

Statistical Mechanics Notes

Ryan D. Reece

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Contents

1	Thermodynamics	3
1.1	State Variables	3
1.2	Inexact Differentials	5
1.3	Work and Heat	5
1.4	Entropy	6
1.5	Thermodynamic Potentials	7
1.6	Maxwell Relations	9
1.7	Heat Capacities	9
2	Ideas of Statistical Mechanics	10
2.1	The Goal	10
2.2	Boltzmann's Hypothesis	10
2.3	Entropy and Probability	11
2.4	The Procedure	12
3	Canonical Ensemble	13
3.1	Definition	13
3.2	The Bridge to Thermodynamics	16
3.3	Example: A Particle in a Box	17
4	Maxwell-Boltzmann Statistics	21
4.1	Density of States	21
4.2	The Maxwell-Boltzmann Distribution	23
4.3	Example: Particles in a Box	24
5	Black Body Radiation	26
5.1	Molecular Beams	26
5.2	Cavity Radiation	26

5.3	The Planck Distribution	26
6	Thermodynamics of Multiple Particles	27
6.1	Definition	27
6.2	Chemical Potential	27
6.3	The Gibbs-Duhem Relation	28
7	Identical Particles	29
7.1	Exchange Symmetry of Quantum States	29
7.2	Spin	30
7.3	Over Counting	31
8	Grand Canonical Ensemble	32
8.1	Definition	32
8.2	The Bridge to Thermodynamics	33
8.3	Fermions	34
8.4	Bosons	35
8.5	Non-relativistic Cold Electron Gas	36
8.6	Example: White Dwarf Stars	38
8.7	Relativistic Cold Electron Gas	41
8.8	Example: Collapse to a Neutron Star	42

Chapter 1

Thermodynamics

1.1 State Variables

Given a function $f(x, y)$, its differential is

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad (1.1)$$

The function is called *analytic* if its mixed partials are equal.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (1.2)$$

In this case, the differential of f , equation 1.1, is called an *exact differential*. Because the mixed partials are equal, Green's Theorem says that any closed line integral of f in x - y -space is zero.

$$\iint \left(\frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x} \right) dx dy = \oint \left(\frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \right) \quad (1.3)$$

$$0 = \oint df \quad (1.4)$$

Suppose we break some closed path into two paths α and β which begin at point Λ and end at point Γ (see Figure 1.1). If f is analytic, the path integrals of f along the two paths α and β must be equal because the integral along the closed path, equal to the difference of the the two path integrals, is zero.

$$\oint df = \int_{\alpha} df - \int_{\beta} df = 0 \quad (1.5)$$

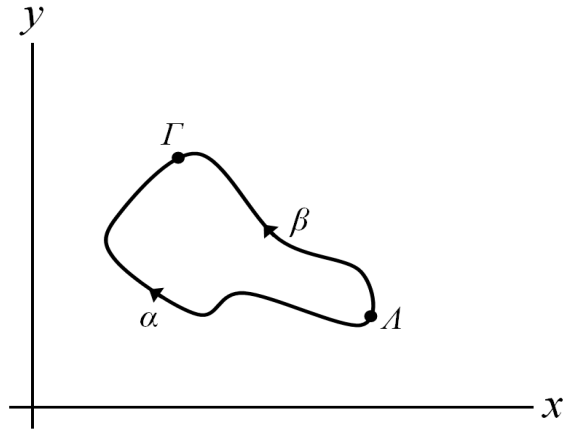


Figure 1.1: Path Independence of State Variables

This means the value of f , is a function of the endpoints alone and independent of the path.

$$f = \int df = f(\Lambda, \Gamma) \rightarrow f(\Delta x, \Delta y) \quad (1.6)$$

Concerning thermodynamics, if x and y are macroscopic variables that we can measure (temperature, pressure, volume, etc.), and we can find some variable f with an exact differential in terms of x and y , then f is called a *state variable*. State variables have defined values when a system has come to equilibrium, regardless of what processes (paths) brought the system there. The macroscopic variables x and y , are themselves state variables. An *equation of state* can be derived relating state variables independent of path, for example the equation of state for an ideal gas¹ is

$$p V = N k T \quad (1.7)$$

where pressure (p), volume (V), number of particles (N), and temperature (T) are all state variables and k is Boltzmann's constant.

¹We prove that this is the equation of state for an ideal gas, using statistical mechanics in Section 3.3

1.2 Inexact Differentials

Suppose we had derived the following differential equation for f

$$\delta f = A(x, y)dx + B(x, y)dy \quad (1.8)$$

and f is not analytic.

$$\frac{\partial A}{\partial y} \neq \frac{\partial B}{\partial x} \quad (1.9)$$

Then δf is an *inexact differential*, denoted by δ . It may be possible to multiply δf by some expression called an *integrating factor* to make an exact differential. Consider the following example.

$$\delta f = (2x + yx^2)dx + x^3dy \quad (1.10)$$

We see that δf is indeed inexact.

$$\frac{\partial^2 f}{\partial y \partial x} = x^2, \quad \frac{\partial^2 f}{\partial x \partial y} = 3x^2 \quad (1.11)$$

Choosing an integrating factor of e^{xy} gives

$$dS \equiv e^{xy} \delta f = e^{xy} (2x + yx^2)dx + e^{xy} x^3dy \quad (1.12)$$

dS is exact.

$$\frac{\partial^2 S}{\partial x \partial y} = \frac{\partial^2 S}{\partial y \partial x} = (x^3y + 3x^2)e^{xy} \quad (1.13)$$

We will use this method when we define entropy in Section 1.4.

1.3 Work and Heat

Naïve application conservation of energy requires that the change in the energy of a system, ΔU , is the work done on it, W . But this ignores thermal processes as a means to take and give energy. Introducing a quantity for the heat added to a system, Q , accounts for these thermal processes. This is the *First Law of Thermodynamics*.

$$\Delta U = W + Q \quad (1.14)$$

Considering the traditional example of a cylinder of gas with a piston such that we may vary the volume, V , and pressure, p , of the gas, we note that a differential change in volume, dV , does the following differential work on the system

$$\delta W = - p dV \quad (1.15)$$

For some less ideal system, this can be generalized. If some system has X_j variables that when varied do work on the system, then there are p_j “generalized pressures” that satisfy

$$\delta W = - \sum_j p_j dX_j \quad (1.16)$$

But, equation 1.15 is an *inexact differential* meaning that the work is dependent on the path through P - V -space and not just on the endpoints. That is, it is also dependent on how much heat comes in or out of the system. This implies that the differential heat is also an inexact differential.

$$dU = \delta W + \delta Q \quad (1.17)$$

1.4 Entropy

Our goal is to make equation 1.17 an exact differential in terms of state variables. We have seen that in our traditional system of a cylinder of gas, we can write δW in terms of state variables p and V . Now we need to find a way of writing δQ in terms of state variables.

$$\delta Q = dU + p dV \quad (1.18)$$

From the equation of state for an ideal gas (equation 1.7) we have

$$P = \frac{NkT}{V} \quad (1.19)$$

$$P dV = \frac{NkT}{V} dV \quad (1.20)$$

Then knowing that the energy of an ideal gas² is

$$U = \frac{3}{2}NkT \quad (1.21)$$

²We prove the equation of state and equation 1.21 for an ideal gas in Section 3.3

$$dU = \frac{3}{2} Nk dT \quad (1.22)$$

Plugging equations 1.20 and 1.22 into 1.18 gives

$$\delta Q = \frac{3}{2} Nk dT + \frac{NkT}{V} dV \quad (1.23)$$

Indeed, δQ is inexact.

$$\frac{\partial^2 Q}{\partial V \partial T} = \frac{\partial}{\partial V} \left(\frac{3}{2} Nk \right) = 0 \quad (1.24)$$

$$\frac{\partial^2 Q}{\partial T \partial V} = \frac{\partial}{\partial T} \left(\frac{NkT}{V} \right) = \frac{Nk}{V} \quad (1.25)$$

If equation 1.25 had not had that factor of T before taking the derivative, then both mixed partials would equal zero, and the differential would be exact. This motivates us to pick an integrating factor of T^{-1} . We define the *entropy*, S , to have the differential

$$dS \equiv \frac{\delta Q}{T} \quad (1.26)$$

$$= \frac{3}{2} \frac{Nk}{T} dT + \frac{Nk}{V} dV \quad (1.27)$$

It is an exact differential

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V} = 0 \quad (1.28)$$

meaning S is a state variable. With entropy defined, we can now write dU in terms of state variables.

$$\boxed{dU = T dS - p dV} \quad (1.29)$$

1.5 Thermodynamic Potentials

Sometimes it is convenient to create other state variables from our existing ones, depending on which variables are held constant in a process. The *thermodynamic potentials*, other than the total energy (U), are *enthalpy* (H), *Helmholtz Free Energy* (F), and *Gibbs Free Energy* (G). They are created by adding pV and/or subtracting TS from U (see Figure 1.2).

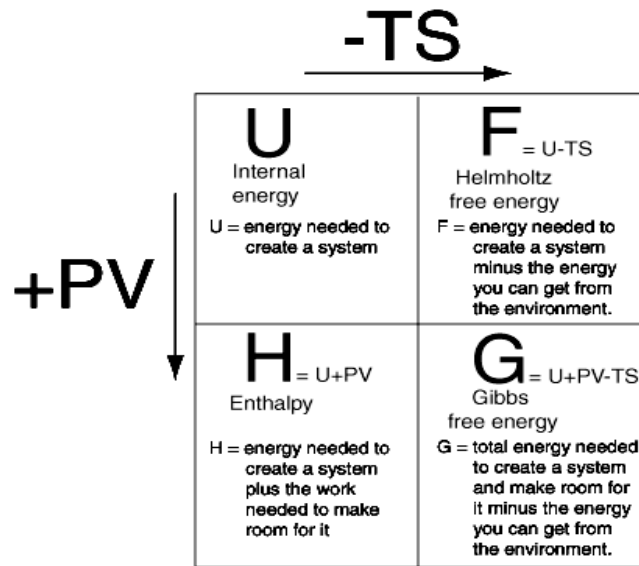


Figure 1.2: Mnemonic for the thermodynamic potentials

We can derive the exact differentials of these potentials, simply by differentiating their definitions and plugging in our exact differential for dU .

$$dH = T dS - \cancel{p dV} + \cancel{p dV} + V dp = T dS + V dp \quad (1.30)$$

$$dF = \cancel{T dS} - p dV - \cancel{T dS} - S dT = -S dT - p dV \quad (1.31)$$

$$dG = \cancel{T dS} - \cancel{p dV} + \cancel{p dV} + V dp - \cancel{T dS} - S dT \quad (1.32)$$

$$= V dp - S dT \quad (1.33)$$

1.6 Maxwell Relations

By recognizing that each of the thermodynamic potentials has an exact differential, we can derive the *Maxwell Relations* by equating the mixed partials.

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \Rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_T \quad (1.34)$$

$$\frac{\partial^2 H}{\partial S \partial p} = \frac{\partial^2 H}{\partial p \partial S} \Rightarrow \left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial T}{\partial p} \right)_S \quad (1.35)$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \Rightarrow \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad (1.36)$$

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p} \Rightarrow - \left(\frac{\partial S}{\partial p} \right)_T = \left(\frac{\partial V}{\partial T} \right)_p \quad (1.37)$$

1.7 Heat Capacities

Heat capacity is defined as the amount of differential heat that must be supplied to a system to change the system's temperature, per the differential change in temperature.

$$C \equiv \frac{\delta Q}{dT} \quad (1.38)$$

Because gases expand significantly upon heating, their heat capacity depends on whether pressure or volume is held fixed. For most solids and liquids the differences between C_V and C_p is less pronounced. From

$$\delta Q = dU + p dV \quad (1.39)$$

we see that when V is held fixed

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (1.40)$$

To express C_p , it is convenient to note the differential enthalpy.

$$dH = \delta Q + V dp \quad (1.41)$$

Therefore, when pressure is held fixed, $dH = \delta Q$, and we have that

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad (1.42)$$

Chapter 2

Ideas of Statistical Mechanics

2.1 The Goal

The goal of statistical mechanics is to form a theoretical foundation for the empirical laws of thermodynamics based on more fundamental physics (*i.e.* quantum mechanics).

2.2 Boltzmann's Hypothesis

Boltzmann's insightful hypothesis to define entropy in terms of the number of microstates.

$$\boxed{S = k_B \ln \Omega} \quad (2.1)$$

One way to see why this is a convenient definition is to recognize that this makes entropy *extensive*, that is, it is proportional to the number of particles or subsystems in our system, N . Other extensive state variables are U , V , and trivially N . If subsystem 1 has Ω_1 microstates and entropy S_1 , and subsystem 2 has Ω_2 microstates and entropy S_2 , then the combined system has $\Omega_T = \Omega_1 \times \Omega_2$ different microstates. The entropy of the combined system is

$$S = k_B \ln \Omega_T \quad (2.2)$$

$$= k_B \ln(\Omega_1 \times \Omega_2) \quad (2.3)$$

$$= k_B \ln \Omega_1 + k_B \ln \Omega_2 \quad (2.4)$$

$$= S_1 + S_2 \quad (2.5)$$

All extensive quantities are proportional to each other, with the constant of proportionality equal to the corresponding partial derivative. Therefore, instead of writing U in differential form as in equation 1.29, we may write

$$U = \left(\frac{\partial U}{\partial V}\right)_S V + \left(\frac{\partial U}{\partial S}\right)_V S \quad (2.6)$$

$$= -p V + T S \quad (2.7)$$

2.3 Entropy and Probability

Suppose a huge number of systems, N , are in thermal contact. N_1 of which are in microstate 1, N_2 in microstate 2, etc. The number of ways to make this arrangement is

$$\Omega = \frac{N!}{N_1! N_2! N_3! \dots} \quad (2.8)$$

The entropy of the entire ensemble of systems is

$$S_N = k \ln \Omega = k \ln N! - k \sum_i \ln N_i! \quad (2.9)$$

Using Stirling's approximation that $\ln N \approx N \ln N - N$ for large N gives

$$S_N = k(N \ln N - N - \sum_i N_i \ln N_i + \sum_i N_i) \quad (2.10)$$

Noting that $N = \sum_i N_i$ simplifies this to

$$S_N = k \left(\sum_i N_i \ln N - \sum_i N_i \ln N_i \right) \quad (2.11)$$

$$= k \sum_i N_i (\ln N - \ln N_i) \quad (2.12)$$

$$= -k \sum_i N_i \ln \frac{N_i}{N} \quad (2.13)$$

$$= -k N \sum_i \frac{N_i}{N} \ln \frac{N_i}{N} \quad (2.14)$$

The probability of finding any given system in the i -th microstate is $P_i = N_i/N$. Therefore,

$$S_N = -k N \sum_i P_i \ln P_i \quad (2.15)$$

The entropy per system, $S = S_N/N$, is

$$\boxed{S = -k \sum_i P_i \ln P_i} \quad (2.16)$$

2.4 The Procedure

- Determine the spectrum of energy levels and their degeneracies using quantum mechanics or some other means.
- Calculate the partition function.
- Use “the bridge to thermodynamics” ($F = -k_B T \ln Z$ in Canonical Ensemble or $\Phi = -k_B T \ln \Xi$ in the Grand Canonical Ensemble) to calculate any desired thermodynamic variable.

Chapter 3

Canonical Ensemble

3.1 Definition

Suppose system A is in contact with a reservoir (heat bath) R and has come to equilibrium with a temperature T . The total number of microstates in the combined system is

$$\Omega = \Omega_A(U_A) \times \Omega_R(U_R) \quad (3.1)$$

where U_A and U_R denote the energy in system A and the reservoir respectively. We choose to write quantities in terms of the energy in system A . E_i is the energy of the i -th energy level of system A . If the energy levels of system A have degeneracy g_i , the total number of microstates with $U_A = E_i$ is

$$\Omega(E_i) = g_i \times \Omega_R(U_T - E_i) \quad (3.2)$$

where $U_T = U_A + U_R$ is the total energy of the combined system.

From equation 1.29, we have that

$$dU = TdS - pdV \quad (3.3)$$

$$\Rightarrow \left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad (3.4)$$

Combining this with the statistical definition of entropy, $S = k \ln \Omega$, gives

$$\frac{1}{kT} = \left(\frac{\partial \ln \Omega_R}{\partial U_R} \right)_V \quad (3.5)$$

When energy is added to the reservoir, the temperature does not change. This is the property that defines a heat bath. Therefore, we can integrate equation 3.5 to get

$$C + \frac{U_R}{kT} = \ln \Omega_R \quad (3.6)$$

where C is some integration constant.

$$\Omega_R = e^C e^{U_R/kT} \quad (3.7)$$

$$\Omega(E_i) = g_i e^C e^{(U_T - E_i)/kT} \quad (3.8)$$

The total number of states is

$$\Omega_{\text{total}} = \sum_j \Omega(E_j) \quad (3.9)$$

$$= e^C e^{U_T/kT} \sum_j g_j e^{-E_j/kT} \quad (3.10)$$

where j indexes the energy levels of A . The probability that A has an energy E_i is

$$P(E_i) = \frac{\Omega(E_i)}{\Omega_{\text{total}}} \quad (3.11)$$

$$= \frac{g_i e^{\mathcal{C}} e^{(U_T - E_i)/kT}}{e^{\mathcal{C}} e^{U_T/kT} \sum_j g_j e^{-E_j/kT}} \quad (3.12)$$

$$= \frac{g_i e^{-E_i/kT}}{\sum_j g_j e^{-E_j/kT}} \quad (3.13)$$

$$= \frac{g_i e^{-E_i/kT}}{Z} \quad (3.14)$$

where we defined the *partition function*, Z , as

$$Z = \sum_j g_j e^{-E_j/kT} \quad (3.15)$$

We could have chosen to index the microstates instead of the energy levels, in which case the probability of the system being in the i -th microstate would simply be

$$\boxed{P_i = \frac{e^{E_i/kT}}{Z}} \quad (3.16)$$

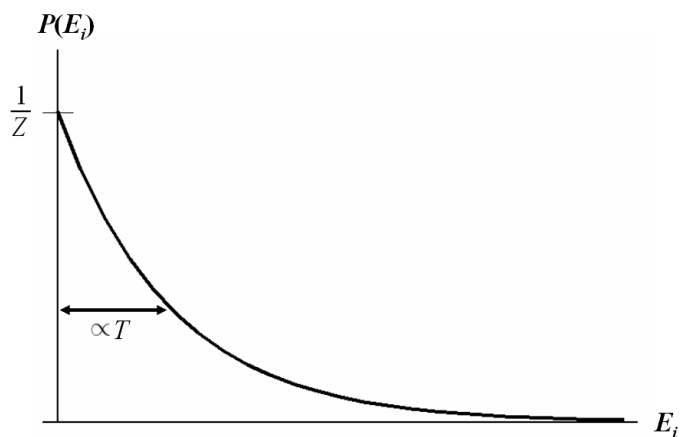


Figure 3.1: Boltzmann Distribution for nondegenerate energy levels

and the partition function would be

$$\boxed{Z = \sum_j e^{-E_j/kT}} \quad (3.17)$$

This probability distribution is called the *Boltzmann Distribution*. The partition function serves as a normalization factor for the distribution. For nondegenerate states and finite T , lower energy levels are always more likely. As T approaches infinity, all states are equally likely. A large number of distinguishable systems in thermal contact can be treated as a heat bath for any one of the individual systems in the group. This is called the *Canonical Ensemble*, in which case the the distribution of energies should fit the Boltzmann Distribution.

3.2 The Bridge to Thermodynamics

Plugging in the Boltzmann Distribution to equation 2.16 gives

$$S = -k \sum_i P_i \ln P_i \quad (3.18)$$

$$= -k \sum_i \frac{e^{-E_i/kT}}{Z} \ln \left(\frac{e^{-E_i/kT}}{Z} \right) \quad (3.19)$$

$$= k \sum_i \frac{e^{-E_i/kT}}{Z} \left(\frac{E_i}{kT} + \ln Z \right) \quad (3.20)$$

$$= \frac{1}{T} \sum_i \frac{e^{-E_i/kT}}{Z} E_i + k \ln Z \sum_i \frac{e^{-E_i/kT}}{Z} \quad (3.21)$$

$$= \frac{1}{T} \sum_i \frac{e^{-E_i/kT}}{Z} E_i + k \ln Z \quad (3.22)$$

Recognizing that the first term in equation 3.22 contains an express for the average energy of any one of the systems

$$U = \langle E \rangle = \sum_i P_i E_i = \sum_i \frac{e^{-E_i/kT}}{Z} E_i \quad (3.23)$$

equation 3.22 can be rewritten as

$$S = \frac{U}{T} + k \ln Z \quad (3.24)$$

We can now calculate the *Helmholtz Free Energy*, F , from equation 3.24

$$U - TS = -k T \ln Z \quad (3.25)$$

$$\boxed{F = -k T \ln Z} \quad (3.26)$$

It is now apparent that the partition function is more than just a normalization factor for the probability distribution of energies. If one can calculate the partition function of some system, then F can be calculated using equation 3.26. From F one can determine relations between the thermodynamic state variables.

Another way to see how Z is directly related to state variables, specifically U , is the following. For convenience, define $\beta \equiv 1/kT$.

$$U = \langle E \rangle \quad (3.27)$$

$$= \frac{1}{Z} \sum_i E_i P_i \quad (3.28)$$

$$= \frac{1}{Z} \sum_i E_i e^{-\beta E_i} \quad (3.29)$$

Noting that

$$Z = \sum_i e^{-\beta E_i} \quad (3.30)$$

$$\frac{\partial Z}{\partial \beta} = - \sum_i E_i e^{-\beta E_i} \quad (3.31)$$

means that equation 3.29 can be written as

$$U = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (3.32)$$

$$= - \frac{\partial \ln Z}{\partial \beta} \quad (3.33)$$

3.3 Example: A Particle in a Box

Imagine our system is a single particle confined to a one-dimensional box. This system is replicated a huge number of times and the systems are all in thermal contact making a Canonical Ensemble.

The time independent Schrödinger wave equation in one dimension is

$$- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x) \quad (3.34)$$

For a particle in a square potential of width L and with infinite barriers, the energy eigenvalues are

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad n \in 1, 2, 3, 4 \dots \quad (3.35)$$

For convenience, we define the constant ε to be

$$\varepsilon \equiv \frac{\hbar^2 \pi^2}{2mL^2}, \quad E_n = \varepsilon n^2 \quad (3.36)$$

Now that we know the spectrum of energies of the system, we can calculate¹ the partition function.

$$Z = \sum_{n=1}^{\infty} e^{-E_n/kT} \quad (3.37)$$

$$= \sum_{n=1}^{\infty} e^{-\varepsilon n^2/kT} \quad (3.38)$$

$$\approx \int_0^{\infty} e^{-\varepsilon n^2/kT} dn \quad (3.39)$$

$$= \sqrt{\frac{\varepsilon}{kT}} \frac{\sqrt{\pi}}{2} \quad (3.40)$$

$$= \sqrt{\frac{L^2 m k T}{2\pi \hbar^2}} \quad (3.41)$$

If we define the *de Broglie* wavelength² as

$$\lambda_D \equiv \sqrt{\frac{2\pi \hbar^2}{m k T}} \quad (3.42)$$

then we can write the partition function as

$$Z = \frac{L}{\lambda_D} \quad (3.43)$$

We can now calculate the Helmholtz Free Energy, and other macroscopic thermodynamic quantities.

$$F = -kT \ln(Z) = -kT \ln \left(\sqrt{\frac{L^2 m k T}{2\pi \hbar^2}} \right) \quad (3.44)$$

$$= -\frac{k}{2} T \ln \left(\frac{L^2 m k T}{2\pi \hbar^2} \right) \quad (3.45)$$

¹In equation 3.40, we use the integral $\int_0^{\infty} e^{-x^2} = \frac{\sqrt{\pi}}{2}$

²According to de Broglie, a particle in an eigenstate of momentum with momentum p has a corresponding wavelength $\lambda = \hbar/p$. A thermal distribution of particles therefore has a distribution of wavelengths. λ_D represents the average wavelength.

The entropy is

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = - \left(\frac{\partial F}{\partial T} \right)_L \quad (3.46)$$

$$= \frac{k}{2} \ln \left(\frac{L^2 m k T}{2\pi \hbar^2} \right) + \frac{k}{2} \cancel{\mathcal{F} \left(\frac{2\pi \hbar^2}{L^2 m k T} \right)} \cancel{\left(\frac{L^2 m k}{2\pi \hbar^2} \right)} \quad (3.47)$$

$$= \frac{k}{2} \left[\ln \left(\frac{L^2 m k T}{2\pi \hbar^2} \right) + 1 \right] \quad (3.48)$$

Using equation 1.40, the heat capacity is

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_L \quad (3.49)$$

$$= \cancel{\mathcal{F}} \frac{k}{2} \cancel{\left(\frac{2\pi \hbar^2}{L^2 m k T} \right)} \cancel{\left(\frac{L^2 m k}{2\pi \hbar^2} \right)} \quad (3.50)$$

$$= \frac{k}{2} \quad (3.51)$$

What if the particle is in a three-dimensional box? Solving this basic quantum mechanical problem gives the spectrum of energies.

$$E_{n_1, n_2, n_3} = \varepsilon (n_1^2 + n_2^2 + n_3^2) \quad (3.52)$$

where ε is the same as we defined in equation 3.36. The partition function is

$$Z = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} e^{-\varepsilon(n_1^2 + n_2^2 + n_3^2)/kT} \quad (3.53)$$

$$= \left(\sum_{n_1=1}^{\infty} e^{-\varepsilon n_1^2/kT} \right) \left(\sum_{n_2=1}^{\infty} e^{-\varepsilon n_2^2/kT} \right) \left(\sum_{n_3=1}^{\infty} e^{-\varepsilon n_3^2/kT} \right) \quad (3.54)$$

$$= \left(\frac{L^2 m k T}{2\pi \hbar^2} \right)^{3/2}, \quad V = L^3 \quad (3.55)$$

$$= V \left(\frac{m k T}{2\pi \hbar^2} \right)^{3/2} = \frac{V}{\lambda_D^3} \quad (3.56)$$

The Helmholtz Free Energy is

$$F = -kT \ln Z \quad (3.57)$$

$$= -kT \ln V + \frac{3}{2} \ln \left(\frac{m k T}{2\pi \hbar^2} \right) \quad (3.58)$$

The pressure is

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{kT}{V} \quad (3.59)$$

We have derived an equation of state for this system!

$$p V = k T \quad (3.60)$$

Imagine our box contains N particles instead of one. If the particles do not interact, this defines an *ideal gas*, then the pressure of the system is just N times the pressure due to a single particle, giving equation 3.59 an extra factor of N . This gives the equation of state for an ideal gas.

$$p V = N k T \quad (3.61)$$

Back to the case of only one particle, the entropy of the system is

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = k \left[\ln V + \frac{3}{2} \ln \left(\frac{mkT}{2\pi\hbar^2} \right) + \frac{3}{2} \right] \quad (3.62)$$

The heat capacity is

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (3.63)$$

$$= \cancel{\mathcal{X}} \frac{3k}{2} \left(\frac{2\pi\hbar^2}{L^2 mkT} \right) \left(\frac{L^2 mk}{2\pi\hbar^2} \right) \quad (3.64)$$

$$= \frac{3k}{2} \quad (3.65)$$

We see that the heat capacity of a particle in a three-dimensional box is three times that for a particle in a one-dimensional box. This makes sense because each dimension of translational motion independently adds to the capacity of the system to store energy in thermal motion. Each translation degree of freedom gives a $\frac{k}{2}$ term to the heat capacity for a system with constant volume.

Because the heat capacity is not dependent on temperature, we can easily integrate it from zero to the some temperature to find out how much thermal energy is stored in the system.

$$\int_0^T \left(\frac{\partial U}{\partial T'} \right)_V dT' = \int_0^T C_V dT' \quad (3.66)$$

$$U = C_V T \quad (3.67)$$

$$U = \frac{3}{2} kT \quad (3.68)$$

Chapter 4

Maxwell-Boltzmann Statistics

4.1 Density of States

We know that a free particle in a three-dimensional box has energy eigenstates:

$$\psi_{n_1, n_2, n_3}(x, y, z) = C \sin\left(\frac{n_1 \pi x}{L_x}\right) \sin\left(\frac{n_2 \pi y}{L_y}\right) \sin\left(\frac{n_3 \pi z}{L_z}\right) \quad (4.1)$$

$$= C \sin(k_x x) \sin(k_y y) \sin(k_z z) \quad (4.2)$$

with energies

$$E_{n_1, n_2, n_3} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{L_x^2} + \frac{n_2^2}{L_y^2} + \frac{n_3^2}{L_z^2} \right) \quad (4.3)$$

$$= \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad (4.4)$$

These states correspond to lattice points in a space, k -space, whose axes are k_x , k_y , and k_z . A vector in this space is called a *wave vector*

$$\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z} \quad (4.5)$$

with a magnitude, or *wavenumber*¹

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2} \quad (4.6)$$

¹We will now use k_B to denote Boltzmann's constant in order not to confuse it with the magnitude of a wave vector k .

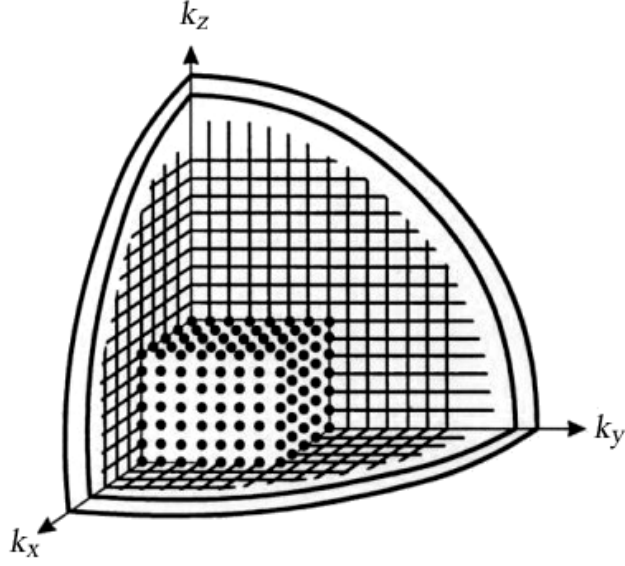


Figure 4.1: k -space

In polar coordinates,

$$\theta = \arccos\left(\frac{k_z}{k}\right), \quad \phi = \arctan\left(\frac{k_y}{k_x}\right) \quad (4.7)$$

$$\text{volume element in } k\text{-space} = k^2 \sin\theta \, dk \, d\theta \, d\phi \quad (4.8)$$

$$\text{density of points in } k\text{-space} = \frac{L_x L_y L_z}{\pi^3} = \frac{V}{\pi^3} \quad (4.9)$$

Therefore, the number of states in a differential volume is

$$dN = \frac{V}{\pi^3} k^2 \sin\theta \, dk \, d\theta \, d\phi \quad (4.10)$$

Integrating $d\theta$ and $d\phi$ gives the number of states in a differential shell of thickness dk .

$$dN = \frac{V}{\pi^3} k^2 \, dk \int_0^{\pi/2} d\phi \int_0^{\pi/2} \sin\theta \, d\theta \quad (4.11)$$

$$= \frac{V}{\pi^3} k^2 \, dk \cdot \frac{\pi}{2} \cdot 1 = \frac{V}{2\pi^2} k^2 \, dk \quad (4.12)$$

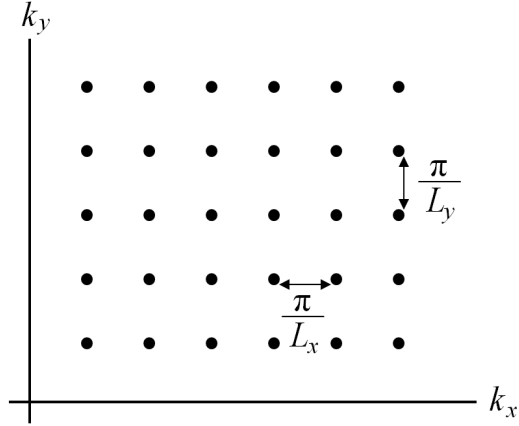


Figure 4.2: Density of points in k -space

We define that *density of states*, $D(k)$, such that

$$dN = \frac{V}{2\pi^2} k^2 dk = D(k) dk \quad (4.13)$$

In this discussion, we have ignored the possibility of there being multiple spin states at a single point in k -space. For future reference, we define $D_0(k)$ to be the density of states ignoring any spin degeneracy.

$$\boxed{D_0(k) \equiv \frac{V}{2\pi^2} k^2} \quad (4.14)$$

In general, if there are g_s spin states with the same energy at the same point in k -space, the density of states is

$$D(k) = g_s D_0(k) \quad (4.15)$$

We can now write down the partition function, using k to integrate over all states.

$$Z = \int_0^\infty D(k) e^{-E_k/k_B T} dk \quad (4.16)$$

4.2 The Maxwell-Boltzmann Distribution

If we allow multiple particles to occupy the same state, the probability the i -th state is occupied if we “toss” N particles among the states at random

is²

$$P_{\text{ocp}} = 1 - P(N_i = 0) \quad (4.17)$$

$$= 1 - (1 - P_i)^N \quad (4.18)$$

$$= \mathcal{X} - \mathcal{X} + NP_i - \frac{N(N-1)}{2}P_i^2 + \dots \quad (4.19)$$

where N_i denotes the number of particles occupying the i -th state and P_i is the probability that a particle gets tossed into the i -th states. If the density of states is sufficiently large, and the temperature high, then $P_i \ll 1$, and we can ignore higher terms in P_i . In this regime, it does not even matter if we allow multiple particles to occupy the same state, be them fermions or bosons, because the probability of multiple occupancies is so low.

$$P_{\text{ocp}} \simeq N P_i \quad (4.20)$$

Using this approximation, the number of states occupied in a differential k -shell is

$$dN_{\text{ocp}} = P_{\text{ocp}} dN \quad (4.21)$$

$$= \frac{N e^{-E_k/k_B T}}{Z} D(k) dk \quad (4.22)$$

$$= f_{\text{MB}}(k) dk \quad (4.23)$$

where we have defined the *Maxwell-Boltzmann Distribution*, $f_{\text{MB}}(k)$, to be

$$\boxed{f_{\text{MB}}(k) = \frac{N D(k) e^{-E_k/k_B T}}{Z}} \quad (4.24)$$

4.3 Example: Particles in a Box

Back to our example of particles in a box, we can plug in the partition function from equation 3.56 and the density of states from equation 4.13 into equation 4.22.

$$f_{\text{MB}}(k) dk = N e^{-E_k/k_B T} \left(\frac{\lambda_D^3}{\mathcal{V}} \right) \left(\frac{\mathcal{V}}{2\pi^2} k^2 \right) dk \quad (4.25)$$

$$= \frac{N \lambda_D^3}{2\pi^2} k^2 e^{-E_k/k_B T} dk \quad (4.26)$$

²We have used that the probability of r successful tosses out of N tosses, with a probability p for the success of each toss, is given by the *binomial distribution*. $P(x = r) = \binom{N}{r} p^r (1-p)^{(N-r)}$

Let us say we want to calculate the average velocity squared of the particles. We first have to calculate

$$\langle k^2 \rangle = \frac{\int_0^\infty k^2 f_{\text{MB}}(k) dk}{\int_0^\infty f_{\text{MB}}(k) dk} \quad (4.27)$$

$$= \frac{\int_0^\infty k^4 e^{-E_k/k_B T} dk}{\int_0^\infty k^2 e^{-E_k/k_B T} dk} \quad (4.28)$$

$$= \frac{\int_0^\infty k^4 e^{-\hbar^2 k^2/2mk_B T} dk}{\int_0^\infty k^2 e^{-\hbar^2 k^2/2mk_B T} dk} \quad (4.29)$$

Substitute³ $x^2 \equiv \frac{\hbar^2 k^2}{2mk_B T}$

$$\langle k^2 \rangle = \frac{2mk_B T}{\hbar^2} \frac{\int_0^\infty x^4 e^{-x^2} dx}{\int_0^\infty x^2 e^{-x^2} dx} \quad (4.30)$$

$$= \frac{2mk_B T}{\hbar^2} \left(\frac{3\sqrt{\pi}}{8} \right) \left(\frac{4}{\sqrt{\pi}} \right) \quad (4.31)$$

$$= \frac{3mk_B T}{\hbar^2} \quad (4.32)$$

In the non-relativistic limit,

$$\langle v^2 \rangle = \frac{\langle p^2 \rangle}{m^2} = \frac{\hbar^2}{m^2} \langle k^2 \rangle \quad (4.33)$$

$$= \frac{3k_B T}{m} \quad (4.34)$$

For each particle, the average energy is

$$U = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \quad (4.35)$$

which is the same result we got for the ideal gas using a different method in equation 3.68.

³We used the integrals $\int_0^\infty x^4 e^{-x^2} dx = \frac{3\sqrt{\pi}}{8}$ and $\int_0^\infty x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}$.

Chapter 5

Black Body Radiation

5.1 Molecular Beams

5.2 Cavity Radiation

5.3 The Planck Distribution

Chapter 6

Thermodynamics of Multiple Particles

6.1 Definition

Now we will consider systems consisting of distinguishable types of particles, where all the particles in a given type are identical. In addition to the exchange of work and heat between subsystems, now the number of particles of one type can be transferred to another type. One example of this is a cylinder of gas with a semipermeable membrane dividing the cylinder. There are two types of gas molecules that are distinguishable by which side of the membrane they are on. Another example is a single container of gas holding A type molecules, B type molecules, and a third AB type that is the product of some kind of combination of A and B type molecules.

6.2 Chemical Potential

Introducing the ability for particles to change type within a system gives a new way to exchange energy. *We define the chemical potential, μ , to be the internal energy gained by a system when the average number of particles, N , of some type increases by one.* This means we must add a term to equation 2.7.

$$U = -p V + T S + \mu N \tag{6.1}$$

Therefore,

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{V,S} \quad (6.2)$$

and we can add this term to equation 1.29, giving

$$\boxed{dU = T dS - p dV + \mu dN} \quad (6.3)$$

This also leads to a noteworthy equation for the Gibbs Free Energy:

$$G \equiv U - T S + p V = \mu N \quad (6.4)$$

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P} = \frac{G}{N} \quad (6.5)$$

Flipping around equation 6.3 gives a relation for μ that is often convenient.

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \quad (6.6)$$

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \quad (6.7)$$

6.3 The Gibbs-Duhem Relation

Differentiating equation 6.1 directly gives

$$dU = T dS + S dT - p dV - V dP + \mu dN + N d\mu \quad (6.8)$$

but then using equation 6.3, we cancel some terms, leaving

$$0 = S dT - V dp + N d\mu \quad (6.9)$$

This is called the *Gibbs-Duhem Relation*. We can generalize this for a system with various work variables X_i and particle types indexed by j .

$$0 = S dT - \sum_i X_i dp_i + \sum_j N_j d\mu_j \quad (6.10)$$

Chapter 7

Identical Particles

7.1 Exchange Symmetry of Quantum States

Suppose we have a system of two identical particles. Because they are identical, the square of the wavefunction that describes the state should be unchanged if two particles are exchanged. \mathcal{X} denotes the exchange operator.

$$|\psi(x_1, x_2)|^2 = |\mathcal{X}\psi(x_1, x_2)|^2 \quad (7.1)$$

$$= |\psi(x_2, x_1)|^2 \quad (7.2)$$

This implies that the exchanged wavefunctions differ only by a complex factor whose modulus squared is one.

$$\psi(x_1, x_2) = e^{i\theta} \psi(x_2, x_1) \quad (7.3)$$

If we exchange the particles twice, we have done nothing. Therefore the wavefunctions should be identical.

$$\psi(x_1, x_2) = \mathcal{X}^2\psi(x_1, x_2) \quad (7.4)$$

$$\Rightarrow e^{i2\theta} = 1 \quad (7.5)$$

which only has solutions $\theta = \dots - 2\pi, -\pi, 0, \pi, 2\pi \dots \Rightarrow e^{i\theta} = \pm 1$.

Particles with an exchange factor of $+1$, *i.e.* symmetric under exchange, are called *bosons*. Those with an exchange factor of -1 , *i.e.* antisymmetric under exchange, are called *fermions*.

Larger numbers of identical bosons or fermions must still obey the appropriate exchange symmetry. The ways to construct a wavefunction for several identical particles with the correct symmetry are the following:

$$\psi_{\text{Bose}}(x_1, x_2, x_3 \dots) = \psi_i(x_1) \psi_j(x_2) \psi_k(x_3) \dots + \text{permutations of } i, j, k \dots \quad (7.6)$$

$$\psi_{\text{Fermi}}(x_1, x_2, x_3 \dots) = \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) & \psi_i(x_3) & \dots \\ \psi_j(x_1) & \psi_j(x_2) & \psi_j(x_3) & \dots \\ \psi_k(x_1) & \psi_k(x_2) & \psi_k(x_3) & \dots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \quad (7.7)$$

The determinate in equation 7.7 is called a *Slater Determinate* and gives the correct signs for the total wavefunction to be asymmetric under exchange.

Consider a system of two fermions, for example two electrons bound to an atom. The Slater Determinate gives

$$\psi_{\text{Fermi}}(x_1, x_2) = \psi_i(x_1) \psi_j(x_2) - \psi_i(x_2) \psi_j(x_1) \quad (7.8)$$

Immediately one can see that if the two particles are in the same state ($i = j$), $\psi_{\text{Fermi}} \equiv 0$. This explains the *Pauli Exclusion Principle*, that no two identical fermions can exist in the same quantum state.

7.2 Spin

There is a very important result from relativistic quantum mechanics called the *Spin-Statistics Theorem*, which is beyond the scope of this work. It holds that fermions have half-integer spin and bosons have integer spin.

$$\text{fermions: } s = 1/2, 3/2, 5/2 \dots \quad (7.9)$$

$$\text{bosons: } s = 0, 1, 2, 3 \dots \quad (7.10)$$

The total wavefunction must obey the exchange symmetry.

$$\psi_{\text{total}} = \phi(\text{space}) \chi(\text{spin}) \quad (7.11)$$

This allows fermions to exist in a symmetric spacial state, as long as their combined spin state is antisymmetric. For two spin 1/2 fermions, the combined spin states with spin, s , and z -projection of the spin, m , are $\chi = |s m\rangle$.

$s = 1$ symmetric triplet:

$$|1\ 1\rangle = \uparrow\uparrow \quad (7.12)$$

$$|1\ 0\rangle = \uparrow\downarrow + \downarrow\uparrow \quad (7.13)$$

$$|1\ -1\rangle = \downarrow\downarrow \quad (7.14)$$

$s = 0$ antisymmetric singlet:

$$|0\ 0\rangle = \uparrow\downarrow - \downarrow\uparrow \quad (7.15)$$

The spin singlet allows two electrons (which are fermions) to exist in the same spacial state (orbital) without violating Pauli's Exclusion Principle.

$$\psi_{ee}(x_1, x_2) = \phi_i(x_1) \phi_i(x_2) |0\ 0\rangle \quad (7.16)$$

7.3 Over Counting

Chapter 8

Grand Canonical Ensemble

8.1 Definition

Suppose system A is in contact with a with a huge reservoir with which the system can exchange both heat and particles. We use Ω_R to denote the number of microstates in the some macrostate specified by a number of particles and a temperature. Plugging $S = k_B \ln \Omega_R$ into equation 6.7 gives

$$\frac{-\mu}{k_B T} = \left(\frac{\partial \ln \Omega_R}{\partial N_R} \right)_{U_R, V_R} \quad (8.1)$$

Similar to the Canonical Ensemble in equation 3.5, we also have that

$$\frac{1}{k_B T} = \left(\frac{\partial \ln \Omega_R}{\partial U_R} \right)_{V_R, N_R} \quad (8.2)$$

The reservoir is so large that its temperature and chemical potential do not significantly change when heat or particles are added to it. Therefore, we may trivially integrate both equations. They have the simultaneous solution (where C is some combined constant of integration):

$$\ln \Omega_R = C + \frac{U_R - \mu N_R}{k_B T} \quad (8.3)$$

$$\Omega_R = e^C e^{(U_R - \mu N_R)/k_B T} \quad (8.4)$$

The total number of microstates of the combined system is

$$\Omega = \Omega_A(U_A, N_A) \times \Omega_R(U_R, N_R) \quad (8.5)$$

The number of microstates with system A in its i -th microstate is

$$\Omega_i = 1 \times \Omega_R(U_T - U_A, N_T - N_A) = \Omega_R(U_T - E_i, N_T - N_i) \quad (8.6)$$

where $U_T = U_A + U_R$ and $N_T = N_A + N_R$.

$$\Omega_i = e^C e^{(U_T - E_i - \mu N_T + \mu N_i)/k_B T} \quad (8.7)$$

Since U_T and N_T are conserved, they can be absorbed into the leading constant.

$$\Omega_i = C' e^{-(E_i - \mu N_i)/k_B T} \quad (8.8)$$

The total number of states is

$$\Omega_{\text{total}} = \sum_j \Omega_j \quad (8.9)$$

The probability that A is in the i -th state is

$$P_i = \frac{\Omega_i}{\Omega_{\text{total}}} \quad (8.10)$$

$$= \frac{\mathcal{C}' e^{-(E_i - \mu N_i)/k_B T}}{\mathcal{C}' \sum_j e^{-(E_j - \mu N_j)/k_B T}} \quad (8.11)$$

$$= \frac{e^{-(E_i - \mu N_i)/k_B T}}{\Xi} \quad (8.12)$$

where we defined the *Grand Partition Function* as

$$\boxed{\Xi = \sum_j e^{-(E_j - \mu N_j)/k_B T}} \quad (8.13)$$

8.2 The Bridge to Thermodynamics

Plugging in the distribution function in equation 8.12 into equation 2.16 gives

$$S = -k_B \sum_i P_i \ln P_i \quad (8.14)$$

$$= -k_B \sum_i P_i \ln \left(\frac{e^{-(E_i - \mu N_i)/k_B T}}{\Xi} \right) \quad (8.15)$$

$$= -k_B \sum_i P_i \left[\frac{-(E_i - \mu N_i)}{k_B T} - \ln \Xi \right] \quad (8.16)$$

Recognizing that

$$U = \sum_i P_i E_i \quad \text{and} \quad N = \sum_i P_i N_i \quad (8.17)$$

we have that

$$S = \frac{U}{T} - \frac{\mu N}{T} + k_B \ln \Xi \quad (8.18)$$

Rearranging this, we define the *Grand Potential* to be

$$\Phi \equiv U - T S - \mu N \quad (8.19)$$

$$\boxed{\Phi = -k_B T \ln \Xi} \quad (8.20)$$

Differentiating Φ and plugging in the differential of U from equation 6.3 gives

$$d\Phi = dU - T dS - S dT - \mu dN - N d\mu \quad (8.21)$$

$$= \cancel{T dS} - p dV + \mu dN - \cancel{T dS} - S dT - \mu dN - N d\mu \quad (8.22)$$

$$= -p dV - S dT - N d\mu \quad (8.23)$$

By taking various partial derivatives, we can calculate p , S , and N from Φ . We can then calculate any thermodynamic state variable we want using the various Maxwell Relations.

Most notably, we can calculate the average number of particles in the system.

$$N = - \left(\frac{\partial \Phi}{\partial \mu} \right)_{T,V} \quad (8.24)$$

8.3 Fermions

For our system we choose the i -th *single quantum state of a fermion*, a state with a specific wave vector and spin state. Pauli's exclusion principle forbids more than one particle to exist in this state. Therefore, the spectrum of energies for this system is only $\{0, E_i\}$, 0 for the state being unoccupied, and E_i , being the energy of that state, for when it is occupied. Then the grand partition function for this system is

$$\Xi = 1 + e^{-(E_i - \mu)/k_B T} \quad (8.25)$$

The grand potential is

$$\Phi = -k_B T \ln(1 + e^{-(E_i - \mu)/k_B T}) \quad (8.26)$$

The average number of particles in this state is

$$N = - \left(\frac{\partial \Phi}{\partial \mu} \right)_{T,V} \quad (8.27)$$

$$= \frac{1}{e^{(E_i - \mu)/k_B T} + 1} \quad (8.28)$$

Now considering all of the quantum states, if we use the magnitude of the wave vector, k , to index the energy levels, and let the density of states, $D(k)$, handle the spin and other degeneracies, we can write the distribution of occupied states for fermions, called the *Fermi-Dirac Distribution*.

$$f_{\text{FD}}(k) = \frac{D(k)}{e^{(E_k - \mu)/k_B T} + 1} \quad (8.29)$$

8.4 Bosons

We choose our system to be the i -th *single quantum state of a boson*, a state with a specific wave vector and spin state. Any nonnegative integer number of bosons can occupy a single state. Therefore, the spectrum of energies for our system is $\{0, E_i, 2E_i, 3E_i, \dots\}$. The grand partition function is¹

$$\Xi = 1 + e^{-(E_i - \mu)/k_B T} + e^{-2(E_i - \mu)/k_B T} + e^{-3(E_i - \mu)/k_B T} + \dots \quad (8.30)$$

$$= \sum_{j=0}^{\infty} \left(e^{-(E_i - \mu)/k_B T} \right)^j \quad (8.31)$$

$$= \frac{1}{1 - e^{-(E_i - \mu)/k_B T}} \quad (8.32)$$

where $(E_i - \mu)$ must be positive for the series to converge. The grand potential is

$$\Phi = k_B T \ln(1 - e^{-(E_i - \mu)/k_B T}) \quad (8.33)$$

¹Recognize that the sum in equation 8.31 is a geometric series.

The average number of particles in this state is

$$N = - \left(\frac{\partial \Phi}{\partial \mu} \right)_{T,V} \quad (8.34)$$

$$= \frac{1}{e^{-(E_i - \mu)/k_B T} - 1} \quad (8.35)$$

Just like we did for fermions, if we use k to index the energy levels, and let $D(k)$ handle the spin and other degeneracies, we can write the distribution of occupied states for bosons, called the *Bose-Einstein Distribution*.

$$f_{\text{BE}}(k) = \frac{D(k)}{e^{(E_k - \mu)/k_B T} - 1} \quad (8.36)$$

8.5 Non-relativistic Cold Electron Gas

Electrons have a spin degeneracy of 2. Therefore, the density of states of an electron gas is

$$D(k) = 2 D_0(k) = \frac{V}{\pi^2} k^2 \quad (8.37)$$

As temperature approaches zero, the particles in a fermion gas stack in the allowed states, starting at the ground states. This means that the particles pile up in the states in the corner of k -space closest to the origin, making an eighth of a sphere. The surface of that sphere is called the *Fermi surface*. The states on that surface all have the same radius or wavenumber, k_F , called the *Fermi wavenumber*. In order to calculate the Fermi wavenumber, we equate the number of electrons, N_e , with number of states, stacking them in the corner.

$$N_e = \int_0^{k_F} D(k) dk = \frac{V}{\pi^2} \int_0^{k_F} k^2 dk = \frac{V k_F^3}{3\pi^2} \quad (8.38)$$

$$k_F = \left(3\pi^2 \frac{N_e}{V} \right)^{1/3} = (3\pi^2 n)^{1/3} \quad (8.39)$$

where n is the number density of electrons. In the non-relativistic limit, the energy of a state with a wavenumber k is

$$E_k = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m_e} \quad (8.40)$$

Therefore, the energy of the states on the Fermi surface, called the *Fermi energy*, is

$$E_F = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3} \quad (8.41)$$

The total internal energy of the electron gas at $T = 0$ is

$$U = \int_0^{k_F} E_k D(k) dk \quad (8.42)$$

$$= \int_0^{k_F} \left(\frac{\hbar^2 k^2}{2m_e} \right) \left(\frac{V k^2}{\pi^2} \right) dk \quad (8.43)$$

$$= \frac{\hbar^2 V}{2\pi^2 m_e} \int_0^{k_F} k^4 dk \quad (8.44)$$

$$= \frac{\hbar^2 V}{10\pi^2 m_e} k_F^5 \quad (8.45)$$

From equations 8.39 and 8.41

$$k_F^3 = 3\pi^2 n = 3\pi^2 \frac{N_e}{V} \quad (8.46)$$

$$k_F^2 = \frac{2m_e E_F}{\hbar^2} \quad (8.47)$$

Therefore,

$$U = \frac{\hbar^2 V}{10\pi^2 m_e} \left(3\pi^2 \frac{N_e}{V} \right) \left(\frac{2m_e E_F}{\hbar^2} \right) \quad (8.48)$$

$$= \frac{3}{5} E_F N_e \quad (8.49)$$

Even at $T=0$, an electron gas has positive internal energy and therefore a positive pressure. To calculate this *degeneracy pressure*, we write the explicit dependence of U on V . Plugging equation 8.39 into 8.45 gives

$$U = \frac{\hbar^2 V}{10\pi^2 m_e} \left(3\pi^2 \frac{N_e}{V} \right)^{5/3} \quad (8.50)$$

$$= \frac{\hbar^2}{10\pi^2 m_e} (3\pi^2 N_e)^{5/3} V^{-2/3} \quad (8.51)$$

$$p = - \left(\frac{\partial U}{\partial V} \right)_{T, N_e} \quad (8.52)$$

$$= \frac{2}{3} \frac{\hbar^2}{10\pi^2 m_e} \left(3\pi^2 \frac{N_e}{V} \right)^{5/3} \quad (8.53)$$

$$= \frac{2}{3} \frac{\hbar^2 k_F^2}{10\pi^2 m_e} \left(3\pi^2 n \right) \quad (8.54)$$

$$= \frac{2}{5} E_F n \quad (8.55)$$

Notice that the degeneracy pressure increases with the number density, and that the Fermi energy also increases with the number density.

8.6 Example: White Dwarf Stars

When a star can no longer perform fusion of its matter, creating heat and pressure to suppress its collapse, the star collapses until the electron degeneracy pressure increases enough to halt the collapse. Such a star is called a *white dwarf*.

In order to calculate the stable radius, R , of a white dwarf, we write U as a function of R .

$$U = \frac{\hbar^2}{10\pi^2 m_e} (3\pi^2 N_e)^{5/3} V^{-2/3}, \quad V = \frac{4}{3} \pi R^3 \quad (8.56)$$

$$= \frac{\hbar^2}{10\pi^2 m_e} (3\pi^2 N_e)^{5/3} \left(\frac{4}{3} \pi R^3 \right)^{-2/3} \quad (8.57)$$

$$= \frac{9}{20} \left(\frac{3}{2} \right)^{1/3} \pi^{2/3} \frac{\hbar^2}{m_e R^2} \quad (8.58)$$

Now we calculate the gravitational potential energy for the star.

$$dU_G = \frac{-Gm}{r} dm \quad (8.59)$$

$$m = \frac{4}{3} \pi r^3 \rho, \quad dm = 4\pi r^2 \rho dr \quad (8.60)$$

$$dU_G = \frac{-G}{r} \left(\frac{4}{3} \pi r^3 \rho \right) (4\pi r^2 \rho) dr \quad (8.61)$$

$$= \frac{-16\pi^2}{3} G \rho^2 r^4 dr \quad (8.62)$$

$$U_G = \frac{-16\pi^2}{3} G \rho^2 \int_0^R r^4 dr \quad (8.63)$$

$$= \frac{-16\pi^2}{15} G \rho^2 R^5 \quad (8.64)$$

The density in terms of the number of nucleons, N_N , and the mass of a nucleon, m_N , is

$$\rho = \frac{N_N m_N}{4\pi R^3/3} \quad (8.65)$$

Therefore,

$$U_G = \frac{-16\pi^2}{15} G \left(\frac{N_N m_N}{4\pi R^3/3} \right)^2 R^5 \quad (8.66)$$

$$= \frac{-3GN_N^2 m_N^2}{5R} \quad (8.67)$$

The total energy, U_T , is

$$U_T = U + U_G \quad (8.68)$$

For convenience, we define the constants

$$A \equiv \frac{9}{20} \left(\frac{3}{2} \right)^{1/3} \pi^{2/3} \frac{\hbar^2}{m_e} \quad (8.69)$$

$$B \equiv \frac{3}{5} GN_N^2 m_N^2 \quad (8.70)$$

$$U_T = \frac{A}{R^2} - \frac{B}{R} \quad (8.71)$$

$$U_T = \frac{A}{R^2} - \frac{B}{R} \quad (8.72)$$

The stable minimum in energy is found by calculating the critical point.

$$\frac{dU_T}{dR} = \frac{-2A}{R^3} + \frac{B}{R^2} = 0 \quad (8.73)$$

$$\Rightarrow R = \frac{2A}{B} = \left(\frac{9\pi}{4} \right)^{2/3} \frac{\hbar^2 N_e^{5/3}}{GN_N^2 m_N^2 m_e} \quad (8.74)$$

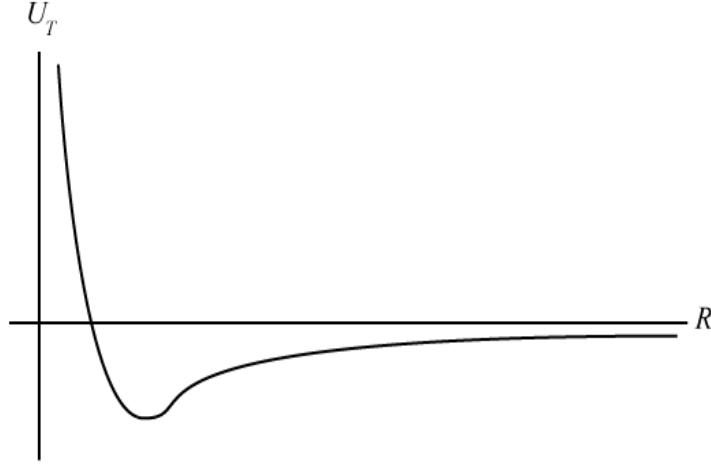


Figure 8.1: Potential well for white dwarf with non-relativistic electrons

Most elements have approximately as many neutrons as protons, and will have the same number of electrons as protons. Therefore,

$$N \equiv N_e \approx \frac{1}{2} N_N \quad (8.75)$$

The mass of the star, M , is almost entirely due to nucleons

$$M \approx N_N m_n, \quad m \equiv m_e \approx \frac{1}{1800} m_N \quad (8.76)$$

$$\Rightarrow N = \frac{M}{2m_N} = \frac{M}{2(1800 m)} = \frac{M}{3600 m} \quad (8.77)$$

$$R = \left(\frac{9\pi}{4} \right)^{2/3} \frac{\hbar^2 N^{5/3}}{GM^2 m} \quad (8.78)$$

$$= \left(\frac{9\pi}{4} \right)^{2/3} \frac{\hbar^2 \left(\frac{M}{3600 m} \right)^{5/3}}{GM^2 m} \quad (8.79)$$

$$= \left(\frac{9\pi}{4} \right)^{2/3} (3600)^{-5/3} \frac{\hbar^2}{G M^{1/3} m^{8/3}} \quad (8.80)$$

For a star with the mass of the sun, $M = m_\odot \approx 2.0 \times 10^{30}$ kg, and $R \approx 7.4 \times 10^6$ m.

The Fermi energy of such a white dwarf can be calculated by combining the following equations

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad (8.81)$$

$$n = \frac{N}{4\pi R^3/3} \quad (8.82)$$

$$N = \frac{M}{2(1800 m)} \quad (8.83)$$

which gives that $E_F \approx 0.18$ MeV. Note that the rest mass energy of an electron is 0.51 MeV, indicating that the most energetic electrons in our example white dwarf star (those on the Fermi surface) are getting near relativistic.

8.7 Relativistic Cold Electron Gas

As we confine an electron gas into a smaller and smaller volume, the allowed quantum states get higher and higher in energy. In a small enough volume, even the lowest energy electrons will be relativistic. In the relativistic limit, the energy of an electron with a wavenumber k is

$$E_k = pc = \hbar kc \quad (8.84)$$

So the Fermi energy is

$$E_F = \hbar k_{Fc} = \hbar c (3\pi^2 n)^{1/3} \quad (8.85)$$

The total internal energy of the electron gas at $T = 0$ is

$$U = \int_0^{k_F} E_k D(k) dk \quad (8.86)$$

$$= \int_0^{k_F} (\hbar k c) \left(\frac{V k^2}{\pi^2} \right) dk \quad (8.87)$$

$$= \frac{\hbar c V}{\pi^2} \int_0^{k_F} k^3 dk \quad (8.88)$$

$$= \frac{\hbar c V}{4\pi^2} k_F^4 \quad (8.89)$$

$$= \frac{E_F V}{4\pi^2} k_F^3 \quad (8.90)$$

$$= \frac{E_F V}{4\pi^2} \left(3\pi^2 n \right) \quad (8.91)$$

$$= \frac{3}{4} E_F N_e \quad (8.92)$$

8.8 Example: Collapse to a Neutron Star

Following the same procedure we used in Section 8.6, we write the the internal energy as a function of radius of the star.

$$U = \frac{\hbar c V}{4\pi^2} k_F^4 \quad (8.93)$$

$$= \frac{\hbar c V}{4\pi^2} \left(3\pi^2 \frac{N_e}{V} \right)^{4/3} \quad (8.94)$$

$$= \frac{\hbar c}{4\pi^2} (3\pi^2 N_e)^{4/3} V^{-1/3} \quad (8.95)$$

$$= \frac{\hbar c}{4\pi^2} (3\pi^2 N_e)^{4/3} \left(\frac{4}{3} \pi R^3 \right)^{-1/3} \quad (8.96)$$

$$= \frac{3}{4} \left(\frac{3}{2} \right)^{2/3} \pi^{1/3} \hbar c N_e^{4/3} R^{-1} \quad (8.97)$$

For convenience, we define the constant

$$C \equiv \frac{3}{4} \left(\frac{3}{2} \right)^{2/3} \pi^{1/3} \hbar c N_e^{4/3} \quad (8.98)$$

The gravitational potential energy is the same as we calculated in Section 8.6. The total energy is

$$U_T = U + U_G \quad (8.99)$$

$$= \frac{C}{R} - \frac{B}{R} \quad (8.100)$$

$$= \frac{C - B}{R} \quad (8.101)$$

There is no stable radius for a white dwarf star with relativistic electrons. The critical point is when $C = B$. Using the same assumptions from equations 8.75, 8.76, and 8.77, we have that

$$\frac{3}{4} \left(\frac{3}{2}\right)^{2/3} \pi^{1/3} \hbar c N_e^{4/3} = \frac{3}{5} G N_N^2 m_N^2 \quad (8.102)$$

$$\frac{5}{4} \left(\frac{3}{2}\right)^{2/3} \pi^{1/3} \left(\frac{\hbar c}{G}\right) \left(\frac{M}{2 m_N}\right)^{4/3} = M^2 \quad (8.103)$$

$$M^{2/3} = \frac{5}{4} \left(\frac{3}{2}\right)^{2/3} \left(\frac{1}{2}\right)^{4/3} \pi^{1/3} \left(\frac{\hbar c}{G}\right) m_N^{-4/3} \quad (8.104)$$

$$M = 3 \left(\frac{5}{16}\right)^{3/2} \sqrt{\pi} \left(\frac{\hbar c}{G}\right)^{3/2} m_N^{-2} \quad (8.105)$$

The *Planck Mass* is defined as

$$m_P = \sqrt{\frac{\hbar c}{G}} \quad (8.106)$$

We call the critical mass, M , the *Chandrasekhar limit*, M_{Ch} .

$$M_{\text{Ch}} = 3 \left(\frac{5}{16}\right)^{3/2} \sqrt{\pi} m_P^3 m_N^{-2} \quad (8.107)$$

$$\approx m_P^3 m_N^{-2} \quad (8.108)$$

$$\approx 3 \times 10^{30} \text{ kg} \quad (8.109)$$

$$\approx 1.5 m_{\odot} \quad (8.110)$$

If mass of the star is less than M_{Ch} , then $C - B$ is positive and the star will expand, lowering its energy levels until it is in the non-relativistic regime. If

the mass of the star is greater than M_{Ch} , then $C - B$ is negative and the star will continue to collapse. The star is forced to perform an enormous number of inverse beta-decays, converting its electrons into electron neutrinos that radiate away and converting its protons into neutrons. Then the star can reach a new equilibrium supported by neutron degeneracy pressure. Such a star is called a *neutron star*. It is virtually a huge single nucleus consisting of only neutrons. If the neutron degeneracy pressure is not enough to stop the collapse, the star becomes a *black hole*.