

# Statistical Mechanics and Thermodynamics

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# 1 Introduction to Statistical Methods

## 1.1 Simple Random Walk and Binomial Distribution

In one dimension, the random walk can be seen as a particle moving a distance  $l$  to the left or right with probability  $p$  and  $q(1-p)$  respectively in each timestep. Note that we assume the direction of movement is independent of previous decisions. After a total of  $N$  steps, the position of the particle is given by

$$x = ml \quad -N \leq m \leq N$$

The general problem statement is to calculate  $P_N(x)$  the probability that the particle is at location  $x$  after  $N$  iterations. We can decompose  $m$  into the number of movements right  $n_1$  and the number of movements left  $n_2$  such that  $m = n_1 - n_2$ . Next, notice that  $n_1 + n_2 = N$ , so we can express  $m = 2n_1 - N$  as solely a function of  $n_1$ .

For a given value  $m$ , we have a set  $n_1$  and  $n_2$ . Since each movement is independent, we can calculate the probability of achieving this value as  $p^{n_1}q^{n_2}$ . However, before finalizing our answer, we must notice that there are  $\binom{N}{n_1}$  different ways to order these movements. Therefore, our final probability is given by:

$$W_N(n_1) = \binom{N}{n_1} p^{n_1} q^{n_2}$$
$$P_N(m) = \binom{N}{\frac{N+m}{2}} p^{\frac{N+m}{2}} q^{\frac{N-m}{2}}$$

The probability expression presented above is the binomial distribution. The distribution has mean  $Np$  and variance  $Npq$ .

Majority of this section was skipped

## 2 Statistical Descriptions of Systems of Particles

### 2.1 Basic Postulate

In an isolated system conservation of energy tells us that the system is characterized by a singular energy. All states accessible to our system must therefore have this energy. We say that the system is in equilibrium if the probability of being in any given state is independent of time. Consequently, all macroscopic parameters describing the system are also time-independent. Liouville's Theorem from classical mechanics tells us that if the system is uniformly distributed across these accessible states, then it will remain uniformly distributed across these states. With this in mind, we come to our first postulate:

**Postulate 1** *The probability that  $n$  isolated system at equilibrium is uniformly distributed across all accessible states*

Note that this postulate does not make any remarks on the time required to reach the state of equilibrium.

### 2.2 Probability Calculations

This schema lends itself to simple probability calculations. For a given energy band  $[E, E + \delta E]$  we define the states in this band to be  $\Omega(E)$ . For another arbitrary parameter  $y$ , we denote the states with energy  $E$  and parameter  $y = y_k$  to be  $\Omega(E, y_k)$ . The probability that our system takes value  $y_k$  is simply given by:

$$P(y_k) = \frac{\Omega(E, y_k)}{\Omega(E)}$$

Similar calculations can be applied to find the expected value and variance of the parameter  $y$  in our system.

$$\bar{y} = \frac{\sum \Omega(E, y_k) y_k}{\Omega(E)}$$

## 2.3 First Law of Thermodynamics

We define external parameters to be the independent parameters that specify a macroscopic system. Consider two thermal systems that can interact and exchange energy.

### 2.3.1 Thermal Interaction

First, consider the case where all external parameters remain fixed. In this case, all energy transfer is done via thermal interaction. We refer the mean energy transferred across these systems to be the heat.

$$Q = d\bar{E}$$

Conservation of energy tells us that  $\Delta E + \Delta E' = 0$  so we can conclude that the heat transferred for each system is equal in magnitude and opposite in sign.

### 2.3.2 Mechanical Interaction

If two systems are thermally isolated, there can be no heat transfer. Instead, interactions between the systems occurs via changes to their external parameters. We define the mean energy change due to these interactions to be work.

$$W = \Delta_x \bar{E}$$

We can generalize these results a system with both mechanical and thermal interaction. In this case, we expect energy transfer both work and heat.

$$\Delta \bar{E} = W + Q$$

## 2.4 Quasistatic Processes

Consider a process in which the system remains arbitrarily close to equilibrium. In order to ensure these conditions we require the process to move sufficiently slowly. Recall that we can think of energy in a given state  $r$  as some function of the external parameters:

$$E_r = E(x_1, \dots, x_n)$$

For an infinitesimal change in the external parameters  $x_a \rightarrow x_a + dx_a$  we see that the energy change corresponds to

$$dE_r = \sum_i \frac{\partial E}{\partial x_i} dx_i$$

Work is therefore given by

$$dW_r = -dE_r = \sum_i X_{i,r} dx_i \quad X_{i,r} = -\frac{\partial E_r}{\partial x_i}$$

We refer to each of these  $X$  terms as the generalized force. If the external parameter is varied quasistatically then we have well-defined mean values for each of the corresponding generalized forces. Taking the appropriate average over all equilibrium states,

$$dW = \sum \bar{X}_i dx_i$$

## 2.5 Exact and Inexact Differentials

Exact differentials are characterized by the following:

$$dF = A(x, y)dx + B(x, y)dy \quad A = \frac{\partial F}{\partial x}, B = \frac{\partial F}{\partial y}$$

Exact differentials are path independent.

$$\Delta F = \int_i^f dF = \int_i^f A(x, y)dx + B(x, y)dy$$

In our definition for the energy differential, we see that  $dE$  is exact since it is the difference of a well defined quantity. On the other hand, work is an inexact differential since it is the process between going two states and is necessarily path dependent. Consequently,  $Q$  also depends on the path taken.

If the system is thermally isolated, we have that  $Q = 0$  and consequently  $dE = -dW$  and work is path independent. This follows analogously for situations in which  $dW = 0$ .

### 3 Statistical Thermodynamics

**Postulate 2** *If some constraints of an isolated system are removed, the parameters of the system tend to readjust themselves in a way such that  $\Omega(y_1, \dots, y_n)$  approaches a maximum*

A irreversible process is one in which reintroducing a constraint after removing it does not cause the system to return to its original state. Otherwise, the process is said to be reversible. If the number of accessible states stays the same after the removal of a constraint, we can consider the process to be reversible. If it increases, the process is irreversible.

#### 3.1 Entropy

Consider a composite system of 2 parts. The total energy of the system  $E$  can be broken down into components  $E_1$  and  $E_2$ . Technically, we require an interaction term, but for the purpose of this argument we can assume that the interaction term is inconsequential in the scale of each  $E$ .

$$E = E_1 + E_2$$

For a given energy  $E$ , we can describe our system solely in terms of  $E_1$  by expressing  $E_2 = E - E_1$ . Under this notation, we have a set of total accessible states  $\Omega(E_1)$ . The probability that our composite system has the first portion with energy  $E_1$  is then proportional to this value.

$$P(E_1) = C\Omega(E_1)$$

If the first system has energy  $E_1$  there are  $\Omega_1(E_1)$  states with equal probability available to the system. Consequently, there are  $\Omega_2(E - E_1)$  states available to the second system. In total, we see that the system has  $\Omega(E_1) = \Omega_1(E_1)\Omega_2(E - E_1)$  states accessible.

From our earlier discussion, we know that  $\Omega_1(E_1)$  is rapidly increasing with  $E_1$  and consequently  $\Omega_2(E - E_1)$  is rapidly decreasing with  $E_1$ . This behavior results in a sharp maximum for  $\Omega(E_1)$  and  $P(E_1)$ .

By introducing the quantity  $S = k \ln \Omega$  and the dimensionless parameter  $T$ ,  $kT = \frac{\partial S}{\partial E}$ , we can see that this maximum  $P(E_1)$  is obtained when  $S_1 + S_2$  is maximized. Given our definition of  $T$ , this equivalent to the statement that  $T_1 = T_2$ . In words, the maximum probability state is that which maximizes  $S$ , the entropy, which is equivalent to the state in which both systems have the same temperature.

#### 3.2 Temperature

The above discussion yields two observations. First, if two systems are separately in equilibrium and have the same parameter  $T$ , then when put in thermal contact, the systems will remain in equilibrium. Second, if two systems in separate equilibrium are characterized by different temperature values, then when placed in thermal contact, the systems will not remain in equilibrium.

The quantity  $kT$  can be thought of as an estimate of the mean energy per degree of freedom of the system.

### 3.3 Heat Reservoir

Consider the thermal interaction between two systems with a large size difference. The larger system acts as a heat reservoir with respect to the smaller system in that the temperature of the system does not change in response to heat transfer from the smaller object. Heat reservoirs are relative to the object they interact with. Consider a Taylor expansion the number of accessible states at energy  $E$  given a heat transfer of  $Q$  into the system:

$$\ln \Omega'(E + Q) = \ln \Omega(E) + \left( \frac{\partial \ln \Omega(E)}{\partial E} \right) Q + \frac{1}{2} \left( \frac{\partial^2 \ln \Omega(E)}{\partial E^2} \right) Q^2$$

With the heat reservoir assumption, we can assume that change in temperature is relatively small. Recalling our relationship between temperature and entropy, we can kill all higher order terms.

$$\ln \Omega'(E + Q) - \ln \Omega(E) = \frac{Q}{kT}$$

The resulting entropy change is simply  $\delta S = \frac{Q}{T}$

### 3.4 Quasistatic Process

Consider a quasistatic process in which a system is changed from  $E$  to  $E + \delta E$  and  $x_a$  to  $x_a + \delta x_a$ . The change in accessible states is given by:

$$d \ln \Omega = \frac{\partial \ln \Omega}{\partial E} dE + \sum \frac{\partial \ln \Omega}{\partial x_a} dx_a$$

We can equivalently write this as

$$dQ = TdS = dE + dW \quad dS = \frac{dQ}{T}$$

Notice that this implies that in an adiabatic quasistatic process, we have that  $S = 0$  regardless of external parameter changes. Since the number of accessible states does not change, this means that the process is reversible.

### 3.5 Entropy

Entropy is an exact differential despite heat not being one. Entropy also becomes exceedingly small as energy and temperature decrease.

### 3.6 Thermodynamic Laws

**0th Law of Thermodynamics:** If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other

**1st Law of Thermodynamics:**  $\Delta E = -W + Q$

**2nd Law of Thermodynamics:** In any process in which a thermally isolated system goes from one macrostate to another, entropy cannot decrease.

$$\Delta S \geq 0$$

If the system is not isolated undergoes a quasistatic process, then

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

This also implies the following relations:

$$\begin{aligned} dS &= \frac{dQ}{T} = \frac{1}{T} \left( dE + \sum X_a dx_a \right) && \text{Basic Relation} \\ dS &= \frac{\partial S}{\partial E} dE + \sum \frac{\partial S}{\partial x_a} dx_a && \text{S is exact} \\ \frac{1}{T} &= \frac{\partial S}{\partial E} && \frac{X_a}{T} = \frac{\partial S}{\partial x_a} \end{aligned}$$

Below are a series of equivalent statements to the 2nd Law of Thermodynamics:

- **Carnot's Theorem:** The basic relation holds for simple systems and in each infinitesimal quasistatic step  $dQ = TdS$
- **Absolute Temperature:** T is a temperature scale that abides by the 0th law of thermodynamics
- **Entropy:** S is entropy and it is the sum of its parts in a simple system
- **Claussius Inequality:**  $\Delta S_{TOT} \geq 0$  for any thermally isolated system
- In any infinitesimal process in a simple system,  $TdS \geq dQ$  and  $\sum J_i dx_i \leq dW$  (equality holds for quasistatic)

**3rd Law of Thermodynamics:** The entropy of a system has a limiting property that  $S \rightarrow 0$  as  $T \rightarrow 0$

## 4 Macroscopic Parameters and their measurement

### 4.1 Heat Capacity and Specific Heat

We define the heat capacity of a system as its temperature response to an infinitesimal heat transfer:

$$C_v = \left( \frac{\partial Q}{\partial T} \right)_X$$

To make this quantity independent of the amount of matter in the system, we can scale it by the moles present to find the specific heat of the system. This value is then comparable across systems and corrects for the size of the system. Notice that this value is dependent on the external parameters present. In a simple system, we can consider volume as our external parameter. Therefore, the macrostate can be defined by T and V. In this case, we have two possibilities: constant volume and constant pressure. Since at constant volume  $dQ = dE$  and at constant pressure  $dQ = dE + pdV$ , we see that for the same  $dQ$ , the constant pressure case results in a smaller change in internal energy. Therefore, it requires more heat to produce the same temperature change as its constant volume counterpart.

$$c_p > c_v$$

From the second law of thermodynamics, we have that  $dS = \frac{dQ}{T}$  in a quasistatic process. Substituting this into our heat capacity expression, we find

$$C_v = T \left( \frac{\partial S}{\partial T} \right)_X$$

If we further restrict our external parameters, we can write  $dQ = dE$

$$C_v = T \left( \frac{\partial S}{\partial T} \right)_X = \left( \frac{\partial E}{\partial T} \right)_X$$

If we consider a quasistatic path between two states, we can find the entropy difference by integrating  $\frac{dQ}{T}$

$$S_b - S_a = \int_a^b \frac{dQ}{T}$$

However, if we know the heat capacity, we can rewrite this expression as

$$S_b - S_a = \int_a^b \frac{dQ}{T} = \int_a^b \frac{C_v dT}{T} = C_v \ln \frac{T_b}{T_a}$$

Note that we implicitly assume that  $C_v$  is independent of T.

### 4.2 Extensive and Intensive Parameters

Extensive parameters get doubled if the size of the system is doubled, while intensive parameters remain the same.

## 5 Simple Applications of Macroscopic Thermodynamics

Recall from our earlier discussions the following equations:

$$\begin{aligned}dQ &= dE + dW && \text{First Law of Thermodynamics} \\TdS &= dE + pdV && \text{Second + First Laws of Thermodynamics}\end{aligned}$$

### 5.1 Ideal Gases

An ideal gas is dictated by the following equation:

$$pV = nRT$$

#### 5.1.1 Internal Energy

One would expect the energy of an ideal gas to be a function of volume and temperature,  $E = E(T, V)$ .

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

If we substitute in an expression for  $p$  into the basic relation provided by the 2nd law of thermodynamics, we find the following equation:

$$TdS = \frac{1}{T}dE + \frac{nR}{V}dV$$

We can now plug in our expression for the energy differential into the equation above:

$$TdS = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_T + \frac{nR}{V}\right]dV$$

We can now exploit the fact that  $dS$  is exact. By definition, we have

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left[\frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_T + \frac{nR}{V}\right]\end{aligned}$$

Now, by the symmetry of second derivatives, we require the cross derivatives to be equivalent. Evaluating the second derivatives results in  $\left(\frac{\partial E}{\partial V}\right)_T = 0$

Thus, energy of an ideal gas is solely dependent on temperature  $T$ .

#### 5.1.2 Specific Heat

Next, let's consider the specific heat of an ideal gas at constant volume ( $dV = 0 \rightarrow dQ = dE$ )

$$c_v = \frac{1}{v} \left(\frac{\partial Q}{\partial T}\right)_V = \frac{1}{v} \left(\frac{\partial E}{\partial T}\right)_V$$

As shown above, we know that  $E$  is only a function of  $T$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT$$

Putting the two together,

$$dE = v c_v dT$$

At constant pressure, we reintroduce the  $pdV$  term. From the ideal gas law, we see that change in volume corresponds to  $pdV = vEdT$ .



$$dQ = v c_v dT + v R dT$$

By definition,

$$c_p = \frac{1}{v} \left( \frac{\partial Q}{\partial T} \right)_p = c_v + R$$

We define the ratio between specific heats

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{R}{c_v}$$

If we apply microscopic calculations into the calculations, for a monoatomic ideal gas, we find the following:

$$\begin{aligned} E &= \frac{3}{2} v R T \\ c_v &= \frac{3}{2} R \\ c_p &= \frac{5}{2} R \end{aligned}$$

### 5.1.3 Adiabatic Expansion and Compression

Suppose a gas is allowed to expand isothermally. From the ideal gas law, we have that

$$pV = \text{constant}$$

However, under adiabatic expansion, we expect different results. In fact, we expect the gas to do work at the expense of energy. Since we have an adiabatic process, we know that  $dQ = 0$ .

$$0 = v c_v dT + p dV$$

We can use the ideal gas law to relate these differentials by considering  $p dV + V dp = v R dT$ . Solving for and plugging in  $dT$  into the equation above,

$$\begin{aligned} (c_v + R) p dV + c_v V dp &= 0 \\ \gamma \frac{dV}{V} + \frac{dp}{p} &= 0 \end{aligned}$$

$c_v$  is independent of temperature, so we can integrate the above expression and find

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

Alternatively, we also get the following equations:

$$V^{\gamma-1} T = \text{constant} \quad p^{\frac{1}{\gamma}} T = \text{constant}$$

### 5.1.4 Entropy

For a quasistatic process, we can substitute  $dQ = T dS$  into the earlier expression.

$$T dS = v c_v dT + \frac{v R T}{V} dV$$

We can simply integrate this expression to find the change in entropy between two states.

## 5.2 Maxwell's Relations

Beginning with the basic relation

$$dE = TdS - pdV$$

we can derive Maxwell's relations:

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

## 5.3 Free Expansion

Consider the free expansion of a gas in an adiabatic container. Since the expansion is without resistance  $dW = 0$  and since the process is adiabatic  $dQ = 0$ . Therefore, internal energy remains constant. For an ideal gas, since energy is only dependent on temperature, we know that  $E_1 = E_2$  so  $T_1 = T_2$ .

## 5.4 Heat Engines

A heat engine is a machine that can capture internal energy from a heat reservoir and produce macroscopic work. To make the machine feasible, we require the process to end up in the same macrostate in which it begins. The problem statement can also be phrased as extracting energy that is distributed across many degrees of freedom in a heat reservoir into a single degree of freedom in the external parameter of an external device.

Unfortunately an engine that does so with perfect efficiency, that is  $w = q$ , is impossible. According to the second law of thermodynamics, we require the total entropy change to increase in a cycle. Since we require the engine itself to return to its original macrostate, we know that its entropy remains the same as it was initially. As stated in the problem statement, the action of the heat engine does not increase the entropy of the outside device. However, the entropy change of the heat reservoir is given by  $-q/T$ . In an ideal heat engine we have  $w = -q$ , so we see that  $w/T \leq 0$ . This does not produce positive work! Therefore, we see that it is impossible to produce a perfect heat engine.

Heat engines can work if they are coupled with another heat reservoir in which entropy does increase. One way of doing so is to introduce a reservoir at  $T_2 < T_1$ . This new heat engine takes in  $q_1$  from the first heat reservoir to produce  $q_2$  to the second reservoir and some work  $w$ .

$$q_1 = w + q_2$$

The second law of thermodynamics is satisfied if

$$\Delta S = \frac{-q_1}{T_1} + \frac{q_2}{T_2} \geq 0$$

Combining these equations we can introduce  $\eta$  the efficiency of our heat engine.

$$\eta = \frac{w}{q_1} \leq \frac{T_1 - T_2}{T_1}$$

Equality is only realized when the process is quasistatic.

### 5.4.1 Carnot Engine

Carnot Engines are theoretical heat engines that operate quasistatically between two heat reservoirs. The cycle goes through 4 macrostates (a,b,c,d)

1.  $a \rightarrow b$ : Engine is thermally isolated and the external parameter is slowly tuned until the engine temperature reaches  $T_1$ .  $x_a \rightarrow x_b$   $T_2 \rightarrow T_1$
2.  $b \rightarrow c$ : Engine is put in thermal contact with reservoir at  $T_1$  and the external parameter is slowly tuned to  $x_c$  as temperature remains constant.  $x_b \rightarrow x_c$   $q_1$  into heat engine
3.  $c \rightarrow d$ : Engine is thermally isolated and the external parameter is slowly tuned until the engine temperature reaches  $T_2$ .  $x_c \rightarrow x_d$   $T_1 \rightarrow T_2$
4.  $d \rightarrow a$ : Engine is put in thermal contact with reservoir at  $T_2$  and the external parameter is slowly tuned to  $x_a$  as temperature remains constant.  $x_d \rightarrow x_a$   $q_2$  into heat reservoir

## 5.5 Refrigerators

Refrigerators take heat from a lower temperature reservoir and reject it into a higher temperature reservoir.

$$w + q_2 = q_1$$

Since the Carnot cycle runs quasistatically, we can reverse it and effectively create a refrigerator.

$$\Delta S = \frac{q_1}{T_1} + \frac{-q_2}{T_2} \geq 0$$

## 6 Basic Methods and Results of Statistical Mechanics

### 6.1 Ensembles Representative of Situations of Physical Interest

#### 6.1.1 Isolated System

The fundamental postulate of statistical mechanics postulates that any of the equilibrium states are equally probable. Therefore, for an state with energy in the range  $E \leq E_r \leq E + \delta E$ , we can define the probability of being in state  $r$  as

$$P_r = \begin{cases} C & E \leq E_r \leq E + \delta E \\ 0 & \text{else} \end{cases}$$

$C$  is chosen such that the total probability across all accessible states sums to 1. This distribution is known as the microcanonical ensemble.

### 6.2 System in Contact with Heat Reservoir

In this situation, instead of considering the energy of the system, we say that the energy of the system + reservoir is fixed.

$$E^0 = E' + E_r$$

If our system has an energy  $E_r$ , then the energy of the reservoir is given by  $E' = E^0 - E_r$ . Therefore, if the system has a single state  $r$  then the number of accessible states for the combined reservoir system is given by  $\Omega(E^0 - E_r)$ . The probability of being in state  $r$  is consequently given by:

$$P_r = C' \Omega'(E^0 - E_r)$$

Typically, the system is much smaller than the reservoir and  $E_r \ll E^0$ . You can therefore approximate the natural log as

$$\ln \Omega'(E^0 - E_r) = \ln \Omega'(E^0) - \frac{\partial \ln \Omega'}{\partial E'} E_r$$

We represent the first derivative term

$$\beta = \frac{\partial \ln \Omega'}{\partial E'}$$

Note that this term is constant and independent of  $E_r$ . This can be interpreted as the reservoir being so large that its temperature is unaffected by interactions with the system in question. The equations above simplify into:

$$\begin{aligned} \Omega'(E^0 - E_r) &= \Omega(E^0) e^{-\beta E_r} \\ P_r &= C e^{-\beta E_r} \end{aligned}$$

This exponential factor and associated distribution are known as the boltzmann factor and the canonical distribution respectively.

### 6.3 Simple Applications of the Canonical Distribution

#### Paramagnetism

Consider an object with  $N_0$  magnetic atoms with magnetic moment  $\mu$  in an external magnetic field  $H$ . We can approach this system by considering a single atom with either parallel or antiparallel spin in a heat reservoir consisting of the remaining atoms at temperature  $T$ . The magnetic energy corresponding to each of these states is given by  $\epsilon_+ = -\mu H$  and  $\epsilon_- = \mu H$ . The corresponding probabilities are

$$P_+ = C e^{B\mu H} \quad P_- = C e^{-B\mu H}$$

The higher energy state (-) corresponds to a lower probability and thus the mean magnetic moment points in the direction of  $H$ . The mean energy can be simply calculated:

$$\bar{\mu}_H = \mu \tanh \frac{\mu H}{kT}$$

#### Molecule in an Ideal Gas

Consider a monoatomic ideal gas in a box of volume  $V$  and absolute temperature  $T$ . Suppose that interactions between molecules are insignificant and that the energy of the system is simply the energy of each molecule. We can select a single molecule and consider the remainder of the gas as a heat reservoir at temperature  $T$ . The energy of this particle is purely kinetic so we can represent it as:

$$E = \frac{1}{2} \frac{p^2}{m}$$

We can capture the position and momentum of this particle by restricting the position of the particle between  $r$  and  $r + dr$  and the momentum between  $p$  and  $p + dp$ . Under the canonical distribution the probability of finding the particle in this phase space is proportional to the number of boxes in this phase space box.

$$P(r, p) d^3r d^3p \propto \left( \frac{d^3r d^3p}{h_0^3} \right) e^{-\beta p^2/2m}$$

Notice that the probability is independent of position. Physically, this can be interpreted as the lack of positional preference when no external forces are present. The probability of finding the particle in a certain momentum range is then given by summing up the probabilities over all possible  $r$  values. This calculation can be equivalently calculated for velocities to recover the maxwell distribution of molecular velocities.

$$P(v) d^3v \propto C e^{-\beta m v^2/2} d^3v$$

## Molecule in an Ideal Gas in the Presence of Gravity

Consider an analogous situation to above with the introduction of gravity.

$$E = \frac{1}{2} \frac{p^2}{m} + mgz$$

The probability of finding the particle at given position and momentum is no longer independent of the position.

$$P(r, p) d^3r d^3p \propto d^3r d^3p e^{-\beta p^2/2m} e^{-\beta mgz}$$

Since the exponential factors, we can simply integrate over the other variable and find the probability of finding a particle at given momentum or height.

$$\begin{aligned} P(p) d^3p &= C e^{-\beta p^2/2m} d^3p \\ P(z) d^3z &= C' e^{-\beta mgz} d^3z \end{aligned}$$

## 6.4 System with specified mean energy

Consider the situation of a system with a fixed number of particles  $N$  in a given volume  $V$ , but the only available information is the mean energy of the system:  $\bar{E}$ . Suppose  $E_r$  denotes the energy of a system in state  $r$ . If we have  $a$  such states,

$$\frac{1}{a} \sum_s a_s E_s = \bar{E}$$

We can equivalently write this as  $\sum a_s E_s = a\bar{E}$ . Notice that this statement is equivalent to having a total energy of  $a\bar{E}$  with an equal change of the system being in any state. If a system in the ensemble has energy  $E_r$  then the remainder of the system has energy  $a\bar{E} - E_r$ . This is an equivalent formulation to the canonical distribution of a heat reservoir where instead of the reservoir is now the other systems in the ensemble rather than an external reservoir.  $\beta = \frac{\partial \phi(E')}{\partial E'}$  does not have physical significance in this formulation. This beta can be calculated by the setting the mean energy of this ensemble distribution to  $\bar{E}$ .

$$\frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = \bar{E}$$

## 6.5 Calculation of Mean Values in a canonical ensemble

Consider the mean energy for the canonical distribution. By introducing a variable  $Z = \sum_r e^{-\beta E_r}$  known as the partition function, we can reexpress the mean energy as:

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

With the distribution of system over possible energies we can easily calculate statistical quantities:

$$\overline{\Delta E^2} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

Consider a system characterized by a single external parameter  $x$ . If we have a quasistatic change of this parameter by  $dx$  the energy of the system will respond by  $\Delta_x E_r = \frac{\partial E_r}{\partial x} dx$ . Work is correspondingly the change in mean energy of the states:

$$dW = \frac{\sum_r e^{-\beta E_r} \left(-\frac{\partial E_r}{\partial x} dx\right)}{\sum_r e^{-\beta E_r}}$$

With the partition function we can rewrite this as

$$dW = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} dx$$

In this formulation we can represent the mean generalized force as  $\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}$ . If our external parameter is  $V$  we can write our mean pressure as this generalized force.

## 6.6 Connection with Thermodynamics

Notice that we can represent all physically relevant quantities with the partition function. Let's consider an infinitesimal change in  $Z$  with respect to the parameters  $x$  and  $\beta$ :

$$d \ln Z = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta$$

If we plug in the relations derived above, we can connect the partition function to mean energy and work.

$$d \ln Z = \beta dW - \bar{E} d\beta$$

If we represent the  $d\beta$  term as a change in  $\bar{E}$  we can recover heat:

$$\begin{aligned} d \ln Z &= \beta dW - d(\bar{E}\beta) + \beta d\bar{E} \\ d(\ln Z + \beta\bar{E}) &= \beta(dW + d\bar{E}) = \beta dQ \end{aligned}$$

We see that this equality arises from the second law of thermodynamics. We can further define entropy using  $dS = \frac{dQ}{T}$

$$S = k(\ln Z + \beta\bar{E})$$

As temperature approaches 0 we see that the only appreciable terms in the partition function are those corresponding to the ground state energy.

$$Z \rightarrow \Omega_0 e^{-\beta E_0}$$

Mean energy simply approaches  $E_0$  and the entropy approaches  $k \ln \Omega_0$ .

If we consider two weakly interacting systems index by variables  $s$  and  $r$ , the partition function clearly factors.

$$Z^0 = \sum_{r,s} e^{-\beta E^0} = \sum_{r,s} e^{-\beta(E_r + E_s)} = \sum_r e^{-\beta E_r} \sum_s e^{-\beta E_s}$$

Consequently we see that both energy and entropy are additive according to their relations to the partition function.

We can now apply express basic thermodynamic quantities based on canonical probability by exploiting the partition function derivations.

$$\begin{aligned} P_r &= \frac{e^{-\beta E_r}}{Z} && \text{Canonical Probability} \\ \bar{E} &= \sum_r E_r P_r && \text{Mean Energy} \\ dE &= \sum_r (E_r dP_r + P_r dE_r) && \text{Quasistatic Change in Energy} \\ dW &= - \sum_r P_r dE_r && \text{Work} \\ dQ &= \sum_r E_r dP_r && \text{Heat} \\ S &= -k \sum_r P_r \ln P_r && \text{Entropy} \end{aligned}$$

## 6.7 Approximation Methods

## 6.8 Grand Canonical and Other Ensembles

The grand canonical distribution is concerned with systems with an indefinite number of particles. For example consider a system in contact with a reservoir of both particles and heat.

$$E^0 = E + E'$$

$$N^0 = N + N'$$

The total energy and number of particles is held constant across both the reservoir and the system. We can apply analogous reasoning as the canonical distribution and argue that if the system is in a defined state  $r$ , then the number of accessible states for the joint system is just the number of states accessible to the reservoir.

$$P_r(E_r, N_r) \propto \Omega'(E^0 - E_r, N^0 - N_r)$$

Using the same natural log expansion argument, we can write the grand canonical distribution

$$P_r \propto e^{\beta E_r - \alpha N_r} \quad \beta = \frac{\partial \ln \Omega}{\partial E'} \quad \beta = \frac{\partial \ln \Omega}{\partial N'}$$

The new term corresponds to the chemical potential of the system  $\mu = -kT\alpha$ .

## 6.9 Alternative Derivation of Canonical Distribution

# 7 Simple Applications of Statistical Mechanics

## 7.1 Partition Functions and their properties

If an arbitrary constant is added to the energy term, the partition function is modified by a  $e^{-\beta \epsilon_0}$  term. In terms of calculated thermodynamic quantities the mean energy is appropriately shifted while entropy and generalized forces are unchanged. The partition function also factors into simple parts if the system consists of distinct non-interacting parts.

We can also classically formalize the partition function by splitting our phase space into cells of volume  $h_0^f$ . The partition function is then the sum of cells abiding by the volume and energy conditions and then summing over all possible cells.

$$Z = \int e^{\beta E(q_1, \dots, q_f)} \frac{dq_1 \dots dq_f}{h_0^f}$$

## 7.2 Calculation of Thermodynamic Quantities

Consider a gas of  $N$  identical monoatomic gas particles with mass  $m$  in a volume  $V$ . The total energy of this gas is given by

$$E = \sum_{i=1}^N \frac{p_i^2}{2m} + U(r_1, \dots, r_N)$$

In a dilute gas we can set the interaction term to 0  $U \rightarrow 0$ . In the classical framework we can write our partition function as

$$Z^c = \int \exp \left[ -\frac{\beta}{2m} (p_1^2 + \dots + p_f^2) + U(r_1, \dots, r_f) \right] \frac{d^3 p_1 \dots d^3 p_f d^3 r_1 \dots d^3 r_f}{h_0^{3N}}$$

Evaluating the potential energy term is difficult, but when  $U = 0$ , the partition function can be written as

$$\ln Z^c = N \ln \zeta \quad \zeta = \frac{V}{h_0^3} \int_{-\infty}^{\infty} e^{-\beta \frac{p^2}{2m}} d^3 p$$

$\zeta$  represents the partition function of a single molecule. We can solve for  $\zeta = V \left( \frac{2\pi m}{h_0^2 \beta} \right)^{3/2}$ . Consequently, the partition function simplifies to

$$\ln Z^c = N \left( \ln V + \frac{3}{2} \ln \left( \frac{2\pi m}{h_0^2} \right) \right)$$

We can use this form to write our other quantities:

$$\bar{p} = \frac{N}{\beta V}$$

which recovers the ideal gas law!

$$\bar{E} = \frac{3}{2}kTN$$

$$C_v = \left( \frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3}{2}Nk$$

The molar heat capacity is consequently  $c_v = \frac{3}{2}R$ .

### 7.3 Gibbs Paradox

The classical formulation mischaracterizes the indistinguishability of particles. In fact, the above partition function does not yield the correctly additive entropy expression. We can account for indistinguishability of the particles by introducing a  $\frac{1}{N!}$  term in our partition function.

$$Z = \frac{Z^c}{N!} = \frac{\zeta^N}{N!}$$

Our expression for entropy then takes the form:

$$S = kN \left( \ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0 \right) \quad \sigma_0 = \frac{3}{2} \left( \frac{2\pi mk}{h_0^2} \right) + \frac{5}{2}$$

### 7.4 Validity of Classical Approximation

The classical approximation is valid under:

$$\left( \frac{V}{N} \right)^{1/3} \gg \frac{h}{\sqrt{3mkT}}$$

### 7.5 Equipartition Theorem

The energy of a system is a function of its coordinates and momentum. Often times the total energy can be split additively in terms of a quadratic function of momentum. The mean value of this term  $\bar{\epsilon}_i = \frac{1}{2}kT$ . This statement is only valid in classical statistical mechanics.

### 7.6 Simple Applications

#### 7.6.1 Mean Kinetic Energy of a Molecule in a Gas

The kinetic energy of a molecule in a gas with mass  $m$  and momentum  $p$  is given by:

$$K = \frac{1}{2}m(p_x^2 + p_y^2 + p_z^2)$$

Since there are 3 quadratic terms the mean equilibrium energy is given by  $\frac{3}{2}kT$ . The entire energy is simply  $\bar{E} = N \cdot \frac{3}{2}kT = \frac{3}{2}RT$ . Molar specific heat capacity is consequently  $c_v = \frac{3}{2}R$ .

#### 7.6.2 Brownian Motion

A macroscopic particle immersed in a liquid. The mean velocity of the particle in the  $x$  direction must vanish by symmetry. However, if we consider the a collection of particles, the equipartition theorem yields:

$$\overline{\frac{1}{2}mv_x^2} = \frac{1}{2}kT \quad \bar{v}_x = \frac{kT}{m}$$



### 7.6.3 Harmonic Oscillator

A 1-D oscillator in thermal equilibrium by a heat reservoir has its energy described by the equation:

$$E = \frac{1}{2}k_0x^2 + \frac{p^2}{2m}$$

Since each term is quadratic we can apply the equipartition theorem to each one and conclude that the average energy  $\bar{E} = \bar{K} + \bar{U} = kT$

Now let's consider the quantum mechanics approach. Energy of the system for each state  $n = 1, 2, 3, \dots$

$$E_n = (n + \frac{1}{2})\hbar\omega$$

We write our partition function as

$$Z = e^{-\frac{\beta}{2}\hbar\omega} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = e^{-\frac{\beta}{2}\hbar\omega} (1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots)$$

This is simply a geometric series so we can write the partition function as

$$Z = e^{-\frac{\beta}{2}\hbar\omega} \frac{1}{1 - e^{-\beta\hbar\omega}}$$

From the partition function we recover the mean energy:

$$\bar{E} = \hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

At high temperatures this expression recovers the classical result. However, at low temperatures it approaches the zero-point energy of the system.

## 7.7 Specific Heat of Solids

Consider a lattice of atoms with  $N_a$  atoms per mole. We can write the energy of lattice vibrations as

$$E = \sum_i^{3N_a} \left( \frac{p_i^2}{2m} + \frac{1}{2}k_iq_i^2 \right)$$

Since each term is quadratic and independent we can immediately apply the equipartition theorem and find  $\bar{E} = 3N_a kT$ . This is only true at sufficiently high temperatures. At low temperatures, we can add the assumption that each atom vibrates with the same angular frequency  $\omega$ . Under this model we just get  $3N_a$  quantum harmonic oscillators.

$$\bar{E} = 3N_a \hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

Under this model as  $T$  approaches 0 the specific heat of solids exponentially approaches 0.

## 7.8 Paramagnetism

## 7.9 Maxwell Velocity Distribution

Consider a molecule of mass  $m$  in a dilute gas. We can represent the center of mass and momentum of each particle as  $r$  and  $p$  respectively. Under the canonical distribution, the probability of finding the molecule in with center of mass and momentum in the ranges specified is given by

$$P_s(r, p) d^3r d^3p \propto e^{-\beta p^2/2m} e^{-\beta \epsilon_s^{int}} d^3r d^3p$$

To recover the probability of finding the particle in the specified range independent of internal state, we simply sum over all possible states. We can then drop the  $e^{-\beta \epsilon_s^{int}}$  term as it becomes a constant of proportionality. With this probability statement we can find the mean number of particles in the provided momentum and position range.

We can now introduce a function that returns the mean number of molecules in the provided position and velocity range.

$$f(r, v)d^3rd^3v = Ce^{-\beta mv^2/2}d^3rd^3v$$

If we integrate this expression over r and v we see that f is independent of r and thus returns the volume when integrated over position. The total integral over both r and v must return N, the total number of molecules.

$$CV \int_{-\infty}^{\infty} e^{\beta mv^2/2}d^3v = CV \left(\frac{2\pi}{\beta m}\right)^{3/2} = N$$

The constant of proportionality is thus  $C = \frac{N}{V} \left(\frac{2\pi}{\beta m}\right)^{3/2}$  We now have the distribution of velocities of particles.

$$f(r, v)d^3rd^3v = \frac{N}{V} \left(\frac{2\pi}{\beta m}\right)^{3/2} e^{-\beta mv^2/2}d^3rd^3v$$

## 7.10 Related Velocity Distributions and Mean Values

### 7.11 Number of molecules striking a surface

### 7.12 Effusion

### 7.13 Pressure and Momentum Transfer

## 8 Equilibrium between phases or Chemical Species

### 8.1 Isolated System

For a thermally isolated system, the stable equilibrium state is the state at which entropy is maximized.

### 8.2 System in contact with a reservoir at constant temperature

If a system whose external parameters are fixed is in thermal contact with a heat reservoir, the stable equilibrium condition is the state where helmholtz free energy is minimized.

### 8.3 System in contact with a reservoir at constant temperature and pressure

If a system is in contact with a reservoir at constant temperature and pressure and if its external parameters are fixed so that it can only do work on the pressure reservoir, then the stable equilibrium is the state where gibbs free energy is minimized.

### 8.4 Stability Conditions for Homogenous substance

## 9 Quantum Statistics of Ideal Gases

### 9.1 Identical Particles and Symmetry Requirements

Consider a gas of N identical particles in a container of volume V. Let  $Q_i$  denote the coordinates of the ith particle and  $s_i$  represent the possible quantum states for the ith particle. Therefore the entire state of the gas is given by  $s_1 \dots s_N$ . The corresponding wavefunction is given by  $\psi = \psi_{[s_1, \dots, s_N]}(Q_1, \dots, Q_N)$ .

#### Maxwell-Boltzmann Statistics

This model does not impose any symmetry requirements on the wavefunction. Each particle is distinguishable and can occupy any state. Quantum mechanical models on the otherhand do impose symmetry on the wavefunction. Physically, this implies that the state of the gas does not change if we swap two particles. Therefore, when we introducing counting arguments it is essentially that the particles are indistinguishable.

### Bose-Einstein Statistics

Bose-einstein statistics refers to the case where each particle has an integer total angular momentum. This requires that the wavefunction is symmetric. Particles that obey these statistics are known as bosons.

### Fermi-Dirac Statistics

The second case refers to particles with half-integer spins. These particles are referred to as fermions and require the wavefunction to be antisymmetric. Since the wavefunction must be antisymmetric we require the sign to change when swapping two particles. However, if the particles were in the same state  $s$ , then the only way antisymmetry is preserved is if the wavefunction vanishes. Therefore, fermions cannot occupy the same quantum state (Pauli-exclusion principle)

For example, consider a system of two particles across 3 different energy levels:

#### Maxwell-Boltzmann

0	$\epsilon$	$3 \epsilon$
AB		
	AB	
		AB
A	B	
A		B
B	A	
	A	B
	B	A
B		A

#### Bose-Einstein

Since the particles are indistinguishable, we have a total of 6 states.

0	$\epsilon$	$3 \epsilon$
AA		
	AA	
		AA
A	A	
A		A
	A	A

#### Fermi-Dirac

Since the particles are indistinguishable and cannot occupy the same state, we have a total of 3 states.

0	$\epsilon$	$3 \epsilon$
A	A	
A		A
	A	A

## 9.2 Formulation of the Statistical Problem

For a gas of identical particles in a volume  $V$  in equilibrium at a temperature  $T$  we define the following parameters:  $r$  is label of the possible states of a particle,  $\epsilon_r$  is the energy corresponding to the state  $r$ ,  $n_r$  is the number of particles in state  $r$ , and  $R$  is the state of the entire gas system. In this notation we can write the total energy of the gas as:

$$E_R = \sum_r n_r \epsilon_r$$

If we know the total number of particles in the gas we can set  $\sum_r n_r = N$ . Our partition function then takes the form

$$Z = \sum_R e^{-\beta(n_1 \epsilon_1 + \dots)}$$

The average number of particles in a state is then just

$$\bar{n}_s = \frac{\sum_R n_s e^{-\beta(n_1 \epsilon_1 + \dots)}}{\sum_R e^{-\beta(n_1 \epsilon_1 + \dots)}} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s}$$

The dispersion is similarly

$$\overline{(\Delta n_s)^2} = -\frac{1}{\beta} \frac{\partial \bar{n}_s}{\partial \epsilon_s}$$

How we sum over all states R is dependent on the statistical framework we use.

### Maxwell-Boltzmann

In this case summing over R refers to summing over all possible numbers of particles in each state over all values subject to the total  $\sum n_r = N$  restriction. We also consider each particle distinguishable so any permutation of particles are considered distinct.

### Bose-Einstein

This case is similar to maxwell-boltzmann statistics; however, now the particles are indistinguishable so we are only concerned with the number of particles in each state. Photon statistics refers to the special case in which the number of total particles is not constant.

### Fermi-Dirac

Since particles cannot occupy the same state we sum  $n_r = 0$  or  $1$  for each r subject to any particle constraint.

## 9.3 The Quantum Distribution Functions

When  $T = 0$  in the Bose-Einstein case we will find that all N particles will occupy the lowest energy state  $\epsilon_1$ . However, in the case of Fermi-Dirac statistics, the particles will occupy the N lowest energy levels which results in a considerably higher energy level than the BE counterpart.

### Photon Statistics

Photon statistics refers to BE statistics with an unrestricted number of particles. The average number of particles in each state is calculated as follows:

$$\begin{aligned} \bar{n}_s &= \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s}}{\sum_{n_s} e^{-\beta n_s \epsilon_s}} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln \left( \sum e^{-\beta n_s \epsilon_s} \right) \\ &= \frac{1}{e^{\beta \epsilon_s} - 1} \end{aligned}$$

The final form is referred to as the plank distribution.

### Fermi-Dirac Statistics

Now we return to a fixed number of particles N. Skipping some derivations, we find the resulting distribution of the form:

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1} \quad \alpha = \frac{\partial \ln Z}{\partial N}$$

$\alpha = \beta \mu$  so we can equivalently be write the fermi-dirac distribution using the chemical potential:

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$

## Bose-Einstein Statistics

The results for BE statistics are very similar to FD.

$$\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s} - 1} \quad \alpha = \frac{\partial \ln Z}{\partial N}$$

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}$$

## 9.4 Maxwell-Boltzmann Statistics

The partition function in the general case is

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

For  $N$  particles in split across  $n_1, n_2, \dots$  states we can count the number of states using combinatorics. The partition function can then be written as

$$\ln Z = N \ln \left( \sum_r e^{-\beta\epsilon_r} \right)$$

We can recover the maxwell-boltzmann distribution by differentiating with respect to the energy of the state:

$$\bar{n}_s = N \frac{e^{-\beta\epsilon_s}}{\sum_r e^{-\beta\epsilon_r}}$$

The dispersion takes the form:

$$\overline{(\Delta n_s)^2} = \bar{n}_s - \frac{\bar{n}_s^2}{N}$$

## 9.5 Photon Statistics

The partition function takes the form

$$\ln Z = - \sum_r \ln(1 - e^{-\beta\epsilon_r})$$

The corresponding plank distribution is

$$\bar{n}_s = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = \frac{1}{e^{-\beta\epsilon_s} - 1}$$

The associated dispersion is

$$\overline{(\Delta n_s)^2} = \bar{n}_s(1 + \bar{n}_s)$$

## 9.6 Bose-Einstien Statistics

Skipping derivations the partition function simplifies to

$$\ln Z = \alpha N - \sum_r \ln(1 - e^{-\alpha - \beta\epsilon_r})$$

The corresponding distribution is

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta\epsilon_s} - 1}$$

The associated dispersion is

$$\overline{(\Delta n_s)^2} = \bar{n}_s(1 + \bar{n}_s) \left(1 + \frac{1}{\beta} \frac{\partial \alpha}{\partial \epsilon_s}\right) \approx \bar{n}_s(1 + \bar{n}_s)$$

## 9.7 Fermi-Dirac Statistics

Skipping derivations the partition function simplifies to

$$\ln Z = \alpha N + \sum_r \ln(1 + e^{-\alpha - \beta \epsilon_r})$$

The corresponding distribution is

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1}$$

The associated dispersion is

$$\overline{(\Delta n_s)^2} = \bar{n}_s(1 - \bar{n}_s)\left(1 + \frac{1}{\beta} \frac{\partial \alpha}{\partial \epsilon_s}\right) \approx \bar{n}_s(1 - \bar{n}_s)$$

## 9.8 Quantum Statistics in the classical limit

In the classical limit, sufficiently low concentration or high temperature, both BE and FD statistics reduce to:

$$\bar{n}_r = e^{-\alpha - \beta \epsilon_r}$$

Solving for  $\alpha$  using the N particle constraint, we see that this statement is equivalent to the MB distribution.

## 9.9 Quantum States of a Single Particle

Consider a nonrelativistic particle of mass  $m$ , position  $\mathbf{r}$ , and momentum  $\mathbf{p}$ . If we apply boundary conditions and results from quantum mechanics, we find the following energy levels:

$$\epsilon = \frac{2\pi^2 \hbar^2}{m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

Where from boundary conditions we have that  $k_i = \frac{2\pi}{L_i} n_i$  for some integers  $n_i$ .

The number of translational states between  $k$  and  $k + dk$  is given by  $\rho d^3k = \frac{V}{2\pi^2} k^2 dk$

## 9.10 Evaluation of the Partition Function

Under this scheme we find that the partition function for a single particle is given by

$$\zeta = \frac{V}{h^3} (2\pi m k T)^{3/2}$$

These results are identical to the classical derivation with planks constant subbed into  $h_0$ .

## 9.11 Physical Implications of the quantum-mechanical enumeration of states

### Vapor Pressure of a Solid

At equilibrium  $\mu_1 = \mu_2$ , the chemical potential of the solid and the gas phases must be equal. Using the identity  $\mu = -kT \ln \frac{\zeta}{N}$  we can solve for the chemical potential of the vapor phase.

$$\mu_1 = -kT \ln \left( (2\pi m k T)^{3/2} \right)$$

For the solid, we calculate the chemical potential as follows:

$$\mu_2 = \left( \frac{\partial F}{\partial N_2} \right)_{V_2, T} = -kT \left( \frac{\partial \ln Z}{\partial N_2} \right)_{V_2, T}$$

We can solve for the partition function of the solid by considering the mean energy expression.

$$\bar{E}(T) = kT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_V$$

We can integrate this expression to give:

$$\ln Z(T) = \int_{T_0}^T \frac{\bar{E}(T)}{kT^2} dT + \ln Z(T_0)$$

Writing the mean energy as a function of specific heat and latent heat of vaporization and plugging in the  $T_0 = 0$  limit for the partition function,

$$\ln Z(T) = \frac{N_2 \eta}{kT} + N_2 \int_0^T \frac{dT}{kT^2} \int_0^T c(T) dT$$

The chemical potential is thus

$$\mu_2(T) = -\eta - T \int_0^T \frac{dT}{T^2} \int_0^T c(T) dT$$

We can then solve for pressure by using the ideal gas law  $p_1 V_1 = N_1 kT$

## 9.12 Partition Functions of Polyatomic Molecules

## 9.13 Electromagnetic Radiation in thermal equilibrium inside an enclosure

Consider electromagnetic radiation in thermal equilibrium at temperature  $T$  in an enclosure of volume  $V$ . The electric field of the collection of photons must obey the wave equation.

$$\nabla^2 \mathcal{E} = \frac{1}{c^2} \frac{\partial^2 \mathcal{E}}{\partial t^2}$$

This admits solutions of planewaves in the form  $\mathcal{E} = \mathcal{E}_0 e^{i\omega t}$  where  $k = \frac{\omega}{c}$ . We can describe the relativistic energy and momentum of a photon using  $\epsilon = \hbar\omega$  and  $p = \hbar k$ . Next, let's consider the mean number of photons in a certain polarization direction with wavenumber between  $k$  and  $k + dk$

$$f(k) d^3 k = \frac{1}{e^{\beta \hbar \omega} - 1} \frac{d^3 k}{(2\pi)^3}$$

Now, we can consider the mean energy density of system by summing the above expression for both polarization directions and angular frequency values in the specified  $[\omega, \omega + d\omega]$  band

$$\bar{u}(\omega, T) d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\beta \hbar \omega} - 1}$$

If we introduce  $\eta = \frac{\hbar\omega}{kT}$  we can write this in the more familiar

$$\bar{u}(\omega, T) d\omega = \frac{h}{\pi^2 c^3} \left( \frac{kT}{h} \right)^4 \frac{\eta^3 d\eta}{e^\eta - 1}$$

Wein's displacement law follows immediately (for the frequency of maximum energy density at a given  $T$ ):

$$\frac{\bar{\omega}_1}{T_1} = \frac{\bar{\omega}_2}{T_2}$$

The mean total energy is given by integrating over all angular frequencies (Stefan-Boltzmann Law):

$$u_0(T) = \frac{\pi^2}{15} \frac{(kT)^4}{(ch)^3}$$

## Radiation Pressure

The mean pressure exerted by the enclosed photons is given by

$$\bar{p} = \sum_s \bar{n}_s \left( -\frac{\partial \epsilon_s}{\partial V} \right)$$

Using the expansion  $\epsilon_s = \hbar c \frac{2\pi}{L} (N_x^2 + n_y^2 + n_z^2)^{1/2}$ , we find that  $\frac{\partial \epsilon_s}{\partial V} = -\frac{1}{3} \frac{\epsilon_s}{V}$ . Radiation pressure is thus related to mean energy density.

$$\bar{p} = \sum_s \bar{n}_s \frac{1}{3} \frac{\epsilon_s}{V} = \frac{1}{3V} \bar{E} = \frac{1}{3} \bar{u}_0$$

### 9.14 Nature of Radiation inside arbitrary enclosure

### 9.15 Radiation emitted by a body at temperature T

A good emitter of radiation is a good absorber of radiation and vice versa. Glossing over the derivations,

$$P(\omega)d\omega = \alpha(\omega) \left[ \frac{1}{4} c \bar{u} \omega d\omega \right] = \alpha(\omega) \frac{\hbar}{4\pi^2 c^2} \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}$$

by integrating over all frequencies we can find the total power (Stefan-Boltzmann Law):

$$P^0 = \alpha(\sigma T)^4 \quad \sigma = \frac{\pi^2}{60} \frac{k^4}{c^2 \hbar^3}$$

### 9.16 Consequences of Fermi-Dirac Distribution

Consider the Fermi-function:

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

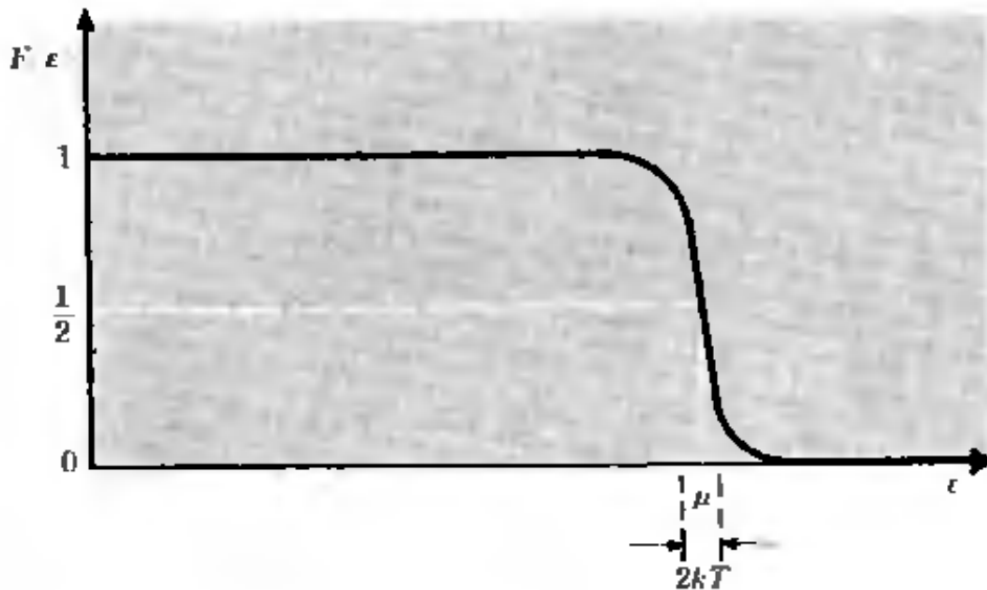


Figure 1: Fermi Function

We see that the transition region is on the order  $kT$ . As  $T$  approaches 0 the fermi function becomes a step function. The fermi energy of a gas at  $T = 0$  corresponds to the energy of the particles occupying the lowest  $k_F$  states. The fermi sphere thus has a radius  $\frac{V}{(2\pi)^3} (\frac{4}{3} \pi k_F^2)$ . Since each electron can have two spin states there are a total of  $2 \frac{V}{(2\pi)^3} (\frac{4}{3} \pi k_F^3)$  states occupied.



$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

Energy is then given by

$$\mu_0 = \frac{p_F^2}{2m} = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

## 10 Sections Skipped

- 1-5 Probability Distribution for large N
- 1-6 Gaussian Probability Distribution
- General Discussion of Random Walk
- 2-5 Behavior of density of states
- 3-7 Sharpness of probability distribution
- 3-8 Dependence of the density of states on the external parameters
- 4-6 Consequences of absolute definition of entropy
- 5-5 Derivations of General Relations
- 5-7 Specific Heats
- 5-8 Entropy and Internal Energy
- 5-10 Joule Thompson Process
- 6-8 Approximation Methods
- 6-10 Alternative Derivation of Canonical Distribution
- 7-4 Proof of Equipartition Theorem
- 7-8 Paramagnetism
- 7-10 Related Velocity Distributions and Mean Values
- 7-11 Number of molecules striking a surface
- 7-12 Effusion
- 7-13 Pressure and Momentum Transfer
- 8: Equilibrium between phases or Chemical Species
- 9-12 Partition Functions of Polyatomic Molecules
- 9-14 Nature of Radiation inside arbitrary enclosure
- 9-16 Heat Capacity of Electrons
- 9-17 Quantitative Calculation of Electronic Specific Heat