm$ indicates heat. Consider figure 3.4. If we perform work on the magnet, we find that we do not change the spin ratio, so we decrease the magnetic field within the paramagnet, increase its energy, and decrease its temperature. This process is known as *adiabatic demagnetisation*. If we look at figure 3.5, we find that we can change the temperature of a paramagnet by magnetising and demagnetising it. We lower the temperature in two steps,

1. Have a sample in contact with a heat bath at T_1 , and increase the magnetic field to B_1 , known as *isothermal magnetisation*.
2. Reduce the field to B_1 slowly, to perform adiabatic demagnetisation. The temperature of the sample has now been decreased without changing the entropy or magnetisation.

Let us note that we can perform this process for subsystems, however it will take infinite steps to reach 0K. There is always a minimum energy ground state ε , and for $k_B T \ll \varepsilon$, the probability of being in the ground state tends to 1 and the entropy tends to 0.

For $T \rightarrow \infty$, we find that $S \rightarrow \text{const}$, however this is only the case for systems with a finite number of microstates. In this case, the probability of each state is equal.

3.5 Energies of Diatomic Molecules

3.5.1 Vibrational Energies

The energy levels for a simple harmonic oscillator are,

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \hbar \omega, n \in \mathbb{Z} \quad (3.29)$$

For a single oscillator, the partition function is,

$$\begin{aligned} Z_1 &= e^{-\varepsilon_0 \beta} + e^{-\varepsilon_1 \beta} + e^{-\varepsilon_2 \beta} + \dots \\ &= e^{-\frac{1}{2} \hbar \omega \beta} \sum_{n=0}^{\infty} e^{-n \hbar \omega \beta} \end{aligned} \quad (3.30)$$

which is a geometric series, so can be evaluated,

$$Z_1 = \frac{e^{-\frac{1}{2} \hbar \omega \beta}}{1 - e^{-\hbar \omega \beta}} = \frac{1}{2 \sinh\left(\frac{\hbar \omega \beta}{2}\right)}. \quad (3.31)$$

From this we can evaluate the average energy,

$$\begin{aligned} \langle E_1 \rangle &= \frac{\partial}{\partial \beta} \left[\ln 2 + \ln \left(\frac{\hbar \omega \beta}{2} \right) \right] \\ &= \frac{\hbar \omega}{2} \frac{\cosh\left(\frac{\hbar \omega \beta}{2}\right)}{\sinh\left(\frac{\hbar \omega \beta}{2}\right)} = \frac{\hbar \omega}{2} \coth \left(\frac{\hbar \omega \beta}{2} \right). \end{aligned} \quad (3.32)$$

Analysing the limits as $T \rightarrow 0$, we find that $\coth\left(\frac{\hbar \omega \beta}{2}\right) \rightarrow 1$, and $E \rightarrow \frac{\hbar \omega}{2}$, which is the ground state, and what we expect at low temperatures. In the limit $T \rightarrow \infty$, $\coth\left(\frac{\hbar \omega \beta}{2}\right) \rightarrow \frac{1}{x}$, thus $E \rightarrow k_B T$, which is what we expect as this is a result of the equipartition theorem.

3.6 Translational Energies of a Molecule in an Ideal Gas

Consider a particle confined in a 3D box, i.e., in a potential,

$$V(x, y, z) = \begin{cases} \infty & x > L_x \\ \infty & y > L_y \\ \infty & z > L_z \\ 0 & \text{Otherwise} \end{cases} \quad (3.33)$$

for which the Schrodinger equation is,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi \quad (3.34)$$

with boundary conditions, $\psi(L_x, L_y, L_z) = \psi(0, 0, 0) = \psi(L_x, 0, 0) = \dots = 0$. Thus, the solution will have a form,

$$\psi = A \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right). \quad (3.35)$$

And our energy levels are given by,

$$E = \frac{\hbar^2 \pi^2}{2m} \underbrace{\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)}_{k^2} \quad (3.36)$$

where $k = |\mathbf{k}|$. The partition function is then given by,

$$Z_1 = \sum_{n_x, n_y, n_z}^{\infty} e^{-E(n_x, n_y, n_z) \beta} \quad (3.37)$$

which we can separate into 3 sums,

$$\begin{aligned} Z_1 &= \left(\sum_{n_x=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} n_x^2 \beta} \right) \left(\sum_{n_y=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} n_y^2 \beta} \right) \left(\sum_{n_z=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2m} n_z^2 \beta} \right) \\ &= \left(\int_0^{\infty} e^{-\frac{\hbar^2}{2m} \beta k_x^2} \frac{L_x}{\pi} dk_x \right) \left(\int_0^{\infty} e^{-\frac{\hbar^2}{2m} \beta k_y^2} \frac{L_y}{\pi} dk_y \right) \left(\int_0^{\infty} e^{-\frac{\hbar^2}{2m} \beta k_z^2} \frac{L_z}{\pi} dk_z \right) \end{aligned} \quad (3.38)$$

which are Gaussian integrals,

$$\begin{aligned} Z_1 &= \frac{L_x L_y L_z}{2^3 \pi^3} \left(\frac{2m\pi}{\hbar^2 \beta} \right)^{\frac{3}{2}} \\ &= V \underbrace{\left(\frac{mk_B T}{2\pi \hbar^3} \right)^{\frac{3}{2}}}_{n_Q} \end{aligned} \quad (3.39)$$

where $n_Q = n_Q(T)$ known as the *quantum concentration*, with dimensions of number density. We were able to convert the sums to integrals as even for every low temperatures, the energy spacing is much higher than the spacing between the energy levels, so we can use the continuum limit. We can then proceed to find the average energy,

$$\langle E_1 \rangle = \frac{3}{2} k_B T \quad (3.40)$$

as expected.

3.6.1 The density of states

Let us return to the particle in a box, and let's assume we cannot factorise the integral. We can then evaluate the integral over k -space in spherical polars,

$$\begin{aligned} Z_1 &= \frac{V}{\pi^3} \int_0^{\infty} \int_0^{\frac{\pi}{2}} d\theta_k \int_0^{\frac{\pi}{2}} d\phi_k k^2 e^{-\epsilon(k) \beta} \sin \theta_k dk \\ &= \frac{V}{\pi^3} 4\pi \int_0^{\infty} k^2 e^{-\frac{\hbar^2 \beta}{2m} k^2} dk \\ &= V g_s n_Q \end{aligned} \quad (3.41)$$

as before. It is useful to write this integral as,

$$Z_1 = \int_0^\infty g(k) e^{-\varepsilon(k)\beta} dk \quad (3.42)$$

where $g(k)$ is a degenerate factor, representing many states with the same energy, but different direction in k -space. We can find $g(k)$ by considering how many states lie in a thin strip $k \rightarrow k + dk$, i.e., the volume of a spherical shell in k space and the volume per state,

$$g(k) = \frac{1}{8} 4\pi^2 k^2 dk \cdot \frac{1}{\frac{\pi}{L_x} \frac{\pi}{L_y} \frac{\pi}{L_z}} = \frac{V}{2\pi^2} k^2 dk. \quad (3.43)$$

If we have spin in our particles, we require k_x, k_y, k_z and m_s to full specify the state. The degenerate factor is then,

$$g(k) = \frac{V g_s}{2\pi^2} k^2 \quad (3.44)$$

where $g_s = 2s + 1$.

3.6.2 Maxwell Boltzmann Distribution

The probability of finding a particle in k space,

$$P(k \rightarrow k + dk) = g(k) \frac{e^{-\varepsilon\beta}}{Z_1} dk \quad (3.45)$$

and similarly, the probability of finding a particle with a given velocity is,

$$P(v \rightarrow v + dv) \propto v^2 e^{-\frac{1}{2}mv^2\beta} \quad (3.46)$$

which is the Maxwell-Boltzmann distribution.

3.7 Factorisation of the partition function

The total partition function for a single particle is the product over each degree of freedom which contributes, i.e.,

$$Z_1^{\text{tot}} = \prod_f Z^f = Z_1^{\text{trans}} Z_2^{\text{vib}} Z_3^{\text{rot}} \quad (3.47)$$

and thus the total energies are the sum of the contribution from each degree of freedom,

$$\varepsilon_1 = \varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}}. \quad (3.48)$$

3.8 Equipartition Theorem

For $T \gg E_{\text{spacing}}/k_B$,

$$E \rightarrow n_f \cdot \frac{1}{2} k_B T. \quad (3.49)$$

where n_f are the number of degrees of freedom which contribute quadratically in coordinate or momentum. These are summarised below,

Type	Contribution / $\varepsilon \propto$	n_f
Translational	$p_x^2 + p_y^2 + p_z^2$	3
Rotational	$\frac{1}{2}\omega_1^2 I_1 + \frac{1}{2}\omega_2^2 I_2$	2
Vibrational	$\frac{1}{2}kx^2 + \frac{1}{2}mv^2$	2

For linear degrees of freedom, e.g., relativistic kinetic energy where $\varepsilon \propto pc$, $E \rightarrow n_f \cdot k_B T$.

For $T \ll E_{\text{spacing}}/k_B$, the degrees of freedom are "frozen out", and thus their contributions to the heat capacity $C_V \rightarrow 0$.

3.8.1 Heat Capacity of a Crystal

Let us consider a crystal as $3N$ independent oscillators. We have,

$$Z = (Z_1^{\text{vib}})^{3N} \quad \langle E \rangle = \frac{3}{2} N \hbar \omega \cosh\left(\frac{1}{2} \hbar \omega \beta\right) \quad C_V = \frac{3}{4} N k_B (\hbar \omega \beta)^2 \sinh\left(\frac{1}{2} \hbar \omega \beta\right) \quad (3.50)$$

At $T \rightarrow \infty$, we find $C_V \rightarrow 3Nk_B (\hbar \omega \beta)^2 e^{-\hbar \omega \beta}$. However, this does not agree with experiment, and where $C_V \propto T^3$. In order to get a complete picture we would need to consider modelling the crystal as a chain of vibrating molecules with multiple nodes.

3.9 *N*-Particle Partition Function for Indistinguishable Particles

Let us recall the partition function for a single molecule under translational degrees of freedom,

$$Z_1 = V g_s \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} = V g_s n_\phi. \quad (3.51)$$

We may expect that $Z_N = (Z_1)^N$, however this is not correct. If we do this, we find that F , which is an extensive variable, depends on $\ln(V)$, so does not behave extensively. This is because there are less microstates, as some of them become indistinguishable. We can fix this by supposing that, *if* the number of single particle states available is much greater than the number of particles, then almost all N -particle microstates have the particles all in different levels. We then have that $(Z_1)^N$ overcounts the number of microstates by $N!$, so we have,

$$Z_N \simeq \frac{(Z_1)^N}{N!}. \quad (3.52)$$

3.9.1 Diatomic Molecules

We can extend the N -particle partition function for indistinguishable particles to diatomic molecules, by,

$$\begin{aligned} Z_N &= \frac{(Z_1^{\text{Trans}})^N (Z_1^{\text{Rot}})^N (Z_1^{\text{Vib}})^N}{N!} \\ &= Z_N^{\text{Trans}} (Z_1^{\text{Rot}})^N (Z_1^{\text{Vib}})^N \end{aligned} \quad (3.53)$$

3.10 Ideal Gas in the Classical Limit

We will be considering a monatomic gas. We can conclude whether or not the equation (3.52) is a good approximation if we consider how likely it is for two atoms to be in the same energy level. For an ideal gas, we can calculate the number of energy levels below $2k_B T$ from,

$$\int_0^{k_m a x} g(k) dk \quad (3.54)$$

where,

$$\frac{\hbar^2 k_m a x^2}{2m} = 2k_B T \quad (3.55)$$

and we find, that it equals $2.1 n_Q V$. We see then that the quantum concentration n_Q is a measure of the states available, and we can use the approximation (3.52) if $\frac{N}{V} = n < n_Q$. We can then proceed to find the Helmholtz free energy by equation (3.18),

$$\begin{aligned} F &= -k_B T \ln Z_N = -k_B T (\ln Z_N - \ln N!) \\ &= -k_B T (N \ln V g_s n_Q - N \ln N + N) \\ &= -N k_B T \left(\ln \left(\frac{V g_s n_Q}{N} \right) + 1 \right) \\ &= -N k_B T \left(\ln \left(\frac{g_s n_Q}{n} \right) + 1 \right). \end{aligned} \quad (3.56)$$

Let us now consider the pressure by a Maxwell relation as in equation (3.19),

$$\begin{aligned} P &= - \left(\frac{\partial F}{\partial V} \right)_{T,N} \\ &= \frac{Nk_B T}{V} \implies PV = Nk_B T \end{aligned} \quad (3.57)$$

thus we have derived the ideal gas law. We can further consider the entropy by $S = -\frac{\partial F}{\partial T}$, where we find,

$$\boxed{S = Nk_B \left(\ln \frac{g_s n_Q}{n} + \frac{5}{2} \right)} \quad (3.58)$$

which is known as the Sackur-Tetrode equation. Let us note that we can re-write equation (3.58) to be,

$$S = Nk_B \left(\ln V + \frac{3}{2} \ln T + \text{Const.} \right) \quad (3.59)$$

which is exactly as in classical thermodynamics. We may say that this expression is invalid as we can only measure the difference in entropy, however, if we consider the entropy from a starting point of a very low energy, we can consider the absolute entropy, i.e.,

$$\int_{T_0}^T \frac{dQ}{T} = S(T) - S(T_0) \simeq S(T) \quad (3.60)$$

as for $T_0 \rightarrow 0$, $S(T_0) \rightarrow 0$. However, let us note that the Sackur-Tetrode equation is only valid in the classical limit, i.e., $n \ll n_Q(T)$.

3.10.1 Chemical potential of an ideal gas

Let us recall the formulation for chemical potential,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} \quad \mu = \frac{G}{N} \quad (3.61)$$

where $G = E - TS + PV$ is the Gibbs free energy. We can calculate the Gibbs energy by

$$G = \frac{3}{2} Nk_B T - Nk_B T \left(\ln \frac{g_s n_Q}{n} + \frac{5}{2} \right) + Nk_B T \quad (3.62)$$

where we then obtain,

$$\boxed{\mu = -k_B T \ln \frac{g_s n_Q}{n}} \quad (3.63)$$