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1.5	*3*	*Bose Einstein distribution, Bose gas and its application*	*إحصاء بوز-أينشتين (البوزونات وتطبيقاته)*

Textbook:

Kerson Huang , Introduction to statistical Physics 2nd Edition, CRC Press , 2009

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Chapter 1

Introduction

What is the thermodynamics? What is the statistical mechanics?

1.1 **Thermodynamics*: phenomenological theory*[1]** of the macroscopic properties of system at certain ***equilibrium*** state. This theory describes the system in terms of a few experimentally measurable parameters like - Volume V , Pressure P, Temperature T , Density ρ,...etc.

1.2 **Statistical mechanics:** They belong to ***a branch of mechanics*** which explains the laws of thermodynamics on mechanical principles.

But before we venture deeply into this subject, it is useful to begin by considering what is meant by "equilibrium" and the energetics associated with removing ***macroscopic*** systems from equilibrium. This is the subject of thermodynamics. While students may be somewhat familiar with this subject, we take this point as our beginning because of its central importance to statistical mechanics.

1.3 Thermodynamic variables: The properties of a macroscopic system can be classified as either extensive or intensive.

- **Extensive quantities**: *quantities proportional to the amount of matter present*. Suppose we have a system and we double it. That

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[1] *Phenomenological theory means that it does not provide the microscopic origin of a phenomenon*

means that we double the volume V, double the number of particles N, double the internal energy U, and double the entropy S. Quantities such as V , N, U and S which are ***additive*** are called extensive.

- **Intensive quantities**: *quantities independent of the amount of matter present*. the variables which arise from differentiating the entropy, such as temperature $1/T = \partial S/\partial E$ and pressure $p = T\,\partial S/\partial V$ and chemical potential $\mu = T\partial S/\partial N$ involve the ratio of two extensive quantities and so do not change as we scale the system: they are called ***intensive*** quantities.

1.4 **Thermodynamic limit:** Consider a material body that consists of N atoms in a volume V . The limit

$N \to \infty$

$V \to \infty$

But N/V = fixed

this is called the *thermodynamic limit*, in which the system is translationary *invariant.* In the thermodynamic limit we use intensive quantities. Instead of V we use the specific volume $v = V/N$ or the density $n = N/V$.

1.5 Thermodynamic state is a state specified by a number of thermodynamic variables, which are assumed to be either extensive (proportional to N) or intensive (independent of N). Usually we consider generic systems described by the three variables P, V , and T. For magnetic systems we consider such variables as M (magnetization) and H (magnetic field).

1.6 The zeroth law of thermodynamics,

> *"If each of two systems is in thermal equilibrium with a third, then they are also in thermal equilibrium with each other".*

This implies the existence of ***a property*** called ***temperature***. Two systems that are in thermal equilibrium with each other must have the same temperature.

1.7 **Thermal equilibrium and thermodynamic transformations**

Thermal equilibrium*:* from our experience we know that a macroscopic system generally relaxes to a **stationary** state after a short time. This stationary state is called a state of thermal equilibrium.

1.8 Equation of state: if a system is in thermal equilibrium, the thermodynamic variables are not independent of one another, but constrained by the so-called equation of state of the form:

$$f(P, V, T) = 0 \qquad (1.1)$$

where *f* is a characteristic function of the system under study.

Example: the equation of state of a classical ideal gas (a real gas in the limit of low density and high temperature) is

$$f(P, V, T) = PV - Nk_B T \qquad (1.2)$$

where *T* is the ideal gas temperature measured in Kelvin (K), and $k_B = 1.381\times10^{-23}$ J/K is the Boltzmann constant, and N is the number of particles. The equation of state of the ideal gas leaves two independent variables out of the original three.

1.8.1 Geometrical representation of the equation of state: The equation of state of the ideal gas can be represented by a surface in the *state space* spanned by P, V, and T (see Fig. 1). All equilibrium states must be on this surface. *f* is a *continuous, differentiable* function, except at some special points.

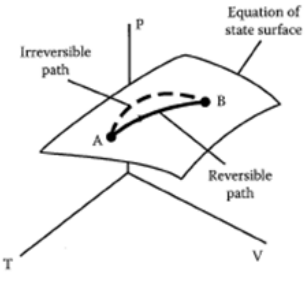


Fig. 1: The state space in thermodynamics

1.9 Thermodynamic transformation: a change in *the external conditions* changes the equilibrium state of the system. This transformation of the equilibrium state is called a *thermodynamic transformation* or *process*. For example, application of external pressure causes the volume of the body to decrease. *The initial and final states are equilibrium states*. Thermodynamic transformations are classified as:

1) **quasi-static transformation (process):** the transformation proceeds **sufficiently slowly *(*** *a mathematically infinitesimal paths)* so that the system can be considered to remain in equilibrium.

2) **reversible transformation (process):** *quasi-static transformation* is usually *reversible*, that is, the system will trace the transformation in reverse, when the external change is reversed. A reversible transformation can be represented by a continuous path on the equation of state surface, as illustrated in **Fig.1**.

3) **irreversible transformation (process):** an *irreversible* transformation cannot be retraced by reversing the external conditions. Such a transformation cannot be represented by a path in the equation-of-state space (**see fig.1**). An example of an irreversible transformation is mixing of two gases by removing the separation wall

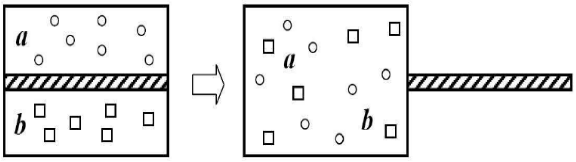


Fig. 2: Mixing of two gases as an example of an irreversible thermodynamic transformation. An example of irreversible process.

1.10 Mechanical work

Mechanical work is defined as an energy transfer either into or out of the system, through the change of an *external parameter*. *Work is the only energy which is transferred to the system through external macroscopic forces*.

Example: The mechanical work performed on a gas due to an infinitesimal volume change (reversible transformation) is

$$dW = PdV \qquad (1.3)$$

Along a finite path reversible path $A \longrightarrow B$, the work done is given by

$$\Delta W = \int_A^B PdV \qquad (1.4)$$

Which **<u>depend on the path connecting</u>** A to B. This is the area underneath the path in PV diagram.

Cycle process*:* When the path is closed cycle, the work done in one cycle is the area enclosed, as shown in fig. 3.

The work done along *irreversible* path is generally not $\int PdV$. For example, the free expansion of a gas into vacuum, the system does not perform work on any external agent, so $\Delta W = 0$.

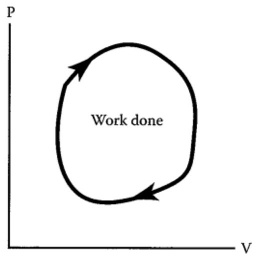


Figure 3: Cycle process.

Note:

- Mechanical work is positive when it is performed ***on*** the system.
- dW is not an *exact differential*, i.e., $W(P, V)$ does not define any state property. Not always, $\oint PdV \neq 0$

1.11 Heat transfer: Heat is a uniquely thermodynamic process. Heat can be defined as follows;

1) **From the atomic point of view** (statistical mechanics view): it represents a transfer of energy because of temperature difference.

If a system absorbs an amount of heat ΔQ, its temperature rises proportionally by an amount ΔT:

$$\Delta Q = C\Delta T \qquad (1.5).$$

The proportionality constant C is called ***heat capacity*** of the substance. It is *an extensive quantity.*

specific heat *c*: is the *intensive* heat capacity per particle C/N , per mole C/n, or per unit volume C/V.

The fact *that heat is a form of energy* was established experimentally, by observing that one can increase the temperature of a body by ΔT either by transferring heat to the body or performing work on it. The unit of heat is ***calorie:***

$$1\,cal \equiv 4.184\ \mathrm{J} \qquad (1.6)$$

the heat absorbed by a body and the work done by a body are path dependence (*not state functions*). We can speak of the amount of heat absorbed in a process, but the "heat of the body" , like the "work of a body", is meaningless.

Since the heat absorbed by a body depends on the path of transformation, one can define
various heat transfer processes:

- T = const *(isothermal process),*
- P = const *(isobaric process),*
- V = const *(isochoric process),*
- $\Delta Q = 0$ *(Adiabatic process).*

A corresponding subscript is used to distinguish the various types of paths. For example, C_V for *heat capacity at constant volume*, C_P for *heat capacity at constant pressure*.

Other thermodynamic coefficients that measure the linear response of the system to an external source are

- compressibility

$$\kappa = -\frac{1}{V}\frac{\Delta \mathrm{P}}{\Delta V} \qquad (1.7)$$

- the coefficient of thermal expansion

$$\alpha = \frac{1}{V}\frac{\Delta V}{\Delta T} \qquad (1.8)$$

Reminder: our convention is that
$\delta Q > 0$ when heat is transferred to the system
$\delta W > 0$ when work is done on the system with ;

$$\delta W = -PdV \qquad (1.9)$$

1.12: Classical Ideal Gas: is a gas in the limit of low density and high temperature.

The equation of state is given by the *ideal gas law*

$$PV = Nk_BT \qquad (1.10)$$

Where T is the ideal gas temperature, measured in kelvins (K), and

$$k_B = 1.38 \times 10^{-23}\ \text{J/K} \qquad (1.11) \quad \text{(Boltzmann constant)}$$

According to the second law of thermodynamics, $T > 0$, and $T = 0$ is called the ***absolute zero*** so T is called the ***absolute temperature***.

The heat capacity of an idela gas is given as

$$C_V = \frac{3}{2}Nk_B \qquad (1.12)$$

These properties is established experimentally, and can be derived theoretically, as we will see, in statistical mechanics. Thermodynamics does not assume the concept of atoms, instead of the number of atoms, we can use the number of grams moles n , the two are related through,

$$nR = Nk_B \qquad (1.13)$$

$$R = 8.31\,\text{J/mol.K} \qquad (1.14) \quad (\mathit{Gas\ constant})$$

The ration R/k_B is Avogadro's number N_A, the number of atoms per mole:

$$N_A = \frac{R}{k_B} = 6.022 \times 10^{23} \qquad (1.15)$$

1.12: Internal energy: *Internal energy is* a measure of the *total energy* of the system. If it were possible, we could measure the position and velocity of every particle of the system and calculate the total energy by summing up the individual kinetic and potential energies.

$$U = E = \frac{1}{2}\sum_{i=1}^{N} p_i^2 + \sum_{i=1}^{N} \phi(\vec{\mathrm{r}}_\mathrm{i}) + \frac{1}{2}\sum_{i \neq j}^{N} V\left(\vec{\mathrm{r}}_\mathrm{i} - \vec{\mathrm{r}}_\mathrm{j}\right) \qquad (1.16)$$

where $\phi(\vec{r}_i)$ is the external potential and $\mathrm{V}(\vec{\mathrm{r}}_\mathrm{i} - \vec{\mathrm{r}}_\mathrm{j})$ is the potential of interaction between particles (i.e, Coulomb interaction potential between charged particles).

1.13: The First Law of thermodynamics

For a closed system, the first law of thermodynamic is given as

$$\Delta U = Q + W \qquad (1.17)$$

In words it say that" ***the change in the internal energy of a closed system is equal to the energy transferred to the system as a heat plus the work done on the system***[2]".

In differential for it given as

$$dU = dQ + dW \qquad (1.18)$$

Where $dW = -PdV$

---

[2] Here dQ and dW ,unlike $\mathrm{d}U$, are path dependence; that is, there are no such functions as $Q(p.V)$ and $W(p.V)$ that depend only on the state of the system. The quantities dQ and dW are called ***inexact differentials*** and are usually represented by the symbols dQ and dW. For our purposes, we can treat them simply as infinitesimally small energy transfers.

1.13: Heat equations: The internal energy is an exact differential state function . Since the constraint imposed by the equation of state reduces the number of independent variables to two, we may consider the internal energy to be a function of any two of the variables. Then, under infinitesimal increments of the variables, we will have for dU:

$dU(P,V)=\left(\frac{\partial U}{\partial P}\right)_V dP+\left(\frac{\partial U}{\partial V}\right)_P dV$ $dU(P,T)=\left(\frac{\partial U}{\partial P}\right)_T dP+\left(\frac{\partial U}{\partial T}\right)_P dT$ $dU(V,T)=\left(\frac{\partial U}{\partial V}\right)_T dV+\left(\frac{\partial U}{\partial T}\right)_V dT$	(1.19)

The partial derivative, such as $\left(\frac{\partial U}{\partial P}\right)_V$, are thermodynamic coefficient to be taken from experiments.

The heat absorbed by the system can be obtained from the first law as

$$dQ = dU + PdV \qquad (1.20)$$

Then

$dQ=\left(\frac{\partial U}{\partial P}\right)_V dP+\left[\left(\frac{\partial U}{\partial V}\right)_P+P\right] dV$ $dQ=\left(\frac{\partial U}{\partial P}\right)_T dP+\left(\frac{\partial U}{\partial T}\right)_P dT+PdV$ $dQ=\left[\left(\frac{\partial U}{\partial V}\right)_T+P\right] dV+\left(\frac{\partial U}{\partial T}\right)_V dT$	(1.21)

In the second of these equations, there are three variables, we can change it to two variables by rewrite V as a function of P and T, so

$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$	(1.22)

The second equation then becomes:

$dQ = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left(\frac{\partial(U+PV)}{\partial T}\right)_P dT$	(1.23)

Now, We define the state function ***enthalpy***

$$H \equiv U + PV$$

So, the heat equations in dQ can be summarize as follow,

$dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV$ $dQ = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left(\frac{\partial H}{\partial T}\right)_P dT$ $dQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT$	(1.24)

The heat capacities at constant V and P can then be expressed as derivatives of state functions:

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

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Prob**lem ():** knowing that:$dU = dQ - PdV$, $H = U + PV$, $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$, $C_P = \left(\frac{\partial Q}{\partial T}\right)_P$, apply the internal energy U as a function of state $U(P,V)$, $U(P,T)$, $and\ U(V,T)$ to show that

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

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

1.14: Application to Ideal Gas

Joule performed a classical experiment on free expansion consisting on the following:

A thermally isolated ideal gas was allowed to expand freely into an isolated chamber, which had been initially empty (**Fig. 4**). After a new equilibrium state was established, the final temperature was be the same as initial temperature.

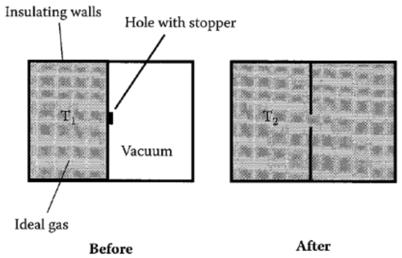


Figure 3: Free expansion of ideal gas

From this experiment we have the following conclousion :

- $\Delta W = 0$ (since the gas pushes into a vacuum)
- $\Delta Q = 0$ (since the temperature was unchanged)
- $\Delta U = 0$ (by the first law)

Choosing V, T as independent variables, we conclude $U(V_1, T) = U(V_2, T)$, that is, U is independent of V:

$$U = U(T)$$

Note: U is proportional to the number of particles N, which has been kept constant for this experiment.

Now we can express the heat capacity at constant volume as a total derivative

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT}$$

Assuming that C_V is constant, we can integrate the above to get $U(T)$ as

$$U(T) = \int C_V \, dT = C_V T$$

Where the constant of integration has been set to zero by defining $U = 0$ at $T = 0$

Also, C_P is given as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial(U + PV)}{\partial T}\right)_P$$

$$= \frac{dU}{dT} + \frac{\partial(Nk_B T)}{\partial T}$$

$$= C_V + Nk_B$$

but from eq. ( ), $C_V = \frac{3}{2} Nk_B$

Then $C_P = \frac{3}{2} Nk_B + Nk_B = \frac{5}{2} Nk_B$

- **Adiabatic Process**

  An adiabatic process happens without heat transfer:

Setting $dQ = 0$, in the first law of thermodynamic, we have $dU = -PdV$. Since $dU = C_V dT$, we obtain

$$C_V dT + PdV = 0$$

Using the equation of state $PV = Nk_B T$, then

$$T = \frac{PV}{Nk_B}$$

$$dT = \frac{d(PV)}{Nk_B} = \frac{PdV + VdP}{Nk_B}$$

Thus

$$C_V\,(PdV + VdP) + Nk_B PdV = 0$$

$$C_V\,VdP + (C_V + Nk_B)PdV = 0$$

$$C_V\,VdP + C_P PdV = 0$$

or

$$\frac{dP}{P} + \gamma\frac{dV}{V} = 0$$

where

$$\gamma \equiv \frac{C_P}{C_V}$$

Assuming that γ is a constant, we obtain through an integration

$$\ln P = -\gamma\,\ln V + \text{constant}$$

or

$$PV^{\gamma} = \text{constant}$$

Using the equation of state, we can rewrite this in the equivalent form

$$TV^{\gamma-1} = \text{constant}$$

Since $\gamma > 1$, ***an adiabatic path has a steeper slope than an isotherm in a P - V diagram***

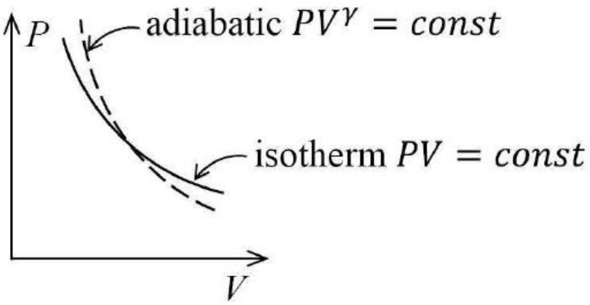


Figure 4: An adiabatic line has steeper slope than isothermal

Q. Prove that the slope of the adiabatic path is steeper than the slope of isothermal path in a $P - V$ diagram.

Chapter 2

Entropy and Second Law of Thermodynamics

2.1 Carnot Cycle:

Now, it's well known that U is a state function. In a cyclic transformation, the final state is the same as the initial state, and therefore

$$\Delta U = 0 \qquad (2.1)$$

A reversible cyclic process can be represented by a closed loop in the PV diagram, **Fig. 2.1**

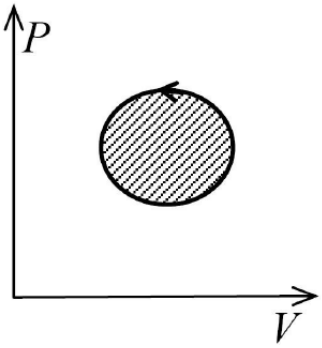


Figure: 2.1 Reversible cyclic process. The shaded area of the loop is the total work done by the system in one cycle.

The area of the loop is the total work done by the system in one cycle. Since $\Delta \boldsymbol{U} = \boldsymbol{0}$, it is also equal the heat absorbed.

$$|\Delta W| = |\Delta Q| \cdots (2 \cdot 2)$$

A Carnot cycle a reversible cycle bounded by two isotherms and two adiabatic lines, see figure 2.2.

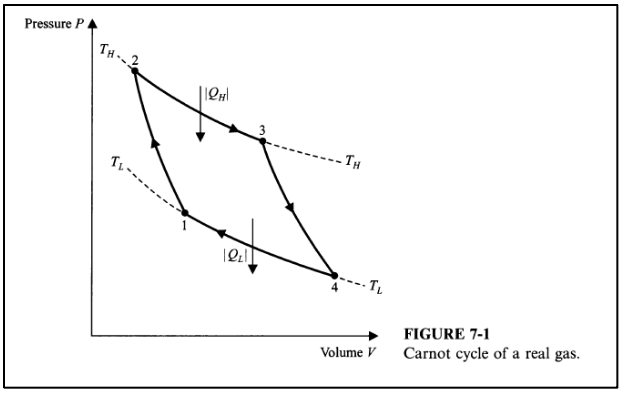


Figure: 2.2 Carnot cycle on the PV diagram of ideal gas.

With the condition $T_h > T_L$, the system absorbs heat $|Q_H|$ along the isotherm T_H and rejects heat $|Q_L|$ along T_L , with $|Q_H| > |Q_L|$. Using the first law of thermodynamics, the net work output is

$$W = |Q_H| - |Q_L| \qquad (2.3)$$

The efficiency of the Carnot engine is defined as

$$\eta = \frac{W}{Q_H} = 1 - \frac{|Q_L|}{|Q_H|} \qquad (2.4)$$

Which is 100% if there is no waste heat, that is, $|Q_L| = 0$. *But, this is impossible , according to the second law of thermodynamics.*

The Carnot engine is represented by the schematic diagram shown in fig. 2.3

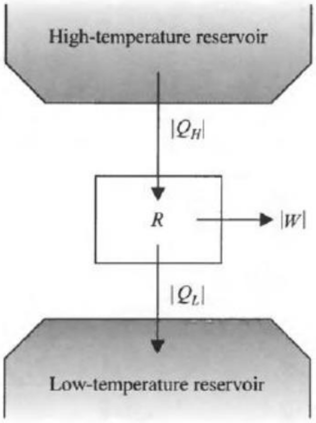


Figure 2.3 Schematic representation of Carnot engine.

The importance of Carnot's cycle originates from the fact that it is not only to be interpreted as an idealized limiting case of real cycles, but that it will make some principle ideas (such as entropy) clear to us.

The Carnot cycle is performed in four successive reversible steps, as illustrate in PV diagram in figure 2.2.

To compute $|Q_L|$ and $|Q_H|$,we need only to consider the isothermal processes. For any infinitesimal reversible process of *an ideal gas*, the first law of thermodynamic can be written as;

$$dQ = C_V dT + PdV$$

- Applying this equation to the isothermal process $2 \rightarrow 3$, the heat absorbed is

$$|Q_H| = \int_{V_2}^{V_3} PdV$$

$$= nRT_H \ln \frac{V_3}{V_2}$$

Similarly, for the isothermal process $4 \rightarrow 1$

$$|Q_L| = nRT_L \ln \frac{V_1}{V_4}$$

Therefore

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L} \frac{\ln \frac{V_3}{V_2}}{\ln \frac{V_1}{V_4}} \cdots\cdots (2 \cdot 5)$$

Since the process $1 \rightarrow 2$ is adiabatic, we may write, for any infinitesimal portion

$$-C_V dT = PdV.$$

Or

$$-C_V dT = \frac{nRT}{V} dV$$

Integrating from $1 \rightarrow 2$, we get

$$-\frac{1}{nR} \int_{T_L}^{T_H} C_V \frac{dT}{T} = ln \frac{V_2}{V_1}$$

$$\frac{1}{nR}\int_{T_L}^{T_H} C_V\frac{dT}{T} = ln\frac{V_1}{V_2}$$

Similarly, for the adiabatic process $3 \rightarrow 4$,

$$-\frac{1}{nR}\int_{T_H}^{T_L} C_V\frac{dT}{T} = ln\frac{V_4}{V_3}$$

$$\frac{1}{nR}\int_{T_L}^{T_H} C_V\frac{dT}{T} = ln\frac{V_3}{V_4}$$

Therefore

$$\begin{array}{c} ln\frac{V_1}{V_2} = ln\frac{V_3}{V_4} \\ or \\ ln\frac{V_3}{V_2} = ln\frac{V_1}{V_4} \end{array} \quad \cdots\cdots (2\cdot 6)$$

Combining eq.(2.5) and eq.(2.6) obtain

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L} \cdots (2.7)$$

Then with eq.(2.4)

$$\eta = 1 - \frac{T_L}{T_H}$$

2.4 Entropy

From eq.(2.7), then

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L}$$

or

$$\frac{Q_H}{Q_L} = -\frac{T_H}{T_L} \Rightarrow Q_H T_L = -Q_L T_H$$

So actually, during this reversible process we have

$$\sum_{n}\left(\frac{Q_L}{T_L}+\frac{Q_H}{T_H}\right)_n = 0 \Rightarrow \oint \frac{dQ}{T} = 0 \cdots (2.8) \quad (\text{reversible process})$$

Let us consider the following theorem stated by *Clausius:*

> *⇒ "In an arbitrary cyclic process P, the following inequality holds:*
>
> $$\oint_P \frac{dQ}{T} \le 0 \cdots (2.9)$$
>
> *where the equality holds for P reversible."*

Since $\oint \frac{\mathrm{dQ}}{\mathrm{T}} = 0$ for reversible process, then $\frac{\mathrm{dQ}}{\mathrm{T}}$ is *exact differential*. This implies that there a state function *S* called *entropy* whose differential is given as

$$dS = \frac{\mathrm{dQ}}{\mathrm{T}}$$

The entropy is defined up to an additive constant. The difference between entropies of any two states A and B is

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

❖ THE INCREASE OF ENTROPY PRINCIPLE

Consider a cycle that is made up of two processes: process 1-2, which is arbitrary (reversible or irreversible), and process 2-1, which is internally reversible, as shown in Figure 2–4.

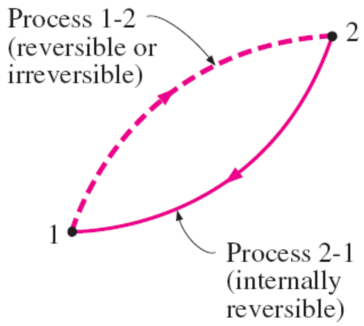


Figure 2-4: A cycle composed of a reversible and an irreversible process.

From the Clausius inequality,

$$\oint \frac{\delta Q}{T} \leq 0$$

Or

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \leq 0$$

The second integral in the previous relation is recognized as the entropy change $S_1 - S_2$. Therefore,

$$\int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0$$

Which can be regards as

$$S_1 - S_2 \geq \frac{dQ}{T} \cdots (2.10)$$

It can also be expressed as

$$dS \geq \frac{\delta Q}{T} \cdots (2.11)$$

where the equality holds for an internally ***reversible*** process and the inequality for an ***irreversible*** process.

We may conclude from these equations that:

- In the limiting case of a reversible process, these two quantities become equal.

$$dS = \frac{dQ}{T}$$

- The entropy change of a closed system during an ***irreversible process*** is greater than the integral of dQ/T evaluated for that process.

$$dS > \frac{dQ}{T}$$

This means that, the entropy change of a closed system during an irreversible process is always greater than the entropy transfer. That is, some entropy is ***generated*** or ***created*** during an irreversible process, and this generation is due entirely to the presence of ***irreversibilities***. The entropy generated during a process is called ***entropy generation*** and is denoted by S_{gen}. Noting that the difference between the entropy change of a closed system and the entropy transfer is equal to entropy generation,

$$\Delta S_{system} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

Now, for an isolated system (or simply an adiabatic closed system), the heat transfer is
zero, and Eq. 2.10 reduces to

$$\Delta S_{isolated} \geq 0 \cdots (2.12)$$

This means that the entropy of an isolated system never decreases and remains constant during a reversible transformation.

Note:

i) The joint system of a system and its environment is called" *<u>universe</u>". Defined in this* *way, the" universe" is an isolated system and, therefore, its entropy never decreases.*

However, the entropy of a non-isolated system may decrease at the expense of the system's environment.

ii) Since the entropy is a state function, $S(B) - S(A)$ is independent of the path, regardless whether it is reversible or irreversible. For an irreversible path, the entropy of the environment changes, whereas for a reversible one it does not.

iii) Remember that the entropy difference

$$S_A - S_B = \int_A^B \frac{dQ}{T}$$

only when the path is reversible; otherwise, the difference is larger than the integral

---

Example Problem (   ): *The heat capacity at constant volume of a number of substances can be represented empirically by an equation of the form*

$$C_V = a + bT + CT^2$$

where a, b, and c are constants. Calculate the change in internal energy and the change in entropy when the temperature changes fromT_1toT_2 at constant volume.

Solution

At constant volume, we have $dU = dQ = C_V dT$ then

$\Delta U = \int_{T_1}^{T_2} C_V\, dT = \int_{T_1}^{T_2} (a + bT + cT^2) dT$. Thus,

$$\Delta U = (aT + b\,T^2/2 + c\,T^3/2)|_{T_1}^{T_2}$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_V/T\,\mathrm{d}T = a \ln T + bT + cT^2/2\Big|_{T_1}^{T_2} .$$

2.5 The Second Law of Thermodynamics

Definition by Clausius:

" There is no thermodynamic transformation whose sole effect is to deliver heat from a reservoir of lower temperature to a reservoir of higher temperature."

Summary: heat does not flow upwards.

Definition by Kelvin:

"There is no thermodynamic transformation whose sole effect is to extract heat from a reservoir and convert it entirely to work".

Summary: a perpetuum mobile of second type does not exist.

2.5 Entropy of Ideal Gas

As we have seen, the first law for a closed PVT system is given in differential form as

$$dU = dQ - dW = dQ - PdV$$

Now for reversible process we have

$$\mathrm{dS} = \frac{\mathrm{dQ}}{\mathrm{T}} \Longrightarrow \mathrm{dQ} = \mathrm{TdS}$$

Combining the two equations we get

$$\boxed{\boldsymbol{dU = TdS - PdV}}$$

This is the ***central*** equation in thermodynamic . It is in fact ***the fundamental equation*** for closed PVT systems and for PVT systems of fixed composition, and all other property relations are derived from it.

For the special case of an ideal gas, we have ; $\boldsymbol{dU = C_V dT}$ so the last equation becomes

$$C_V dT = TdS - PdV$$

Or

$$dS = C_V \frac{dT}{T} + \frac{P}{T} dV$$

However by the ideal gas law $P/T = Nk_B/V$, and $C_V = 3/2\, Nk_B$ we get

$$dS = \frac{3}{2} Nk_B \frac{dT}{T} + Nk_B \frac{dV}{V}$$

This equation prove that the entropy of an ideal gas is a function of *T* and *V*, i.e.
$S = S(V,T)_N$. If we integrate the last equation the starting from T_0 and V_0 with entropy S_0 we find

$$S(V,T) = S_0(V,T) + \frac{3}{2}Nk_B\ln\frac{T}{T_0} + Nk_B\ln\frac{V}{V_0}$$
$$= C_0 + Nk_B\ln\left(VT^{3/2}\right)$$

Where the constants includes V_0 and T_0 is absorbed by the constant C_0.
Since the entropy is an extensive quantity, it has to be proportional to the particle number *N*. This can not exist unless C_0 somehow contain a term $Nk_B\ln N$. As we shall see, this is supplied by quantum effects, through " ***correct Boltzmann counting***".
Looking forward, let us here quote ***Sackur –Tetrode equation*** for the absolute entropy:

$$S = Nk_B\left[\frac{5}{2} - \ln(n\lambda^3)\right]$$

Which will be derived further. Hence $n = N/V$ and λ is the ***thermal wavelength*** , the wavelength of a particle with energy k_BT:

$$\lambda = \sqrt{2\pi\hbar/mk_BT}$$

Where $\hbar$ is the reduced Planck's constant. It is interesting to note that this quantum constant appears even in high-temperature macroscopic physics.

2.6 Condition for equilibrium

The first law of thermodynamic states that $\Delta U = \Delta Q - PdV$. Using Clausius' theorem $\Delta Q \leq T\Delta S$, we have;

$$\Delta U \leq T\Delta S - \Delta W$$

Therefore, when $\Delta S = \Delta W = 0$

$$Then,\ \ \Delta U \leq 0$$

"This means that, for thermally and mechanically isolated system, the internal energy will tend to have the lowest possible value".

- **Maxwell equation from the internal energy *U***

  For infinitesimal reversible changes we have

  $$dU = TdS - PdV$$

  Then the natural variables of *U* are *S* and *V.* If the function $U(S, V)$ is known, we can obtain all thermodynamic properties through the formula;

  $$P = -\left(\frac{\partial U}{\partial V}\right)_S$$

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

  We emphasize that these equations holds for all infinitesimal changes of *U(S, V)* within the field of ***equilibrium states***.Thes second equation is concidered as the ***real definition of temperature***.

If the second partial derivatives of *U* are continuous, as we shall assume to be the case for thermodynamic functions, the order of partial differentiation does notmatter and we obtain

$$\left(\frac{\partial}{\partial V}\right)\left(\frac{\partial U}{\partial S}\right) = \frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial}{\partial S}\right)\left(\frac{\partial U}{\partial V}\right) = \frac{\partial^2 U}{\partial S \partial V}$$

But

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_s$$

And

$$\frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

Then,

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

The last equation is the first ***Maxwell relation, dervied from U***

2.7 Helmholtz Free Energy

Remember that up to now we have four thermodynamic variables, P, V, T, S. In the laboratory it is difficult to manipulate S, V, but far easier to change V, T. The question know is "what is the ***equilibrium condition*** at constant, T ?

The answer as follow,

From the inequality $\Delta U \leq T\Delta S - \Delta W$. If T is kept constant we can rewrite it as

$$\Delta \boldsymbol{W} \leq -\Delta(\boldsymbol{U} - \boldsymbol{TS})$$

If $\Delta W = 0$,

Then

$$(\boldsymbol{U} - \boldsymbol{TS}) \leq \mathbf{0}$$

This motivates us to define ***Helmholtz Free energy*** or simply *free energy*

$$\boldsymbol{F} \equiv \boldsymbol{U} - \boldsymbol{TS}$$

Then

$$\Delta \boldsymbol{W} \leq -\Delta(\boldsymbol{F})$$

If $\Delta \boldsymbol{W} = \mathbf{0}$**, then** $\Delta(\boldsymbol{F}) \leq \mathbf{0}$ **.** ***The equilibrium condition for a mechanically isolated body at constant temperature is that the free energy be minimum.***

- **Maxwell equation from Helmholtz free energy**

  For infinitesimal reversible transformations we have

$$dF = dU - TdS - SdT$$
$$dU = TdS - PdV$$

  Then

$$dF = -SdT - PdV$$

Then knowing $F(V,T)$, then all thermodynamic properties can be obtained through Maxwell relations

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

and from the formula for *Helmholtz Free energy*, $F \equiv U - TS = TdS - PdV - TS$, and assuming the natural variables of F are *T* and *V*, we have,

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

The last equation is the second ***Maxwell relation, dervied from F***

2.8 Gibbs Potential

We have seen that the thermodynamic properties of a system can be obtained from the function $U(S,T)$ or from $F(V,T)$. Let us now consider $G(P,T)$;

$$G = F + PV$$

- Maxwell equation from Gibbs free energy

$$dG = dF + PdV + VdP$$

$$dG = dF + PdV + VdP$$

$$dG = -SdT - PdV + PdV + VdP$$

$$dG = -SdT + VdP$$

Then

$$S = -\left(\frac{\partial G}{\partial T}\right)_P , \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

and from the formula for the Gibbs free energy,

$$G = F + PV = U - TS + PV$$

And assuming the natural variables of G are *T* and *P*, we have,

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

The last equation is the third *Maxwell relation, dervied from G*

2.8 Enthalpy

We have seen the functions $U(S,T)$ or from $F(V,T)$, $G(P,T)$. Let us now consider $H(S,P)$

$$H = U + PV$$

- Maxwell equation from Enthalpy

$$dH = dU + PdV + VdP$$

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

$$dH = TdS + VdP$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad , \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

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

The last equation is the fourth ***Maxwell relation, dervied from H***

2.9 Using Maxwell Relations

We can summarize basic functions (Potentials) and its inter-relations as follow;

$$\Delta U = Q + W$$
$$F = U - TS$$
$$G = F + PV$$
$$H = U + PV$$

The differential forms are as follow

$$U(S,V): \qquad dU = TdS - PdV$$
$$F(V,T): \qquad dF = -SdT - PdV$$
$$G(P,T): \qquad dG = -SdT + VdP$$
$$H(S,P): \qquad dH = TdS + VdP$$

Each function is expressed in terms of its natural variables. *When these variables are held fixed, the corresponding function is at a minimum in thermal equilibrium*.

Figure 2.6 Summarize the Maxwell relations.

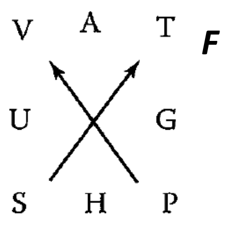


Figure 2.6:

Mnemonic diagram summarizing the Maxwell relations. Each quantity at the center of a row or column is flanked by its natural variables. The partial derivative with respect to one variable, with the other kept fixed, is arrived at by following the diagonal line originating from that variable. Attach a minus sign if you go against the arrow.

2.10 Chemical Potential

So far we have kept the number of particles N constant in thermodynamic transformations. When N does change, the first law is generalized to the form where μ is called the *chemical potential,* the energy needed to add one particle to a thermally and mechanically isolated system. For a gas-liquid system we have

$$dU = TdS - PdV + \mu dN$$

The change in free energy is given by

$$dF = -SdT - PdV + \mu dN$$

which gives the Maxwell relation

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

Similarly, for processes at constant P and T, we consider the change in the Gibbs potential:

$$dG = -SdT - VdP + \mu dN$$

and obtain

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

CHAPTER 3

The statistical approach

3.1 Introduction

Given certain information about a substance (e.g., *equation of state, heat capacity*), thermodynamics allows us to derive various other quantities. *What is the missing in this way is the bridge between the macroscopic level of thermodynamics and the mechanical (classical or quantum) description at the atomic level.*

Since the number of particles in a macroscopic system is huge ($\sim 10^{23}$ particles in a cubic centimeter), one cannot expect an exact solution of the equations of motion. Not only because one would need a supercomputer to deal with 10^{23} coupled equation, but also because it is not at all clear how useful it would be to deal with the large amount of data resulting out of these equations.

Therefore, in statistical physics we will be dealing ***with average quantities and probability predictions***. For example, ***the pressure*** of a gas is due ***to the collisions of the molecules with a surface***, whereas, ***temperature is directly given by the mean kinetic energy of the particles***. ***Fluctuations*** around the average value are also possible within the statistical physics, but for large numbers of particles, $N \to \infty$, these fluctuations will become less and less important. In order to make ***rigorous predictions***, the statistical physics needs to have the limit $N \to \infty$.

We can distinguish the following branches of statistical physics.

- ***Classical statistical physics:*** the microscopic equations of motion of the particles are given by classical mechanics.
- ***Quantum statistical physics:*** the microscopic equations of motion of the particles

are given by quantum mechanics.

- ***Statistical physics in equilibrium***: the macroscopic variables are time-independent

and the macroscopic world can be described in terms of microscopic average values,
distribution functions or probabilities.

- ***Statistical physics in non-equilibrium***: the macroscopic variables are time dependent

.In this case, the microscopic treatment is more complicated.

In this course, we will restrict ourselves *to classical and quantum statistical physics in equilibrium.*

3.2 Phase Space

How we classify the state of a system of N-particle?

3.2.1: Γ–space (one point with 6N- components in 6N –dimensional space)

In classical mechanics, a state of a particle at any instant of time is specified by its ***momentum*** $\vec{\boldsymbol{p}}$ and ***position*** $\vec{\boldsymbol{r}}$. The six components of these vector quantities ***span* the phase space** (the space of all coordinates and momenta) ***of one particle***. For ***N*** particles, the total number of ***degrees*** is $\boldsymbol{6N}$, and ***the total phase space is 6N-dimensional***. The motion of the particle is governed by the Hamiltonian

$$H(p,r) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} U(r_i - r_j) \qquad (3.1)$$

Where $\boldsymbol{U}(\boldsymbol{r})$ is *the interatomic potential*

The point in this space is given as;

$$(p,r) = (p_1, p_2, p_3 \dots\dots, p_{3N}, r_1, r_2, r_3, \dots\dots r_{3N}) \qquad (3.2)$$

The set (p,r) can now be understood as *a point in* 6N –dimensional space which is called Γ *–space*, or *classical phase space*. *The point in this phase space is called representative point and corresponds to one microstate of motion of the whole system at particular time.* As time *evolves*, *the representative point* traces out *a trajectory*. It never intersects itself, because the solution of the equations of motion is unique. *If* H *does not depend explicitly on time,* in which case *energy is a conserved quantity, all trajectories in phase space lie on an energy surface which is a hypersurface in* Γ *–space defined by*

$$H(p,r) = E \qquad (3.3)$$

A symbolic representation of Γ –space is shown in **figure (3.1a)**.

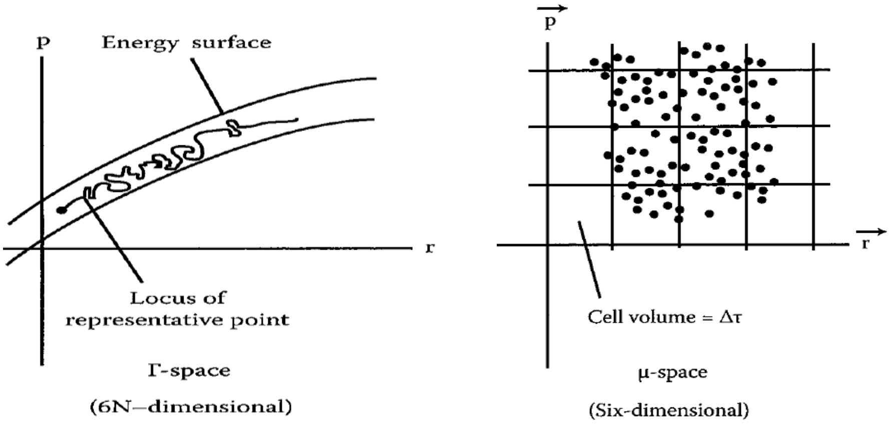


Figure 3.1

3.2.2: μ–space (N- points with 6- components in 6 -dimensional space)

Another way to specify the state of the system is to describe each atom *separately* (one-particle phase space). The motion of each atom is described by momentum and position $(\vec{p},\vec{r})$, *which span a 6-dimensional phase space called the μ-space* (*N- points phase space).* The overall system is represented by $N \approx 10^{19}$ points (number of atoms in the dilute limit), as illustrated schematically in figure (3.1b)

3.4 Microstates and Macrostates

A microstate; is *a state that specifies the parameters of all the particles of the system*. In a system of N particles, we know *the position* and *momentum* of each particle**.** *One microstate* can be described by either *one point with one point of 6N-components in Γ – space* or *N-points with 6 –components in μ-space*.

A macrostate; is a state *that describes the system as whole*. For example, a system with a fixed *pressure*, *volume* and *temperature* is in *a particular macrostate*. There are *many different possible microstates that can give rise to a particular macrostate*.

3.4.1 Number of microstates *Ω*

Consider a system of two particles A and B that can both exist in one of two energy levels, E_1 and E_2. The *macrostate* of this system can be defined by the total energy of the system.

Macrostate	(1) $E_1 + E_1$	(2) $E_1 + E_2$	(3) $E_2 + E_2$
Microstate	$A(E_1),B(E_1)$	$A(E_1),B(E_2)$ $A(E_2),B(E_1)$	$A(E_2),B(E_2)$
Ω	1	2	1

Therefore if both energy levels, E_1 and E_2 are equally likely, the system has a 50% chance of being in macrostate *(2)* and a 25% chance each of being in macrostates *(1)* and *(3)*.

However, in general not every energy level is equally likely so the most likely macrostate is also governed by the probability of energy level occupation.

This leads on to the concept of the *partition function, Z,* for a system, which we will cover later.

3.5 Ergodic Hypothesis

Given a sufficiently long time, the representative point of an isolated system will come arbitrarily close to any given point on the energy surface.

Essentially, this means that *for an isolated system in equilibrium, all accessible microstates are equally likely*. This is the "*assumption of equal a priori probability*" .This means that, "*There is no preferred microstate*".

This is ***the fundamental assumption of statistical physics***. It is very difficult to prove that a system will even ***visit*** every allowed point much less prove that all are equally probable. In the absence of a mathematical proof, we use ***the postulate*** of equal probabilities as a working hypothesis (that happens to be well supported by experiments and numerical simulations).

3.6 Distribution function:

After establishing *the space* that describe the atoms, we seek *distribution function* $f(\vec{p},\vec{r},t)$ which describe *the statistical* *properties of the entire system*, rather than the behavior of the individual atoms.

3.6.1 $\boldsymbol{f(\vec{p},\vec{r},t)}$ in *μ-space*

Divide the *μ-space* into *cells* which are *6–dimensional volume element*

$$\Delta\tau = \Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z \qquad (3.4)$$

Each cell is distinguished *on a microscopic level*, but *is infinitesimal on a macroscopic scale*. We assume that a cell contains a large number of atoms. From a macroscopic view, particles in the *i*th cell have the same *energy* ε_i.

<u>Definition</u>: The number of particles, n_i ,in cell i at time t;, is called *<u>the occupation number.</u>*

<u>Definition:</u> The distribution function, $f(\vec{p},\vec{r},t)$, is defined as *<u>the occupation number per unit volume:</u>*

$$f(\vec{p},\vec{r},t) = \frac{n_i}{\Delta\tau} \qquad (3.5)$$

$$\Rightarrow \; f(\vec{p},\vec{r},t)\Delta\tau = n_i \qquad (3.6)$$

Since there are N-atoms with total energy, $\boldsymbol{E}$, we have the conditions;

$$\sum_i n_i = N \qquad (3.7)$$

$$\sum_i n_i \varepsilon_i = E \qquad (3.8)$$

The phase-space unit volume $\Delta\tau$ is so *arbitrary*. Sometimes, this leads to the appearing *undetermined constant*, as in the expression for entropy, as we shall see later. In quantum mechanics determines the unit volume is found to be h^3 , where h is planck's constant.

In *the <u>thermodynamic limit</u>* $(N \rightarrow \infty, V \rightarrow \infty)$, $f(\vec{p},\vec{r},t)$ is assumed to be a *continuous function*, and one also can write

$$\Delta\tau \rightarrow d^3p\, d^3r$$

So $(\mathbf{3.6})$ and $(\mathbf{3.7})$ can be rewritten as;

$$\int d^3p\ d^3r\, f(\vec{p},\vec{r},t) = N \qquad (3.9)$$

$$\int d^3p\ d^3r\, f(\vec{p},\vec{r},t)\,\frac{p^2}{2m} = E \qquad (3.10)$$

If the density *is uniform* , then $f(\vec{p},\vec{r},t)$ is *independent* of $\vec{r}$. We denote it by $f(\vec{p},t)$

$$\int d^3p f(\vec{p},t) = \frac{N}{V} \qquad (3.11)$$

$$\int d^3p f(\vec{p},t)\,\frac{p^2}{2m} = \frac{E}{V} \qquad (3.12)$$

Thus, it is possible to find the state of a system once we know the distribution function. The distribution function that we have defined, $f(\vec{p},\vec{r},t)$, *evolves* in time following the microscopic equations of motion. When *thermal equilibrium* is reached, $f(\vec{p},\vec{r},t)$ should acquire a time-independent form $f(\vec{p},\vec{r})$.

Our aim is to find the equilibrium distribution, and to deduce from it the thermodynamics of the system

3.7 Entropy in statistical physics

As we mentioned before, there are *many different possible microstates that can give rise to a particular macrostate*. *Then the states with the largest value of Ω are those that are most likely occurs. However, the states with the largest value Ω are also with most disorder*-simply because there are so many microstates to give one macrostate. This means that there must be relationship between *Ω* and the entropy *S* of a system.

Therefore if

Ω tends to a maximum,

Then,

S tends to a maximum.

3.7.1 The Boltzmann-Planck entropy formula

The Boltzmann-Planck equation for entropy is written,

$$\boxed{S = k_B \ln\Omega \qquad (3.13)}$$

where Ω is is *the number of possible microstates* corresponding to *a given macrostate*., or *the number of arrangements* , or *the multiplicity* of the state of the system. The states with the largest value of Ω. will be the ones most likely to occur. This equation is carved on Boltzmann's tombstone in Vienna. The reason why we use logarithms is because for two systems with entropy *S₁, S₂*; the total entropy is S_1+ S_2. However, looking in terms of the microstates of the systems, Ω_1, Ω_2; the total number of microstates is $\Omega_1\Omega_2$; . This is reconciled with logarithms.

3.7.2 Entropy and information theory

Entropy can be thought of as a measure of information. For a macrostate with only one microstate (highly ordered), e.g. all particles are stationary, the entropy is a minimum. The macrostate with the most microstates available (highly disordered) has maximum entropy and is the most likely state.

Consider a system with a number of possible states, $i = 1, 2, 3, \dots, r$
And there is a probability P_i that the system is in state i
Let's measure the state of this system a very large number of times, N. The number of times we get the state i (number of microstates belong to the state i) is

$$n_i = NP_i \qquad (3.14)$$

The total number of microstates of this system is;

$$\Omega_N = \frac{N!}{\prod_{i=1}^{r} NP_i} \qquad (3.15)$$

` Applying this to the Boltzmann-Planck equation gives us,

$$S_N = k_B \ln\Omega_N$$

$$S_N = k_B \ln\left(\frac{N!}{n_1!\, n_2!\, n_3! \dots .\, n_r!}\right)$$

$$= k_B \ln N! - \ln(n_1!\, n_2!\, n_3! \dots .\, n_r!)$$

$$= k_B \left[N \ln N - \sum_i n_i \ln n_i \right]$$

The entropy of a single system is related to the entropy of the ensemble as;

$$S = \frac{S_N}{N} = \frac{k_B}{N} \left[N \ln N - \sum_i n_i \ln n_i \right]$$

$$= k_B \left[\ln N - \sum_i P_i \ln P_i \right] =$$

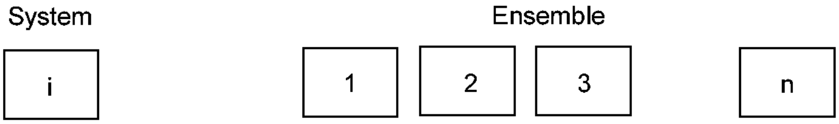
$$= -k_B \sum_i P_i \ln P_i \qquad (3.16) \quad (for\ large\ i)$$

3.8 Statistical Ensemble

To measure a physical quantity in statistical mechanics we take *the average* over a suitably *chosen collection of systems* called *statistical ensemble*.

The *statistical ensemble*; *is an infinite collection of identical copies (replica) of the system, with identical specifications e.g. volume, temperature, chemistry, number of particles…etc.*

The ensemble represents the *microstate* of the system while each individual replica represents one of the possible *microstates.*



This collection of systems is characterized by *a density function* $\rho(p, r, t)$ in *Γ–space*. From eq. (3.5), this is defined as;

$$\boxed{\begin{aligned}&\rho(p, r, t) dpdr \\ &= Number\ of\ system\ copies\ in\ the\ vloume\ element\ dpdr\ at\ time\ t\end{aligned}}$$

Where each *system copy* in this space is characterized by the point

$$(p,r) = (p_1, p_2, p_3 \dots\dots, p_{3N}, r_1, r_2, r_3, \dots\dots r_{3N}) \qquad (3.17)$$

And ***the volume element*** in this space is given as:

$$dp\,dr = d^{3N}p\, d^{3N}\, r \qquad (3.18)$$

The probability of finding the system in $dpdr$ at time t is given as;

$$\widetilde{P} = \frac{number\ of\ microstates\ (\ systems)\ in\ the\ volume\ (dp\ dr)\ at\ time\ t}{total\ number\ of\ microstates}$$

$$\widetilde{P} = \frac{\rho(p,r,t)dpdr}{\int \rho(p,r,t)dpdr} \qquad (3.19)$$

This can also be expressed ***as a probability density*** (i.e., ***probability per unit phase-space volume),***

$$P = \frac{\widetilde{P}}{dp\,dr} = \frac{\rho(p,r,t)}{\int \rho(p,r,t)dpdr} \qquad (3.20)$$

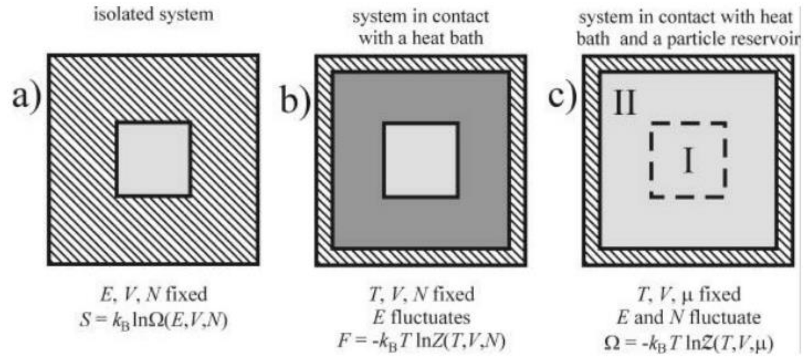
The probability for the system to be in certain microstate is

$$P(1) = \frac{1}{\int \rho(p,r,t)dpdr} \qquad (3.21)$$

The ensemble average of a physical quantity $O(p,r)$ is:

$$\langle o \rangle = \frac{\int dpdr\rho(p,r,t)O(p,r)}{\int \rho(p,r,t)dpdr} \qquad (3.22)$$

It is important to keep in mind that *members of the ensemble are* <u>*mental copies*</u> *of the system* and do not interact with each other. There are several different ensembles that we might encounter. The type of ensemble is governed by the measurable parameters.



1. **Micro-canonical ensemble:** _isolated system_, the total internal energy, *U*, and number of particles, *N*, is well defined.
2. **Canonical ensemble**: systems in _thermal equilibrium_, the temperature, *T*, and number of particles, N, is well defined.
3. **Grand canonical ensemble**: systems in thermal and chemical contact, the temperature, T, and chemical potential, μ, is well defined.

3.8.1 Microcanonical Ensemble

A simple example

There are 3 (_distinguishable, independent and identical_) particles A, B and C. They are allowed to occupy 4 different energy states: $\varepsilon_0 = 0$, ε_1, $\varepsilon_2 = 2\varepsilon_1$ and $\varepsilon_3 = 3\varepsilon_1$
(e.g. harmonic oscillator).
The total energy of the system amounts to $3\varepsilon_1$.
The occupation numbers are n_0, n_1, n_2 and n_3.
Now we are going to try to find the number of macro-states by which the system can be realized.

Macro-state	n_0	n_1	n_2	n_3	$N = \sum_{i=1}^{3} n_i$	$E = \sum_{i=1}^{3} n_i \varepsilon_i$
I	**2**	**0**	**0**	**1**	**3**	$3\varepsilon_1$
II	**1**	**1**	**1**	**0**	**3**	$3\varepsilon_1$
III	**0**	**3**	**0**	**0**	**3**	$3\varepsilon_1$

We see that there are only 3 possible macro-states for the system.
The next question is then: How many micro-states are possible to realize each macro-state?
Note: We recall/realize that exchange of particles in the same micro-state doesn't generate a new micro-state!

Energy state	***Macro-state I***			***Macro-state II***						***Macro-state III***
ε_3	**A**	**B**	**C**	**-**	**-**	**-**	**-**	**-**	**-**	**-**

ε_2	-	-		A	A	B	B	C	C	-
ε_1	-	-		B	C	A	C	A	B	ABC
ε_0	BC	AC	AB	C	B	C	A	B	A	–
No. of micro-states	3			6						1

Hence macro-state II has the highest number of microstates, or number of arrangements Ω (often written as W for German „Wahrscheinlichkeit" = probability) , $\Omega_{II} = 6$, in this example.

- **Generalization**

Inspired from this example we want to generalize this for N particles. For single occupation $n_i = 1$ it can be directly concluded that the highest number of microstates is given by all permutations, or $\Omega = N!$ However, if we consider cases in which the occupation number can eventually become larger than 1 ($n_i > 1$) we are overestimating by this method. This is because the permutation of particles in each individual micro-state doesn't generate a new micro-state. Hence, we need the following correction:

$$\Omega_N = \frac{N!}{n_0!\, n_1!\, n_2! \ldots}$$

Note: The meaning of this equation can easily be checked on the previous example

macro-state I: $\Omega_{\text{I}} = \frac{3!}{2!\,0!\,0!\,1!} = \frac{6}{2} = 3$ ✓

macro-state II: $\Omega_{\text{II}} = \frac{3!}{1!\,1!\,1!\,0!} = \frac{6}{1} = 6$ ✓

macro-state III: $\Omega_{\text{III}} = \frac{3!}{0!\,0!\,3!\,0!} = \frac{6}{6} = 1$ ✓

We also know that in equilibrium the Boltzmann (entropy) equation tells us that the most probable is realized (for maximum entropy), or (eq. 3. 13)

$$S = k_B \ln \Omega_{\max}$$

Additionally we can establish the following constraints:

$$N = \sum_{i=1}^{3} n_i \qquad \text{(total number of particles)} \qquad (3.23)$$

$$E = \sum_{i=1}^{3} n_i \varepsilon_i \qquad \text{(total energy)} \qquad (3.24)$$

our goal is summarized in eq. (3.20): We have to find the maximum number of microstates

$$\Omega_N = \frac{N!}{\prod_{i=0}^{r-1} n_i!} \rightarrow \text{maximum} \qquad (3.25)$$

To simplify this task, we notice that when Ω has a maximum, ln Ω also must have a maximum (because the logarithm is a monotonic function). This enables us to use Stirling's approximation:

$$\ln N! = N \ln N - N \qquad (3.26)$$

Hence, eq. [3.1.5] becomes:

$$\ln \Omega = \ln \frac{N!}{\prod_{i=0}^{r-1} n_i!} = \ln N! - \ln \prod_{i=0}^{r-1} n_i! \qquad (3.27)$$

$$= N \ln N - N - \sum_{i=0}^{r-1} (n_i \ln n_i - n_i) \qquad (3.28)$$

Note: we will later see that for realistic conditions the last step (applying Stirling's formula to n_i, hence n_i = large) is satisfied.

$$\ln \Omega = N \ln N - N - \sum_{i=0}^{r-1} n_i \ln n_i + \sum_{i=0}^{r-1} n_i \qquad (3.29$$

$$\ln \Omega = N \ln N - N - \sum_{i=0}^{r-1} n_i \ln n_i + N$$

$$= N\ln N - \sum_{i=0}^{r-1} n_i \ln n_i \qquad (3.30)$$

The maximum number of microstates then gives,

$$\left(\frac{\partial \ln \Omega}{\partial n_i}\right)_{N,E} = 0 \qquad (3.31)$$

Rather than differentiating with respect to the occupation numbers n_i (ϵN), it is instructive to consider small changes (symbol δ) of the occupation number. Then;

$$\delta(\ln\Omega) = \frac{1}{\Omega}\delta\Omega \qquad (3.32)$$

Hence eq. [3.28] become

$$\delta(\ln\Omega) = \delta(N\ln N) - \delta\sum_{i=0}^{r-1} n_i \ln n_i \qquad (3.33)$$

$$\delta(\ln\Omega) = 0 - \delta\sum_{i=0}^{r-1} n_i \ln n_i \qquad (3.34)$$

$$-\delta(\ln\Omega) = \delta\sum_{i=0}^{r-1} n_i \ln n_i = \qquad (3.35)$$

$$-\delta(\ln\Omega) = \sum_{i=0}^{r-1} n_i \delta \ln n_i + \sum_{i=0}^{r-1} \ln n_i \;\; \delta n_i \qquad (3.36)$$

$$-\delta(\ln\Omega) = \sum_{i=0}^{r-1} n_i \frac{\delta n_i}{n_i} + \sum_{i=0}^{r-1} \ln n_i \;\; \delta n_i \qquad (3.37)$$

$$-\delta(\ln\Omega) = \sum_{i=0}^{r-1} \delta n_i + \sum_{i=0}^{r-1} \ln n_i \;\; \delta n_i = 0 \qquad (3.38)$$

Equation [3.38] can be combined with the constant boundary conditions in eqs. [3.23] and [3.24], to give

$$\text{i)}\qquad -\delta(\ln\Omega) = \sum_{i=0}^{r-1}\delta n_i + \sum_{i=0}^{r-1}\ln n_i\ \delta n_i$$
$$= 0 \qquad \text{(maximun)}$$
$$\text{ii)}\qquad -\delta N = \sum \delta n_i$$
$$= 0 \qquad \text{(constant)}$$
$$\text{ii)}\qquad -\delta E = \sum \varepsilon_i \delta n_i$$
$$= 0 \qquad \text{(constant)}$$

The easiest way to solve such an equation system or to combine the conditions is the method of undetermined Lagrange Multipliers. This gives

$$\sum \delta n_i + \sum \ln n_i\ \delta n_i + \lambda \sum \delta n_i + \beta \sum \varepsilon_i \delta n_i$$
$$= 0 \qquad (3.39)$$

$$\sum \delta n_i\,[1 + \ln n_i + \lambda + \beta\varepsilon_i] = 0 \qquad (3.40)$$

where λ and β are the (yet) undetermined multipliers. The first term (δn_i) in [3.40] can be chosen arbitrarily to be any number as long as the last two are chosen to fulfil ii) and iii) in the conditions above. But generally the following condition must hold:

$$1 + \ln n_i + \lambda + \beta\varepsilon_i = 0 \qquad (3.41)$$
$$\ln n_i = -(\lambda + 1) - \beta\varepsilon_i$$
$$n_i = \exp[-(\lambda + 1)]\exp[-\beta\varepsilon_i]$$

putting

$$C = \exp[-(\lambda + 1)]$$

Then

$$n_i = C\exp[-\beta\varepsilon_i] \qquad (3.42)$$

The constant C can be determined by plugging n_i into the constraints (3.23);

$$\sum n_i = N = C\sum \exp[-\beta\varepsilon_i] \qquad (3.43)$$

$$C = \frac{N}{\sum \exp[-\beta\varepsilon_i]} \qquad (3.44)$$

Where $\sum \exp[-\beta\varepsilon_i]$ is called partition function Z. Hence

$$n_i(\varepsilon_i, \beta\,) = \frac{N}{Z}e^{-\beta\varepsilon_i} \qquad (3.45\ )$$

This is Boltzmann distribution. This function corresponds to the most probable macrostate. Later we will see that $\beta = \frac{1}{k_B T}$. At fixed temperature and total particle number, this function tells us the number of particles in the energy state ε_i , i.e. how the energy is distributed amongst the particles.

Chapter 4:

Canonical Ensemble

A far better alternative appears to be to speak *of a fixed temperature T* of the system — a parameter that is not only directly observable (by placing a “thermometer” in contact with the system) but also controllable (by keeping the system in contact with an appropriate *“heat reservoir”*). However, in most cases the properties of such reservoir do not interest us, all one needs is that it should have an infinitely large *heat capacity*, so that, with energy exchange between the system and *the reservoir*, an overall constant temperature can be maintained.

4.1 Traditional approach

Consider an isolated system divided into two subsystems a "large " one regarded as a ***heat reservoir,*** and a "small" one on which ***is the canonical ensemble*** we focus our attention, as shown in **Figure (4.1).**

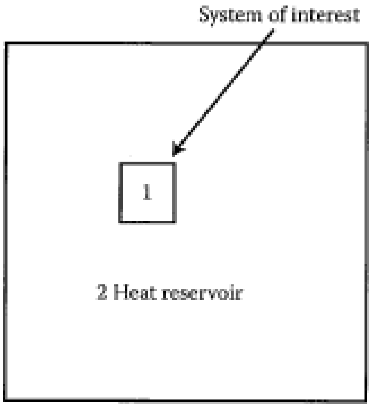


Figure (4.1) We study the small system 1 which is a part of a large system. The rest of the system 2 acts as a heat reservoir for system 1.

The system 1 is characterized by (E_1, V_1, N_1) and system 2 (*the heat reservoir*) is characterized by (E_2, V_2, N_2). The total Hamiltonian is

$$H(p_1, r_1, p_2, r_2) = H_1(p_1, r_1) + H_2(p_2, r_2) \qquad (4.1)$$

Also the two systems satisfy the following.

$$\begin{gathered} N = N_1 + N_2 \\ E = E_{1+}E_2 \\ E_2 \gg E_1 \\ N_2 \gg N_1 \end{gathered} \qquad (4.2)$$

The phase space volume occupied by system 2 is given by

$$\Gamma_2(E_2) = \int_{H_2(p_2,r_2) \leq E_2} dp_2 dr_2 \qquad (4.3)$$

The probability that system 1 is in dp_1dr_1 is proportional to dp_1dr_1 and $\Gamma_2(\mathrm{E}-E_1)$. Dependence on Γ_2 comes by the virtue that**,** *the larger Γ_2, then the larger number of microstates available to the reservoir, to have the macrostate E_2, which means the larger the system 1 to be in the corresponding energy value E_1) , so porobability (P) that 1 is in dp_1dr_1 is given as*

$$P \propto dp_1dr_1\Gamma_2(E_2) \qquad (4.4)$$

At the same time the probability P proportional to the number of microstates in dp_1dr_1**.** This gives a definition for the distribution function (*the occupation number per unit volume)* of system 1 where;

$$P \propto dp_1dr_1\Gamma_2(E_2) \ \propto \rho_1(p_1,r_1)dp_1dr_1 \qquad (4.5)$$

Then;

$$\begin{aligned} P &= const \times dp_1dr_1\Gamma_2(E_2) \\ &= const \times \rho_1(p_1,r_1)dp_1dr_1 \qquad (4.6) \end{aligned}$$

Since $E_1 \ll E$, we can expand (4.6) around the value $E_2 = E - E_1$. It is convenient to expand the logarithm of Γ_2 which can be expressed in terms of the entropy of system 2:

$$\begin{aligned} k_B \ln \Gamma_2(E-E_1) &= S_2(E-E_1) = S_2(E) - E_1\frac{\partial S_2(E)}{\partial E} + \cdots \\ &\approx S_2(E) - \frac{E_1}{T} \qquad (4.7) \end{aligned}$$

Where T is the temperature of the heat reservoir. Hence

$$\Gamma_2(E-E_1) \approx \mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}\ \mathrm{e}^{(-\beta E_1)} \qquad (4.8)$$

Where $\beta = \frac{1}{k_BT}$ **.** Substituting eq.(4.8) in eq.(4.5), we get the probability for the system 1 to be in $dpdr$ as a function of E_1 ;

$$P(E_1) \propto dp_1dr_1\ \mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}\ \mathrm{e}^{(-\beta E_1)} \qquad (4.9)$$

Here the probability decreases with increasing E_1 . So, we can *normalize P* to 1, so that $\int P(E_1) = 1$, then

$$\int P(E_1) = C\int dp_1 dr_1 \mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}\ \mathrm{e}^{(-\beta E_1)} = 1$$

Then;

$$C = \frac{1}{\int dp_1 dr_1 \mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}\ \mathrm{e}^{(-\beta E_1)}}$$

So, equation(4.9) could be written as

$$P(E_1) = \frac{dp_1 dr_1 \mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}\ \mathrm{e}^{(-\beta E_1)}}{\int dp_1 \mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}\ \mathrm{e}^{(-\beta E_1)}} \qquad (4.10)$$

The term $\mathrm{e}^{\left[\frac{1}{k_B}S_2(E)\right]}$ is constant and can be omitted from numerator and denominator, them eq. (4.10) becomes

$$P(E_1) = \frac{dp_1 dr_1 \mathrm{e}^{(-\beta E_1)}}{\int dp_1 dr_1 \mathrm{e}^{(-\beta E_1)}} \qquad (4.11)$$

Since we will refer only to the small system from now on, the ***subscript 1 is unnecessary**, **and will be omitted***. Then;

$$P(E) = \frac{dpdre^{e^{(-\beta E)}}}{\int dpdr\ e^{e^{(-\beta E)}}} \qquad (4.12)$$

Now *the canonical distribution function* $\rho_1(p_1, r_1)$ of eq. (4.6) (see eq.(3.11)) could be written as;

$$\rho(E) = e^{(-\beta E)} \qquad (4.13)$$

Using the Hamiltonian form this becomes

$$\rho(p, r) = \mathrm{e}^{(-\beta H(p,r))} \qquad (4.14)$$

Where; $\beta = 1/k_B T$

<u>This is the canonical ensemble, appropriate for a system of a fixed number of particles, in contact with a heat reservoir of temperature, T.</u>

Schematic representation of the microcanonical and canonical ensemble are given in **figure 4.2** .

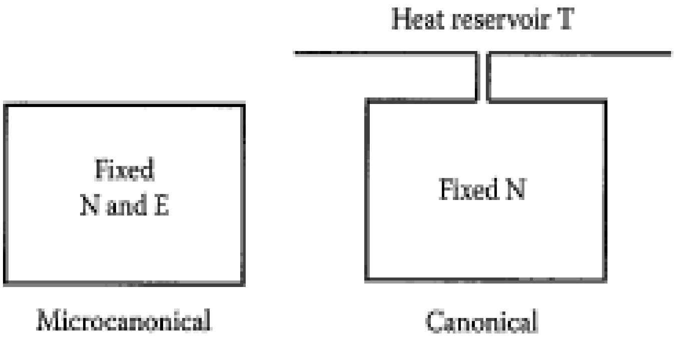


Figure 4.2

4.1.1 The Partition function

The volume in $\Gamma -$ space occupied by the canonical ensemble (or the total number of microstates with a norm factor h^{3N}) is ***called the partition function***.

$$Z_N = \int \frac{d^{3N}pd^{3N}r}{N!\,h^{3N}} e^{-\beta H(p,r)} \qquad (4.15)^3$$

Where we have introduced a constant h, of the dimension of momentum × distance, in order to make Z_N dimensionless. The factor $1/N!$ appears, in accordance with the rule of "correct Boltzmann counting." It takes into account Factor $N!$ arises from the fact that particles are _indistinguishable_. These constants are of no importance for the equation of state. Without this constant we face Gibbs paradox.

4.2 Information approach

In the canonical ensemble, the number of particles is constant but the energy can change. Consider a system of N particles. Let p_i be the probability that the system has energy E_i. We require the constriant that the system has an average energy,

---

[3] In this equation we notice that $e^{-\beta H(p,r)}$ is the density function $\rho(E) = \exp(-\beta H)$, then dividing this function by h^{3N} , gives the number of microstate ....الى ان تكتمل الصورة

$$\sum_i p_m E_m = \langle E \rangle \equiv E \qquad (4.16)$$

Also require normalization.

$$\sum_i p_i = 1 \qquad (4.17)$$

The entropy is $S = -\sum_i k p_i \ln\ p_i$. If we maximise the entropy subject to these constraints, we want to maximize the function

$$-\sum_i k p_\mathrm{i} \ln p_\mathrm{i} + \lambda \sum_i (p_\mathrm{i} - 1) \\ - \beta \sum_i (p_i E_\mathrm{i} - E) \qquad (4.18)$$

Taking the derivative $\frac{\partial}{\partial p_i}$ and setting to zero,

$$\begin{aligned} -k\ln\ p_\mathrm{i} \quad & -k + \lambda - \beta E_\mathrm{i} = 0 && (4.19) \\ p_\mathrm{i} \quad & = e^{\lambda - k} e^{-\beta E_\mathrm{i}} && \\ & = C e^{-\beta E_\mathrm{i}} && (4.20) \end{aligned}$$

To find C, we use the constraints.

$$\sum_i p_i = \sum_i C e^{-\beta E_i} = 1$$

$$\Rightarrow C = \frac{1}{\sum_i\ e^{-\beta E_i}}$$

Call

$$Z = \sum\nolimits_i e^{-\beta E_i} \qquad (4.21)$$

the partition function of the canonical ensemble.

Hence, the distribution of the canonical ensemble is

$$p_i = \frac{1}{Z} e^{-\beta E_1} \qquad (4.22)$$

Although this has the same form as the microcanonical ensemble, this distribution has different meaning, it is the probability for the system to be in energy E_{i} whereas in the microcanonical ensemble, it's the number of particles with energy $E_{\text{i.}}$

4.3 Connection with Thermodynamics

Let's see how we get thermodynamics from this. If p_n is the probability of finding the system in some energy E_n, then we can find the average energy to be

$$\langle E \rangle = p_n E_n = \frac{\sum_n E_n e^{-\beta \Sigma_n}}{Z} \qquad (4.23)$$

Upon inspection, this can be written nicely as[4]

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \equiv U \qquad (4.24)$$

Physically, *the expectation value* of the energy is the internal energy.

4.3.1 Energy Fluctuation

Consider now the variance in the energy.

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 \qquad (4.25)$$

If you expand these out, it turns out that you can write this nicely as

$$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z \qquad (4.26)$$

But we know that the heat capacity is defined as $\frac{\partial U}{\partial T}$. Using $\beta = \frac{1}{k_B T}$, then

$$(\Delta E)^2 = k_B T^2 C_V \qquad (4.27)$$

This equation tells us the system's ability to absorb/dissipate energy is related to its energy fluctuations. Note that

---

[4]

$$E \sim N \text{ and } C_v \sim N \Rightarrow \frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \qquad (4.28).$$

As $N \to \infty$ in *the thermodynamic limit, the energy fluctuation goes to zero* and the canonical and microcanonical ensembles coincide. Since the system we are normally looking at have large N, we can consider ourselves in the thermodynamic limit.

4.3.2 Helmholtz Free energy

This will finally be shown. Lets substitute the distribution into the entropy of eq. (3. 16). We get

$$\begin{aligned} S &= -k \sum_t \frac{1}{Z} e^{-\beta E_i} \ln\left(\frac{1}{Z} e^{-\beta E_i}\right) \\ &= -k \sum_i \frac{1}{Z} e^{-\beta E_i} (-\beta E_i - \ln Z) \\ &= k\beta U + k \ln Z \\ \Rightarrow U &= \frac{1}{k\beta} S - \frac{1}{\beta} \ln Z \qquad (4.29) \end{aligned}$$

We connect this with the expression from thermodynamics,

$$U = TS + A \qquad (4.30)$$

Equating (4.30 and 4.29), we get

$$\beta = \frac{1}{k_B T} \qquad (4.31)$$

And also

$$A = -kT \ln Z \qquad (4.32)$$

It is now possible to derive thermodynamic quantities from the Maxwell relations involving the free energy.

4.3.3: The Ideal Gas

For the ideal gas, the Hamiltonian is

$$H = \textstyle\sum_i \dfrac{p^2}{2m} \qquad (4.33)$$

Therefore, the partition function becomes

$$Z = \int \frac{d^{3N}pd^{3N}q}{N!\,h^{3N}} e^{-\beta\left(\Sigma_i \mathrm{P}_i^2/2m\right)} \qquad (4.34)$$

where the $N!$ comes from correct Boltzmann counting (all particles are indistinguishable) and the k is some arbritrary constant to nondimensionalise Z. The integral is straightforward, and goes as follow;

Now we calculate the partition function Z_N for ideal gas

$$Z_N = \int \frac{d^{3N}rd^{3N}p}{h^{3N}\,N!} e^{-\beta H} \qquad (4.35)$$

$$Z_N = \int \frac{d^{3N}rd^{3N}p}{h^{3N}\,N!} e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}} \qquad (4.36)$$

$$Z_N = \frac{V^N}{N!}\left(\int \frac{dp}{h} e^{-\beta\frac{p^2}{2m}}\right)^{3N} \qquad (4.37)$$

In the last expression we factorized the integral over p_i.Now we use the integral

$$\int_{-\infty}^{+\infty} dxe^{-x^2} = \sqrt{\pi} \qquad (4.38)$$

With

$$x^2 = \frac{p^2}{2mk_BT} \Longrightarrow x = \frac{p}{\sqrt{2mk_BT}} \Rightarrow dx = \frac{dp}{\sqrt{2mk_BT}} \qquad (4.39)$$

$$\int\left(\frac{dp}{h}e^{-\beta\frac{p^2}{2m}}\right)^{3N}=\frac{\sqrt{2mk_BT}}{h}\int_{-\infty}^{+\infty}dxe^{-x^2}$$

$$=\frac{\sqrt{2\pi mk_BT}}{h}\qquad(4.40)$$

Substituting in eq. (4.28), then

$$Z_N=\frac{V^N}{N!}\left(\frac{\sqrt{2\pi mk_BT}}{h}\right)^{3N}\qquad(4.41)$$

With the thermal wavelength, λ_T;

$$\lambda_{th}=\frac{h}{\sqrt{2\pi mk_BT}}\qquad(4.42)$$

So we can rewrite eq. (4.32) as;

$$Z_N=\frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N\qquad(4.43)$$

Helmholtz free energy of an ideal gas

14 Computing the Helmholtz Free Energy, $-kT\ln\,Z=A$,

$$A=-\,kT\ln\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$=-k_BT\ln\left(\frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N\right)\qquad(4.44)$$

$$=-k_BT\left(ln\frac{1}{N!}+ln\left(\frac{V}{\lambda_T^3}\right)^N\right)\qquad(4.45)$$

$$=-k_BT\left(-NlnN+N+Nln\frac{V}{\lambda_T^3}\right)\qquad(4.46)$$

$$= -Nk_BT\left(ln\frac{V}{N\lambda_T^3}+1\right) \qquad (4.47)$$

$$= -Nk_BT\left(-ln\frac{N\lambda_T^3}{V}+1\right) \qquad (4.47)$$

$$A = -kT(\ln(n\lambda_T^3)-1) \qquad (4.48)$$

where $n = \frac{N}{V}$ and Stirling's apprcximation has been used. The entropy can abo be found using thermodynamic relation $S = -\left(\frac{\partial A}{\partial T}\right)_V$,

$$S = -Nk\left(\ln(n\lambda^3)+\frac{T}{n\lambda^3}n\left(\frac{-3}{2}\right)\left(\frac{h^2}{2\pi mkT}\right)^{\frac{2}{2}}T^{-\frac{3}{2}}-1\right. \qquad (4.49)$$

which simplifies nicely to

$$S = Nk\left[\frac{5}{2}-\ln\left(n\lambda^3\right)\right] \qquad \text{(Sackur-Tetrode equation)}$$

$$(4.50)$$

If we didn't have the original $\frac{1}{N!}$ Boltzmann factor in the partition function, we would get Gibb's Paradox. We need to use a semiclassical interpretation that all particles are *indistinguishable.*

Gas law

Lets also use the thermodynamic relation, $P = -\frac{\partial A}{\partial V}$.

$$\Rightarrow PV = NkT$$

which is the familiar equation of state.

4.4 Equipartition of Energy

The average energy is

$$E = -\frac{\partial}{\partial \beta}\ln\, Z = \frac{3}{2}NkT$$

The 3 comes from the lambda $Z = \frac{1}{N!}\left(\frac{V}{\lambda^2}\right)$ which is directly related to the degrees of freedom that the particle has. Every degree of freedom contributes $\frac{1}{2}kT$ to the system. It is also easy to see that

$$C_V = \frac{\partial E}{\partial T_V} = \frac{3}{2}Nk$$

This shows that the heat capacity does not depend on temperature.

Chapter 5:
Grand canonical ensemble

5.1: Chemical Potential

So far we kept the number of particles constant, when *N* does change change, the first law is generalized to the form:

$$dU = dQ + dW + \mu dN \qquad (5.1)$$

Definition: μ is called ***the chemical potential***, the energy needs to add one particle to a thermally and mechanically isolated system.

$$dU = TdS - PdV + \mu dN \qquad (5.2)$$

We can define Helmholtz free energy as

$$F(V,T,N) = U - Ts - \mu N \qquad (5.3)$$

Then

$$dF = -SdT - PdV - N \qquad (5.4)$$

This gives the thermodynamic functions as;

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\mu,} \qquad (5.5)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,\mu} \qquad (5.6)$$

$$P$$

$$\mu = -\left(\frac{\partial F}{\partial \mu}\right)_{T,V} \qquad (5.7)$$

Similarly, we can write the change in Gibbs free energy as;

$$dG = -SdT + VdP + \mu dN \qquad (5.8)$$

Then

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} \qquad (5.9)$$

5.2 Grand Canonical Ensemble

- In *microcanonical ensemble*, we considered *isolated system* (everything is constant).

- In *canonical ensemble* we considered *closed system*. It is built in the microcanonical ensemble by relaxing the restriction of fixed energy (the system can exchange energy with the surrounding reservoir, at fixed temperature.

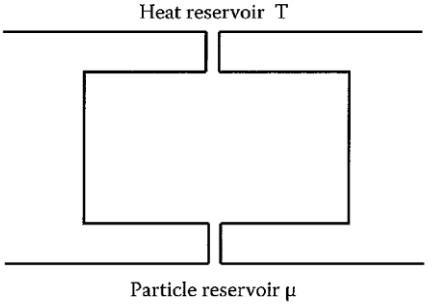
The *grand canonical ensemble* consider an *open system* (the system can exchange both energy and matter with reservoir).

$N_1 \gg N_2$ (5.10)

$E_1 \gg E_2$ (5.11)

$N_1 + N_2 = N$ (5.12)

$E_1 + E_2 = E$ (5.13)



So our constraints are given by the average value of energy and particle number which are

$$\sum_j p_j E_j = E$$

$$\sum_j p_j N_j = N$$

where E, N denote the average. p_j is the probability to find the system in the jth state ie with energy E_j and particle number N_j . The probabilities are normalized

$$\sum_j p_j = 1$$

The entropy S is given as

$$S = -k_B \sum_j p_j \ln p_j$$

We want to maximize S. This is done with Lagrange multipliers and it works out to be

$$p_j = \frac{e^{-\beta E_j + \beta \mu N_j}}{\sum_j e^{-\beta E_j + \beta \mu N_j}}$$

where the Lagrange multipliers can be found from

$$TdS = dU + PdV - \mu dN$$

We define the partition function of the grand canonical ensemble to be

$$Z_{gr} = \sum_j e^{-\beta E_j + \beta\mu N_j} = \sum_N e^{\beta\mu N} Z(V,T,N_j)$$
$$= \sum_N z^N Z(V,T,N_j)$$

$z = \mathrm{e}^{\beta\mu}$ is the fugacity. Then we can write the grand partition function as

$$Z_{gr} = \sum_{N=0}^{N=\infty} z^N Z_N \qquad (5.16)$$

Where Z_N is the canonical partition function. The canonical partition function depends on N_j which is a particular number of particles for a given state. So the grand canonical partition function is a weighted sum of the canonical ensemble partition function.

5.3 Thermodynamics

By averaging the canonical ensemble over the number of particles, we get the ensemble average over grand canonical ensemble. For example the internal energy is given as

$$U = \frac{\sum E_N z^N Z_N}{\sum z^N Z_N} \qquad (5.17)$$

E_N is the average energy in the canonical ensemble.

$$Z_N = \sum e^{-\beta E_j}$$

In terms of Z_{gr} we can write . So

$$U = \frac{\sum E_N z^N Z_N}{\sum z^N Z_N} \qquad (5.18)$$

$$U = -\frac{\frac{\partial}{\partial\beta}\sum Z_N}{\sum z^N Z_N} = -\frac{1}{Z_{gr}}\frac{\partial Z_{gr}}{\partial\beta} \qquad (5.19)$$

The average number of particles is (which I will denote N, I should technically use $\bar{N}$ but more on that later)

$$N \equiv \langle N\rangle = \frac{\sum_N \; N e^{\beta\mu N} Z}{\sum \; e^{8\mu N} Z} = \frac{1}{\beta\mathcal{Z}} \frac{\partial}{\partial\mu}\left(\sum \; e^{\beta\mu N} Z\right)$$
$$= \frac{1}{\beta}\frac{\partial}{\partial\mu} \ln \, \mathcal{Z}$$

Noting that $\frac{\partial}{\sigma\mu} = \frac{\partial z}{\partial\mu}\frac{\partial}{dz} = \beta z \frac{\partial}{\partial z}$

$$N = z\frac{\partial}{\partial z} \ln \mathcal{Z} \qquad (5.20)$$

We can also find what the variance in the particle number is.

$$(\Delta N)^2 = \langle N^2\rangle - \langle N\rangle^2$$

This works out nicely to be

$$(\Delta N)^2 = z\frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln \, \mathcal{Z}$$
$$= (kT)^2 \frac{\partial^2}{\partial\mu^2} \ln \, \mathcal{Z}$$

Dividing by V^2 gives the number density fluctuation,

$$(\Delta n)^2 = \frac{(kT)^2}{V^2}\frac{\partial^2}{\partial\mu^2} \ln \mathcal{Z} \qquad (5.21)$$

We see that $\frac{\Delta N}{(N\rangle} \sim \frac{1}{\sqrt{QN})}$. Therefore, for $N \to \infty$, the number fluctuations go to zero. The three ensembles coincide in the thermodynamic of infinite volume and infinite particle number. This is why I don't bother with writing N and denote it N.

• Helmholtz free energy and the Grand partition function

In the canonical ensemble, we were able to connect the Helmholtz Potential with the partition function. It is also possible to do it with the grand canonical partition function. Define the grand canonical potential to be,

$$\Phi = E - TS - \mu N$$

Recalling the Helmholtz Free Energy,

$$\Phi = F - \mu N$$

The grand canonical partition function in terms of the Helmholtz free energy is,

$$Z_{gr} = \sum_{N=0}^{N=\infty} \mathrm{e}^{\beta\mu N} e^{-\beta F}$$

This suggests that

$$\Phi = -kT\ln Z_{gr} \qquad (5.22)$$

This connects the potential with the grand canonical partition function. From the thermodynamic definition,

$$d\Phi = -SdT - PdV - Nd\mu$$

We can then derive thermodynamic relations from this. One of them is

$$\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -P = -= -k_B T \ \frac{\partial}{\partial V}\ln Z_{gr} \qquad (.5.23)$$

5.4 Ideal gas in Grand Canonical ensemble

$$Z_{gr} = \sum_{N=0}^{N=\infty} z^N Z_N \qquad (5.24)$$

But

$$Z_N = \int \frac{dpdr}{N!\,h^{3N}} e^{-\beta H(p,r)} \qquad (5.25)$$

then

$$Z_{gr} = \sum_{N=0}^{N=\infty} e^{\beta\mu N} \int \frac{dpdr}{N!\,h^{3N}} e^{-\beta \sum_i^N \frac{p_i^2}{2m}(p,r)} \qquad (5.26)$$

We have seen before in canonical ensemble that the integral is given by

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$$

So,

$$Z_{gr} = \sum_{N=0}^{N=\infty} e^{\beta\mu N} \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$$

$$Z_{gr} = \sum_{N=0}^{N=\infty} \frac{1}{N!}\left(\frac{e^{\beta\mu} V}{\lambda_T^3}\right)^N$$

But this is the definition of the exponential function. Then

$$Z_{gr} = exp\left(\frac{e^{\beta\mu} V}{\lambda_T^3}\right) \qquad (5.27)$$

The average particle number is

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} = \frac{e^{\beta\mu} V}{\lambda^3} \qquad (5.28)$$

This gives an expression for the chemical potential.

$$\mu = kT\ln\left(\frac{\lambda^3 N}{V}\right) \qquad (5.29)$$

Now take the grand canonical potential,

$$\Phi = -kT\ln\ Z_{gr} = -kTe^{\beta\mu}\frac{V}{\lambda^3}$$

The pressure is

$$P = -\left(\frac{\partial\Phi}{\partial V}\right)T_{T,\mu}$$

$$P = kT\frac{e^{\beta\mu}}{\lambda^3}$$

With equation (5.28) this gives

$$P = kTN\frac{\lambda^3}{V\lambda^3}$$

$$\Rightarrow PV = NkT \qquad (5.30)$$

which is the familiar equation of state.

Chapter 6

Interacting Gas

So far we have considered an ideal gas in which the particles do not interact. The ideal gas is a good starting point as an approximation to interacting gas. We expect that when the interactions become negligible, the ideal gas equation holds. So we consider the ideal gas equation and look at how we can correct it for an interacting gas.

The most general equation of state is the ***virial expansion***

$$\frac{P}{k_B T} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \cdots \; (6 \cdot 1)$$

$B_i(T)$ is known as the ***virial coefficients***.

Our goal is to compute the virial coefficients starting from a knowledge of the underlying potential energy $U(r)$ between two neutral atoms separated by a distance r. This potential has two important features:

- An attractive $1/r^6$ force. This arises from ***induced dipole*** of the particles (***Van der Walls interaction)***.
- Repulsive force at short distances, arising from the ***Pauli exclusion principle*** that prevents two atoms from occupying the same space.

One very common potential that is often used to model the force between atoms is the

Lennard-Jones potential which looks like

$$U(r) \sim \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \; \ldots (6 \cdot 2)$$

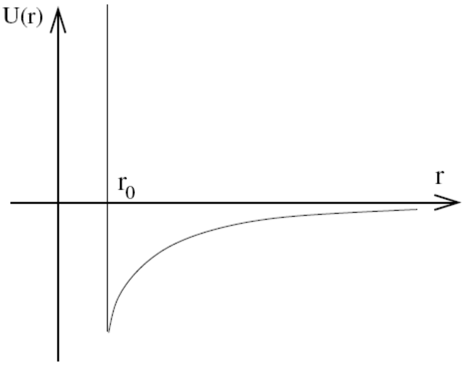
The exponent 12 is chosen only for convenience: it simples certain calculations because $12 = 2 \times 6$

Equation (5.28) could be written as;

$$U(r) \sim \left(\frac{r_0}{r}\right)^6 \left(\left(\frac{r_0}{r}\right)^6 - 1\right) \ldots (6 \cdot 3)$$

For $r < r_0 \Longrightarrow U(r) > 0$ (the repulsive potential dominates), and for $r > r_0 \Longrightarrow U(r) < 0$ (the attractive potential dominates).

However, although this is a nice model, it is not easy to compute . We replace it with a simple form of the potential incorporates ***a hard core repulsion***, in which the particles are simply forbidden from closer than a fixed distance (see the figure) ;



$$U(r) = \left\{ \begin{matrix} \infty & if\ r < 0 \\ -U_0 \left(\frac{r_0}{r}\right)^6 & if\ r > r_0 \end{matrix} \right\} \quad (6 \cdot 4)$$

6.1 Computing the partition function:

Then the Hamiltonian of the system is

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i>j} U(r_{ij}) \quad (6 \cdot 5) \qquad r_{ij} \equiv r_j - r_i$$

The restriction $i > j$ on the final sum ensures that we sum over each pair of particles exactly once. Inserting into the ***canonical partition function*** ,

$$Z(N,V,T) = \frac{1}{N!\,h^{3N}} \int d^{3N}p\, d^{3N}r\, e^{-\beta H}$$

$$= \frac{1}{N!\,h^{3N}} \int d^{3N}p\, e^{-\beta p_i^2/2m} \int d^{3N}r\, e^{-\beta \sum_{i>j} U(r_{ij})} \quad (6.7)$$

The momentum integral has been done before and is just a Gaussian, then

$$Z(N,V,T) = \frac{1}{N!\,\lambda^{3N}} \int d^{3N}r\, e^{-\beta \sum_{i>j} U(r_{ij})} \quad (6.8)$$

The second integral is not as easy, the interactions mean that the integrals don't factor in any obvious way. We could try **Taylor expansion**, but this doesn't work since as $r_{ij} \to 0,\ U(r_{ij}) \to \infty$ so this would not converge. Instead, define

$$f(r) = e^{-\beta U(r)} - 1 \quad (6.9)$$

Which is known as the ***Mayer f function***. This is a nicer expansion parameter because;

$$r \to \infty \implies f(r) \to 0, \qquad r \to 0 \quad \Rightarrow f(r) \to -1$$

We define

$$f_{ij} = f(r_{ij}) \Rightarrow e^{-\beta \sum_{j>k} U(r_{jk})} = 1 + \prod_{j>k} (1 + f_{jk}) \quad (6.10)$$

Then taking the arithmetic sum out of the exponential to give a geometric sum and replacing with f, then

$$Z(N,V,T) = \frac{1}{N!\,\lambda^{3N}} \int d^{3N}r \prod_{j>k} (1 + f_{jk}) \qquad (6.11)$$

$$= \frac{1}{N!\,\lambda^{3N}} \int d^{3N}r \left(1 + \sum_{j>k} f_{jk} + \sum_{j>k} \sum_{l>m} f_{jk} f_{lm} + \cdots \right) \quad (6.12)$$

The first integral gives V^{N} . Ignoring quadratic terms, the second term works out such that the partition function looks like,

$$Z(N,V,T) = \frac{V^N}{N!\,\lambda^{3N}} \left(1 + \frac{N}{2V} \int d^3r\, f(r) \right)^N \qquad (6.13)$$

The Helmholtz free energy is,

$$F = -k_B T \ln \mathrm{Z} = -k_B T \ln \frac{V^N}{N!\,\lambda^{3N}} - N k_B T \ln \left(1 + \frac{N}{2V} \int d^3r\, f(r) \right) \quad (6.14)$$

Now we want to find out how to integrate the f function. Using the potential mentioned above,

$$\int d^3r\, f(r) = \int_0^{r_0} d^3r(-1) + \int_0^{\infty} d^3r \left(e^{\beta U_0 (r_0/r)^6} - 1 \right) \quad (6.15)$$

We assume $\beta \ll 1$ for high temperature. Then we can use ***Taylor expand,*** then

$$e^{\beta U_0 (r_0/r)^6} = 1 + \beta U_0 \left(\frac{r_0}{r} \right)^6 \quad (5 \cdot 41)$$

Then

$$\int d^3r\, f(r) = -4\pi \int_0^{r_0} dr\, r^2 + \frac{4\pi U_0}{k_B T}\int_{r_0}^{\infty} dr\, \frac{r_0^6}{r^4} \tag{6.16}$$

$$-4\pi \int_0^{r_0} dr\, r^2 = \frac{-4\pi r_0^3}{3} \quad ,$$

And

$$\frac{4\pi U_0}{k_B T}\int_{r_0}^{\infty} dr\, \frac{r_0^6}{r^4} = \frac{4\pi U_0 r_0^3}{3k_B T}$$

So

$$-4\pi \int_0^{r_0} dr\, r^2 + \frac{4\pi U_0}{k_B T}\int_{r_0}^{\infty} dr\, \frac{r_0^6}{r^4} = \frac{4\pi r_0^3}{3}\left(\frac{U}{k_B T} - 1\right) \tag{6.17}$$

then

$$\int d^3r\, f(r) = \frac{4\pi r_0^3}{3}\left(\frac{U}{k_B T} - 1\right) \qquad (5\cdot 43)$$

Then eq.(5.) becomes

$$F = -k_B T \ln Z = -k_B T \ln \frac{V^N}{N!\,\lambda^{3N}} - N k_B T \ln\left(1 + \frac{N}{2V}\left(\frac{4\pi r_0^3}{3}\left(\frac{U}{k_B T} - 1\right)\right)\right) \tag{6.18}$$

We can use the free energy to compute the pressure of the gas. Expanding the logarithm as $\ln(1 + x) = x$ we get,

$$F = -k_B T \ln Z = -k_B T \ln \frac{V^N}{N!\,\lambda^{3N}} - N k_B T \left(\frac{N}{2V}\left(\frac{4\pi r_0^3}{3}\left(\frac{U}{k_B T} - 1\right)\right)\right) \tag{6.19}$$

$$= -\left\{ N k_B T \ln V - k_B T N!\,\lambda^{3N} + N k_B T \left(\frac{N}{2V} \left(\frac{4\pi r_0^3}{3} \left(\frac{U}{k_B T} - 1 \right) \right) \right) \right\}$$

$$P = -\frac{\partial F}{\partial V}$$

$$= -\left\{ \frac{N k_B T}{V} + \frac{N k_B T}{V^2} \left(\frac{N}{2} \left(\frac{4\pi r_0^3}{3} \left(\frac{U}{k_B T} - 1 \right) \right) \right) \right\} \quad (6.20)$$

$$= \frac{N k_B T}{V} \left\{ 1 - \frac{N}{2V} \left(\frac{4\pi r_0^3}{3} \left(\frac{U}{k_B T} - 1 \right) \right) \right\} \quad (6.21)$$

$$\frac{PV}{N k_B T} = \left\{ 1 - \frac{N}{2V} \left(\frac{4\pi r_0^3}{3} \left(\frac{U}{k_B T} - 1 \right) \right) \right\} \quad (6.22)$$

$$\frac{PV}{N k_B T} = 1 - \frac{N}{V} \left(\frac{a}{k_B T} - b \right) \quad (6.23)$$

$$a = \frac{2\pi r_0^3 U}{3}, \quad b = \frac{2\pi r_0^3}{3} \quad (6.24)$$

It is actually slightly more useful to write this in the form $k_B T =$ …..We can multiply through by $k_B T$ then, rearranging we have

$$k_B T = \frac{V}{N} \left(P + \frac{N^2}{V^2} \right) \left(1 + \frac{N}{V} b \right)^{-1} \approx \left(P + \frac{N^2}{V^2} \right) \left(\frac{V}{N} - b \right) \quad (6.25)$$

Van der Walls equation of state valid at low $\frac{N}{V}$ and high T

6.2 Cluster Expansion:

In deriving the Van Der Walls equation of state, higher order terms were neglected. It is possible to compute the higher order terms to get the correct terms. This will not be done here.

Chapter 7

Magnetism

Consider N fixed magnetic dipoles with magnetic moment μ. Let B be an external magnetic field. Then the interaction Hamiltonian is,

$$H = -\sum_{l=1}^{N} \mu_l \cdot \mathbf{B}$$

$$= -\mu B \sum_{l=1}^{N} \cos\theta_l$$

We choose our coordinate system so the z-axis aligns with the magnetic field. The partition function looks like

$$Z = \prod_{i=1}^{N} \int_0^{\pi} d\theta_i \int_0^{2\pi} d\phi_i \; e^{-\beta \mu B \cos\theta_i}$$

This integrates to

$$Z = \left(4\pi \frac{\sinh(\beta\mu B)}{\beta\mu B}\right)^N$$

The magnetization is the expectation value of the z component.

$$\langle \mu_z \rangle = \frac{1}{Z} \mu \cos\theta_i \int_0^{\pi} d\theta_i \int_0^{2\pi} d\phi_i \; e^{-\beta\mu B \cos\theta_i}$$

It might be possible to compute this but this is tedious so recognize that we can rewrite this as

$$\langle \mu_z \rangle = \frac{1}{ZB} \frac{\partial}{\partial\beta} Z$$

Recall the Z computed earlier. The magnetization is the total magnetization of N particles,

$$M_z = N\langle \mu_z \rangle = N\mu \mathcal{L}(\beta\mu B)$$

where L is the Langevin function. For the high temperature limit, Taylor expanding and ignoring higher order terms gives

$$M_z = \frac{N\mu^2}{3kT} B$$

This is the Curie Law.

Chapter 8

Quantum statistical mechanics

We now move into a quantum framework. In classical mechanics, the microstates are described by momentum and position and in quantum mechanics, the microstates are described by wavefunctions. Consider a system with N particles. Each particle is described by a wavefunction ψ_a, $a = 1, \ldots, N$. Observables correspond to a Hermitian operator O. The expectation value of O in state $|\psi_a\rangle$ is,

$$\langle O\rangle_a = \langle\psi_a|O|\psi_a\rangle$$

Define the average expectation value to be,

$$\begin{aligned}\langle O\rangle &= \frac{1}{N}\sum_{a=1}^{N}\langle\psi_a|O|\psi_a\rangle \\ &\equiv \langle\psi|O|\psi\rangle\end{aligned}$$

Now consider an orthonormal basis of the Hilbert space $\{|\phi_n\rangle\}_{n=1,2,\ldots}$. We can express the states as a linear combination.

$$|\psi_a\rangle = \sum_{n=1}^{\infty} c_n^a|\phi_a\rangle$$

This gives,

$$\langle\psi|O|\psi\rangle = \frac{1}{N}\sum_{a=1}^{N}\sum_{n,m} c_n^{a*}c_m^a\langle\phi_n|O|\phi_m\rangle$$

Define $\rho_{mn} = \frac{1}{N}\sum_a c_n^{a*}c_m^a$ and $O_{nm} = \langle\phi_n|O|\phi_m\rangle$. Then,

$$\langle O\rangle = \sum_{n,m}\rho_{mn}O_{nm}$$

ρ_{mn} can be interpreted as matrix elements of an operator ρ such that $\rho_{mn} = \langle\phi_m|\rho|\phi_n\rangle$. ρ is called the density operator/matrix.

ρ is equivalent to $\rho = \sum |\psi_a\rangle\langle\psi_a|$ where p_a can be thought of as the probability for the system to be in th. This can be seen by getting the matrix elements of ρ,

$$\langle\phi_m|\rho|\phi_n\rangle = \sum \langle\phi_m|\psi_a\rangle\langle\psi_a|\phi_n\rangle = \sum c_m^a c_n^{a\,*}$$

Expressing in terms of a basis, it will look like

$$\rho = \sum_a \sum_{n,m} c_n^{a\,*} c_m^a |\phi_m\rangle\langle\phi_n| = \sum_a \sum_n |c_n^a|^2 |\phi_n\rangle\langle\phi_n| = \sum p_n |\phi_n\rangle\langle\phi_n|$$

(that may be slightly wrong, if it is just take the last bit as a definition) Interpret p_n as the probability to be in the state ϕ_n.

Finally,

$$\begin{aligned}\langle O\rangle &= \sum_{n,m} \langle\phi_m|\rho|\phi_n\rangle\langle\phi_n|O|\phi_m\rangle \\ &= \sum_m \langle\phi_m|\rho O|\phi_m\rangle \\ &= \mathrm{Tr}(\rho O)\end{aligned}$$

Properties of ρ

1. $\mathrm{Tr}\rho = 1$
2. $\rho = \rho^\dagger$
3. $\rho \geq 0$

The proof will be left as an exercise for the reader. (I've always wanted to do that) They're pretty trivial anyway.

8.1 Time Evolution of the Density Operator

Choose an orthonormal basis $\{\phi_n\}$ that are eigenfunctions of the Hamiltonian of our system. Then we have,

$$H\phi_n = E_n\phi_n$$

Our wavefunction can be expressed in terms of the basis as

$$\psi_a(t) = \sum_n c_n^a(t)\phi_n$$

Then the time dependent Schrodinger equation is,

$$i\hbar\frac{\partial}{\partial t}\psi_a(t) = H\psi_a(t)$$

Putting in $\psi_a(t)$ in terms of the basis,

$$\sum_n i\hbar\dot{c}_n^a(t)\phi_n = \sum_n i\hbar c_n^a(t)H\phi_n$$

$$\sum_n i\hbar\dot{c}_n^a(t)\phi_n = \sum_n i\hbar c_n^a(t)E_n\phi_n$$

We project out the kth component by taking $(\phi_k, \cdot)$.

$$i\hbar\dot{c}_k^a(t) = E_k c_k^a(t)$$

and the complex conjugate is

$$-i\hbar\dot{c}_k^{a*}(t) = E_k c_k^{a*}(t)$$

Now lets consider the derivative of the density matrix.

$$\rho_{mn} = \frac{1}{N}\sum_a c_n^{a*}c_m^a$$

$$\Rightarrow i\hbar\dot{\rho}_{mn} = i\hbar\frac{1}{N}\sum_a[\dot{c}_n^{a*}c_m^a + c_n^{a*}\dot{c}_m^a]$$

We computed the values for $\dot{c}$ above. This gives,

$$\begin{aligned} i\hbar\dot{\rho}_{mn} &= \frac{1}{N}\sum_a[-E_n c_n^{a*}c_m^a + E_m c_n^{a*}c_m^a] \\ &= (E_m - E_n)\frac{1}{N}\sum_a c_n^{a*}c_m^a \\ &= (E_m - E_n)\rho_{mn} \end{aligned}$$

Denoting $\rho_{mn} = (\phi_m, \rho\phi_n)$ to be the matrix element,

$$\begin{aligned} \Rightarrow i\hbar(\phi_m, \dot{\rho}\phi_n) &= (E_m - E_n)(\phi_m, \rho\phi_n) \\ &= (E_m\phi_m, \rho\phi_n) - (\phi_m, \rho E_n\phi_n) \\ &= (H\phi_m, \rho\phi_n) - (\phi_m, \rho H\phi_n) \\ &= (\phi_m, H\rho\phi_n) - (\phi_m, \rho H\phi_n) \\ &= (\phi_m, [H, \rho]\phi_n) \end{aligned}$$

Since this holds for arbitrary basis and m, n,

$$i\hbar\dot{\rho} = [H, \rho]$$

This is a very important result. What this says that if we want $\langle O\rangle$ to be time independent at equilibrium, then ρ must also be time independent since $\langle O\rangle = \mathrm{Tr}(\rho O)$. Therefore, $[H, \rho] = 0$.

8.2 Partition Functions

We want to find expressions for ρ in our ensembles. Recall the derivations for the canonical ensemble. When we were deriving the probability for the system to be in the E_nth state, we did not use classical mechanics so the derivation should also work for quantum mechanics. Therefore, the probability to be in the E_nth state is,

$$p_n = \frac{1}{Z} e^{-\beta E_n}$$

But we have from earlier,

$$\begin{aligned} \rho &= \sum p_n |\phi_n\rangle\langle\phi_n| \\ \Rightarrow \rho &= \frac{1}{Z}\sum e^{-\beta E_n}|\phi_n\rangle\langle\phi_n| \\ \rho &= \frac{1}{Z}\sum e^{-\beta H}|\phi_n\rangle\langle\phi_n| \end{aligned}$$

Since ϕ_n is complete,

$$\rho = \frac{e^{-\beta H}}{\text{Tr } e^{-\beta H}}$$

Similarly, the density operator looks like

$$\rho = \frac{e^{-(\beta H - \mu\hat{N})}}{\text{Tr } (e^{-(\beta H - \mu\hat{N})})}$$

where $\hat{N}$ is the particle number operator and denote $\mathcal{Q} = \text{Tr } (e^{-(\beta H - \mu\hat{N})})$. Also the fugacity is given by $z = e^{\beta\mu}$.

Since we have the expectation of an operator to be $\langle O\rangle = \text{Tr}(\rho O)$, in the canonical ensemble,

$$\langle O\rangle = \frac{1}{Z}\text{Tr}(Oe^{-\beta H})$$

For the internal energy, this is,

$$\begin{aligned} U = \langle H\rangle &= \frac{1}{Z}\text{Tr}(He^{-\beta H}) \\ &= \frac{1}{Z}(-\frac{\partial}{\partial\beta})\text{Tr}(He^{-\beta H}) \\ &= \frac{1}{Z}(-\frac{\partial}{\partial\beta})Z = -\frac{\partial}{\partial\beta}\ln Z \end{aligned}$$

The free energy is identified by

$$F = -kT\ln Z$$

And thermodynamics falls from the usual thermodynamic relations like $P = -\frac{\partial F}{\partial V}$.

In the grand canonical ensemble, we have

$$\langle \hat{N} \rangle = \bar{N} = z\frac{\partial}{\partial z} \ln Q$$

$$F = \bar{N}\mu - kT \ln Q$$
$$PV = kT \ln Q$$

The grand canonical potential is

$$\Omega = -kT \ln Q$$

So nothing too special and pretty similar to the classical case. Most of the things derived above in the classical case can be applied here like how the energy and number fluctuations are negligible in the thermodynamic limit.

Chapter 9

Identical Particles

There are two types of particles, *bosons* and *fermions* which are either *symmetric* or *antisymmetric* under particle exchange. This gives rise to the Pauli exclusion principle for fermions. Let us define the occupation number n_i to be the number of particles in the system to be in the ith state where this state contains all of the particle's properties like momentum, position and spin. While I use i to denote a state that has complete information, at times I may switch to denote a state by p, λ where λ is the polarization state e.g. spin. We have

$$n_i = \begin{cases} 0, 1 & \text{for fermions} \\ 0, 1, 2, \dots & \text{for bosons} \end{cases}$$

We then have a set of occupation numbers of a system {n$_i$}. Also, there is a constraint that the sum is the total number of particles in the system.

$$\sum_i n_i = N$$

And if ϵ_i is the energy of the ith state, then the total energy must be the total sum

$$\sum_i n_i \epsilon_i = E$$

Now consider the grand canonical partition function,

$$Z_{gr} = \sum_N \mathcal{Z}^N Z_N = \sum_N \sum_{n_i} \mathcal{Z}^N e^{-\beta \sum \epsilon_i n_i}$$

$$= \sum_{n_i} \prod_i \mathcal{Z} e^{-\beta (\epsilon_i)^{n_i}} = \prod_i \sum_{n_i} \mathcal{Z} e^{-\beta (\epsilon_i)^{n_i}}$$

9.1 Bose-Einstein Distribution

For bosons, $n_i = 0, 1, 2, \dots$. Using $\sum_{n=1}^{\infty} x^n = \frac{1}{1-x}$

$$Z_{gr} = \prod_i \frac{1}{1 - \mathcal{Z} e^{-\beta \in_i}}$$

This only converges of course if | $\mathcal{Z} e^{-\beta \in_i}$ | < 1 which is valid but we will discuss the physics of this later.

Having computed the partition function, we can get

$$\frac{PV}{kT} = \ln Z_{gr}$$

$$= -\sum_i \ln\left(1 - \mathcal{Z} e^{-\beta \epsilon_i}\right)$$

The average particle number is

$$\langle N \rangle = \mathcal{Z} \frac{\partial}{\partial \mathcal{Z}} \ln Z_{gr}$$

$$= \sum_i \frac{\mathcal{Z} e^{-\beta \epsilon_i}}{1 - \mathcal{Z} e^{-\beta \epsilon_i}}$$

Then

$$\langle N \rangle = \sum_i \frac{1}{\mathcal{Z}^{-1} e^{\beta \epsilon_i} - 1}$$

9.2 Fermi-Dirac Distribution

For fermions, $n_i \; = \; 0, 1$ Using $\sum_{n=1}^{\infty} x^n = \frac{1}{1-x}$

$$Z_i = \sum_{n_i = 0,1} \left[\mathcal{Z} e^{-\beta \epsilon_i}\right]^{n_i} \Rightarrow Z_i = 1 + \mathcal{Z} e^{-\beta \epsilon_i}$$

$$Z_{gr} = \prod_i \left(1 + z e^{-\beta \epsilon_i}\right)$$

$$\frac{PV}{kT} = \ln Z_{gr}$$

$$= \sum_i \ln\left(1 - \mathcal{Z}e^{-\beta\epsilon_i}\right)$$

The average number of particles is

$$\langle N \rangle = \mathcal{Z}\frac{\partial}{\partial \mathcal{Z}}\ln Z_{gr}$$

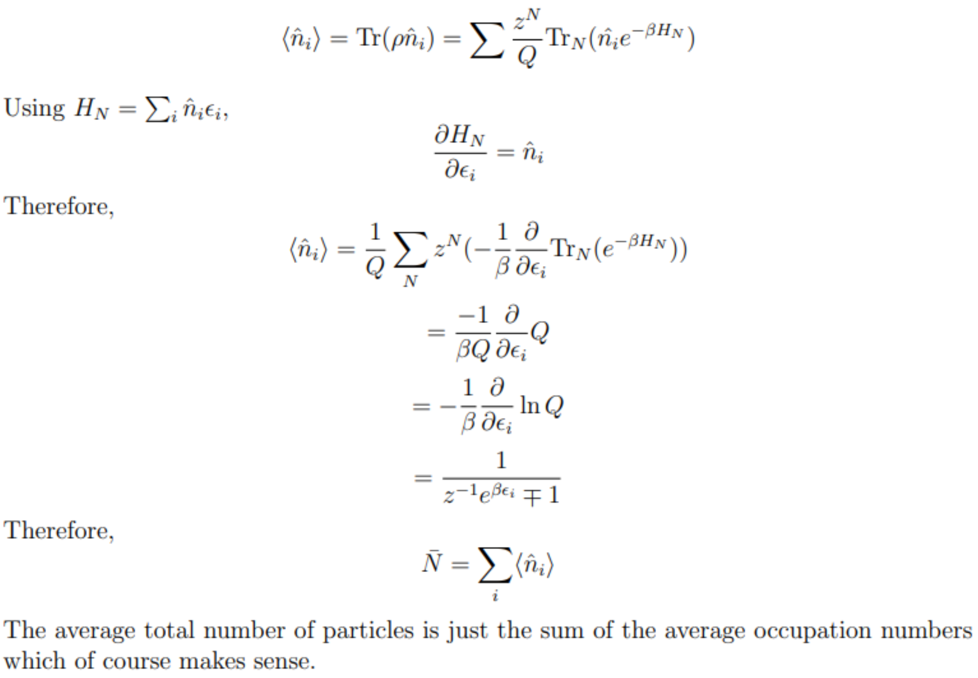
$$= \sum_i \frac{\mathcal{Z}e^{-\beta\epsilon_i}}{1 - \mathcal{Z}e^{-\beta\epsilon_i}}$$

Then

$$\langle N \rangle = \sum_i \frac{1}{\mathcal{Z}^{-1}e^{\beta\epsilon_i} + 1}$$

9.3 Expected Occupation Numbers

Consider the expectation value of the occupation number.



$$\langle \hat{n}_i \rangle = \mathrm{Tr}(\rho \hat{n}_i) = \sum \frac{z^N}{Q}\mathrm{Tr}_N(\hat{n}_i e^{-\beta H_N})$$

Using $H_N = \sum_i \hat{n}_i \epsilon_i$,

$$\frac{\partial H_N}{\partial \epsilon_i} = \hat{n}_i$$

Therefore,

$$\langle \hat{n}_i \rangle = \frac{1}{Q}\sum_N z^N\left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\mathrm{Tr}_N(e^{-\beta H_N})\right)$$

$$= \frac{-1}{\beta Q}\frac{\partial}{\partial \epsilon_i}Q$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\ln Q$$

$$= \frac{1}{z^{-1}e^{\beta\epsilon_i} \mp 1}$$

Therefore,

$$\bar{N} = \sum_i \langle \hat{n}_i \rangle$$

The average total number of particles is just the sum of the average occupation numbers which of course makes sense.

To summarize, we call

$$\langle \hat{n}_i \rangle = \left\{ \frac{1}{\mathcal{Z}^{-1} e^{\beta \epsilon_i} \pm a} \right\} \left\{ \begin{matrix} a = +1\, fermions \\ a = -1\, bosons \end{matrix} \right\}$$

the Bose-Einstein/Fermi-Dirac distribution function. It tells us the average number of particles that occupy the state i

Chapter 10

Ideal Quantum Gas

10.1 Density of States

Consider an ideal gas in a cubic box with volume $V = L^3$. Due to the boundary conditions, the momenta must satisfy,

$$\mathbf{p} = \hbar \frac{2\pi\mathbf{n}}{L}$$

$$\Rightarrow \Delta p_i = \hbar \frac{2\pi}{L}$$

Suppose now we have a distribution function $f(\mathbf{p})$. Taking the large volume limit $V \to \infty$, where V is the volume in $\mathbf{p}$ space, then

$$\Delta p_x \Delta p_y \Delta p_z \sum_{\mathbf{p}} f(\mathbf{p}) \to \int d^3\mathbf{p} f(\mathbf{p})$$

since the LHS becomes a Riemann sum in the limit.

$$\sum_{\mathbf{p}} f(\mathbf{p}) \to \left(\Delta p_x \Delta p_y \Delta p_z\right)^{-1} \int d^3\mathbf{p} f(\mathbf{p})$$

$$\sum_{\mathbf{p}} f(\mathbf{p}) \to \frac{V}{h^3} \int d^3\mathbf{p} f(\mathbf{p})$$

To change this to an integral over the magnitude of p, use spherical coordinates and integrate over all angles to get a factor of 4π,

$$\frac{4\pi V}{h^3} \int_0^\infty dp p^2 f(p)$$

It is often more useful to integrate over the energies. Use the fact that $\sqrt{2m\epsilon} = p$. Then we get,

$$\frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \int_0^\infty d^3\epsilon \epsilon^{\frac{1}{2}} f(\epsilon)$$

The quantity;

$$g(\epsilon) \equiv \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \in^{\frac{1}{2}}$$

is referred to as *the density of states*. The quantity $g(\epsilon) d\epsilon$ measures the number of states within energy $\epsilon, \epsilon + d\epsilon$.

Let’s find the equation of state. This is given by,

$$\frac{PV}{kT} = \ln\ \mathcal{Q}(z, \mathbf{p}, V) = \frac{V}{h^3}\int d^3\mathrm{p}\textstyle\sum_{\mathbf{p}}\left[\mp\ln\left(1 \mp ze^{-\beta\epsilon_{\mathrm{p}}}\right)\right]$$

$$= \frac{V}{h^3}g_{pol^{\alpha}}4\pi\int_0^\infty p^2dp\left(\mp\ln\left(1 \mp ze^{-\beta\epsilon_{\mathrm{p}}}\right)\right)$$

where g_{pol} is the number of polarization states (such as spin). This is due to *degeneracy that may arise*. It's very important for fermions since only one fermion can occupy one state.

Sticking in our density of states stuff,

$$= \mp\frac{2\pi}{h^3}(2m)^{8/2}g_{poi}\int_0^\infty d\epsilon\epsilon^{1/2}\ln\left(1 \mp ze^{-\beta\epsilon}\right)$$

Integrating by parts gives

$$P = \frac{2}{3}g_{pol}\frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\int_0^\infty \frac{\epsilon^{\frac{3}{2}}}{z^{-1} \mp 1} \qquad (10.1.1)$$

Similarly, since the expression for the average particle number from above is,

$$N = \sum \frac{1}{z^{-1}e^{-\beta\epsilon} \pm 1}$$

Changing this to an integral and working it out gives,

$$\frac{N}{V} = g_{pol}\frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\int_0^\infty d\epsilon\frac{\epsilon^{\frac{1}{2}}}{z^{-1}e^{-\beta\epsilon} \mp 1} \qquad (10.1.2)$$

Finally, lets compute the internal energy.

$$U = -\frac{8}{\partial\beta}\ln\ Z_{gr}$$

We have

$$\ln\ Z_{gr} = \mp g_{\mathrm{pol}}V\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\epsilon^{1/2}\ln\left(1 \mp ze^{-\beta\epsilon}\right)$$

So

$$U = n_{\mathrm{pol}}\,V\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\frac{\epsilon^{3/2}}{z^{-1}e^{\beta^2 \neq 1}}$$

$$U = \frac{3}{2}PV$$

This is a result that can also be computed classically.

Chapter 11

Fermi Gas

So far we have some general expressions for both distributions. Lets now examine the Fermi-Dirac distribution. Examples of Fermi gases are electrons in a metal. Recall the thermal wavelength,

$$\lambda^3 = \left(\frac{h^2}{2\pi mkT}\right)^{3/2}$$

ow recall the significance of λ_T in QM:

So we can infer that

*$\lambda_T\sim$ minimum **size** of quantum wavepackets describing atoms in a quantum ideal gas.*

As shown in the figure , the classical picture of atoms as billiard balls with well-defined trajectories only makes sense If;

$$\lambda_T \ll \text{ the average interparticle distance } r_0 \sim \left(\frac{V}{N}\right)^{1/3} = \frac{1}{n^3}$$

Where $n = N/V$ is ***the density*** of particles. Then the classical condition can be stated as;

$$\lambda_T \ll r_0 \sim \frac{1}{n^3}\,, \quad \text{that is } (\,\lambda_T \ll r_0)$$

$$\equiv (\,\lambda_T\, n^3 \ll 1\,) \quad (\text{classical regime})$$

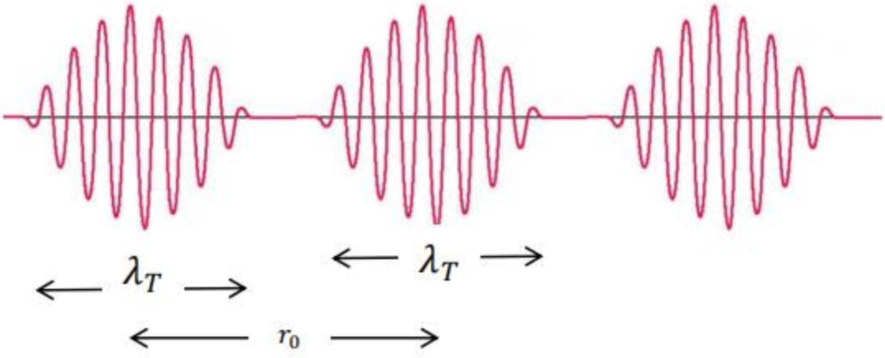


Figure 1

This inequality is ***violated*** *at low T or high density*. Then the quantum regime become more significant at temperatures lower than the ***degeneracy temperature T_0*** corresponding to.

$$\lambda_T\, n^3 \approx 1 \quad (Onset\ of\ quantum\ effect)$$

When this condition is fulfilled***, the wave functions*** of different particles begin to ***overlap***

and the system has to be treated according to quantum mechanics.

The condition

$$\lambda_T\, n^3 \approx 1$$

Or

$$n\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2} = 1 \qquad (6.5)$$

defines a line in the $T\ -\ n$ plane that sets the division between the classical and the

quantum regimes, as indicated in figure (2).

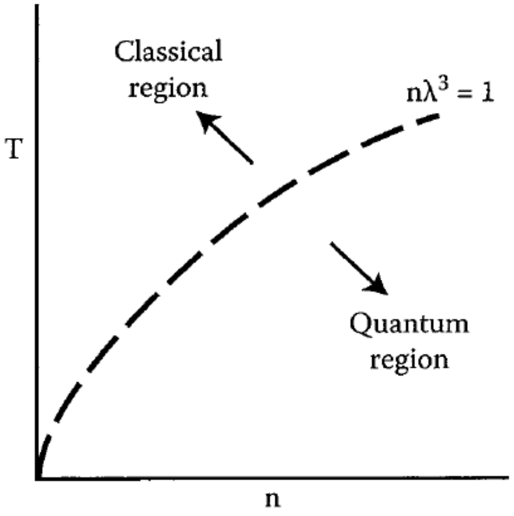


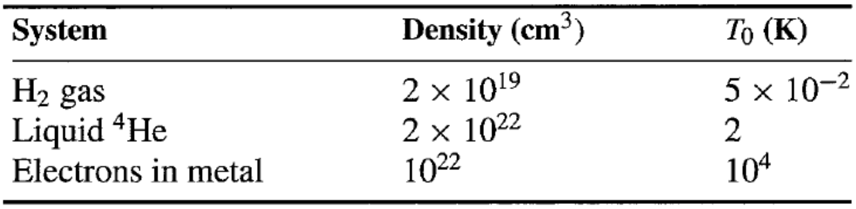
Figure 2

The degeneracy temperature T_0 is then given as;

$$k_B T_0 = \left(\frac{2\pi\hbar^2}{m}\right) n^{2/3}$$

T_0 can have very different values, depending on the physical system under study, as indicated in table 6.1. For example, at room temperature, a gas at STP can be described classically , whereas electrons in a metal are in the extreme quantum region. Liquid helium has a degeneracy temperature in between. At 2.17 it makes a transition to a quantum phase that exhibits superfluidity.

Table 3: Examples of quantum degeneracy temperatures



System	**Density (cm^3)**	T_0 **(K)**
H_2 gas	2×10^{19}	5×10^{-2}
Liquid ^{4}He	2×10^{22}	2
Electrons in metal	10^{22}	10^4

For a Fermi-Dirac system, we have from equation (10.1.2)

$$\frac{N}{V} = g_{pol}\frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\int_0^\infty d\epsilon \frac{\epsilon^{\frac{1}{2}}}{z^{-1}e^{-\beta\epsilon}+1}$$

$$\frac{N}{V} = g_{pol}\frac{2\pi}{h^3}(2m)^{\frac{3}{2}}\int_0^\infty d\epsilon \frac{\epsilon^{\frac{1}{2}}}{z^{-1}e^{-\beta\epsilon}+1}$$

To solve this integral, change variable $x = \beta\epsilon$ so $dx = \beta d\epsilon$.

$$\frac{N}{V} = g_{pol}\frac{2\pi}{\lambda^3(\pi)^{3/2}}(\beta)^{\frac{3}{2}}\int_0^{\infty}\frac{d\epsilon}{(\beta)^{3/2}}\frac{x^{\frac{1}{2}}}{z^{-1}e^{\mathrm{x}}+1}$$

$$\frac{N}{V} = g_{pol}\frac{2}{\sqrt{pi}}\lambda^{-3}\int_0^{\infty} dxx^{1/2}ze^{-x}\frac{1}{1+ze^{-x}}$$

Expend in powers of z assuming that $|ze^{-x}| < 1$,

$$\frac{N}{V} = g_{pol}\frac{2}{\sqrt{P}}\lambda^{-3}\int_0^{\infty} dzz^{1/2}ze^{-x}\sum_{k=0}^{\infty}(-z)^k e^{-kr}$$

Recall the definition of the gamma function, $\Gamma(n) = \int_0^{\infty 0} dtt^{n-1}e^{-t}$. We define,

$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^{\infty}\frac{x^{n-1}dx}{z^{-1}e^{x}+1}$$

It can be shown that,

$$\frac{1}{\Gamma(n)}\int_0^{\infty}\frac{x^{n-1}dx}{z^{-1}e^{x}+1} = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^n}$$

Therefore, uting the fact that $\Gamma\left(\frac{3}{2}\right) = \frac{\pi}{2}$,

$$\frac{N}{V} = g_{pol}\lambda^{-3}f_{3/2}(z)$$

Now equation (I0.1.1) can be analysed in the same way to give

$$\frac{PV}{kT} = g_{pol}\frac{V}{\lambda^{-3}}f_{5/2}(z)$$

We can obtain an equation of state then from the two expressions.

$$\frac{PV}{NkT} = \frac{f_{5/2}(z)}{f_{3/2}(z)} = \frac{\sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^{5/2}}}{\sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^{3/2}}}$$

$$= \frac{-(-z + \frac{z^2}{2^{5/2}} - \frac{z^3}{3^{5/2}} + \mathcal{O}(z^3))}{-(-z + \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} + \mathcal{O}(z^3))}$$

$$= 1 - (\frac{1}{2^{5/2}} - \frac{1}{2^{3/2}})z + \mathcal{O}(z^2)$$

Denote

$$\mathrm{t} \equiv \frac{N\lambda^2}{Vn_{\mathrm{pe}i}} = f_{2//2}(z)$$

Writing out f explicitly givest,

$$t = f_{3/2}(z) = \sum_{k=1}^{\infty} (-1)^{k-1}\frac{z^k}{k^{3/2}} = -\frac{z^3}{2^{3/2}} + O(z^3)$$

We want z in tetans of pomets of t. Use an ansatz $z = z_1 t + z_2 t^2 + O(t^3)$,

$$t = [z_1 t + z_2 t^2 + \mathcal{O}(t^3)] - \left[\frac{1}{2^3/2}\left(z_1 t + z_2 t^2 + O(t^3)\right)^2\right] + O(z^2)$$

We equate the coefficients on the LHS and RHS to find z_1, z_2, ... This gives,

$$z = t + \frac{1}{2^{3/2}} t^2 + \mathcal{O}(t^3)$$

Plugging in $\frac{PV}{NkT}$ gives,

$$\frac{PV}{NkT} = 1 + \left(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\right) t + \mathcal{O}(t^2)$$

Recalling that $t \equiv \frac{N\lambda^3}{Vg_{pol}}$ '

$$\frac{PV}{NkT} = 1 + \frac{1}{4\sqrt{2g_{pol}}} \frac{N\lambda^3}{V} + O(t^2)$$

Also, nobe that since $t \equiv \frac{N\lambda^3}{\mathrm{V}g_{pol}}$, which is related to the conditions for noticeable quantum effects, we see that for small t, get the classical limit. Also, the correction to the classical ideal gas is positive. This mesns the preasure due to the fermionic nature of particlen is larger.

11.1 Fermi Gas at Zero Temperature

It has been sbown that a Fermi Gas at high temperature is just a chssical ideal gas and quantum effects are negligible. Lets examuine the properties when $T \to 0$.
Consider the Fermi-Dirae distribution,

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

When $T \to 0, \beta \to \infty$. Henoe,

$$\lim_{\beta\to\infty} \frac{1}{e^{8(\epsilon-\mu)} + 1} = \begin{cases} 0 & \text{if } \epsilon > \mu \\ 1 & \text{if } \epsilon < \mu \end{cases}$$

$$= \theta(\mu - \varepsilon)$$

where θ is the Henvivide step function. Then,

$$\frac{N}{V} = n_p x^2 \frac{2\pi}{h^2} (2m)^{2/2} \int_0^\infty \mathrm{d}\epsilon\, e^{1/2} \theta(\mu - \epsilon)$$

$$= g_{pol} \frac{2\pi}{h^3} (2m)^{1/2} \int_0^k d\epsilon \epsilon^{1/2}$$

$$= g_{\mathrm{pol}}\frac{2\pi}{h^3}(2m)^{3/2}\frac{2}{3}\mu^{3/2}$$

We also have for the pressure,

$$P = \frac{2}{3}g_{pol}d\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\epsilon^{3/2}\theta(\mu - \epsilon)$$
$$P = \frac{2}{3}g_{pol}\frac{2\pi}{h^2}(2m)^{2/2}\frac{2}{5}\mu^{5/2}$$

Dividing tav expressions gives,

$$PV = \frac{2}{5}N\mu$$

Eliminate μ to get,

$$PV = \frac{2}{5}N\left[\frac{2}{3}g_{pol}d\frac{2\pi}{h^3}(2m)^{3/2}\frac{V}{N}\right]^{-2/3}$$
$$\Rightarrow PV^{s/2} = \frac{2h^2N^{-5/2}}{10m}\left(\frac{4\pi}{3}g_{pol}\right)^{-2/3}$$

This is the equation of state for $T = 0$. What it shows it that pressure does not vanish at $T = 0$

We also see that

$$\mu \sim N^{2/3}$$

This means that the chemical potential can be quite large at $T = 0$. Since the porticles we are dealing with are fermions, only one particle can fill one state. Define $\mu(T = 0) \equiv \epsilon_F$ to be the Fermi energy which is the energy of the highest occupied state ot $T = 0$. It also means that it is the minimal energy of any new particle that is added to the system.

11.2 Fermi Gas near Zero Temperature

We have examined the properties of a Fermi gas at zero temperature. We now want to find how it behaves near zero. This can be done by Taylor expanding our integral. Lets obtain a general form. Consider the integral of some function along with the Fermi-Dirac distribution,

$$I(\mu) = \int_0^\infty \frac{f(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon$$

Splitting integrals, Taylor expanding and doing some generally tricky manipulation gives,

$$I(\mu) = \int_0^w d\epsilon f(\epsilon) + \frac{2}{\beta^2}\frac{\pi^2}{12} f'(\mu) + O(\beta^{-4})$$

Lets get

$$\frac{N}{V} = g_{pol}\frac{2\pi}{h^3}(2m)^{1/2}\int_a^\infty d\epsilon \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon} + 1}$$

Call $A = n_{\text{pad}}\, V \frac{2r}{E}(2m)^{3/2}$ for convenience. Tben using the tesult above gives,

$$\begin{aligned} N \quad &= A\left[\int_0^\mu d\epsilon\epsilon^{1/2} + \frac{2}{\beta^2}\frac{\pi^2}{12}\frac{d}{d\epsilon}e^{1/2} + O(\beta^{-4})\right] \\ &= A\left[\frac{2}{3}\mu^{3/2} + \frac{1\pi^2}{\beta^2 12}\mu^{-1/2} + O\left(\beta^{-1/4}\right)\right] \end{aligned}$$

I'm going to skip a be of things here since it's all maths and no pbysics. We can use an ansatz method again to get μ in posers of β^{-2}. Then we abo coanpute the integral for the grand canonical potentinl $\Omega = -kT\ln\, Q = -PV$. An ansatz method is used agnin to get μ. Putting everytbing together gives the equation of state

$$PV = \frac{4}{15}A\left(\frac{3N}{2A}\right)^{5/2} + \frac{\pi^2}{9}\beta^{-2}A\left(\frac{3N}{2A}\right)^{1/2} + O(\beta^{-4})$$

I haven't done it yet but Im pretty sure for $\beta \to \infty$, gou can monipulate this into the equation of state at zero temperature.

11.3 Entropy

Recall from the definition of the grand canonical potential, the entropy is

$$S = -\left(\frac{\delta\Omega}{\delta T}\right)_{V,}$$

This works out to be

$$S = \frac{\pi^2}{3} A\mu_0^{1/2} k^2 T + O(T^3)$$

or

$$S = \frac{\pi^2}{3} Nk \frac{kT}{e_F} + O(T^a)$$

Note that thin is in agreement with the third law of thermodynamics.

11.4 Heat Capacity

The heat capacity is

$$\begin{aligned} C_v = \frac{dQ}{dT}_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} &= T\left(\frac{\partial S}{\partial T}\right)_{V,N} \\ &= Nk\frac{\pi^2}{3}\frac{kT}{\epsilon_F} + \mathcal{O}(T^3) \end{aligned}$$

This is a divergence from classical mechanics and predicts that the heat capacity goes to zero when the temperature does.

Chapter 12

Bose Gas

We now lock at the Bose gas, The treatment is quite similar as the Fermi gas. Start with the grand canonical potential and the average particle number.

$$-PV = \Omega = -kT'\ln\, Z_{gr} = -\frac{2}{3}A\int_0^\infty \,\mathrm{d}\epsilon\,\frac{\epsilon^{2/2}}{z^{-1}e^{\beta\epsilon}-1}$$

$$N = A\int_0^\infty d\epsilon\,\frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon}+-1}$$

with

$$A = n_{px}V\frac{2}{\sqrt{\pi}}\lambda^{-3}\beta^{3/2}$$

Lets define a function,

$$g(z) = \frac{1}{\Gamma(l)}\int_0^\infty dx\,\frac{x^{l-1}}{z^{-1}e^{x}-1}$$

Which can be written as a geometrical series

$$\begin{aligned} g_l(z) \quad &= \frac{1}{\Gamma(l)}\int_0^\infty dxx^{l-1}\left(ze^{-x}\sum_{n=0}^{\infty}(ze^{-x})^n\right. \\ &= \frac{1}{\Gamma(l)}\sum_{n=1}^{\infty} z^n\int_0^\infty dxx^{l-1}e^{-nx} \end{aligned}$$

The integral is just the gamma function.

$$\Rightarrow g(z) = \sum_{n=1}^{\infty}\frac{z^n}{n^l}$$

Note that this expansion converges only if $0 \leq z \leq 1$ so it is not defined for $z > 1$. This is iaportant later since it defines a critical

temperature..
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Note the relationship between the Riemann Zeta functioa wben $z = 1(\mu = 0)$,

$$g_l(1) = \sum_{n=1}^{\infty} \frac{1}{n^l} = \zeta(l)$$

One thing we should know is that

$$g_2/2(1) = \zeta\left(\frac{3}{2}\right) \approx 2.612$$

and also that it is an increasing function.

So we can now rewrite the density in terms of this new function. The next section examines what happens when we change the temperature of the system and how we must change g to *compensate*.

12.1 Bose Einstein Condensation

We can write the density now as

$$\frac{N}{V} = g_{pol}\lambda^{-3}g_{3/2}(z)$$

Suppose we want to keep the density $\frac{N}{V}$ fixed whilst decreasing the temperature (ie λ). Then $g_{3/2}(z)$ must increases so z must increase. However, z $\text{can't take value greater than 1}$. Denote this temperature at $z = 1$ to be the critical teruperature $T = T_{\text{c.}}$ This can be solved pretty easily by recalling that $\lambda = \frac{h}{\sqrt{2\pi mkt}}$. Setting $z = 1$ gives

$$T_c = \frac{h^2}{2\pi mk}\left(\frac{N}{Vg_{pol}\zeta\left(\frac{2}{2}\right)}\right)^{2/3}$$

Now there's another problem that we run into. Suppose we go below the critical temperature. z can only go at most to 1 so g can no longer change. This means that $\frac{N}{V}$ decreases when tbe temperoture goes down which doesn't physically make sense. The problem is to do with the change from a sum to an integml. The contribution of the ground sitate $\epsilon = 0$ does not contribute to the integral to we must explicitly sum it. Therefore, the correct expression is,

$$\frac{N}{V} = \frac{g_{pol}}{V}\frac{z}{1-z} + g_{p0l}\lambda^{-3}g_{\frac{3}{2}}(z) \qquad (12.1.1)$$

and denote

$$N_0 = g_{p0l}\frac{z}{1-z}$$

For small z, thete is a negligible amount of particks in the ground state. Homever, as the temperature begins to decrease, the number *diverges* and a macroscopic amount of particles are in the ground state. This is the phenomenon of ***Bose-Einstein condensation***.

What's incredible is that once tbere are a buge number of particles in the ground state, it's as if the particles merge into a colkctive single state such that quantum effects are noticeable on the macroscopic level.

We can also find the ratio of the perticles in the ground state to the total number of particles. Some simple manipuhtion of (12.1.1) leads to,

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{2/2}$$

Past the point T_c, corresponds to a phase thinsition.

12.2 Equation of State for $T < T_c$

Up until pow, the pressure has been completely ignoted. Well, it can be written as

$$\frac{PV}{kT} = g_{pol} V \lambda^{-3} g_{5/2}(z)$$

Fot $T < T_c$

$$\frac{PV}{kT} = g_{\mathrm{pol}} V \lambda^{-3} \zeta\left(\frac{5}{2}\right)$$

and this includes careful integrating and summing of the ground state. It's also handy to know that $\zeta\left(\frac{5}{2}\right) = 1.324$

Rewrite the number density to get

$$g_{pol} V \lambda^{-3} = \frac{N - N_0}{\zeta\left(\frac{3}{2}\right)}$$

Then combining the two equations gives,

$$\begin{aligned} \frac{PV}{kT} &= \frac{N - N_0}{\zeta\left(\frac{3}{2}\right)} \zeta\left(\frac{5}{2}\right) = \left(\frac{T}{T_e}\right)^{3/2} N \frac{\zeta(5/2)}{\zeta(3/2)} \\ \Rightarrow \quad \frac{PV}{NkT} &= \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_e}\right)^{3/2} \approx 0.513 \left(\frac{T}{T_c}\right)^{3/2} \end{aligned}$$

This can aloo be written as

$$\frac{PV}{kT} \approx 0.513N\left(\frac{T}{T_c}\right)^{3/2}$$

The second last teo quantities can be interpreted as the number of particles with $\epsilon \neq 0$. The pressure comes from particles with nonzero momentum/energy.

12. 3 Equation of State for $T > T_c$For $T > T_c$ we have

for $T > T_c$ we have

$$\frac{PV}{kT} = g_{pol}V\lambda^{-3}g_{5/2}(z)$$
$$\frac{N}{V} = \frac{N_0}{V} + g_{pol}\lambda^{-3}g_{3/2}(z)$$

For $T > T_{c,}$, $\frac{N_0}{V} \to 0$. Combining the two equations gives,

$$\frac{PV}{NkT} = \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

Recall that

$$g(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^t}$$

For $T \to \infty, z \to 0$. We can then expand and get,

$$\frac{PV}{NkT} = 1 + O(z)$$

So we get the classical ideal gas for high temperature. The term of $O(z)$ can be computed using an ansatz method by expanding in a power series of $t = g_{3/2}(z) = \frac{N\lambda^3}{Vg_{pol}}$ which may do at some point

12.4 Heat Capacity

We look at states where there is bo degeneracy, ie $g_{pol} = 1$. Recall that

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

Recall equation (10.1.3). For a Bose gas, we bave

$$U = \frac{3}{2}PV = \begin{cases} \frac{2}{2}VkT\lambda^{-3}g_{5/2}(z) & (T > T_c) \\ \frac{1}{2}VKT\lambda^{-2}\zeta\left(\frac{5}{2}\right) & (T < T_c) \end{cases}$$

There are 3 straightforward computations then for each case of T.

- **Heat Capacity when $T < T_c$**

$$C_V = \frac{\partial}{\delta T}\left(\frac{3}{2}VkT\lambda^{-3}\zeta\left(\frac{5}{2}\right)\right)$$
$$C_V = \frac{15}{4}Vk\lambda^{-3} \propto T^{2/2}$$

- **Heat Capacity when $T = T_c$**

At $T = T_{c,}$ use $\frac{N}{V} = \lambda^{-3}g_{5/2}(1)$

$$C_V = \frac{15}{4}Vk\frac{N\zeta(5/2)}{V\zeta(3/2)} \approx 1.925Nk$$

- **Heat Capacity when $T > T_c$**

$$C_V = \frac{\partial}{\delta T}\left(\frac{3}{2}VkT\lambda^{-3}g_{\frac{5}{2}}(z)\right)$$

$$= \frac{3}{2}Vk\lambda^{-3}g_{5/2}(z) + \frac{3}{2}VkT(-3)\lambda^{-4}\frac{\partial\lambda}{\partial T}g_{5/2}(z) + \frac{3}{2}VkT\lambda^{-3}\frac{\partial g_{5/2}(z)}{\partial z}\frac{\partial z}{\partial T}$$

Most of the derivatives are easy enough. $\frac{\partial g_{5/2}(z)}{\partial z} = \frac{1}{z}g_{3/2}(z)$ = 1 z g3/2(z) can be obtained from the series definition. To find ∂z/ ∂T , take

$$\frac{N}{V} = \lambda^{-3}g_{3/2}(z)$$

Differeatinbe w.r.t T.

$$0 = \frac{\partial}{\partial T}\lambda^{-3}g_{3/2}(z)$$

Using the product rule,

$$\Rightarrow \frac{\partial z}{\delta T} = -z\frac{3}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)}$$

Therefore,

$$C_V = \frac{3}{2}Nk\left[\frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right]$$
$$= \frac{3}{2}Nk\left[\frac{5}{2}\frac{z + O(z^2)}{z + O(z^2)} - \frac{3z + O(z^2)}{2z + O(z^2)}\right]$$

For $T \to \infty, z \to 0$

$$C_V = \frac{3}{2}Nk + O(z)$$

which is the same as a classical ideal gas.

More importantly, plotting a graph of this shows a discontinuity of the slope of the heat capacity. This is an example of a phase transition.

Chapter 13

Heat Capacity of a Solid

13.1 Classical Heat Capacity of a Solid

Consider a solid which consists of atoms held in place that are allowed to undergo small vibrations, so essentially this is a system of N harmonic oscillation. The Hamiltonian is

$$H = \sum_{i=1}^{\mathrm{IN}} \left(\frac{p_1^2}{2m} + \frac{1}{2} k {q_i}^2 \right)$$

The canonical partition function is

$$Z = \int d^{3N}p \; d^{3N}q \; e^{-\beta H}$$

$$= \left[\int_{\infty}^{\infty} dp \int_{\infty}^{\infty} dq \; e^{-\beta \frac{p^2}{2m}} e^{-\frac{1}{2}\beta k q^2} \right]^{3N}$$

These are Gaussian integrals.

$$= \left[\left(\frac{2m\pi}{\beta} \right)^{1/2} \left(\frac{2\pi}{\beta k} \right)^{1/2} \right]^{3N}$$

The internal energy is

$$U = -\frac{8}{\partial \beta} \ln\, Z = -\frac{\partial}{\partial T} \left(-\frac{3N}{2} \ln\, \beta - \frac{3N}{2} \ln\, \beta \right) + 0$$

$$= \frac{3N}{\beta} = 3NkT$$

Therefore, the heat capacity is,

$$C_V = 3Nk$$

This is the heat capacity predicted for a classical solid. While this is true for high temperature, experiments show that the heat capacity goes to zero as temperature goes to zero so clearly, we need a quantum explanation.

I3.2 Einstein Model

In quantum mechanics, a. harmonic oscillator's energy is quantized. Therefore, the solid's energy should have the form,

$$E = \sum_{i=1}^{3N} \left(n_i + \frac{1}{2}\right) \hbar\omega_i$$

where n_i is a quantum number, $i = 1, \dots, N$. Interpret n_i to be the number of 'particles' with energy $\hbar\omega_i$. These particles are known as phonons. Note that the number of particles is not conserved. This means that $\mu = 0$ so $z = 1$

Let's compute the grand canonical partition function.

$$Z_{gr} = \sum_{N_q=0}^{\infty} z^{N_q} \sum_{\{n_i\}_{i=1,\dots,3N}} e^{-\beta \sum_{i=1}^{3N} \left(n_i + \frac{1}{2}\right)\hbar\omega_i}$$

Use N_q to label the number of quanta or 'particles', $\sum_{i-1}^{3N} = N_{q^*}$ Since $z = 1$,

$$\sum_{\{n_i\}_{i=1,.....3\mathrm{N}}} e^{-\beta\sum_{t=1}^{3N}\left(n_1+\frac{1}{2}\right)h\omega_1}$$

$$\sum_{\{n_i\}}\prod_{i=1}^{3N} e^{-\beta\sum_{t=1}^{3N}\left(n_\mathrm{i}+\frac{1}{2}\right)h\omega_\mathrm{i}}$$

$$\prod_{i=1}^{3N}\sum_{\{n_i\}} e^{-\beta\sum_{t=1}^{3N}\left(n_\mathrm{i}+\frac{1}{2}\right)h\omega_\mathrm{i}}$$

$$= \prod\nolimits_{i=1}^{3N} e^{-\frac{1}{2}\beta\hbar\omega_i}\sum\nolimits_{n_i=0}^{\infty}\left(e^{-\beta h\omega_i}\right)^{n_i}$$

since the quantum number n_i has no limit.

$$Z_{gr} = \prod_{i=1}^{3N} e^{-\frac{1}{2}\beta t\omega_i}\frac{1}{1-e^{-\beta h\omega_\mathrm{i}}}$$

The internal energy is

$$U = -\frac{\partial}{\partial\beta}\ln\,Q$$

$$= -\frac{\partial}{\partial\beta}\left(\sum_{i=1}^{\infty}\left(-\frac{1}{2}\beta\hbar\omega_i - \ln\left(1-e^{-\beta\hbar\omega_i}\right)\right)\right)$$

$$= \sum_{i=1}^{3N}\hbar\omega_i\left(\frac{1}{2}+\frac{1}{e^{\beta\pi\Delta i}-1}\right)$$

Then the heat capacity is,

$$C_V = \frac{\partial U}{\partial T} = \sum_{t=1}^{3N} k(\beta\hbar\omega_i)^2 \frac{e^{\beta\hbar\omega_i}}{(e^{\beta\hbar\omega_i}-1)^2}$$

We now make an assumption that all the particles vibrate at the same angular frequency which is a feature of the Einstein model. Set $\omega_{\mathrm{i}} = \omega$.

$$\Rightarrow C_V = 3\mathrm{Nk}(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta/\omega}-1)^2}$$

This is the Einstein heat capacity.

Lets look at the limits

For $T \to \infty, \beta \to 0$.

$$C_V = 3Nk(\beta\hbar\omega)^2 \frac{1+\beta\hbar\omega+O(\beta^2)}{\left(B\hbar\omega+\frac{(\beta\hbar\omega)^2}{2}+O(\beta^3)\right)^2}$$

$$C_V = 3Nk \frac{1+\beta\hbar\omega+O(\beta^2)}{1+\frac{\beta\hbar\omega}{2}+O(\beta^2)}$$

$$= 3Nk(1+\beta\hbar\omega)\big(1-\beta\hbar\omega+\mathcal{O}(\beta^2)\big)+\mathcal{O}(\beta^2)$$
$$= 3Nk + O(\beta^2)$$

agreeing with the classical limit.

For $T \to 0, \beta \to \infty$

$$C_V = 3Nk(B\hbar\omega)^2 e^{-2\beta\hbar\omega} \frac{e^{\beta\hbar\omega}}{(1 - e^{-\hbar\omega})^2}$$

$$= 3Nk(\beta\hbar\omega)^2 e^{-\beta\hbar\omega} \left(1 + O\left(e^{-\beta}\right)\right)$$

Since the exponential goes to zero much faster than β goes to infinity,

$$C_V \to 0$$

Chapter 14

Blackbody Radiation

The next section examines the properties of a gas consisting of photons which gives rise to blackbody radiation.

14.1 Relativistic Bose Gas

Consider a system of N bceons with mass m. The relativistic energy is,

$$\epsilon = \sqrt{p^2c^2 + m^2c^4}$$

We need to reconsider how we change a momentum integral to an energy integral.

$$\begin{aligned} \frac{P}{kT} &= \frac{g_{\text{poi}}}{h^3}\int d^3\text{p}\left(-\ln\left(1 - ze^{-\beta\epsilon}\right)\right) \\ &= \frac{4\pi p_{pol}}{h^3}\int_0^\infty p^2 dp\left(-\ln\left(1 - ze^{-\beta\epsilon}\right)\right) \end{aligned}$$

Use the fact that

$$\begin{aligned} d\varepsilon &= \frac{1}{2\sqrt{p^2c^2 + m^2c^4}}2pc^2dp \\ \Rightarrow p^2dp &= \frac{\sqrt{\epsilon^2 - m^2c^4}}{c^3}\epsilon d\epsilon \end{aligned}$$

Therefore, our relativistic expressions for the pressure and density are,

$$\frac{P}{kT} = g_{pol}\frac{4\pi}{(hc)^3}\int_{mc^2}^\infty d\epsilon\epsilon\sqrt{\epsilon^2 - m^2c^4}\left[-\ln\left(1 - ze^{-\beta\epsilon}\right)\right]$$

$$\frac{N}{V} = g_{pol}\frac{4\pi}{(hc)^3}\int_{mc^2}^{\infty} d\epsilon \in \sqrt{\epsilon^2 - m^2c^4}\,\frac{1}{z^{-1}e^{\beta\epsilon} - 1}$$

14.2 Photon Gras

For photons, set $m = 0$. Then we get,

$$\frac{P}{kT} = g_{pol}\frac{4\pi}{(hc)^3}\int_0^{\infty} d\epsilon\epsilon^2\left[-\ln\left(1 - ze^{-\beta\varepsilon}\right)\right]$$

$$\frac{N}{V} = g_{pol}\frac{4\pi}{(hc)^3}\int_0^{\infty} d\epsilon\frac{\epsilon^2}{z^{-1}e^{\beta c} - 1}$$

The first expression can be integrated by parts to give,

$$\frac{P}{kT} = n_{pd}\frac{4\pi\beta}{3(hc)^8}\int_0^{\infty} d\epsilon\frac{\epsilon^3}{z^{-1}e^{\beta\epsilon} - 1}$$

One of the first things we need to note is that photons can be created and destroyed without changing the free energy.

$\left(\frac{\partial P}{\partial V}\right)v_1T = \mu = 0 \Rightarrow z = 1$

The energy of a photon is $\epsilon = \hbar\omega$. We change vatiables to integrate over $\omega. d\epsilon = \hbar d\omega$. So our expressions now look like.

$$PV = g_{\mathrm{pol}}\frac{4\pi}{3}V\frac{\hbar^4}{(hc)^3}\int_0^{\infty} d\omega\frac{\omega^a}{e^{\beta\hbar\omega} - 1}$$

$$\frac{N}{V} = g_{pd}\frac{4\pi}{(hc)^3}\hbar^3\int_0^{\infty} d\omega\frac{\omega^2}{e^{\beta\hbar\omega} - 1}$$

Ok, so lets now look at the internal energy of the system which in discrete form is,

$$U = \sum_k (n_k)\epsilon_k = \sum_k \frac{\epsilon_k}{z^{-1}e^{\beta\epsilon_k} - 1}$$

When $V \to \infty$, it is possible to change this to an energy integral and then to a frequency integral. We find that

$$U = V\frac{g_{pol}\hbar}{2\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

Denote

$$u(\omega, T) = \frac{g_{pol}\hbar}{2\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

This is known as Plenck's Law for Radiation. It gives the distribution of energy per frequency per unit volume.
By inspection, we get an equation of state

$$U = 3P$$

Carrying out the integral,

$$\frac{U}{V} = \int_0^\infty d\omega u(\omega, T)$$
$$= \frac{\hbar}{\pi^2 c^3}\int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

Using the fact that $\int_0^\infty dx \frac{x^{2n-1}}{e^x - 1} = \frac{(2\pi)^{2n}B_n}{4n}$ where B_n are the Bernoulli numbers and $g_{pol} = 2$ for photons,

$$\frac{U}{V} = \frac{\pi^2}{15}\frac{(kT)^4}{(\hbar c)^3}$$

This is related to the Stefan-Boltzmann Law which scales $\sim T^4$. It gives the energy density of the photons and we can derive the Stefan-Boltzmann Law from it.

Consider the limit $\omega \to 0$. Then Planck's formula looks like

$$u(\omega, T) \sim \frac{kT}{\pi^2 c^3} \omega^2 + \cdots$$

This is the Rayleigh-Jean Law.

Consider the limit $\omega \to \infty$. Then Planck's formula looks like

$$u(\omega, T) \sim \frac{\hbar}{\pi^2 c^3} \omega^3 e^{-\beta \hbar \omega}$$

This is Wien's approximation.

Finally, we can find the maximum ω_{max} of $u(\omega, T)$ by diferentiating. This gives,

$$\hbar \omega_{\mathrm{maz}} = 2.822 \mathrm{kT}$$

This is Wien's Law.

Chapter 15

Magnetic Systems

In a magnetic system, the state variables that we are concerned with are the temperature T, magnetic field B and the magnetisation M. Like the earlier systems we considered, the magnetic system can then be described by an equation of state,

$$f(M,B,T)=0$$

The work performed by the system is $dW=-BdM$. Hence, the first law of thermodynamics for a magnetic system looks like

$$dU=dQ+BdM$$

15.1 Magnetic Susceptibility

Define the magnetic susceptibility to be

$$\chi_T=\left(\frac{\partial M}{\partial B}\right)_T$$
$$\chi_S=\left(\frac{\partial M}{\partial B}\right)_S$$

They can be interpreted as how magnetized something gets when there is a magnetic field present.

15.2 An Example of Paramagnetism

Consider N fixed magnetic dipoles with magnetic moments μ_{i}. Each particle's magnetic moment points in a certain direction. The magnetic moment's direction can be described by the angles (θ_i,ϕ_i). With no magnetic field, they point in random directions and the weral magnetisation is 0 . Let there be a B field applied to the system. The magnetic moments will try to align with the field to minimise the potential. The Hamiltonian for the system is,

$$H = -\sum_{i=1}^{N} \mu_i \cdot \mathbf{B}$$

Let the magnitude of each particle's magnetic moment be the same. If we choose our coordinate system such that $\mathbf{B} = (0,0,B)$,

$$H = -\sum_{i=1}^{N} \mu B \cos\ \theta_{\mathrm{i}}$$

The distribution over the angles follows Maxwell-Boltzmann statistics. The canonical partition function is,

$$Z_N = \prod_{i=1}^{N} \sum e^{-\beta E_{\mathrm{i}}}$$

Summing over all configurations gives,

$$= \prod_{i=1}^{N} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta_i \sin\ \theta_i e^{\beta\mu B \cos\ \theta_i}$$

Integrating this gives,

$$Z_N = \left(\frac{4\pi}{\beta\mu B} \sinh\,(\beta\mu B)\right)^N$$

Let us now compute the expectation value of the overall magnetic moment.

$$\langle\mu\rangle = \frac{1}{Z} \int\ d\theta_1 d\phi \mu e^{\beta\mu B c x \phi_i}$$

If we express μ in Cartesian coordinates, it is found that the x, y components are 0 . This makes sense since the B field is in the z direction so the alignment of the magnetic moments are random in the x, y direction which will average to 0. Therefore,

$$\langle\mu_z\rangle \equiv \langle\mu\rangle = \frac{1}{Z} \int\ d\theta_i d\phi \mu \cos\ \theta_i e^{-\beta\mu B \cos\ \theta_i}$$

observe that this can be rewritten as,

$$(\mu\rangle = \frac{1}{\beta}\frac{\partial}{\partial B}\ln\ Z_1$$

This is equivalent to the magnetisation of one particle. The total magnetisation then is the sum of the magnetic moments,

$$M = \frac{N}{\beta}\frac{\partial}{\partial B}\left[\ln\left(\frac{4\pi}{\beta\mu B}\sinh\left(\beta\mu B\right)\right)\right]$$

This works out to be,

$$M = N\mu\left(\coth\left(\beta\mu B\right) - \frac{1}{\beta\mu H}\right) = N\mu L(\beta\mu B)$$

where $L(x) = \coth\left(x\right) - \frac{1}{2}$ is *the Langevin function*. This is an equation of state.
Oteerve what happens in the high temperature limit $\beta \to 0$.

$$\begin{aligned} M \quad &= N\mu\frac{\beta\mu B}{3} + O(T^{-3}) \\ &= \frac{N\mu^2 B}{3kT} + \mathcal{O}(T^{-3}) \end{aligned}$$

The susceptibility is

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = \frac{N\mu^2}{3kT} + O(T^{-3})$$

Notice that magnetisation goes to 0 for high temperature. Also, the susoeptibility is positive and non-zero even when the magnetic field is turned off.

15.3 Paramagnetism and Diamagnetism

We can classify a system into two classes. We call a system paramagnetic if $\chi_T > 0$ This means that the magnetisation is in the direction of the applied magnetic field.

We call a system *diamagnetic* if $\chi_T < 0$. This means that the magnetisation oppoes the magnetic field. The next sections will develop a simple model that exhibits diamagnetism.

15.4 Electron Moving in a Magnetic Field with no Spin

It can be shown that a charged particle moving in a magnetic field with no spin does not exhibit magnetisation classically s o we look at a quantum picture. The Hamiltonian for the particle is

$$H = \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\ \mathbf{A}(\mathrm{q})\right)^2$$

with

$$\mathbf{B} = \nabla \times \mathbf{A}$$

Due to gauge invariance, we chocse $\mathbf{A}(\mathbf{q}) = (-B_y, 0,0)$ and this gives the magnetic field pointing in the z direction. Then the Hamiltonian becomes,

$$H = \frac{1}{2m}\left(\left(p_x - \frac{eB}{c}y\right)^2 + p_y^2 + p_z^2\right)$$

Solving the S-eqn gives,

$$\epsilon(p_z, j) = \frac{p_z^2}{2m} + \hbar\omega_0\left(j + \frac{1}{2}\right)$$

where $\omega_0 = \frac{\epsilon B}{mc}$. We refer to a state with quantum number j as a Landau Level. The Landau Levels are degenerate due to the allowed values of k_z. (see Michael Fry) For example, for a particle in a box of volume L^3, the allowed values of k_z are,

$$k_x = \frac{2\pi n_{\mathrm{x}}}{L_x}$$

It is found the largest n_x is $\frac{eBL^2}{he}$. Since, n_2 is positive and is integers, this is the number of degeneracies.

15.5 Landau Diamagnetism

Consider now N spinless electrons in a magnetic field and neglect the interaction between them. The Hamiltonian is

$$H = \frac{1}{2m}\sum_{i=1}^{N}\left(\mathbf{p}_{\mathrm{i}} + \frac{e}{c}\mathbf{A}\right)^2$$

We wish to compute the magnetisation and susceptibility. Define the magnetisation per unit volume $\mathcal{M} = \frac{M}{V}$. Then,

$$\mathcal{M} = \frac{kT}{V}\frac{\partial}{\partial B}\ln Z_{gr}$$

Sinoe electrons are fermions, we use the Fermi-Dirac distribution.

$$Z_{gr} = \prod_{\lambda}\left(1 + ze^{-\beta\epsilon_\lambda}\right)$$

λ here is an index that is identified with p_z, j, α where $\alpha = 1, \dots, g$ is a degeneracy factor.

Lets compute $\ln\, Q$.

$$\ln Z_{gr} = \prod \ln\left(1 + ze^{-\beta\epsilon_\lambda}\right)$$

$$\ln\, Z_{gr} = g\frac{L}{h}\sum_{j=0}^{\infty}\sum_{p_z} \ln\left(1 + ze^{-\beta\epsilon_{pzj}}\right)$$

$$= g\frac{L}{h}\sum_{j=0}^{\infty}\int_{-\infty}^{\infty} dp_z \ln\left(1 + ze^{-\beta\epsilon}\right)$$

The $\frac{L}{R}$ factor comes from the density of states stuff. The average number of electrons is,

$$N = z\frac{\partial}{\partial z}\ln Z_{gr} \ = \frac{2gL}{h}\sum_{j=0}^{\infty}\int_{0}^{\infty} dp_z \frac{1}{z^{-1}e^{\beta\epsilon} + 1}$$

where we recognise the integral is an even integral.

Consider the high temperature limit $\beta \to 0$. For the particle number to remain finite, $z \to 0$. (not sure about this). Then the integral can be expanded in powers of z.

$$\ln\, Z_{gr} \approx \frac{2gL}{h}\textstyle\sum_{j=0}^{\infty}\int_{0}^{\infty} dpze^{-\beta\epsilon}$$

$$= \frac{2gLz}{h}\sum_{j=0}^{\infty}\int_{0}^{\infty} dp\; e^{\frac{-\beta p^2}{2m}} e^{-\beta\hbar\omega_0(j+1/2)}$$

$$= \frac{gLz}{h}e^{-\frac{\beta\hbar\omega_0}{2}}\sum_{j=0}^{\infty}(e^{-\beta\hbar\omega_0})^j\sqrt{\frac{2m\pi}{\beta}}$$

$$= \frac{gLz}{\lambda_{th}}e^{-\frac{\beta\hbar\omega_0}{2}}\frac{1}{1 - e^{-\beta\hbar\omega_0}}$$

$$= \frac{gLz}{2\lambda_{th}}\frac{1}{\sinh(\frac{\beta\hbar\omega_0}{2})}$$

$$= \frac{2gLz}{h} e^{-\frac{\mathrm{Sl}_2}{2}} \frac{1}{1 - e^{-\hat{\rho}\|_0}}$$

$$= \frac{gLz}{2\lambda_{\mathrm{th}}} \frac{1}{\sinh\left(\frac{j\hbar_0}{2}\right)}$$

Now expand the sinh since $\beta \to 0$,

$$\ln\, Z_{gr} \approx \frac{gLz}{\lambda_{th}} \left(1 - \frac{1}{24} (\beta \hbar \omega_0)^2 + \mathcal{O}(\beta^4)\right)$$

Plugging in values for g and ω_{b} gives,

$$\ln Z_{gr} \; = \frac{Vz}{\lambda_{\mathrm{t}\hbar}^{\mathrm{a}}} \left(1 - \frac{1}{24} (\beta \hbar \omega_0)^2\right.$$

Therefore, the magnetisation density is,

$$\mathcal{M} = \frac{kT}{V} \frac{\partial}{\partial B} \ln\, Q$$

$$= 2 \frac{kT}{\lambda_{th}^3} \left(-\frac{\hbar^2}{24 (kT)^2} \frac{\partial}{\partial B} \left(\frac{eB}{mc}\right)^2\right)$$

$$= -\frac{2z}{24 \lambda_{\mathrm{th}}^3 kT} \left(\frac{e\hbar}{mc}\right)^2 B$$

So the susceptibility density is,

$$\frac{\chi_T}{V} = \frac{\partial \mathcal{M}}{\partial B} = \frac{-z}{3kT\lambda^3} \left(\frac{e\hbar}{2mc}\right)^2$$

This is an example of a diamagnetic system which has a negative susceptibility. What's essentially happening is that the magnetic field causes circular orbits and according to Lenz's Law, an opposing magnetic field must be created.

15.6 De Haas-Van Alphen Effect

Consider the low temperature limit of Landau diamagnetism where the system approaches its ground state. We also assume that motion only occurs in the xy plane. The energy can be rewritten to be

$$\epsilon_j = 2\mu_B B\left(j + \frac{1}{2}\right)$$

where $\beta_B = \frac{e\hbar}{2mc}$ is *the Bohr magneton.*

Rewrite the degeneracy as

$$g = N\frac{B}{B_0}$$

where $B_0 = \frac{Nhc}{L^2 e}$
If $B \geq B_0$, then $g \geq N$ all the particles can fit into the ground state.
The energy of the ground state is $E_0 = N\mu_B B$.
However, if $B < B_0$, then some particles are forced into the next state by the Pauli exclusion principle. Suppose $B < B_0$ and the levels j and below are filled and the level $j + 1$ is partly filled and all higher levels are empty. Then (not sure about this)

$$(j + 1)g < N < (j + 2)g$$
$$\Rightarrow \frac{1}{j+2} < \frac{B}{B_0} < \frac{1}{j+1}$$

The energy of the system is,

$$E = g\sum_{i=1}^{1} \epsilon_1 + (N - (j + 1)g)\epsilon_{j+1}$$

where $N - (j + 1)g$ is the number of remaining particles. This gives,

$$E = N_{\mu_B} Bx(2j + 3 - (j + 1)(j + 2)x)$$

Where $\frac{B}{B_0}$

To summarise, the energy per particle of the system is,

$$\frac{E}{N} = \begin{cases} \mu_B B x & \text{if } x > 1 \\ \mu_B B x(2j+3-(j+1)(j+2)x) & \text{if } \frac{1}{j+2} < x < \frac{1}{j+1} \end{cases}$$

The magnetisation per unit area $\mathcal{M} = \frac{-1}{L^2}\frac{\partial}{\partial B}E$ is

$$\mathcal{M} = \begin{cases} \frac{-N\mu_B}{L^2} & \text{if } x > 1 \\ \mu_B B x(2j+3-(j+1)(j+2)x) & \text{if } \frac{1}{j+2} < x < \frac{1}{j+1} \end{cases}$$

Something is really wrong so stop here.

Chapter 16

Ferromagnetism

We now look at a different class of magnets called ferromagnets. These are magnets that have magnetisation even when not in the presence of a magnetic field. It is due to the electron's spin. It is energetically favored to have parallel spin. In this model, we assume that the spins can either point in the pceitive or negative direction in the z direction (i.e. we measure S_z, for convenience the z is dropped). Consider a system of N particles. The Heisenberg model has the Hamiltonian

$$H = -\frac{1}{2}\sum_{\mathrm{I},j} J_{\mathrm{ij}} S_i S_j - g\mu_B \sum_{i=1}^{N} \mathbf{S}_{\mathrm{i}} \cdot \mathbf{B}$$

where $\mathbf{B}$ is the magnetic feld, S is the spin of the particle, g is the g - factor. $J_{\mathrm{i}j} = J_{\mathrm{i}j} > 0$ is a term that measures the interaction between the spins of neighbouring particles. There is $-J$ energy for parallel spins and J energy for antiparallel spins.

Firstly, lets develop a bit of the framework we will be using later. The spins follow the usual commutator relations for spin and the spin for the i and j particle commute. This means we can find a simultaenous diagonalised eigenstate for all the particles. The partition function looks like

$$Z = Tr(e^{-\beta H}) = \sum_{m_1=\pm\frac{1}{2}} \cdots \sum_{m_N=\pm\frac{1}{2}} \langle \psi_{m_1 \dots m_N} | e^{-\beta H} | \psi_{m_1 \dots m_N} \rangle$$

We also have the Gibbe potential energy to be

$$G(T, B) = -kT \ln Z$$

The expectation value of the energy is,

$$(H) = \frac{1}{Z} \mathrm{Tr}\left(He^{-\beta H}\right)$$

$$= -\frac{\partial}{\partial \beta} \beta G(T, B)$$

The magnetiation is

$$M^{\alpha} = g\mu_B \left(\sum_{j=1}^{N} S_j^{\alpha} \right)$$

$$= \frac{1}{Z} \mathrm{Tr} \left(g\mu_B \sum_{j=1}^{N} S_i^{\alpha} e^{-\beta H} \right)$$

$$= \frac{1}{\beta Z} Tr \left(\frac{\partial}{\partial B^{\alpha}} e^{-\beta H} \right) = \frac{1}{\beta} \frac{\partial}{\partial B^{\alpha}} \ln Z$$

α labels the coordinate x, y, z.

16.1 Non-Interacting Case

Lets now consider the case where $J = 0$ so the spins do not interact with each other. However, the spins interact with the magnetic field. Choose the coordinate system so that B points in the z-direction. Then the Hamiltonian is

$$H = -g\mu_B B \sum_{i=1}^{N} S_i^{z}$$

Therefore, the partition function is,

$$\begin{aligned}
Z &= \sum_{m_1=\pm\frac{1}{2}} \cdots \sum_{m_N=\pm\frac{1}{2}} \langle \psi_{m_1\ldots m_N} | e^{\beta g \mu_B B \sum S_i^z} | \psi_{m_1\ldots m_N} \rangle \\
&= \sum_{m_1=\pm\frac{1}{2}} \cdots \sum_{m_N=\pm\frac{1}{2}} e^{\beta g \mu_B B \sum m_i} \langle \psi_{m_1\ldots m_N} | \psi_{m_1\ldots m_N} \rangle \\
&= \sum_{m_1=\pm\frac{1}{2}} \cdots \sum_{m_N=\pm\frac{1}{2}} e^{\beta g \mu_B B \sum m_i} \\
&= \left(\sum_{m=\pm\frac{1}{2}} e^{\beta g \mu_B B m} \right)^N \\
&= (e^{\frac{1}{2}\beta g \mu_B B} + e^{-\frac{1}{2}\beta g \mu_B B})^N \\
&= 2^N \cosh^N\left(\frac{\beta g \mu_B B}{2}\right)
\end{aligned}$$

Therefore the magnetisation is,

$$M = kT \frac{\partial}{\partial B} \ln\, Z = M_0 \tanh \frac{\beta g \mu_B B}{2}$$

where $M_0 = \frac{Ng\mu\, m}{2}$

16.2 Mean Field Approximation

In the mean field approximation, we assume that the spin has the form

$$\mathbf{S}_i = \langle \mathbf{S}_i \rangle + \Delta \mathbf{S}_i$$

We treat $\Delta \mathbf{S}_i$ as a small approximation. So,

$$\mathbf{S}_i \cdot \mathbf{S}_j = \langle \mathbf{S}_i \rangle \langle \mathbf{S}_j \rangle + \Delta \mathbf{S}_i \langle \mathbf{S}_j \rangle + \Delta \mathbf{S}_j \langle \mathbf{S}_i \rangle + \mathcal{O}(\Delta \mathbf{S}^2)$$

The Hamiltonian becomes,

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \Big[\langle \mathbf{S}_i \rangle \langle \mathbf{S} \rangle + 2 \Delta \mathbf{S} \langle \mathbf{S}_j \rangle \Big] - g\mu_B \sum \mathbf{S}_i \cdot \mathbf{B}$$

$$= -\sum J_{ij} \Big[\langle \mathbf{S}_i \rangle (\mathbf{S}_j - \langle \mathbf{S}_j \rangle) + \frac{1}{2} \langle \mathbf{S}_i \rangle \langle \mathbf{S}_j \rangle \Big] - g\mu_B \sum \mathbf{S}_i \cdot \mathbf{B}$$

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