Statistical Physics

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Contents

0 Introduction

0.1 Preface

These notes are predominantly based on the lectures given by Professor Clark in Michaelmas 2023, following the content of *Statistical Physics* by *T. Guénault*. They are not intended to be complete and, in some places, they diverge a little from the course. In particular, content from the last two lectures on Bose-Einstein gases and condensate is missing.

0.2 Useful Results from Probability

For n distinguishable particles, there are $n!$ ways of arranging them. There are

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} \tag{0.1}$$

ways of splitting them into two groups of sizes $n-k$ and k. This leads us to the binomial distribution.

Definition (Binomial distribution)**.** The discrete probability distribution of the number of successes in sequences of n boolean (success/failure) experiments, each with a probability of success p. The probability of getting exactly k successes in n independent trials is

$$\Pr(k; n, p) = \binom{n}{k} p^k (1-p)^{n-k}. \tag{0.2}$$

1 Basic Ideas

The basic task of statistical physics is to take a system in a well-defined thermodynamic state and to compute the various thermodynamic properties of that system from an (assumed) microscopic model. We start by defining some useful terms.

Definition (The macrostate)**.** The macrostate is a specification of the thermodynamic state of a system based on a bulk property. From its macrostate, we can extract all the information needed to make its thermodynamic state well-defined, but no more.

Definition (The microstate)**.** The microstate is a complete specification of the state of a system based on its microscopic properties. For a given macrostate, there is an enormous number, Ω, of possible microstates.

Definition (Statistical ensemble)**.** A statistical ensemble is an idealisation consisting of a large number of virtual copies (often infinitely many) of the system, each copy representing a possible state the real system could be in.

Definition (Microcanonical ensemble)**.** The microcanonical ensemble is a statistical ensemble that represents the possible states of a system for which the volume, number of particles and total energy are specified.

Definition (Canonical ensemble)**.** The canonical ensemble is a statistical ensemble that represents the possible states of a system for which the volume, number of particles and temperature are specified.

Definition (Chemical potential)**.** The chemical potential, μ, is another word for the Fermi energy - the energy of the highest occupied state.

Definition (Grand canonical ensemble)**.** The grand canonical ensemble is a statistical ensemble that represents the possible states of a system for which the volume, chemical potential and temperature are specified.

Definition (Distributions)**.** Distributions are an intermediate description of different sets of microstates within the ensemble. We will use two alternative definitions of a distribution:

1. *Distribution in states*: A set of numbers $\{n_i\}$ where the distribution number n_i is defined as the number of particles in state i, which has energy ε_i.

2. *Distribution in levels*: A set of numbers $\{n_i\}$ where the distribution number n_i is defined as the number of particles in level i, which has energy ε_i and degeneracy g_i.

In the first case, the total energy, U, is given by

$$U = \sum_i n_i \varepsilon_i. \tag{1.1}$$

In the second case, however, we must account for degeneracy,

$$U = \sum_i n_i g_i \varepsilon_i. \tag{1.2}$$

In both cases, we have, of course,

$$N = \sum_i n_i. \tag{1.3}$$

1.1 Entropy and Microstates

To find an appropriate statistical description of some macrostate, we need to be able to count the number of possible microstates it describes.

Example 1. Suppose we have five *distinguishable* particles $\{A, B, C, D, E\}$, and we divide them into two piles. There are

$$\binom{5}{3} = \frac{5!}{3!2!} = 10 \tag{1.4}$$

ways of doing this ($\underline{ABC}\ \underline{DE}$, $\underline{ABD}\ \underline{CE}$ etc.). If we have five *indistinguishable* particles, then there is just 1 possible arrangement ($\underline{AAA}\ \underline{AA}$). $\triangle$

The number of microstates $\Omega(\{n_i\})$ for a distribution $\{n_i\}$ is

$$\Omega(\{n_i\}) = \frac{N!}{\prod_i n_i!}. \tag{1.5}$$

Boltzmann postulated that the entropy S of a system and the number of microstates Ω of a distribution are related,

$$S = k_B \ln \Omega. \tag{1.6}$$

Counting microstates is inherently combinatorial and, as such, we often have to calculate the log of a factorial to calculate S. A useful approximation, and one we will use frequently, is Stirling's,

$$\ln N! = N \ln N - N + \mathcal{O}(N) \approx N \ln N - N. \tag{1.7}$$

2 The Most Probable Distribution

A macrostate describes many possible distributions which, in turn, have many microstates associated with them. The number of microstates $\Omega(\{n_i\})$ for some possible distribution $\{n_i\}$ is its statistical weight. The distribution with the highest number of microstates (or, equivalently, the highest *entropy*) is most likely to be found. For a system with large N, the distribution of energy states becomes so steep that we can approximate the number of microstates Ω to the number of microstates of the most probable state.

Applying Stirling's approximation to Equation 1.6, we can link our microscopic definition of matter to entropy, a macroscopic property,

$$S(\{n_i\}) = -N k_B \sum_i \frac{n_i}{N} \ln \frac{n_i}{N}. \tag{2.1}$$

Defining $p_i \equiv n_i/N$ as the probability of finding a particle in state i, we can make the link from microscopic probability to macroscopic entropy explicit,

$$S(\{n_i\}) = -N k_B \sum_i p_i \ln p_i. \tag{2.2}$$

2.1 Distinguishable Particles - Boltzmann

Let's find the most probable distribution for a system of N distinguishable particles with non-degenerate energy levels ε_i. To find the most probable distribution, we can use the method of Lagrange multipliers, maximising S as a function of $\{n_i\}$ subject to the distribution constraints defined in Equations 1.1 to 1.3. Finding the Euler-Lagrange equation for each state occupancy n_i, we find

$$\frac{\partial}{\partial n_i} \left[N \ln N - \sum_i n_i \ln n_i - \alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i \right] = 0, \tag{2.3}$$

where α, β are Lagrange multipliers. Solving this, we find

$$n_i = \mathrm{e}^{-1-\alpha} \mathrm{e}^{-\beta \varepsilon_i}. \tag{2.4}$$

This looks familiar! To determine the Lagrange multipliers, we first apply the particle number constraint from Equation 1.3,

$$N = \sum_i n_i = \mathrm{e}^{-1-\alpha} \sum_i \mathrm{e}^{-\beta \varepsilon_i} \tag{2.5}$$

which implies

$$e^{-1-\alpha} = \frac{N}{\sum_i \exp{-\beta\varepsilon_i}} = \frac{N}{Z}, \tag{2.6}$$

were we have defined the partition function Z,

$$Z \equiv \sum_i e^{-\beta\varepsilon_i}, \tag{2.7}$$

which 'normalises' the probability a particle is in a given state.

Now, we apply the internal energy constraint from Equation 1.1,

$$U = \sum_i n_i\varepsilon_i = \frac{N}{Z} \sum_i \varepsilon_i e^{-\beta\varepsilon_i}. \tag{2.8}$$

Differentiating with respect to the Lagrange multiplier β, we find

$$\frac{\mathrm{d}}{\mathrm{d}\beta}Z = \sum_i \varepsilon_i e^{-\beta\varepsilon_i}, \tag{2.9}$$

and hence find a new relation between the macroscopic and microscopic pictures,

$$\begin{aligned} U &= -\frac{N}{Z}\frac{\mathrm{d}Z}{\mathrm{d}\beta} \\ &= -N\frac{\mathrm{d}}{\mathrm{d}\beta}\ln Z, \end{aligned} \tag{2.10}$$

where we have used the chain rule in reverse in the last step. Looking at this equation, we can deduce the physical meaning of the multiplier β - it must depend on temperature T in some way. We choose to define it as [1]

$$\beta \equiv \frac{1}{k_B T}. \tag{2.11}$$

All together, we arrive at the Boltzmann distribution,

$$f_{\mathrm{B}}(\varepsilon_i) \equiv n_i = \frac{N}{Z}e^{-\beta\varepsilon_i} = \frac{N}{Z}e^{-\varepsilon_i/k_B T}. \tag{2.12}$$

2.2 Distinguishable Particles with Degeneracy - Maxwell-Boltzmann

Consider a similar system of N distinguishable particles, but, now, let each energy level ε_i have degeneracy g_i. The number of microstates of a distribution $\{n_i\}$ is now

$$\Omega(\{n_i\}) = N! \prod_i \frac{g_i^{n_i}}{n_i!}. \tag{2.13}$$

Following the same process as above, we can find the distribution that minimises entropy. Applying Stirling's approximation to the entropy equation, and subtracting the constraints, the function to minimise is

$$\ln N! + \sum_i \left(n_i \ln g_i - n_i \ln n_i + n_i - \alpha n_i - \beta n_i g_i \right). \tag{2.14}$$

---

[1]Note that, annoyingly, Guénault defines β as $-1/k_B T$, so keep an eye out for extra/missing minus signs.

Finding the Euler-Lagrange equations for this function and solving for α and β, we arrive at the most probable distribution

$$f_{\mathrm{MB}}(\varepsilon_i) \equiv \frac{n_i}{g_i} = \frac{N}{Z}e^{-\beta\varepsilon_i}, \tag{2.15}$$

the familiar Maxwell-Boltzmann distribution function.

2.3 Fermions - Fermi-Dirac

Once again, let's repeat the above analysis. This time, we consider a system of N (indistinguishable) fermions with energy levels ε_i and degeneracy g_i. By Pauli's exclusion principle, each state can be occupied by one fermion at most. For a given energy level ε_i, we want to know the number of ways the g_i states can be occupied, i.e. the number of microstates associated with that energy level. There are n_i particles with energy ε_i, and each one can occupy any of the g_i states. This matches the problem solved by the binomial theorem, and so there are

$$\Omega(\varepsilon_i) = \frac{g_i!}{n_i!(g_i - n_i)!} \tag{2.16}$$

ways of dividing the different states. From this, the total number of microstates corresponding to an allowable distribution $\{n_i\}$ is therefore given by

$$\Omega(\{n_i\}) = \prod_i \frac{g_i!}{n_i!(n_i - g_i)!}, \tag{2.17}$$

where we have multiplied the number of microstates associated with each energy level. From this, the same method of Lagrange multipliers can be applied to arrive at the Fermi-Dirac distribution function,

$$f_{\mathrm{FD}}(\varepsilon_i) \equiv \frac{n_i}{g_i} = \frac{1}{\exp(\alpha + \beta\varepsilon_i) + 1}, \tag{2.18}$$

where the Lagrange multiplier α is adjusted to give the correct number of gas particles.

2.4 Bosons - Bose-Einstein

For the last time, let's follow the same process. Consider a system of N (indistinguishable) bosons with energy levels ε_i and degeneracy g_i. Pauli's exclusion principle doesn't apply to bosons; each state can contain many particles. First, calculate the contribution from the ith group of the distribution. This group has g_i states containing n_i identical particles with no restriction on occupation numbers.

Example 2. Imagine we have 5 identical balls and 3 groups to put them in, how many ways can we arrange the balls? Each group could contain anywhere from 0 to 5 balls. Some possible arrangements are:

$$\circ | \circ\ \circ | \circ\ \circ$$

$$\circ\ \circ\ |\ \circ\ |\ \circ\ \circ$$

$$\circ \, \circ \, \circ | \circ \, \circ |$$

In total, there are $5 + (3 - 1) = 7$ symbols, with

$$\frac{(5 + (3 - 1))!}{5!(3 - 1)!} \tag{2.19}$$

unique ways of arranging them. $\triangle$

We can generalise this example to help solve our boson counting problem. Our n_i bosons map to n_i circles, and our g_i degenerate states map to g_i groups, so there are $(g_i - 1)$ vertical lines. The ith group therefore has

$$\Omega(\varepsilon_i) = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \approx \frac{(n_i + g_i)!}{n_i! g_i!}, \tag{2.20}$$

where we have used that, in most cases, $n_i, g_i \gg 1$. The (slightly approximate) number of microstates for an allowable distribution is therefore given by

$$\Omega(\{n_i\}) = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!}. \tag{2.21}$$

By the same process as above, it can be shown that the Bose-Einstein distribution function minimises entropy for this system, where

$$f_{\mathrm{BE}}(\varepsilon_i) \equiv \frac{n_i}{g_i} = \frac{1}{\exp(\alpha + \beta \varepsilon_i) - 1}, \tag{2.22}$$

where, again, the Lagrange multiplier α is adjusted to give the correct number of gas particles.

2.5 Distribution Functions Summary

A distribution function gives the fractional occupancy of an energy state. The Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distribution functions are remarkably similar, differing only by the choice of $-1, 0, +1$ in the denominator.

Definition (Dilute limit)**.** Also called the classical or Maxwell-Boltzmann limit, in the dilute limit the probability of a state being occupied is small. Simply put, there are fewer particles than 'places they can be put'.

In the *dilute* limit, the distribution functions for fermions (Fermi-Dirac) and bosons (Bose-Einstein) both tend to the distribution function for classical particles (Maxwell-Boltzmann). This makes sense; in our treatment of fermions, we applied the Pauli-exclusion principle which has negligible effects when most states are unoccupied anyway. In our treatment of bosons, we accounted for the multiple occupancy of a single state, which becomes unnecessary in the dilute limit. More

explicitly, in the dilute limit $g_i \gg n_i$. For fermions,

$$
\begin{aligned}
\Omega_{\mathrm{FD}}(\{n_i\}) &= \prod_i \frac{g_i!}{n_i!(n_i - g_i)!} \\
&= \prod_i \frac{(g_i - n_i + 1)\dots(g_i - 1)g_i}{n_i!} \\
&\approx \prod_i \frac{g_i^{n_i}}{n_i!}.
\end{aligned}
\tag{2.23}
$$

For bosons,

$$
\begin{aligned}
\Omega_{\mathrm{BE}}(\{n_i\}) &= \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \\
&= \prod_i \frac{(g_i + 1)\dots(g_i + n_i)}{n_i!} \\
&\approx \prod_i \frac{g_i^{n_i}}{n_i!}.
\end{aligned}
\tag{2.24}
$$

For classical, distinguishable particles, we had

$$
\Omega_{\mathrm{MB}}(\{n_i\}) = N! \prod_i \frac{g_i^{n_i}}{n_i!}.
\tag{2.25}
$$

Clearly, in the dilute limit, the number of microstates of bosons and fermions is similar to that of classical particles, differing only by a factor of $N!$, which accounts for distinguishability.

3   Thermodynamic Functions

We have talked about internal energy U and defined entropy S and the partition function Z. Let's define another thermodynamic function, the Helmholtz free energy.

Definition (Helmholtz free energy). The Helmholtz free energy F is a thermodynamic potential that measures the useful work obtainable from a closed, isothermal (at constant temperature) thermodynamic system. We define

$$
F \equiv U - TS
\tag{3.1}
$$

Substituting the statistical formulae for U and S of localised particles, we can write

$$
\begin{aligned}
F &= \sum_i n_i \varepsilon_i - k_B T \ln \Omega \\
&= \sum_i n_i \varepsilon_i - k_B T \left(N \ln N - \sum_i n_i \ln n_i \right) \\
&= -N k_B T \ln Z.
\end{aligned}
\tag{3.2}
$$

In the last step, we inserted the logarithm of Equation 2.12 to obtain

$$
\ln n_j = \ln N - \ln Z - \varepsilon_i / k_B T.
\tag{3.3}
$$

3.1 Examples

Example 3 (Harmonic oscillator). Consider a system of 1D harmonic oscillators with energy levels given by

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n \in \mathbb{N}. \tag{3.4}$$

Let's calculate the thermodynamic properties of this quantum system. We start by calculating the partition function,

$$
\begin{aligned}
Z &= \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n} \\
&= \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} \\
&= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} \\
&= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n
\end{aligned}
\tag{3.5}
$$

The series in the last step is geometric and the modulus of the ratio between terms is less than one! Thus, applying the formula for the infinite sum of a geometric series, we find

$$Z = \frac{\exp\left(-\beta\hbar\omega/2\right)}{1 - \exp\left(-\beta\hbar\omega\right)}. \tag{3.6}$$

Now we have Z, we can calculate free energy F and internal energy U. Starting with F, we have

$$
\begin{aligned}
F &= -\frac{N}{\beta}\ln Z \\
&= -\frac{N}{\beta}\left(-\beta\frac{\hbar\omega}{2} - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right). \\
&= \frac{N\hbar\omega}{2} + \frac{N}{\beta}\ln\left(1 - e^{-\beta\hbar\omega}\right).
\end{aligned}
\tag{3.7}
$$

Similarly for U,

$$
\begin{aligned}
U &= -N\frac{\mathrm{d}}{\mathrm{d}\beta}\ln Z \\
&= N\hbar\omega\left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1}\right).
\end{aligned}
\tag{3.8}
$$

From here, it is simple to calculate entropy S and heat capacity C_V

$$S = \frac{1}{T}(U - F), \tag{3.9}$$

and

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \tag{3.10}$$

where the subscript indicates volume V is held constant when differentiating. $\triangle$

Example 4 (Two distinguishable particles). Consider two distinguishable particles allowed in two energy levels $\varepsilon_1, \varepsilon_2$. There are 4 possible microstates: $(\varepsilon_1, \varepsilon_1)$, $(\varepsilon_1, \varepsilon_2)$, $(\varepsilon_2, \varepsilon_1)$, $(\varepsilon_2, \varepsilon_2)$.

We can calculate the partition function directly,

$$
\begin{aligned}
Z_2 &= \sum_i e^{-\beta E_i} \\
&= e^{-2\beta\varepsilon_1} + 2e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-2\beta\varepsilon_2} \\
&= \left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}\right)^2 \\
&= (Z_1)^2,
\end{aligned}
\tag{3.11}
$$

where Z_1 is the partition function for a single, isolated particle allowed in two energy levels $\varepsilon_1, \varepsilon_2$.
△

This is a useful result; we have shown that, for *distinguishable* particles, the partition function multiplies! Generalising to a system of N distinguishable particles each represented by the single particle partition function Z_1, the partition function is given by

$$
Z_N = (Z_1)^N.
\tag{3.12}
$$

For a system of N classical *indistinguishable* particles, we can write the partition function as

$$
Z_N = \frac{1}{N!}(Z_N)^N,
\tag{3.13}
$$

where the factor of $1/N!$ removes the permutations of particles [2]. This result isn't exact. To understand why, consider an identical system to the one above, but with indistinguishable particles: there would be just 3 possible microstates, as $(\varepsilon_1, \varepsilon_2)$ and $(\varepsilon_2, \varepsilon_1)$ are equivalent, and the partition function would be

$$
Z_2 = e^{-2\beta\varepsilon_1} + e^{-2\beta(\varepsilon_1+\varepsilon_2)} + e^{-2\beta\varepsilon_2}.
\tag{3.14}
$$

Equation 3.13, on the other hand, yields

$$
Z_2 = \frac{1}{2}e^{-2\beta\varepsilon_1} + e^{-2\beta(\varepsilon_1+\varepsilon_2)} + \frac{1}{2}e^{-2\beta\varepsilon_2}.
\tag{3.15}
$$

Example 5 (Localised, distinguishable spins in a magnetic field). A particle with spin magnetic moment μ in a magnetic field B has energy $\varepsilon_\pm = \pm\mu B$, where the sign is positive if the fields are aligned and negative if they are anti-aligned. This one-spin system has a partition function

$$
\begin{aligned}
Z &= e^{-\beta\mu B/2} + e^{\beta\mu B/2} \\
&= e^{\beta\mu B}\left(1 + e^{-\beta\mu B}\right).
\end{aligned}
\tag{3.16}
$$

As we said earlier, Z 'normalises' the probability of finding a particle in a given state. Hence,

$$
P(\varepsilon_+) = \frac{1}{1 + \exp(-\beta\mu B)} = \begin{cases} 1 & \beta \to \infty \\ \frac{1}{2} & \beta \to 0 \end{cases}
\tag{3.17}
$$

---

[2] I have written this section as it was taught, but I find it a bit misleading. As far as I can tell, the Gibbs factor $1/N!$ comes from the Gibbs paradox, see Section 5.3.4, and is a way of obtaining the correct answers in classical thermodynamics. It doesn't arise from any real consideration of (in)distinguishability, despite what was written above.

$$P(\varepsilon_-) = \frac{\exp(-\beta\mu B)}{1 + \exp(-\beta\mu B)} = \begin{cases} 0 & \beta \to \infty \\ 1 & \beta \to 0. \end{cases} \tag{3.18}$$

For a system of N distinguishable spins, recalling Z multiplies for distinguishable particles, the magnetisation M is therefore

$$\begin{aligned} M &= N\left(P(\varepsilon_+)(\mu) + P(\varepsilon_-)(-\mu)\right) \\ &= N\mu\tanh(\beta\mu B/2). \end{aligned} \tag{3.19}$$

As in Example 3, we can use our Z to find the internal energy, free energy, entropy and specific heat of the system. From these results, interesting phenomena arise such as cooling by adiabatic demagnetisation: a magnetic is cooled by reducing its magnetisation adiabatically. $\triangle$

4 The Density of States

Consider a cube of macroscopic length a. We want to find the degeneracy of a particle with energy ε. Starting in one dimension, consider the particle trapped in a 1D box of length a, so

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \tag{4.1}$$

with wavefunction

$$\psi_k = A\sin(kx), \quad \text{where } k = \frac{n\pi}{a}, n \in \mathbb{Z}^+. \tag{4.2}$$

For some small δk, the number of states between k and $k + \delta k$ is given by

$$\begin{aligned} g(k)\delta k &= \frac{n(k + \delta k) - n(k)}{\delta k}\delta k \\ &= \frac{\mathrm{d}n(k)}{\mathrm{d}k}\delta k, \end{aligned} \tag{4.3}$$

where $n(k')$ is the number of states with $|k| \leq k'$. Defining the separation between points in k-space as π/a^3, it follows that

$$n(k) = \frac{ka}{\pi}. \tag{4.4}$$

From Equation 4.3, we find the density of states in one-dimension to be

$$g(k)\delta k = \frac{a}{\pi}\delta k. \tag{4.5}$$

We can expand this notion to three dimensions, considering only the positive octant. Wavenumber k goes to wavevector $\mathbf{k} = (k_x, k_y, k_z) = \frac{\pi}{a}(n, m, l)$, where $n, m, l \in \mathbb{Z}^+$. The density of states in three dimensions is

$$g(k)\delta k = \frac{4\pi|\mathbf{k}|^2\delta k}{\left(\frac{\pi}{a}\right)^3} \cdot \frac{1}{8}, \tag{4.6}$$

where the factor of 1/8 comes from our considering only positive components of $\mathbf{k}$. It is worth noting that the density of states for electrons is double this, as a spin-up and a spin-down can occupy each energy state simultaneously.

---

[3]Note that this differs from other courses, where we define this as $2\pi/a$.

We can find the density of states in energy space via a change of variables. Rearranging Equation 4.1 for k in terms of ε, we find

$$k = \sqrt{\frac{2m\varepsilon}{\hbar^2}} \tag{4.7}$$

and

$$\delta k = \sqrt{\frac{m}{2\hbar^2\varepsilon}}\delta\varepsilon \tag{4.8}$$

Substituting in to Equation 4.6, we find

$$\tilde{g}(\varepsilon)\delta\varepsilon = \frac{a^3}{\pi^2}\left(\frac{m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{1}{2}\varepsilon\right)^{\frac{1}{2}}\delta\varepsilon \propto \varepsilon^{\frac{1}{2}}\delta\varepsilon, \tag{4.9}$$

where $\tilde{g}$ signifies the change of variables from k to ε.

5 Maxwell-Boltzmann Gases

5.1 Thermal Averages

Consider some single particle with an associated quantity Q_i when particle i is in energy state ε_i with occupancy n_i. For a bulk system of N particles, let ε_i have degeneracy g_i such that $n_i = f_i g_i$, where

$$f_i = \frac{N}{Z}e^{-\beta\varepsilon_i}, \tag{5.1}$$

with

$$Z = \sum_i g_i e^{-\beta\varepsilon_i}. \tag{5.2}$$

The average (expectation) value of Q is given by

$$\begin{aligned}\langle Q \rangle &= \frac{1}{N}\sum_{i=1}^{N} n_i Q_i \\ &= \frac{1}{Z}\sum_i g_i e^{-\beta\varepsilon_i} Q_i.\end{aligned} \tag{5.3}$$

In a bulk system, we can approximate these discrete properties with continuous ones. We swap g_i for $g(\varepsilon)\delta\varepsilon$ and n_i/g_i for $f(\varepsilon) = \delta n/g(\varepsilon)\delta\varepsilon$. This yields

$$\langle Q \rangle = \frac{1}{Z}\int_0^\infty g(\varepsilon)Q(\varepsilon)e^{-\beta\varepsilon}d\varepsilon, \tag{5.4}$$

where the bulk partition function is given by

$$Z = \int_0^\infty g(\varepsilon)e^{-\beta\varepsilon}d\varepsilon. \tag{5.5}$$

Example 6 (De Broglie thermal wavelength). As we found earlier, particles in a three-dimensional solid have a density of states given by

$$g(\varepsilon) \propto \varepsilon^{\frac{1}{2}} \iff g(k) \propto k^2. \tag{5.6}$$

Inserting this and their energy function (Equation 4.1), we find the partition function is given by

$$
\begin{aligned}
Z &= \frac{a^3}{(2\pi)^3} 4\pi \int_0^\infty k^2 \mathrm{e}^{-\beta \hbar^2 k^2 / 2m} \mathrm{d}k. \\
&= \left(\frac{a}{\lambda_{\mathrm{D}}} \right)^3,
\end{aligned} \tag{5.7}
$$

where

$$\lambda_{\mathrm{D}} \equiv h \sqrt{\frac{\beta}{2\pi m}} \tag{5.8}$$

is defined as the de Broglie thermal wavelength. λ_{D} has units of length and is a useful quantity that lets us determine if treating a system classically is appropriate. If $\lambda_{\mathrm{D}} \geq a$, the wavefunctions of neighbouring particles overlap and the system should be treated with quantum mechanics. If not, the system is in the dilute limit. $\triangle$

5.2 The Maxwell-Boltzmann Distribution of Speeds

Making a simple linear transformation, we can write the density of states as a function of speed. As before, a gas particle with wave-vector k and mass m has energy

$$\varepsilon = \frac{\hbar^2 k^2}{2m}. \tag{5.9}$$

Equating expressions for momentum, we have that $\hbar k = mv \implies k = mv/\hbar$. Substituting this for k, we find the familiar result for kinetic energy

$$\varepsilon = \frac{mv^2}{2}, \tag{5.10}$$

and

$$\delta\varepsilon = 2mv\delta v. \tag{5.11}$$

Substituting into Equation 4.9, we find the density of states as a function of speed v,

$$g(v)\delta v = Cv^2 \mathrm{e}^{-\beta mv^2/2} \delta v, \tag{5.12}$$

where C is a constant. Similarly, we can express the Maxwell-Boltzmann distribution as a function of speed,

$$f_{\mathrm{MB}}(v) = \frac{N}{Z} \mathrm{e}^{-\beta mv^2/2} \tag{5.13}$$

Sometimes, we want to calculate the most probable speed from a given distribution. We have a few different options:

1. $v_{\max} = \sqrt{2}v_T$, the most probable speed corresponding to the maximum of $g(v)$

2. $\bar{v} = \langle v \rangle = \sqrt{\frac{8}{\pi}} v_T$, the mean speed of the molecules obtained via the same method as in Section 5.1.

3. v_{rms}, the root-mean-square speed calculated by the same method ($v_{\mathrm{RMS}} = \sqrt{\langle v^2 \rangle}$).

v_{RMS} is particularly useful, since the average kinetic energy per molecule is given by

$$\bar{\varepsilon} = m v_{\mathrm{RMS}}^2 / 2 = \frac{3}{2} k_{\mathrm{B}} T, \tag{5.14}$$

as in the Equipartition theorem.

5.3 Thermodynamics

Let's calculate the properties of a gas of weakly interacting, spinless, *indistinguishable* particles in the limit of low density - an *ideal* gas - via Maxwell-Boltzmann statistics.

5.3.1 Internal Energy

First, subbing our expression for Z, Equation 5.12, into Equation 2.10, we derive the familiar expression for internal energy U,

$$U = \frac{3}{2} N k_{\mathrm{B}} T. \tag{5.15}$$

From this, the heat capacity at constant volume can be derived,

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N k_{\mathrm{B}}, \tag{5.16}$$

which, it must be noted, applies *only* in the dilute limit.

5.3.2 Entropy

Substituting Ω_{MB}, Equation 2.13, into Equation 1.6, we can derive the entropy,

$$\begin{aligned}
\frac{1}{k_{\mathrm{B}}} S &= \ln \Omega_{\mathrm{MB}} \\
&= \sum_i \left(n_i \ln g_i - \ln(n_i!) \right) \\
&= \sum_i n_i \left(\ln(g_i/n_i) + 1 \right) \\
&= \sum_i n_i \left(\ln Z - \ln N + \beta \varepsilon_i + 1 \right) \\
&= N(\ln Z - \ln N + 1) + \beta U \\
&= N \ln Z - \ln(N!) + \beta U
\end{aligned} \tag{5.17}$$

16

where Stirling's approximation was applied between the second and third lines, the Maxwell-Boltzmann distribution was substituted for n_i/g_i between the third and fourth lines, the internal energy was identified in the penultimate line, and Stirling's approximation was applied in reverse in the final line.

5.3.3 Free Energy

Now, we can evaluate the free energy,

$$F \equiv U - TS = -Nk_\mathrm{B}T(\ln Z - \ln N + 1) = -Nk_\mathrm{B}T \ln Z + k_\mathrm{B}T \ln(N!), \tag{5.18}$$

applying Stirling's approximation in reverse to obtain the final form. This closely resembles our expression of the free energy for localised, *distinguishable* particles in Equation 3.2, but with an extra $N!$ term as introduced earlier. This term, often called the Gibbs term, is where Maxwell-Boltzmann statistics differs from Boltzmann statistics.

5.3.4 The Gibbs Paradox

Consider a box of fixed volume V and temperature T containing a mixture of ideal gases A and B. If the two gases are different then they behave independently, occupying different states. The system has total microstates Ω, entropy S, free energy F and pressure P given by

$$\Omega = \Omega_A \cdot \Omega_B \tag{5.19}$$

$$S = S_A + S_B \tag{5.20}$$

$$F = F_A + F_B, \tag{5.21}$$

$$P = P_A + P_B, \tag{5.22}$$

where the subscripts refer to the properties each gas would have in the absence of the other. They behave as if the other gas is not present. If, however, we say gases A and B are identical, then we still have the same expression for pressure, but $S \neq 2S_A$ and $F \neq 2F_A$. The molecules are now competing for states, so the statistical properties of the second gas are modified by the existence of the first. Explicitly, gas A has entropy given by

$$
\begin{aligned}
S_A &= N_A k_\mathrm{B} \ln Z - k_\mathrm{B} \ln N_A! + \frac{U_A}{T} \\
&= N_A k_\mathrm{B} \ln Z - N_A k_\mathrm{B} \ln N_A + N_A k_\mathrm{B} + \frac{U_A}{T}.
\end{aligned}
\tag{5.23}
$$

The total entropy S of a system with two lots of gas A is given by

$$
\begin{aligned}
S &= 2N_A k_\mathrm{B} \ln Z - k_\mathrm{B} \ln(2N_A)! + \frac{2U_A}{T} \\
&= 2N_A k_\mathrm{B} \ln Z - 2N_A k_\mathrm{B} \ln(2N_A) + 2N_A k_\mathrm{B} + \frac{2U_A}{T} \\
&= 2N_A k_\mathrm{B} \ln Z - 2N_A k_\mathrm{B} \ln(N_A) - 2N_A k_\mathrm{B} \ln 2 + 2N_A k_\mathrm{B} + \frac{2U_A}{T} \\
&= 2S_A - 2N_A k_\mathrm{B} \ln 2.
\end{aligned}
\tag{5.24}
$$

The negative sign implies the competition between molecules for energy states lessens the degree of disorder.

5.4 Diatomic Gases

The energy of a diatomic molecule has contributions due to the electronic potential energy and translational, vibrational and rotational kinetic energy [4], i.e.

$$\varepsilon = \varepsilon_{\text{elec}} + \varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}}. \tag{5.25}$$

We can, therefore, write the single-particle partition function as

$$
\begin{aligned}
Z_1 &= \sum_{\text{all states}} e^{-\beta(\varepsilon_{\text{elec}} + \varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}})} \\
&= \sum_{\text{elec}} e^{-\beta\varepsilon_{\text{elec}}} \sum_{\text{trans}} e^{-\beta\varepsilon_{\text{trans}}} \sum_{\text{vib}} e^{-\beta\varepsilon_{\text{vib}}} \sum_{\text{rot}} e^{-\beta\varepsilon_{\text{rot}}} \\
&= Z_{\text{elec}} \cdot Z_{\text{trans}} \cdot Z_{\text{vib}} \cdot Z_{\text{rot}},
\end{aligned}
\tag{5.26}
$$

and the partition function of a gas of N identical diatomic molecules as

$$Z_N = \frac{1}{N!}(Z_{\text{elec}})^N \cdot (Z_{\text{trans}})^N \cdot (Z_{\text{vib}})^N \cdot (Z_{\text{rot}})^N. \tag{5.27}$$

Let's look at each contribution individually and evaluate their effect on the heat capacity.

5.4.1 Translational Contribution

There is nothing new here; we can describe the translational motion with the 'waves in a box' technique. The partition function is given by Equation 5.7, for reference (writing λ_D in full),

$$Z_{\text{trans}} = a^3 \left(\frac{mk_{\text{B}}T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{5.28}$$

where m is the mass of the diatomic molecule. The heat capacity is given by

$$
\begin{aligned}
C_{\text{trans}} &= \frac{\partial U}{\partial T} \\
&= \frac{3}{2}Nk_{\text{B}}.
\end{aligned}
\tag{5.29}
$$

5.4.2 Electronic Contribution

Let the electrons have energy levels $\{\varepsilon_i\}$, then

$$
\begin{aligned}
Z_{\text{elec}} &= e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1} + \dots \\
&= e^{-\beta\varepsilon_0}\left(1 + e^{-\beta(\varepsilon_1 - \varepsilon_0)} + \dots\right).
\end{aligned}
\tag{5.30}
$$

---

[4]This is a (good) approximation; we assume each energy term is independent.

The quantity $(\varepsilon_i - \varepsilon_0)$ is the i-th excitation energy. For many diatomic molecules, $(\varepsilon_1 - \varepsilon_0) \approx 10$ eV. If $T \ll 10^5$ K (s.t. $k_{\mathrm{B}} T \approx \varepsilon_1 - \varepsilon_0$), then a good approximation is

$$Z_{\mathrm{elec}} \approx \mathrm{e}^{-\beta \varepsilon_0}. \tag{5.31}$$

Hence, the energy of the system is approximately constant at ε_0, and the contribution C_{elec} to the heat capacity is negligible.

Truncating the sum as we have done here is a useful trick for approximating the partition function in the low-temperature limit.

5.4.3 Vibrational Contribution

The vibrational kinetic energy is quantised as

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega. \tag{5.32}$$

We have already calculated the thermodynamic functions for such a system in Example 3. For reference,

$$Z_{\mathrm{vib}} = \mathrm{e}^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega n} \tag{5.33}$$

The specific heat capacity is given by

$$C_{\mathrm{vib}} = \frac{N k_{\mathrm{B}} (\hbar\omega\beta)^2 \mathrm{e}^{\beta\hbar\omega}}{(\mathrm{e}^{\beta\hbar\omega} - 1)^2} \tag{5.34}$$

Each diatomic molecule has a temperature T_{vib} at which it oscillates the most. For $T \ll T_{\mathrm{vib}}$, the contribution to heat capacity is negligible. For higher T, the contribution increases. In the high-temperature limit, the sum is well-approximated by an integral,

$$
\begin{aligned}
(Z_{\mathrm{vib}})_{\mathrm{high\ T}} &\approx \mathrm{e}^{-\beta\hbar\omega/2} \int_0^{\infty} \mathrm{d}n\, \mathrm{e}^{-\beta\hbar\omega n} \\
&= \frac{1}{\beta\hbar\omega} \mathrm{e}^{-\beta\hbar\omega/2}.
\end{aligned}
\tag{5.35}
$$

From this, it can be shown that the contribution to the heat capacity in the high-temperature $(T \gg T_{\mathrm{vib}})$ is $N k_{\mathrm{B}}$. [5]

5.4.4 Rotational Contribution

Similarly, rotational energy is quantised. For a diatomic molecule with moment of inertia I, the energy due to rotation with total orbital angular momentum quantum number l is given by

$$\varepsilon_l = \frac{L^2}{2I} = \frac{l(l+1)\hbar^2}{2I}. \tag{5.36}$$

---

[5] In practice, diatomic gasses often dissociate before reaching such high temperatures, as the vibrational energy overcomes the bonding energy.
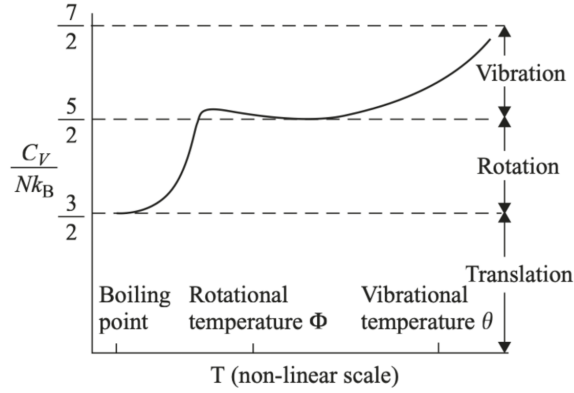
Figure 1: The variation of heat capacity C_V with temperature for a diatomic gas. (Copied form Statistical Physics by Guénault)

Making sure we account for degeneracy $(2l + 1)$ [6], the partition function is given by

$$Z_{\mathrm{rot}} = \sum_{l=0}^{\infty}(2l + 1)\mathrm{e}^{-\beta\hbar^2 l(l+1)/2I}. \tag{5.37}$$

This sum is difficult to solve analytically. We can, however, evaluate Z_{rot} in the low- and high-temperature limits as before. Similar steps as before yield

$$C_{\mathrm{rot}} = \begin{cases} 0 & T \ll T_{\mathrm{rot}} \\ Nk_{\mathrm{B}} & T > T_{\mathrm{rot}}. \end{cases} \tag{5.38}$$

5.4.5 Heat Capacity

Combining all the contributions, we have

$$C_V = \frac{1}{2}k_{\mathrm{B}} \cdot \begin{cases} 3 & T \ll T_{\mathrm{rot}} \\ 5 & T_{\mathrm{rot}} < T < T_{\mathrm{vib}} \\ 7 & T_{\mathrm{vib}} < T < T_{\mathrm{elec}} \end{cases} \tag{5.39}$$

as shown for diatomic Hydrogen in Fig. 1.

6 Fermi-Dirac Gases

Fermions are objects with half-integer spin. They obey the Pauli-exclusion principle. As before, we have the Fermi-Dirac distribution,

$$f_{\mathrm{FD}}(\varepsilon) = \frac{1}{\mathrm{e}^{\beta(\varepsilon-\mu)} + 1} \tag{6.1}$$

---

[6]Think about how many values of m you can get for some l.

where we have defined the Lagrange multiplier $\alpha \equiv -\beta\mu$, with μ representing the chemical potential (Fermi) energy.

For single-particle states, we have

$$f_i \equiv \frac{n_i}{g_i} \in [0, 1] \tag{6.2}$$

as each state can be occupied by at most one Fermion. At absolute zero temperature, all states up to and including the Fermi energy μ are occupied, and all above are unoccupied. At higher temperatures, the distribution relaxes and we get some particles with higher energy than μ. Of course, the total number of particles

$$N = \int_0^\infty g(\varepsilon) f_{\mathrm{FD}}(\varepsilon) \mathrm{d}\varepsilon \tag{6.3}$$

is the same for all T.

6.1 Paramagnetism

In a metal, electrons with spin up and down will interact with an applied magnetic field. The energy of applying a field B to electrons with magnetic moment μ[7] is

$$\varepsilon_\pm = \pm\mu B. \tag{6.4}$$

The distribution function splits, shifting to the left for spin-up particles and to the right for spin-down particles (for $B > 0$). A paramagnet will have induced magnetisation M in a field B, where M is the net magnetic moment per unit volume,

$$M = g(\varepsilon_F)\mu = \frac{\mu^2 3N g(\varepsilon_F)}{2\varepsilon_F} B. \tag{6.5}$$

7 Bose-Einstein Gases

The Bose-Einstein distribution function is

$$f_{\mathrm{BE}}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} \geq 0, \tag{7.1}$$

where, again, we have replaced the Lagrange multiplier α with chemical potential μ. The requirement that f_{BE} is positive comes from its definition as the fractional occupancy of energy levels. To preserve positivity, it follows that we must have $\mu \leq \varepsilon$.

---

[7]Not Fermi energy!