



Class Note for Physics 406

Thermodynamics and Statistical Mechanics

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Chapter 1

Thermodynamics

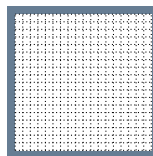
1.1 Basic concepts of thermodynamics

1.1.1 Thermodynamic System

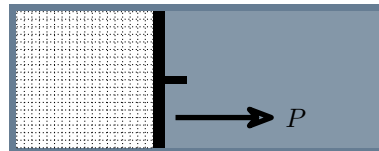
Definition 1.1.1 We define a **thermodynamic system** as a portion of the universe that we select for investigation.

Below are some examples of a thermodynamic system.

1. Gas in a *rigid, thermally insulating*¹ container.



2. Fluid in a *metal* cylinder with a *tight-fitting metal piston*.



Now, consider a more general system with a boundary, we want to know what can this system exchange with its surroundings.

	No	Yes
Mechanical Work	Rigid	Soft / Deformable / Movable
Heat	Thermally Insulating / "adiabatic"	Thermally Conducting
Particles (Matter)	Closed	Open / Permeable

Now, consider the example of atmosphere of the earth:

1. What is the content of the system? - Gas particles of the atmosphere, possibly birds, planes, etc.
2. What is the surrounding? - Earth, matters in space
3. How should we describe this boundary? - The boundaries are the surface of the Earth and the open outer boundary. It exchange work mechanical work (volcano for example), it exchange heat with the radiation of the sun, and it exchanges particles with the outer space (solar winds) as well as the earth surface (rains and snow).

¹Think: why are we using these extra adjectives?

Conclusion: In real world, there are no 100% rigid, 100% adiabatic, or 100% closed boundaries. However, depending on the problem we want to study, we can approximate the boundary to be of any properties above. It is important to know which approximation is important in thermodynamics.

1.1.2 Thermodynamic variables

Thermodynamic variables are macroscopic variables that describe the exchange of work of the system. For example, P, V, B, M .

Intensive Variables	P (Pressure)	B (Magnetic induction)	T (Temperature)	μ (Chemical Potential)
Extensive Variables	V (Volume)	M (Dipole moment)	S (Entropy)	N (# of particles)

Intensive variables describes the local intensity; **Extensive variables** describes the system size. The reason we pair the variables is that each pair contributes to a type of energy change in the system. We call the pairs *conjugate pairs*. For example, $[P] \cdot [V] = [B] \cdot [\mu] = [E]$. The conjugate pairs are defined through Legendre transforms.

1.1.3 Thermodynamic equilibrium

Definition 1.1.2 (Thermodynamic equilibrium) *Empirically, in the absence of any changes of external conditions, after some time, a system will reach a state in which NO macroscopic variables continue to change. The time required for the system to reach equilibrium is called the relaxation time.*

Now consider **microscopic variables**. They describe individual particles in the system. They may still change even the system has reached thermodynamic equilibrium.

The process to reach thermodynamic equilibrium during the relaxation time is irreversible. To reverse the process, we need to supply the system initial condition in forms of external energy.

1.1.4 Thermal equilibrium

Definition 1.1.3 *If systems A, B are in thermal contact and are both in thermodynamic equilibrium. We claim that the systems A and B are in **thermal equilibrium** with one another.*

1.2 The Zeroth and First Law of Thermodynamics

1.2.1 Useful mathematical identities

Theorem 1.2.1 *If $F(x, y, z) = 0$ then*

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1 \quad (\text{reciporcity theorem})$$

$$\left. \frac{\partial z}{\partial x} \right|_y = \left(\left. \frac{\partial x}{\partial z} \right|_y \right)^{-1} \quad (\text{reciporcal theorem})$$

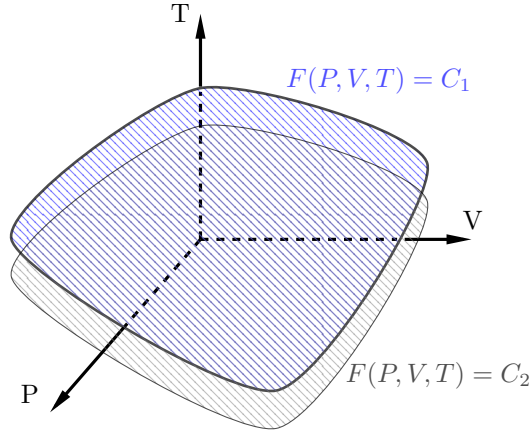
Note here $F(x, y, z) = 0$ defines a surface. The two theorems above will be proven in homework.

An example in thermodynamics is $F(P, V, T) = 0$:

$$PV = nRT \quad (\text{Ideal Gas Equation})$$

$$\left(PV + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad (\text{Van der Waals Equation})$$

We need the system to be in equilibrium for the equations of states to hold. This is because when the system is not in equilibrium, the macroscopic variables are not homogeneous, therefore, we are unable to select a variable value that represent the system uniquely.



Theorem 1.2.2 (*Symmetry of second partial derivative*) If $x = x(y, z)$, then

$$\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y}$$

$$\left. \frac{\partial}{\partial y} \right|_z \left. \frac{\partial x}{\partial z} \right|_y = \left. \frac{\partial}{\partial z} \right|_y \left. \frac{\partial x}{\partial y} \right|_z$$

Theorem 1.2.3 (Exact differential) If $x = x(y, z)$, then $dx = \partial_y x dy + \partial_z x dz$. Integration over exact differentials are independent of paths.

1.2.2 Zeroth law of thermodynamics

Fundamental questions in thermodynamics:

1. What quantifies hot and cold?
2. What is the fundamental relation between heat and work?

Theorem 1.2.4 (Zeroth law) If 2 systems are in separately in thermal equilibrium with a third, they must be in thermal equilibrium with one another.

Suppose there are three thermodynamic systems A, B, C , the first law says suppose that the

The zeroth law says that the thermal equilibrium is a transitive relation. It is a necessary condition for us to define temperature as a real number.

However, it is not sufficient: suppose we have multiple systems, $\mathbf{s}_1, \dots, \mathbf{s}_9$, suppose that the systems with s_i satisfying $i \equiv 0(\text{mod}3)$, $i \equiv 1(\text{mod}3)$, and $i \equiv 2(\text{mod}3)$ are in thermal equilibrium respectively. This gives $\phi(\mathbf{s}_1) = \phi(\mathbf{s}_4) = \phi(\mathbf{s}_7) = \Phi_1$, $\phi(\mathbf{s}_2) = \phi(\mathbf{s}_5) = \phi(\mathbf{s}_8) = \Phi_2$, $\phi(\mathbf{s}_3) = \phi(\mathbf{s}_6) = \phi(\mathbf{s}_9) = \Phi_3$. However, we are unable to know the temperature or hotness relation between systems in different groups, i.e., the relation between Φ_1, Φ_2 and Φ_3 . We will use second law to obtain the sufficiency.

1.2.3 Equation of State

Definition 1.2.1 An **equation of state** is an equation that describes variables in thermodynamic equilibrium. It has the form of:

$$f(\mathbf{S}, T) = 0,$$

where \mathbf{S} is the state of the system.

Definition 1.2.2 Quasi-static processes are thermodynamics processes that are infinitely slow so that at any instance the system is at thermodynamic equilibrium.

The curve of the quasi-static process is on that plane $f(\mathbf{S}, T) = 0$ that the process started on. It is therefore a reversible process.

1.2.4 First Law of Thermodynamics

Theorem 1.2.5 (First law of thermodynamics) *The increase of internal energy of a system is equal to the increase of heat plus work done to the system.*

$$\Delta U = \Delta Q + \Delta W \quad \Rightarrow \quad dU = dQ + dW$$

The notation indicates the differential is path independent. The differential of work can be expressed with conjugate pairs of variables:

$$dW = \sum_i X_i dx_i,$$

in which X_i are the intensive variables and x_i are the extensive variables.

Example 1.2.1 *Suppose a gas pushes a piston of cross section A by a distance dl , the work done to the system by the hydrostatic pressure is given by:*

$$dW = -pA \, dl = -p \, dV$$

Note that conventionally, we set the work to be positive when it is done to the system. Since in this example, $p dV$ actually describes the work done by the system to the environment, we therefore make it negative.

Example 1.2.2 (Joule Heating) *Suppose a resistor R is immersed in water with voltage V . The work done by the system is given by:*

$$\Delta W = \frac{V^2}{R} \Delta T = V \Delta Q$$

Note in this example, there is no negative sign.

Example 1.2.3 *Suppose a rubber is pulled longer with a constant force f over a small distance Δl , the work is given by:*

$$\Delta W = f \Delta l$$

We see that a generalized form of work done to a thermodynamic system can be express as:

$$\Delta W = \mathbf{X} \cdot \mathbf{x} = \sum_i X_i \Delta x_i$$

1.3 Ideal Gases and Their Processes

1.3.1 Heat Capacity

Joule's experiment: Joule tried many ways to do work on a system, and increase its temperature. He discover that to his experimental precision, the work needed to increase the temperature of a given system by certain amount is the same and independent of the type of work. (resistor, heating, friction, ...)

Definition 1.3.1 *The general definition of heat capacity C is:*

$$\begin{aligned} C &= \lim_{\Delta T \rightarrow 0, path} \frac{\Delta Q}{\Delta T} \\ &= \left. \frac{\partial Q}{\partial T} \right|_P \quad \text{or} \quad \left. \frac{\partial Q}{\partial T} \right|_V \end{aligned}$$

It states the heat required for a system to increase it temperature by a unit amount.

Note: The expression is path dependent and cannot be simply expressed as $C = \frac{dQ}{dT}$.

From the heat capacity C , we are able to define the specific heat c :

$$c = \frac{C}{m},$$

where C is the heat capacity of the system and m is the mass of the system. Specific heat is an intrinsic property of the material the system consists.

Question: For a gas system, which is greater C_P or C_V ?

Consider the differential form of the first law of thermodynamics:

$$dU = \bar{d}Q + \bar{d}W$$

The bar on the d indicates the differential is path dependent. However, with fixed volume:

$$dU = dQ - PdV \Rightarrow C_V = \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V + P \left. \frac{\partial V}{\partial T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V$$

We are unable to cancel the dV/dT term when we are moving along the path of constant pressure, so we obtain:

$$C_P = \left. \frac{\partial Q}{\partial T} \right|_P = \left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P$$

We define **Enthalpy** as:

$$H = U + PV$$

Consider the differential form of enthalpy:

$$dH = d(U + PV) = dU + PdV + VdP$$

Rewrite $\bar{d}Q$ in dH :

$$\bar{d}Q = dH - VdP$$

With enthalpy, we can rewrite C_P and C_V :

$$C_P = \left. \frac{\partial H}{\partial T} \right|_P$$

$$C_V = \left. \frac{\partial H}{\partial T} \right|_V - V \left. \frac{\partial P}{\partial T} \right|_V$$

1.3.2 Ideal Gas

Definition 1.3.2 *Ideal gas is a dilute gas of molecules that only has kinetic energy, indicating no interaction between particles. We always consider ideal gas in the classical limit.*

In thermodynamics, ideal gas is defined with 2 assumptions:

1. *Boyle's Law (EOS): $PV = nRT$;*
2. *Joule's Law: internal energy U is only a function of T .*

Neglecting the potential energy leads to Joule's Law, as T is only dependent on the kinetic energy. These laws are not obeyed strictly by any real gas. A more general way of Boyle's law expresses the accurate isothermal measurement of PV is:

$$PV = A + BP + CP^2 + DP^3 + \dots$$

This expression is known as a Virial expansion and the coefficients are known as Virial coefficients. Boyle's law in the definition provides a good approximation for real gases at *low pressure*.

Microscopic picture of an ideal gas is a group of *free, non-interacting* particles in the *classical* regime.

“Free” indicates the particles have a flat potential; “non-interacting” indicates there is only kinetic energy among the particles; “classical” is the opposite to “quantum”, we talk about atoms and molecules more but in the quantum regime, we talk about bosons and fermions.

Question: what are C_V and C_P for ideal gases?

We choose (T, V) as independent variables, by Joule’s law we have that $\frac{\partial U}{\partial T}|_T = 0$. Therefore, we have:

$$U = \int C_V dT + U_0 \quad \Rightarrow \quad C_V = \frac{\partial U}{\partial T}$$

The term $P \frac{\partial V}{\partial T}|_P = nR$. Therefore, $C_P = \frac{\partial H}{\partial T}|_P = C_V + nR$. Also, $P \frac{\partial U}{\partial T}|_P = P \frac{\partial U}{\partial T}|_V$ for ideal gases. Define $\gamma = \frac{C_P}{C_V}$, we have:

$$C_V = \frac{nR}{\gamma - 1}, \quad C_P = \frac{\gamma nR}{\gamma - 1}$$

1.3.3 Quasistatic Process of ideal gas

Quasi-static indicates that the processes is reversible and never out of equilibrium. Therefore, quasistatic processes of an ideal gas follows curves on the surface defined by their equation of state. There are some frequently used examples:

1. Isothermal Process, $dT = 0$. In this process: $PV = \text{Const}$.
2. Adiabatic Process, $dQ = 0$.

With the first law, we have $dU = dQ - pdV$. Note that $dU = C_V dT$ and $dQ = 0$. We have:

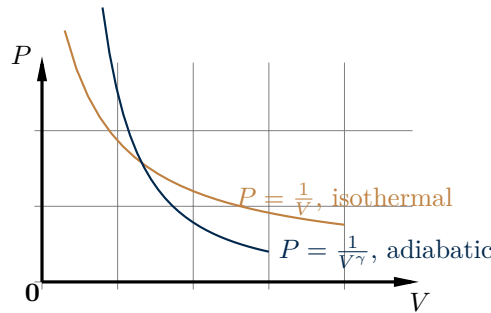
$$dT = -\frac{P}{C_V} dV$$

Substitute in the equation of state and we obtain:

$$PdV + VdP = nRdT \quad \Rightarrow \quad \left(1 + \frac{nR}{C_V}\right) PdV + VdP = 0$$

Note the coefficient is γ . Solve the differential equation we obtain

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



Example 1.3.1 (Irreversible adiabatic expansion) Consider a box half filled with some atomic gas. When the partition that separates the space is removed, the gas occupies all space of the box.

In the example, the initial and final states are both in thermal equilibrium. We therefore have the EOS at initial and final states:

$$P_i V_i = nRT_i, \quad P_f V_f = nRT_f$$

However, between the two states, the system go through non-equilibrium states as it expands. Note since the expansion is adiabatic, $\Delta Q = 0$. There is no volume change in the box, so $\Delta W = 0$. The internal energy is therefore the same. Since U is only dependent on T , $T_i = T_f$. We still have:

$$P_i V_i = P_f V_f = nRT$$

1.4 Heat Engines and the Second Law

1.4.1 Comparison between reversible and irreversible processes

From last lecture, we want to compare the differences between reversible and irreversible expansion.

Isothermal reversible expansion process happens at constant T . The work done in the process is given by:

$$\begin{aligned}\Delta W &= - \int_{V_i}^{V_f} P \, dV \\ &= - \int_{V_i}^{V_f} \frac{nRT}{V} \, dV = -nRT \ln \left(\frac{V_f}{V_i} \right) < 0\end{aligned}$$

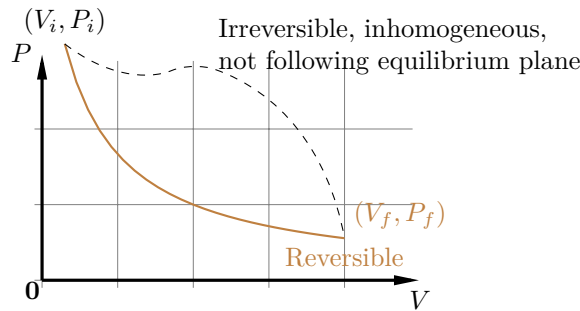
$\Delta Q = -\Delta W = nRT \ln(V_f/V_i) > 0$, there is a conversion from heat to work; for *adiabatic irreversible* process (free expansion), $\Delta Q = -\Delta W = 0$, there is no heat-to-work conversion.

Now, consider the case of *irreversible adiabatic expansion*, more specifically, free expansion in our case. Suppose there is an insulated container separated into two parts by a plate. One side is filled with gas of pressure P_i , volume V_i while the other side is vacuum. Now, we remove the barrier. The process that the gas permeates over the box is an adiabatic expansion. Since the gas goes through non-equilibrium states until it reaches expansion, the process is irreversible.

During the process, we have:

$$\Delta Q = 0 \text{ (adiabatic); } \Delta W = 0 \text{ (no work is done since the otherside is vacuum, } P = 0)$$

Therefore, the total change of internal energy is 0. Since the gas is ideal, by Joule's Law, the temperature of the final state satisfies $T_f = T_i$. We notice that the both the initial and final states satisfies the relation $PV = nRT$. However, this is not a reversible process as its path does not follow the equilibrium surface.

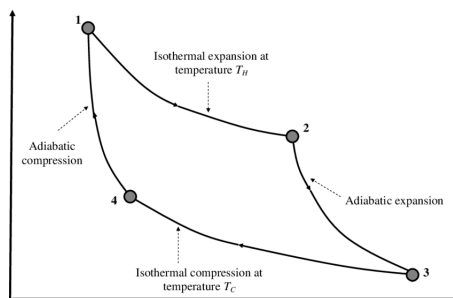


1.4.2 Heat Engine

Heat engines are devices that convert heat to work. Now, we start the discussion on the second law, which answers the following questions:

1. Why some processes are irreversible?
2. What is the efficiency of engine that transfer heat to work?

One simple example of heat engines is the *Carnot Engine*, which follows the *Carnot Cycle*. Consider the process of Carnot cycle of ideal gases:



Consider the isothermal expansion process $1 \rightarrow 2$, the work done to the system is given by:

$$\Delta_{12} = - \int_{V_1}^{V_2} P dV = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

Since this process is isothermal, temperature stays the same during the process, and the internal energy stays the same. The heat transferred to the system is given by:

$$\Delta Q_{12} = -\Delta W_{12} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

The adiabatic expansion process $2 \rightarrow 3$ has no heat exchange, and the internal energy change is equal to the work done to the system ($\Delta U_{23} = \Delta W_{23}$). We will solve the work done in this adiabatic process in homework.

The isothermal compression process $3 \rightarrow 4$ is similar to the isothermal expansion of $1 \rightarrow 2$:

$$\Delta Q_{34} = nRT_2 \ln \left(\frac{V_4}{V_3} \right), \quad \Delta W_{34} = -nRT_2 \ln \left(\frac{V_4}{V_3} \right)$$

The adiabatic compression $4 \rightarrow 1$ is similar to the $2 \rightarrow 3$ process. In this case, the surrounding does work to the system and the system is pushed back to its original position.

How do we know the efficiency of this Carnot Engine?

1. Net work the system exports: The area enclosed by the cycle;
2. Heat absorbed from the high temperature side: ΔQ_{12}

1.4.3 Efficiency of the Carnot Engine

Definition 1.4.1 *Efficiency of a heat engine is defined to be:*

$$\eta = \frac{|\Delta W|}{Q_H} = \frac{|\Delta W|}{Q_{12}} = \frac{\text{Work output}}{\text{Heat intake at hot reservoir}}$$

We first calculate the total heat absorbed done in the Carnot Cycle:

$$\Delta Q = \Delta Q_{12} + \Delta Q_{34} = nRT_1 \ln \frac{V_2}{V_1} + nRT_2 \ln \frac{V_4}{V_3}$$

There is no heat transfer from process $2 \rightarrow 3$ and $4 \rightarrow 1$ as they are adiabatic. Since the engine goes through a cyclic process, the total internal energy is the same at the start and end of a cycle. The total work done in the process is therefore:

$$\Delta W = \Delta U - \Delta Q = -nRT_1 \ln \frac{V_2}{V_1} - nRT_2 \ln \frac{V_4}{V_3}$$

We want to simplify this expression. Since $2 \rightarrow 3$ and $4 \rightarrow 1$ are adiabatic, we have the relations:

$$P_2 V_2^\gamma = P_3 V_3^\gamma, \quad P_1 V_1^\gamma = P_4 V_4^\gamma$$

Substitute the relations above into the isothermal EOS:

$$\frac{nRT_1}{V_2} V_2^\gamma = \frac{nRT_2}{V_3} V_3^\gamma \quad \Rightarrow \quad T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

Switching V_1 to V_2 and V_3 to V_4 , we obtain a similar relation, from which we get:

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

We therefore obtain the relation:

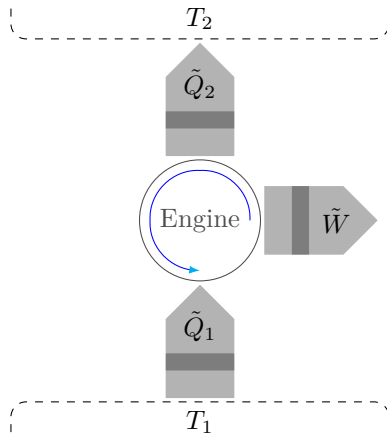
$$\Delta W = -nR(T_1 - T_2) \ln \frac{V_2}{V_1}$$

We have calculated ΔQ_{12} in the previous subsection. The efficiency is therefore given by:

$$\eta = \frac{\tilde{W}}{\tilde{Q}_1} = \frac{-\Delta W}{\Delta Q_{12}} = \frac{T_1 - T_2}{T_1}$$

We observe that for ideal gas Carnot cycles, the efficiency is independent of the type or amount of ideal gas.

We also introduce the abstract diagram of a generic heat engine as well as the historical notations.



Historically, the notation is:

$$\tilde{Q}_1 = \Delta Q_{12}$$

$$\tilde{Q}_2 = -\Delta Q_{34}$$

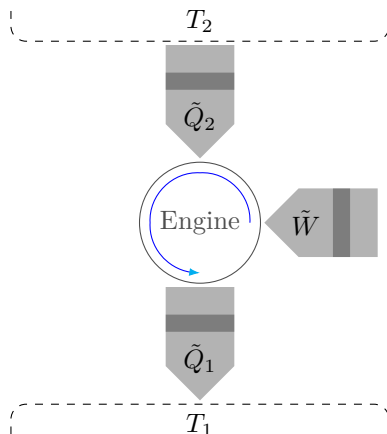
$$\tilde{W} = \tilde{Q}_1 - \tilde{Q}_2 = -\Delta W$$

From this point of class, we will use the historical notation.

1.5 The Second Law of Thermodynamics

1.5.1 Running the engines backwards

We want to investigate the effect of running heat engine backwards. Still, we need to suppose the engine we are interested in is a Carnot engine, or at least an engine that goes through reversible cyclic processes. Otherwise, we wouldn't be able to reverse the engine in an ideal way.



We obtain *refrigerator* and *heat pump* by running the engine backwards. We apply work to the reversed pump and it transfer heat from the colder sink to the hotter sink. For the refrigerator, we want the cooler side to be cooler whereas in the heat pump case we want the hot side to be hotter. The efficiency of a fridge and a heat pump is respectively given by:

$$\eta_{\text{fridge}} = \frac{\tilde{Q}_2}{\tilde{W}} \xrightarrow{\text{Reversible}} \frac{T_2}{T_1 - T_2}$$

$$\eta_{\text{pump}} = \frac{\tilde{Q}_1}{\tilde{W}} \xrightarrow{\text{Reversible}} \frac{T_1}{T_1 - T_2}$$

A key to deriving the reversible efficiency is to recall that $\frac{\tilde{Q}_1}{\tilde{Q}_2} = \frac{T_1}{T_2}$.

For engines that involve irreversible processes, we can run it backwards, but in a lower efficiency than the reversible cases. The statement “running an engine backwards” does not indicate the engine is going through all reversible processes.

1.5.2 Second Law of Thermodynamics

In this subsection, we will rigorously define **Temperature** from the second law of thermodynamics.

The second law of thermodynamics has two statements, which are equivalent:

1. **Kelvin statement:** No process is possible in which the sole result is the complete conversion of heat into work.
2. **Clausius statement:** No process is possible in which the sole result is the transfer of heat from a colder to a hotter body.

Note: Kelvin stated that the efficiency of any heat engine (not only Carnot) must be strictly less than 1, a portion of heat is converted to work while the other portion is released. Clausius' statement defined a direction of spontaneous heat transfer, which is useful in defining thermodynamic temperature.

Now, we want to prove the two relations above equivalent, that is, showing that when either one of the statement fail to stand, the other one fail automatically.

proof.

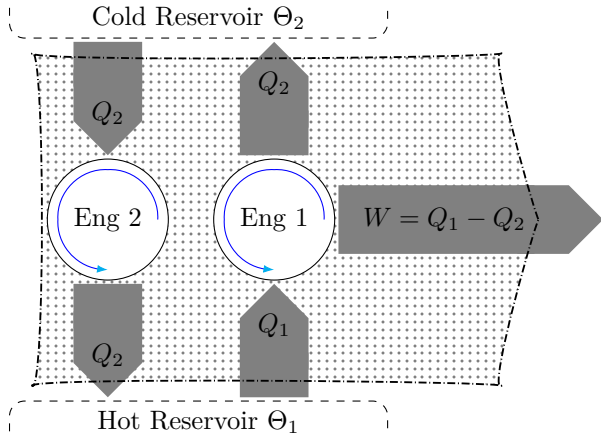


Figure 1.5.1

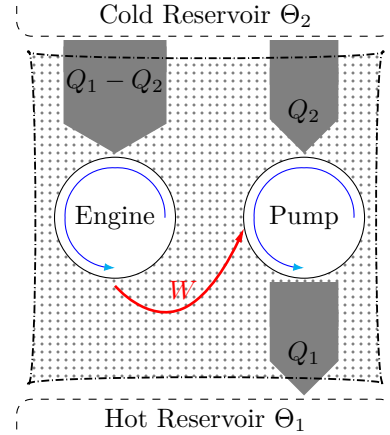


Figure 1.5.2

Suppose we have an engine that violates the Clausius statement of the second law by extracting heat from a cold reservoir of hotness² Θ_2 to a hot reservoir of hotness Θ_1 . Since no work is involved, the heat absorbed must equal that delivered in each cycle. Referring to Figure 1.5.1, we now take any engine and operate it in the normal way so that the heat is absorbed at the hotter reservoir and rejected at the colder one while some work is done by the engine. Suppose that in some given time the first engine transfers Q_2 from Θ_2 to Θ_1 . Then, we operate the second engine at such a rate that during the same period it rejects Q_2 at Θ_2 . If the heat it absorbs in that period is Q_1 , the work done is $W = Q_1 - Q_2$. We now consider the two engines, taken together to form a composite engine. We see that the net effect of the composite engine is to exchange no heat at the cold reservoir but only to extract heat $Q_1 - Q_2$ at Θ_1 and do an equal amount of work. This indicates an engine of efficiency $\eta = 1$. Therefore, Kelvin's statement fail to hold.

We can prove the other direction in a similar method. We suppose that Kelvin's statement fails to hold. Referring to Figure 1.5.2, suppose we have a heat pump working between the two reservoirs. The pump takes work $W = Q_1 - Q_2$, absorbs heat Q_2 from the cold reservoir of hotness Θ_2 and reject heat Q_1 to the hot reservoir of hotness Θ_1 . Since Kelvin's statement fail to hold, we can add a heat engine of efficiency $\eta = 1$ that absorbs heat $Q = Q_1 - Q_2$ from the cold reservoir and provide work $W = Q$ to the heat pump. Combining the heat engine and heat pump, we obtained a net heat flow from the cold reservoir to the hot reservoir, without any external work. Therefore, Clausius' statement fails to hold.

The proof is therefore complete. Kelvin's statement and Clausius' statement are equivalent. □

Now, from the proof above we are able to make new statement: *Adiabatic free expansion of ideal gas is irreversible / No process is possible in which the sole result is the spontaneous compression of an ideal gas to half of the container.*

We want to prove that the new statement is equivalent to the old ones.

proof.

We only need to prove that the new statement is equivalent to Kelvin's statement. We proceed in a similar way to the previous proof.

Suppose the new statement fails to hold, then there exist a process that consists solely of a spontaneous compression of an ideal gas from V to $\frac{1}{2}V$. We are able to construct an isothermal expansion that connects the start and end point of the adiabatic compression, but in a different direction. Now, the two processes form a cycle. In the compression part, since it is spontaneous and adiabatic, it gives $\Delta W = \Delta Q = \Delta U = 0$. The isothermal part has $\Delta Q = -\Delta W = nRT \ln 2 > 0$. Therefore, the whole process form an engine that absorbs heat ΔQ and does work $-\Delta W$ to. It has an efficiency of $\eta = 1$ and violates Kelvin's statement.

²When proving this, we use "hotness" rather than the thermodynamic temperature.

Similarly, suppose Kelvin's statement fails to hold, we are able to use engine of $\eta = 1$ to create a spontaneous compression, which violates our new statement. This completes the proof. \square

Note, the new statement involves new assumptions of ideal gas and is thus not as fundamental as the Kelvin or the Clausius statement. We will be rigorously defining thermodynamic temperature in the following section.

Theorem 1.5.1 (Carnot theorem) *No engines operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.*

Corollary 1.5.1.1 *All reversible engines operating between the same 2 reservoirs are equally efficient: If engine A is more efficient than engine B, we can use the work from engine A to reverse engine B and violate the Kelvin statement of the second law.*

We have an inequality to describe the efficiency of different engines:

$$\eta_{\text{irreversible}} \leq \eta_{\text{reversible}} = \eta_{\text{Carnot}}$$

Second law gives Carnot theorem and its corollary. If Carnot's theorem is violated, second law is violated as well.

1.6 Thermodynamic temperature

Zeroth law states that $\Phi(S)$ is a real number. When the two systems are in thermal equilibrium, we have $\Phi_1 = \Phi_2$. How do we quantitatively define the temperature?

Consider an heat engine operating between two systems of hotness Φ_1 and Φ_2 , we have:

$$\frac{\tilde{Q}_1}{\tilde{Q}_2} = F_1(\Phi_1, \Phi_2),$$

where F_1 is a universal function for all reversible heat engines. Similarly, an engine operating between Φ_2 and Φ_3 can be expressed as:

$$\frac{\tilde{Q}_2}{\tilde{Q}_3} = F_2(\Phi_2, \Phi_3)$$

If we combine the two processes to obtain an engine operating between Φ_1 and Φ_3 , we obtain:

$$\frac{\tilde{Q}_1}{\tilde{Q}_3} = F_3(\Phi_1, \Phi_3)$$

Apply the corollary of Carnot theorem, we have:

$$F_3(\Phi_1, \Phi_3) = F_1(\Phi_1, \Phi_2)F_2(\Phi_2, \Phi_3)$$

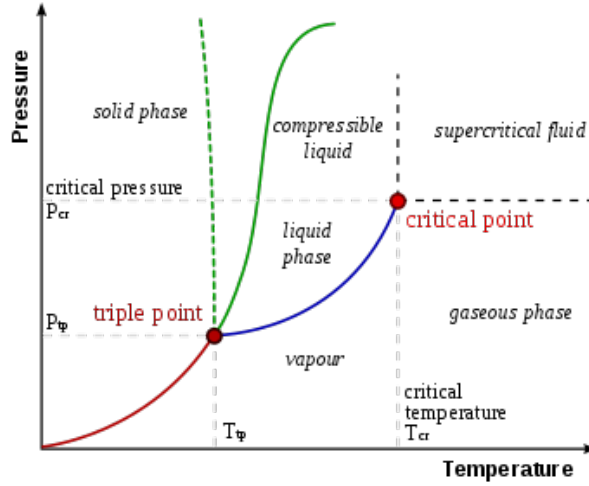
We see that the function F has a form of:

$$F(\Phi_1, \Phi_2) = \frac{f(\Phi_1)}{f(\Phi_2)}$$

We can therefore define the thermodynamic temperature of $T = f(\Phi)$ such that for a reversible heat engine operating between Φ_1 and Φ_2 , we have:

$$\frac{\tilde{Q}_1}{\tilde{Q}_2} = \frac{T_1}{T_2}$$

We still need a constant prefactor to define the scale of the temperature: **The triple point of water is 273.16 Kelvin.** It is a well defined point.



We modify the equation when we define the thermodynamic temperature:

$$\frac{\tilde{Q}_1}{T_1} = \frac{\tilde{Q}_2}{T_2}$$

But recall in the correct notation of thermodynamics, $Q_1 = \tilde{Q}_1$ is the heat taken out from the reservoir of temperature T_1 and $Q_2 = -\tilde{Q}_2$ is the heat taken out of the system T_2 . We are therefore able to write:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Theorem 1.6.1 (Clausius theorem) *For generic cyclic process (systems has been in contact with n reservoirs), we have*

$$\sum_{i=1}^n \frac{Q_i}{T_i} = 0, \text{ or } \oint \frac{\delta Q}{T} = 0$$

proof.

Consider n systems of T_1, T_2, \dots, T_n . we have a base case of $n = 2$: when $n = 2$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Consider an additional system of T_0 , and there are cyclic engines acting between T_0 and all other n sinks. For engine \mathcal{E}_i between T_0 and T_i , we have:

$$Q_{0,i} = \frac{Q_1}{T_1} T_0$$

Since the Q_i cancels at each sink of T_i , the only term left is $Q_{0,i}$. And by Kelvin's theorem:

$$T_0 \sum_{i=1}^n \frac{Q_n}{T_n} \leq 0$$

Note this process is reversible, when reversing it, the inequality becomes:

$$T_0 \sum_{i=1}^n \frac{Q_n}{T_n} \geq 0$$

We obtain:

$$\sum_{i=1}^n \frac{Q_i}{T_i} = 0$$

Note, when the process is not cyclic (not reversible), we have the Clausius inequality:

$$T_0 \sum_{i=1}^n \frac{Q_n}{T_n} \leq 0$$

1.7 Entropy

1.7.1 Definition of entropy

The change of entropy between two states is defined to be:

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} \quad (5-3)$$

Note that dQ is path independent. However, suppose that the process between $1 \rightarrow 2$ is reversible, by Clausius theorem, we have:

$$\oint \frac{dQ}{T} = 0,$$

The process $1 \rightarrow 2$ and $2 \rightarrow 1$ together forms a loop, we therefore write:

$$\int_1^2 \frac{dQ}{T} \Big|_A + \int_2^1 \frac{dQ}{T} \Big|_B = 0 \Rightarrow \int_1^2 \frac{dQ}{T} \Big|_A = \int_1^2 \frac{dQ}{T} \Big|_B$$

This indicates that the variable dQ/T is path independent and S is a state variable. We can derive an equation of state using equation 5-3.

IN reversible processes, we can rewrite the first law of thermodynamics:

$$dU = dQ + dW \Rightarrow dQ = TdS$$

In irreversible processes, we have:

$$dU = TdS - pdV$$

1.7.2 Change of entropy in processes

Reversible processes

$$\Delta S = \int_1^2 \frac{dQ}{T} \Big|_{\text{reversible}}$$

Irreversible process

$$\Delta S \leq \int_1^2 \frac{dQ}{T} \Big|_{\text{irreversible}}$$

By Clausius inequality, we have:

$$\oint_{A^+, B^-} \frac{dQ}{T} \leq 0,$$

Rearrange it we obtain:

$$\int_A \frac{dQ}{T} \Big|_{\text{irreversible}} \leq \int_B \frac{dQ}{T} \Big|_{\text{reversible}} = \Delta S$$

To get the entropy change during an irreversible process, we can find a reversible process that connects the start and end.

1.7.3 Law of increase entropy

We have derived above that:

$$\begin{aligned} dQ &= TdS & (\text{reversible}) \\ dQ &\leq TdS & (\text{irreversible}) \end{aligned}$$

Recall in adiabatic processes, $dQ = 0$

$$dS \geq 0, \begin{cases} dS = 0 & \text{reversible} \\ dS > 0 & \text{irreversible} \end{cases}$$

General statement of the second law: in adiabatic processes, entropy never decreases. Entropy measures irreversibility in adiabatic processes.

1.7.4 Entropy of ideal gases

The definition of ideal gases give:

$$\begin{cases} PV = nRT \\ dU = nC_V dT \end{cases}$$

The entropy is then given by:

$$dS_{\text{rev}} = \frac{dQ}{T} = \frac{1}{T} (dU + pdV) = \frac{nC_V}{T} dT + \frac{nR}{V} dV$$

Integrate both sides we obtain:

$$\begin{aligned} S &= \int_{T_0}^T \frac{nC_V}{T} dT + \int_{V_0}^V \frac{nR}{V} dV + S_0 \\ &= nC_V \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0} + S_0 \\ &= nC_V \ln T + nR \ln V + (S_0 - nC_V \ln T_0 - nR \ln V_0) \end{aligned}$$

If choose T, P as free variables, we have:

$$S = nC_p \ln T - nR \ln P + S_0''$$

1.7.5 Adiabatic free expansion of ideal gas

Consider the free (adiabatic) expansion of gas from V_1 to V_2 . To calculate the entropy change, we want to find a reversible process that connects the two states. Note the initial and end state in this case can be connected with an isothermal curve. On this curve we have $dQ = -dW$

$$\Delta S = \int_1^2 \frac{dQ}{T} = - \int_1^2 \frac{dW}{T} = \int_1^2 \frac{PdV}{T} = nR \ln \left(\frac{V_2}{V_1} \right) > 0$$

Or, we can directly apply the formula:

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1} \right)$$

Example 1.7.1 A engine is working between reservoirs of temperature T_1 and T_2 . The heat transfer from $1 \rightarrow 2$ is $Q > 0$. We want to find the entropy change ΔS between the reservoirs.

We can rewrite the entropy change as $\Delta S = \Delta S_1 + \Delta S_2$:

$$\begin{aligned} \Delta S_1 &= \frac{dQ}{T_1} = \frac{-Q}{T_1}; \quad \Delta S_2 = \frac{dQ}{T_2} = \frac{Q}{T_2}; \\ \Rightarrow \Delta S &= Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) > 0 \end{aligned}$$

Example 1.7.2 (Entropy change in heat transfer) Suppose gases in two boxes has temperatures T_1 and T_2 . They have the same C_p and the (deformable) boxes are put into contact. We want to know what is the entropy change during the heat exchange process until the two objects are in thermal equilibrium.

Rewrite ΔS as $\Delta S_1 + \Delta S_2$. We want to find a reversible that connects the initial and final states of the heat transfer processes.

Note the temperature of the two gases are all $\frac{T_1+T_2}{2}$ after reaching thermal equilibrium with each other.

Consider infinitesimal processes:

$$\Delta S_1 = \int \frac{dQ}{T_1} = C_p \ln \left(\frac{T_1 + T_2}{2T_1} \right); \quad \Delta S_2 = \int \frac{dQ}{T_2} = C_p \ln \left(\frac{T_1 + T_2}{2T_2} \right)$$

We have:

$$\Delta S = C_p \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} > 0$$

Example 1.7.3 (Problem 3 in Homework 2) Finite system instead of big reservoir

Method we used in HW: Carnot theorem and $dW = \eta(Q)dQ = \eta(T)dT$:

$$\tilde{W} = \int_i^f d\tilde{Q}_1 = \int_i^f \frac{T - T_0}{T} d\tilde{Q}_1 = \int_i^f \frac{T - T_0}{T} (-C_V dT) = C_V \left(T_i - T_0 - T_0 \ln \left(\frac{T_i}{T_0} \right) \right)$$

We use another approach here (with entropy): To achieve the max efficiency, we expect a reversible process. We put the water tank and the reservoir together to create an adiabatic system, so there is no heat exchange between the system and the environment. The system can still do work to the environment. We have the equation:

$$\begin{aligned} \Delta S &= \Delta S_{\text{tank}} + \Delta S_{\text{reservoir}} + \Delta S_{\text{engine}} \\ &= \int_i^f \frac{dQ}{T} + \frac{\tilde{Q}_2}{T_0} + 0 \\ &= \int_i^f \frac{C_V dT}{T} + \frac{\tilde{Q}_2}{T_0} \\ &= C_V \ln \left(\frac{T_0}{T_i} \right) + \frac{\tilde{Q}_2}{T_0} = 0 \end{aligned}$$

Note the entropy change in the engine is zero as it is a cyclic reversible process. Since the system is adiabatic, we have: $\Delta S = 0$. We have:

$$\tilde{Q}_2 = C_V T_0 \ln \left(\frac{T_i}{T_0} \right) > 0$$

We also have $\tilde{Q}_1 = C_V(T_0 - T_i)$. The work done is therefore:

$$\tilde{W} = \tilde{Q}_1 - \tilde{Q}_2$$

1.7.6 Summary on entropy

1. S is a function of state;
2. S is a measure of irreversibility and $\Delta S \geq 0$ in adiabatic processes;
3. S helps us to find what is the upper limit of the transfer from heat to work.

Consider the general work output from a system with the first law of thermodynamics:

$$dU = dW + dQ,$$

rewrite is we obtain:

$$-dW = -dU + dQ \leq -dU + TdS$$

Note $TdS \geq dQ$. So in word, the work done in a process from point p_1 to p_2 is the drop of the internal energy plus the correction from entropy.

1.8 Helmholtz and Gibbs free energies

1.8.1 Helmholtz free energy

We continue to use the form:

$$\delta W \leq -dU + TdS$$

We define the **Helmholtz free energy**:

$$F = U - TS \quad (\text{Helmholtz free energy})$$

It has a differential form of:

$$dF = dU - TdS - SdT$$

In isothermal process, $-\delta W = -dF$ as the term SdT goes away. It indicates in general we have:

$$-\delta W \leq -dF$$

The max work output of an isothermal process is the decrease of F . Consider an isothermal and reversible process without work exchange, we have:

$$0 = -\delta W = -dF$$

However, if reversibility not indicated, we have:

$$0 = -\delta W \leq -dF$$

We have $dF \leq 0$. The decrease of F measures irreversibility of a process.

Consider isothermal processes: $-\delta W \leq dF$, $-\delta W$ has two components: mechanical work PdV and non-mechanical work δW_1

$$-\delta W_1 = \delta W - PdV \leq -dF - PdV$$

1.8.2 Gibbs free energy

Define the Gibbs free energy:

$$G = U - TS + PV = F + PV \quad (\text{Gibbs free energy})$$

1.9 Thermodynamic potentials

Consider you have n conjugate pairs such as (T, S) , (P, V) , (f, L) , \dots . This gives n independent variables to determine the state of the system. An example of this is (T, S) and (p, V) . The equilibrium is maintained on a 2d-surface, which is described by the EOS.

Consider the partial differential differential $\left. \frac{\partial C_P}{\partial P} \right|_T$, we can rewrite it as:

$$\begin{aligned} \left. \frac{\partial C_P}{\partial P} \right|_T &= \left. \frac{\partial}{\partial P} \right|_T \left(T \left. \frac{\partial S}{\partial T} \right|_P \right) \\ &= T \left. \frac{\partial}{\partial T} \right|_P \left. \frac{\partial S}{\partial P} \right|_T \end{aligned}$$

Consider the Maxwell relation:

$$P = - \left. \frac{\partial U}{\partial V} \right|_S$$

Substitute it in we get:

$$\left. \frac{\partial C_P}{\partial P} \right|_T = T \left. \frac{\partial^2 V}{\partial T^2} \right|_P$$

1.9.1 Applications of thermodynamics

For ideal gases, $C_P - C_V \rightarrow R$. However, we want to obtain the generic relation, that is, to simplify the expression below.

$$C_P - C_V = T \left. \frac{\partial S}{\partial T} \right|_P - T \left. \frac{\partial S}{\partial T} \right|_V$$

By implicit function theorem, we express V as $V(P, T)$. Now by rules of derivatives, we have:

$$\left. \frac{\partial S}{\partial T} \right|_P = \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P + \left. \frac{\partial S}{\partial T} \right|_V \quad (9-1)$$

Substitute it in we get:

$$C_P - C_V = T \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P = T \left. \frac{\partial P}{\partial T} \right|_V \left. \frac{\partial V}{\partial T} \right|_P$$

Another approach to this problem is to consider the differential form of dS and dV :

$$\begin{aligned} dS &= \left. \frac{\partial S}{\partial T} \right|_V dT + \left. \frac{\partial S}{\partial V} \right|_V dV \\ dV &= \left. \frac{\partial V}{\partial T} \right|_P dT + \left. \frac{\partial V}{\partial P} \right|_T dP \end{aligned}$$

Substitute dV back in dS we obtain equation (9-1). Define isobaric expansivity β_P and isothermal compressibility κ_T as:

$$\begin{aligned} \beta_P &= \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P \\ \kappa_T &= -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T \end{aligned}$$

To express $C_P - C_V$ in β_P and κ_T , we use the reciprocity theorem:

$$\left. \frac{\partial P}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial T}{\partial P} \right|_V = -1 \quad \Rightarrow \quad -\left. \frac{\partial P}{\partial T} \right|_V = \left. \frac{\partial P}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_P$$

Substitute it back in we obtain:

$$C_P - C_V = \frac{VT\beta_P^2}{\kappa_T}$$

Example 1.9.1 Show relation $C_P/C_V = K_T/K_S$ with compressibility:

$$\begin{aligned} \kappa_S &= -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_S \\ \kappa_T &= -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T \end{aligned}$$

Given C_P and C_V , we have:

$$\frac{C_P}{C_V} = \frac{\left. \frac{\partial S}{\partial T} \right|_P}{\left. \frac{\partial S}{\partial T} \right|_V}, \quad \frac{\kappa_S}{\kappa_T} = \frac{\left. \frac{\partial V}{\partial P} \right|_T}{\left. \frac{\partial V}{\partial P} \right|_S}$$

Using reciprocity relation, rewrite κ_S/κ_T :

$$\frac{\kappa_S}{\kappa_T} = \frac{\left. \frac{\partial V}{\partial P} \right|_T}{\left. \frac{\partial V}{\partial P} \right|_S} = \frac{\left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial T}{\partial P} \right|_V}{\left. \frac{\partial V}{\partial S} \right|_P \left. \frac{\partial S}{\partial P} \right|_V} = \frac{\left. \frac{\partial S}{\partial T} \right|_P}{\left. \frac{\partial S}{\partial T} \right|_V} = \frac{C_P}{C_V}$$

Chapter 2

Statistical Mechanics

2.1 Basics on Probability Distributions

2.1.1 Introduction

Definition 2.1.1 (Probability) Probability $P(i)$ is a measure of the expectation that an event i will occur. $P(i) \in [0, 1]$. $P(i) = 0$ indicates event i will never happen whereas $P(i) = 1$ indicates event i will always happen.

Definition 2.1.2 (Probability distribution) Consider an operation or a process that has different outcomes. The information of the probability of all the possible outcomes is the probability distribution of the operation.

Example 2.1.1 Consider the process of flipping a coin. It has two possible outcomes: head and tail. Note these two results are mutually exclusive and they represents all the possible outcomes. It therefore has the property:

$$P(\text{Head}) + P(\text{Tail}) = 1$$

In a more general case where there are multiple outcomes that are complete and mutually exclusive, we have:

$$\sum_i P(i) = 1$$

Below are some basic rules:

$$P(i \text{ or } j) = P(i) + P(j), \quad P(\text{not } j) = 1 - P(j), \quad P(i \text{ then } j) = P(i)P(j), \quad P(i, \text{ each one time}) = 2P(i)P(j)$$

For an operation total of N outcomes, conducting the operation 2 times offers a total of N^2 outcomes.

2.1.2 Characterization of probability distribution

Definition 2.1.3 Suppose x is some quantity that has a unique value x_i in each outcome i with $i = 1, 2, \dots, N$. $\bar{x} = \langle x \rangle$ describes the mean value of x_i 's when you conduct the measurement of x for infinite times.

$$\bar{x} = \lim_{m \rightarrow \infty} \frac{\sum_m x_i}{m} = \sum P(i)x(i)$$

We define the m -th moment $\overline{x^m} = \langle x^m \rangle = \sum_{i=1}^N P(i)x(i)^m$.

Definition 2.1.4 (Variance and standard deviation) We define the variance of an operation x to be:

$$\sigma_x^2 = \overline{(\Delta x)^2} = \overline{x^2 - 2x\bar{x} + \bar{x}^2} = \overline{x^2} - 2\bar{x}\bar{x} + \bar{x}^2 = \overline{x^2} - 2\bar{x}^2 + \bar{x}^2 = \overline{x^2} - \bar{x}^2 = \langle x^2 \rangle - \langle x \rangle^2$$

We define the standard deviation to be the square root of variance:

$$\sigma_x = \sqrt{\overline{x^2} - \bar{x}^2}$$

Variance and standard deviation describes how wide the dispersion of x is.

Example 2.1.2 (Flipping an unfair coin) Consider the operation of tossing coins. The probabilities of getting heads and tails is given by $P(H) = p$, $P(T) = 1 - p \equiv q$. One win 1 point when getting head and loses 1 point when getting tail. We want to know the mean and standard deviation point get by tossing the coin one time.

$$\bar{x} = \sum x_i P(i) = p - q, \quad \overline{x^2} = p + q = 1 \quad \Rightarrow \quad \sigma_x = \sqrt{\overline{x^2} - \bar{x}^2} = 2\sqrt{pq}$$

Now we want to find the the mean and standard deviation of point earned after tossing two coins.

$$\begin{aligned} \bar{x} &= \overline{x^{(1)} + x^{(2)}} = \overline{x^{(1)}} + \overline{x^{(2)}} = 2(p - q) \\ \sigma_x &= \sqrt{\overline{\Delta x^2}} = \sqrt{\overline{(\Delta x^{(1)} + \Delta x^{(2)})^2}} = \sqrt{\overline{(\Delta x^{(1)})^2} + \overline{(\Delta x^{(2)})^2} + 2\overline{(\Delta x^{(1)}) (\Delta x^{(2)})}} = \sqrt{2 \times 4pq} = \sqrt{2} (2\sqrt{pq}) \end{aligned}$$

Note the standard deviation of tossing 2 coins is $\sqrt{2}$ of that of tossing 1 coin. However, the mean of tossing 2 coins is 2 times of that of tossing 1 coin. This shows standard deviation grows slower.

2.1.3 Binomial distribution

Still, we consider the operation of tossing coins. The number of coins we toss is N , however. We want to discuss in a more general way.

There are total 2^N outcomes, if order matters. If order does not matter, we have a total of $N + 1$ situations of combining different numbers of heads and tails. This leads to the binomial expansion terms $p^N, p^{N-1}q, \dots, q^N$

$$(p + q)^N = \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} \equiv \sum_n P_N(n)$$

$P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$ describes the probability of getting n heads out of N flips.

2.2 Introduction to statistical mechanics

A starting question for statistics mechanics is “how a large number of particles choose to populate quantum states?”

Case 1: Recall the example in quantum mechanics. The particles in a 3D cube has eigenstates in sinusoidal functions. To obtain this solution, we need to solve the Schrödinger equation in the 3D box:

$$i\hbar\partial_t\psi(x, y, z) = -\frac{\hbar^2\nabla^2}{2m}\psi(x, y, z) = E\psi(x, y, z)$$

Given a periodical boundary condition which requires $\psi(x + a, y, z) = \psi(x, y + a, z) = \psi(x, y, z + a) = \psi(x, y, z)$. Suppose the solution is of the form:

$$\psi(x, y, z) = \exp(i(k_x x + k_y y + k_z z)) = \exp(i(k_x(x + a) + k_y y + k_z z))$$

We obtain $\exp(ik_x a) = 1$, and therefore $k_x = \frac{2\pi}{a}n_x$, with $n \in \mathbb{N} \cup \{0\}$. The energy $E(n_x, n_y, n_z)$ is given by:

$$\frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2\pi^2}{2ma} (n_x^2 + n_y^2 + n_z^2)$$

Case 2: Consider the example of a hydrogen atom:

$$E_n = -\frac{e^2}{2a} \frac{1}{n^2}, \quad a = \frac{\hbar^2}{\mu e^2}, \quad n \in \mathbb{N}$$

Case 3: Consider the harmonic oscillator:

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

Case 4: Spins in a magnetic field.

$$\epsilon = \begin{cases} mB & \uparrow \\ -mB & \downarrow \end{cases}$$

2.2.1 Examples of systems of multiple particles

We start from the case 4 in the previous subsection. When we have multiple particles, we have:

$$\begin{array}{lcl} 1 \text{ spins} & \uparrow & \downarrow \\ 2 \text{ spins} & \uparrow\uparrow & \uparrow\downarrow \quad \downarrow\uparrow \quad \downarrow\downarrow \\ 3 \text{ spins} & \uparrow\uparrow\uparrow & (\uparrow\downarrow\uparrow \quad \uparrow\uparrow\downarrow \quad \downarrow\uparrow\uparrow) \quad (\downarrow\uparrow\downarrow \quad \uparrow\downarrow\downarrow \quad \downarrow\downarrow\uparrow) \quad \downarrow\downarrow\downarrow \end{array}$$

For the case of N -spins, we have:

$$(\uparrow + \downarrow)^N = \sum_{t=0}^N \frac{N!}{(N-t)!t!} \uparrow^{N-t} \downarrow^t$$

We define microscopic states and macroscopic states. Micro-states is the total number of different arrangement where the order matters; macro-states refers to the number of different combinations, where the order does not matter.

Definition 2.2.1 *Multiplicity function is a number of micro-states a given macro-state correspond to.*

Consider the multiplicity of N -spin problem, the multiplicity function is given by:

$$g(N, t) = \sum_{t=0}^N \frac{N!}{(N-t)!t!}$$

To express it in a more symmetric way, we define the *spin-excess*:

$$S = \frac{1}{2} (N_{\uparrow} - N_{\downarrow}),$$

from which we obtain:

$$\begin{aligned} t &= \frac{N}{2} + S, \quad N - t = \frac{N}{2} - S \\ \Rightarrow g(N, S) &= \frac{N!}{\left(\frac{N}{2} + S\right)! \left(\frac{N}{2} - S\right)!} \end{aligned}$$

We now want to discuss the behavior of the multiplicity function at large N . Apply Sterling's approximation, which states:

$$\ln(N!) = \frac{1}{2} \log(2\pi) + \left(N + \frac{1}{2}\right) \ln N - N + \mathcal{O}\left(\frac{1}{N}\right)$$

The multiplicity function becomes:

$$\begin{aligned} \ln(g(N, S)) &= \ln N! - \ln N_{\uparrow}! - \ln N_{\downarrow}! \\ &= -\frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln N - \left(N_{\uparrow} + \frac{1}{2}\right) \ln \left(\frac{N_{\uparrow}}{N}\right) - \left(N_{\downarrow} + \frac{1}{2}\right) \ln \left(\frac{N_{\downarrow}}{N}\right) \\ &= \frac{1}{2} \ln \frac{1}{2\pi N} - (N+1) \ln \frac{1}{2} - \left(\frac{N}{2} + S + \frac{1}{2}\right) \ln \left(1 + \frac{2S}{N}\right) - \left(\frac{N}{2} - S + \frac{1}{2}\right) \ln \left(1 - \frac{2S}{N}\right) \end{aligned}$$

Apply Taylor expansion to the last term, we obtain:

$$\lim_{N \rightarrow \infty} \ln(g(N, S)) = \frac{1}{2} \ln \left(\frac{2}{\pi N}\right) + N \log 2 - \frac{2S^2}{N},$$

Take exponential at both sides we obtain:

$$g(N, S) = \left(\frac{2}{\pi N}\right)^{1/2} 2^N \exp\left(\frac{-2S^2}{N}\right) = g(N, 0) \exp\left(\frac{-2S^2}{N}\right)$$

which indicates at large N , we have

$$g(N, S) \propto e^{\frac{2S^2}{N}}.$$

Normalizing each multiplicity function we see that the multiplicity function gets narrower at larger N .

2.3 Fundamental assumptions of statistical mechanics

In statistical mechanics, we assume that an isolated system is equally likely to be in any of the quantum states (microscopic state) accessible to it.

In the assumption, **quantum states** refers to the microscopic states; **isolated** indicates there is no exchange of heat, work, or matter with the surrounding, meaning constant internal energy; **accessible** means the states need to be achievable with the number of particle in the system.

The probability of each macro-state is given by:

$$P(N, S) = \frac{g(N, S)}{\sum_{S'=-N/2}^{N/2} g(N, S')}$$

Without sterling approximation, we have:

$$\sum_{S'=-N/2}^{N/2} = \frac{N!}{\left(\frac{N}{2} + S\right)! \left(\frac{N}{2} - S\right)!} \Rightarrow \sum_{S'=-N/2}^{N/2} g(N, S') = 2^N$$

With sterling approximation, we need to compute the normalization constant:

$$\sum_{S'=-N/2}^{N/2} g(N, S') \rightarrow \int_{\mathbb{R}} g(N, 0) \exp\left(-\frac{2S'^2}{N}\right) dS'$$

Define the variable X :

$$X = g(N, 0) \sqrt{\frac{\pi N}{2}}$$

2.3.1 Micro-canonical ensemble

An ensemble is a process that introduces many replicas of the same system.

Micro-canonical ensemble refers to an ensemble that acts on an isolated system that follows the fundamental assumption.

The micro-canonical ensemble is denoted as:

$$\langle X \rangle = \sum_S X(S) P(S) = \sum_S X(S) \frac{1}{g}$$

2.3.2 Most probable configuration

The most probable macro-state occurs at the max value of the multiplicity function.

2.4 General case of 2 systems in thermal contact

Fundamental assumption only hold in isolated systems that are in equilibrium. It states in such systems, all accessible microscopic states are equally probable.

Example 2.4.1 Consider the two systems S_1 and S_2 in thermal contact, but them together is isolated. We know that $U_1 + U_2$ is constant. Now, we obtained a thermal equilibrium between S_1 , S_2 , what can we say about U_1 and U_2 ?

Define the value of U_1 to be the macroscopic state. We want to find the most probable macroscopic state. To do this we find the max value of the multiplicity function.

Suppose we are able to express the multiplicity function of the combined system as $g_{\text{combined}}(U_1)$. To find a extremum, we require:

$$\frac{\partial}{\partial U_1} g_{\text{combined}}(U_1) = 0 \tag{2-4-1}$$

Redefine the multiplicity function to be the multiplication of $g_1(U_1)$ and $g_2(U_2)$, representing the possible microstates in system S_1 and S_2 respectively at U_1 and U_2 :

$$g_{\text{combined}} := g_1(U_1)g_2(U_2)$$

Reconsider the derivative in equation(2-4-1):

$$\frac{\partial}{\partial U_1} g_{\text{combined}} = g_2 \frac{\partial g_1(U_1)}{\partial U_1} + g_1 \frac{\partial g_2(U - U_1)}{\partial U_1} = g_2 \frac{\partial g_1(U_1)}{\partial U_1} - g_1 \frac{\partial g_2(U_2)}{\partial U_2} \Big|_{U_2=U-U_1}$$

In expression above we assumed that $U_1 + U_2 = U$. We therefore obtain:

$$\frac{1}{g_1} \frac{\partial g_1}{\partial U_1} = \frac{1}{g_2} \frac{\partial g_2}{\partial U_2} \quad \Rightarrow \quad \frac{\partial \log g_1}{\partial U_1} = \frac{\partial \log g_2}{\partial U_2}$$

Note the statement of thermal equilibrium in thermodynamics states that the two systems must be of the same temperature. We introduce the Boltzmann constant k_B ¹, there must be an one-to-one correspondence between $\frac{\partial \log g}{\partial U}$ to the temperature T . We come to the relation:

$$\frac{\partial \log g}{\partial U} = \pm \frac{1}{k_B T}$$

To determine the sign of the expression above, we want to see how the internal energy changes with the increase of of the multiplicity function. Suppose that we move a small amount of internal energy from S_1 to S_2 , the change in the multiplicity function of the combined system is given by:

$$\begin{aligned} \Delta g_{\text{combined}} &\approx \frac{\partial g_c}{\partial U_1} \Delta U_1 \\ &= \left(\frac{1}{g_1} \frac{\partial g_1}{\partial U_1} - \frac{1}{g_2} \frac{\partial g_2}{\partial U_2} \right) g_1 g_2 \Delta U_1 \end{aligned}$$

Note before we apply the change, the system is at the most probable macrostate, $\Delta g_{\text{combined}}$ is therefore less than 0. We have:

$$\left(\frac{1}{g_1} \frac{\partial g_1}{\partial U_1} - \frac{1}{g_2} \frac{\partial g_2}{\partial U_2} \right) g_1 g_2 \Delta U_1 < 0$$

Since $\Delta U_1 < 0$, we require:

$$\frac{\partial \log g_1}{\partial U_1} > \frac{\partial \log g_2}{\partial U_2}$$

After the change, $T_1 < T_2$. Given this relation, we know that when $\frac{\partial \log g_1}{\partial U_1}$ is greater, T is smaller. Therefore the relation between the multiplicity function and temperature is given by:

$$\frac{\partial \log g}{\partial U} = \frac{1}{k_B T}$$

$\frac{\partial \log g}{\partial U}$ is a quantity that describes the capability/tendency for a system to gain energy at thermal contact. We also obtained the expression of entropy:

$$S = k_B \log g$$

Note: in Kittle's book, $k_B T = \tau$; $\sigma = \frac{S}{k_B} = \log g$. We will use these notation as temperature and entropy from now on.

From Kittle's convention, we obtain:

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial U}$$

¹ $k_B = 1.381 \times 10^{-23}$ Joules/Kelvin; The ideal gas equation has the form $pV = nRT = Nk_B T$.

2.4.1 Change of Entropy

Suppose we move δU from \mathcal{S}_1 to \mathcal{S}_2 .

Initial State: $\mathcal{S}_1(U_1, \tau_1, \sigma_1), \mathcal{S}_2(U)_2, \tau_2, \sigma_2$

Final State: $\mathcal{S}_1(U_1 - \delta U, \tau'_1, \sigma'_1), \mathcal{S}_2(U)_2 + \delta U, \tau'_2, \sigma'_2$

The change of σ of the combined system is given by:

$$\begin{aligned}\Delta\sigma &= \Delta\sigma_1 + \Delta\sigma_2 \\ &= -\frac{\sigma_1}{\partial U_1} \delta U + \frac{\partial \sigma_2}{\partial U_2} \delta U \\ &= \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2}\right) \delta U\end{aligned}$$

Suppose $\tau_1 > \tau_2 > 0$, $-\frac{1}{\tau_1} + \frac{1}{\tau_2} > 0$. We have:

$$\begin{cases} \Delta\sigma > 0 & \delta U > 0 \\ \Delta\sigma < 0 & \delta U < 0 \end{cases}$$

This gives the spontaneous direction of heat flow.

Note when the system size approaches to infinity, the process that the system proceed from a non-equilibrium state to the most probable (equilibrium) state is irreversible.

Note: In statistical mechanics, any value of $\delta U \in (-U_2, U_1)$ is possible. At some state $\mathcal{S}_1(U + \delta U'), \mathcal{S}_1(U - \delta U')$ the system achieve the most probable configuration, or the max of $g_1(\delta U)g_2(\delta U)$. If the systems are large, the maximum with respect to changes in δU will be extremely sharp, close to a δ -function.

2.5 Canonical Ensemble

2.5.1 Recap

The combined multiplicity function g_{combined} is proportional to $P_{\text{macro/configuration}}$. Consider you release a particle at a particular position that is not the most probable one. After a long time, when observing again, the particle is most probably to be observed at the peak of the multiplicity function $g_{\text{max}}(\hat{x})$.

Microscopically, all micro-states are equally possible. **Macroscopically**, we observe a operator \hat{x} at its most probable configuration. The final standard deviation is given by:

$$\sigma_{\text{final}} = \begin{cases} \log g_{\text{combined}} \\ \log(g_1 g_2)_{\text{max}} \end{cases}$$

We then obtain the relation:

$$\begin{aligned}\log(g_1 g_2)_{\text{max}} &\sim \sigma_{\text{final}} \propto \text{system size } N \\ \log g_c - \log(g_1 g_2)_{\text{max}} &\ll N\end{aligned}$$

Relations we established between thermodynamics and statistical mechanics:

$$\begin{aligned}\frac{1}{\tau} = \frac{1}{k_B T} &= \left. \frac{\partial \log g}{\partial U} \right|_{N, V} \\ \sigma = \frac{S}{k_B} &= \log g\end{aligned}$$

2.5.2 Law of increase entropy

Consider a large system divided into 2 parts starting at a state that is not the most probable one (meaning the two parts are not of same temperature). When the system is released, it spreads to explore all possible states.

When equilibrium is reached, a peak in the distribution will be observed at the most probable configuration \hat{U} . It is extremely unlikely that the system will go back to its initial configuration in a statistical sense, and this is the origin of **irreversibility**.

Note: the discussion above are about isolated systems; in thermodynamics, only the most probable configuration is allowed.

Question: instead of isolated systems, what happens if we keep the system at a constant temperature τ ?

2.5.3 Boltzmann Factor

Consider a system in thermal contact with a reservoir of temperature τ . What is the probability of each state?

Let the reservoir has energy $U_0 - \epsilon$, and the system has energy ϵ . The total energy of the reservoir and system combined is U_0 . What is the probability of each microscopic state now?

Define $P(\epsilon)$ to be the probability of the state that the system has energy ϵ , we are then able to express $\frac{P(\epsilon_1)}{P(\epsilon_2)}$ as:

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g_s(\epsilon_1) g_R(U_0 - \epsilon_1)}{g_s(\epsilon_2) g_R(U_0 - \epsilon_2)}$$

Note, g_s is the one specific energy partition state that the system choose to be in. Therefore, $g_s(\epsilon_1) = g_s(\epsilon_2) = 1$. We have:

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g_R(U_0 - \epsilon_1)}{g_R(U_0 - \epsilon_2)} = \exp(\sigma_R)((U_0 - \epsilon_1) - (U_0 - \epsilon_2)) \approx \exp\left(-\frac{\partial \sigma_R}{\partial U}\bigg|_{U,N}(\epsilon_1 - \epsilon_2)\right)$$

By definition, we obtain:

$$\boxed{\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\exp(-\epsilon_1/\tau)}{\exp(-\epsilon_2/\tau)}}$$

We therefore claim that $P_s(\epsilon) \propto \exp(-\epsilon/\tau)$, where $\exp(-\epsilon/\tau)$ is called the **Boltzmann Factor**.

Partition function

To normalize the probability distribution function, we define the partition function, which is the sum of the probability of all accessible microstates:

$$Z(\tau) = \sum_s \exp(-\epsilon_s/\tau)$$

$P_s(\epsilon)$ is then normalized by:

$$P(\epsilon_s) = \frac{1}{Z} \exp(-\epsilon_s/\tau)$$

2.6 Canonical Ensemble II

2.6.1 Partition function Z

From the previous lecture, we defined the partition function for a system:

$$Z(\tau) = \sum \exp\left(-\frac{\epsilon}{\tau}\right)$$

The expectation of the total internal energy is given by the weighted average:

$$U(\tau) = \sum_s \epsilon_s P_s = \sum_s \epsilon_s \left(\frac{1}{Z} \exp\left(-\frac{\epsilon_s}{\tau}\right) \right)$$

We have another form of the internal energy U :

$$\begin{aligned}
 U &= \tau^2 \left. \frac{d}{d\tau} \log Z(\tau) \right|_{N,V} \\
 &= \tau^2 \frac{\partial}{\partial \tau} \log \left(\sum_s \exp \left(-\frac{\epsilon_s}{\tau} \right) \right) \\
 &= \frac{\tau^2}{Z} \sum_s \frac{\partial}{\partial \tau} \exp \left(-\frac{\epsilon_s}{\tau} \right) \\
 &= \frac{\tau^2}{Z} \sum_s \left(\frac{\epsilon_s}{\tau^2} \exp \left(-\frac{\epsilon_s}{\tau} \right) \right) \\
 &= \frac{1}{Z} \sum_s \epsilon_s \exp \left(-\frac{\epsilon_s}{\tau} \right)
 \end{aligned}$$

2.6.2 Helmholtz Free Energy

In thermodynamics, we defined Helmholtz free energy as:

$$F = U - TS = U - \tau \sigma$$

It as a corresponding definition in statistical mechanics:

$$F = -\tau \log Z(\tau)$$

The entropy is given by:

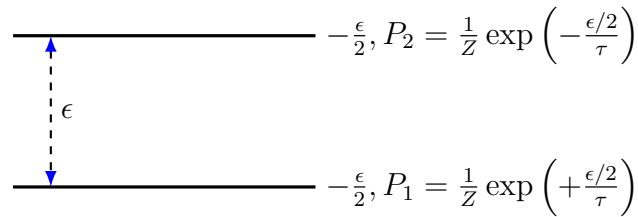
$$\begin{aligned}
 \sigma &= - \left. \frac{\partial F}{\partial \tau} \right|_{N,V} = \log Z(\tau) + \frac{\tau}{Z} \frac{\partial Z(\tau)}{\partial \tau} \\
 \Rightarrow F + \tau \sigma &= -\tau \log Z + \tau \log Z + \tau^2 \frac{\partial \log Z}{\partial \tau} = U
 \end{aligned}$$

We then obtain:

$$\exp \left(-\frac{F}{\tau} \right) = Z = \sum_s \exp \left(-\frac{\epsilon_s}{\tau} \right)$$

2.6.3 Apply canonical ensemble to a 2-level system

Suppose we have a system of only two possible energy levels:



Note $Z = \frac{1}{Z} \exp \left(-\frac{\epsilon/2}{\tau} \right) + \frac{1}{Z} \exp \left(+\frac{\epsilon/2}{\tau} \right)$, at limit of $\epsilon \ll \tau$, we have $P_1 \rightarrow \frac{1}{2}$ and $P_2 \rightarrow \frac{1}{2}$ as $\exp \left(\pm \frac{\epsilon/2}{\tau} \right) \rightarrow 1$ and $Z \rightarrow 2$.

However, at the limit of $\tau \gg \tau$, we have $P_1 \rightarrow 1$ and $P_2 \rightarrow 0$. Meaning the ground state is a more probable state than the excited state. To make the excited state the more probable state, we require negative temperature.

The internal energy is given by:

$$U = \left\{ \begin{array}{l} \tau \left. \frac{\partial}{\partial \tau} \right|_{N,V} \log Z \\ \frac{(-\epsilon) \exp(\epsilon/2\tau) + (+\epsilon) \exp(-\epsilon/2\tau)}{\exp(\epsilon/2\tau) + \exp(-\epsilon/2\tau)} = -\frac{\epsilon}{2} \tanh \left(\frac{\epsilon}{2\tau} \right) \end{array} \right.$$

We then obtain the Helmholtz free energy and heat capacity:

$$F = -\tau \log \left(2 \cosh \frac{\epsilon}{2\tau} \right)$$

$$C_V = \left. \frac{\partial U}{\partial \tau} \right|_{N,V} = \left(\frac{\epsilon}{\tau} \right)^2 \frac{1}{4 \cosh^2 (\epsilon/2\tau)}$$

2.7 Ideal Gas in Statistical Mechanics

2.7.1 Atom in crystal as QHO

Consider one atom in a crystal with constant temperature. The it is difficult for the atom to escape from its position, which is a potential well created by other surrounding atoms. We model it as a quantum harmonic oscillator (QHO), whose energy of each mode is given by $\epsilon_s = (s) + \frac{1}{2}\hbar\omega$. The partition function is given by:

$$Z = \sum_{s(n_x, n_y, n_z)} \exp \left(-\frac{\epsilon_s}{\tau} \right)$$

It's a geometric series, so the sum will simply be:

$$Z = \frac{1}{1 - \exp \left(-\frac{\hbar\omega}{t} \right)}$$

This resembles the Planck distribution function:

$$\langle s \rangle = \frac{\exp \left(-\frac{\hbar\omega}{t} \right)}{1 - \exp \left(-\frac{\hbar\omega}{t} \right)} = \frac{1}{\exp \left(\frac{\hbar\omega}{t} \right) - 1}$$

2.7.2 Classical Harmonic Oscillator

Starting with the Hamiltonian of a classical HO, we have:

$$\mathcal{H} = \frac{1}{2}kx^2 + \frac{p^2}{2m}$$

The partition function is given by:

$$\begin{aligned} Z_{\text{classical}} &= \int_{\mathbf{x}, \mathbf{p}} \exp \left(-\frac{H}{\tau} \right) d\mathbf{x} d\mathbf{p} \\ &= \left(\int \exp \left(-\frac{kx^2}{2\tau} \right) dx \right) \left(\int \exp \left(-\frac{p^2}{2m\tau} \right) dp \right) \\ &= \sqrt{\frac{2\pi k_b T}{k}} \sqrt{2m k_b T \pi} \end{aligned}$$

The expectation of the energy of the harmonic oscillator is given by:

$$\langle \epsilon \rangle = \frac{1}{Z_{\text{classical}}} \int_{\mathbf{x}, \mathbf{p}} \exp \left(-\frac{H}{\tau} \right) \left(\frac{1}{2}kx^2 + \frac{p^2}{2m} \right) d\mathbf{x} d\mathbf{p} = \frac{\tau}{2} + \frac{\tau}{2} = \tau$$

This has an implication that each quadratic degree of freedom gives $\frac{\tau}{2}$ in internal energy.

2.7.3 Ideal Gas

For free particles in a box, we have:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \mathcal{E}_n \psi$$

This is a 3D time-independent Schrödinger equation. The eigenstates are given by

$$\psi_n(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

with n_x, n_y, n_z being positive integers. The energy of this eigenstate is given by:

$$\mathcal{E}_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

The energy become a continuum when $L \rightarrow \infty$.

Example 2.7.1 *What is the partition function for one atom in a box?*

$$Z_1 = \sum_{n_x, n_y, n_z} \exp\left(-\frac{1}{\tau} \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)\right)$$

Define $\alpha^2 := \frac{\hbar^2 \pi^2}{2mL^2 \tau}$, we have the continuum form:

$$Z_1 = \int_0^\infty \exp(-\alpha^2 (n_x^2 + n_y^2 + n_z^2)) dn_x dn_y dn_z$$

2.8 Ideal Gas II

In the classical limit, which is large systems, the partition function becomes:

$$\begin{aligned} Z_1 &= \int_0^\infty \exp(-\alpha^2 (n_x^2)) dn_x \int_0^\infty \exp(-\alpha^2 (n_y^2)) dn_y \int_0^\infty \exp(-\alpha^2 (n_z^2)) dn_z \\ &= \prod_{x,y,z} \frac{1}{2} \left(\frac{\pi}{\alpha^2}\right)^{1/2} \\ &= \frac{\pi^{3/2}}{8\alpha^3} = \frac{\pi^{3/2}}{8} \left(\frac{2mL^2 \tau}{\hbar^2 \pi^2}\right)^{3/2} \\ &= \frac{\pi^{3/2}}{8} (2m\tau)^{3/2} \frac{L^3}{\hbar^3 \pi^3} \\ &= \frac{V}{V_Q}, \end{aligned}$$

Where

$$V_Q := \left(\frac{2\pi \hbar^2}{m\tau}\right)^{3/2}$$

is defined to be the quantum volume of the particle. If we interpret this quantity as some wavelength cubed, then the wavelength should look like:

$$\lambda_Q = \sqrt{\frac{2\pi \hbar^2}{m\tau}}$$

We convert it into wave vector:

$$k := \frac{1}{\lambda_Q} = \sqrt{\frac{m\tau}{2\pi \hbar^2}}$$

Commonly known de-Broglie relation is given by:

$$\begin{aligned} \mathcal{E} &= \hbar \omega \\ \mathbf{p} &= \hbar \mathbf{k} = \frac{\pi}{L} \hbar \mathbf{n} \end{aligned}$$

Apply this relation to the wave vector, we obtain:

$$p = \hbar k = \sqrt{\frac{m\tau}{2\pi}}$$

Ignoring the 2π as it is unitless, we obtain:

$$\frac{p^2}{m} \sim \tau = k_B T$$

This indicates that when one has a classical molecular gas, each particle has kinetic energy proportional to $k_B T$.

2.9 Ideal Gas III

Consider there are multiple particles in a box, and they don't interact with each other. In this case, as an approximation, single particle states are still good description of the quantum states.

2.9.1 Distinguishable Particles

If the particles are of different species, the partition function in this configuration is given by

$$Z_N = Z_1^N$$

This is because the new system consists of states of N different particles, meaning the possible states are given by:

$$\begin{aligned} Z_N &= \prod_{i=1}^N Z_{1,i} \\ &= \left(\prod_{i=1}^N \sum_j \exp\left(-\frac{\epsilon_{s_j(i)}}{\tau}\right) \right), \end{aligned}$$

where $Z_{1,i}$ is the partition function of the i -th particle.

For example, a system of 2 distinct particles and each of the particles has 5 accessible states. The particle function of the system is given by $Z_N = 5^2 = 25$

2.9.2 Identical Particles

If the particles are identical, assume the gas is dilute, the partition function is given by:

$$Z_N = \frac{1}{N!} Z_1^N$$

This is because one state is counted $N!$ times.

2.9.3 Thermodynamic Variables of the Ideal Gas

- Internal Energy:

$$U = \tau^2 \left(\frac{\partial \log Z_N}{\partial \tau} \right) = \frac{3}{2} N \tau = \frac{3}{2} N k_B T$$

- Free Energy:

$$\begin{aligned} F &= -\tau \log Z_N \\ &= -\tau N \log Z_1 + \tau \log N! \\ &\sim -\tau N \log \left(\frac{V}{N V_Q} \right) - \tau N \end{aligned}$$

- Pressure

$$P = - \left. \frac{\partial F}{\partial V} \right|_{\tau} = \frac{N\tau}{V}$$

- Entropy

$$\sigma = - \left. \frac{\partial F}{\partial \tau} \right|_V = N \left(\log \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right) \quad (\text{Sackur-Tetrode Equation})$$

2.9.4 Gibbs Paradox

For distinguishable particles, what is the problem if F and S are not extensive?

Consider the configuration of two systems separated by a barrier. The two systems each contains N distinguishable particles and have the same volume τ, V . What is the change in entropy after removing the partition barrier (so $N \rightarrow 2N$, $V \rightarrow 2V$)?

In a thermodynamic point of view, it seems that the entropy should not change after removing the barrier. Nothing really happened in a macroscopic level.

However, in a statistical mechanic sense, before removing:

$$\sigma_b = \sigma_{1,b} + \sigma_{2,b} = 2N \left(\log \frac{V}{V_Q} + \frac{3}{2} \right)$$

After removing the barrier:

$$\sigma_a = 2N \left(\log \frac{2V}{V_Q} + \frac{3}{2} \right)$$

Therefore, the change in entropy is given by:

$$\Delta\sigma = 2N \log 2 \neq 0$$

This is due to the assumption that the particles are distinguishable. However, in thermodynamic, the particles are considered identical when being considered microscopically. This reconciles why the entropy change is 0 in the sense of thermodynamics. To reconcile it, we need to calculate following the rule for indistinguishable particles.

2.10 Electromagnetic Radiation

Recap

Expressing the partition function from 1 particle to n particles $Z_1 \rightarrow Z_n$:

1. When the particles are distinguishable:

$$Z_1 \rightarrow Z_N = Z_1^N \rightarrow \sigma_N = N \left(\log \frac{V}{v_Q} + \frac{3}{2} \right)$$

v_Q represents the quantum volume. However, this caused the Gibbs paradox, where σ_N become a non-extensive quantity as it does not scale with volume.

2. When the particles are not distinguishable:

$$Z_1 \rightarrow Z_N = \frac{Z_1^N}{N!} \rightarrow \sigma_N = N \left(\log \frac{V}{N v_Q} + \frac{5}{2} \right)$$

2.10.1 Mixing Entropy

Consider a lattice with N sites. t sites are red and the other $N - t$ sites are white. Initially, particles of different colors are aligned in separate spaces in a box. When we let the particles to diffuse freely, after a long time, the two types particles reaches thermal equilibrium. We hope to find the entropy change in this process.

Note: We are unable to distinguish particles of same color while we can distinguish white and red particles.

Consider the multiplicity function:

$$g(N, t) = \frac{N!}{(N - t)!t!}$$

Apply Stirling approximation, at large N , we have:

$$\begin{aligned}\sigma(N, t) &= \log g(N, t) = -(N - t) \log \left(\frac{N - t}{N} \right) - t \log \frac{t}{N} \\ &= -N \left(\left(1 - \frac{t}{N} \right) \log \left(1 - \frac{t}{N} \right) + \frac{t}{N} \log \frac{t}{N} \right) \\ &= -N ((1 - x) \log (1 - x) + x \log x)\end{aligned}$$

Note $\sigma \rightarrow 0$ when $x \rightarrow 0$ and $x \rightarrow 1$. σ attains its maximum when $x = \frac{1}{2}$:

$$\sigma = -N \left(\frac{1}{2} \log \frac{1}{2} + \frac{1}{2} \log \frac{1}{2} \right) = N \log 2$$

2.10.2 EM waves in a cavity

Consider a square cavity. The Maxwell equation that describes the electric field in the cavity is given by:

$$\begin{aligned}c^2 \nabla^2 \vec{E} &= \frac{\partial^2}{\partial t^2} \vec{E} \\ \Rightarrow c^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) E_i &= \frac{\partial^2}{\partial t^2} E_i, \quad i = x, y, z\end{aligned}$$

The field in different directions are given by:

$$\begin{aligned}E_x &= E_{x,0} \sin(\omega t) \cos(k_x x) \sin(k_y y) \sin(k_z z) \\ E_y &= E_{y,0} \sin(\omega t) \sin(k_x x) \cos(k_y y) \sin(k_z z) \\ E_z &= E_{z,0} \sin(\omega t) \sin(k_x x) \sin(k_y y) \cos(k_z z)\end{aligned}$$

Let $\vec{k} = \frac{\pi}{L} (n_x, n_y, n_z) = \frac{\pi}{L} \vec{n}$, plug the solutions E_i back into the equation, we obtain:

$$\begin{aligned}\omega^2 &= c^2 (k_x^2 + k_y^2 + k_z^2) \\ \Rightarrow \omega^2 &= \left(\frac{\pi c}{L} \right)^2 n^2 \\ \Rightarrow \omega_n &= \frac{\pi c}{L} n \\ \Rightarrow \omega_{\text{EM}} &= c |\vec{k}|\end{aligned}$$

With de Broglie's relation, $\mathcal{E} = \hbar \omega$ and $\vec{p} = \hbar \vec{k}$. In this setting, therefore,

$$\mathcal{E}_{\text{EM}} = c |\vec{p}|$$

If we obtain the wave function using Schrödinger equation, we will obtain:

$$\omega = \frac{\hbar |\vec{k}|^2}{2m} = \frac{|\vec{p}|^2}{2m}$$

We see that $\omega(k)$ relation is actually a $\mathcal{E}(p)$ (energy-momentum) relation.

Let us go back to the configuration using Maxwell equation. Choosing the wavemode k , we can express the wave equation in:

$$E(\vec{k}, t) = \exp(ik\vec{r}) E_k(t)$$

Plug it into equation of motion of eigen mode \vec{k} , we obtain:

$$\frac{\partial^2}{\partial t^2} E_k = -c^2 k^2 E_k$$

Observe we see that this represents a harmonic oscillator with the energy level:

$$\left(s + \frac{1}{2}\right) \hbar\omega$$

The eave function is given by:

$$\psi = A \exp(i(kx - \omega t))$$

Energy of one photon in this configuration is therefore given by:

$$\mathcal{E}_{\vec{k},s} = \left(s + \frac{1}{2}\right) \hbar\omega(\vec{k})$$

At a wave mode k , we have:

$$\langle \mathcal{E}_k \rangle = \frac{\hbar\omega_k}{\exp \frac{\hbar\omega_k}{\tau} - 1} + \frac{1}{2} \hbar\omega_k$$

Sum it up we obtain the internal energy:

$$U = 2 \sum_k \langle \mathcal{E}_k \rangle$$

The coefficient is introduced by polarization. Note, as $\tau \rightarrow 0$, there is still energy left in the vacuum. If one observe, he might find the term $\frac{1}{2} \hbar\omega_k$ contributes to an infinite energy. Therefore, there must be a cut-off at some $k = N$.

Typically, in statistical mechanic, we omit the $\frac{1}{2} \hbar\omega_k$ term in the sum. The total energy therefore becomes:

$$U = 2 \sum_k \frac{\hbar\omega_k}{\exp \frac{\hbar\omega_k}{\tau} - 1}$$

Note $\omega_k = \frac{\pi c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\pi c}{L} \vec{n}$. We can therefore rewrite the sum of total internal energy:

$$U = 2 \sum_{n_x, n_y, n_z}^{\infty} \frac{\hbar\omega_k}{\exp \frac{\hbar\omega_k}{\tau} - 1}$$

In the limit of large \vec{n} , the sum becomes an integral:

$$\begin{aligned} U &= 2 \int_0^\infty \int_0^\infty \int_0^\infty \frac{\hbar\omega_k}{\exp \frac{\hbar\omega_k}{\tau} - 1} dn_x dn_y dn_z \\ &= \frac{2}{8} \int_{\mathbb{R}^3} \frac{\hbar\omega_k}{\exp \frac{\hbar\omega_k}{\tau} - 1} dn_x dn_y dn_z \end{aligned}$$

Apply the coordinate change to we can integrate in spherical coordinate:

$$\begin{aligned} U &= \frac{2}{8} \int_0^\infty \frac{\hbar\omega_k}{\exp \frac{\hbar\omega_k}{\tau} - 1} 4\pi n^2 dn \\ &= \pi \tau \left(\frac{L\tau}{\hbar c \pi} \right)^3 \int_0^\infty x^2 \frac{x^3}{\exp x - 1} dx \\ &= \frac{\pi^2}{15 \hbar^3 c^3} V \tau^4 \end{aligned}$$

Divide both side by V , we obtain the **Stephan-Boltzmann Law of Radiation**:

$$\frac{U}{V} = \frac{\pi^2}{15 \hbar^3 c^3} \tau^4$$

2.10.3 Planck radiation law

From previous section, we obtained a form:

$$\frac{U}{V} = \int d\omega dU_\omega$$

Bring the constant $2/8$ in we obtain:

$$U = \int_0^\infty \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} \pi n^2 dn$$

Apply a change of variable by letting $\omega = \frac{\pi c}{L} n$, the integral becomes:

$$U = \pi \left(\frac{L}{\pi c} \right)^3 \int \omega^2 \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} d\omega$$

Therefore, we obtain U_ω in the form:

$$U_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar\omega/\tau) - 1}$$

We explore the asymptotic behavior of U_ω as $\omega \rightarrow 0$ and $\omega \rightarrow \infty$.

When $\hbar \gg \tau$,

$$U_\omega \rightarrow \frac{\hbar}{\pi^2 c^3} \exp\left(-\frac{\hbar\omega}{\tau}\right) \rightarrow 0$$

τ is small in this setting, the spectrum becomes discrete and it it therefore a quantum limit.

When $\hbar \ll \tau$,

$$\begin{aligned} U_\omega &\rightarrow \frac{\hbar}{\pi^2 c^2} \frac{\omega^3}{1 + \frac{\hbar\omega}{\tau} + \mathcal{O}\left(\frac{\hbar\omega}{\tau}\right) - 1} \\ &= \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 \tau}{\hbar\omega} \\ &= \frac{\omega\tau}{\pi^2 c^3} \end{aligned}$$

τ is large in this setting, the spectrum becomes continuous and it it therefore a classical limit. If we extend the classical limit outside its range, we find the integral $\int U_\omega d\omega$ diverges. This is called the *ultraviolet catastrophe* and was resolved by the quantum limit term. It was one of the driving forces that led to the development of quantum mechanics.

2.10.4 energy flux density

Definition 2.10.1 *Energy flux density is defined to be the energy emission per unit area. It is denoted as J_U .*

Consider a hole on the cavity, we want to find the energy that is emitted from the hole. Since energy is transferred by photons through radiation, it propagates at a speed of light. Therefore, it has an expression:

$$J_U = \frac{U}{V} c = \frac{\pi^2}{15\hbar^3 c^2} \tau^4$$

2.10.5 Emission and absorption

Definition 2.10.2 *Black surface in a given temperature range is a surface that absorbs all incident radiation upon the surface over the temperature range.*

If the system is in thermodynamic equilibrium, the absorbed and emitted radiation is equal. For a blackbody in thermodynamic equilibrium, the emitted flux density is also:

$$[J_U]_{\text{emitted}} = \frac{\pi^2}{15\hbar^3 c^2} T^4$$

For a non-black surface in thermodynamic, we have the relation:

$$\begin{cases} \text{absorption} = aJ_U \\ \text{emission} = eJ_U \end{cases}$$

2.10.6 Radiation and surface temperature

Given the frequency ω_{max} at the peak U_ω , the temperature of a energy spectrum can be obtained by the **Wein's distribution law**:

$$\hbar\omega_{\text{max}} = 2.82k_B T$$

2.10.7 cosmic background radiation (CMB)

From observation, CMB can be modeled ideally as a black body radiation with temperature ~ 2.7 Kelvin.

2.11 Systems with a diffusive boundary

Two incompressible systems in thermal contact with a diffusive boundary. Suppose they are also in contact with a infinitely large reservoir of temperature τ . This indicates that the systems are able to exchange particles at the boundaries in contact. When the two systems reaches thermal equilibrium, we have $\tau_1 = \tau_2$. During the process to reach the equilibrium, the total energy $U = U_1 + U_2$, is also constant.

Recall from the chapter where we derived temperature, we have:

$$\frac{\partial (g_1 g_2)}{\partial U_1} = 0 \Rightarrow \frac{\partial \log g_1}{\partial U_1} = \frac{\partial \log g_2}{\partial U_2}$$

However, even a system is at the same temperature and pressure, if there composition are different, there will still be particle exchanges when the two systems are put into diffusive contact. Therefore, the two systems are not in equilibrium in diffusion sense. We introduce the concept of chemical potential.

Recall in thermodynamics, we have $dF = -SdT - pdV$, we want to minimize $F = F_1 + F_2$ in this case as T and V are fixed.

$$0 = \frac{\partial F}{\partial N_1} = \left. \frac{\partial F_1}{\partial N_1} \right|_{\tau_1, N_1} + \left. \frac{\partial F_2}{\partial N_1} \right|_{\tau_2, N_2}$$

We therefore have:

$$\frac{\partial F_1}{\partial N_1} = \frac{\partial F_2}{\partial N_2}$$

We therefore define chemical potential to be:

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{\tau, V}$$

When the two systems are in diffusive equilibrium, their chemical potential must equal:

$$\mu_1 = \mu_2$$

Example 2.11.1 (Spontaneous Flow) Consider an example of two system in diffusive contact and $\mu_1 > \mu_2$. We have:

$$\frac{\partial F}{\partial N_1} = \frac{\partial F_1}{\partial N_1} - \frac{\partial F_2}{\partial N_2} = \mu_1 - \mu_2 > 0 \quad (*)$$

In order to minimize dF , the particles must move in a direction such that dF is negative.

$$dF = \frac{\partial F}{\partial N_1} dN_1$$

Since $\frac{\partial F}{\partial N_1} > 0$ from (*), N_1 should be negative in order for F to minimize. This defined a spontaneous flow direction of particles in a field of varying chemical potential.

Example 2.11.2 (Chemical potential of ideal gas) Chemical potential is defined to be:

$$\mu := \left. \frac{\partial F}{\partial N} \right|_{\tau, V}$$

In thermodynamics, F is given by:

$$F = -\tau \left(N \log \frac{V}{V_Q} - \log N! \right)$$

We therefore have:

$$\begin{aligned} \mu &= \left. \frac{\partial F}{\partial N} \right|_{\tau, V} = -\tau \log Z_1 - \tau \frac{d}{dN} \log N! \\ &\approx -\tau \log Z_1 - \tau \frac{d}{dN} \left(\frac{1}{2} \log 2\pi + \left(N + \frac{1}{2} \right) \log N - N \right) \\ &= -\tau \log Z_1 - \tau \left(\log N + \left(N + \frac{1}{2} \right) - 1 \right) \end{aligned}$$

At large N , this value becomes :

$$\begin{aligned} \mu &= -\tau \log Z_1 - \tau \log N \\ &= \tau \log \left(\frac{N v_Q}{V} \right) \\ &= \tau \log \left(\frac{\rho}{\rho_Q} \right) \end{aligned}$$

2.11.1 Internal vs total chemical potential

In a configuration of two systems at different places of a gravitational fields $g(\vec{x})$. The free energy becomes:

$$F_{1,tot} = F_{1,idea} + N_1 mg \Delta h \quad F_{2,tot} = F_{2,idea}$$

The equation that describes equilibrium becomes:

$$\tau \log \left(\frac{\rho_1}{\rho_Q} \right) = \tau \log \left(\frac{\rho_2}{\rho_Q} \right) + mg \Delta h$$

Solve it we obtain:

$$\rho_1 = \rho_2 \exp \left(-\frac{mg \Delta h}{\tau} \right)$$

2.12 Thermodynamic identities including N change

With a change in number of particles, the thermodynamics identities becomes:

$$\begin{aligned} dU &= TdS - pdV & dU &= TdS - pdV + \mu dN \\ dF &= -SdT - pdV & dF &= -SdT - pdV + \mu dN \\ dH &= TdS + Vdp & dH &= TdS + Vdp + \mu dN \\ dG &= -SdT + Vdp & dG &= -SdT + Vdp + \mu dN \end{aligned} \Rightarrow$$

Rearrange the expression, we obtain:

$$dS = \frac{1}{T} (dU + pdV - \mu dN) \quad \Rightarrow \quad d\sigma = \frac{1}{\tau} (dU + pdV - \mu dN)$$

2.12.1 Gibbs Factor

Definition 2.12.1 *Gibbs factor describes the probability for a system to be at a certain microscopic state with particle number N and energy \mathcal{E} at given (τ, U, V) .*

$$\begin{aligned}
 P_s(N_s, \mathcal{E}_s) &\propto g_R(N - N_s, E - \mathcal{E}_s) \\
 &= \exp(\log g_R(N - N_s, E - \mathcal{E}_s)) \\
 &= \exp\left(\log g_R(N, E) - \frac{\partial \log g_R}{\partial N_R} N_s - \frac{\partial \log g_R}{\partial E_R} \mathcal{E}_s\right) \\
 &\propto \exp\left(-\frac{\partial \log g_R}{\partial N_R} N_s - \frac{\partial \log g_R}{\partial E_R} \mathcal{E}_s\right) \\
 &= \exp\left(\frac{\mu}{\tau} N - \frac{\mathcal{E}}{\tau}\right) \\
 &= \exp\left(\frac{\mu N - \mathcal{E}}{\tau}\right) \quad (\text{Gibbs Factor})
 \end{aligned}$$

Grand Canonical Ensemble

We denote the grand canonical ensemble as:

$$\zeta(\mu, \tau) = \sum_{\text{microstates}} \exp\left(\frac{\mu N - \mathcal{E}}{\tau}\right)$$

For the sum, we usually denote it as:

$$\sum_{N=1}^{\infty} \sum_{S(N)} := \sum_{ASN}$$

Probability of a microstate is given by:

$$P(N, \mathcal{E}) = \frac{1}{\zeta} \exp\left(\frac{\mu N - \mathcal{E}}{\tau}\right)$$

Example 2.12.1 (Expectation Value of N) *The expectation values of particle number is given by:*

$$\begin{aligned}
 \langle N \rangle &= \frac{1}{\zeta} \sum_{ASN} N \exp\left(\frac{\mu N - \mathcal{E}}{\tau}\right) \\
 &= \frac{1}{\zeta} \sum_{ASN} \frac{\partial}{\partial \mu} \bigg|_{\tau, V} \exp\left(\frac{\mu N - \mathcal{E}}{\tau}\right)
 \end{aligned}$$

We also have:

$$\frac{\tau}{\zeta} \frac{\partial}{\partial \mu} \bigg|_{\tau, V} \zeta = \tau \frac{\partial}{\partial \mu} \bigg|_{\tau, V} \log \zeta$$

Define $\lambda = \exp\left(\frac{\mu}{\tau}\right)$ to be *absolute activity*, we have:

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \bigg|_{\tau, V} \log \zeta$$

Example 2.12.2 (Expectation Value of \mathcal{E}) *The total internal energy is defined to be the expectation value of \mathcal{E} :*

$$\langle \mathcal{E} \rangle = \frac{1}{\zeta} \sum_{ASN} \mathcal{E} \exp\left(\frac{\mu N - \mathcal{E}}{\tau}\right)$$

Let $\beta = \frac{1}{\tau}$, we have:

$$\left. \frac{\partial}{\partial \beta} \right|_{\mu, V} \log Z = \frac{1}{\zeta} \sum_{ASN} (N\mu - \mathcal{E}) \exp(\beta(N\mu - \mathcal{E}))$$

Therefore, we have:

$$U = \langle \mathcal{E} \rangle = - \left. \frac{\partial}{\partial \beta} \right|_{\mu, V}$$

2.12.2 Review of statistical ensembles

Ensemble: Many copies, and each copy represent a microstate.

Ensembles	Fixed Variables	Probability P_s
Microcanonical	(U, V, N) , Isolated	$1/g$
Canonical	(τ, V, N) , heat reservoir	$\frac{1}{Z} \exp(-\mathcal{E}_s/\tau)$
Grand Canonical	(τ, V, μ) , heat & particle reservoir	$\frac{1}{\zeta} \exp(-(\mathcal{E} - \mu N)/\tau)$

Ensembles	U	σ	F
Microcanonical	U as given	$\log g$	$U - \tau\sigma$
Canonical	$\tau^2 \left. \frac{\partial}{\partial \tau} \log Z \right _{V, N}$	$- \left. \frac{\partial F}{\partial \tau} \right _{V, N}$	$-k_b \log Z$
Grand Canonical	$\left(\tau\mu \left. \frac{\partial}{\partial \mu} \right _{\tau, V} - \left. \frac{\partial}{\partial (1/\tau)} \right _{\mu, V} \right) \log \zeta$	$\log \zeta + \tau \left. \frac{\partial}{\partial \tau} \log \zeta \right _{\mu, V}$	$U - \tau\sigma$

2.13 Quantum Gas

How to describe a gas?

In thermodynamics, we have the gas equations, for example, $pV = nRT, U = U(T)$. In statistical ensemble, we have canonical ensembles.

2.13.1 Fermi Gas

Consider the Grand canonical ensemble of a subsystem, which is defined be a single particle state (wave function, or “orbitals”). Fermions have half-integer spins, and an orbital can be occupied by 0 or 1 Fermions of the same species (Pauli exclusion principle).

The grand canonical ensemble of a subsystem is:

$$\begin{aligned} \zeta &= \sum_{ASN} \exp\left(-\frac{\mathcal{E} - \mu N}{\tau}\right) \\ &= 1 + \exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right) \\ &= 1 + \lambda \exp\left(\frac{\mu}{\tau}\right) \end{aligned}$$

The first term is from the case of no fermions and the second term is from the case of 1 fermion.

The average occupancy is given by:

$$\langle N \rangle_{\text{fermion}} = \frac{\exp\left(\frac{\mathcal{E} - \mu}{\tau}\right)}{1 + \exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right)} = \frac{1}{1 + \exp\left(\frac{\mathcal{E} - \mu}{\tau}\right)} \quad (\text{Fermi-Dirac Distribution})$$

2.13.2 Boson Gas

Bosons have integer spins. Occupancy on an orbital s can be $0, 1, 2, \dots, \infty$. The grand canonical ensemble is given by:

$$\zeta = 1 + \exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right) + \exp\left(-\frac{2(\mathcal{E} - \mu)}{\tau}\right) + \dots = \frac{1}{1 - \exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right)}$$

Average occupancy is given by:

$$\langle N \rangle_{\text{boson}} = \lambda \frac{\partial}{\partial \lambda} \log \zeta = \frac{1}{\exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right) - 1} \quad (\text{Bose-Einstein Distribution})$$

Note, for bosons, the chemical potential must be smaller than the energy. Otherwise, the average occupancy will become negative, which does not make sense physically. In large limit of $\mu \ll \mathcal{E}$ or $\frac{\mathcal{E} - \mu}{\tau} \gg 1$, then

$$\frac{1}{\exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right) \pm 1} \sim \exp\left(-\frac{\mathcal{E} - \mu}{\tau}\right)$$

This is the **Classical Limit**.

2.13.3 Classical Limit

What does the classical limit mean by having bosons and fermions behave the same?

$$\langle N \rangle = \sum_s \langle N_s \rangle$$

s represents possible orbitals/ wave functions. We then have:

$$\langle N \rangle = \sum_s \frac{1}{\exp\left(-\frac{\mathcal{E}_s - \mu}{\tau}\right) \pm 1} = \exp\left(\frac{\mu}{\tau}\right) \sum_s \exp\left(-\frac{\mathcal{E}_s}{\tau}\right) = \exp\left(\frac{\mu}{\tau}\right) \frac{V}{v_Q}$$

In grand canonical ensemble, we have

$$\frac{\mu}{\tau} = \log\left(\frac{\rho}{\rho_Q}\right)$$

Substitute the result in we obtain:

$$\mu = \tau \log\left(\frac{N/V}{\rho_Q}\right)$$

Therefore, in the classical limit, $\exp\left(-\frac{\mathcal{E}_s - \mu}{\tau}\right) \gg 1$ for all orbitals. We therefore require the ground state to also have:

$$\exp\left(-\frac{\mu}{\tau}\right) \gg 1,$$

which leads to:

$$\frac{N}{V} \ll \frac{1}{v_Q}, \text{ or } \frac{V}{N} \gg v_Q$$

The quantity $(V/N)^{1/3}$ describes the typical distance between particles. The quantity $v_Q^{1/3} \sim \lambda_{\text{th}}$, where λ_{th} is the **thermal de Broglie wave length**, which describes the characteristic size of the wave packet.

At **high** temperature, the wave packets becomes points, and the particles behave in the classical limit. At **low** temperature, the characteristic length of wave packets increases and the particles has wavy behaviors in the quantum limit.

2.14 Fermi Energy

Recall the Fermi-Dirac distribution from previous lecture:

$$f_{FD}(\mathcal{E}) = \frac{1}{1 + \exp\left(\frac{\mathcal{E}-\mu}{\tau}\right)}$$

It describes the occupancy of one single-particle state at energy \mathcal{E} . What would happen when $\tau \rightarrow 0$? The distribution function becomes a step function:

$$f_{FD} = \begin{cases} 1 & x < 0 \\ 0 & x > 0 \end{cases}$$

This indicates that there exist some energy \mathcal{E}_n where for all $m \geq n$, the \mathcal{E}_m orbital is empty and for all $m < n$, the \mathcal{E}_m orbital is filled. We call the energy of higher cut-off **Fermi energy**.

2.14.1 Fermi gas in 3D

The orbitals in 3D has the wave function:

$$\psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z),$$

where k_x, k_y, k_z are given by:

$$k_x = \frac{\pi}{L}n_x; \quad k_y = \frac{\pi}{L}n_y; \quad k_z = \frac{\pi}{L}n_z, \quad n_x, n_y, n_z \in \mathbb{N}$$

Define $n^2 = n_x^2 + n_y^2 + n_z^2$:

$$\mathcal{E}(k) = \frac{\hbar^2 |k|^2}{2m} = \frac{\hbar^2 \pi^2}{2m L^2} n^2$$

To obtain the Fermi Energy in 3D quantum configuration, we calculate the number of particles enclosed by the spherical shell of radius n_F .

$$N = \frac{1}{8} \frac{4\pi}{3} n_F^3 \times 2 = \frac{\pi}{3} n_F^3$$

We include the constant $1/8$ because the particles will only fill the region with $n_x, n_y, n_z \geq 0$, which is $1/8$ of the whole space and the coefficient 2 comes from the spin of Fermions.

We have:

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

The Fermi energy is therefore given by:

$$\mu = \mathcal{E}_F = \frac{\hbar^2}{2m} \left(3\pi^3 \frac{N}{V} \right)^{2/3} \equiv \tau_F \quad (\text{Fermi Temperature})$$

The total energy in such configuration is given by:

$$\begin{aligned} U(\tau = 0) = U_0 &= 2 \sum_{n \leq n_F} \mathcal{E}_n = 2 \times \frac{1}{8} \int_{\mathbb{R}^3} d^3n \mathcal{E}_n \\ &= \pi \int_0^{n_F} 4\pi n^2 dn \left(\frac{\hbar^2 \pi^2}{2m L^2} n^2 \right) \\ &= \frac{\pi^3 \hbar^2}{2m L^2} \int_0^{n_F} n^4 dn \\ &= \frac{3}{5} N \mathcal{E}_F \end{aligned}$$

Then, we have:

$$P_0 = \left. \frac{\partial U_0}{\partial V} \right|_{\tau, N} = \frac{2U_0}{3V}$$

2.14.2 Density of States for Fermions in 3D

We want to convert the sum into an integral for summing over wave functions:

$$2 \sum_{n_x, n_y, n_z} A(n_x, n_y, n_z) \longrightarrow \int \mathcal{D}(\mathcal{E}) d\mathcal{E},$$

$A(n_x, n_y, n_z)$ is any summable quantity.

$$\begin{aligned} 2 \sum_{n_x, n_y, n_z} A(n_x, n_y, n_z) &\rightarrow \frac{1}{8} \times 2 \int A(n_x, n_y, n_z) 4\pi n^2 dn \\ &= \int A(n_x, n_y, n_z) \pi n^2 dn = \int A(n_x, n_y, n_z) \mathcal{D}(n) dn \end{aligned}$$

Note, we have:

$$\mathcal{E} = \frac{\hbar^2}{2m} \left(\frac{\pi n}{L} \right)^2$$

Rearrange:

$$n = \left(\frac{2m\mathcal{E}}{\hbar^2} \right)^{1/2} \frac{L}{\pi}$$

Take the derivative of n with respect to n , we obtain:

$$dn = \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{L}{\pi} \frac{1}{2\mathcal{E}^{1/2}} d\mathcal{E}$$

We require the relation

$$\mathcal{D}(\mathcal{E}) d\mathcal{E} = \mathcal{D}(n) dn$$

We know that $\mathcal{D}(n) = \pi n^2$, we have:

$$\mathcal{D}(\mathcal{E}) = \pi n^2 \frac{dn}{d\mathcal{E}} = \pi \left(\left(\frac{2m\mathcal{E}}{\hbar^2} \right)^{1/2} \frac{L}{\pi} \right)^2 \left(\left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{L}{\pi} \frac{1}{2\mathcal{E}^{1/2}} \right)$$

2.14.3 Applications of Fermi Gas

Electron in metals is one example of a Fermi gas. Atoms, such as ^3He , is also Fermions. Neutrons are Fermions, they form neutron stars.

The classical limit of a Fermion Gas system is reached when $\frac{V}{N} \gg v_Q$, where v_Q is given by:

$$v_Q = \left(\frac{2\pi\hbar^2}{m\tau} \right)^{3/2}$$

We then have:

$$\frac{V}{N} \gg \left(\frac{2\pi\hbar^2}{m\tau} \right)^{3/2} \Rightarrow \tau \gg \left(\frac{N}{V} \right)^{2/3} \frac{2\pi\hbar^2}{m}$$

Note, we have derived in previous section, the Fermi Temperature is given by:

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

We then claim that at the classical regime, $\tau \gg \tau_F$.

2.15 Bose Gas

Bose Gas is gas made of bosons. It follows the distribution that describes the average occupancy at energy level \mathcal{E} :

$$f_{BE}(\mathcal{E}) = \frac{1}{\exp\left(\frac{\mathcal{E}-\mu}{\tau}\right) - 1}$$

At fixed N , the relation between f_{BE} and E is given by:

$$N = \int \mathcal{E}(\mathcal{E}) f(\mathcal{E}) d\mathcal{E}$$

The density function is given by:

$$\mathcal{D} = \frac{V}{4\pi} \left(\frac{2m}{\hbar^2}\right)^{3/2} \mathcal{E}^{1/2}$$

2.15.1 Bose-Einstein Condensation

Consider the equation:

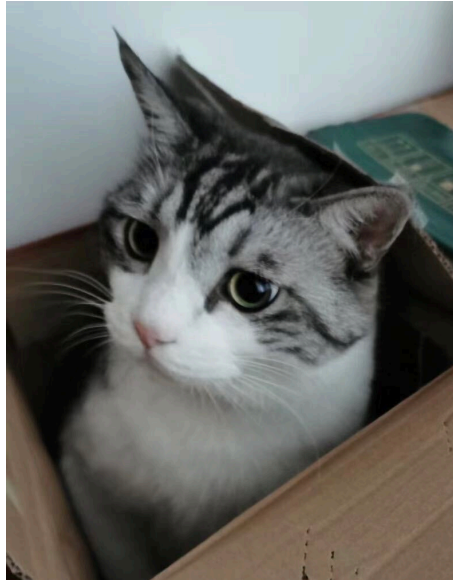
$$\begin{aligned} N &= \int_0^\infty \mathcal{D}(\mathcal{E}) f(\mathcal{E}) d\mathcal{E} \\ &= \int_0^\infty \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \mathcal{E}^{1/2} \frac{d\mathcal{E}}{\exp\left(\frac{\mathcal{E}-\mu}{\tau}\right) - 1} \end{aligned}$$

We hope to see what happens at $\mu = 0$, the equation becomes:

$$N = \int_0^\infty \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \exp(1/2) \frac{d\mathcal{E}}{\exp\left(\frac{\mathcal{E}}{\tau}\right) - 1}$$

Let $\chi = \frac{\mathcal{E}}{\tau}$, we have the expression below:

$$N = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \tau^{3/2} \int_0^\infty \frac{\chi^{1/2}}{\exp(\chi) - 1}$$



Thank you for reading my notes!!

