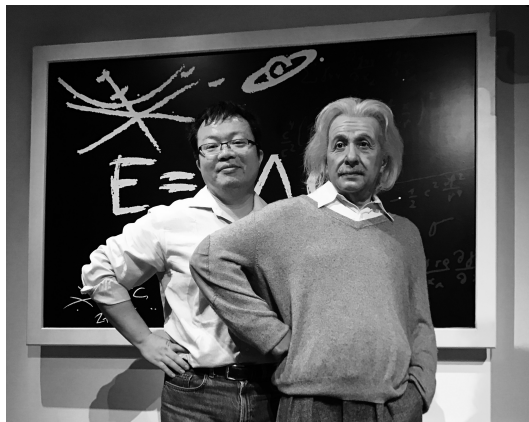# INTRODUCTION TO STATISTICAL MECHANICS

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Lecture note for Statistical Mechanics II at SUSTech

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Lecture Note

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CONTACTS

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Simplicity is the ultimate sophistication. — Leonardo da Vinci

CONTENTS

1 | INTRODUCTION

This part contains a brief introduction of statistical mechanics. The statistical mechanics contains two parts, one is how to obtain the macroscopic properties from microscopic structure, i.e. the microscopic distribution of some physical quantities. The other one is how to obtain the microscopic distribution.

1.1 TO OBTAIN MACROSCOPIC PROPERTIES FROM MICROSCOPIC DISTRIBUTION

In our daily life or in our interaction with the nature, we are facing macroscopic system which consists of many-particles (atoms, moleculas) systems at a room temperature. We also faces different many-particle systems in the lab at some circumstance where we can control the temperature. The properties of those systems varies with varying temperature and they absorb or emit heat. These phenomena related to temperature or heat are so-called the thermal phenomena. The discipline study thermal phenomena is thermodynamics which is a phenomenological theory. How the thermodynamics and the thermal properties of the macroscopic system emerge from a many-particle system which is describe by a Hamiltonian is the purpose of statistical mechanics (SM).

STATISTICAL MECHANICS (SM) is discipline studying many-particle (or more generally, many-agents) system. Its purpose is to deduct the macroscopic thermodynamic properties of the systems from their microscopic structure.

Here the microscopic knowledge of the microscopic structure means informations such as Hamiltonian of the system, the distribution of the velocity of all particles,.... Let us start from an example in case, the ideal gas.

TWO TYPICAL METHODS TO ANALYZE PROBLEMS IN PHYSICS:

1) DISSECTING A SPARROW —— To analyze a typical case,

2) THE BLIND MAN PATTING AN ELEPHANT ——To make an overall judgement of something on the basis of partial understanding.

The state function and the equation of state for ideal gas are listed in the following table.

Macroscopic Properties	Analog of mechanical system
P: Presure V: Volume T: Temperature N: Particle Number	like coordinate of a particle
Equation of State: $PV = Nk_B T$	like equation of motion
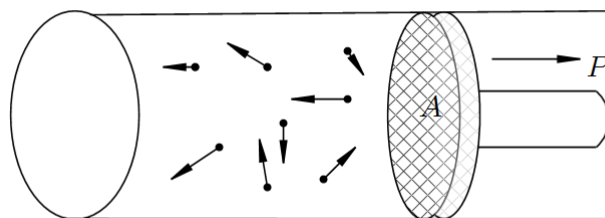
Figure 1: A container full of gas

Figure 2: The pressure of the gas

$$
\boxed{\begin{array}{c}\vec{v} \text{ of each individual particles} \\ P\,(v)\ \text{distribution}\end{array}} \overset{SM}{\Longrightarrow} \boxed{\begin{array}{l}\text{Eq. of State} \\ \text{macroscopic properties}\end{array}}
$$

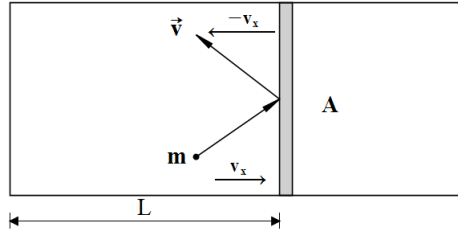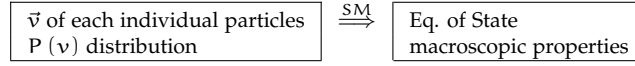### 1.1.1 Macroscopic Properties: State Equation

How to get the equation of state from the microscopic knowledge of the system? We assume velocity of the particles are $\vec{v}_i$, and the mass are all m, then the pressure of the gas are due to the collision of the particles with the wall of the container,

$$
\begin{aligned}
P \overset{\text{def}}{=} \frac{F}{A} &= \frac{\overline{\Delta p/\Delta t}N}{A} \\
&= \frac{1}{A}\overline{\left(\frac{2mv_x}{2L/v_x}\right)}N \qquad * \\
&= \frac{1}{A}\frac{\overline{2mv_x}}{L}N = \frac{N}{V}m\overline{v_x^2} = \frac{N}{V}\frac{1}{3}m\overline{v^2}
\end{aligned}
$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$, and * N particles with average velocity v_x.

1.1.2 Microscopic Distribution: Maxwell-Boltzman distribution

The distribution function of the velocities of the particles satisfy the Maxwell-Boltzman distribution,

$$
\begin{aligned}
\mathbf{P}\,(v) &= \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}\,4\pi v^2 e^{-\frac{mv^2}{2k_B T}} \\
&= \prod_{i=1}^{3}\sqrt{\frac{m}{2\pi k_B T}}\,e^{-\frac{mv_i^2}{2k_B T}}
\end{aligned}
$$

where $dv_x dv_y dv_z = 4\pi v^2 dv$.

$$
\begin{aligned}
\langle mv_x^2 \rangle &= \frac{m}{2}\int \mathbf{P}\,(v_x)\,dv_x = \frac{1}{2}2k_B T = k_B T \\
\frac{1}{2}\langle mv^2 \rangle &= \frac{m}{2}\int v^2 \mathbf{P}\,(v)\,dv = \frac{3}{2}k_B T \\
\langle mv^2 \rangle &= 3k_B T
\end{aligned}
$$

so we have

$$
\begin{aligned}
P &= \frac{N}{V}\frac{1}{3}m\overline{v^2} = \frac{N}{V}\frac{1}{3}\,(3k_B T) = \frac{Nk_B T}{V} \\
&\Longrightarrow PV = Nk_B T
\end{aligned}
$$

We can see from above that from the knowledge of microscopic structure $\mathbf{P}\,(\vec{v})$, we can deduce the macroscopic equation of State $PV = Nk_B T$. This process is the main purpose of SM.

We can not only derive the macroscopic properties from microscopic structure, but also derive the macroscopic statistical law as well.
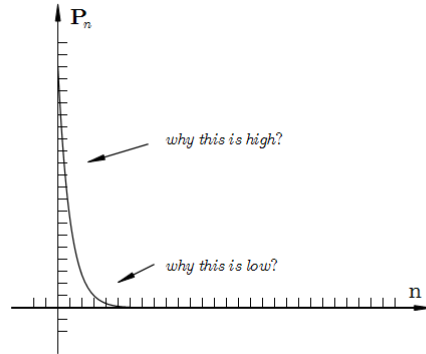
1.2 TO OBTAIN MICROSCOPIC DISTRIBUTION: HOW STATISTICAL LAW EMERGENT

1.2.1 Number game: To give you a sense of why "statistics" play the role.

Let us play a game. Everyone bring a piece of paper, and prepare for a scissor-stone-cloth (SSC) game.

- (1) Write down a table in your paper

1	3
2	4
3	
4	
5	
...	
19	
20	

- (2) Play a game with another student in your class.

    (a) You two play the SSC game, the person who win the game get one point, the other people lose one point only if both of your points are positive or zero. Otherwise, keep the same points.

    (b) If you two play even, don't change you points.

    Each person has to play with different people at each time. Stop when you play 19 times.

- (3) When all the people finish, we do the statistics where P_n is the number of people whose points are n,

Each P_n curve is a macroscopic configuration of the system. You can take it as a macroscopic state (it is called macrostate) of the system. You will find that as time evolves P_n is approaching a stable configuration $\overline{P}_n$. And use a function to fit $\overline{P}_n$, you will get

$$\overline{P}_n = N_0 e^{-\beta n}$$

Why is that?

1.2.2 An simple explanation

$n \longrightarrow n + 1$ the probability to win 1 point is $\frac{1}{2}$

$n \longrightarrow n + 2$ the probability to win 2 points $\left(\frac{1}{2}\right)^2$

....

$n \longrightarrow n + s$ the probability to win s points is $\left(\frac{1}{2}\right)^s = e^{\ln\left(\frac{1}{2}\right)^s} = e^{s \ln \frac{1}{2}} = e^{-s \ln 2}$

So to get a large point, you need to be very lucky, it is with low probability, so only very few people can achieve.

On the other hand

$n \longrightarrow n - s$ the probability to lose s the points is also $\left(\frac{1}{2}\right)^s$, but there is a lower limit of n (zero), when $n = 0$, you can not lose any points again, but you are still in the game, you can win back. So the number # of people are accumulate at small n.

So $\overline{P}_n = N_0 e^{-\beta n}$ is reasonable.

1.2.3 More formally explanation

We have totally N_s people and N_p points with $N_p = 3 \times N_s = 3 \times 40 = 120$ in this example.

No matter how points are transfered from one person to another person. We have the following constraints

$$\begin{cases} \sum_n P_n & = N_s \\ \sum_n n P_n & = N_p \end{cases}$$

This problem is actually the problem "that how do you put N_p balls into N_s boxes." For

$$N_p = 4, \qquad N_s = 3$$

We have following configurations (here is the macroscopic state, i.e. macrostate) and number of possible microscopic state (i.e. microstate)

marcrostates	0	1	2	3	4	number of microstates	probability
0+0+4	2	0	0	0	1	$\frac{3!}{2!1!} = 3$	20%
0+1+3	1	1	0	1	0	$\frac{3!}{1!1!1!} = 6$	40%
0+2+2	1	0	2	0	0	$\frac{3!}{1!2!} = 3$	20%
1+1+2	0	2	1	0	0	$\frac{3!}{2!1!} = 3$	20%

Here we assume each ball has an index, different arrangement of index are different microscopic states (it is called microstate). For example, macrostate $P_4 = 1, P_0 = 2$ has three macrostates. One of them is that the balls with index 1, 2 have zero point and the ball with index 3 has 4 points, denoted as $P_0 = \{1, 2\}, P_4 = \{3\}$. And macrostates $P_0 = \{1, 3\}, P_4 = \{2\}$ and $P_0 = \{2, 3\}, P_4 = \{1\}$ are all corresponding to the same macrostate. The other macrostate and corresponding number of microstates are calculated in the same way. The probability is calculated by assuming all microscopic states have the same probabilities. So the macroscopic configuration with larger number of microscopic states have higher probabilities.

Generally, each macroscopic P_n is plot in the following figure,
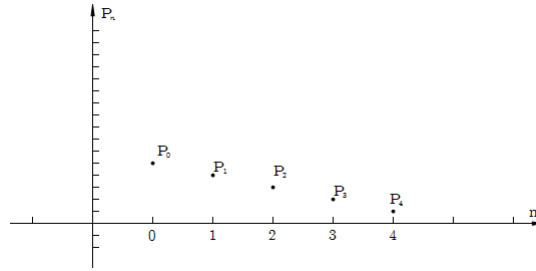
Such configuration has the following number of microscopic states

$$\Omega = \frac{N_p!}{P_1! P_2! \cdots P_{N_s}}$$

To get the maximum number of microscopic state, we try to find the maximum value of $S = \ln \Omega$ (which is proportional to the entropy of the system).

$$S = \ln \Omega$$
$$= \ln \frac{N_p!}{P_1! P_2! \cdots P_{N_s}}$$

By using the method of Lagrange multipliers to get

$$\delta \left[\ln \Omega \{P_n\} - \alpha \sum_n P_n - \beta \sum_n n P_n \right] = 0$$

where

Why it throw up lnPn

$$\ln \Omega \{P_n\} = \ln N_p! - \sum_n \ln P_n!$$
$$= \ln N_p! - \sum_n P_n \ln P_n + \sum_n P_n$$

by using Stirling approximation $\ln P_n! = P_n \ln P_n - P_n$.

$$0 = \delta \sum_n \left[-P_n \ln P_n + P_n - \alpha P_n - \beta n P_n \right]$$
$$= \sum_n \left[-\ln P_n - P_n \frac{\delta \ln P_n}{\delta P_n} + 1 - \alpha - \beta n \right] \delta P_n$$
$$= \sum_n \left[-\ln P_n - \alpha - \beta n \right] \delta P_n$$

for each n, δP_n are independent, so the let $0 = \left[-\ln P_n - \alpha - \beta n \right] \delta P_n$, we need $-\ln P_n - \alpha - \beta n = 0$, then

$$P_n = e^{-\alpha - \beta n} = N_0 e^{-\beta n}$$

So from the maximum number of microscopic state (or so-called the maximum entropy principle), we get the most probable distribution $P_n = N_0 e^{-\beta n}$.

From the SSC game, we have the following correspondings,

| 1. Most probable distribution	Equilibrium state
2. Time-evolution of distribution	Approaching equilibrium state
3. Initial state	Nonequlibrium state

Here, we assume that:

- All microscopic states are possible, and equally weighted.

And we conclude that:

- The macroscopic configuration with maximum number of microscopic states win. It is the most probable configuration described by distribution P_n.

1.2.4 Think about this game

Game	Ideal gas	Distribution of wealth
Students	Particles	People
Points	Energy	Wealth
Playing a game between two students	Collisions of particles	Transfer of wealth
Students number is fixed	Particle number is conservation	number of people is fixed
Total # of points are fixed	Energy conservation	Wealth is conserved (pure exchange)
Most probable configuration	Equlibrium state of the system	
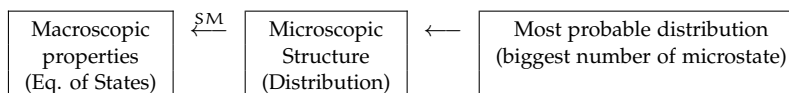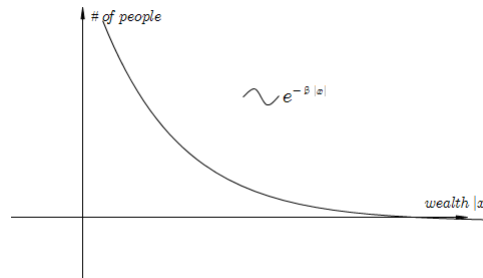
STATISTICAL MECHANICS (2ND DEFINITION) More generally, SM describe the global (macroscopic) properties of a system which consist of many interacting degree of freedom. (particles/ fields/ stocks/ people/ cars. . .). Its purpose is to deduct the macroscopic properties of the systems from their microscopic structure.

MAXWELL–BOLTZMAN DISTRIBUTION: Here n can be replaced by the energy of particles, thus the distribution is $P(E) = \exp[\alpha - \beta E]$. For free particles in 1D case, $E = \frac{1}{2}mv^2$, we get the Maxwell-Boltzman distribution, $P(v_i) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{mv_i^2}{2k_B T}}$ and $P(\mathbf{v}) = \prod_{i=1}^{3} P(v_i)$.

Let me give you a few examples:

1.2.5 Distribution of wealth

Social scientists have investigate the wealth (income and other kind of wealth) of one area of a city, or a city. They found that the distribution of wealth has the following distributions, where the horizontal axle is the wealth, vertical axle is the number of people,
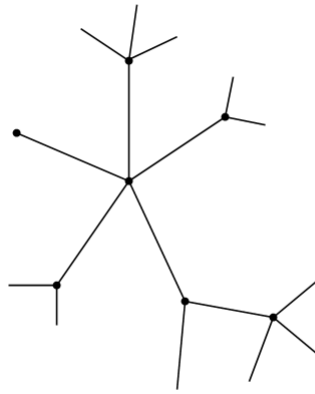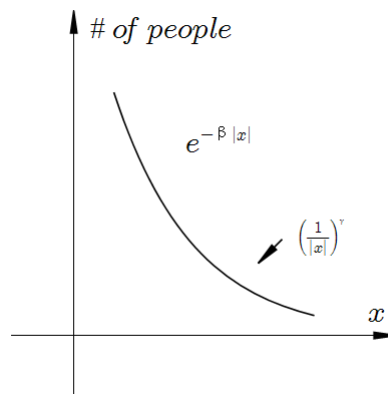
Figure 3: Each node represent one person, a connection between two nodes mean that these two people know each other.

It is found that at small x, the distribution is in forms of $e^{-\beta|x|}$ which decay very fast. But investigation found that at large value of x, P_x(number of very rich people) are not that rare, it decay as the power law.

Can any one explain why?

- Mathew Effect: Mathew Effect is the phenomena where "The richer get richer, and the poor get poorer."

- 20/80 rule: 20% of the people own 80% of the wealth.

  The 80-20 rule (The Pareto principle)

  For many events, roughly 80% of the effects come from 20% of the causes. Pareto observed in 1906 that 80% of the land in Italy was owned by 20% of the population. Common rule of thumb in bussiness: "80% of your sales come from 20% of your clients." Mathematically, the 80-20 rule is roughly followed by a power law distribution for a particular set of parameters.

1.2.6 6–degree of seperation

If two people know each other, it is called zero-degree of seperation.

If two people don't know each other, but they can build a connect by another person. It is call 1-degree of seperation.

In this word, you only need to go through 6-people to know anyone (on average).
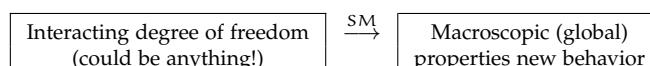
1.2.7 Econphysics

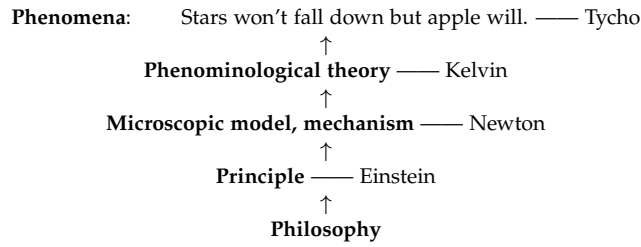Econphysics is using method of Statistical Physics to study economy.

So we get eh more general definition of SM:

Statistical Physics attempts to describe macroscopic (global) properties of the system in terms of its constituent degree of freedom. It is to describes how new behavior emerges from interaction of many degree of freedom.

More is different!

$$\boxed{\begin{array}{c} \text{Interacting degree of freedom} \\ \text{(could be anything!)} \end{array}} \xrightarrow{SM} \boxed{\begin{array}{c} \text{Macroscopic (global)} \\ \text{properties new behavior} \end{array}}$$

1.2.8 The structure of knowledge and statistical physics #

Phenomena: Stars won't fall down but apple will. —— Tycho
↑
Phenominological theory —— Kelvin
↑
Microscopic model, mechanism —— Newton
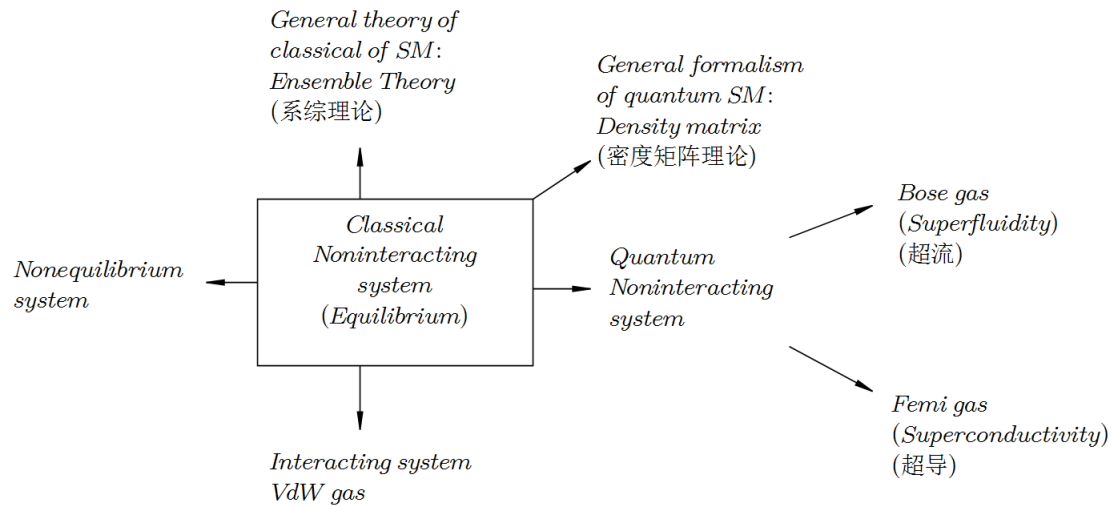↑
Principle —— Einstein
↑
Philosophy

If we view SM from a higher level, what can we get?

The structure of knowledge

1. Phenomena	Thermal phenomena
2. Phenomenological theory	↑ Thermodynamics (TD) * P, V, T; State function to represent the state of the system Eq. of state $PV = Nk_B T$
3. Microscopic theory (mechanism)	↑ Statistical Mechanics
4. Principle	↑ Information theory (complexity, entropy)

* TD is a phenomenological description of properties of macroscopic system in thermal equilibrium.

1.3 ROAD MAP OF THIS COURSE

General theory of classical of SM:
Ensemble Theory
(系综理论)

General formalism of quantum SM:
Density matrix
(密度矩阵理论)

Bose gas
(*Superfluidity*)
(超流)

Nonequilibrium system ← **Classical Noninteracting system (Equilibrium)** → *Quantum Noninteracting system*

Femi gas
(*Superconductivity*)
(超导)

Interacting system
VdW gas

- Probability: $P(x) \longrightarrow \langle f(x) \rangle$ (Equilibrium)

- Statistics: $x_i \longrightarrow P(x)$

- Random Process: Eq. of $P(x) \longrightarrow P(x)$ (Nonequilibrium)

1. Thermodynamics Review	Preparation knowledge
2.Fundamental knowledge Probability Entropy, density of state (macrostate, microstates)	
3. SM of noninteracting system (Classical & Quantum)	Macroscopic quantities $\langle O(\Gamma) \rangle$ $\uparrow$ Distribution $P(\Gamma)$ $\uparrow$ Microscopic structure $H(\Gamma), \Gamma = (\vec{p}_i, \vec{q}_i)$ (Distribution function and moments)
4. Classical SM (Ensemble Theory) Microcannonical Ensemble Cannonical Ensemble Grand Cannonical Ensemble	
5. SM of Interacting System VdW gas 1st order phase transition	
6. Quantum Statistical Mechanics Why quantum? General formalism	
7. Bosonic gas $\longrightarrow$ Superfluidity	
8. Femionic gas $\longrightarrow$ Superconductivity	
9. Nonequilibrium System	$P(\Gamma, t) \longleftarrow$ by time-dependent differential equations

1.4 PROJECT

1. 4-5 peoples form a group.

2. Find a system which consist of many individual agents.
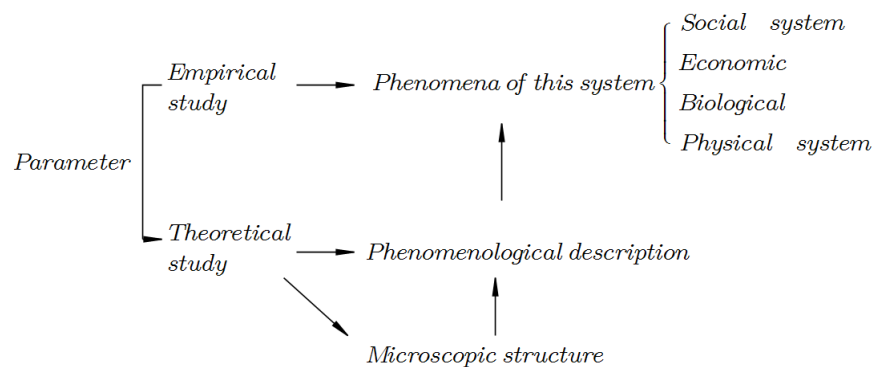
3. Write a paper & give a representation.
1st experience of doing research.

   1.
   2.
   3.

R. V

1.5 HOW DO YOU DO RESEARCH ON PHYSICS?

Physics is different from other science, three main points you need to care about:

1. Physical picture

   a) Everything has a simple, straight forward explaination. No matter how difficult, how complicated your caculation is.

   b) Two different ways to get the same results.

   c) Reproduce the derivative without refering any materials.

2. Simplicity

   The aim of science is to make difficult things understandable in a simpler way.

   a) Idealized model

   b) Typical case, limit case.

   c) Low complexity, then increase the complexity.

3. Test

   a) Limit case, typical case.

   b) Numerical simulation

   c) Experiments

1.6 HOMEWORKS

PROBLEM 1: Find a the most probable distribution P_n such that,

$$\sum_n P_n = N$$

$$\sum_n n P_n = N n_a$$

$$\sum_n n^2 P_n = N n_d^2$$

Here the most probable distribution is defined as the distribution P_n of which the following quantity

$$\ln \Omega \{P_n\} = \ln N_p! - \sum_n \ln P_n!$$

$$= \ln N_p! - \sum_n P_n \ln P_n + P_n$$

is maximized.

PROBLEM 2: For a ideal gas with distribution

9. 10

$$P(\nu) = \prod_{i=1}^{3} \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m(\nu_i - \bar{\nu}_i)^2}{2 k_B T}}$$

Please find out the state equation.

Part I

Basic Knowledge

This part contains some basic mathematical tools we used in statistical mechanics and a short review on thermal dynamics.

2 | MATHEMATICS

2.1 SUMMARY OF BASIC KNOWLEDGE

- Probability related Kardar, <Statistical Mechanics of Particles>, Chap. 2

- Physics related Liang XX ,Chap. 1

PROBABILITY

1. distribution$P(x) \longrightarrow$ moment $\langle x \rangle \longrightarrow$ characteristic function (univariate)

2. simultaneous distribution (multivariate)

3. stable distribution: Gauss and exponent. (Law of large number and Central limit theorem)

4. maximum entropy principle, entropy S definition.

5. To get the sum or integration of exponential function (Stirling Formula)

6. Gaussian Integral and Γ-integral.

PHYSICS

1. The description of the ensemble microscopic state

   - μ-Space $(\vec{r}_i, \vec{p}_i)$ $6 \times N$.

   - Γ-Space $\left(\vec{R}, \vec{Q}\right)$ $6N$.

   - Microscopic state function $\prod\limits_{i=1}^{N} \int \frac{d^D \vec{r}_i d^D \vec{p}_i}{n^D}$.

   - density of states $\int d^D \vec{k} = \int \rho(\varepsilon) d\varepsilon$.

2. common microscopic state $\vec{\varepsilon}, \vec{k}$ Free particle; Harmonic oscillator; spin

3. The description of the system microscopic state (multiparticle)$\neq$The description of the particle microscopic state(Single particle) (more think about the hypothesis of identical particles)

4. Nearly independent system.

FEYNMAN: WHAT I CAN NOT CREATE, I DON'T UNDERSTAND. He mean that, starting with a blant piece of paper and the knowledge already in his mind, he could take any theoretical result and receive it.

2.2 PROBABILITY

2.2.1 Why do we need probability in SM?

Two approaches to get the thermodynamical properties.
Kinetic theory
Using the equation of motion to track the system, and thermodynamical properties is the time average.
Ensemble theory
Ignore the actual dynamics, using distribution. (so we need probability) Probability (Statistics) made simple!

2.2.2 Random variable

Random variable x: value of throw a dice.
Outcome: $S = \{1, 2, 3, 4, 5, 6\}$
Events: Subset of outcome. $A = \{1\}$, $B = \{1, 3\}$.
Probability: $P\{i\} = \frac{1}{6}$, $P\{A\} = \frac{1}{6}$, $P\{B\} = \frac{1}{3}$.
Probability is a measurement of likeliness that an event will occur. Events are defined using sets. Probability is a mapfrom sets to numbers:

1. Positivity: $P(E) \geqslant 0$.

2. Additivity: $P(A \cup B) = P(A) + P(B)$ if $A \cap B = A\grave{o}$.

3. Normalization: $P(S) = 1$.

How to assign probability values to varies outcomes?

- Objective (experimentally): frequency

$$P(A) = \lim_{N \to \infty} \frac{N_A}{N}$$

- Subjective (theoretically): without any prior reasons, all outcomes are equally likely.

$$S = \{1, 2, 3, 4, 5, 6\}$$
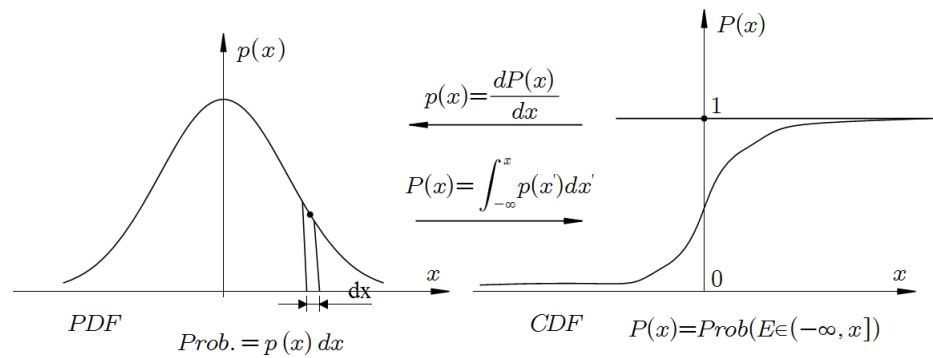
$$P\{i\} = \frac{1}{6}$$

2.2.3 One continous random variable

1. Outcome $S_x = \{-\infty < x < \infty\}$

Distribution (probability) can be characterized by

1. Cumulative Probability Function (CPF)
   & Probability Density Function (PDF)

2. Expectation & Moments

3. Characteristic Function

(1) CPF & PDF

$$p(x) = \frac{dP(x)}{dx}$$

$$P(x) = \int_{-\infty}^{x} p(x')dx'$$

$$P(x) = Prob(E \in (-\infty, x])$$

PDF $Prob. = p(x)\,dx$ *CDF*

CDF & PDF can determine each other

Ex: exponential distribution

$$f(x) = \begin{cases} \lambda e^{-\lambda x} & x \geqslant 0 \\ 0 & x < 0 \end{cases}$$

$$F(x) = \int_{-\infty}^{x} f(x')\,dx' \begin{cases} 1 - e^{-\lambda x} & x \geqslant 0 \\ 0 & x < 0 \end{cases}$$
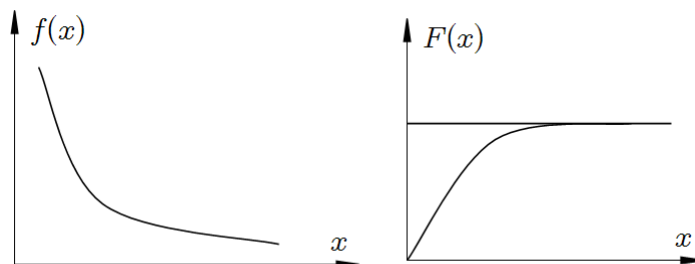
(2) Moments

$$M_n = \langle x^n \rangle = \int p(x)\,x^n dx$$

(3) Expectation Value (mean)

$$E\left(x\right) = \int_{-\infty}^{\infty} xp\left(x\right) dx$$

(4) Variation & Standard deviation

$$Var\left[x\right] = E\left[\left(x - E\left[x\right]\right)^2\right]$$
$$= E\left[x^2\right] - \left(E\left[x\right]\right)^2$$

$$\sigma = \sqrt{Var\left[x\right]}$$

(5) Expenential distribution

$$E\left[x\right] = \frac{1}{\lambda}$$
$$Var\left[x\right] = \frac{1}{\lambda^2}$$
$$E\left[x^n\right] = \frac{n!}{\lambda^n}$$

(6) Change of variables *
How to get PDF of $F\left(x\right)$ from $p\left(x\right)$ is

$$p_F\left(F\right) = Prob\left(E \subset \left(-\infty, F\right]\right) = Prob\left(E \subset \left(-\infty, x\right)\right) = p\left(x\right)$$
$$\Longrightarrow p_F\left(F\right) dF = \sum_i p\left(x_i\right) dx_i$$
$$\Longrightarrow p_F\left(F\right) = \sum_i p\left(x_i\right) \left.\left|\frac{dx}{dF}\right|\right._x$$
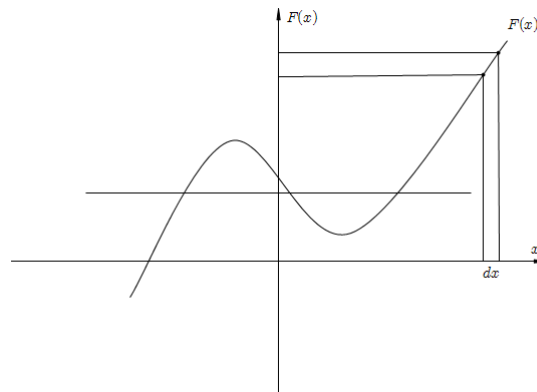
(7) Characteristic Function *

$$\widetilde{p}\left(k\right) = \langle e^{-ikx} \rangle = \int dxp\left(x\right) e^{-ikx}$$

- Fourier transform of PDF

$$p\left(x\right) = \int \frac{dk}{2\pi} \widetilde{p}\left(k\right) e^{ikx}$$
$$p\left(x\right) = \begin{cases} 1 & -1 \leqslant x \leqslant 1 \\ 0 \end{cases}$$

get $\widetilde{p}\left(k\right) =$?

- Generating function of all moments

$$\widetilde{p}\left(k\right) = \langle \sum_{n=0}^{\infty} \frac{\left(-ik\right)^n}{n!} x^n \rangle$$
$$= \sum_{n=0}^{\infty} \frac{\left(-ik\right)^n}{n!} \langle x^n \rangle$$

with all moments, you can construct characteristic function the PDF.

Exponential distribution

$$\widetilde{p}(k) = E\left[e^{-ikx}\right] = \int_0^\infty \lambda e^{-\lambda x} e^{-ikx} dx$$

$$= \int_0^\infty \lambda e^{-(\lambda+ik)x} dx$$

$$= \frac{-\lambda}{\lambda+ik} e^{-(\lambda+ik)x}\Big|_0^\infty$$

$$= \frac{\lambda}{\lambda+ik}$$

$$\langle x^n \rangle = \frac{i^n \partial^n}{\partial^n k} \widetilde{p}(k)\Big|_{k=0}$$

$$= \frac{i^n \partial^n}{\partial^n k} \left(\frac{\lambda}{\lambda+ik}\right)$$

$$= \frac{\lambda (i)^n (-i)^n n!}{(\lambda+ik)^{n+1}}$$

$$= \frac{n!}{\lambda^n}$$

$$CPF \; P(x) \xrightarrow[\text{differentiate}]{\text{integral}} PDF \; p(x) \xrightarrow{\tilde{p}(k)=\langle e^{-ikx}\rangle} CF \; \tilde{p}(k) \xrightarrow[\substack{\text{if all moments} \\ \text{are given}}]{\tilde{p}(k)=\sum_{n=0}^\infty \frac{(-ik)^n}{n!}\langle x^n\rangle \\ \text{Taylor expansion}} \langle x^n \rangle$$

2.2.4 Some distribution

- Gaussian

  PDF $\frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \longrightarrow$ CPF $\frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{x-\mu}{\sqrt{2}\sigma}\right)\right]$

- Binomial distribution

  - Tossing a coin.

    Head $P_H = 0.4$
    Tail $P_T = 1 - P_H = 0.6$

  Tossing $N = 3$ times, what is the probability to get $n = 2$ H

  $$P_N(N_A) = \binom{N}{N_A} P_A^{N_A} P_B^{N-N_A}$$

  $$\binom{N}{N_A} = \frac{N!}{N_A!(N-N_A)!}$$

2.2.5 Many Random Variable

$$\vec{x} = \{x_1, x_2, \cdots, x_N\}, d^N\vec{x} = \prod_{i=1}^N dx_i \quad \text{(Volumn elements)}$$

- If variables are independent

$$p(\vec{x}) = \prod_{i=1}^N p_i(x_i) \qquad p(x,p) = p(x)p(p)$$

- unconditional join PDF (integrate unintested variables)

$$p(x_1, x_2, \cdots, x_m) = \int \prod_{i=m+1}^{N} p(x_1, x_2, \cdots, x_N) \, dx_i \qquad p(x) = \int p(x, p) \, dp$$

- Conditional joint prob.

$$p(x_1, \cdots, x_m | x_{m+1}, \cdots, x_N) = \frac{p(x_1, \cdots, x_N)}{p(x_{m+1}, \cdots, x_N)}$$

$$p(x|p) = \frac{p(x, p)}{p(p)}$$

2.3 LAW OF LARGE NUMBER (LLN)

The average of the results obtained from a large number of trials should be close to the expected value, and will tend to become closer as more trials are performed.

2.3.1 Central limit theorem

Sum of N random varibales satisfy the Gaussian distribution as N approach infinity if the moments of each individual distribution B finite.

If the moment of each individual distribution is infinity, we get power law (Levy distribution)

$$P_\alpha(y) = \frac{1}{\pi} \sum_{n=1}^{\infty} (-1)^{n+1} \sin\left(\frac{n\pi}{2}\alpha\right) \frac{\Gamma(1 + n\alpha)}{n!} \frac{a^n}{y^{1+n\alpha}}$$

when $\alpha = 1$, $\qquad P_y = \frac{a}{\pi(y^2 + a^2)}$

$$\widetilde{P}_y(k) = -a|k|^\alpha$$

Gaussian distribution decay very fast! You can not find a person twice higher than you.

Power law distribution decay not that fast, you can easily find person 2000 times richer than you.

CENTRAL LIMIT THEOREM

If one random varibale has $\langle x \rangle = \mu$, $\langle x^2 \rangle - \langle x \rangle^2 = \sigma^2$, sum of N independent random variables. x, $\Xi = \sum_i x_i$ and setting $y = \frac{\Xi - N\mu}{\sqrt{N}}$, we have

$$\lim_{N \to \infty} P(y) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\left(\frac{y^2}{2\sigma^2}\right)}$$

$$P(\Xi) = \frac{1}{\sqrt{2\pi N\sigma^2}} e^{-\frac{(\Xi - N\mu)^2}{2N\sigma^2}}$$

The motion of a particle in 1 D, its probability of moving 1 step.

Along +x -axle is p, and moving along opposite direction is P, and at each step, the probability are independent of previous step and its position. After N step, what is the distribution of this particle's position?

1 STEP

$$\langle x \rangle = p + (1 - p)(-1) = 2p - 1$$

$$\langle x^2 \rangle = 1p^2 + (-1)^2 (1 - p) = 1$$
$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$
$$= 1 - (2p - 1)^2$$
$$= 1 - \left(4p^2 - 4p + 1\right)$$
$$= 2p(1 - p)$$

$$p_N(x) = \frac{1}{\sqrt{2\pi N 2p(1-p)}} e^{-\frac{(x-(2p-1)N)^2}{4Np(1-p)}}$$

2.3.2 Rule of large numbers

Physical quantities vs N

- Intensive quantities. $T, \quad \vec{B}, \quad P$

- Extensive quantities. $E, \quad S, \quad V, \quad \vec{M}$

- Exponential dependence. $\mathcal{O}(\exp(N\phi))$
  is encounted in enumerating discrete micro-states, or computing availiable Volumes in phase space.

$$S = \sum_{i=1}^{\aleph} \varepsilon_i$$

$$0 \leqslant \varepsilon_i \sim \mathcal{O}(\exp(N\phi_i)) \qquad \aleph \propto N^p$$

Approximation

$$0 \leqslant \varepsilon_i \leqslant \varepsilon_{max}$$
$$\varepsilon_{max} \leqslant S \leqslant \aleph \varepsilon_{max}$$
$$\frac{\ln \varepsilon_{max}}{N} \leqslant \frac{\ln S}{N} \leqslant \frac{\ln \varepsilon_{max}}{N} + \frac{\ln \aleph}{N}$$

For $\aleph \propto N^p$

$$\frac{\ln \aleph}{N} = \frac{p \ln N}{N} \overset{N\to\infty}{\longrightarrow} 0$$

1.
2.

$$\lim_{N\to\infty} \frac{\ln S}{N} = \frac{\ln \varepsilon_{max}}{N} = \phi_{max}$$

2.3.3 Saddle point integral

$$I = \int \exp(N\phi(x))\, dx$$

Approximation

$$I = \int \exp\left\{ N\left[\phi(x_{max}) - \frac{1}{2}\left|\phi''(x_{max})\right|(x-x_{max})^2 + \cdots \right] \right\} dx$$

$$= e^{N\phi(x_{max})} \int \exp\left[-\frac{N}{2}\left|\phi''(x_{max})\right|(x-x_{max})^2 \right] dx$$

$$\cong \sqrt{\frac{2\pi}{N\left|\phi''(x_{max})\right|}} e^{N\phi(x_{max})}$$

Method of steepest decent

2.3.4 Stirling formula

Rewrite N! by a integral

$$\int_0^\infty x^N e^{-\alpha x} dx = \frac{N!}{\alpha^{N+1}}$$

$$\int_0^\infty e^{-\alpha x} dx = \frac{1}{\alpha}$$

$\alpha = 1$

$$\Gamma(N+1) = N! = \int_0^\infty x^N e^{-x} dx$$

$$= \int \exp[N\phi(x)]\, dx$$

$$\phi(x) = \ln x - \frac{x}{N}$$

$$0 = \frac{d\phi}{dx}\bigg|_{x_{max}} = \frac{1}{x_{max}} - \frac{1}{N} = 0 \qquad x_{max} = N$$

$$\frac{d^2\phi}{d^2x} = -\frac{1}{x_{max}^2} = -\frac{1}{N^2}$$

$$N! = \int \exp\left[N\phi(x_{max}) - \frac{1}{2}\frac{1}{N^2}(x - x_{max})^2\right] dx$$

$$= \int \exp\left[N\ln N - N - \frac{1}{2N^2}(x - N)^2\right] dx$$

$$\approx N^N e^{-N}\sqrt{\frac{2\pi}{N|-1/N^2|}}$$

$$= N^N e^{-N}\sqrt{2\pi N}$$

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

2.4 ENTROPY

Information contents of a probability distribution.

- A string with length N using M possible letter $N\ln_2 M$.

A	B		A	B	C	D
0	1		00	01	10	11
$\ln_2 2 = 1$				$\ln_2 4 = 2$		

or $g = M^N$ total # of possible string

$$\ln_2 g = \ln_2 M^N = N\ln_2 M$$

- discrete set of outcomes $S = \{x_i\}, \quad i = 1, 2, \cdots, M$ occurring with probability P_i.
A message from N indept outcomes of random varibales. There are M possibilities for each character in this message expect the message contain $N_i = N P_i$ occur of each symbol.
Number of typical messages correspords to the number of ways of arranging the $\{N_i\}$ occurences of $\{x_i\}$

$$g = \frac{N!}{\prod\limits_{i=1}^{M} N_i!}$$

EX:

$\{x_i\} = \{1, 2, 3\}, \qquad M = 3.$

$N = 100 \qquad P_i = \{30\%, 30\%, 40\%\}$

1. $100 \times 30\% = 30$
2. $100 \times 30\% = 30$
3. $100 \times 40\% = 40$

30 ones	30 twos	40 threes

$$N_1 + N_2 + N_3 = N$$

$$\binom{N}{N_1}\binom{N - N_1}{N_2}\binom{N - N_1 - N_2}{N_3}$$

$$= \frac{N}{N_1!(N - N_1)!}\frac{(N - N_1)!}{N_2!(N - N_1 - N_2)!}\frac{(N - N_1 - N_2)!}{N_3!(N - N_1 - N_2 - N_3)!}$$

$$= \frac{N!}{N_1!N_2!N_3!}$$

$$\ln_2 g = \ln_2 \frac{N!}{\prod_{i=1}^{M} N_i!}$$

$$= \ln_2 \frac{N!}{(N_{P_i})!}$$

$$\approx \ln_2 \frac{N^N}{\prod_{i=1}^{M} (N_{P_i})^{N_{P_i}}}$$

$$= N \ln_2 N - \sum_{i=1}^{M} (N_{P_i}) \ln_2 (N_{P_i})$$

$$= N \ln_2 N - \sum_{i=1}^{M} N_{P_i} \ln_2 N - \sum_{i=1}^{M} N_{P_i} \ln_2 P_i$$

$$= -N \sum_{i=1}^{M} P_i \ln_2 P_i$$

So we need $N\left(-\sum_{i=1}^{M} P_i \ln_2 P_i\right)$ bits of information.

For uniform distribution $P_i = \frac{1}{M}$

$$N\left(-\sum_{i=1}^{M} \frac{1}{M} \ln_2 \frac{1}{M}\right)$$

$$= N\left(\sum_{i=1}^{M} \frac{1}{M}\right) \ln_2 M$$

$$= N \ln_2 M$$

It is the most chaotic one. It is like nothing is told about the possible distribution.

If P_i is a δ-like function

$$P_i = \begin{cases} 1 & i = k \\ 0 & i \neq k \end{cases}$$

then

$$N\left(-\sum_{i=1}^{M} P_i \ln P_i\right) = N(-1 \ln_2 1) = 0$$

It is the most determined one. It is a certain case.

So the information content of a probability distribution is

$$I[\{P_i\}] = \ln_2 M + \sum_{i=1}^{M} P_i \ln P_i = \ln_2 M - S$$

when P_i is uniform distribution $\qquad I = 0$.

when P_i is determmistic $\qquad I = \ln_2 M$.

we can define an entropy for any probability as

$$S = -\sum_{i=1}^{M} P(i) \ln P(i)$$

$$= -\langle \ln P(i) \rangle$$

The most important formular in SM!

S take minimal value of 0, if the distribution is a delta function. And maximal value of $\ln_2 M$ if the distribution is uniform. $\qquad P(i) = \frac{1}{M}$.

S is a measure of dispersity (disorder) of the distribution.

From the deriving process of S, we know, we actually calculate the total number of possible combination generated by the letters $\{N_{P(i)}\}$ from distribution $P(i)$, and that is similar to the Boltzman's relation

$$S = k_B \ln_2[W]$$

where W is the total number of possible microstates. And the only differences are two: one is the constant factor k_B which grantee the correct dimension of physical entropy and the second we take log of 2 instead of e. So we know the information entropy for one distribution has the same meaning of the physical entropy.

PROPERTIES:

A one-to-one mapping to $f_i = F(x_i)$ leaves the entropy unchanged.

A many-to-one mapping make the distribution more ordered and decrease S

if

$$
\begin{array}{ccc}
x_1, x_2 & \longrightarrow & f \\
P_1, P_2 & & P_1 + P_2
\end{array}
$$

$$
\begin{aligned}
\triangle S &= -\left[P_1 \ln P_1 - P_2 \ln P_2\right] + \left[-\left(P_1 + P_2\right) \ln \left(P_1 + P_2\right)\right] \\
&= P_1 \ln \frac{P_1}{P_1 + P_2} + P_2 \ln \frac{P_2}{P_1 + P_2} \\
&< 0
\end{aligned}
$$

A one-to-many mapping will increase S.

ESTIMATION OF A DISTRIBUTION FROM MAXIMUM ENTROPY PRINCIPLE

Entropy S can be used to quantify subjective estimation of probabilities. In the absence of any information, the best unbiased estimate is that all M outcomes are equally likely. This is the distribution of maximum entropy!

If additional information is availiable, the unbiased estimate is obtained by maximizing the entropy subject to constraints imposed by this information.

EX: If we know

$$\langle x \rangle = \mu$$

$$\langle x^2 \rangle - \langle x \rangle^2 = \sigma^2 \implies \langle x^2 \rangle = \sigma^2 + \mu^2$$

what is the $P(x)$?

$$S\left(\alpha, \beta, \gamma, \{P_i\}\right) = -\sum_i P(i) \ln P(i) - \alpha\left(\sum_i P_i - 1\right) - \beta\left(\sum_i P_i x_i - \mu\right) - \gamma\left(\sum_i P_i x_i^2 - \left(\sigma^2 + \mu^2\right)\right)$$

$$\frac{\delta S}{\delta P(i)} = -\ln P(i) - 1 - \alpha - \beta x_i - \gamma x_i^2 = 0$$

$$P(i) = e^{-\alpha - \beta x_i - \gamma x_i^2}$$

and using

$$
\begin{aligned}
\langle x_i \rangle &= \mu \\
\langle x_i^2 \rangle &= \left(\sigma^2 + \mu^2\right) \qquad \text{to determine } \alpha, \beta, \gamma \\
\langle 1 \rangle &= 1
\end{aligned}
$$

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

If information is $\quad \langle F(x) \rangle = f$

then $\qquad P(x) \propto e^{-\beta F(x)}$

2.5 GAUSSIAN INTEGRAL AND Γ–INTEGRAL

$$I = \int_0^\infty e^{-x^2} dx = ?$$

$$\int_{-\infty}^\infty \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx = 1$$

$$I = \int_{-\infty}^\infty e^{-x^2} dx = 2 \int_0^\infty e^{-x^2} dx$$

$$I^2 = \int_{-\infty}^{\infty} e^{-x^2} dx \int_{-\infty}^{\infty} e^{-y^2} dy$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy$$

$$= \int_{0}^{\infty} r dr \int_{0}^{2\pi} d\theta e^{-r^2} \quad \text{Polar coordinate } dx dy = r dr d\theta, \quad r^2 = x^2 + y^2$$

$$= 2\pi \int_{0}^{\infty} \frac{1}{2} dr^2 e^{-r^2} = 2\pi \frac{1}{2} e^{-r^2} \Big|_{0}^{\infty} = \pi$$

$$I = \int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

Let $y = \frac{x-\mu}{\sqrt{2\sigma^2}}$, we can get $dx = \sqrt{2\sigma^2} dy$, so

$$\int_{-\infty}^{\infty} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx$$

$$= \int_{-\infty}^{\infty} \sqrt{2\sigma^2} e^{-y^2} dy$$

$$= \sqrt{2\pi\sigma^2}$$

$$I_n = \int_{0}^{\infty} x^n e^{-ax^2} dx \quad y = \sqrt{a}x \to x = \frac{y}{\sqrt{a}} \to dy = \sqrt{a} dx$$

$$I_n = \int_{0}^{\infty} \frac{y^n}{a^{\frac{n}{2}}} e^{-y^2} \frac{dy}{\sqrt{a}}$$

$$= \frac{1}{a^{(1+n)/2}} \int_{0}^{\infty} y^n e^{-y^2} dy$$

$$I_0 = \frac{1}{a^{\frac{1}{2}}} \int_{0}^{\infty} y^0 e^{-y^2} dy = \frac{\sqrt{\pi}}{2} \frac{1}{a^{\frac{1}{2}}}$$

$$I_1 = \frac{1}{a} \int_{0}^{\infty} y e^{-y^2} dy = \frac{1}{2a} \int_{0}^{\infty} e^{-y^2} dy^2 = \frac{1}{2a}$$

$$I_n = \frac{1}{a^{(1+n)/2}} \int_{0}^{\infty} y^n e^{-y^2} dy$$

$$= \frac{1}{a^{(1+n)/2}} \int_{0}^{\infty} y^{n-1} e^{-y^2} dy^2 \frac{1}{2}$$

$$= \frac{1}{a^{(1+n)/2}} \int_{0}^{\infty} y^{n-1} de^{-y^2} \left(-\frac{1}{2}\right)$$

$$= \frac{1}{a^{(1+n)/2}} \left[e^{-y^2} y^{n-1} \Big|_{0}^{\infty} - \int_{0}^{\infty} e^{-y^2} (n-1) y^{n-2} dy \right] \left(-\frac{1}{2}\right)$$

$$= \frac{n-1}{2} \frac{1}{a^{(1+n)/2}} \int_{0}^{\infty} y^{n-2} e^{-y^2} dy$$

$$= \left(\frac{n-1}{2a}\right) \int_{0}^{\infty} x^{n-2} e^{-ax^2} dx$$

$$= \left(\frac{n-1}{2a}\right) I_{n-2}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{(2n-1)}{2} \frac{(2n-3)}{2} \cdots \frac{3}{2} \cdot \frac{1}{2} \frac{\sqrt{\pi}}{a^n a^{\frac{1}{2}}}$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2 a^{n+1}}$$

$$\Gamma(\alpha) = \int_0^\infty x^{\alpha-1} e^{-x} dx$$

$$\Gamma(\alpha+1) = \alpha \Gamma(\alpha)$$

$$\Gamma(1) = 1$$

$$\Gamma(n+1) = n!$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

$$\Gamma\left(n+\frac{1}{2}\right) = \frac{(2n-1)!}{2^n} \sqrt{\pi}$$

2.6   HOMEWORKS

PROBLEM 1:   At time t_n, the *stock price* of a certain stock is P_n. Then the *return* of such stock at time t_n is defined as,

$$r_n = \ln \frac{P_n}{P_{n-1}} \approx \frac{P_n}{P_{n-1}} - 1$$

We don't know the distribution of r_n, but we know that r_n are independent of each other and that

$$\langle r_n \rangle = \mu$$
$$\langle r_n^2 \rangle - \langle r_n \rangle^2 = \sigma^2$$

Use the central limit theorem to calculate the distribution of stock price at t_N when N is very large. (Hint: Calculate the distribution of R_N defined as

$$R_N = \ln \frac{P_N}{P_0} = \ln \frac{P_N}{P_{N-1}} \frac{P_{N-1}}{P_{N-2}} \cdots \frac{P_2}{P_1} \frac{P_1}{P_0} = \sum_{n=1}^N r_n.$$

And then get $P_N = P_0 \exp(R_N)$.)

PROBLEM 2:   Find a the most probable distribution $P(x)$ such that,

$$\int P(x) dx = 1$$

$$\langle x \rangle = \int P(x) x \, dx = \mu$$

$$\langle x^2 \rangle - \langle x \rangle^2 = \int P(x) x^2 dx - \left(\int P(x) x \, dx \right)^2 = \sigma^2$$

Here the most probable distribution is defined as the distribution $P(x)$ of which the entropy

$$S = - \int P(x) \ln P(x) dx$$

is maximized.

Compared the result with the problem 1 of chapter 1. What do you find?

PROBLEM 3:   For different $N = 1, 10, 100, 1000$, numerically calculate the following functions,

$$\sum_{n=1}^{100} \exp\left[N/n^2\right]$$

Compared it with the function $\exp[N]$ (the $n = 1$ term, the largest term, in the above function), what do you find?

3 THERMALDYNAMICS

3.1 PHENOMENOLOGICAL THEORY

> Thermodynamics is a phenomenological description of properties of macroscopic systems in thermal equilibrium

HOW? (How phenomenological theory are constructed.)

1. Idealize the system under study as much as possible. For example: ideal gas.

2. Describe the system by a number of thermodynamic coordinates or state functions.
(P, V) (μ, N) (J, x) (T, S)

3. Find the relationship between state functions, which is described by the laws of thermodynamics. (By empirical observations)

WHAT? laws of thermodynamics

TWO KIND OBJECTS IN THERMAL DYNAMICS

1. Carnot engine

2. gas (ideal gas; VdW gas)

3.2 LAW OF THERMAL DYNAMICS

3.2.1 1st law: What is heat?

$d E = d Q + d W$

$$\bcancel{d} W = \sum_i J_i d x_i \, , \, d Q = T d S$$

It is used to define heat. Heat is a kind of energy
J_i is generalized force; x_i is generalized displacement.

	J_i	x_i
Wine	Tension L	Length x
Film	Surface tension S	Area A
Fluid	Pressure $-P$	Volume V
Magnet	Magnetic field H	magnetization M
Dielectric	Electric field E	Polarization $\mathbb{P}$
Chemical reaction	Chemical potential μ	Particle number N
Heat	Temperature T	Entropy S

- Intensive quantities: It is independent of system size.

  J_i are intensive quantities.

- Extensive quantities: It is proportional to system size.

  x_i are extensive quantities

3.2.2 0-th Law: What is at equilibrium?

0-TH LAW : When two systems are in contact (interact with each other) $J_i^1 = J_i^2$.

3.2.3 2nd Law: How do we define the "quality" of energy?

2ND LAW : Heat (thermal energy) is a special kind of energy. It has "low quality". Certain amount of heat can not be transfered into work completely.

KELVIN'S STATEMENT: No process is possible whose sole result is the complete conversion of heat into work.

CLAUSIUS'S STATEMENT: No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

How can we define the "quality" of the energy? $\longrightarrow$ entropy.
All other energy other than heat has zero entropy.

$$d S = \frac{d Q}{T}$$
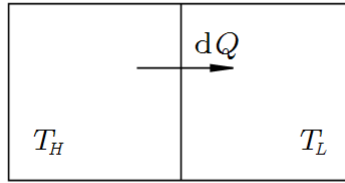
Figure 4: Heat transfer between two objects

MAXIMUM ENTROPY PRINCIPLE: A closed system will approach to a state of which the enropy is maximized. Then it arrives the thermoequilibrium.

$$dS_{ToT} = dS_L + dS_R = -\frac{dQ}{T_H} + \frac{dQ}{T_L}$$
$$= dQ\left(-\frac{1}{T_H} + \frac{1}{T_L}\right) \geqslant 0$$

So heat transfer from hotter body to colder one!

$dS_{ToT} = 0$ for reversible process

3.2.4 3rd Law:

3RD LAW: $dS = \frac{dQ}{T}$ define the change of entropy. To get a absolute value of entropy, you need a referencing point, at $T = 0$, the entropy of arbitrary system is zero.

$$S(T) = S(0) + \int_0^T \frac{dQ}{T'} dT'$$

3.3 RESPONSE FUNCTIONS

Response functions useful method to characterizing the macroscopic behavior of a system. They are experimentally measured from the changes of thermodynamic coordinates with external probes.

HEAT CAPACITIES:

$$C_V = \left.\frac{dQ}{dT}\right|_V = \left.\frac{dE - dW}{dT}\right|_V = \left.\frac{dE + PdV}{dT}\right|_V = \left.\frac{dE}{dT}\right|_V$$

$$C_V = \left.\frac{dQ}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{dE}{dT}\right|_P + \left.P\frac{\partial V}{\partial T}\right|_P$$

FORCE CONSTANT:

$$\chi_T = \left.\frac{1}{V}\frac{\partial M}{\partial B}\right|_T$$

THERMAL RESPONSE

$$\alpha_P = \left.\frac{1}{V}\frac{\partial V}{\partial T}\right|_P$$

3.4 MAXWELL RELATIONS

MAXWELL Relation
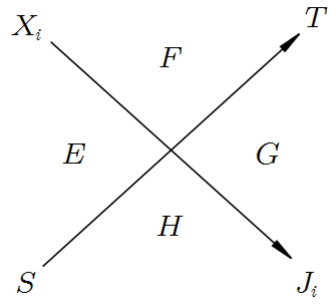
$$
\begin{cases}
dE &= J_i dx_i + T dS \\
dF &= J_i dx_i - S dT \\
dG &= -S dT - x_i dJ_i \\
dH &= -x_i dJ_i + T dS
\end{cases}
$$

What thermodynamical coordinate you used?
Which thermal potential you used?

Part II

Noninteracting Many–particle Systems

4 | DISTRIBUTIONS

4.1 HOW TO DESCRIBE A MANY–PARTICLES SYSTEM?

- Microscopic

  Hamiltonian:

  $$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} U\left(\vec{r}_i - \vec{r}_j\right)$$

  Equation of motion

  $$\begin{cases} \dot{\vec{p}}_i = \frac{\partial H}{\partial \vec{r}_i} & N \times 3 \\ \dot{\vec{r}}_i = -\frac{\partial H}{\partial \vec{p}_i} & N \times 3 \end{cases}$$

  Two approaches

$\Gamma - Space$	$p = (\vec{p}_1, \vec{p}_2, \cdots, \vec{p}_N)$
6N	$r = (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$

  The whole system is represented by 1 point in $6N$ dimensional space

  | $\mu - Space$ | $(\vec{p}_i, \vec{r}_i)$ |

  Each particles is represented by 1 point in 6D space.
  The whole system is represented by N points.

4.1.1 Γ–Space —— 6N D space for arbitrary system

$$p = (\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$$

$$r = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$
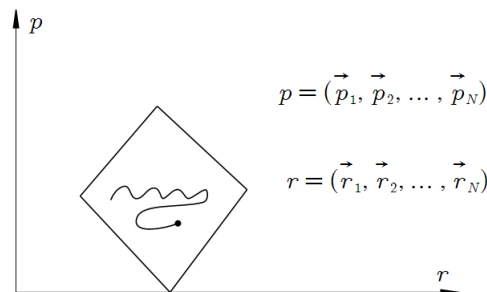
1. 1 point in 6N dimensional space "representing point"

2. The Dynamics of the system is represented by a "trajectory"
   Because of atomic collisions, the trajectory is jagged and exceedly sensitive to initial condition.

3. Because

   - We don't know the initial microscopic state the system

   - Or after a long time, the system will approach a equlilibrium state. (No change in macroscopic states, but still change in microscopic states or one macrostate corresponds to many microstates)

We need a phase space "density" instead of a specific trajectory to charocterize the system.

$\rho(r, p, t) \Longleftrightarrow$ distribution function

$\begin{cases} \text{from Eq. of motion for } r \& p \\ \text{initial density } \rho(r, p, t_0) \end{cases}$

$\Longrightarrow \rho(r, p, t) \longrightarrow$ | Kinetic theory | Nonequilibrium SM

Kinetic theory studies the macroscopic properties of large number of particles, starting from their (classical) equation of motion. $\rho(r, p, t)$

After a long time, the system approach a stationary distribution

$\rho(r, p) \longrightarrow$ | Emsemble theory |

All physical quantity are just the expectation values of certain physical operator on $\rho\,(r,p,t)$

$$A = \langle A\,(r,p)\rangle_{\rho(r,p,t)}$$

$\rho\,(r,p,t)\,dp\,dr/h^{3N} =$ Number (ensembles) of system in $dp\,dr$ at time t.
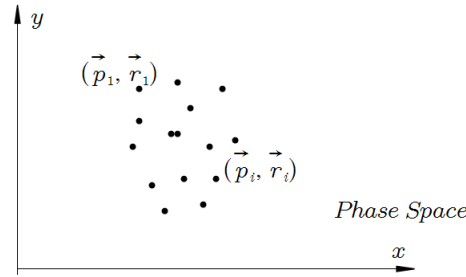$(dp\,dr/h^{3N} = d^{3N}p\,d^{3N}r/h^{3N})$

$$\text{probability density} = \frac{\rho\,(r,p,t)}{\int \rho\,(r,p,t)\,dp\,dr/h^{3N}}$$

The emsemble average of a physical quantity is

$$\langle O \rangle = \frac{\int \rho\,(r,p,t)\,O\,(r,p)\,dp\,dr/h^{3N}}{\int \rho\,(r,p,t)\,dp\,dr/h^{3N}}$$

4.1.2 μ-Space —— 6 D Space for free particle system

The description is good for free particle system or week interacting system (Nearly Independent Particles)

1. Each particle is represented by 1 points.
   The whole system is represented by N-points.
   They forms a "cloud".

2. As time evolues, these points move and collide with each other.
   The distribution of clould characterize the whole system. $f\,(\vec{p},\vec{r},t)$

$$\longrightarrow \text{ideal gas} \begin{cases} \text{Classical} \\ \text{Quantum} \begin{cases} \text{Bose} \\ \text{Fermion} \end{cases} \end{cases}$$

   or nearly independent particles.

$f\,(\vec{p}_\lambda,\vec{r}_\lambda,t)\,d^3\vec{p}_\lambda d^3\vec{r}_\lambda = n_i$(occupation number), distribution function is the occupation number per unit volume.

$$\begin{cases} \sum_\lambda n_\lambda = N \\ \sum_\lambda n_\lambda \varepsilon_\lambda = E \end{cases}$$

can be rewritten as

$$\begin{cases} \int f\,(\vec{p},\vec{r},t)\,d^3\frac{\vec{p}d^3\vec{r}}{h^3} = N \\ \int f\,(\vec{p},\vec{r},t)\,\frac{\vec{p}^2}{2m}\frac{d^3\vec{p}d^3\vec{r}}{h^3} = E \end{cases}$$

if $f\,(\vec{p},\vec{r},t)$ is independent of $\vec{r}$

$$\int f\,(\vec{p},t)\,d^3\vec{p}d^3\vec{r}/h^3 = V\int f\,(\vec{p},t)\,d^3\vec{p}/h^3 = N$$

$$\begin{cases} \int f\,(\vec{p},t)\,\frac{d^3\vec{p}}{h^3} = \frac{N}{V} \\ \int f\,(\vec{p},t)\,\frac{\vec{p}^2}{2m}\frac{d^3\vec{p}}{h^3} = \frac{E}{V} \end{cases}$$

For ideal gas (classical), we know

$$f\,(\vec{p},t) = \frac{N}{V}\left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3 e^{-\frac{\vec{p}}{2m k_B T}}$$

4.2 THREE TYPICAL SINGLE PARTICLE STATES

(1) Free particle

- 1D case

$$\begin{cases} H = \dfrac{\vec{p}^2}{2m} = \dfrac{-\hbar^2}{2m}\dfrac{d^2}{dx^2}, & H\phi = \varepsilon\phi \\ \text{periodic boundary condition (PBC)} & \text{eigen problem} \end{cases}$$

$$k_x = \frac{2\pi}{\lambda} = \frac{2\pi n_x}{L}, \qquad (L = n_x\lambda), \quad n_x = 0, \pm 1, \pm 2, \cdots$$

Solution:

$$\begin{cases} \phi(k_x) = \dfrac{1}{\sqrt{L}}e^{ik_x x} & \text{(method of undetermined coefficients)} \\ \varepsilon(n_x) = \dfrac{p_x^2}{2m} = \dfrac{2\pi^2\hbar^2}{m}\dfrac{n_x^2}{L^2} \end{cases}$$

energy difference between two near energy levels is

$$\triangle\varepsilon_{n_x} = \varepsilon_{n_x+1} - \varepsilon_{n_x} = \frac{2\pi^2\hbar^2}{m}\frac{2n_x+1}{L^2}$$

- 3D case

$$\varepsilon_n = \sum_i \frac{p_i^2}{2m} = \frac{2\pi^2\hbar^2}{m}\frac{n_x^2 + n_y^2 + n_z^2}{L^2}, \qquad n_i = 0, \pm 1, \pm 2, \cdots$$

energy degeneracy is complicated.

In solid

$$k_x, k_y, k_z \in [-\pi, \pi] \qquad \text{continous}$$

$$\varepsilon(k_x, k_y, k_z) = \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m} \qquad \int |\phi(\vec{k}, x)|^2 dV = 1$$

$$\phi(\vec{k}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{x}} \qquad \text{Box normalization}$$

$$\sum_{n_x} f(n_x) = \sum_{n_x} (n_x + 1 - n_x) f(n_x)$$

$$= \frac{L_x}{2\pi} \sum_{k_x} \left(k_{n_x+1} - k_{n_x}\right) f(n_x)$$

$$= \frac{L_x}{2\pi} \int dk_x \tilde{f}(k_x)$$

$$\sum_{n_x n_y n_z} f(n_x, n_y, n_z) = \frac{L_x L_y L_z}{(2\pi)^3} \int dk_x dk_y dk_z \tilde{f}(\vec{k})$$

$$= \frac{V}{(2\pi)^3} \int f(\vec{k}) d^3\vec{k}$$

(2) Linear harmonic oscillator

$$H = \frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2\vec{r}^2, \quad H\phi = \varepsilon\phi, \quad \lim_{r\to\infty}\phi(r) = 0$$

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \qquad n = 0, 1, 2, \cdots$$

$$\triangle\varepsilon_n = \varepsilon_{n+1} - \varepsilon_n = \hbar\omega$$

The energy distributed uniformly.

$$\begin{array}{ll} \overline{\quad\quad} & \left(n + \frac{1}{2}\right)\hbar\omega \\ \vdots & \\ \overline{\quad\quad} & \frac{3}{2}\hbar\omega \\ \overline{\quad\quad} & \frac{1}{2}\hbar\omega \\ \overline{\quad\quad} & 0 \end{array}$$

(3) Electron spin

$$H = -\vec{\mu}\cdot\vec{B} = -\mu B\cos\theta$$

$$\vec{\mu} = -\frac{e}{m}\vec{S}$$

$$\varepsilon_e = -\vec{\mu} \cdot \vec{B} = \pm\frac{e\hbar}{2\,m}B \qquad \text{descrete and finite energy level}$$

$\vec{\mu}$ magnetic moment of one electron.

(4) Rotor

4.3   NUMBER OF MICROSTATE IN μ SPACE (CLASSICAL MECHANICS)
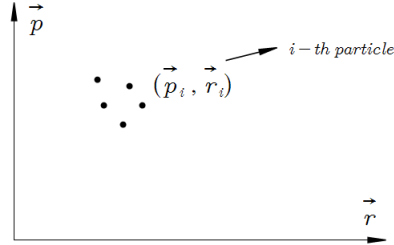
Motion in $(\vec{p}, \vec{r})$ (μ-Space) are continous, so the number of state are uncountable. Real number are uncountable. Natural number are countable.

But due to Heisenberg uncertainty principle, $\triangle p_x \triangle x \geqslant \hbar$, so a volume h in μ-Space represent.

- 1 microstate of single particle

  $\triangle x \sim L$

  $\triangle p_x = \hbar\triangle k_x = \hbar\left[\frac{2\pi(n_x+1)}{L} - \frac{2\pi n_x}{L}\right] = \frac{2\pi\hbar}{L}$

  $\triangle p_x \triangle x \sim 2\pi\hbar = h$

  So in p_x- x plane, a microstate corresponds a space with volume h.

  So the total possible microstate is $\int \frac{dp_x dx}{h}$.

- 3D

$$\int \frac{dp_x dx dp_y dy dp_z dz}{h^3} = \int \frac{d^3\vec{p}\,d^3\vec{r}}{h^3}$$

3D N-particle

$$\prod_{i=1}^{N} \int \frac{d^3\vec{p}_i d^3\vec{r}_i}{h^3} = \frac{1}{h^{3N}}\prod_{i=1}^{N}\int d^3\vec{p}_i d^3\vec{r}_i$$

For example: A free particle is with momentum inside the domain $\vec{p} \longrightarrow \vec{p} + d\vec{p}$, then find out the microstate of such particle.

$$\frac{1}{h^3}dp_x dp_y dp_z \int dx dy dz = \frac{V}{h^3}\int dp_x dp_y dp_z$$

If its momentum $\vec{p}$ is inside the domain

$$p \longrightarrow p + dp, \qquad p = |\vec{p}|$$

what is the number of microstate?

$$\frac{1}{h^3}\int_{p}^{p+dp} dp_x dp_y dp_z \int dx dy dz$$

$$= \frac{V}{h^3}\int_{p}^{p+dp} p^2 dp \int_{0}^{\pi}\sin\theta d\theta \int_{0}^{2\pi} d\varphi$$

$$= \frac{4\pi V}{h^3}p^2 dp$$

$$\equiv g(p)\,dp$$

$g(p)$ is defined as density of state (DoS) in momentum.

DoS is a very important concept in SM. $\vec{p} = \hbar \vec{k}$

$$\int f(\varepsilon)\,d\varepsilon \Longrightarrow \int g(p)\,f(\varepsilon(p))\,dp$$

$g(\varepsilon)$ *a function which reflect the system properties*

$\varepsilon = \dfrac{p^2}{2m}$
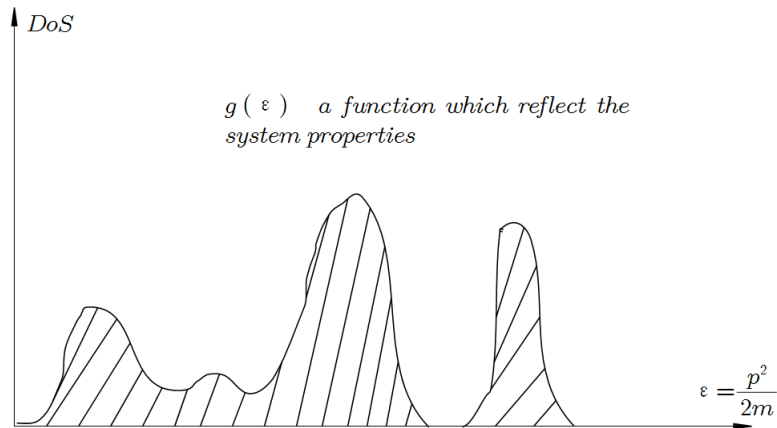
4.4   THE MICROSTATE OF A MANY–PARTICLE SYSTEM

$\displaystyle\prod_{i=1}^{N}$ The microstate of i-th particle (particles are independent of each other)	$\neq$	The microstate of N-particle system

"=" is valid only at classical mechanics.

"$\neq$" at the case of Quantum Mechanics.

EX: 2 particle, 2 state

CM:

$4-states$

QM: Particles are inclistinguishable, if they are overlap in space.

Boson $3-states$

same particles can occupy the same state

wave function overlap

$$\text{Fermion} \qquad \overline{\quad\circ\quad} \qquad 1-state$$
$$\overline{\quad\circ\quad}$$
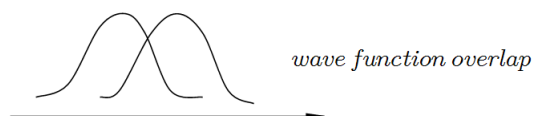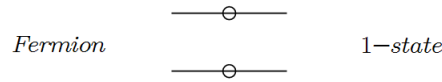
Same particles can not occupy the same state

Pauli Exlusion Principle

If particles are localized and they can not overlap with each other in space. They are distinguishable. The are just like classical particle.

localized particles   *delocalized particles*
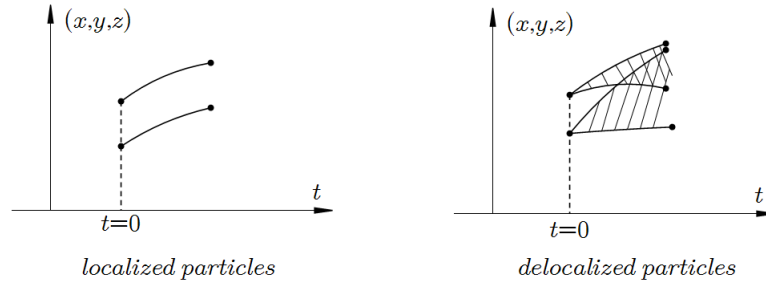
4.5 NEARLY INDEPENDENT PARTICLE SYSTEM (NON-INTERACTING PARTICLE SYSTEM)

A system consist of particles which are free to move in space except the collisions between themselves. Collisions here make them approach to equilibrium.

4.5.1 Equal Probability Principle

$$\boxed{\text{microstates}} \quad \xrightarrow{\text{statistical approach}} \quad \boxed{\text{macrostates}}$$
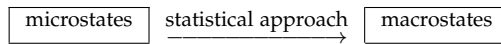
$(\vec{p}_i, \vec{r}_i) \qquad$ μ-Space
$(p, r) \qquad$ Γ-Space $\longrightarrow$ govered by Eq. of motion
$N \sim 10^{23} \qquad 6N \sim 6 \times 10^{23}$ degree of freedom
State function$(P, V, \mu, N, T, S) \longrightarrow$ govered by Eq. of states (5-6 degree of freedom)
There exist many-to-one mapping between microstate and macrostate.

$$\boxed{\begin{array}{c}\text{microstate} \\ M\end{array}} \quad \longrightarrow \quad \boxed{\begin{array}{c}\text{macrostate} \\ 1\end{array}}$$
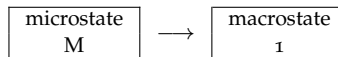
If given a macrostate, what is the microstate? They are all possible and the probability of each possible microstate are equal. (Equal Probability Principle)

It can be "derived" from Maximum Entropy Principle.

$P(x)$ is the probability of possible state x

$$S = -p(x)\ln p(x)$$

$$\mathcal{L} = S - \alpha \left(\int p(x)\,dx - 1 \right)$$

$$\frac{\partial \mathcal{L}}{\partial p(x)} = -\ln p(x) + 1 - \alpha = 0$$

$$p(x) = e^{1-\alpha} = \frac{1}{const} \qquad \text{uniform distribution}$$

All possible states (x) have equal probability.

4.5.2 The most probable distribution for distinguishable particle system (classical system)

A nearly independent particle system.

Energy is conserved and it's the sum of energy of each individual particle. (Interaction energy is ignored!)

$$E = \sum_{i=1}^{N} \tilde{\varepsilon}_i$$

If the particles have energy level as $\varepsilon_1, \varepsilon_2, \cdots, \varepsilon_\lambda, \cdots$

And the degeneracy for each energy level is $g_1, g_2, \cdots, g_\lambda, \cdots$

Define $n_1, n_2, \cdots, n_\lambda, \cdots$ as the occupation number of each energy level. (n_λ particles are with energy ε_λ) Then since particle number & energy is conserved. We have

$$\begin{cases} \sum_\lambda n_\lambda = N \\ \sum_\lambda \varepsilon_\lambda n_\lambda = E \end{cases}$$

$n_1, n_2, \cdots, n_\lambda, \cdots \overset{\text{denoted as}}{\equiv} \{n_\lambda\}$ represent a possible distribution satisfy the above constraint.
For each possible distribution $\{n_\lambda\}$, the exist corresponding possible microstates.
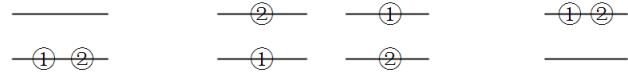
$n_1=2, n_2=0$　　　　$n_1=1, n_2=1$　　　　$n_1=0, n_2=2$
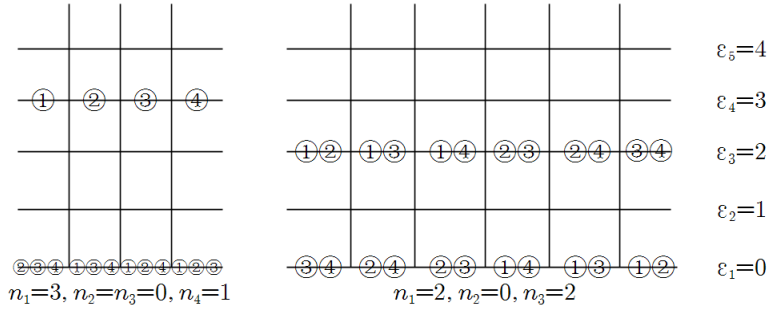
A. $4-microstate$　　　　　　B. $6-microstate$
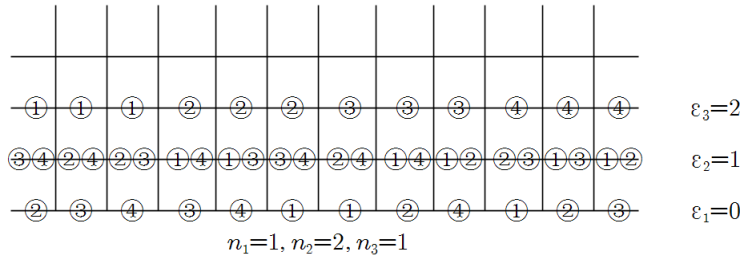
C. $12-microstates$

$$\begin{cases} \sum_\lambda n_\lambda = 4 \\ \sum_\lambda \varepsilon_\lambda n_\lambda = 3 \end{cases}$$

	0	1	2	3		Probability
A	3	0	0	1	$\frac{4!}{3!1!} = 4$	$\frac{4}{22}$
B	2	0	2	0	$\frac{4!}{2!2!} = 6$	$\frac{6}{22}$
C	1	2	1	0	$\frac{4!}{1!2!1!} = 12$	$\frac{12}{22}$

$W(\{n_\lambda\})$ =total # of possible microstates correspond to the distribution $\{n_\lambda\}$ (a macrostate)

$$W(\{n_\lambda\}) = \frac{N!}{n_1! n_2! \cdots n_\lambda! \cdots} g_1^{n_1} g_2^{n_2} \cdots g_\lambda^{n_\lambda} \cdots$$

n_λ particles have same energy ε_λ. Each has g_λ different way to choose ε_λ and they are independent
$g_\lambda^{n_\lambda}$

$$\mathcal{L} = \ln W\left(\{n_\lambda\}\right) - \alpha\left(\sum_\lambda g_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda n_\lambda \varepsilon_\lambda - E\right) \qquad \text{"ln" make it small}$$

$$\ln N! = N \ln N - N \simeq N \ln N$$

$$\mathcal{L} = N \ln N - \sum_\lambda n_\lambda \ln n_\lambda + n_1 \ln g_1 - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda n_\lambda \varepsilon_\lambda - E\right)$$

$$\frac{\partial \mathcal{L}}{\partial n_\lambda} = -\ln n_\lambda + 1 + \ln g_\lambda - \alpha - \beta \varepsilon_\lambda$$

$$n_\lambda = g_\lambda e^{1 - \alpha g_\lambda - \beta \varepsilon_\lambda} \qquad \text{Maxwell-Boltzman-distribution}$$

α, β are determined by

$$\begin{cases} \sum_\lambda n_\lambda = N = \sum_\lambda g_\lambda e^{-\alpha - \beta \varepsilon_\lambda} \\ \sum_\lambda \varepsilon_\lambda n_\lambda = E = \sum_\lambda \varepsilon_\lambda g_\lambda e^{-\alpha - \beta \varepsilon_\lambda} \end{cases}$$

Introducing function

$$Z \equiv \sum_\lambda g_\lambda e^{-\beta \varepsilon_\lambda} \quad Z$$

Then

$$N = e^{-\alpha} Z \qquad \alpha = \ln \frac{Z}{N}$$

$$E = \sum_\lambda \varepsilon_\lambda g_\lambda e^{-\alpha - \beta \varepsilon_\lambda}$$

$$= \sum_\lambda -g_\lambda \frac{\partial}{\partial \beta} e^{-\alpha - \beta \varepsilon_\lambda}$$

$$= -\frac{\partial}{\partial \beta} \sum_\lambda g_\lambda e^{-\alpha - \beta \varepsilon_\lambda}$$

$$= -\frac{\partial}{\partial \beta}\left[(e^{-\alpha}) Z\right]$$

$$= -e^{-\alpha} \frac{\partial Z}{\partial \beta}$$

$$= -\frac{N}{Z} \frac{\partial Z}{\partial \beta}$$

$$= -N \frac{\partial \ln Z}{\partial \beta}$$

We will proof later than Z is partition function and $\beta = \frac{1}{k_B T}$.
$k_B = 1.38 \times 10^{-23} J \cdot k^{-1}$ (Blotzman constant)

4.5.3 The most probable distribution for indistinguishable particle system (Quantum system)

We still have the constraint

$$\begin{cases} \sum_\lambda n_\lambda = N \\ \sum_\lambda \varepsilon_\lambda n_\lambda = E \end{cases}$$

EX:

$$\begin{cases} \sum_\lambda n_\lambda = 4 \\ \sum_\lambda \varepsilon_\lambda n_\lambda = 3, \quad g_\lambda = 2 \end{cases}$$

$$\begin{array}{ll} \underline{\hspace{4cm}} & \varepsilon_4 = 3 \\ \underline{\hspace{4cm}} & \varepsilon_3 = 2 \\ \underline{\hspace{4cm}} & \varepsilon_2 = 1 \\ \underline{\hspace{4cm}} & \varepsilon_1 = 0 \end{array}$$

	ε_1	ε_2	ε_3	ε_4	Boson # of microstate	Fermion # of microstate $n_\lambda \leqslant g_\lambda$
A	3	0	0	1	$\frac{(3+2-1)!}{3!(2-1)!} \cdot \frac{(1+2-1)!}{1!(2-1)!} = 8$	$\frac{2!}{3!(2-3)!} \cdot \frac{2!}{1!1!} \begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = 0$
B	2	0	2	0	$\frac{(2+2-1)!}{2!(2-1)!} \cdot \frac{(2+2-1)!}{2!(2-1)!} = 9$	$\frac{2!}{2!(2-2)!} \frac{2!}{2!(2-2)!} = 1$
C	1	2	1	0	$\frac{(1+1-1)!}{1!(1-1)!} \cdot \frac{(1+1-1)!}{1!(1-1)!} \cdot \frac{(2+2-1)!}{2!(2-1)!} = 3$	$\frac{2!}{1!(2-1)!} \frac{2!}{1!(2-1)!} \frac{2!}{2!(2-2)!} = 4$

- Boson

$$\frac{(3+2-1)!}{3!(2-1)!} = 4 \qquad \bigcirc\bigcirc\triangle\bigcirc \quad \bigcirc\triangle\bigcirc\bigcirc \quad \bigcirc\bigcirc\bigcirc\triangle \quad \triangle\bigcirc\bigcirc\bigcirc$$

$$\frac{(2+2-1)!}{2!(2-1)!} = 3 \qquad \bigcirc\bigcirc\triangle \quad\quad \bigcirc\triangle\bigcirc \quad\quad \triangle\bigcirc\bigcirc$$

$$\frac{(1+2-1)!}{1!(2-1)!} = 2 \qquad \bigcirc\triangle \quad\quad \triangle\bigcirc$$

$$\begin{pmatrix} n_\lambda + g_\lambda - 1 \\ n_\lambda \end{pmatrix} = \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!}$$

Total # of microstate for distribution $\{n_\lambda\}$ is

$$W_B\left(\{n_\lambda\}\right) = \prod_\lambda \begin{pmatrix} n_\lambda + g_\lambda - 1 \\ n_\lambda \end{pmatrix}$$

$$= \prod_\lambda \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!}$$

$$
\begin{aligned}
\mathcal{L} &= \ln W_B - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= \sum_\lambda \ln \frac{(n_\lambda + g_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!} - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= (n_\lambda + g_\lambda - 1)\ln(n_\lambda + g_\lambda - 1) - n_\lambda \ln n_\lambda - (g_\lambda - 1)\ln(g_\lambda - 1) \\
&\quad - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial \mathcal{L}}{\partial n_\lambda} &= \ln(n_\lambda + g_\lambda - 1) + 1 - \ln n_\lambda - 1 - \alpha - \beta\varepsilon_\lambda \\
&= \ln\left(1 + \frac{g_\lambda - 1}{n_\lambda}\right) - \alpha - \beta\varepsilon_\lambda = 0
\end{aligned}
$$

$$n_\lambda = \frac{g_\lambda - 1}{e^{\alpha + \beta\varepsilon_\lambda} - 1} \overset{g_\lambda \gg 1}{\approx} \frac{g_\lambda}{e^{\alpha + \beta\varepsilon_\lambda} - 1} \qquad \text{Bose-Einstein distribution}$$

- Fermion

$\bigcirc\bigcirc\bigcirc$ on $\underline{\ }\,\underline{\ }$ impossible # $= \bigcirc$

$\underline{\bigcirc}\;\underline{\bigcirc}$ #=1

$\underline{\bigcirc}-$ $-\underline{\bigcirc}$

$$\begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!}$$

Total # of microstate for distribution $\{n_\lambda\}$ is

$$W_F\left(\{n_\lambda\}\right) = \prod_\lambda \begin{pmatrix} g_\lambda \\ n_\lambda \end{pmatrix} = \prod_\lambda \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!}$$

$$
\begin{aligned}
\mathcal{L} &= \ln W_F - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= \sum_\lambda \ln \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!} - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right) \\
&= \sum_\lambda g_\lambda \ln g_\lambda - \sum_\lambda n_\lambda \ln n_\lambda - \sum_\lambda (g_\lambda - n_\lambda)\ln(g_\lambda - n_\lambda) \\
&\quad - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)
\end{aligned}
$$

$$0 = \frac{\partial \mathcal{L}}{\partial n_\lambda} = -\ln n_\lambda + 1 + \ln(g_\lambda - n_\lambda) + 1 - \alpha - \beta\varepsilon_\lambda$$

$$
\begin{aligned}
\ln \frac{g_\lambda - n_\lambda}{n_\lambda} - \alpha - \beta\varepsilon_\lambda &= 0 \\
\ln\left(\frac{g_\lambda}{n_\lambda} - 1\right) - \alpha - \beta\varepsilon_\lambda &= 0
\end{aligned}
$$

$$n_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\varepsilon_\lambda}+1} \qquad \text{Fermi-Dirac distribution}$$

- Summary

	$W(\{n_\lambda\})$	most probable distribution	
localized particles (Classical Mechanics)	$W_C(\{n_\lambda\}) = \dfrac{N!}{\prod\limits_\lambda n_\lambda!} g_\lambda^{n_\lambda}$	$n_\lambda = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}$ can be numbered	Heat capacity of solid Equal Partition Theorem Spin - System (magnetization)
delocalized particles (Quantum Mechanics)	$W_B(\{n_\lambda\})$ $= \prod\limits_\lambda \dfrac{(n_\lambda+g_\lambda-1)!}{n_\lambda!\,(g_\lambda-1)!}$	$n_\lambda = \dfrac{g_\lambda}{e^{\alpha+\beta\varepsilon_\lambda}-1}$ can not be numbered	Breaking down of Equal Partion Theorem Heat capacity of solid (QM) Black - body Radiation Bose - Einstein condensation
indistinguishable particles	$W_F(\{n_\lambda\})$ $= \prod\limits_\lambda \dfrac{g_\lambda}{n_\lambda!\,(g_\lambda-n_\lambda)!}$	$n_\lambda = \dfrac{g_\lambda}{e^{\alpha+\beta\varepsilon_\lambda}+1}$	Pauli exclusion principle Fermi - Liquid Superconductivity

4.5.4 The most probable distribution (MPD) $\approx$ The real distribution

	$\varepsilon_1 = 0$	$\varepsilon_2 = 1$	$\varepsilon_3 = 2$	$\varepsilon_4 = 3$	# of microstate	
A	3	0	0	1	4	$\frac{4}{22} = 18.2\%$
B	2	0	2	0	6	$\frac{6}{22} = 27.3\%$
C	1	2	1	0	12	$\frac{12}{22} = 54.5\%$

$$\begin{cases} \sum_\lambda n_\lambda = 4 \\ \sum_\lambda \varepsilon_\lambda n_\lambda = 3 \end{cases}$$

As $N \longrightarrow \infty$ what is probability of most probable distribution?

Take classical particle as a example.

$$W_C(\{n_\lambda\}) = \frac{N!}{\prod\limits_\lambda n_\lambda!} g_\lambda^{n_\lambda}$$

$n_\lambda = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}$ are the most probable distribution.

$$\mathcal{L} = \ln W_C(\{n_\lambda\}) - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)$$

$$= -\sum_\lambda n_\lambda \ln n_\lambda + n_\lambda \ln g_\lambda - \alpha\left(\sum_\lambda n_\lambda - N\right) - \beta\left(\sum_\lambda \varepsilon_\lambda n_\lambda - E\right)$$

$$\frac{\partial \mathcal{L}}{\partial n_\lambda} = -\ln n_\lambda - 1 + \ln g_\lambda - \alpha - \beta\varepsilon_\lambda = 0$$

$$n_\lambda = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}$$

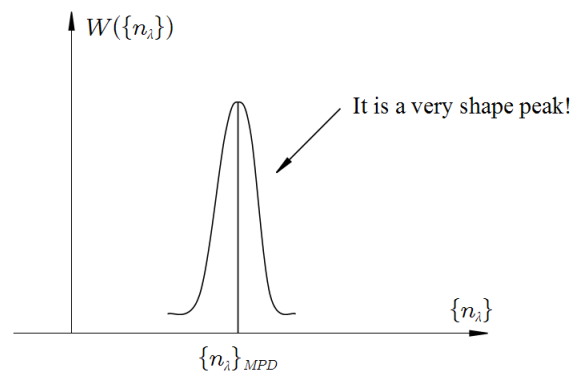$$\frac{\partial^2 \mathcal{L}}{\partial n_\lambda^2} = -\frac{1}{n_\lambda} < 0$$

So it is a maximum value for $W_C(\{n_\lambda\})_{MPD}$

$$\ln W_C(\{n\}) = \ln W_C(\{n_\lambda\}_{MPD}) + \sum_\lambda \frac{\delta \mathcal{L}}{\delta n_\lambda}\delta n_\lambda - \sum_\lambda \frac{1}{n_\lambda}(\delta n_\lambda)^2$$

$$\ln \frac{W_C(\{n_\lambda\})}{W_C(\{n_\lambda\}_{MPD})} = -\sum_\lambda \frac{1}{n_\lambda}(\delta n_\lambda)^2$$

$$I = \frac{W_C(\{n_\lambda\})}{W_C(\{n_\lambda\}_{MPD})} = e^{\sum_\lambda \left(\frac{\delta n_\lambda}{n_\lambda}\right)^2 n_\lambda}$$

δn_λ the small deviation from MPD n_λ. Set $\frac{\delta n_\lambda}{n_\lambda} \sim 10^{-6}$

$$\begin{aligned} I &= e^{-\sum_\lambda (10^{-6})^2 n_\lambda} = e^{-(10^{-6})^2 \sum_\lambda n_\lambda} \\ &= e^{-10^{-12}N} = e^{-10^{-12}10^{20}} = e^{-10^8} \sim 0 \end{aligned}$$

At begining, you need to consider all possible distribution.
Now, you just need to consider the MPD! (Power of large number N)

5 | CLASSICAL STATISTICAL MECHANICS FOR NON-INTERACTING SYSTEM

5.1 NEARLY INDEPENDENT MANY–PARTICLE SYSTEMS

What is the nearly independent many-particle systems? It is mention a system with many particles in which particles don't interact with each other except collisions. Here the collision means particles change their moments in a very short distance and out this this distance, particles are free.

5.2 PHASE SPACE AND DISTRIBUTION FUNCTIONS[1]

1. Nearly independent particle system. $\longrightarrow$ using μ-Space

1 point $\longrightarrow$ 1 particle
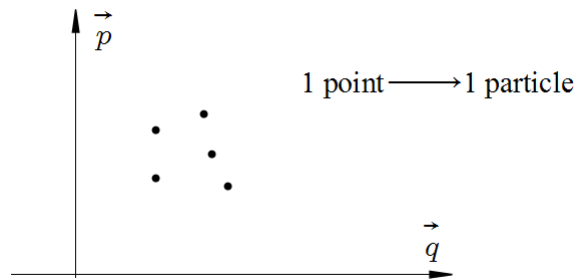
The state of 1 particle is described by $(\vec{q}_i, \vec{p}_i)$
$\downarrow$
Many-particle N $(\vec{q}_i, \vec{p}_i)_{i=1}^N$
$\downarrow$
distribution of $(\vec{q}_i, \vec{p}_i)$

$f(\vec{q}, \vec{p}, t)$ s.t $\begin{cases} \frac{1}{h^3} \int f(\vec{q}, \vec{p}, t) \, d^3\vec{q} d^3\vec{p} = N \\ \frac{1}{h^3} \int \varepsilon(\vec{q}, \vec{p}) f(\vec{q}, \vec{p}, t) \, d^3\vec{q} d^3\vec{p} = E \end{cases}$

2. Classical particle

The most probable distribution is $n_\lambda = g_\lambda e^{-\alpha - \beta \varepsilon_\lambda}$ $\qquad \lambda \equiv (\vec{q}, \vec{p})$ index of states.

$$n(\vec{q}, \vec{p}) = g(\vec{q}, \vec{p}) e^{-\alpha - \beta \varepsilon(\vec{q}, \vec{p})}$$
$$f(\vec{q}, \vec{p}) = g(\vec{q}, \vec{p}) e^{-\alpha - \beta \varepsilon(\vec{q}, \vec{p})}$$

$g(\vec{q}, \vec{p}) = 1$ on one point of space, only one particle can exist.

$$\boxed{f(\vec{q}, \vec{p}) = e^{-\alpha - \beta \varepsilon(\vec{q}, \vec{p})}}$$

5.3 THEMODYNAMICAL PROPERTIES OF IDEAL GAS

IDEAL GAS

$$\varepsilon(\vec{q}, \vec{p}) = \frac{\vec{p}^2}{2m}, \qquad \beta = k_B T$$

$$\sum_\lambda n_\lambda = N \longrightarrow \frac{1}{h^3} \int f(\vec{q}, \vec{p}, t) \, d^3\vec{q} d^3\vec{p} = N;$$

$$\sum_\lambda \varepsilon_\lambda n_\lambda = E \longrightarrow \frac{1}{h^3} \int \varepsilon(\vec{q}, \vec{p}) f(\vec{q}, \vec{p}, t) \, d^3\vec{q} d^3\vec{p} = E$$

---

1 k.h chap.6 & chap.5.4

If $f(\vec{q}, \vec{p}, t)$ is independent of $\vec{q}$

$$\int d^3\vec{q} = V$$

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

$$\frac{1}{h^3}\int f(\vec{p}, t)\, d^3\vec{p} = \frac{N}{V}, \qquad \frac{1}{h^3}\int f(\vec{p}, t)\, \frac{\vec{p}^2}{2m}\, d^3\vec{p} = \frac{E}{V}$$

1. Determining the Parameter

$$\int\limits_{-\infty}^{\infty} e^{-\lambda x^2}\, dx = \sqrt{\frac{\pi}{\lambda}}$$

$$
\begin{aligned}
\int\limits_{-\infty}^{\infty} x^2 e^{-\lambda x^2}\, dx &= \sqrt{\frac{\pi}{2\lambda^{\frac{3}{2}}}} \\
&= -\frac{\partial}{\partial\lambda}\int\limits_{-\infty}^{\infty} e^{-\lambda x^2}\, dx \\
&= -\frac{\partial}{\partial\lambda}\sqrt{\frac{\pi}{\lambda}}
\end{aligned}
$$

QW

$$\int\limits_{-\infty}^{\infty} x^4 e^{-\lambda x^2}\, dx = \frac{3\sqrt{\pi}}{4\lambda^{\frac{5}{2}}} = -\frac{\partial}{\partial\lambda}\frac{\sqrt{\pi}}{2\lambda^{\frac{3}{2}}} = \frac{3}{2}\frac{\sqrt{\pi}}{2\lambda^{\frac{5}{2}}}$$

Trick calculate $\int_{-\infty}^{\infty} e^{-\lambda x^2}\, dx$ first the other can be obtain by $\left(-\frac{\partial}{\partial\lambda}\right)$

$$
\begin{aligned}
Z &\equiv \frac{1}{h^3}\int e^{-\beta\frac{\vec{p}^2}{2m}}\, d^3\vec{q}\, d^3\vec{p} \\
&= \frac{V}{h^3}\int e^{-\beta\frac{\vec{p}^2}{2m}}\, d^3\vec{p} \\
&= \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} V
\end{aligned}
$$

$$ZC = N \qquad C = \frac{N}{Z}$$

Distribution

$$f(\vec{q}, \vec{p}) = \frac{N}{Z} e^{-\beta\frac{\vec{p}^2}{2m}}$$

Normalized to N

$$
\begin{aligned}
E &= C\int \frac{\vec{p}^2}{2m} e^{-\beta\frac{\vec{p}^2}{2m}}\, d^3\vec{q}\, d^3\vec{p} \\
&= VC\int \frac{-\partial}{\partial\beta} e^{-\beta\frac{\vec{p}^2}{2m}}\, d^3\vec{p} \\
&= -C\frac{\partial}{\partial\beta} Z(\beta) \\
&= -\frac{N}{Z}\frac{\partial}{\partial\beta} Z(\beta)
\end{aligned}
$$

$$
\begin{aligned}
\frac{E}{N} &= -\frac{\frac{\partial}{\partial\beta} Z(\beta)}{Z(\beta)} = -\frac{\partial}{\partial\beta}\ln Z(\beta) \\
&= -\frac{\partial}{\partial\beta}\ln\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V \\
&= -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{1}{\beta^{3/2}}\right) + \ln\left(\frac{2\pi m}{h^2}\right)^{3/2} V\right] \\
&= \frac{3}{2\beta}
\end{aligned}
$$

$$\frac{1}{\beta} = \frac{2E}{3N}$$

From experiment

$$\frac{E}{N} = \frac{3}{2}k_B T \Rightarrow \beta = \frac{1}{k_B T}$$

2. Pressure of ideal gas

$$
\begin{aligned}
f(\vec{p}) &= e^{-\alpha}e^{-\beta\varepsilon(\vec{p})} \\
&= \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}} e^{-\frac{\vec{p}^2}{2\pi m k_B T}} \qquad \beta = \frac{1}{k_B T}
\end{aligned}
$$

We notice that if we keep $1/h^3$ factor for all integral $\frac{d^3\vec{q}d^3\vec{p}}{h^3}$, the constant on the front of $f(\vec{p},\vec{q})$ will have a factor of h^3.

Maxwell-Boltzman distribution
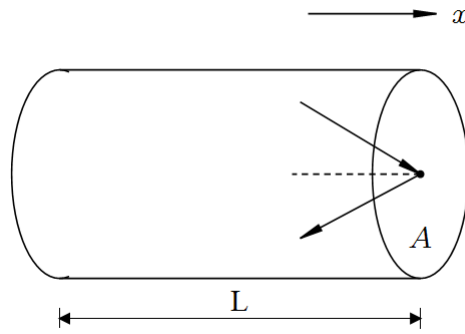
$$
\begin{aligned}
P = \frac{\overline{F}}{A} = \frac{\overline{\frac{F\Delta t}{\Delta t}}}{A} &= \frac{\overline{\left(\frac{\Delta(mv_x)}{2L/v_x}\right)}}{A} \\
&= \frac{\overline{\frac{2mv_x}{2L/v_x}}}{A} = \frac{\overline{mv_x^2}}{LA} \\
&= \frac{1}{V}\int \frac{p_x^2}{m}f(\vec{p})\frac{d^3\vec{q}d^3\vec{p}}{h^3} \\
&= \frac{1}{V}\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\int \frac{p_x^2}{m}e^{-\frac{\vec{p}^2}{2m k_B T}}\frac{d^3\vec{q}d^3\vec{p}}{h^3} \\
&= \frac{1}{V}\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}V\left(\frac{2\pi m k_B T}{h}\right)^{\frac{2}{2}}\int \frac{p_x^2}{m}e^{-\frac{p_x^2}{2m k_B T}}\frac{dp_x}{h} \\
&= \frac{1}{V}\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}k_B T \\
&= \frac{N k_B T}{V}
\end{aligned}
$$

$$\boxed{PV = N k_B T}$$

3. Entropy

Entropy of a distribution (information theory)

$$S = -\int p(x)\ln p(x)\,dx$$

entropy of physics

$$\mathcal{S} = -k_B \int p(x)\ln p(x)\,dx$$

$$f(\vec{p}) = n\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}} e^{-\frac{\vec{p}^2}{2m k_B T}}$$

Let $C = n \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}}$ $\qquad \frac{1}{2 m k_B T} = \lambda$

$$\int p\,(x) \ln p\,(x)\, d^3\vec{x} = C \int e^{-\lambda \vec{p}^2} \ln \left(C e^{-\lambda \vec{p}^2} \right) \frac{d^3\vec{p}\, d^3\vec{q}}{h^3}$$

$$= C \int e^{-\lambda \vec{p}^2} \left(\ln C - \lambda \vec{p}^2 \right) \frac{d^3\vec{p}\, d^3\vec{q}}{h^3}$$

$$= \ln C \left(C \int e^{-\lambda \vec{p}^2} \frac{d^3\vec{p}\, d^3\vec{q}}{h^3} \right) - \lambda C \int \vec{p}^2 e^{-\lambda \vec{p}^2} \frac{d^3\vec{p}\, d^3\vec{q}}{h^3}$$

$$= N \ln C - 4\pi \lambda C \int_0^\infty p^4 e^{-\lambda p^2}\, dp$$

$$= N \ln C - \frac{3}{2} N$$

Or more generally, we replace the above distribution as $f(\varepsilon_\lambda) = \frac{N}{Z} e^{-\beta \varepsilon_\lambda}$, we get the information entropy as $-N \ln Z - \beta E$ where E is the average energy of the system.

$$\mathcal{S}\,(V, T) = -k_B \left[N \ln C - \frac{3}{2} N \right]$$

$$= -N k_B \ln \left[n \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B$$

$$= -N k_B \ln \left[\frac{N}{V} \lambda_T^3 \right] + \frac{3}{2} N k_B$$

$$= N k_B \ln \left[n^{-1} T^{\frac{3}{2}} \left(2\pi m k_B / h^2 \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B$$

$$= N k_B \ln \left(n^{-1} T^{\frac{3}{2}} \right) + \frac{3}{2} N k_B + \frac{3}{2} N k_B \ln \left(2\pi m k_B / h^2 \right)$$

$$= \frac{3}{2} N k_B \ln T + N k_B \ln V + \mathrm{Const}$$

where $\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal wave length for particle with thermal energy $k_B T / 2$. It can be view as the length of the wave package of a particle (view from the quantum mechanics)

4. Derivation of Thermodynamics

Equation of state

$$PV = N k_B T$$

Total energy

$$E = \int \frac{\vec{p}^2}{2m} f\,(\vec{p}) \frac{d^3\vec{p}\, d^3 q}{h^3}$$

$$= \int \frac{\vec{p}^2}{2m} \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} e^{-\frac{\vec{p}^2}{2 m k_B T}} \frac{d^3\vec{p}\, d^3 q}{h^3}$$

$$= N \int \frac{\vec{p}^2}{2m} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} e^{-\frac{\vec{p}^2}{2 m k_B T}} \frac{d^3\vec{p}}{h^3}$$

$$= N \frac{3}{2} k_B T = \frac{3}{2} N k_B T = U$$

$$C_V = \left. \frac{dE}{dT} \right|_V = \frac{3}{2} N k_B$$

$$PV = N k_B T = \frac{2}{3} U$$

$$\frac{\mathcal{S}}{N k_B} = \frac{3}{2} \ln T + \ln V$$

$$\frac{d\mathcal{S}}{N k_B} = d \ln V + \frac{3}{2} d \ln T$$

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

$$= \frac{dV}{V} + \frac{3}{2} \frac{dU}{U} \qquad dU = \frac{3}{2} N k_B dT$$

$$\frac{dV}{V} = \frac{PdV}{Nk_BT} \qquad \frac{3}{2}\frac{dU}{U} = \frac{dU}{\frac{2}{3}U} = \frac{dU}{Nk_BT}$$

$$\frac{dS}{Nk_B} = \frac{PdV}{Nk_BT} + \frac{dU}{Nk_BT}$$
$$dS = \frac{PdV + dU}{T}$$
$$= \frac{dQ}{T}$$

$$\boxed{dQ = TdS}$$

Or more generally, for occupation $n_\lambda(\varepsilon) = g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}$, the changes of occupation number can be obtained from two path, one is change the temperature T, the other is to change the ε_λ. we have

$$E = \sum_\lambda \varepsilon_\lambda n_\lambda$$

$$dE = \sum_\lambda [(d\varepsilon_\lambda)n_\lambda + \varepsilon_\lambda(dn_\lambda)]$$

We can see the change of inner energy of the system can be divided into two parts, one is when external work is done on the system which change the energy level ε_λ. For example an external force is acting on the system and change the volume (changes of length along three directions L_x, L_y and L_z) which lead to the change of energy level $\varepsilon_{\vec{k}} = \frac{\hbar \vec{k}^2}{2m}$ where $(k_x, k_y, k_z) = (\frac{2n_x\pi}{L_x}, \frac{2n_y\pi}{L_y}, \frac{2n_z\pi}{L_z})$ and $n_{x,y,z}$ are integers. The other part of the inner energy is due to changes of temperature which means that ε_λ doesn't change but the occupation number on each level vary.

On the other hand, the distribution function (the probability of one particle to stay in state λ) is

$$f(\varepsilon) = \frac{n_\lambda}{N} = \frac{g_\lambda e^{-\alpha-\beta\varepsilon_\lambda}}{N} = \frac{g_\lambda e^{-\beta\varepsilon_\lambda}}{Z}$$
$$Z = \sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}$$
$$dZ = \sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}\left[-\beta(d\varepsilon_\lambda) + \frac{\varepsilon_\lambda}{k_BT^2}dT\right]$$
$$= -\frac{1}{k_BT}\sum_\lambda \frac{Z}{N}n_\lambda(d\varepsilon_\lambda) + \frac{dT}{k_BT^2}\sum_\lambda \frac{Z}{N}\varepsilon_\lambda n_\lambda$$
$$= -\frac{1}{k_BT}\frac{Z}{N}\sum_\lambda n_\lambda(d\varepsilon_\lambda) + \frac{Z}{N}\frac{EdT}{k_BT^2}$$
$$\sum_\lambda n_\lambda(d\varepsilon_\lambda) = \frac{EdT}{T} - \frac{Nk_BTdZ}{Z}$$

So the entropy is,

$$\frac{S}{N} = -k_B\sum_\lambda f(\varepsilon_\lambda)\ln f(\varepsilon_\lambda)$$
$$= -k_B\sum_\lambda f(\varepsilon_\lambda)\ln \frac{g_\lambda e^{-\beta\varepsilon_\lambda}}{Z}$$
$$= -k_B\sum_\lambda f(\varepsilon_\lambda)\ln \frac{1}{Z} + k_B\sum_\lambda f(\varepsilon_\lambda)[\beta\varepsilon_\lambda - \ln g_\lambda]$$
$$= k_B\ln Z + \frac{E}{NT}$$
$$dS = Nk_B d\ln Z + \frac{dE}{T} - \frac{EdT}{T^2}$$
$$= \frac{Nk_B}{Z}dZ + \frac{dE}{T} - \frac{EdT}{T^2}$$
$$TdS = \frac{Nk_BTdZ}{Z} - \frac{EdT}{T} + dE = dE - \sum_\lambda n_\lambda(d\varepsilon_\lambda)$$
$$TdS = \sum_\lambda \varepsilon_\lambda(dn_\lambda)$$

where we set $g_\lambda = 1$ for simplicity, usually $g_\lambda = g$ is independent of λ and it is just a constant.

5.4 GENERAL ROUTINE TO GET THERMAL PROPERTIES FROM DISTRIBUTIONS

$$f(\vec{p})=n\left(\frac{1}{2\pi mk_B T}\right)^{\frac{3}{2}}e^{-\frac{\vec{p}^2}{2mk_B T}}$$

Assumption : Equal probability principle of microstate

$\downarrow$

most probable distribution $\approx$ real distribution

distribution

$\downarrow$

average values

$$E=\frac{3}{2}Nk_B T \qquad \mathcal{S}=\frac{dQ}{T} \qquad PV=Nk_B T$$

$\downarrow$

$$C_V$$
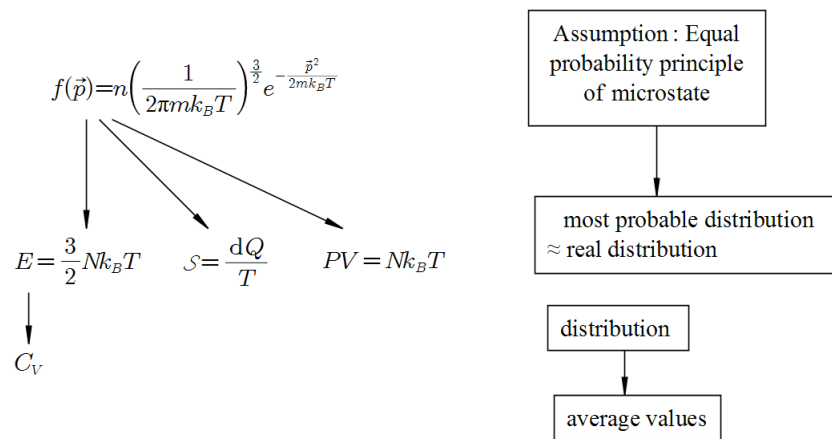
- Another method

distribution

$$p(\varepsilon_\lambda)=\frac{g_\lambda e^{-\beta\varepsilon_\lambda}}{\mathcal{Z}}$$

$$Z=\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda} \qquad \beta=\frac{1}{k_B T}$$

is the <u>partition function</u>. All other physical quantities can be obtained from it.

(1) It is calculated from microstate $g_\lambda, \varepsilon_\lambda$

(2) Other physical quantities can be obtained from it.

So it build a connection between microscopic structure and the macroscopic thermal properties.

All SM calculate start from the calculation of Z (in equilibrium case)

$$Z=\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}$$

In continuous case,

$$\mathcal{Z}=\int e^{-\beta\varepsilon(\vec{p},\vec{q})}\frac{d^3\vec{q}d^3\vec{p}}{h^3}$$

$$\frac{E}{N}=\frac{\sum_\lambda\varepsilon_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}{\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}=\frac{-\frac{\partial}{\partial\beta}\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}{\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}=\frac{-\frac{\partial}{\partial\beta}Z}{\mathcal{Z}}=-\frac{\partial\ln\mathcal{Z}}{\partial\beta}$$

distribution

$$f(\varepsilon_\lambda)=\frac{1}{\mathcal{Z}}e^{-\beta\varepsilon_\lambda} \qquad \text{From the n\_lamba/N}$$

$$\sum_\lambda f(\varepsilon_\lambda)=1$$

$$\frac{S}{N}=-k_B\sum_\lambda f(\varepsilon_\lambda)\ln f(\varepsilon_\lambda)$$

$$=-k_B\sum_\lambda f(\varepsilon_\lambda)\ln\frac{e^{-\beta\varepsilon_\lambda}}{\mathcal{Z}}$$

$$=-k_B\sum_\lambda f(\varepsilon_\lambda)(-\beta\varepsilon_\lambda)+k_B\sum_\lambda f(\varepsilon_\lambda)\ln\mathcal{Z}$$

$$=k_B\beta\sum_\lambda f(\varepsilon_\lambda)\varepsilon_\lambda+k_B\ln\mathcal{Z}$$

$$=\frac{E/N}{T}+k_B\ln\mathcal{Z}$$

$$-k_B T\ln\mathcal{Z}=\frac{E}{N}-\frac{T\mathcal{S}}{N}\equiv\frac{\mathcal{F}}{N}$$

where $\mathcal{F}$ is Free energy.

$$(X)$$
$$V \qquad\qquad\qquad T$$
$$F$$
$$E \qquad G$$
$$H$$
$$S \qquad\qquad\qquad -P$$
$$(F)$$
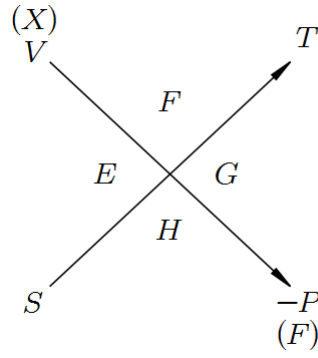
$$d\mathcal{F} = -PdV - \mathcal{S}dT + FdX$$

$$\mathcal{S} = -\left.\frac{\partial \mathcal{F}}{\partial T}\right|_V \qquad P = -\left.\frac{\partial \mathcal{F}}{\partial V}\right|_T \qquad F = \left.\frac{\partial \mathcal{F}}{\partial X}\right|_{V,T}$$

$$\mathcal{Z} = N\int e^{-\beta \frac{\vec{p}^2}{2m}} \frac{d^3\vec{q}d^3\vec{p}}{h^3} = NV\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}$$

$$\frac{\mathcal{F}}{N} = -k_B T \ln \mathcal{Z} = -k_B T \ln V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}$$

$$P = -\left.\frac{\partial \mathcal{F}}{\partial V}\right|_T = Nk_B T \frac{\partial \ln V}{\partial V} = \frac{Nk_B T}{V}$$

$$PV = Nk_B T$$

$$\frac{\mathcal{S}}{N} = -\left.\frac{\partial \mathcal{F}}{\partial T}\right|_V = k_B \ln V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} - k_B T \frac{3}{2}\frac{1}{T}$$

$$= k_B \ln V\left(\frac{2\pi m k_B T}{h^2}\right) - \frac{3}{2}k_B$$

5.5 THERMODYNAMICAL PROPERTIES OF TWO LEVEL SYSTEM (TLS)

Model TLS

$$H = \vec{\mu}_B \cdot \vec{B}$$

$$\varepsilon_2 = \varepsilon$$

$$\varepsilon_1 = -\varepsilon$$

$$g_\lambda = 1$$
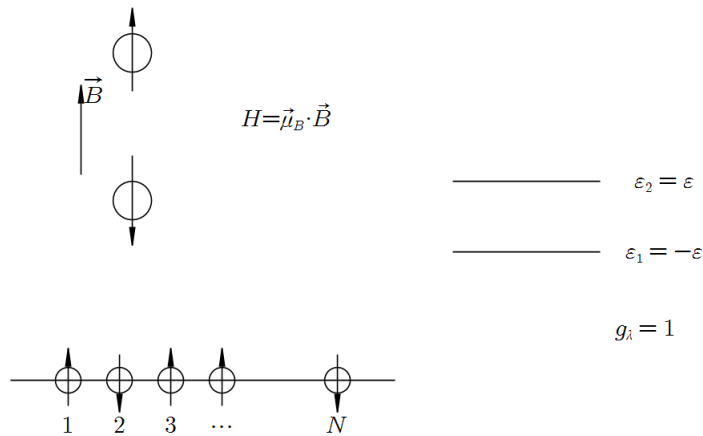
Distribution

$$n_\lambda = g_\lambda e^{-\alpha - \beta \varepsilon_\lambda} \qquad \begin{cases} n_1 &= e^{-\alpha + \beta \varepsilon} \\ n_2 &= e^{-\alpha - \beta \varepsilon} \end{cases}$$

$$\sum_\lambda n_\lambda = N = e^{-\alpha + \beta \varepsilon} + e^{-\alpha - \beta \varepsilon}$$

$$= e^{-\alpha}\left(e^{\beta \varepsilon} + e^{-\beta \varepsilon}\right)$$

$$e^{-\alpha} = \frac{N}{e^{\beta\varepsilon} + e^{-\beta\varepsilon}} \equiv \frac{N}{Z}$$

Partition function

$$n_\lambda = g_\lambda e^{-\alpha - \beta\varepsilon_\lambda} \qquad \beta = \frac{1}{k_B T}$$

$$N = \sum_\lambda n_\lambda = \sum_\lambda g_\lambda e^{-\alpha - \beta\varepsilon_\lambda} = e^{-\alpha} \sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda} = e^{-\alpha} Z$$

$$Z \equiv \sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}$$

$g_\lambda = 1$

$$Z = e^{\beta\varepsilon} + e^{-\beta\varepsilon} = 2\cosh\beta\varepsilon$$

$$e^{-\alpha} = \frac{N}{Z} = N\frac{1}{2\cosh\beta\varepsilon}$$

$$n_1 = \frac{N}{2\cosh\beta\varepsilon}e^{\beta\varepsilon} \qquad n_2 = \frac{N}{2\cosh\beta\varepsilon}e^{-\beta\varepsilon}$$

$$Z = e^{-\beta\mathcal{F}} = e^{-\beta(E-TS)}$$

Energy

$$E = \varepsilon_1 n_1 + \varepsilon_2 n_2 = -\frac{N\partial\ln\mathcal{Z}}{\partial\beta}$$

$$= -\varepsilon n_1 + \varepsilon n_2$$

$$= -\varepsilon\frac{N}{2\cosh\beta\varepsilon}e^{\beta\varepsilon} + \varepsilon\frac{N}{2\cosh\beta\varepsilon}e^{-\beta\varepsilon}$$

$$= \frac{N\varepsilon}{2}\frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{\cosh\beta\varepsilon}$$

$$= -N\varepsilon\frac{\sinh\beta\varepsilon}{\cosh\beta\varepsilon}$$

$$= -N\varepsilon\tanh\beta\varepsilon$$
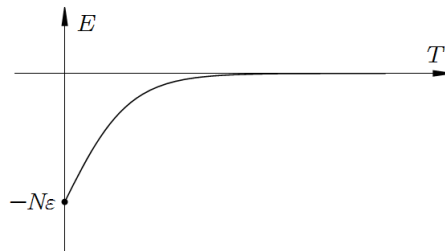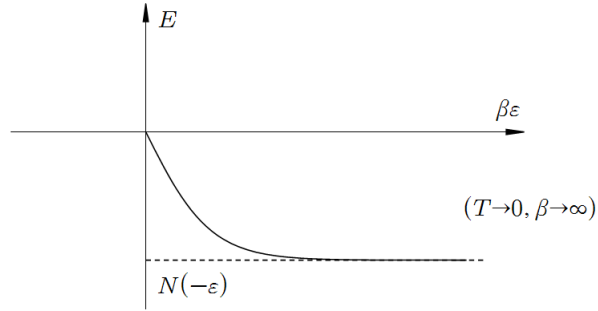
Heat Capacitor

$$C_V = \frac{dE}{dT} = \frac{d}{dT}\left(-N\varepsilon\tanh\beta\varepsilon\right)$$

$$= -N\varepsilon\frac{\sinh\beta\varepsilon\sin\beta\varepsilon - \cosh\beta\varepsilon\cos\beta\varepsilon}{\cosh^2\beta\varepsilon}\varepsilon\frac{-1}{k_BT^2}$$

$$= Nk_B\left(\frac{\varepsilon}{k_BT}\right)^2\frac{1}{\cosh^2\beta\varepsilon} = Nk_B\left(\beta\varepsilon\right)^2\frac{1}{\cosh^2\beta\varepsilon}$$
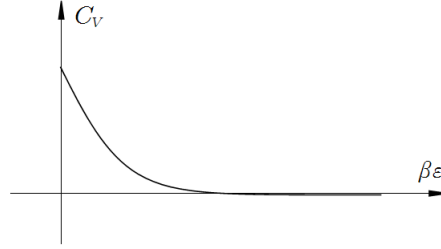
Entropy

$$S = -k_B\left(\frac{e^{\beta\varepsilon}}{\mathcal{Z}}\ln\frac{e^{\beta\varepsilon}}{\mathcal{Z}} + \frac{e^{-\beta\varepsilon}}{\mathcal{Z}}\ln\frac{e^{-\beta\varepsilon}}{\mathcal{Z}}\right)$$

$$= -k_B\left(\frac{e^{\beta\varepsilon}}{\mathcal{Z}}\beta\varepsilon + \frac{e^{\beta\varepsilon}}{\mathcal{Z}}\left(-\beta\varepsilon\right)\right)$$

$$= -k_B\left(\frac{e^{\beta\varepsilon}}{\mathcal{Z}}\ln\frac{1}{\mathcal{Z}} + \frac{e^{-\beta\varepsilon}}{\mathcal{Z}}\ln\frac{1}{\mathcal{Z}}\right)$$

$$= \frac{1}{T}\left(-N\varepsilon\tanh\beta\varepsilon\right) + k_B\ln\mathcal{Z}$$

$$= \frac{1}{T}\left(-N\varepsilon\tanh\beta\varepsilon\right) + k_B\ln 2\cosh\beta\varepsilon$$

$$\mathcal{Z} = 2\cosh\beta\varepsilon \qquad \frac{\mathcal{F}}{N} = -k_BT\ln\mathcal{Z}$$

$$\frac{E}{N} = -\frac{\partial\ln\mathcal{Z}}{\partial\beta} = -\frac{\partial\ln 2\cos\beta\varepsilon}{\partial\beta} = -\frac{2\sinh\beta\varepsilon}{2\cosh\beta\varepsilon}\varepsilon = -\varepsilon\tanh\beta\varepsilon$$

$$E = -N\varepsilon\tanh\beta\varepsilon$$

$$\frac{S}{N} = -\frac{\partial\mathcal{F}}{\partial T}\bigg|_V = k_B\ln\mathcal{Z} + k_BT\frac{\partial\ln\mathcal{Z}}{\partial T}$$

$$= k_B\ln\mathcal{Z} + k_BT\frac{\partial\ln\mathcal{Z}}{\partial\beta}\frac{\partial\beta}{\partial T}$$

$$= k_B\ln\mathcal{Z} + k_BT\left(N\varepsilon\tanh\beta\varepsilon\right)\left(-\frac{1}{k_BT^2}\right)$$

$$= k_B\ln\mathcal{Z} - \frac{1}{T}N\varepsilon\tanh\beta\varepsilon$$

5.6 THERMODYNAMICAL PROPERTIES OF CLASSICAL HARMONIC OSCILATORS

Model
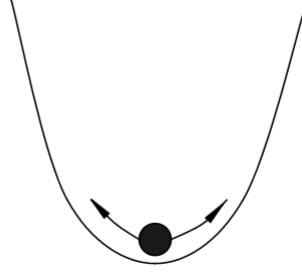
$$H\left(\{\vec{q}_i, \vec{p}_i\}\right) = \sum_{i=1}^{N} \left[\frac{\vec{p}_i^2}{2m} + \frac{1}{2}m\omega^2 \vec{q}_i^2 \right]$$

$$n_\lambda = g_\lambda e^{-\beta\varepsilon_\lambda} \qquad \lambda = (\vec{q}, \vec{p})$$

$$Z = \frac{1}{h^3} \int e^{-\beta\left(\frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2\vec{q}^2\right)} d^3\vec{q}\, d^3\vec{p}$$

$$f(\vec{q}, \vec{p}) = \frac{N}{Z} e^{-\beta\left(\frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2\vec{q}^2\right)}$$

– 1D

$$\int e^{-\beta\frac{1}{2}m\omega^2 q^2} dq = \sqrt{\frac{\pi}{\frac{1}{2}m\omega^2\beta}}$$

$$\int e^{-\beta\frac{p^2}{2m}} dp = \sqrt{\frac{\pi}{\frac{1}{2m}\beta}}$$

$$Z = \frac{1}{h^3}\left(\sqrt{\frac{\pi}{\frac{1}{2m}\beta}}\sqrt{\frac{\pi}{\frac{1}{2}m\omega^2\beta}}\right)^3 = \frac{1}{h^6}\left(\frac{4\pi}{\omega^2\beta}\right)^{\frac{3}{2}}$$

$$= \frac{1}{(\hbar\omega)^3\beta^3} = \left(\frac{k_B T}{\hbar\omega}\right)^3, \quad \hbar = \frac{h}{2\pi}$$

$$\mathcal{F} = -k_B T \ln\left(\frac{1}{(\hbar\omega)^3\beta^3}\right) = -k_B T \ln\left(\frac{k_B T}{\hbar\omega}\right)^3$$

$$\frac{E}{N} = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln\frac{1}{\beta^3} = \frac{3\partial\ln\beta}{\partial\beta} = \frac{3}{\beta} = 3k_B T$$

$$\frac{S}{N} = -\frac{\partial\mathcal{F}}{\partial T} = k_B \ln\left(\frac{k_B T}{\hbar\omega}\right)^3 + 3k_B T\frac{1}{T}$$

$$= k_B \ln\left(\frac{k_B T}{\hbar\omega}\right)^3 + 3k_B$$

5.7 EQUIPARTITION OF ENERGY

$$\int e^{-\beta c p^2} dp \sim \sqrt{\frac{\pi}{\beta c}}$$

$$\int e^{-\beta c q^2} dq \sim \sqrt{\frac{\pi}{\beta c}}$$

$\Longrightarrow$ Contribute $\frac{1}{2}k_B T$ energy per degree of freedom.
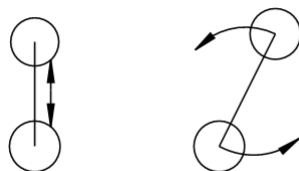
5.8 HOMEWORK

PROBLEM 1: For a many particles system with Hamiltonian,

$$H = \sum_{i=1}^{N} \varepsilon s_i \qquad s_i = -1, 0, 1$$

(a) Calculate the partition function for classical case

$$Z = \sum_{s_i = -1,0,1} e^{-\beta \varepsilon s_i}$$

(b) From the partition function Z, calculate the total energy E, heat capacity C, entropy S of this system.

PROBLEM 2: For a 2D many particles system with Hamiltonian,

$$H = \sum_{i=1}^{N} c|\vec{p}_i|$$

(a) Calculate the partition function for classical case

$$Z = \int \frac{d^2\vec{q} d^2\vec{p}}{h^2} e^{-\beta c|\vec{p}|}$$

(b) From the partition function Z, calculate the energy E, heat capacity C, entropy S and pressure P of this system.

6 | BREAKING DOWN OF CLASSICAL STATISTICAL MECHANICS

6.1 BREAKING DOWN OF CLASSICAL SM

6.1.1 Equipartition of energy

Each degree of freedom will contribute $\frac{N}{2} k_B T$ to energy of the system.

each d.o.f
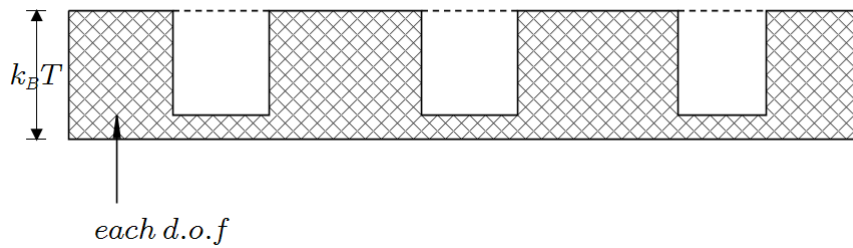
The above physical picture are based on two assumptions:

1. energy can continously change. & the lowest energy of all d.o.f are all zero. (or same number)
2. Energy can transfered from one to another.

At low temperature, where quantum mechanics dominates, (b) still work, but (a) is not valid.

> Energy is descrete and ground state energy is nonzero! (in QM)

Equipartition of energy

$$\frac{\vec{p}^2}{2m}$$

$$\frac{1}{2} m\omega^2 x^2 \quad \text{(oscillation)}$$

$$\frac{1}{2} I\dot{\Theta}^2 \quad \text{(rotation)}$$

In experiment, single atom gas $E = \frac{3N}{2} k_B T$ from translation motion.

6.1.2 Heat capacity for multiple-atom molecule gas

For multiple-atom molecule gas, it is complicated.
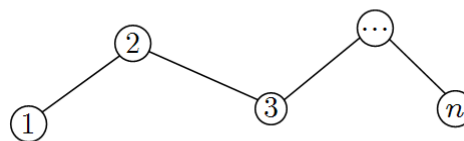
n-atom in one molecule

Kinetic energy: $3n$

Potential energy: depend on the interaction of atoms

$$\vec{q}_i = \vec{q}_i^0 + \vec{u}_i \qquad \vec{q}_i^0 \text{ is the equilibrium position}$$

$$\left. \frac{\partial V(\vec{q}_1, \cdots, \vec{q_n})}{\partial \vec{q}_i} \right|_{\vec{q}_i = \vec{q}_i} = 0$$

The 1st non-zero term

$$\frac{\partial^2 V(\vec{q}_1, \cdots, \vec{q_n})}{\partial \vec{q}_i \partial \vec{q}_j} \rightarrow \frac{\partial^2 V(\vec{q}_1, \cdots, \vec{q_n})}{\partial q_{i\alpha} \partial q_{j\beta}} \qquad \alpha, \beta = 1, 2, \cdots$$

$$V = V^* + \frac{1}{2} \sum_{i,j=1}^{n} \sum_{\alpha,\beta=1}^{3} \frac{\partial^2 V}{\partial q_{i\alpha} \partial q_{j\beta}} u_{i\alpha} u_{j\beta} \qquad 3n \times 3n \text{ matrix}$$

like harmonic oscillator (eigen mode), i.e. diagonalize

$$H = V^* + \sum_{s=1}^{3n} \left[\frac{1}{2} \tilde{p}_s^2 + \frac{K_s}{2} \tilde{u}_s^2 \right]$$

Assuming m non-zero model (eigenstate of $\frac{\partial^2 V}{\partial q \partial q}$. $3n \times 3n$ matrix)
We proof $m = 3n - 3 - r$, r is # of rotational modes depends on n number
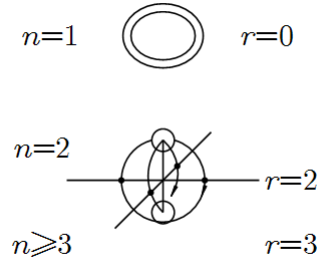
Total degree of freedom

$$N_{d.o.f} = 3n + m \qquad \text{"3n" is from knetic energy, "m" is from potential energy}$$
$$= 3n + (3n - 3 - r) = 6n - 3 - r$$
$$= (3 + r) + (6n - 6 - 2r)$$
$$= 3 + r + 2m$$

We write them in this way because they have different activation energy in QM.

$$\langle H \rangle = (3n + m) \frac{1}{2} k_B T$$
$$= \frac{3 + r + 2m}{2} k_B T$$

$$H = \sum_{s=1}^{3n} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{K_s}{2} \tilde{u}_s^2 \right]$$
$$= \frac{1}{2m} \vec{p}^2 + \frac{1}{2} I\dot{\Theta}^2 + \sum_{s=1}^{m} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{K_s}{2} \tilde{u}_s^2 \right]$$

EXPERIMENTAL RESULTS

(*2 atom molecule* $r = 2 \longrightarrow m = 1$)
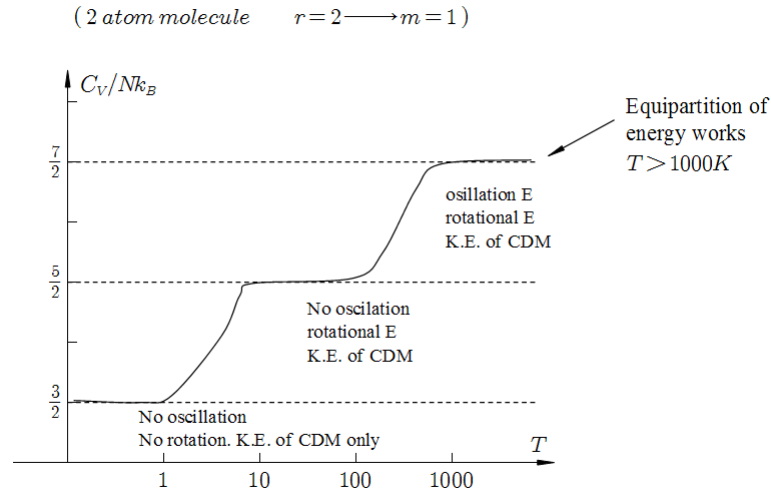
It shown that different mode of motion need different activation energy to active. 3 is for the translation degree of freedom, r is for the rotational degree of freedom, and $2m$ is for the oscillation degree of freedom.

$T < 1000\,\mathrm{K}$ breaking down of equipartion of energy

① *discrete energy level*

② *different ground state energy*

To activate a certain mode, you need a certain minimum energy
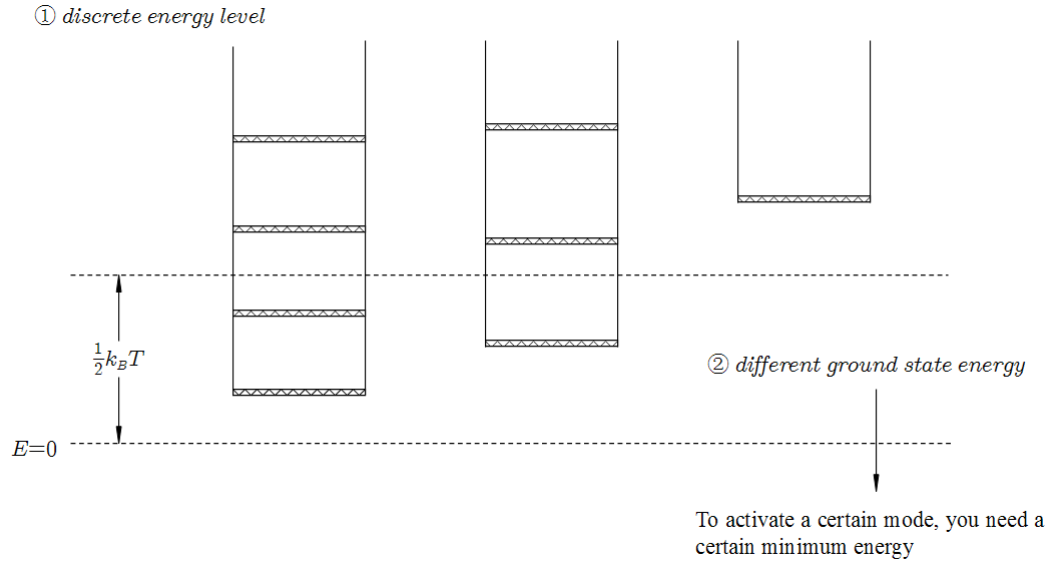
6.1.3   When does classical SM fail?

$$\text{CSM} \qquad n_\lambda = g_\lambda e^{-\alpha - \beta \varepsilon_\lambda}$$

$$\text{QSM} \qquad n_\lambda = \frac{g_\lambda}{e^{\alpha + \beta \varepsilon_\lambda} \pm 1}$$

If $e^\alpha \gg 1$ (i.e. $\frac{n_\lambda}{g_\lambda} = \frac{1}{e^{\alpha + \beta \varepsilon_\lambda} \pm 1} \ll 1$) then we can ignore ± 1

$$
\begin{aligned}
W_{\text{BE}}(\{n_\lambda\}) &= \prod_\lambda \frac{(g_\lambda + n_\lambda - 1)!}{n_\lambda!\,(g_\lambda - 1)!} \\
&= \prod_\lambda \frac{(g_\lambda + n_\lambda - 1)(g_\lambda + n_\lambda - 2)\cdots(g_\lambda)}{n_\lambda!} \\
&= \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}\left[1 + \frac{n_\lambda - 1}{g_\lambda}\right]\left[1 + \frac{n_\lambda - 2}{g_\lambda}\right]\cdots\left[1 + \frac{0}{g_\lambda}\right] \\
&\simeq \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}
\end{aligned}
$$

$$W_{FD}\left(\{n_\lambda\}\right) = \prod_\lambda \binom{g_\lambda}{n_\lambda} = \prod_\lambda \frac{g_\lambda!}{n_\lambda!\,(g_\lambda - n_\lambda)!}$$

$$= \prod_\lambda \frac{g_\lambda\,(g_\lambda - 1)\cdots(g_\lambda - n_\lambda + 1)}{n_\lambda!}$$

$$= \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}\,[1]\left[1 - \frac{1}{g_\lambda}\right]\cdots\left[1 - \frac{(n_\lambda - 1)}{g_\lambda}\right]$$

$$\simeq \prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}$$

$$W_{MB} = \frac{N!}{n_1!\cdots n_\lambda!\cdots}\,g_\lambda^{n_\lambda}$$

$$= N!\prod_\lambda \frac{g_\lambda^{n_\lambda}}{n_\lambda!}$$

So

$$W_{BE} \simeq W_{FD} \simeq \frac{1}{N!}W_{MB}$$

$\frac{1}{N!}$ is a constant. $\frac{\delta \ln W}{\delta n}$ give same results give the same MB distribution. But it will affect the value of entropy.

$$N = \sum_\lambda n_\lambda = \sum_\lambda g_\lambda e^{-\alpha - \beta\varepsilon_\lambda} = e^{-\alpha}Z$$

$$e^\alpha = \frac{Z}{N} = \frac{\sum_\lambda g_\lambda e^{-\beta\varepsilon_\lambda}}{N}$$

For free gas $\varepsilon\left(\vec{k}\right) = \frac{\hbar^2\vec{k}^2}{2m} = \frac{\vec{p}^2}{2m}$

$$Z = \int \frac{d^3\vec{q}\,d^3\vec{p}}{h^3}e^{-\beta\varepsilon}$$

$$= \frac{V}{h^3}\prod_{i=1}^{3}dp_i\, e^{-\beta\frac{p_i^2}{2m}}$$

$$= \frac{V}{h^3}\left(2\pi mk_B T\right)^{\frac{3}{2}}$$

$$e^\alpha = \frac{Z}{N} = \frac{V}{N}\left(\frac{\sqrt{2\pi mk_B T}}{h}\right)^3 = \frac{V}{N}\frac{1}{\lambda_T^3}$$

$$\lambda_T = \frac{h}{\sqrt{2\pi mk_B T}} \qquad \frac{V}{N} = d^3$$

d is the distance of particles, λ_T is the thermal wave length. The size of the wave package for a particle.

If $e^\alpha = \left(\frac{d}{\lambda_T}\right)^3 \gg 1$, particles are not overlap and distinguishable.

If $e^\alpha \sim 1$ or $\ll 1$, particles are indistinguishible.

$\boxed{\frac{V}{N}\frac{1}{\lambda_T\,N,NN^3} \sim 1 \text{ is the criteria.}}$

6.2 THE DIFFERENT BETWEEN CLASSICAL MECHANICS AND QUANTUM MECHANICS

1. Energy is discrete in QM; ground state energy is different for different d.o.f.

2. Particles are indistinguishable.(many-particle case) It has constraints on the filling number of energy level. (How many particle you can put on one energy level.) What is the many-particle state.

   So we first consider cases where energy level is discrete, but we can still use

   $$n_\lambda = g_\lambda e^{-\beta\varepsilon_\lambda}$$

   It is the cases for non-interacting Boson, and with zero chemical potential.

6.3 QUANTUM HARMONIC OSCILATORS, HEAT CAPACITY OF SOLIDS AND BLACKBODY RADIATION

6.3.1 Quantum Harmonic Oscillation– A Semiclassical Approach

– CM (1D)

$$Z_{vib}^{CM} = \int \frac{d\vec{q}d\vec{p}}{h} e^{-\beta\left[\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\right]}$$

$$= \frac{1}{h}\left[\sqrt{\left(\frac{2\pi m}{\beta}\right)\left(\frac{2\pi}{\beta m\omega^2}\right)}\right]$$

$$= \frac{1}{h}\left(\frac{2\pi}{\beta\omega}\right) = \left(\frac{1}{\beta\hbar\omega}\right) = \left(\frac{k_B T}{\hbar\omega}\right)$$

$$\langle H_{vib}^{CM}\rangle = -\frac{\partial\ln Z}{\partial\beta} = \frac{\partial\ln\frac{1}{\beta\hbar\omega}}{\partial\beta} = \frac{1}{\beta} = k_B T$$

$$= \left(\frac{1}{2}k_B T\right)_{K.E.} + \left(\frac{1}{2}k_B T\right)_{P.E.}$$

– QM

$$H_{vib}^{QM} = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$Z_{vib}^{QM} = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$\lim_{\substack{\beta\to 0 \\ T\to\infty}} Z_{vib}^{QM} = \frac{1 - \beta\hbar\omega/2}{1 - (1 - \beta\hbar\omega)} = \frac{1}{\beta\hbar\omega} = Z_{vib}^{CM}$$

$$E_{vib}^{QM} = -\frac{\partial\ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$= -\frac{\partial}{\partial\beta}\left[-\frac{1}{2}\beta\hbar\omega - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

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

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

$\frac{1}{2}\hbar\omega$ is ground state energy, $\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$ is excited state

$$\frac{1}{e^{\beta\hbar\omega} - 1} = \langle n_\omega\rangle$$

Here, the treatment of quantum harmonic oscillator is a semi-classical approach which the summation is over n on $\exp[-\beta(n + 1/2)\hbar\omega]$ instead of using the Bose-Einstein distribution. When Plank use this method to calculate the blackbody radiation, he still don't know the indistinguish of quantum particles and Bose-Einstein distribution is not found yet. So

$$n(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

can also be interpreted as the Bose-Einstein distribution for boson with energy $\hbar\omega$.

$$C_{vib}^{QM} = \frac{dE_{vib}^{QM}}{dT} = \frac{(\hbar\omega)^2\left(-e^{-\beta\hbar\omega}\right) - \frac{k_B}{T^2}}{1 - e^{-\beta\hbar\omega}} + \frac{(\hbar\omega)e^{-\beta\hbar\omega}(-\hbar\omega)\left(-\frac{k_B}{T^2}\right)e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}$$

$$= k_B\left(\frac{\hbar\omega}{k_B T}\right)^2\left[\frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})} - \frac{(e^{-\beta\hbar\omega})^2}{(1 - e^{-\beta\hbar\omega})^2}\right]$$

$$= k_B\left(\frac{\hbar\omega}{k_B T}\right)\frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}$$

$$T\to\infty, \quad e^{-\beta\hbar\omega}\to 1, \quad 1 - e^{-\beta\hbar\omega}\to\beta\hbar\omega$$

$$C_{vib}^{QM} = k_B\left(\frac{\hbar\omega}{k_B T}\right)^2\frac{1}{(\beta\hbar\omega)^2} = k_B = C_{vib}^{CM}$$

$$T \to 0$$

$$k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{-\beta \hbar \omega}}{(e^{-\beta \hbar \omega})^2} = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 e^{-\beta \hbar \omega} \longrightarrow 0$$

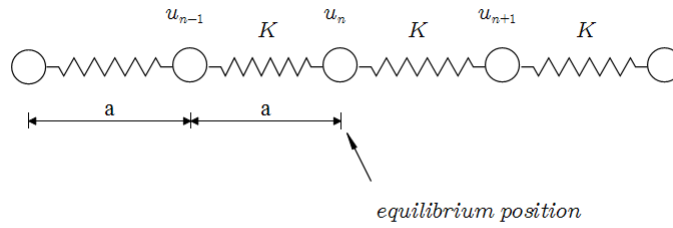$$k_B \Theta_{vib} = \hbar \omega \qquad \Theta_{vib} \sim 10^3 \text{—} 10^4 \text{K}$$
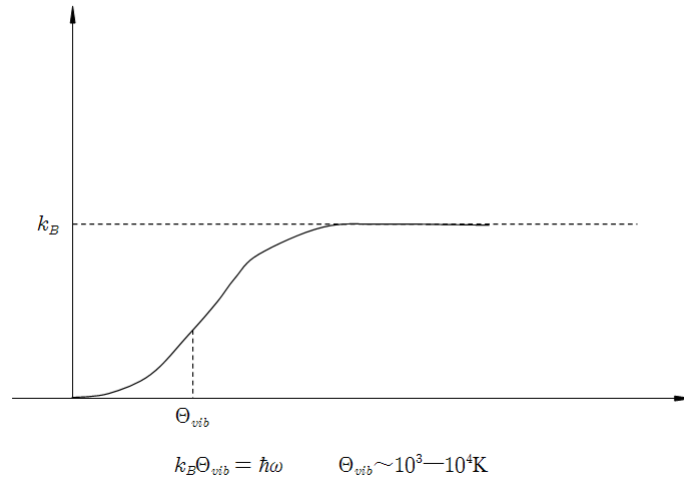
6.3.2 Heat Capacity of Solids : Phonon

Apply the above results in solids

In solids the oscillation of Ions can be represented by phonons with energy spectrum $\omega \left(\vec{k} \right)$

For 1D case

equilibrium position

deviation from equilibrium position $r_n = r_n^* + u_n$

$$m \ddot{u}_n = -k \left(u_n - u_{n-1} \right) - k \left(u_n - u_{n+1} \right)$$
$$= -k \left(2 u_n - u_{n-1} - u_{n+1} \right)$$

Set: $u_n = \sum_K e^{iK(na)} \tilde{u}(K) e^{-i\omega(K)t}$ (Fourier transform)

$$\ddot{u}_n = -\sum_k \omega^2 (k) \tilde{u}(k) e^{ikna} - k \left(2 u_n - u_{n-1} - u_{n+1} \right)$$

$$= -k \sum_k \left(2 e^{ik(na)} \tilde{u}(k) e^{-i\omega(k)t} - e^{ik(n+1)a} \tilde{u}(k) e^{-i\omega(k)t} \right.$$

$$\left. - e^{ik(n-1)a} \tilde{u}(k) e^{-i\omega(k)t} \right)$$

$$= -k \sum_k \left(2 - e^{ika} - e^{-ika} \right) \tilde{u}(k) e^{ina} e^{-i\omega(k)t}$$

$$2 - 2\cos ka = 4\sin^2\left(\frac{ka}{2}\right)$$

$$m\ddot{u}_n = -k\left(2u_n - u_{n-1} - u_{n+1}\right)$$

$$\Rightarrow \sum_K \left[-m\omega^2\left(k\right)\tilde{u}\left(k\right)e^{iKna}e^{-i\omega(K)t}\right]$$

$$= \sum_k -K\left[4\sin^2\left(\frac{ka}{2}\right)\right]\tilde{u}\left(k\right)e^{ikna}e^{-i\omega(k)t}$$

$e^{ikNa} = 1$, for arbitrary k, so

$$\omega^2\left(k\right) = \frac{4k}{m}\sin^2\left(\frac{ka}{2}\right)$$

$$\omega\left(k\right) = 2\sqrt{\frac{k}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

where $k = \frac{2n\pi}{Na}$ is momentum, $\omega\left(k\right)$ is energy.

$E_n = \left(n_{\vec{k}} + \frac{1}{2}\right)\hbar\omega_{\vec{k}}$ $\vec{k} = \frac{2n\pi}{Na}$ N-harmonic oscillator.

From above

1 harmonic oscillator

$$C_{vib} = k_B\left(\frac{\hbar\omega}{k_B T}\right)\frac{e^{-\beta\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)^2}$$

N-harmonic oscillator

$$C_{solid} = \sum_{\vec{k}} k_B\left(\frac{\hbar\omega}{k_B T}\right)^2\frac{e^{-\beta\hbar\omega_k}}{\left(1 - e^{-\beta\hbar\omega_k}\right)^2}$$

– Einstein model (All harmonic oscillators have the same frequency)

$\omega_k \equiv \omega_E$ const $\hbar\omega_E = k_B T_E$

$$C_{solid}^E = Nk_B\left(\frac{\hbar\omega_E}{k_B T}\right)^2\frac{e^{-\beta\hbar\omega_E}}{\left(1 - e^{-\beta\hbar\omega_E}\right)^2}$$

at $T \to 0$

$$\frac{C_{solid}^E}{3Nk_B} \simeq \left(\frac{T_E}{T}\right)^2\frac{e^{-T_E/T}}{\left(1 - e^{-T_E/T}\right)^2} \sim e^{-T_E/T}$$

$3Nk_B$ .... T^3 not $e^{-T_E/T}$ from experiments
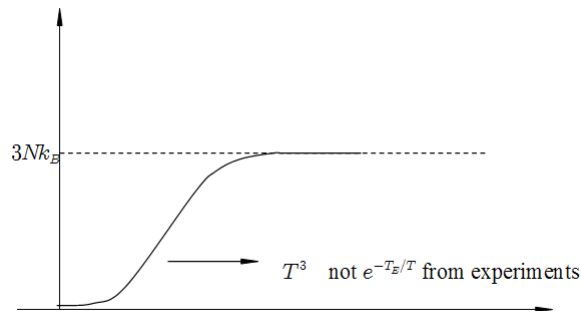
– Debye model

$$\omega\left(k\right) = 2\sqrt{\frac{K}{m}}\left|\sin\frac{ka}{2}\right| = 2\sqrt{\frac{K}{m}}\frac{ka}{2} \approx vk$$

$$\vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right)$$

$$dn_x = \left(n_x + 1\right) - n_x = \frac{L_x}{2\pi}dk_x$$

$$\sum_{n_x} = \sum_{n_x}\left(\left(n_x + 1\right) - n_x\right) = \sum_{n_x}\frac{L_x dk_x}{2\pi} = \frac{L_x}{2\pi}\int dk_x$$

$$\sum_{n_x, n_y, n_z} = \frac{L_x L_y L_z}{\left(2\pi\right)^3}\int dk_x dk_y dk_z = \frac{V}{\left(2\pi\right)^3}\int d^3\vec{k}$$

Here $\sum_{n_x, n_y, n_z}$ is summation over all quantum state which is actually $\sum_\lambda$. We can also define $\lambda = (\vec{p}, \vec{q})$, and we have

$$\sum_\lambda f(\varepsilon_\lambda) = \int \frac{d^3\vec{p}\, d^3\vec{q}}{h^3} f(\vec{p}) = \frac{V}{h^3} \int d^3\vec{p}\, f(\vec{p})$$

And use de broglic relation $\vec{p} = \hbar k = \frac{h\vec{k}}{2\pi}$, we get

$$\int \frac{d^3\vec{p}\, d^3\vec{q}}{h^3} f(\vec{p}) = \frac{V}{h^3} \int d^3\vec{p}\, f(\vec{p}) = \frac{V}{(2\pi)^3} \int d^3\vec{k}\, f(\hbar\vec{k})$$

which completely agree with the previous result.

$$C_{solid} = k_B^3 \frac{V}{(2\pi)^3} \int d^3k \left(\frac{\hbar\omega_k}{k_B T}\right)^2 \frac{e^{-\beta\hbar\omega_{\vec{k}}}}{\left(1 - e^{-\beta\hbar\omega_{\vec{k}}}\right)^2}$$

$$= k_B^3 \frac{V}{(2\pi)^3} \int d^3\vec{k} \left(\frac{\hbar v k}{k_B T}\right)^2 \frac{e^{-\beta\hbar v k}}{(1 - e^{-\beta\hbar v k})^2}$$

$$= k_B^3 \frac{V}{8\pi^3} 4\pi \int \left(\frac{k_B T}{\hbar v}\right)^3 x^2 \frac{e^{-x}}{(1 - e^{-x})^2} dx$$

$$d^3\vec{k} = 4\pi k^2 dk \quad x \equiv \frac{\hbar v k}{k_B T} = \beta\hbar v k \quad dk = \frac{k_B T}{\hbar v} dx$$

We can calculate E first

$$E_{solid} = E_0 + \sum_{\vec{k}} \frac{\hbar\omega_{\vec{k}}}{e^{\beta\hbar\omega\vec{k}} - 1}$$

$$= E_0 + \frac{3V}{(2\pi)^3} \int 4\pi k^2 dk \frac{\hbar v k}{e^{\beta\hbar v k} - 1}$$

$$= E_0 + \frac{3V}{2\pi^2} \left(\frac{k_B T}{\hbar v}\right)^3 k_B T \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

$$= E_0 + \frac{\pi^2}{10} V \left(\frac{k_B T}{\hbar v}\right)^3 k_B T$$

Where $\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$

$$C_{solid}^D = \frac{dE}{dT} = \frac{2\pi^2 v}{5} \left(\frac{k_B T}{\hbar v}\right)^3 k_B \propto \left(\frac{T}{T_D}\right)^3$$

agree with experiments.

6.3.3 Blackbody Radiation : Photon

A phonemena which light and matter interact with each other and arrive equilibrium.

$$\begin{array}{ll} phonon & \longrightarrow \quad photon \\[4pt] \text{collective motion} & \text{collective motion of Electric} \\ \text{of atoms} & - \text{magnetic field} \end{array}$$
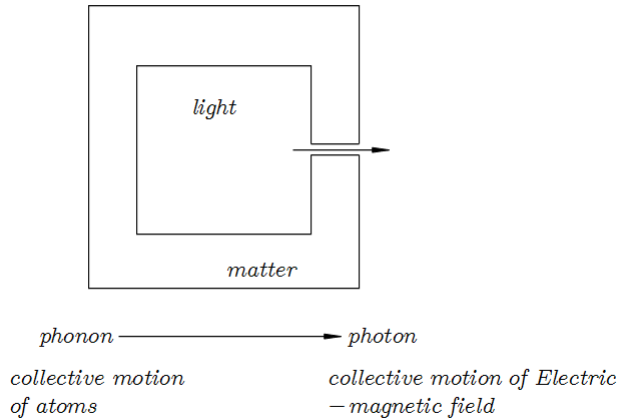
$$H = \frac{1}{2} \sum_{\vec{k},\alpha} \left[|\tilde{P}_{\vec{k},\alpha}|^2 + \omega_\alpha\left(\vec{k}\right) |\tilde{u}_\alpha\left(\vec{k}\right)|^2 \right]$$

$$\omega_\alpha\left(\vec{k}\right) = ck$$

c light of speed, $\alpha = \pm$ only 2 polarization

$$\frac{E}{V} = \frac{\pi^2}{15} \left(\frac{k_B T}{\hbar c}\right)^3 k_B T$$

$$Z = \prod_{\vec{k},\alpha} \frac{e^{-\beta\hbar ck/2}}{1 - e^{-\beta\hbar ck/2}}$$

$$F = -k_B T \ln Z = k_B T \left[\frac{\beta\hbar ck}{2} + \ln\left(1 - e^{-\beta\hbar ck}\right) \right]$$

$$= 2V \int \frac{d^3\vec{k}}{(2\pi)^3} \left[\frac{\hbar ck}{2} + k_B T \ln\left(1 - e^{-\beta\hbar ck}\right) \right]$$

Pressure from light

$$P = -\frac{\partial F}{\partial V} = -\int \frac{d^3k}{(2\pi)^3} \left[\hbar ck + 2k_B T \ln\left(1 - e^{-\beta\hbar ck}\right) \right]$$

$$= P_0 - \frac{2k_B T}{8\pi^3} 4\pi \int_0^\infty k^2 dk \ln\left(1 - e^{-\beta\hbar ck}\right)$$

$$= P_0 - \frac{k_B T}{\pi^2} \int_0^\infty k^2 dk \ln\left(1 - e^{-\beta\hbar ck}\right)$$

$$= P_0 - \frac{k_B T}{3\pi^2} \int dk^3 \ln\left(1 - e^{-\beta\hbar ck}\right)$$

$$= P_0 - \frac{k_B T}{3\pi^2} \left[k^3 \ln\left(1 - e^{-\beta\hbar ck}\right) \Big|_{k=0}^\infty - \int_0^\infty \frac{k^3 e^{-\beta\hbar ck}}{(1 - e^{-\beta\hbar ck})^2} \right]$$

$$= P_0 + \frac{k_B T}{\pi^2} \int_0^\infty dk \frac{k^3}{3} \frac{\beta\hbar ce^{-\beta\hbar ck}}{1 - e^{-\beta\hbar ck}}$$

$$= P_0 + \frac{1}{3}\frac{E}{V}$$
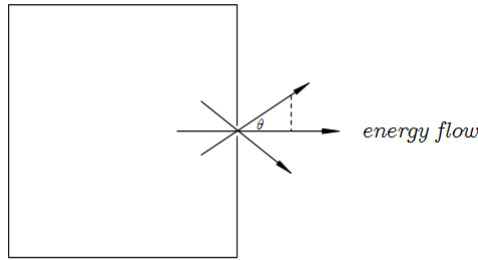
energy flow

energy flow in unit time and unit area

$$\phi = \langle C_\perp \rangle \frac{E}{V}$$

$$\langle C_\perp \rangle = C \frac{1}{4\pi} \int_0^{2\pi} 2\pi \sin\theta d\theta \left(\cos\theta\right) = \frac{C}{4}$$

$$\phi = \frac{C}{4}\frac{E}{V} = \frac{C}{4}\frac{\pi^2}{15}\left(\frac{k_B T}{\hbar C}\right)^3 k_B T = \frac{\pi^2}{60}\frac{k_B^4}{\hbar^3 C^2} \equiv \sigma T^4$$

It's the Stefan-Boltzman law. where $\sigma \simeq 5.67 \times 10^{-8} \mathrm{Wm}^{-2}\mathrm{K}^{-4}$.

$$\frac{E}{V} = \int \varepsilon\,(T, k)\,dk$$
$$= \int \frac{\hbar c}{\pi^2} \frac{k^3}{e^{\beta \hbar c k} - 1}\,dk$$

energy flow per unit area per unit time for certain k.

$$I\,(k, T) = \frac{c}{4}\varepsilon\,(k, T) = \frac{\hbar c^2}{4\pi^2} \frac{k^3}{e^{\beta \hbar c k} - 1}$$

$$\beta\hbar ck \ll 1 \xrightarrow{\quad} \frac{\hbar c^2}{4\pi^2} \frac{k^3}{\beta\hbar ck} \sim \frac{ck_B T}{4\pi^2} k^2$$

$$\beta\hbar ck \gg 1 \xrightarrow{\quad} \frac{\hbar c^2}{4\pi^2} k^3 e^{-\beta\hbar ck}$$

$$k^*\,(T) \sim \frac{k_B T}{\hbar c} \implies \lambda_{max} \approx \frac{b}{T}$$

$$j \propto \sigma T^4$$
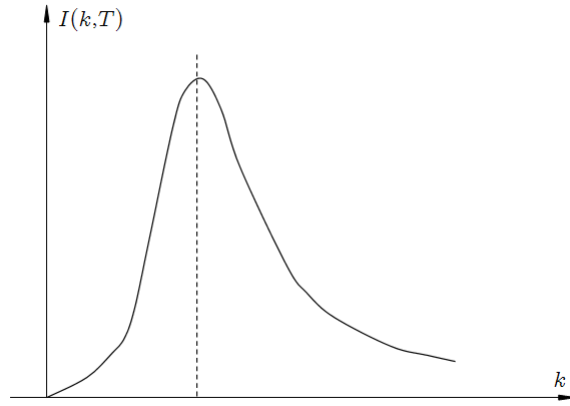
human body radiation $P = \sigma T^4$

$$P_{net} = P_{emit} - P_{absorb} = A\left(T^4 - T_0^4\right)$$

where $T = 37°C, \quad T_0 = 20°C, \quad A = 2\mathrm{m}^2, \quad P_{net} = 100\mathrm{W}$.

6.4 HOMEWORK

PROBLEM 1: For a 3D many particles system with Hamiltonian,

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \frac{1}{2}m\omega^2 \vec{q}_i^2$$

(a) Calculate the partition function for classical case

$$Z = \int \frac{d^3\vec{q}\,d^3\vec{p}}{h^3} e^{-\beta\left[\frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2 \vec{q}^2\right]}$$

$$e^\alpha = \frac{Z}{N}$$

(b) For the classical statistical mechanics to be valid, we should have $e^\alpha \gg 1$, what is the physical meaning of this?

(c) If this system is for 1D case, what is the physical meaning of $e^\alpha \gg 1$?

PROBLEM 2: For a 3D many particles system with Hamiltonian,

$$H = \sum_{i=1}^{N} c|\vec{p}_i|$$

(a) Calculate the partition function for classical case

$$Z = \int \frac{d^3\vec{q}\, d^3\vec{p}}{h^3} e^{-\beta c |\vec{p}|}$$

$$e^\alpha = \frac{Z}{N}$$

(b) For the classical statistical mechanics to be valid, we should have $e^\alpha \gg 1$, what is the physical meaning of this?

(c) From the partition function Z, calculate the energy E, heat capacity C, entropy S and pressure P of this system.

7

QUANTUM STATISTICAL MECHANICS FOR NONINTERACTING SYSTEMS

7.1 QUANTUM GAS

The above chapter for phonon and photon are two cases for many-particle system with zero chemical potential $\mu = 0$. From the following relation,

$$
\begin{array}{ccc}
V, N & & T \\
& F & \\
E & \times & G \\
& H & \\
S & & -P, \mu \\
\text{extensive} & & \text{intensive} \\
\text{quantities} & & \text{quantities}
\end{array}
$$
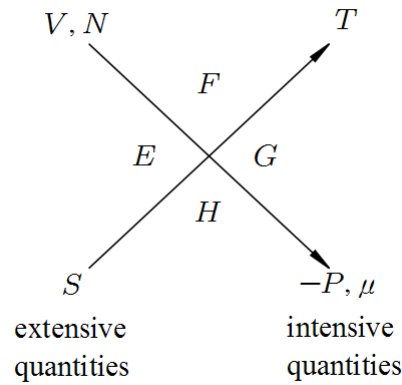
$$E = -PdV + \mu dN + TdS$$

we can see, when particle number changes $N \to N + 1$, you need energy of μ. And $\mu = 0$ means you need zero energy to create a particle, so particle number is not conserved.

From previous chapter, we have occupation number n_λ for quantum level ε_λ

$$n_\lambda = \frac{1}{e^{\alpha + \beta \varepsilon_\lambda} \mp 1} \qquad \alpha = -\beta \mu.$$

7.1.1 Number density and energy density

For a general Bosonic (Fermionic) particle system

$$n_{\vec{k}} = \frac{1}{e^{\beta (\varepsilon(\vec{k}) - \mu)} \mp 1} \qquad \text{particle number with } \vec{k}$$

$$z \equiv e^{\beta \mu}$$

$$\varepsilon\left(\vec{k}\right) = \frac{\hbar^2 k^2}{2m}$$

We have two constraints on total particle number N and total energy E

$$N = \sum_{\vec{k}} n_{\vec{k}} = \frac{V}{(2\pi)^3} \int n_{\vec{k}} d^3 \vec{k}$$

$$= \frac{V}{(2\pi)^3} \int d^3 \vec{k} \frac{1}{e^{\beta (\varepsilon(\vec{k}) - \mu)} \mp 1}$$

$$n = \frac{N}{V} = \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{1}{e^{\beta (\varepsilon_k - \mu)} \mp 1}$$

If N is given, the above equation is used to determine μ, or given μ, we can determine N.

$$E = \sum_{\vec{k}} \varepsilon_{\vec{k}} n_{\vec{k}} \qquad \varepsilon = \frac{E}{V} = \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\varepsilon\left(\vec{k}\right)}{e^{\beta(\varepsilon_k - \mu)} \mp 1}$$

$$= \frac{V}{(2\pi)^3} \int d^3\vec{k} \frac{\varepsilon\left(\vec{k}\right)}{e^{\beta(\varepsilon(\vec{k}) - \mu)} \mp 1}$$

Similarly, the above equation relate the total energy E to temperature T, if we know total energy E, we can determine temperature T or use temperature T to determine the total energy E. Usually, the temperature is give and the total energy is to be determined as a function of temperature T and the capacity can also be obtained as $C = dE(T)/dT$.

$$P = \int_{v_x > 0} d^3p \, (2mv_x) \, v_x f\left(\vec{q}, \vec{p}, t\right)$$
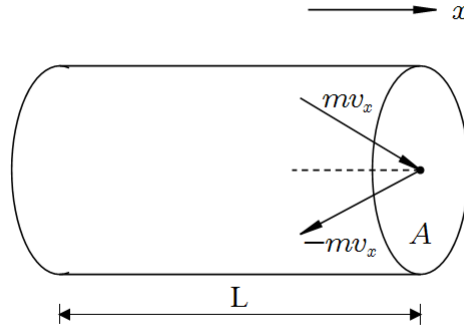
$$P = \frac{F}{A} = \frac{\overline{\Delta(mv_x)/\Delta t}}{A} = \frac{\overline{2mv_x}}{2LA/v_x}$$

$$= \frac{\overline{mv_x^2}}{V} = \frac{1}{3}\overline{mv^2}\frac{1}{V} = \frac{2}{3}\overline{\frac{1}{2}mv^2}\frac{1}{V}$$

$$= \frac{1}{2}\int 2mv_x^2 f\left(\vec{q}, p, t\right) d^3p$$

$$= \frac{2}{3}\int \frac{1}{2}mv^2 f\left(\vec{q}, p, t\right) d^3p$$

$$= \frac{2}{3}\int \frac{d^3\vec{k}}{(2\pi)^3} \varepsilon_{\vec{k}} f\left(\vec{p}, t\right) \frac{1}{V}$$

$$= \frac{2}{3}\frac{E}{V} = \frac{2}{3}\varepsilon$$

where ε is the energy density, which is independent of occupation number or of the distribution $f\left(\vec{q}, \vec{p}, t\right)$

$$n = \frac{N}{V} = g\int \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{z \exp\left(\frac{\beta\hbar^2 k^2}{2m}\right) \mp 1}$$

$$\varepsilon = \frac{E}{V} = g\int \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{z^{-1}\exp\left(\frac{\beta\hbar^2 k^2}{2m}\right) \mp 1}$$

$$P = \frac{2}{3}\varepsilon$$

$$x \equiv \frac{\beta\hbar^2 k^2}{2m} \Rightarrow \frac{\hbar^2 k^2}{2m} = \frac{x}{\beta} \Rightarrow k = \sqrt{\frac{2mx}{\beta\hbar^2}} \Rightarrow dk = \frac{1}{2}\sqrt{\frac{2m}{\beta\hbar^2}}\frac{1}{\sqrt{x}}$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$d^3k = 4\pi k^2 dk$$

$$\begin{cases} n = \frac{g}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{1}{2}} dx}{z^{-1}e^x \mp 1} \\ \beta\varepsilon = \frac{g}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{3}{2}} dx}{z^{-1}e^x \mp 1} \end{cases}$$

Define

$$f_m^\pm (z) = \frac{1}{(m-1)!} \int_0^\infty \frac{x^{m-1}dx}{z^{-1}e^x \mp 1}$$

$$\begin{cases} n = \frac{g}{\lambda^3} f_{\frac{3}{2}}^\pm (z) \\ \beta \varepsilon = \frac{3g}{2\lambda^3} f_{\frac{5}{2}}^\pm (z) \\ \beta P = \frac{2}{3} \varepsilon = \frac{g}{\lambda^3} f_{\frac{5}{2}}^\pm (z) \end{cases}$$

7.1.2 Hight temperature expansion

When the temperature is high, $z \to 0$, then we can expand the distribution function as power series of z. This is the so-call high temperature expansion.

$$f_m^\pm (z) = \frac{1}{(m-1)!} \int_0^\infty \frac{x^{m-1}dx}{z^{-1}e^x \mp 1}$$

$$= \frac{1}{(m-1)!} \int_0^\infty \frac{x^{m-1}ze^{-x}dx}{1 \mp ze^{-x}}$$

$$= \frac{1}{(m-1)!} \int_0^\infty dx\, x^{m-1} z e^{-x} \sum_{n=0}^\infty \left[\pm z e^{-x}\right]^n$$

$$= \frac{1}{(m-1)!} \sum_{n=0}^\infty \int_0^\infty dx\, x^{m-1} (\pm 1)^n z^{(1+n)} e^{-(1+n)x}$$

$$= \sum_{n=0}^\infty (\pm 1)^n z^{(1+n)} \frac{1}{(m-1)!} \int_0^\infty dx\, x^{m-1} e^{-(1+n)x}$$

$$= \sum_{n=0}^\infty (\pm 1)^n \frac{z^{(1+n)}}{(1+n)^m} \left[\frac{1}{(m-1)!} \int_0^\infty dx\, x^{m-1} e^{-x} \right]$$

$$= \sum_{n=0}^\infty (\pm 1)^n \frac{z^{(1+n)}}{(1+n)^m}$$

$$= z \pm \frac{z^2}{2^m} + \frac{z^3}{3^m} \pm \frac{z^4}{4^m} + ...$$

So, we have the number density and energy density as,

$$\frac{n\lambda^3}{g} = f_{\frac{3}{2}}^\pm (z) \approx z \pm \frac{z^2}{2^{(3/2)}} + \frac{z^3}{3^{(3/2)}} + ...$$

$$\frac{\beta P \lambda^3}{g} = f_{\frac{5}{2}}^\pm (z) \approx z \pm \frac{z^2}{2^{(5/2)}} + \frac{z^3}{3^{(5/2)}} + ...$$

We solve the first equation for z and inserted it to the second equation. The first equation can be solve perturbatively

$$z \approx \frac{n\lambda^3}{g} \mp \frac{z^2}{2^{(3/2)}} \approx \frac{n\lambda^3}{g} \mp \frac{1}{2^{(3/2)}} \left(\frac{n\lambda^3}{g}\right)^2 + ...$$

$$\frac{\beta P \lambda^3}{g} = f_{\frac{5}{2}}^\pm (z) \approx z \pm \frac{z^2}{2^{(5/2)}} + ...$$

$$\approx \left(\frac{n\lambda^3}{g} \mp \frac{1}{2^{(3/2)}} \left(\frac{n\lambda^3}{g}\right)^2\right) \pm \frac{1}{2^{(5/2)}} \left(\frac{n\lambda^3}{g} \mp \frac{1}{2^{(3/2)}} \left(\frac{n\lambda^3}{g}\right)^2\right)^2 + ...$$

$$\approx \frac{n\lambda^3}{g} \mp \frac{1}{2^{(5/2)}} \left(\frac{n\lambda^3}{g}\right)^2 + ...$$

We have the state equation as followings,

$$P \approx n k_B T \left[1 \mp \frac{1}{2^{(5/2)}} \left(\frac{n\lambda^3}{g}\right) + ...\right]$$

The second term on the right hand side is due to the Bose (Fermion) statistics, we can see, the Bosons (Fermions) seem to attract (repulse) each other. The above approximation is valid only when $\left(\frac{n\lambda^3}{g} \right) \ll 1$ which is actually what we get from $e^{\alpha} \gg 1$ in previous chapter.

When the temperature is low, Bosonic and Fermionic system behavior differently which is from the different properties of $f^{\pm}_m(z)$. At low temperature, $z \to 1$ for Bosonic system and $z \to \infty$ for Fermionic system. So we treat them separately.

7.2 DEGENERATED BOSE GAS

1. Properties of $f^+_m(z)$

$$f^+_m(z) = \frac{1}{(m-1)!} \int_0^{\infty} \frac{x^{m-1} dx}{z^{-1} e^x - 1}$$

$$\frac{d}{dz} f^-_m(z) = \int_0^{\infty} \frac{dx}{(m-1)!} \frac{d}{dz} \frac{x^{m-1}}{z^{-1} e^x - 1}$$

$$\frac{d}{dz} f\left(z^{-1} e^x\right) = f' \frac{d}{dz} \left(z^{-1} e^x\right) = f' e^x \left(-\frac{1}{z^2}\right) = -\frac{1}{z} \frac{d}{dx} f\left(z^{-1} e^x\right)$$

$$= -\frac{1}{z} \int_0^{\infty} dx \frac{x^{m-1}}{(m-1)!} \frac{d}{dx} \left(\frac{1}{z^{-1} e^x - 1}\right)$$

$$= -\frac{1}{z} \left[\frac{x^{m-1}}{(m-1)!} \frac{1}{z^{-1} e^x - 1} \Big|_0^{\infty} - \int_0^{\infty} \frac{1}{z^{-1} e^x - 1} \frac{d}{dx} \left(\frac{x^{m-1}}{(m-1)!}\right) \right]$$

$$= \frac{1}{z} \int_0^{\infty} dx \frac{1}{z^{-1} e^x - 1} \frac{x^{m-2}}{(m-2)!} = \frac{1}{z} f^+_{m-1}(z)$$

The occupation number is always finite, so for arbitrary energy level ε_k, $\varepsilon_k - \mu$ is always positive (At very low temperature, μ is approaching to the ground state energy from below). For free Bose gas, the ground state energy is zero, so $\mu < 0$. That is $0 \leqslant e^{\beta \mu} \leqslant 1$, i.e. $0 \leqslant z \leqslant 1$.

$$\xi_m \equiv f^+_m(1) = \frac{1}{(m-1)!} \int_0^{\infty} \frac{x^{m-1}}{e^x - 1} dx$$

It has a pole at $x = 0$, when $x \to 0$

$$\int dx \frac{x^{m-1}}{e^x - 1} \simeq \int dx \frac{x^{m-1}}{x} \sim \int x^{m-2} dx \sim \frac{1}{x^{m-1}}$$

It is finite when $m > 1$, and infinite when $m \leqslant 1$, so if $m > 1$

$$\frac{d}{dz} f^+_m(z) = \frac{1}{z} f^+_{m-1}(z) \geqslant 0$$

So it is monotonically increasing function of z. $f^+_m(1)$ is limited. $m > 1$.

$$\xi_m \equiv f^+_m(1) = finite\ value$$

$$\frac{d}{dz} f^+_{\frac{3}{2}} \sim \frac{1}{z} f^+_{\frac{1}{2}} \to \infty$$

$$\xi_{\frac{3}{2}} = \frac{2.6}{2}$$
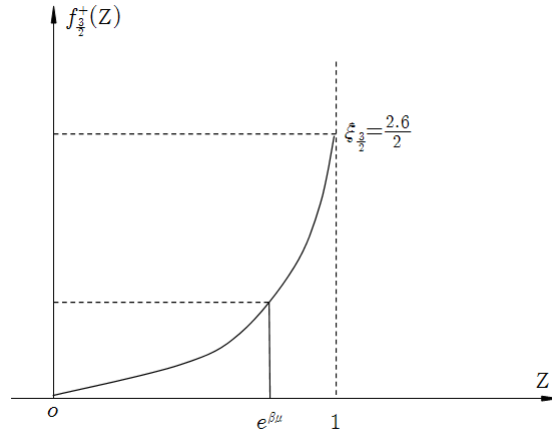
$$n = \frac{g}{\lambda^3} f^+_{\frac{3}{2}}(Z)$$

$$\frac{n\lambda^3}{g} = f^+_{\frac{3}{2}}(Z) = f^+_{\frac{3}{2}}\left(e^{\beta\mu}\right) \leqslant \xi_{\frac{3}{2}}$$

where $\frac{n\lambda^3}{g} = f^+_{\frac{3}{2}}(Z)$ is the density of excited state, n and μ are determining each other.

2. Bose-Einstein Condenstate

So the density of particles for Bose gas in 3D has a maximal value n_*

$$\frac{n_*\lambda^3}{g} = \xi_{\frac{3}{2}} \qquad n_* = \frac{g}{\lambda^3} \xi_{\frac{3}{2}}$$

$$\boxed{\frac{n\lambda^3}{g} = \frac{n}{g}\left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3 \leqslant \xi_{\frac{3}{2}}}$$

When n is too large or T is too low, the above inequality cannot be satisfied. Then how can I put more particles into the system? This is when Bose-Einstein condensation appear.

– Particles can be put in the ground state $\left(\vec{k} = 0\right)$

$$\sum_{\vec{k}} \longrightarrow \int \frac{d^3\vec{k}}{(2\pi)^3} = \int \frac{k^2}{2\pi^2} dk$$

the ground state $k = 0$ is missing when we replace the summation with integral. We have to put it back in the calculation of total number.

– It is so-called Bose-Einstein condensate (BEC).

The phenomena of a macroscopic occupation of a single one-particle state.

$$\langle n_{\vec{k}=0}\rangle = \frac{1}{e^{\beta(\varepsilon_{\vec{k}=0}-\mu)} - 1} = \frac{1}{Z^{-1}e^0 - 1} = \frac{1}{Z^{-1} - 1}$$

$$\lim_{T\to 0} \frac{1}{Z^{-1} - 1} \longrightarrow \infty$$

here we have $\mu \to 0$ and $Z \to 1$ when $T \to 0$.

Macroscopic occupation of one single particle state = Bose-Einstein condensate (BEC)

$$n = \frac{1}{Z^{-1} - 1} + n^* = n_0 + n^*$$

$$n^* = \frac{g}{\lambda^3} \xi_{\frac{3}{2}} = g\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3 \xi_{\frac{3}{2}}$$

where n^* is the upper limit of occupation number for excited state $\left(\vec{k} \neq 0\right)$ if the temperature T is given. On the other hand, if we have a given number density of particles n, if we want these particles to stay int the excited state, we have have the following relation,

$$\frac{n\lambda^3}{g} = \frac{nh^3}{g(2\pi m k_B T)^{3/2}} = f^+_{\frac{3}{2}}(Z) \leqslant \xi_{\frac{3}{2}}$$

thus the temperature should be

$$T > \frac{h}{2\pi m k_B} \left(\frac{n}{\mathcal{E}_{\frac{3}{2}} g} \right)^{2/3}$$

So we define a BEC temperature as

$$T_c(n) \equiv \frac{h}{2\pi m k_B} \left(\frac{n}{\mathcal{E}_{\frac{3}{2}} g} \right)^{2/3}$$
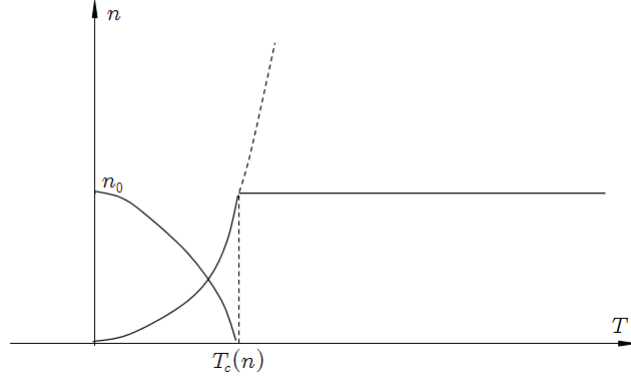
When $T \gg T_c(n)$, $n < n^*$, all states are excited states.

When $T = T_c(n)$, $n = n^*$. Then, when more particles are added in the system, they occupy the ground state. And $z = 1$ for this temperature and below.

When $T \ll T_c(n)$, most of the particles are in ground state (BEC occurs)

3. Properties of BEC system

   When $T < T_c(n)$, $\mu = 0$, $z = 1$, most calculation can be simplified.

$$\begin{aligned}
\beta P &= \frac{g}{\lambda^3} f^+_{\frac{5}{2}}(1) = \frac{g}{\lambda^3} \mathcal{E}_{\frac{5}{2}} \approx 1.341 \frac{g}{\lambda^3} \\
&= 1.341 g \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^3 \sim T^{\frac{3}{2}}
\end{aligned}$$

   $P \propto T^{\frac{3}{2}} T = T^{\frac{5}{2}}$ which is independent of n (not like $P = n k_B T$ in classical gas).

$$\varepsilon = \frac{2}{3} \frac{g}{\lambda^3} f^+_{\frac{5}{2}}(1) = \frac{2}{3} \frac{g}{\lambda^3} \mathcal{E}_{\frac{5}{2}} \sim T^{\frac{3}{2}}$$

   P and ε are independent of n

   – Because $\vec{k} = 0$ particles can not move, they won't collide with the wall of container. So they can not contribute to pressure.

   – $\varepsilon_{\vec{k}=0} = 0$, they don't increase the energy either.

   Decreasing the temperature T, when $T < T_c(n)$, BEC happen. Increasing the number density n (by adding more particles or reducing the volume of the system), when the $n > n_*(T)$ BEC appear. These are the two path to make BEC happen.

   n^* critical density or $v = v^* = \frac{1}{n^*}$ critical volume.

   When $v < v^*$, BEC happen

$$P = \frac{1}{\beta} \frac{g}{\lambda^3} f^+_{\frac{5}{2}}(1) \simeq 1.341 g \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^{\frac{3}{2}} k_B T \propto T^{\frac{5}{2}}$$

   which is independent of v
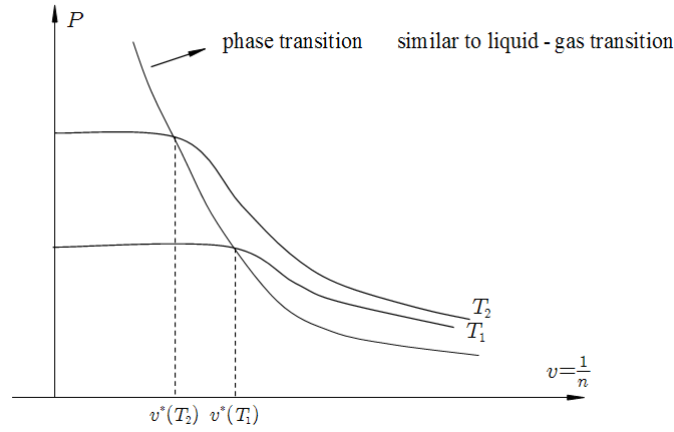
4. Properties above BEC temperature

When the temperature is above the BEC temperature $T_c(n)$, $z \neq 1$, we have to determine μ from the particle number N. In this case

Heat capacity

$$P = \frac{2}{3}\varepsilon = \frac{2}{3}\frac{E}{V}$$

$$E = \frac{3}{2}PV = \frac{3}{2}V\frac{g}{\lambda^3}k_B T f_{\frac{5}{2}}^{+} \propto T^{\frac{5}{2}} f_{\frac{5}{2}}^{+}(z), \quad z = e^{\beta\mu}$$

$$\begin{aligned}
C_{V,N} &= \left.\frac{dE}{dT}\right|_{V,N} = \frac{3}{2}V\frac{g}{\lambda^3}\left[\frac{\frac{5}{2}k_B T}{T}f_{\frac{5}{2}}^{+}(z) + k_B T\frac{d}{dz}f_{\frac{5}{2}}^{+}(z)\left.\frac{dz}{dT}\right|_{V,N}\right] \\
&= \frac{3}{2}V\frac{gk_B T}{\lambda^3}\left[\frac{5}{2T}f_{\frac{5}{2}}^{+}(z) + \frac{1}{z}f_{\frac{3}{2}}^{+}(z)\left.\frac{dz}{dT}\right|_{V,N}\right]
\end{aligned}$$

$\left.\frac{dz}{dT}\right|_{V,N}$ can be obtain by particle number conservation.

$$\begin{aligned}
\left.\frac{dN}{dT}\right|_{V} &= 0 = \frac{d}{dT}\left[\frac{1}{V}\frac{g}{\lambda^3}f_{\frac{3}{2}}^{+}(z)\right] \\
&= \frac{1}{V}\frac{g}{\lambda^3}\left[\frac{3}{2T}f_{\frac{3}{2}}^{+}(z) + \frac{1}{z}f_{\frac{1}{2}}^{+}(z)\frac{dz}{dT}\right]
\end{aligned}$$

$$\frac{dz}{dT}\frac{T}{z} = -\frac{3}{2}\frac{f_{\frac{3}{2}}^{+}(z)}{f_{\frac{1}{2}}^{+}(z)}$$

$$C_{V,N} = \frac{3}{2}V\frac{gk_B}{\lambda^3}\left[\frac{5}{2}f_{\frac{5}{2}}^{+}(z) - \frac{3}{2}\frac{f_{\frac{3}{2}}^{+2}(z)}{f_{\frac{1}{2}}^{+}(z)}\right]$$

Insert the equation of z from high temperature expansion, we get the following figure
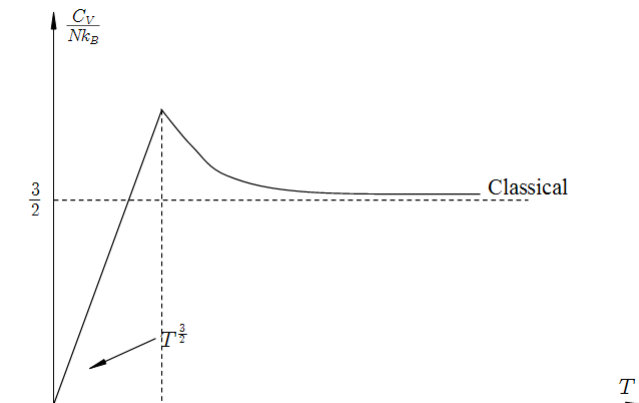
How to understand the behavior of $C_{V,N} \sim T^{\frac{3}{2}}$ as $T \to 0$?

As $T \to 0$ all particles are in the ground state, the highest k can be excited denoted as k_m can be obtained as

$$\frac{\hbar^2 k_m^2}{2m} = k_B T \qquad k_m \sim T^{\frac{1}{2}}$$

And the total number of states in a d-dimensional system is proportional to $\quad k_m^d \sim T^{\frac{d}{2}}$ (from $\int d^d \vec{k}$). While each state carry a energy in order of $k_B T$, the total energy carried is proportional to $T^{\frac{d}{2}+1}$, so we have

$$C_V = \frac{dE}{dT} \sim T^{\frac{d}{2}}$$

5. Superfluid He^4

Superfluidity is actually a properties induced from BEC. The phase diagram of He^4
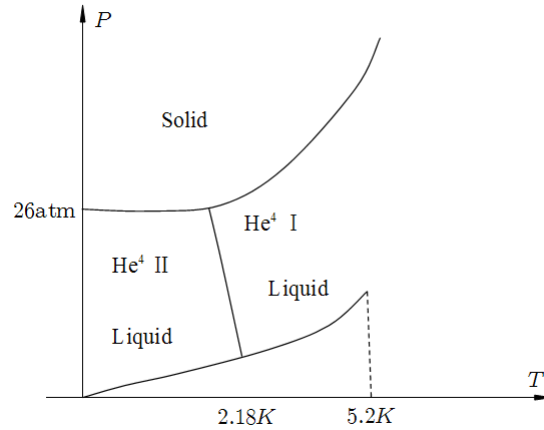
He^4$_{II}$ has unusual hydrodynamic properties.

a) Zero viscosity ($T < T_c$)
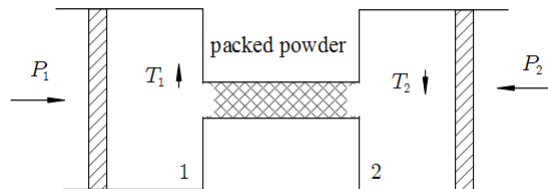
For ordinary fluid, $\Delta P = P_1 - P_2$ is need to maintain the flow from 1 to 2.

He^4$_{II}$ flow even in the limit of zero $\Delta P \longrightarrow$ Zero viscosity (Superfluid)

b) Torsional oscillator: Period of oscillation is proportional to the moment of inertia, which is modified by the fluid dragging the oscillator.
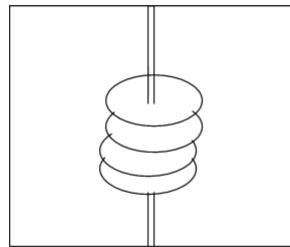
Work like normal fluid even when $T < T_c$, normal density $\longrightarrow 0$ as $T \to 0$.

(a) (b) $\longrightarrow$ two fluid model

– A normal component of density ρ_n, moving with velocity $\vec{v}_n$, having a finite entropy S_n.

– A superfluid component of density ρ_s, flow without viscosity and with no vorticity ($\nabla \times \vec{u}_s = 0$), has zero entropy $S_s = 0$.

many particles occupied the same state (B.E.C.)

$$\nabla \times \vec{u}_s = \nabla \times (\psi \nabla \psi) = \nabla \times \left(|\psi|^2 \nabla \theta\right) = |\psi|^2 \nabla \times \nabla \theta = 0$$
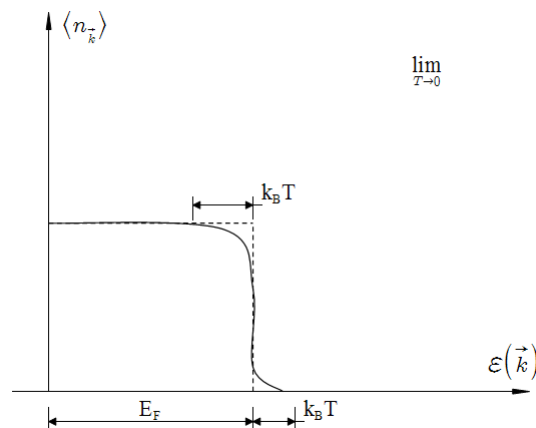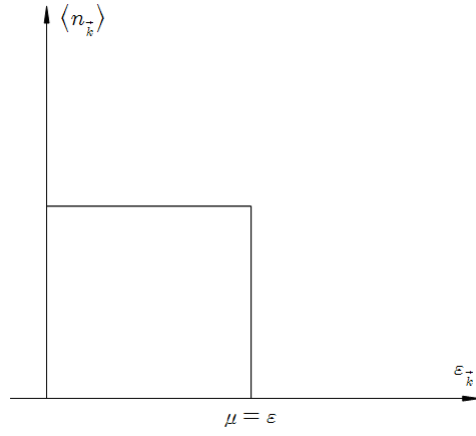
nonzero viscosity	zero viscosity

$$\nabla \times u_s \neq 0 \qquad \nabla \times u_s = 0$$
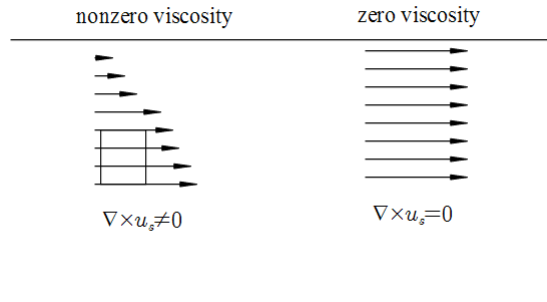
Superfluid with interaction
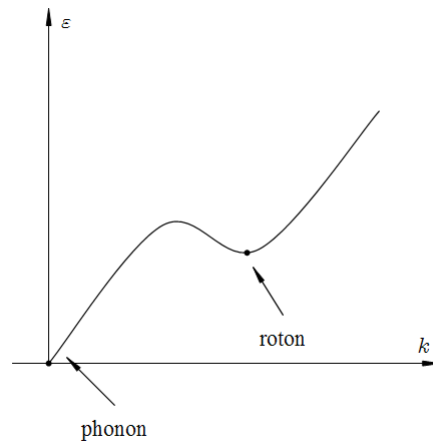
7.3 DEGENERATE FERMI GAS

$$\langle n_{\vec{k}} \rangle = \frac{1}{e^{\beta \varepsilon(\vec{k}) - \mu} + 1}$$

1. T = 0 Case

$$\begin{cases} \varepsilon\left(\vec{k}\right) < \varepsilon_F & n_{\vec{k}} = 1 \\ \varepsilon\left(\vec{k}\right) > \varepsilon_F & n_{\vec{k}} = 0 \end{cases}$$

$$\begin{aligned} N &= \sum_{|\vec{k}| \leqslant k_F, \varepsilon_{\vec{k}} \leqslant \varepsilon_F} (2S+1) = gV \int^{|\vec{k}| \leqslant k_F} \frac{d^3\vec{k}}{(2\pi)^3} \\ &= gV \frac{4\pi k_F^3}{3} \frac{1}{8\pi^3} = g\frac{V}{6\pi^2} k_F^3 \end{aligned}$$

$$S = \frac{1}{2}, \qquad g = 2$$

$$n = \frac{N}{V} = \frac{g}{6\pi^2} k_F^3$$

$$k_F = \left(\frac{6\pi^2 n}{g}\right)^{\frac{1}{3}} \implies \varepsilon_F(n) = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g}\right)^{\frac{2}{3}}$$

In QM, $T = 0$, the system only has one ground state $\Omega = 1$. While in CM, $\Omega_{Classical} \propto \frac{V^N}{N!}$.

2. $T \neq 0$ case

$$n_- = \frac{N_-}{V} = \frac{g}{\lambda^3} f_{\frac{3}{2}}^-(Z) \qquad Z = e^{\beta\mu}$$

$$f_m^-(Z) = \frac{1}{(m-1)!} \int dx \frac{x^{m-1}}{Z^{-1}e^x + 1}$$

We still have

$$\begin{cases} n = \frac{g}{\lambda^3} f_{\frac{3}{2}}^-(Z) \\ \beta P = \frac{g}{\lambda^3} f_{\frac{5}{2}}^-(Z) = \frac{2}{3}\beta\varepsilon, \quad P = \frac{2}{3}\varepsilon \\ \varepsilon = \frac{3}{2}P = \frac{1}{\beta}\frac{3g}{2\lambda^3} f_{\frac{5}{2}}^-(Z) \end{cases}$$

For $T \neq 0$ but is still very low, $Z \to \infty$.

The key problem is how to calculate $f_m^-(Z)$

$$\begin{aligned} f_m^-(Z) &= \frac{1}{(m-1)!} \int_0^\infty dx \frac{x^{m-1}}{Z^{-1}e^x + 1} \\ &= \frac{1}{m(m-1)!} \int_0^\infty \frac{dx^m}{Z^{-1}e^x + 1} \\ &= \frac{1}{m!}\left[\frac{x^m}{Z^{-1}e^x + 1}\Big|_{x=0}^\infty + \int_0^\infty \frac{x^m e^x Z^{-1} dx}{(Z^{-1}e^x + 1)^2} \right] \\ &= \frac{1}{m!} \int_0^\infty x^m \frac{d}{dx}\left(\frac{-1}{Z^{-1}e^x + 1}\right) dx \end{aligned}$$
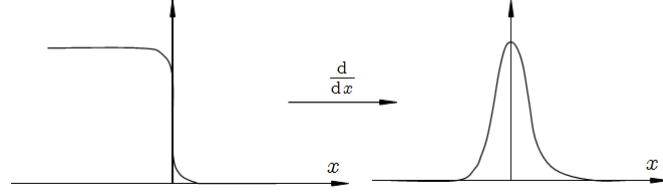
So we can expand, $x = \ln \mathcal{Z} + t, \quad t \in (-\infty, +\infty)$

$$
\begin{aligned}
\mathcal{Z}^{-1} e^x + 1 &= \mathcal{Z}^{-1} e^{\ln \mathcal{Z} + t} + 1 \\
&= e^t + 1
\end{aligned}
$$

$$
\begin{aligned}
f_m^-(\mathcal{Z}) &\cong \frac{1}{m!} \int_{-\infty}^{+\infty} dt \, (\ln \mathcal{Z} + t)^m \frac{d}{dt}\left(\frac{-1}{e^t + 1}\right) \\
&= \frac{1}{m!} \int_{-\infty}^{+\infty} dt \sum_{\alpha=0}^{\infty} \binom{m}{\alpha} t^\alpha (\ln \mathcal{Z})^{m-\alpha} \frac{d}{dt}\left(\frac{-1}{e^t + 1}\right) \\
&= \frac{1}{m!} \sum_{\alpha=0}^{\infty} \frac{m!}{\alpha! \, (m - \alpha)!} (\ln \mathcal{Z})^{-\alpha} \int_{-\infty}^{+\infty} t^\alpha \frac{d}{dt}\left(\frac{-1}{e^t + 1}\right) dt
\end{aligned}
$$

$\dfrac{e^t}{\left(e^t + 1\right)^2}$ Symmetry $t \longrightarrow -t$

$$
\frac{1}{\alpha!} \int_{-\infty}^{+\infty} t^\alpha \frac{d}{dt}\left(\frac{-1}{e^t + 1}\right) = \begin{cases} 0 & \text{for } \alpha \text{ odd} \\ \frac{2}{(\alpha-1)!} \int_0^\infty dt \frac{t^{\alpha-1}}{e^t+1} \equiv 2f_\alpha^-(1) & \text{for } \alpha \text{ even} \end{cases}
$$

$$
\begin{aligned}
\lim_{\mathcal{Z} \to \infty} f_m^-(\mathcal{Z}) &= \frac{(\ln \mathcal{Z})^m}{m!} \sum_{\alpha=0}^{\text{even}} 2 f_\alpha^-(1) \frac{m!}{(m-\alpha)!} (\ln \mathcal{Z})^{-\alpha} \\
&= \frac{(\ln \mathcal{Z})^m}{m!} \left[1 + \frac{\pi^2}{6} \frac{m(m-1)}{(\ln \mathcal{Z})^2} + \frac{7\pi^4}{360} \frac{m(m-1)(m-2)(m-3)}{(\ln \mathcal{Z})^4}\right]
\end{aligned}
$$

In the degenerate limit $\mathcal{Z} \longrightarrow \infty$

$$
\frac{n\lambda^3}{g} = f_{\frac{3}{2}}^-(\mathcal{Z}) = \frac{(\ln \mathcal{Z})^{\frac{3}{2}}}{(3/2)!}\left[1 + \frac{\pi^2}{6} \frac{3}{2} \frac{1}{2} (\ln \mathcal{Z})^{-2} + \cdots\right]
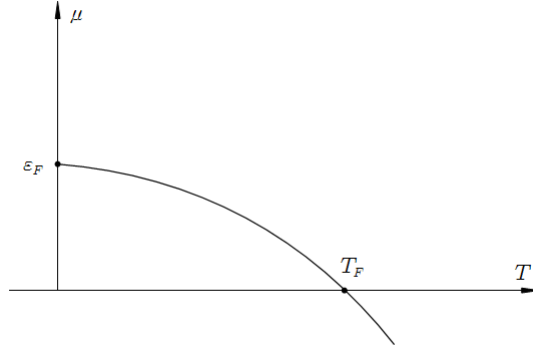$$

$$
\frac{n\lambda^3}{g} = \frac{(\ln \mathcal{Z})^{\frac{3}{2}}}{(3/2)!} = \frac{(\ln \mathcal{Z})^{\frac{3}{2}}}{\frac{3}{4}\sqrt{\pi}}
$$

$$
\lim_{T \to 0} \ln \mathcal{Z} = \left(\frac{n\lambda^3}{g}\right)^{\frac{2}{3}}
$$

$$
\begin{aligned}
\ln \mathcal{Z} &= \left(\frac{4}{3\sqrt{\pi}} \frac{n\lambda^3}{g}\right)^{\frac{2}{3}} \\
&= \left(\frac{6\pi^2 n}{g}\right)^{\frac{2}{3}} \frac{\beta \hbar^2}{2m} \\
&= \frac{\beta \hbar^2 k_F^2}{2m} = \beta \varepsilon_F \qquad (T \to 0)
\end{aligned}
$$

T small but not zero

$$\frac{n\lambda^3}{g} = \frac{(\ln z)^{\frac{3}{2}}}{(3/2)!}\left[1 + \frac{\pi^2}{6}\frac{3}{2}\frac{1}{2}(\ln z)^{-2}\right]$$

$$= \frac{(\ln z)^{\frac{3}{2}}}{(3/2)!}\left[1 + \frac{\pi^2}{8}(\ln z)^{-2}\right]$$

$$\cong \frac{(\ln z)^{\frac{3}{2}}}{(3/2)!}\left[1 + \frac{\pi^2}{8}\left(\frac{1}{\beta\varepsilon_F}\right)^2\right]$$

$$\ln z = \left(\frac{3}{2}\right)!\left(\frac{n\lambda^3}{g}\right)^{\frac{2}{3}}\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]^{-\frac{2}{3}}$$

$$= \beta\varepsilon_F\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]^{-\frac{2}{3}}$$

$$= \beta\varepsilon_F\left[1 + \frac{\pi^2}{8}\left(-\frac{2}{3}\right)\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]$$

$$= \beta\varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]$$

$\mu = k_B T \ln z > 0$ at low T, and $\mu = k_B T \ln z < 0$ at high T. Change sign at $T \approx T_F = \frac{\varepsilon_F}{k_B}$.

3. Pressure

$$\beta P = \frac{g}{\lambda^3}f_{\frac{5}{2}}(z)$$

$$= \frac{g}{\lambda^3}\frac{(\ln z)^{\frac{5}{2}}}{(5/2)!}\left[1 + \frac{\pi^2}{6}\frac{5}{2}\frac{3}{2}(\ln z)^{-2}\right]$$

$$= \frac{g}{\lambda^3}\frac{(\beta\varepsilon_F)^{\frac{5}{2}}}{(5/2)!}\left[1 + \frac{5\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]^{\frac{5}{2}}$$

$$= \frac{g}{\lambda^3}\frac{8(\beta\varepsilon_F)^{\frac{5}{2}}}{15\sqrt{\pi}}\left[1 + \frac{5\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]\left[1 - \frac{5}{2}\frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]$$

$$= \beta P_F\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right] \qquad \text{P for } T = 0$$

With $(5/2)! = \frac{5}{2}\cdot\frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi} = \frac{15}{8}\sqrt{\pi}$, $\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]^{\frac{5}{2}} \to 1 - \frac{5}{2}\frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2$.
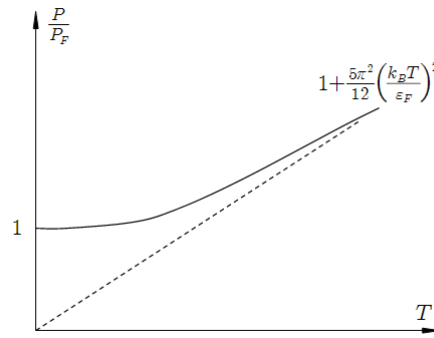
$$\frac{E}{V} = \frac{3}{2}P = \frac{3}{2}\frac{2}{5}n\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \cdots\right]$$

$$P_F = \frac{2}{3}\frac{E}{V} \xrightarrow{T=0} \frac{1}{V}\sum_{|\vec{k}|\leqslant k_F} g = g\frac{V}{V}\int_{k<k_F}\frac{d^3\vec{k}}{(2\pi)^3}\frac{\hbar^2 k^2}{2m}$$

$$= \frac{g\hbar^2}{2\pi^3 2m}4\pi\int_0^{k_F}k^2 k^2 dk = \frac{g\hbar^2}{4\pi^2 m}\frac{1}{5}k_F^5$$

$$= \left(\frac{gk_F^3}{6\pi^2}\right)\frac{3\hbar^2}{2m\cdot 5}k_F^2 = n\frac{3}{5}\left(\frac{\hbar^2 k_F^2}{2m}\right) = \frac{3}{5}n\varepsilon_F$$

4. Heat Capacity

$$C_V = \frac{dE}{dT} = \frac{d}{dT}\left[\frac{5}{12}\pi^2\left(\frac{T}{T_F}\right)^2\right]\frac{3}{5}n\varepsilon_F$$

$$= \frac{\pi^2}{2}Nk_B\left(\frac{T}{T_F}\right)$$

How to understand $C_V \sim T$ at low temperature? We know each degree of freedom carry energy $k_B T$, and only state near Fermi surface ε_F, and within the energy difference $k_B T$ can be excited, so the total number of states which can be excited is $D(\varepsilon_F)k_B T$

$$E \propto D(\varepsilon_F)(k_B T)^2$$

So we have $C_V = \frac{dE}{dT} \propto T$ which is independent of dimension.

7.4 HOMEWORK

PROBLEM 1: For a 2D many-Boson system with Hamiltonian,

$$H = \sum_{i=1}^N \frac{p_i^2}{2m}$$

we know we have the energy level and occupation as

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

$$n_n = \frac{1}{e^{\beta[\hbar^2 k^2/2m - \mu]} - 1}$$

(a) If the particles number is N, what is the chemical potential of this system?

(b) At what the temperature, BEC will occurs? Or BEC won't occur ?

(c) Calculate the total energy as a function of temperature and the heat capacity of this system.

PROBLEM 2: For a 2D many-Fermion system with Hamiltonian,

$$H = \sum_{i=1}^N \frac{p_i^2}{2m}$$

we know we have the energy level and occupation as

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m}$$

$$n_n = \frac{1}{e^{\beta[\hbar^2 k^2/2m - \mu]} + 1}$$

(a) If the particles number is N, what is the chemical potential of this system at zero temperature?

(b) Calculate the total energy as a function of temperature and the heat capacity of this system.

PROBLEM 3: For a 1D many-Boson system with Hamiltonian,

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 x_i^2$$

we know we have the energy level and occupation as

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

$$n_n = \frac{1}{e^{\beta[(n+1/2)\hbar\omega - \mu]} - 1}$$

(a) If the particles number is N, what is the chemical potential of this system?

(b) At what the temperature, BEC will occurs?

(c) Calculate the total energy as a function of temperature and the heat capacity of this system.

PROBLEM 4: For a 1D many-Fermion system with Hamiltonian,

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 x_i^2$$

we know we have the energy level and occupation as

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

$$n_n = \frac{1}{e^{\beta[(n+1/2)\hbar\omega - \mu]} + 1}$$

(a) If the particles number is N, what is the chemical potential of this system at zero temperature?

(b) Calculate the total energy as a function of temperature and the heat capacity of this system.

Part III
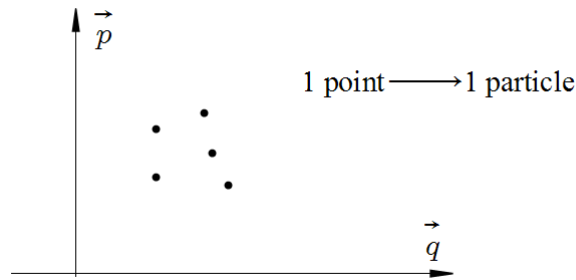
Interacting Many–particle Systems

8 | DISTRIBUTION FUNCTIONS FOR INTERACTING SYSTEMS

8.1 HOW TO DESCRIBE A N–BODY–SYSTEM?

– μ-Space
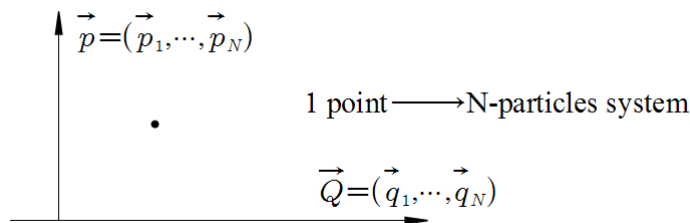
$$6D \; (\vec{q}_i, \vec{p}_i)$$

$$f(\vec{q}, \vec{p}, t) \qquad \# \text{ of microstate in } \mu\text{-Space}$$

(nearly independent system)

– Γ-Space

$$6ND \; (\vec{q}_1, \cdots, \vec{q}_N, \vec{p}_1, \cdots, \vec{p}_N)$$

$$\rho\left(\vec{Q}, \vec{P}, t\right) \qquad \text{(interacting system)}$$

– Kinetic theory

For a given initial macrostate, there exist many-many possible microstate. You don't know the initial microstate, you don't know the trajectory. So you need to guess the distribution of the initial microstate. $\rho\left(\vec{Q}, \vec{P}, t\right)$ is solve from Liouville equation.

– Ensemble theory

After a long time, the system approach a equilibrium state, (macrostate). But there still exist many possible microstates. We assume a distribution for all possible microstates. $\rho\left(\vec{Q}, \vec{P}, t\right)$ is given in this case.

$$O = \langle O\left(\vec{Q}, \vec{P}\right)\rangle = \int \frac{d^{3N}\vec{Q} \, d^{3N}\vec{P}}{h^{6N}} O\left(\vec{Q}, \vec{P}\right) \rho\left(\vec{Q}, \vec{P}, t\right)$$

$$\boxed{\text{Microstate}} \quad \Gamma = \prod_\alpha \{q_\alpha, p_\alpha\}_{\alpha=1}^N \qquad \text{6N-dim}$$
$$\downarrow$$
$$\boxed{\text{Macrostates}} \qquad (P, V, T, S, E) \qquad \text{a few-dim}$$

So there exist many-to-one comespondence between microstate and macrostate.

8.2 KINETIC THEORY AND LIOUVILLE'S THEOREM

N-body system $H\left(\vec{Q}, \vec{P}\right)$

$\Gamma = \prod\limits_{i=1}^{N} \{\vec{q}_i, \vec{p}_i\}$ 6N-dim phase space

$$\begin{cases} \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i} & \longrightarrow \text{definition of velocity} \\ \frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{q}_i} & \longrightarrow \text{Newton's Second Law, Equation of motion (EOM)} \end{cases}$$
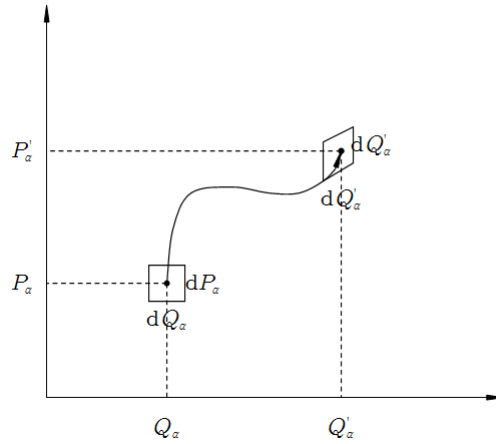
We need initial states.

But for given macrostates, there exist many possible microstates, don't know which one is the right one. We assume a possible distribution $\rho\left(\vec{Q}, \vec{P}, t_0\right)$, then using EOM, we know $\rho\left(\vec{Q}, \vec{P}, t\right)$. (phase space density)

$$\rho\left(\vec{Q}, \vec{P}, t\right) d\Gamma = \lim_{\mathcal{N} \to \infty} \frac{d\mathcal{N}\left(\vec{Q}, \vec{P}, t\right)}{\mathcal{N}}$$
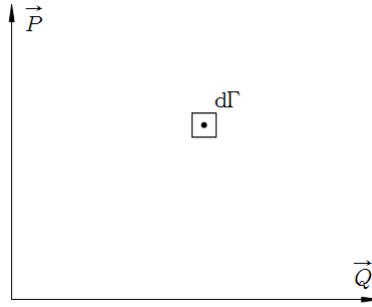
where $\mathcal{N}$ is the number of ensemble. $\int \rho\left(\vec{Q}, \vec{P}, t\right) d\Gamma \equiv 1$ normalized

– Liouville's theorem

$$Q'_\alpha = Q_\alpha + dQ_\alpha = Q_\alpha + \frac{dQ_\alpha}{dt}\delta t + O\left(\delta t^2\right)$$

$$P'_\alpha = P_\alpha + dP_\alpha = P_\alpha + \frac{dP_\alpha}{dt}\delta t + O\left(\delta t^2\right)$$

$$\begin{cases} dQ'_\alpha = dQ_\alpha + \frac{d\dot{Q}_\alpha}{dQ_\alpha}dQ_\alpha\delta t \\ dP'_\alpha = dP_\alpha + \frac{d\dot{P}_\alpha}{dP_\alpha}dP_\alpha\delta t \end{cases}$$

$$dQ'_\alpha dP'_\alpha = dQ_\alpha dP_\alpha \left[1 + \left(\frac{d\dot{Q}_\alpha}{dQ_\alpha} + \frac{d\dot{P}_\alpha}{dP_\alpha}\right)\delta t + O\left(\delta t^2\right)\right]$$

$$\frac{\partial \dot{Q}_\alpha}{\partial Q_\alpha} = \frac{\partial}{\partial Q_\alpha}\left(\frac{\partial H}{\partial P_\alpha}\right) = \frac{\partial^2 H}{\partial Q_\alpha \partial P_\alpha}$$

$$\frac{\partial \dot{P}_\alpha}{\partial P_\alpha} = \frac{\partial}{\partial P_\alpha}\left(-\frac{\partial H}{\partial Q_\alpha}\right) = -\frac{\partial^2 H}{\partial P_\alpha \partial Q_\alpha}$$

So $dQ'_\alpha dP'_\alpha \cong dQ_\alpha dP_\alpha, \quad d\Gamma' = d\Gamma$. (Liouville's theorem)

ρ behaves like the density of an incompressible fluid.

$$\rho\left(Q', P', t + \delta t\right) = \rho\left(Q, P, t\right)$$

$$
\begin{aligned}
0 = \frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{dp_\alpha}{dt} + \frac{\partial \rho}{\partial q_\alpha} \frac{dq_\alpha}{dt} \right) \\
&= \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial p_\alpha} \left(-\frac{\partial H}{\partial q_\alpha} \right) + \frac{\partial \rho}{\partial q_\alpha} \left(\frac{\partial H}{\partial p_\alpha} \right) \right] \\
&= \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right] \\
&= \frac{\partial \rho}{\partial t} + \{\rho, H\}
\end{aligned}
$$

Poisson bracket: $\{A, B\} \equiv \sum_{\alpha=1}^{3N} \left(\frac{\partial A}{\partial q_\alpha} \frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha} \frac{\partial B}{\partial q_\alpha} \right)$

So we have EOM for $\rho\left(\vec{Q}, \vec{P}, t\right)$

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}$$

It's so-called Liouville's Equation. Previous EOM is for $\left(Q_\alpha, P_\alpha\right)$.

Physical quantities

$$\langle O \rangle = \int \rho\left(\vec{Q}, \vec{P}, t\right) O\left(\vec{Q}, \vec{P}\right) d\Gamma$$

$$
\begin{aligned}
\frac{d\langle O \rangle}{dt} &= \frac{d}{dt} \int \rho\left(\vec{Q}, \vec{P}, t\right) O\left(\vec{Q}, \vec{P}\right) d\Gamma \\
&= \int \left(\frac{d}{dt} \rho \right) d\Gamma + \int \rho \frac{dO}{dt} d\Gamma \\
&= 0 + \int \rho \left\{ \frac{\partial Q}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial O}{\partial p_\alpha} \frac{dp_\alpha}{dt} + \frac{\partial O}{\partial q_\alpha} \frac{dq_\alpha}{dt} \right) \right\} d\Gamma \\
&= \int \rho \left\{ O + \sum_{\alpha=1}^{3N} \left[\frac{\partial Q}{\partial p_\alpha} \left(-\frac{\partial H}{\partial q_\alpha} \right) + \frac{\partial Q}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right] \right\} d\Gamma \\
&= \int \rho \{O, H\} d\Gamma \\
&= \langle \{O, H\} \rangle
\end{aligned}
$$

8.3 EQUILIBRIUM STATE AND ENSEMBLE THEORY

If the members of the emsemble comespond to an equilibrium macrostate, the ensemble averages must be indept of time

$$\frac{\partial \rho_{eq}}{\partial t} = 0 = \{\rho_{eq}, H\}$$

It can be used to solve ρ_{eq}. A possible solution is $\rho_{eq}\left(\vec{Q}, \vec{P}\right) = \rho\left(H\left(\vec{Q}, \vec{P}\right)\right)$

$$
\begin{aligned}
\{\rho\left(H\right), H\} &= \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho\left(H\right)}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial \rho\left(H\right)}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right) \\
&= \rho'\left(H\right) \sum_{\alpha=1}^{3N} \left(\frac{\partial H}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial H}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right) \\
&= 0
\end{aligned}
$$

So value of $\rho\left(H\right)$ is constant on surface of constant energy H in phase space.

This is the basic assumption of SM —— microcanonical emsemble.

In microcanonical emsemble, the total energy E is given and fixed. All members of ensemble must be on the surface of $H\left(\vec{Q}, \vec{P}\right) = E$. The above Eq. implies that a uniform density on this surface is stationary in time.

More generally, for same conserved quantities

$$
\begin{aligned}
0 = \frac{dL_n\left(\vec{Q}, \vec{P}\right)}{dt} &= \frac{L_n\left(\vec{Q}\left(t+dt\right), \vec{P}\left(t+dt\right)\right) - L_n\left(\vec{Q}\left(t\right), \vec{P}\left(t\right)\right)}{dt} \\
&= \sum_{\alpha=1}^{3N}\left(\frac{\partial L_n}{\partial p_\alpha}\frac{\partial p_\alpha}{\partial t} - \frac{\partial L_n}{\partial q_\alpha}\frac{\partial q_\alpha}{\partial t}\right) \\
&= -\sum_{\alpha=1}^{3N}\left(\frac{\partial L_n}{\partial p_\alpha}\frac{\partial H}{\partial q_\alpha} - \frac{\partial L_n}{\partial q_\alpha}\frac{\partial H}{\partial p_\alpha}\right) \\
&= \{L_n, H\}
\end{aligned}
$$

So

$$
\rho_{eq}\left(\vec{Q}, \vec{P}\right) = \rho_{eq}\left(H\left(\vec{Q}, \vec{P}\right), L_1\left(\vec{Q}, \vec{P}\right), L_2\left(\vec{Q}, \vec{P}\right), ..., L_n\left(\vec{Q}, \vec{P}\right)\right)
$$

How can we define "Equilibrium" for a system of moving particles?

- microstates are still changing. (moving particles)
- macrostates does not change. denoted by $E, L_1, \cdots, L_n$. distribution ρ doesnot change.

Equilibrium vs Maximum entropy

- Distribution $\rho\left(\vec{Q}, \vec{P}, t\right)$ or $\rho\left(\Gamma, t\right)$ or "phase space density"

  Entropy
  $$
  S\left(t\right) = -\int \rho\left(\Gamma, t\right)\ln \rho\left(\Gamma, t\right)d\Gamma
  $$

  Constraints
  $$
  \begin{cases}
  \int \rho\left(\Gamma, t\right)d\Gamma = 1 \\
  \int \rho\left(\Gamma, t\right)Hd\Gamma = E \quad \text{(energy can fluctuate)}
  \end{cases}
  $$

  Find ρ which has maximum entropy
  $$
  L = -\int \rho\left(\Gamma, t\right)\ln \rho\left(\Gamma, t\right)d\Gamma - \alpha\left[\int \rho\left(\Gamma, t\right)d\Gamma - 1\right] - \beta\left[\rho Hd\Gamma - E\right]
  $$

  $$
  \frac{\delta L}{\delta \rho} = -\ln \rho - 1 - \alpha - \beta H
  $$

  $$
  \rho = Ce^{-\alpha - \beta H(\Gamma)}
  $$

  $$
  \rho_{max} \equiv \frac{1}{Z}e^{-\beta H(\Gamma)}
  $$

  (Canonical ensemble! microcanonical is also included.)

  Show ρ_{max} is stationary
  $$
  \frac{\partial \rho_{max}}{\partial t} = \{\rho_{max}, H\} = 0
  $$

8.4 ENSEMBLE AVERAGE = TIME AVERAGE

- Ensemble average

  $\langle O \rangle_E = \int \rho\left(\Gamma, t\right)O\left(\Gamma\right)d\Gamma$

  $\langle O \rangle_E \longrightarrow$ macrostates, $\Gamma \longrightarrow$ microstates.

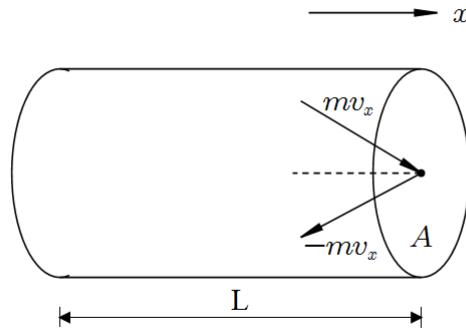 We have a distribution because we don't know the initial microstate. (Kinetic theory)

  Or after a long time, when the system is at equilibrium, the microstates have a stable distribution. (ensemble theory)

  Microstates are still charging macrostates & distribution does not change.

- Time average

  $$
  \langle O \rangle_T = \frac{1}{T_0}\int_0^{T_0} O\left(\Gamma\left(t\right)\right)dt
  $$

For example, when measure the pressure of a gas in container

$$
\begin{aligned}
P \quad &= \quad \frac{F}{A} = \frac{\overline{(\Delta m v_x)/\Delta t}}{A} = \frac{1}{2} \frac{2\overline{m v_x}}{\frac{L}{v_x} A} \\
&= \quad \frac{\overline{m v_x^2}}{V} = \frac{1}{V}\frac{1}{3}\overline{m v^2} \\
&= \quad \frac{1}{V}\frac{2}{3}\overline{\frac{1}{2} m v^2}
\end{aligned}
$$

It is time average.

measurement time τ.

in τ, particles collid with each other and microstates are changing. Γ experience many-many microstates.

So time average $\approx$ microstates average $\approx$ ensemble average

$$
\langle O \rangle_T = \langle O \rangle_E
$$

– Ergodic hypothesis

As time going, system explore all possible microstates with equal probability.

8.5 SHORT SUMMARY

1. Kinetic theory

$$
\begin{cases}
\frac{\partial \rho(\vec{Q},\vec{P},t)}{\partial t} = \{\rho, H\} & \text{EOM} \\
\rho\left(\vec{Q},\vec{P},t_0\right) & \text{ensemble}
\end{cases}
\longrightarrow \text{Solution of } \rho\left(\vec{Q},\vec{P}\right)
$$

2. Equilibrium state (Ensemble Theory)

$$
\frac{\partial \rho_{eq}}{\partial t} = 0 \longrightarrow \rho_{eq} = \rho(H) \quad \text{(sufficient but not necessary) is one of the solutions.}
$$

For isolated system $H = E \quad \rho_{eq} = const$ (microcanonical ensemble)

For closed system H can fluctuate, $\rho_{eq} \sim e^{-\beta H}$ has the maximum entropy. (canonical ensemble)

3. Ensemble average (theory) = time average (experiments)

8.6 DIFFERENT ENSEMBLE THEORY

	Isolated system	Closed system		Open system
Ensemble	Microcannonical	Cannonical	Gibbs Cannonical	Grand Cannonical
δQ	$\times$	$\checkmark$	$\checkmark$	$\checkmark$
δW	$\times$	$\times$	$\checkmark$	$\checkmark$
δN	$\times$	$\times$	$\times$	$\checkmark$
Conserved quantities	(E, N, V)	(T, N, V)	(T, N, P)	(T, μ, V)
$\rho\left(\vec{Q}, \vec{P}, t\right)$	$\frac{1}{\Omega(E,N,V)}$	$\frac{1}{\mathcal{Z}} e^{-\beta H(\mu_s)}$	$\frac{1}{\mathcal{Z}} e^{\beta \vec{J}\cdot\vec{x} - \beta H(\mu_s)}$	$\frac{1}{\Omega} e^{\beta \mu N - \beta H(\mu_s)}$
1st thermal quantity obtained to connect microstate and macrostate	$S = k_B \ln \Omega$ entropy	$F = -k_B T \ln \mathcal{Z}$ free energy	$G = -k_B T \ln \mathcal{Z}$ Gibbs free energy	$g = -k_B T \ln \Omega$ Giant potential
Other quantities	$dE = TdS - PdV$ $+ JdX + \mu dN$ E $\left.\frac{dE}{dS}\right\|_X = \frac{1}{T}$ $\left.\frac{dE}{dX}\right\|_S = J$ $\left.\frac{dS}{dX}\right\|_E = -\frac{J}{T}$	$dF = -SdT - PdV$ $+ JdX + \mu dN$ $F = E - TS$ $\left.S = -\frac{dF}{dT}\right\|_V$ $P = -\frac{dF}{dV}$ $J = \frac{dF}{dX}$	$dG = -SdT + PdV$ $- XdJ + \mu dN$ $G = E - TS - JX$ $P = \frac{dG}{dV}$ $X = -\frac{dG}{dJ}$ $\mu = \frac{dG}{dN}$	$dg = -SdT + JdX$ $- Nd\mu - PdV$ $g = E - TS - \mu N$ $N = -\frac{dg}{d\mu}$
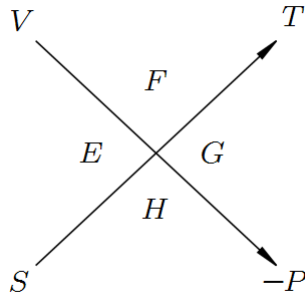
9

MICROCANONICAL ENSEMBLE AND THERMODYNAMICS

9.1 ISOLATED SYSTEM AND DISTRIBUTION

$\delta N = 0$	No particle exchange
$\delta W = 0$	No work done
$\delta Q = 0$	No heat exchange
Macrostate (N, E, V)	

$$\rho\left(E, \vec{X}\right)(\Gamma) = \begin{cases} \frac{1}{\Omega(E,\vec{X})} & \text{for } H(\Gamma) = E \\ 0 & \text{for } H(\Gamma) \neq E \end{cases}$$

where E is energy, $\vec{X}$ is macroscopic variables, Γ is microstate.

For all microstates with $H(\Gamma) = E$, they have equal possibility.

It is the unbiased probability estimation in phase space subject to the constraint of constant energy.

$$L = -\int \rho \ln \rho d\Gamma - \alpha \left[\int \rho d\Gamma - 1\right]$$

$$0 = \frac{\delta L}{\delta \rho} = -\ln \rho - 1 - \alpha = 0$$

$$\rho = e^{-1-\alpha} = \text{const}$$

$\Omega\left(E, \vec{X}\right)$ is the area of surface of const energy E in phase space. i.e. Number of microstates s.t $H(\Gamma) = E$.

- Entropy

$$S\left(E, \vec{X}\right) = k_B \ln \Omega\left(E, \vec{X}\right) \qquad \text{Boltzman}$$

Or from $\rho = \frac{1}{\Omega}$, we have information entropy

$$S_{inf} = -\int \rho \ln \rho d\Gamma$$

$$= -\sum_{\Gamma} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -\ln \frac{1}{\Omega}$$

$$= \ln \Omega$$

$$S = k_B S_{inf} = k_B \ln \Omega$$

$$\boxed{\Omega(E) = e^{\frac{S(E)}{k_B}}}$$

9.2 DERIVE THE THERMODYNAMICS FROM MICROCANONICAL THEORY

interaction between
two parts are small
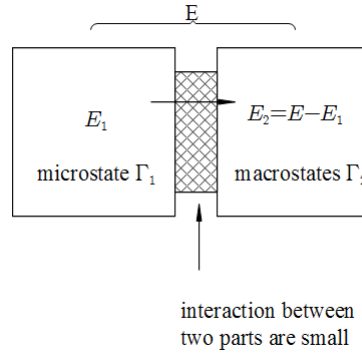
$$\Gamma = \Gamma_1 \otimes \Gamma_2$$

$$H(\Gamma) = H(\Gamma_1) + H(\Gamma_2)$$

i.e. $E = E_1 + E_2$

$$\rho_E(\Gamma) = \rho_E(\Gamma_1 \otimes \Gamma_2) = \begin{cases} \frac{1}{\Omega(E)} & \text{for } H(\Gamma_1) + H(\Gamma_2) = E \\ 0 & \text{otherwise} \end{cases}$$

Total allowed phase space (or number of microstates)

$$\Omega(E) = \int dE_1 \Omega_1(E_1) \Omega(E - E_1)$$

$$= \int e^{S(E_1)/k_B} e^{S(E-E_1)/k_B} dE_1$$

Entropy are extensive quantities and are $\propto N$. (Particle numbers in each container.)

$$\Omega \propto e^{S_i/k_B} \sim e^{N_i f(E_i)/k_B}$$

remenber that

$$\int e^{S(E)/k_B} dE \sim e^{S(E*)/k_B}$$

where E^* is the maximum value, from the lecture on mathematics.

– 2nd Law

$$
\begin{aligned}
\Omega(E) &= \int \exp\left[\frac{S_1(E_1) + S_2(E - E_1)}{k_B}\right] dE_1 \\
&= \exp\left[\frac{S_1(E_1^*) + S_2(E - E_1^*)}{k_B}\right]
\end{aligned}
$$

$$S(E) = k_B \ln \Omega(E) = S_1(E_1^*) + S_2(E_2^*)$$

where

$$
\begin{aligned}
0 &= \left.\frac{\partial[S_1(E_1) + S_2(E - E_1)]}{\partial E_1}\right|_{E_1 = E_1^*} \\
&= \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1 = E_1^*} + \left.\frac{\partial S_2(E_2)}{\partial E_2}\frac{\partial E_2}{\partial E_1}\right|_{E_1 = E_1^*} \quad (E_2 = E - E_1^*) \\
&= \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1 = E_1^*} - \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2 = E_2^*}
\end{aligned}
$$

i.e. $\left.\dfrac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1^*, \vec{X}_1} = \left.\dfrac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2^*, \vec{X}_2}$

From above we can see, the system's propertise can be represented by macrostates of which the entropy is maximized! This is the so-called equilibrium state.

– 2nd Law of thermodynamics

$$S_1(E_1^*) + S_2(E_2^*) \geqslant S_1(E_1) + S_2(E_2)$$

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geqslant 0$$

And when the system arrive equilibrium, we have the statement that

$$\left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1^*,\vec{X}_1} = \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2^*,\vec{X}_2}$$

- Zeroth law of thermodynamics

$$\left.\frac{\partial S_i}{\partial E_i}\right|_{E_i^*,\vec{X}_i} = \frac{1}{T_i}$$

So

$$T_1 = T_2$$

i.e. when two contacted system are at equilibrium. they should have the same temperature.

- 1st law of thermodynamics

$S(E,\vec{X})$ $\vec{X}$ are any coordinate thermal quantities. By changing the coordinate reversibly by $\delta\vec{X}$

$$\begin{aligned}
\delta S &= \delta S\left(E + \vec{J}\cdot\delta\vec{X}, \vec{X} + \delta\vec{X}\right) \\
&= \left.\frac{\partial S}{\partial E}\right|_{\vec{X}} \vec{J}\cdot\delta\vec{X} + \left.\frac{\partial S}{\partial\vec{X}}\right|_{E}\cdot\delta\vec{X} \\
&= \left(\left.\frac{\partial S}{\partial E}\right|_{\vec{X}}\vec{J} + \left.\frac{\partial S}{\partial\vec{X}}\right|_{E}\right)\delta\vec{X}
\end{aligned}$$

at Equilibrium $\frac{\delta S}{\delta\vec{X}} = 0$

$$0 = \left.\frac{\partial S}{\partial E}\right|_{\vec{X}}\cdot\vec{J} + \left.\frac{\partial S}{\partial\vec{X}}\right|_{E}$$

$$\left.\frac{\partial S}{\partial\vec{X}}\right|_{E} = -\frac{\vec{J}}{T}$$

then

$$\begin{aligned}
dS(E,\vec{X}) &= \left.\frac{\partial S(E,\vec{X})}{\partial E}\right|_{\vec{X}} dE + \left.\frac{\partial S(E,\vec{X})}{\partial\vec{X}}\right|_{T} d\vec{X} \\
&= \frac{1}{T}dE - \frac{\vec{J}\cdot d\vec{X}}{T}
\end{aligned}$$

So

$$dE = TdS + \vec{J}\cdot d\vec{X}$$

It's the energy conservation!

Ex: Prove that energy flow from high themperature object to low temperature objects
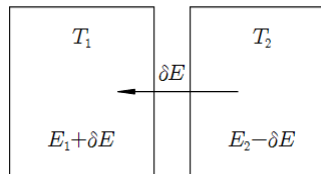
Set $T_1 > T_2$,

$$S(E) = S(E_1) + S(E_2)$$

$$\begin{aligned}
\delta S &= \left.\frac{\partial S_1}{\partial E_1}\right|_{\vec{X}_1}\delta E_1 - \left.\frac{\partial S_2}{\partial E_2}\right|_{\vec{X}_2}\delta E_2 \\
&= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E \geqslant 0
\end{aligned}$$

So if $T_1 > T_2$, $\frac{1}{T_1} - \frac{1}{T_2} < 0$. So $\delta E < 0$.

It is from T_1(high) to T_2(low)

For the point (E_1^*, E_2^*) to be a maximum. The second derivative should be negative

$$\frac{\partial^2 S(E)}{\partial E_1} = \frac{\partial}{\partial E_1}\left[\frac{\partial}{\partial E_1}(S_1(E_1) + S_2(E - E_1))\right]$$

$$= \frac{\partial}{\partial E_1}\left(\frac{\partial S_1(E_1)}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)$$

$$= \frac{\partial^2 S_1(E_1)}{\partial E_1^2} + \frac{\partial S_2(E_2)}{\partial E_2^2} \leqslant 0$$

$$\frac{\partial}{\partial E_i}\frac{\partial S_i}{\partial E_i} = \frac{\partial}{\partial E_i}\left(\frac{1}{T_i}\right) = -\frac{1}{T_i^2}\frac{\partial T_i}{\partial E_i}$$

$$= -\frac{1}{T_i^2}\frac{1}{C_{\vec{X}}}$$

$$\frac{\partial^2 S}{\partial E_1^2} = -\frac{1}{T_1^2}\frac{1}{C_{\vec{X}_1}} - \frac{1}{T_2^2}\frac{1}{C_{\vec{X}_2}}$$

$$= -\frac{1}{T^2}\left(\frac{1}{C_{\vec{X}_1}} + \frac{1}{C_{\vec{X}_2}}\right) \leqslant 0$$

So $\frac{1}{C_{\vec{X}_1}} + \frac{1}{C_{\vec{X}_2}} \leqslant 0$, i.e. $C_{X_i} \geqslant 0$. (Stability condition)

9.3 USE MICROCANONICAL ENSEMBLE TO GET THE THERMAL PROPERTIES OF THE NONINTERACTING SYSTEM

1. Two level systems

   $n_i = 1$ excited state   energy is ϵ.

   $n_i = 0$ ground state   energy is zero.
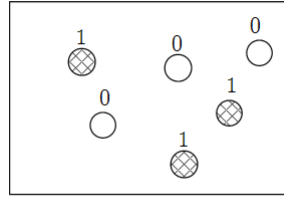
N impurity atoms

$$H(\{n_i\}) = \epsilon \sum_{i=1}^{N} n_i \equiv \epsilon N_1$$

where N_1 is total number of excited impurities.

Given the total energy E, what is the distribution function ρ_E?

$$\rho_E(\{n_i\}) = \frac{1}{\Omega(E,N)}\delta \sum_i \epsilon n_i, E$$

We need to calculate Ω (Number of microstates s.t. $H(\Gamma) = E$)

$$\Omega(E,N) = \binom{N}{N_1} = \frac{N!}{N_1!(N - N_1)!}$$

$$S(E, N) = k_B \ln \Omega(E, N) = k_B \ln \frac{N!}{N_1!(N-N_1)!}$$

$$= k_B [\ln N! - \ln N_1! - \ln(N-N_1)!]$$

$$= k_B [N \ln N - N_1 \ln N_1 - (N-N_1) \ln(N-N_1)]$$

$$= k_B [[N_1 + (N-N_1)] \ln N - N_1 \ln N_1 - (N-N_1) \ln(N-N_1)]$$

$$= -N k_B \left[\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{N-N_1}{N} \ln \frac{N-N_1}{N} \right]$$

$$= -N k_B \left[\left(\frac{E}{N\epsilon} \right) \ln \left(\frac{E}{N\epsilon} \right) + \left(1 - \frac{E}{N\epsilon} \right) \ln \left(1 - \frac{E}{N\epsilon} \right) \right]$$

$$= -N k_B [x \ln x + (1-x) \ln(1-x)]$$

$$\frac{\partial S(E, N)}{\partial E} = \frac{\partial S(E, N)}{\partial x} \frac{1}{N\epsilon}$$

$$= \frac{-N k_B}{N\epsilon} \frac{\partial}{\partial x} [x \ln x + (1-x) \ln(1-x)]$$

$$= -\frac{k_B}{\epsilon} [\ln x + 1 - \ln(1-x) + 1]$$

$$= -\frac{k_B}{\epsilon} \ln \left(\frac{x}{1-x} \right)$$

$$= -\frac{k_B}{\epsilon} \ln \frac{E}{N\epsilon - E} = -\frac{k_B}{\epsilon} \ln \frac{1}{\frac{N\epsilon}{E} - 1}$$

$$= \frac{k_B}{\epsilon} \ln \left(\frac{N\epsilon}{E} - 1 \right)$$

where $N_1 = \frac{E}{\epsilon}$, $\frac{N_1}{N} = \frac{N_1 \epsilon}{N\epsilon} = \frac{E}{N\epsilon}$, $\frac{N-N_1}{N} = 1 - \frac{E}{N\epsilon}$. By using $\ln N! \cong N \ln N$, $N = N_1 + (N - N_1)$

Using $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N = \frac{1}{N\epsilon} \frac{\partial S}{\partial (E/N\epsilon)}$, $x = \frac{E}{N\epsilon}$.

$$\frac{N\epsilon}{E} - 1 = e^{\frac{\epsilon}{k_B T}}$$

$$E = \frac{N\epsilon}{e^{\frac{\epsilon}{k_B T}} + 1} = N \left[\epsilon \frac{e^{\frac{-\epsilon}{k_B T}}}{e^{\frac{-\epsilon}{k_B T}} + 1} + 0 \frac{1}{e^{\frac{-\epsilon}{k_B T}} + 1} \right]$$
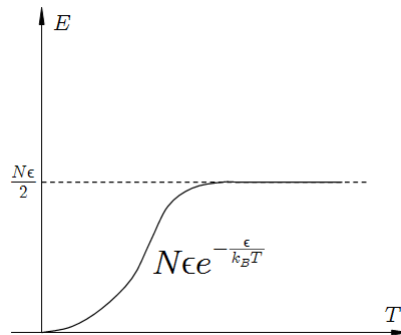
$$C = \frac{dE}{dT} = N k_B \left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{\frac{\epsilon}{k_B T}}}{\left(e^{\frac{\epsilon}{k_B T}} + 1 \right)^2}$$
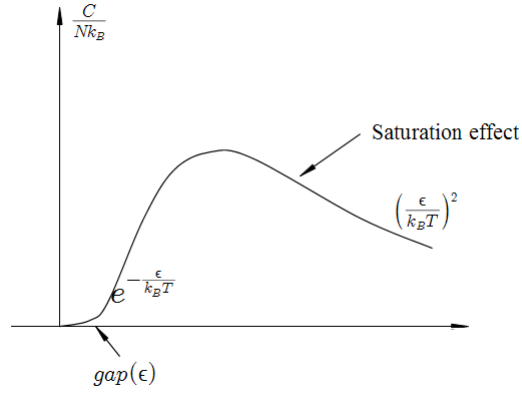
The above is macroscopic information. We can also get information about microstates. The unconditional probability for excited state is

$$P(n_1) = \sum_{\{n_2,n_3,\cdots,n_N\}} \rho(\{n_1,n_2,\cdots,n_N\})$$

$$= \frac{\Omega(E-n_1,N-1)}{\Omega(E,N)}$$

$$P(n_1=0) = \frac{\Omega(E,N-1)}{\Omega(E,N)} = \frac{\frac{(N-1)!}{N_1!(N-N_1-1)!}}{\frac{N!}{N_1!(N-N_1)!}}$$

$$= \frac{N-N_1}{N} = 1 - \frac{N_1}{N} = 1 - \frac{E}{N\epsilon}$$

$$E = \frac{N\epsilon}{e^{\frac{\epsilon}{k_B T}} + 1}$$

$$P(n_1=0) = \frac{1}{e^{\frac{-\epsilon}{k_B T}} + 1}$$

$$P(n_1=1) = \frac{e^{\frac{-\epsilon}{k_B T}}}{e^{\frac{-\epsilon}{k_B T}} + 1} = \frac{1}{e^{\frac{\epsilon}{k_B T}} + 1} = 1 - P(n_1=0)$$

2. Ideal gas

Preliminary

$$R^2 = \sum_{i=1}^{d} x_i^2$$

$$I_d = \int \prod_{i=1}^{d} e^{-x_i^2} dx_i = S_d \int_0^\infty R^{d-1} e^{-R^2} dR$$

$$= \frac{S_d}{2} \int_0^\infty y^{\frac{d}{2}-1} e^y dy = \frac{S_d}{2}\left(\frac{d}{2}-1\right)!$$

$$= \pi^{\frac{d}{2}}$$

where S_d is surface integral. So

$$S_d = \frac{2\pi^{\frac{d}{2}}}{\left(\frac{d}{2}-1\right)!}$$

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}$$

In Γ-Space, the constant energy space is

$$\sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} = E$$

It is a super sphere in $3N$ space, $3N$-space of coordinate is integrated to give a V^N factor.

So the radius for sphere is

$$\frac{R^2}{2m} = E, \qquad R = \sqrt{2mE}$$

So

$$\Omega(E, V, N) = \int \frac{d^3\vec{q}_i d^3\vec{p}_i}{h^{3N}} \delta\left(\sum_i \frac{\vec{p}_i^2}{2m} - E\right)$$

$$= \frac{V^N}{h^{3N}} S_{3N} \cdot R^{3N-1} dR$$

$$= \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (2mE)^{\frac{3N-1}{2}} dR$$

for simplicity $\frac{3N-1}{2} \approx \frac{3N}{2}$

$$S(E, V, N) = k_B \ln \Omega(E, V, N)$$

$$\cong k_B \left[\ln \frac{V^N}{h^{3N}} + \frac{3N}{2} \ln(\pi \cdot 2mE) - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2}\right]$$

$$= Nk_B \left[\ln \frac{V}{h^3} + \frac{3}{2} \ln(2\pi mE) - \frac{3}{2} \ln \frac{3N}{2} + \frac{3}{2}\right]$$

$$= Nk_B \ln \left[\frac{V}{h^3} \left(\frac{4\pi emE}{3N}\right)^{\frac{3}{2}}\right]$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = Nk_B \frac{3}{2} \frac{1}{E}$$

So

$$E = \frac{3}{2} Nk_B T$$

$$C_V = \frac{\partial E}{\partial T} = \frac{3}{2} Nk_B$$

$$dE = TdS - PdV$$

If in a process of $dE = 0$

$$\frac{P}{T} = \frac{dS}{dV}\bigg|_E = \frac{Nk_B}{V}$$

So

$$PV = Nk_B T$$

And the uncondition probability of find a particle in momentum $\vec{p}_1$ is

$$P(\vec{p}_1) = \int d^3\vec{q}_1 \int \prod_{i=1}^N d\vec{q}_i d\vec{p}_i \rho\left(\{\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2, \cdots, \vec{q}_N, \vec{p}_N\}\right)$$

$$= V \frac{\Omega\left(N-1, E - \frac{\vec{p}_1^2}{2m}, V\right)}{\Omega(N, E, V)}$$

$$= \frac{V \frac{V^{N-1}}{h^{3(N-1)}} S_{3N} \left(2m\left(E - \frac{\vec{p}_1^2}{2m}\right)\right)^{[3(N-1)-1]/2} \Delta R}{\frac{V^{3N}}{h^{3N}} S_{3(N-1)} (2mE)^{(3N-1)/2} \Delta R}$$

$$= \left(1 - \frac{\vec{p}_1^2}{2m}\right)^{\frac{3N}{2} - 2} \frac{1}{(2mE)^{\frac{3}{2}}} \frac{\left(\frac{3N}{2} - 1\right)!}{\left(\frac{3(N-1)}{2} - 1\right)!}$$

$$= \left(1 - \frac{\vec{p}_1^2}{2m}\right)^{\frac{3N}{2} - 2} \frac{\left(\frac{3N}{2} - 1\right)^{\left(\frac{3N}{2} - 1\right)}}{(2mE)^{\frac{3}{2}} \left(\frac{3N}{2} - 1 - \frac{3}{2}\right)^{\left(\frac{3N}{2} - 1 - \frac{3}{2}\right)}}$$

$$\cong \left(1 - \frac{\vec{p}_1^2}{2mE}\right)^{\frac{3N}{2} - 2} \frac{1}{(2\pi mE)^{3h}} \left(\frac{3N}{2}\right)^{\frac{3}{2}}$$

$$\cong \left(1 - \frac{3N\vec{p}_1^2}{2 \cdot 2mE}\right) \left(\frac{3N}{4\pi mE}\right)^{\frac{3}{2}}$$

$$\cong \left(\frac{3N}{4\pi mE}\right)^{\frac{3}{2}} e^{-\frac{3N\vec{p}_1^2}{2 \cdot 2mE}}$$

$$= \left(\frac{1}{2\pi mk_B T}\right)^{\frac{3}{2}} e^{-\frac{\vec{p}_1^2}{2mk_B T}}$$

by using $\lim_{N\to\infty}\left(1-\frac{x}{N}\right)^{N}=e^{-x}$, and $E=\frac{3}{2}Nk_{B}T$.

10 CANONICAL, GIBBS CANONICAL AND GRAND CANONICAL ENSEMBLE

10.1 CLOSED SYSTEM AND CANONICAL ENSEMBLES
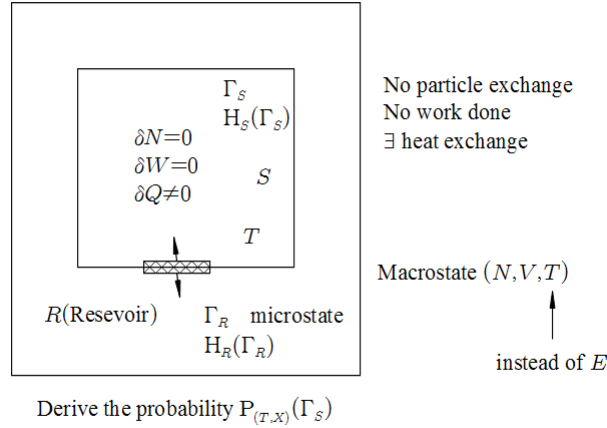
$E_{tot} = E_R + E_S \gg E_S$

$$\text{Reservoir} + \text{System} = \text{isolated System}$$

$$P(\Gamma_S \otimes \Gamma_R) = \begin{cases} \frac{1}{\Omega(\Gamma_S \otimes \Gamma_R)} & H(\Gamma_S) + H(\Gamma_R) = E_{tot} \\ 0 & \text{otherwise} \end{cases}$$

$$P(\Gamma_S) = \int P(\Gamma_S \otimes \Gamma_R) \, d\Gamma_R$$

$$= \int \frac{1}{\Omega_{S+R}(E_{tot})} d\Gamma_R$$

$$= \frac{\Omega_R(E_{tot} - H(\Gamma_S))}{\Omega_{S+R}(E_{tot})}$$

$$= \frac{e^{\frac{1}{k_B} S_R(E_{tot} - H(\Gamma_S))}}{e^{\frac{1}{k_B} S_{S+R}(E_{tot})}}$$

$$\approx \exp\left[\frac{1}{k_B}\left(S_R(E_{tot}) - \frac{\partial S_R(E_{tot})}{\partial E} H(\Gamma_S) - S_{S+R}(E_{tot})\right)\right]$$

$$\propto \exp\left[-\frac{H(\Gamma_S)}{k_B T}\right] = e^{-\beta H(\Gamma_S)}$$

where we have use the Boltzman relation $S = k_B \ln \Omega$ and Taylor expansion.

So

$$P(\Gamma_S) = \frac{e^{-\beta H(\Gamma_S)}}{\sum_{\Gamma_S} e^{-\beta H(\Gamma_S)}} \equiv \frac{e^{-\beta H(\Gamma_S)}}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_{\Gamma_S} e^{-\beta H(\Gamma_S)} \longrightarrow \text{Partition function}$$

Here, $P(\Gamma_S)$ represent the probability with which the system stay in the microstate Γ_S. And then we know the thermal properties of the system, i. e. the physical quantities of macrostate, are in forms of the expectation values.

The internal energy of the system is not a constant since the system in in contact with a reservoir and have energy exchange. The expectation value of the energy is,

$$\langle H \rangle = \sum_{\Gamma_S} H(\Gamma_S) \frac{e^{-\beta H(\Gamma_S)}}{\mathcal{Z}}$$

$$= \sum_{\Gamma_S} -\frac{\partial}{\partial \beta}\left(e^{-\beta H(\Gamma_S)}\right) \frac{1}{\mathcal{Z}}$$

$$= \frac{1}{\mathcal{Z}}\left(-\frac{\partial}{\partial \beta}\right)\sum_{\Gamma_S} e^{-\beta H(\Gamma_S)}$$

$$= \frac{1}{\mathcal{Z}}\left(-\frac{\partial \mathcal{Z}}{\partial \beta}\right) = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\boxed{E = \langle H \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}}$$

$$E = F + TS = F - T\frac{\partial F}{\partial T}\bigg|_X = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

$$= \frac{\partial}{\partial \left(\frac{1}{k_B T}\right)}\left(\frac{F}{k_B T}\right) = \frac{\partial(\beta F)}{\partial \beta}$$

$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

where F is the free energy, $\vec{X}$ is other quantities, $\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$, $\frac{\partial T}{\partial \beta} = -k_B T^2$. So

$$\boxed{F = -k_B T \ln \mathcal{Z}}$$
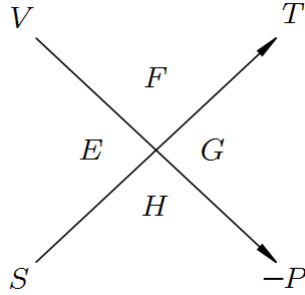
$$dE = -PdV + TdS$$
$$dF = -PdV - SdT$$

$$\begin{cases} S = -\frac{\partial F}{\partial T}\bigg|_V \\ P = -\frac{\partial F}{\partial V}\bigg|_T \end{cases}$$

We can get all other quantities from F.

10.2 FLUCTUATION OF ENERGY

Energy is not a constant in this system, the probability density of the energy ε is in form of,

$$P(\varepsilon) = \sum_{\Gamma_S} P(\Gamma_S) \, \delta(H(\Gamma_S) - \varepsilon)$$

$$= \sum_{\Gamma_S} \frac{e^{-\beta H(\Gamma_S)}}{\mathcal{Z}} \delta(H(\Gamma_S) - \varepsilon)$$

$$= \frac{e^{-\beta \varepsilon}}{\mathcal{Z}} \sum_{\Gamma_S} \delta(H(\Gamma_S) - \varepsilon)$$

$$= \frac{e^{-\beta \varepsilon}}{\mathcal{Z}} \Omega(\varepsilon)$$

$$= \frac{1}{\mathcal{Z}} e^{-\beta \varepsilon} e^{\frac{S(\varepsilon)}{k_B}} = \frac{1}{\mathcal{Z}} e^{-\beta(\varepsilon - TS(\varepsilon))}$$

$$= \frac{1}{\mathcal{Z}} e^{-\beta F(\varepsilon)}$$

Where $\Omega(\varepsilon)$ is the number of microstates of which the energy is ε. Then The variance of the energy is

$$\langle H^2 \rangle - \langle H \rangle^2 \equiv \langle H^2 \rangle_c$$

$$= \frac{1}{\mathcal{Z}} \sum_{\Gamma_S} H^2 e^{-\beta H} - \frac{1}{\mathcal{Z}^2} \left(\sum_{\Gamma_S} H e^{-\beta H} \right)^2$$

$$\frac{\partial \ln \mathcal{Z}}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{\partial}{\partial \beta} \ln \mathcal{Z} \right) = \frac{\partial}{\partial \beta} \left(\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} \right)$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \beta^2} - \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \beta} \right)^2$$

So

$$\langle H^2 \rangle_c = \frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2}$$

$$= -\frac{\partial}{\partial \beta} \left(-\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right) = k_B T^2 \frac{\partial}{\partial T} (\langle H \rangle)$$

$$= k_B T^2 C_{\bar{X}}$$

where $C_{\bar{X}}$ is the heat capacity.

$$\delta \varepsilon = \sqrt{\langle H \rangle_c^2} = \sqrt{k_B T^2 C_X} \propto \sqrt{N}$$

So

$$\frac{\delta \varepsilon}{\varepsilon} = \frac{\sqrt{\langle H^2 \rangle_c}}{\langle H \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \longrightarrow 0$$

as $N \longrightarrow \infty$.
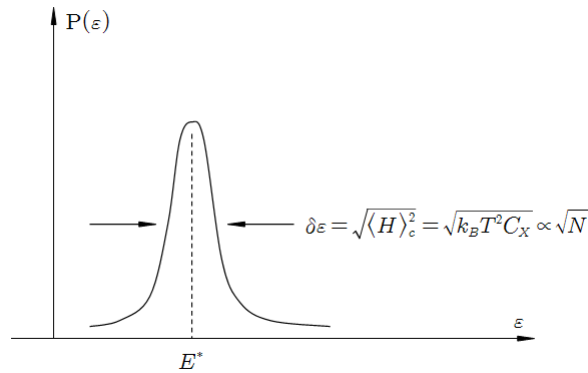
$$S = -k_B \int P\left(\Gamma_S\right) \ln P\left(\Gamma_S\right) d\Gamma_S$$

$$= -k_B \int \frac{e^{-\beta H(\Gamma_S)}}{\mathcal{Z}} \ln \frac{e^{-\beta H(\Gamma_S)}}{\mathcal{Z}} d\Gamma_S$$

$$= -k_B \left[\int P\left(\Gamma_S\right)\left(-\beta H\left(\Gamma_S\right)\right) d\Gamma_S - \int P\left(\Gamma_S\right)\left(-\ln \mathcal{Z}\right) d\Gamma_S \right]$$

$$= \frac{\langle H \rangle}{T} - k_B \ln \mathcal{Z}$$

$$= \frac{E - F}{T}$$

Which is consistent with TD.

10.3 EXAMPLES

In the followings, we calculate three cases as examples.

1. Two-level-systems

   N imparities

   $n_i = 1 \qquad$ Energy ϵ

   $n_i = 0 \qquad$ Energy 0

   $H = \epsilon \sum_i n_i \qquad$ Hamiltonian

   $\Gamma_S = \{n_1, n_2, \cdots, n_N\} \equiv \{n_i\} \qquad$ Microstates

$$P\left(\Gamma_S\right) = P\left(\{n_i\}\right) = \frac{1}{\mathcal{Z}} e^{-\beta \epsilon \sum_i n_i}$$

$$\mathcal{Z}\left(T, N\right) = \sum_{\Gamma_S} e^{-\beta H(\Gamma_S)}$$

$$= \sum_{\{n_i\}} \exp\left[-\beta \sum_i n_i\right]$$

$$= \left(\sum_{n_1=0}^{1} e^{-\beta n_1}\right) \left(\sum_{n_2=0}^{1} e^{-\beta n_2}\right) \cdots \left(\sum_{n_N=0}^{1} e^{-\beta n_N}\right)$$

$$= \left(1 + e^{-\beta \epsilon}\right)^N$$

$$F\left(T, N\right) = -k_B T \ln \mathcal{Z}$$

$$= -k_B T \ln \left(1 + e^{-\beta \epsilon}\right)^N$$

$$= -N k_B T \ln \left(1 + e^{-\beta \epsilon}\right)$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_N = N k_B \ln \left(1 + e^{-\beta \epsilon}\right) + N k_B T \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \left(\frac{\epsilon}{k_B T^2}\right)$$

$$E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = -\frac{\partial}{\partial \beta} N \ln \left(1 + e^{-\beta \epsilon}\right) = \frac{N \epsilon}{1 + e^{-\beta \epsilon}}$$

$$P = \prod_i p_i$$

$$p_i\left(n_i\right) = \frac{e^{-\beta n_i \epsilon}}{1 + e^{-\beta n_i \epsilon_i}}$$

2. Ideal gas

   microstates $\qquad \Gamma_S = \{\vec{p}_i, \vec{q}_i\}, \qquad H\left(\Gamma_S\right) = \sum_i \frac{\vec{p}_i^2}{2m}$

$$\mathcal{Z}\left(T, V, N\right) = \int \prod_{i=1}^{N} \frac{d^3 \vec{q}_i d^3 \vec{p}_i}{N! h^{3N}} \exp\left[-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}\right]$$

   Where

$$\frac{dp_i^{x,y,z}}{h} e^{-\beta \left(p_i^{x,y,z}\right)^2 / 2m} = \sqrt{\frac{2\pi m k_B T}{h^2}} = \frac{1}{\lambda\left(T\right)}$$

So

$$\mathcal{Z} = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} = \frac{1}{N!} \left(\frac{V}{\lambda^3(T)} \right)^N$$

$$\ln N! = N \ln N - N$$

$$F = -k_B T \ln \mathcal{Z}$$

$$= -N k_B T \ln V + N k_B T \ln N - N k_B T - \frac{3N}{2} k_B T \ln \left(\frac{2\pi m k_B T}{h^2} \right)$$

$$= -N k_B T \left[\ln \left(\frac{Ve}{N} \right) + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Pressure

$$P = -\frac{\partial F}{\partial V} \bigg|_{T,X} = \frac{\partial N k_B T \ln V}{\partial V} = \frac{N k_B T}{V}$$

$$PV = N k_B T$$

Chemical potential

$$\mu = \frac{\partial F}{\partial N} = \frac{F}{N} + k_B T$$

$$= -k_B T \left[\ln \frac{V}{N} + \frac{3}{2} \ln \lambda^2(T) \right]$$

$$= k_B T \left[\ln \frac{N}{V} - \ln \lambda^3(T) \right]$$

$$\mu = k_B T \ln \left(n \lambda^3(T) \right)$$

$$S = -\frac{\partial F}{\partial T} \bigg|_{V,N}$$

$$= -N k_B \left[\ln \frac{Ve}{N} + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] - N k_B T \frac{3}{2} \frac{1}{T}$$

$$= \frac{F - E}{T}$$

10.4 GIBBS CANONICAL ENSEMBLE

1. Closed systems with changes by addition of heat and work

$$E_{tot} = H_S(\Gamma_S) + H_R(\Gamma_R)$$
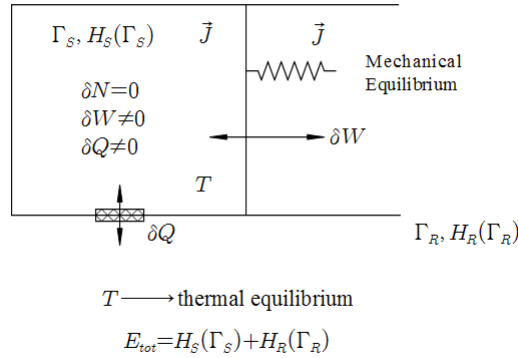
Including the work done by the system against the force, the energy of the combined system is $\left(H - \vec{J} \cdot \vec{X} \right)$.
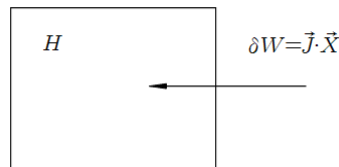
The energy of the system is H and part of it is from external force $\delta W = \vec{J} \cdot \vec{X}$, so the energy from internal degree of freedom is $\left(H - \vec{J} \cdot \vec{X}\right)$.

using canonical ensemble

$$P\left(\Gamma_S, \vec{X}\right) = \frac{e^{-\beta\left(H(\Gamma_S) - \vec{J} \cdot \vec{X}\right)}}{Z} = \frac{e^{\beta \vec{J} \cdot \vec{X} - \beta H(\Gamma_S)}}{Z}$$

$$Z\left(N, T, \vec{J}\right) = \sum_{\Gamma_S, \vec{X}} e^{\beta \vec{J} \cdot \vec{X} - \beta H(\Gamma_S)}$$

The expectation value of the coordinates

$$\langle \vec{X} \rangle = \int \vec{X} \frac{e^{\beta \vec{J} \cdot \vec{X} - \beta H(\Gamma_S)}}{Z} d\Gamma_S$$

$$= k_B T \int \frac{\frac{\partial}{\partial \vec{J}} e^{\beta \vec{J} \cdot \vec{X} - \beta H(\Gamma_S)}}{Z} d\Gamma_S$$

$$= k_B T \frac{\partial \ln Z}{\partial \vec{J}}$$

$$\vec{X} = \frac{\partial (k_B T \ln Z)}{\partial \vec{J}}$$

$$\begin{matrix} \overset{(\vec{X})}{V} & & & T \\ & & F & \\ E & & & G \\ & & H & \\ S & & & \underset{(\vec{J})}{-P} \end{matrix}$$
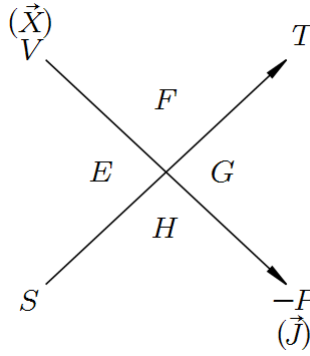
$$dG = -SdT + VdP - \vec{X} \cdot d\vec{J}$$

$$S = -\left.\frac{\partial G}{\partial T}\right|_{P,\vec{X}}$$

$$P = \left.\frac{\partial G}{\partial V}\right|_{T,\vec{J}}$$

$$\vec{X} = -\left.\frac{\partial G}{\partial \vec{J}}\right|_{T,P}$$

So

$$G = -k_B T \ln Z \qquad P\left(\Gamma_S\right) = \frac{e^{\beta(\vec{J} \cdot \vec{X} - H)}}{Z}$$

or from

$$S = -k_B \int P\left(\Gamma_S\right) \ln P\left(\Gamma_S\right) d\Gamma_S$$

$$= -k_B \left[\int P\left(\Gamma_S\right) \beta \left(\vec{J} \cdot \vec{X} - H\right) d\Gamma_S - \int P\left(\Gamma_S\right) \ln Z d\Gamma_S\right]$$

$$= \frac{1}{T}\left[-\vec{J}\langle\vec{X}\rangle + \langle H \rangle\right] + k_B \ln Z$$

$$-k_B T \ln Z = -\vec{J}\langle\vec{X}\rangle + \langle H \rangle - TS$$

$$= E - \vec{J}\langle\vec{X}\rangle - TS$$

$$= G$$

$$G = -k_B T \ln Z$$

$$-\frac{\partial \ln Z}{\partial \beta} = -\vec{J}\langle\vec{X}\rangle + \langle H \rangle \equiv H \quad (\text{enthalpy})$$

2. Examples

a) Ideal gas under pressure

$$P(\Gamma_S, V) = \frac{e^{-\beta PV - H(\Gamma_S)}}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_{\Gamma_S, V} e^{-\beta PV - H(\Gamma_S)}$$

$$= \int dV \int \frac{d^3\vec{q}_i d^3\vec{p}_i}{N! h^{3N}} \exp\left(-\beta \sum_i \frac{\vec{p}_i^2}{2m} - \beta PV\right)$$

$$= \int dV \frac{V^N}{N!} \frac{1}{\lambda^{3N}} e^{-\beta PV}$$

$$= \frac{1}{N!\lambda^{3N}} \left[\int (\beta PV)^N e^{-\beta PV} d(\beta PV)\right] \frac{1}{(\beta P)^{N+1}}$$

$$= \frac{1}{N!\lambda^{3N}} \Gamma(N+1) \frac{1}{(\beta P)^{N+1}}$$

$$= \frac{1}{N!\lambda^{3N}} N! \frac{1}{(\beta P)^{N+1}}$$

$$= \frac{1}{(\beta P)^{N+1} \lambda^{3N}}$$

$$G = -k_B T \ln \mathcal{Z}$$

$$= k_B T \left[\ln(\beta P)^N - \ln\left(\sqrt{\frac{2\pi m k_B T}{h^2}}\right)^3\right]$$

$$= N k_B T \left[\ln P - \frac{5}{2}\ln k_B T + \frac{3}{2}\ln \frac{h^2}{2\pi m}\right]$$

$$V = -\frac{\partial G}{\partial P} = \frac{N k_B T}{P} \longrightarrow PV = N k_B T$$

$$H = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{5}{2} N k_B T$$

$$C_P = \frac{\partial H}{\partial T} = \frac{5}{2} N k_B$$

b) Magnetic dipoles in magnetic field

$$\uparrow \quad \sigma_i = +1 \quad \vec{m}_i = \mu_B \sigma_i \quad \vec{M} = \sum_i \vec{m}_i = \mu_B \sum_i \sigma_i$$

$$\downarrow \quad \sigma_i = -1 \quad \text{energy} \quad \vec{B} \cdot \vec{M} = B \mu_B \sum_i \sigma_i$$

microstates $\{\sigma_1, \sigma_2, \cdots, \sigma_N\} = \{\sigma_i\}$ $H(\{\sigma_i\}) = 0$ no interaction between dipoles

$$P(\{\sigma_i\}) = \frac{1}{\mathcal{Z}} e^{\beta B \mu_0 \sum_i \sigma_i}$$

$$\mathcal{Z} = \sum_M e^{\beta B \mu_0 \sum \sigma_i}$$

$$= \left(e^{\beta B \mu_0} + e^{-\beta B \mu_0}\right)^N$$

$$= [2\cosh(\beta \mu_0 B)]^N$$

$$G = -k_B T \ln \mathcal{Z} = -N k_B T \ln[2\cosh(\beta \mu_0 B)]$$

magnetization

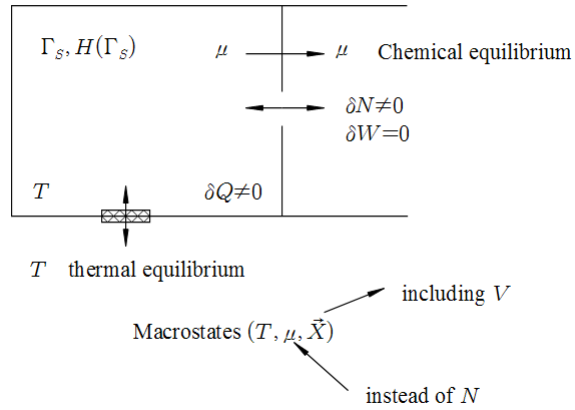$$M = -\frac{\partial G}{\partial B} = N\mu_0 \tanh(\beta\mu_0 B)$$

magnetic susceptibility

$$\begin{aligned}
\chi(T) &= \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{N\mu_0^2}{k_B T}\left.\frac{1}{\cosh^2(\beta\mu_0 B)}\right|_{B=0} \\
&= \frac{N\mu_0^2}{k_B T}
\end{aligned}$$
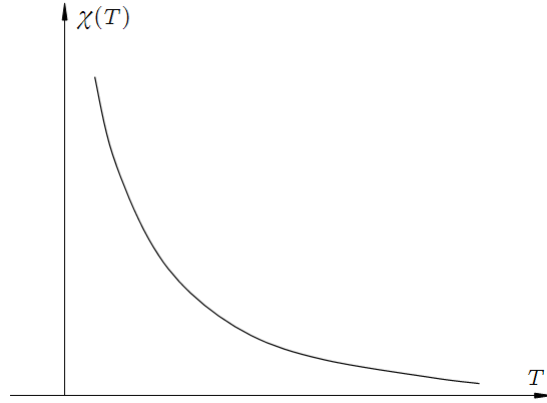
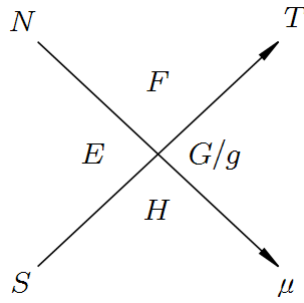## 10.5   GRAND CANONICAL ENSEMBLE

1. Open system

microstates Γ_S contain a indefinitive number of particles N (μ_S)

$$P(\Gamma_S, N) = \frac{e^{\beta\mu N - \beta H(\Gamma_S)}}{Q}$$

$$Q\left(T, \mu, \vec{X}\right) = \sum_N \sum_{\Gamma_S} e^{\beta\mu N - \beta H(\Gamma_S)}$$

$$\begin{aligned}
S &= -k_B \int P(\Gamma_S, N)\ln\frac{e^{\beta\mu N - H(\Gamma_S)}}{Q} d\Gamma_S dN \\
&= -k_B \int P(\Gamma_S, N)\left[\beta(\mu N - H(\Gamma_S))\right]d\Gamma_S dN + k_B \int P(\Gamma_S, N)\ln Q\, d\Gamma_S dN \\
&= -\frac{1}{T}\mu\langle N\rangle + \frac{1}{T}\langle H\rangle + +k_B\ln Q - k_B\ln Q \\
&= \langle H\rangle - TS - \mu N \\
&\equiv g
\end{aligned}$$

$$g = -k_B T\ln Q$$

$$dg = -SdT + PdV - Nd\mu + \vec{J} \cdot d\vec{X}$$

$$g = E - TS - \mu N - \vec{J} \cdot \vec{X}$$

$$S = -\left.\frac{\partial g}{\partial T}\right|_{\mu,\vec{X}}$$

$$N = -\left.\frac{\partial g}{\partial \mu}\right|_{T,\vec{X}}$$

$$\vec{J} = \frac{\partial g}{\partial \vec{X}}$$

2. Example
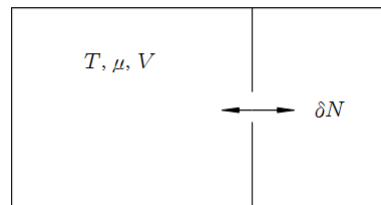
macrostates (T, μ, V)

microstates $\{\vec{p}_i, \vec{q}_i\}$

$$H(\Gamma_S) = \sum_i \frac{\vec{p}_i^2}{2m}$$

$$Q = \sum_{N=0}^{\infty} \sum_{\Gamma_S} e^{\beta\mu N - \beta \sum_i \frac{\vec{p}_i^2}{2m}}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \int \prod_i \frac{d^3\vec{q}_i d^3\vec{p}_i}{N!h^{3N}} e^{-\beta \frac{\vec{p}_i^2}{2m}}$$

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

$$= \exp\left[e^{\beta\mu} \frac{V}{\lambda^3}\right]$$

$$g = -k_B T \ln Q = -k_B T e^{\beta\mu} \frac{V}{\lambda^3}$$

$$P = -\frac{\partial g}{\partial V} = \frac{-g}{V} = k_B T \frac{e^{\beta\mu}}{\lambda^3}$$

$$N = -\frac{\partial g}{\partial \mu} = \frac{e^{\beta\mu} V}{\lambda^3}$$

$$\mu = k_B T \ln\left(\lambda^3 \frac{N}{V}\right) = k_B T \ln\left(\frac{P\lambda^3}{k_B T}\right)$$

$$P = \frac{N k_B T}{V}$$

11 | VAN DE WAALS GAS AND FIRST ORDER PHASE TRANSITION

11.1 OUTLINE

– System: Classical many-particle system with interaction

$$H = \sum \frac{\vec{p}_i^2}{2m} + \sum_{i<j} V(\vec{q}_i - \vec{q}_j)$$

– Method: Ensemble theory

$$\mathcal{Z} = \frac{1}{N!h^{3N}} \prod_i \int e^{-\beta \frac{\vec{p}_i^2}{2m} - \beta \sum\limits_{i<j} V(\vec{q}_i - \vec{q}_j)} d\vec{p}_i d\vec{q}_i$$

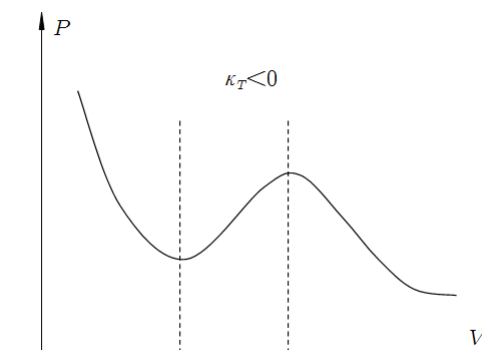$$= \frac{1}{N!\lambda^{3N}} \int \prod_{i=1}^{N} e^{-\beta V(\vec{q}_i - \vec{q}_j)}$$

1. Cluster Expansion

$$\mathcal{Z} = \frac{1}{N!\lambda^{3N}} \int \prod_i d\vec{q}_i \prod_{i<j} \left[e^{-\beta V(\vec{q}_i - \vec{q}_j)} \right]$$

$$= \frac{1}{N!\lambda^{3N}} \int \prod_i d\vec{q}_i \prod_{i<j} \left[1 + \left(e^{-\beta V(\vec{q}_i - \vec{q}_j)} - 1 \right) \right]$$

$$= \frac{1}{N!\lambda^{3N}} \int \prod_i d\vec{q}_i \prod_{i<j} \left[1 + f_{ij} \right]$$

2. Mean Field Method

– VdW gas Equation : $P = \frac{Nk_BT}{V - \frac{N\Omega}{2}} - \frac{\mu N^2}{2V^2}$.

1. Working condition: low density; high T; short range fore

2. Physical interpretation

3. Unstability

4. Phase transition (1st order)

11.2 CLASSICAL INTERACTING MANY-BODY SYSTEM AND ITS PARTITION FUNCTION

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i<j} V\left(\vec{q}_i - \vec{q}_j\right)$$
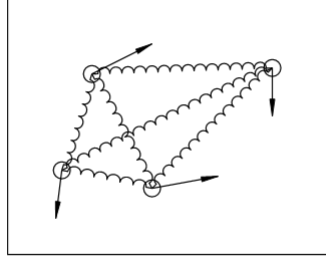
$$\text{microstate} \quad \Gamma_S = \{q_1, q_2, \cdots, q_N, p_1, \cdots, p_N\}$$

Using Canonical Ensemble

$$\rho\left(\Gamma_S\right) = \frac{1}{Z} e^{-\beta H(\Gamma_S)}$$

$$Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{N} e^{-\beta \sum_i \frac{\vec{p}_i}{2m} - \beta \sum_{i<j} V\left(\vec{q}_i - \vec{q}_j\right)} d\vec{p}_i d\vec{q}_i$$

$$\frac{1}{h^3} \int e^{-\beta \frac{\vec{p}_i}{2m}} d\vec{p}_i = \left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \qquad \text{thermal wavelength}$$

$$Z = \frac{1}{N! \lambda^{3N}} \int \prod_i e^{-\beta \sum_{i<j} V\left(\vec{q}_i - \vec{q}_j\right)} d\vec{q}_i$$

$$= \frac{1}{N! \lambda^{3N}} \int \prod_i d\vec{q}_i \left[1 + \left(e^{-\beta \sum_{i<j} V\left(\vec{q}_i - \vec{q}_j\right)} - 1\right)\right]$$

$$= \frac{1}{N! \lambda^{3N}} \int \prod_i d\vec{q}_i \left[1 + f_{ij}\right]$$

If $V = 0$, $f_{ij} = 0$. It is reduced to the noninteracting cases.

Cluster expansion

$$Z = \frac{1}{N! \lambda^{3N}} \int \prod_i d\vec{q}_i \left(1 + f_{12}\right)\left(1 + f_{13}\right)\left(1 + f_{14}\right) \cdots \left(1 + f_{1N}\right)$$

$$\times \left(1 + f_{23}\right)\left(1 + f_{24}\right) \cdots \left(1 + f_{2N}\right)$$

$$\times \left(1 + f_{34}\right) \cdots \left(1 + f_{3N}\right)$$

$$\ddots \qquad \vdots$$

$$\left(1 + f_{N-1,N}\right)$$

For example $N = 3$

$$Z = \frac{1}{3! \lambda^{3 \times 3}} \int dq_1 dq_2 dq_3 \quad \left(1 + f_{12}\right)\left(1 + f_{13}\right)\left(1 + f_{23}\right)$$

$$= \frac{1}{3! \lambda^{3 \times 3}} \int dq_1 dq_2 dq_3 \quad [1 + \left(f_{12} + f_{13} + f_{23}\right) + \left(f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}\right)$$

$$+ f_{12}f_{13}f_{23}]$$

Using a diagram

$$\frac{1}{3!\lambda^9}\int dq_1 dq_2 dq_3 \cdot 1 = \underset{1}{\bigcirc} \quad \underset{2}{\bigcirc} \quad \underset{3}{\bigcirc} = b_1$$

$$\frac{1}{3!\lambda^9}\int dq_1 dq_2 dq_3 \cdot f_{12} = \underset{1}{\bigcirc}\!\!-\!\!\underset{2}{\bigcirc} \quad \underset{3}{\bigcirc} \left.\begin{array}{l} \\ \\ \\ \end{array}\right\}$$

$$+\, f_{13} = \underset{1}{\bigcirc} \quad \underset{2}{\bigcirc} \quad \underset{3}{\bigcirc} \quad \Big\} b_2$$

$$+\, f_{23} = \underset{1}{\bigcirc} \quad \underset{2}{\bigcirc}\!\!-\!\!\underset{3}{\bigcirc}$$

$$\frac{1}{3!\lambda^9}\int dq_1 dq_2 dq_3 \cdot f_{12} f_{23} = \underset{1}{\bigcirc}\!\!-\!\!\underset{2}{\bigcirc}\!\!-\!\!\underset{3}{\bigcirc} \left.\begin{array}{l} \\ \\ \\ \\ \\ \end{array}\right\}$$

$$+ f_{12} f_{13} = \underset{1}{\bigcirc}\!\!-\!\!\underset{2}{\bigcirc} \quad \underset{3}{\bigcirc}$$

$$+ f_{13} f_{23} = \underset{1}{\bigcirc} \quad \underset{2}{\bigcirc}\!\!-\!\!\underset{3}{\bigcirc} \quad \Big\} b_3$$

$$+ f_{12} f_{23} f_{13} = \underset{1}{\bigcirc}\!\!-\!\!\underset{2}{\bigcirc}\!\!-\!\!\underset{3}{\bigcirc}$$

$$b_1 = \int dq_1 dq_2 dq_3 \cdot 1 = V^3 = (Vb)^3 \qquad b \equiv 1$$

$$b_2 = \int dq_1 dq_2 dq_3 \left(e^{-\beta V(q_1 - q_2)} - 1\right)$$

$$= V \int dq_1 dq_2 \left(e^{-\beta V(q_1 - q_2)} - 1\right)$$

$$= V \int dq_2 \int d(q_1 - q_2) \left(e^{-\beta V(q_1 - q_2)} - 1\right)$$

$$= V^2 \int dq \left(e^{-\beta V(q)} - 1\right)$$

$$= (Vb_1)^2 (Vb_2)$$

$$b_2 = \frac{1}{V} \int dq \left(e^{-\beta V(q)} - 1\right)$$

$$b_3 = \int dq_1 dq_2 dq_3 \left(f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{23}f_{13}\right)$$

$$= \int dq_1 d(q_2 - q_1) d(q_3 - q_1) [f(q_2 - q_1) f(q_3 - q_1)$$

$$+ f(q_2 - q_1) f(q_3 - q_1 - (q_2 - q_1)) + f(q_3 - q_1) f(q_3 - q_1 - (q_2 - q_1))$$

$$+ f(q_3 - q_1) f(q_2 - q_1) f(q_3 - q_1 - (q_2 - q_1))]$$

$$= V \int dx dy \left[f(x) f(y) + f(x) f(y - x) + f(y) f(y - x) + f(x) f(y) f(x - y)\right]$$

$$= V^3 b_3$$

$$Z_{N=3} = \frac{V^3}{3!\lambda^{3\times 3}} \left[b_1^3 + 3b_1 b_2 + b_3 + \cdots\right]$$

For arbitrary

$$Z_N = \frac{V^N}{N!\lambda^{3N}} \left[b_1^N + \binom{N}{2} b_1^{N-1} b_2 + \binom{N}{3} b_1^{N-2} b_3 + \cdots\right]$$

$$= \frac{V^N}{N!\lambda^{3N}} \left[b_1^N + \frac{N(N-1)}{2} b_1^{N-1} b_2 + \cdots\right]$$
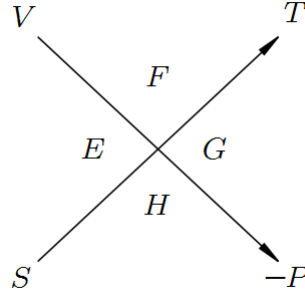
We just consider 1st order correction on free particle case.

$$b_1 = 1$$

$$b_2 = \frac{1}{V} \int dq \left[e^{-\beta V(q)} - 1 \right]$$

For more general case and higher order, please refer to "SM of Particles" Merhan kardar.

$$\mathcal{Z}_N = \frac{V^N}{N! \lambda^{3N}} \left[1 + \frac{N(N-1)}{2} b_2 \right] \approx \frac{V^N}{N! \lambda^{3N}} \left[1 + \frac{N^2}{2V} (Vb_2) \right]$$

$$F = -k_B T \ln \mathcal{Z}$$

$$= -k_B T \ln \frac{V^N}{N! \lambda^{3N}} \left[1 + \frac{N^2}{2V} (Vb_2) \right]$$

Vb_2 indept of V.

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

$$= N k_B T - k_B T \frac{\partial}{\partial V} \left[\ln \left(1 + \frac{N^2}{2V} (Vb_2) \right) \right]$$

$$\cong N k_B T - k_B T \frac{\partial}{\partial V} \left[\frac{N^2}{2V} (Vb_2) \right]$$

$$= \frac{N k_B T}{V} + k_B T \frac{N^2}{2V^2} \left[\int e^{\beta V(q)} dq - 1 \right]$$

$$= \frac{N k_B T}{V} \left[1 - \frac{N}{2V} \int f_{12} dq \right]$$

11.3   VDW GAS

In this section, we focus on gas with weak interaction.

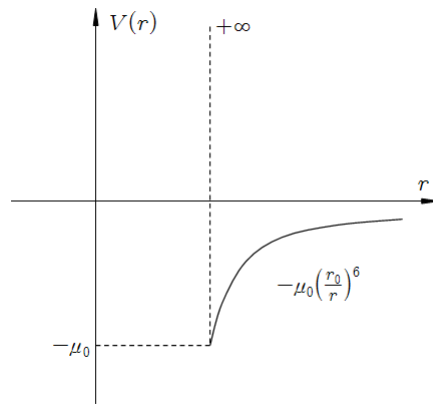### 11.3.1   Ex: Lennard–Jones potential

$$V(r) = 2\mu_0 \left[\frac{1}{2} \left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \qquad 6\text{--}12 \text{ potential}$$

where $\left(\frac{r_0}{r} \right)^{12}$ is repulsive (Pauli replusion), $\left(\frac{r_0}{r} \right)^6$ is attractive (from dipole-dpole interaction)

L-J potential
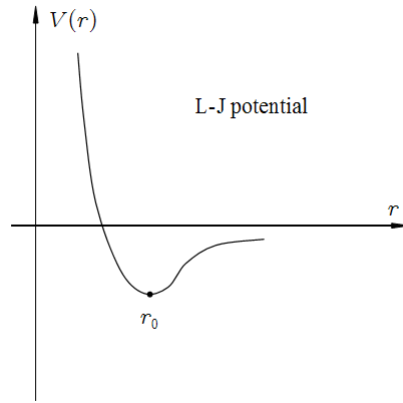
It can be simplified as

$$V(r) = \begin{cases} +\infty & r < r_0 \\ -\mu_0 \left(\frac{r_0}{r}\right)^6 & r \geqslant r_0 \end{cases}$$

$$b_2(T) = \frac{1}{V} \int dq \left(e^{-\beta V(q)} - 1\right)$$

$$= \frac{1}{V} \left\{ \int_0^r d\bar{q} \left(e^{-\beta \infty} - 1\right) + \int_r^{+\infty} d\bar{q} \left[e^{\beta \mu_0 \left(\frac{r_0}{r}\right)^6} - 1\right] \right\}$$

$$\cong \frac{1}{V} \left\{ \int_0^r 4\pi r^2 dr \left[-1\right] + \int_r^{+\infty} 4\pi r^2 dr \left[1 + \beta \mu_0 \left(\frac{r_0}{r}\right)^6 - 1\right] \right\}$$

$$= -\frac{4\pi r_0^3}{3} - \frac{\beta \mu_0}{3} \frac{4\pi r_0^6}{r^3} \Big|_{r=r_0}^{\infty}$$

$$= -\frac{4\pi r_0^3}{3} + \beta \mu_0 \frac{4\pi r_0^3}{3}$$

$$= \frac{4\pi r_0^3}{3} (\beta \mu_0 - 1)$$

$$= \Omega (\beta \mu_0 - 1) \equiv B_2$$

$$\Omega \equiv \frac{4\pi r_0^3}{3}$$

$$P = \frac{N k_B T}{V} \left[1 - \frac{N}{2V} \Omega (\beta \mu_0 - 1)\right]$$

$$\frac{P}{k_B T} = \frac{N}{V} - \frac{1}{2} \left(\frac{N}{V}\right) \Omega (\beta \mu_0 - 1)$$

$$= n + B_2 n^2$$

$$B_2 = -\frac{1}{2} V b_2 = \frac{\Omega}{2} \left(1 - \frac{\mu_0}{k_B T}\right)$$

$$\frac{P}{k_B T} = n + B_2 (T) n^2 \qquad \text{(Eq. of State)}$$
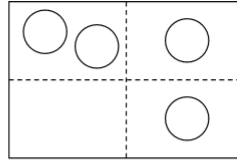
11.3.2 Working Conditions:

1. Short range interaction

$$\frac{1}{r^6} \qquad \checkmark$$

$$\frac{1}{r^\alpha} \qquad \alpha \leqslant 3 \qquad \text{Not working}$$
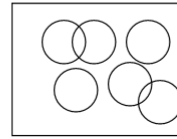
$$\int \frac{4\pi r^2}{r^\alpha} dr \longrightarrow \infty$$

2. Low density

$$\frac{\text{2nd term}}{\text{1st term}} = \frac{B_2 (T) n^2}{n} \ll 1 \qquad \Omega = \frac{4\pi r_0^3}{3}$$

$$\frac{B_2 (T) n^2}{n} = \frac{B_2}{n^{-1}} \approx \frac{\Omega}{V/N}$$

$$= \frac{\text{Volume of a gas particle (now large is a particle)}}{\text{Volume of a gas particle free to move}}$$

$$\frac{\Omega}{V/N} \ll 1$$

$$\frac{\Omega}{V/N} \sim 1$$

3. High temperature

$$\beta \mu_0 \ll 1$$

4. Physical interpretation

$$\frac{P}{k_B T} = n + B_2 (T) n^2$$

$$= \frac{N}{V} + \frac{\Omega}{2} \left(1 - \frac{\mu_0}{k_B T} \right) n^2$$

$$\frac{P}{k_B T} + \frac{n^2 \Omega \mu_0}{2 k_B T} = \frac{N}{V} + \frac{\Omega}{2} \left(\frac{N}{V} \right)^2$$

11.3.3 Volume part

$$\frac{N}{V} + \frac{\Omega}{2} \left(\frac{N}{V} \right)^2 = \frac{N}{V} \left[1 + \frac{\Omega}{2} \frac{N}{V} \right]$$

$$\cong \frac{N}{V} \left(\frac{1}{1 - \frac{\Omega}{2} \frac{N}{V}} \right) = \frac{N}{(V - \frac{N\Omega}{2})}$$

The volume of the system is reduce from V to $\left(V - \frac{N\Omega}{2} \right)$.

Ω volume of a hardcore particle, why $\frac{1}{2}$?

- Hardcore particle
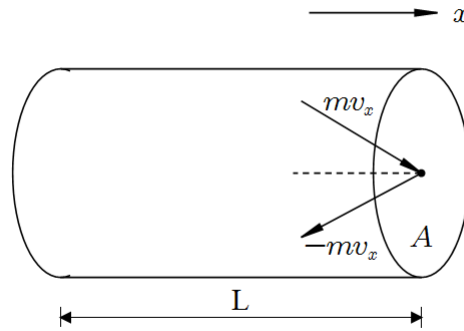
$$
\begin{aligned}
z_{HC} \;=&\; \frac{1}{N!} \int e^{-\beta \sum_{i<j} V(\vec{q}_i - \vec{q}_j)} \, dq_1 dq_2 \cdots dq_N \\
=&\; V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)\frac{1}{N!} \\
=&\; [V(V-(N-1)\Omega)][(V-\Omega)(V-(N-2)\Omega)] \\
&\; \cdots \left[\left(V-\frac{N-1}{2}\Omega\right)\left(V-\frac{N+1}{2}\Omega\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
V(V-(N-1)\Omega) \;=&\; V^2 - (N-1)\Omega \\
=&\; V^2 - N\Omega + \left(\frac{N}{2}\Omega\right)^2 - \left(\frac{N}{2}\Omega\right)^2 + \Omega \\
\cong&\; \left(V-\frac{N}{2}\Omega\right)^2
\end{aligned}
$$

$$
z_{HC} = \frac{1}{N!}\left(V-\frac{N\Omega}{2}\right)^{2\cdot\frac{N}{2}} = \frac{1}{N!}\left(V-\frac{N\Omega}{2}\right)^{N}
$$

V is replace by $V-\frac{N\Omega}{2}$, instead of $V-N\Omega$.
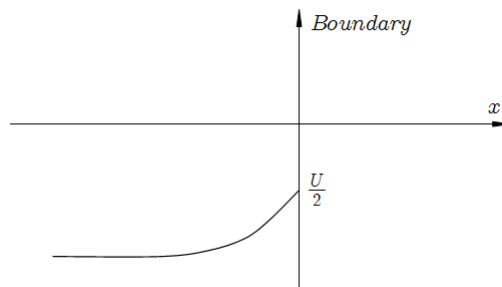
11.3.4 Pressure part

$$
\begin{aligned}
P \;=&\; \frac{\bar{F}}{A} = \frac{N\frac{\Delta p}{\Delta t}}{A} = \frac{[n(v_x \Delta t \cdot A)]2mv_x/\Delta t}{A}\Bigg|_{v_x<0} \\
=&\; n\cdot 2m\overline{v_x^2}\big|_{v_x<0} = n\overline{mv_x^2}
\end{aligned}
$$

For ideal gass

$$
\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}k_B T
$$

$$
P = nm\overline{v_x^2} = nk_B T
$$

$$
\delta P = \delta\left(nm\overline{v_x^2}\right) = (\delta n)\,m\overline{v_x^2} + n\delta\left(m\overline{v_x^2}\right)
$$

interaction energy

$$U = \int V_{attr}(r) \, n(r) \, dr = -\Omega \mu_0 n < 0$$

energy conservation

$$\frac{\delta\left(m\overline{v_x^2}\right)}{2} = \delta U = \frac{U}{2} = -\frac{1}{2}\Omega\mu_0 n$$

$$\delta P = n\delta\left(m\overline{v_x^2}\right) = -n\left(\Omega\mu_0 n\right)/2 \ ?$$

$$v_x < 0$$

$$\delta P = -\frac{1}{2}\Omega\mu_0 n^2$$

reduce of pressure

$$P_{insider} - \frac{1}{2}\Omega\mu_0 n^2 = P_{measured}$$

we care about the properties of the gas

$$P_{measured} + \frac{1}{2}\Omega\mu_0 n^2 = P_{insider} = P_{gas}$$

So $P + \frac{1}{2}\Omega\mu_0 n^2$ replace P

$$\left(P + \frac{1}{2}\Omega\mu_0 n^2\right)\left(V - \frac{N\Omega}{2}\right) = k_B T$$

- Derive the VdW equation using Mean Field Theory

$$Z = \frac{\int\prod d\vec{p}_i d\vec{q}_i}{N! h^{3N}} \exp\left[-\beta\sum_i \frac{\vec{p}_i^2}{2m} - \beta\sum_{i<j} V(\vec{q}_i - \vec{q}_j)\right]$$

$$= \int \frac{\prod d\vec{q}_i}{N!\lambda^{3N}} \exp\left[-\beta\sum_{i<j} V(\vec{q}_i - \vec{q}_j)\right]$$

Assuming: (**1**) hardcore (no penentration of particle into each other); (**2**) particle are uniformly distributed in space.

$$Z = \frac{1}{N!\lambda^{3N}} V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)\, e^{-\beta\tilde{u}}$$

$$\approx \frac{1}{N!\lambda^{3N}}\left(V - \frac{N\Omega}{2}\right)^N e^{-\beta\tilde{u}}$$

where $V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)$ is from hardcore, $\tilde{u}$ is from attractive potential.

$$\tilde{u} = \frac{1}{2}\sum_{i,j} V_{attr}(\vec{q}_i - \vec{q}_j)$$

$$= \frac{1}{2}\int dq_1 dq_2 \, n(q_1) n(q_2) V(\vec{q}_1 - \vec{q}_2)$$

$$= \frac{1}{2}\left(\frac{N}{V}\right)^2 \int dq_1 dq_2 \, V(\vec{q}_1 - \vec{q}_2)$$

$$= \frac{1}{2}\frac{N^2}{V^2}\int dq_1 d(\vec{q}_2 - \vec{q}_1) V(\vec{q}_2 - \vec{q}_1)$$

$$= \frac{1}{2}\frac{N^2}{V}\int dq \, V(q) = \frac{1}{2}\frac{N^2}{V}(-u)$$

$$= -\frac{N^2 u}{2V}$$

$$Z = \frac{1}{N!\lambda^{3N}}\left(V - \frac{N\Omega}{2}\right)^N e^{-\frac{N^2}{2V}u}$$

$$F = -k_B T \ln Z = -Nk_B T \ln\left(V - \frac{N\Omega}{2}\right) + Nk_B T \ln N! + 3Nk_B T \ln\lambda - \frac{uN^2}{2V}$$

$$P = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V - \frac{N\Omega}{2}} - \frac{uN^2}{2V^2}$$

$$\left(P + \frac{uN^2}{2V}\right)\left(V - \frac{N\Omega}{2}\right) = Nk_B T$$

## 11.4 BREAKING DOWN OF VDW GAS EQUATION AND THE 1ST ORDER PHASE TRANSITION

11.4.1 Corresponding states

VdW gas equation is good approximation for varies of gas with weak interaction. Different gas are with different values of a and b. In this section, we use some dimensionless variables to rewrite the VdW equation find a common structure of such gas.

$$P + \frac{1}{2}\Omega\mu_0 \left(\frac{N}{V}\right)^2 = \frac{Nk_B T}{V - \frac{N\Omega}{2}}$$

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_B T$$

$$a = \frac{1}{2}\Omega\mu_0 \qquad b = \frac{\Omega}{2}$$
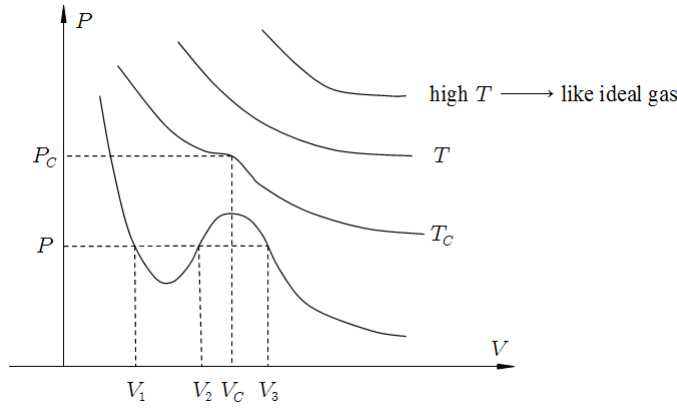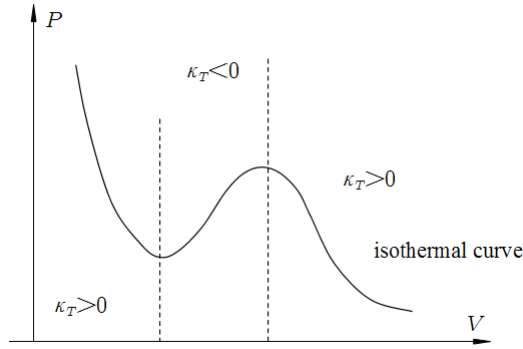
It is monotonic function for $T > T_c$.

Below T_c, a "Kink" exhibit negative compressibility.

Using P_c, V_c to simplify the equation of state

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_B T$$

$$\left[P + a\left(\frac{N}{V}\right)^2\right]\left(\frac{V}{N} - b\right) = k_B T$$

$$\left(P + \frac{a}{v^2}\right)(v - b) = k_B T$$

$$P = \frac{k_B T}{v - b} - \frac{a}{v^2}$$

at P_c, v_c.

$$\left.\frac{\partial P}{\partial v}\right|_{T=T_c} = 0 \qquad -\frac{k_B T_c}{(v_c - b)^2} - \frac{2a}{v_c^3} = 0$$

$$\frac{\partial^2 P}{\partial v^2}\bigg|_{T=T_c} = 0 \qquad \frac{2k_B T_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0$$

and

$$P_c = \frac{k_B T_c}{v_c - b} - \frac{a}{v_c^2}$$

3 Equations give P_c, v_c & T_c.

$$\begin{cases} P_c = \frac{a}{27b^2} = \frac{2\mu_0}{27\Omega} \\ v_c = 3b = \frac{3}{2}\Omega \\ k_B T_c = \frac{8a}{27b} = \frac{8}{27}\mu_0 \end{cases}$$

$$a = \frac{1}{2}\Omega\mu_0 \qquad b = \frac{1}{2}\Omega$$

Scaling

$$\tilde{P} = \frac{P}{P_c}, \quad \tilde{T} = \frac{T}{T_c}, \quad \tilde{v} = \frac{v}{v_c} \qquad \text{(dimensionless)}$$

Then

$$\left(\tilde{P} + \frac{3}{\tilde{v}^2}\right)\left(\tilde{v} - \frac{1}{3}\right) = \frac{8}{3}\tilde{T} \qquad \text{(corresponding state)}$$

or

$$\tilde{P} = \frac{8}{3}\frac{\tilde{T}}{\left(\tilde{v} - \frac{1}{3}\right)} - \frac{3}{\tilde{v}^2}$$

It is universal (material-independent) Equation of State.

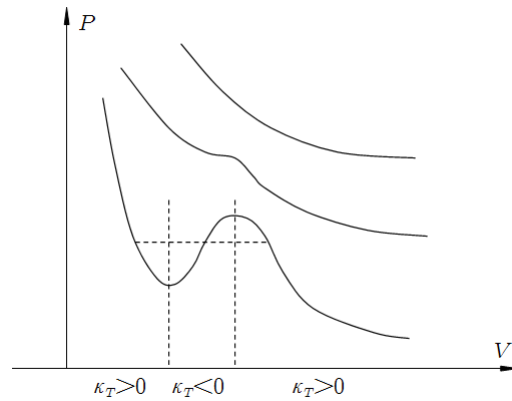3 values P_c, v_c, T_c depend on 2 parameters a, b. There exist a relation

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} = 0.375$$

Experiments show that this value is about $0.28 - 0.33$.

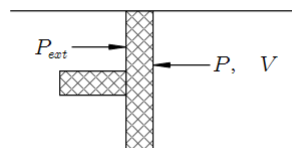It is good for Noble gas Ne, Xe, Kr; Not good for many atom molecular gas.

11.4.2 Breaking down of VdW Equation

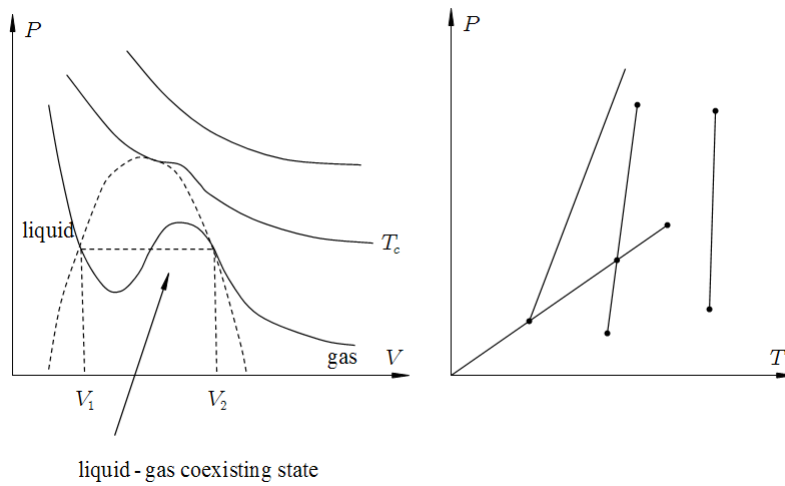Part of the VdW equation show unstability and we need to reconstruct it.

Why it is unstable?

$$\kappa_T = -\frac{1}{T}\frac{\partial V}{\partial P}\bigg|_T \qquad \text{(compressibility)}$$

– $P_{ext} > P$, compress, $V \downarrow \underset{\longrightarrow}{\kappa_T > 0} P \uparrow$, P increase till $P = P_{ext}$.

– $P_{ext} > P$, compressed, $V \downarrow \underset{\longrightarrow}{\kappa_T < 0} P \downarrow$, P decrease, so it can never balance P_{ext}, so the system collapse.

Maxwell construction

liquid - gas coexisting state
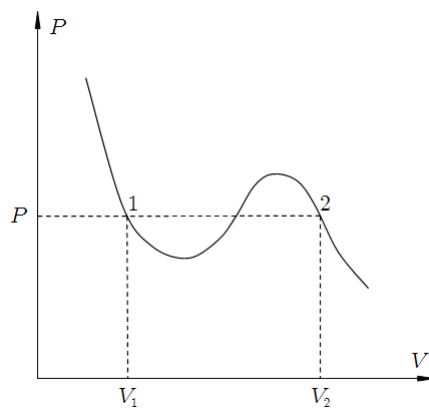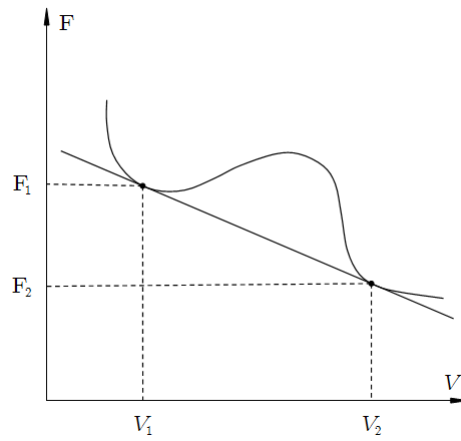
How to determine V_1 & V_2.

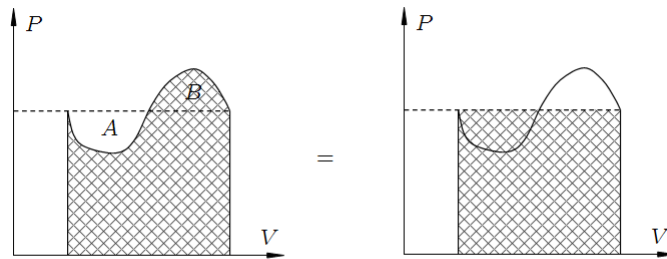From condition that Gibbs free energies of gas and the liquid must be equal when they coexists.

$$F = - \int_{isotherm} PdV \qquad P = -\frac{\partial F}{\partial V}\Big|_T$$

$$P_1 = P_2 \qquad \frac{\partial F}{\partial V_1} = \frac{\partial F}{\partial V_2}$$

$$F = F(V) \qquad P = \frac{\partial F}{\partial V_1} = \frac{F_2 - F_1}{V_2 - V_1}$$

$$\Rightarrow F_2 - F_1 = \frac{\partial F}{\partial V_1}(V_2 - V_1)$$

$$\Rightarrow -(F_2 - F_1) = \left(-\frac{\partial F}{\partial V_1}\right)(V_2 - V_1)$$

$$\Rightarrow \int_{V_1}^{V_2} PdV = P(V_2 - V_1)$$

$$\Rightarrow \text{Area } A = \text{Area } B$$
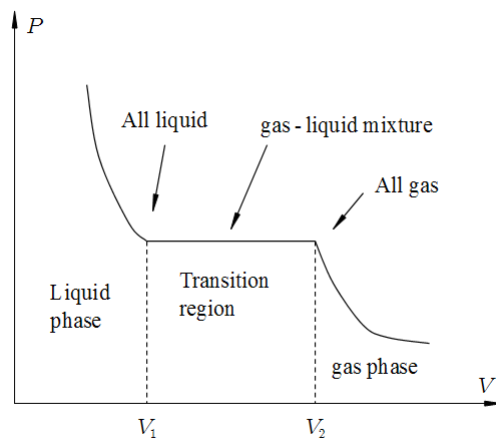
liquid absorb heat (latent heat) becomes gas.

1st order transition

11.4.3 Critical Exponents

$$P = nk_B T - \frac{b}{2}n^2 + \frac{c}{6}n^3$$
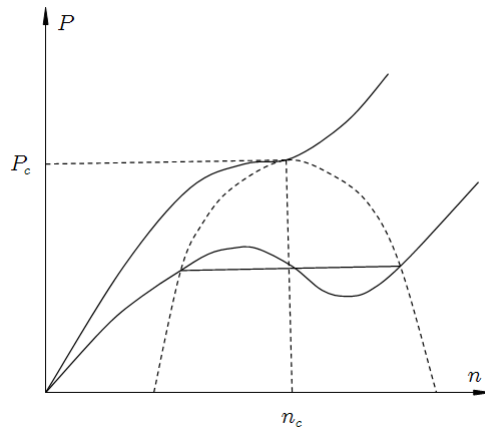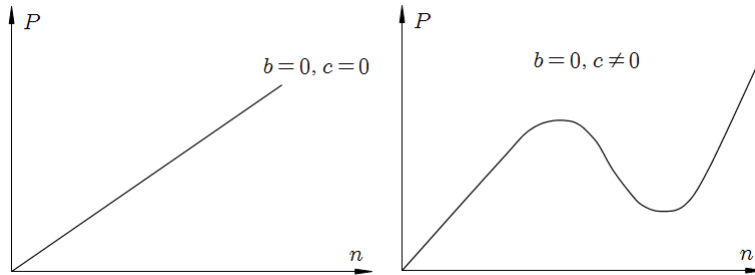
$$\frac{dP}{dn}\bigg|_{n=n_c,T=T_c} = k_B T - bn_c + \frac{c}{2}n_c^2 = 0$$

$$\frac{d^2P}{dn^2}\bigg|_{n=n_c,T=T_c} = -b + cn_c = 0$$

Solution:

$$\begin{cases} n_c = \frac{b}{c} \\ k_B T_c = \frac{b^2}{2c} \\ P_c = \frac{b^3}{6c^2} \end{cases}$$

1. Exponent γ with $\kappa_T(T) \propto (T - T_c)^{-\gamma}$

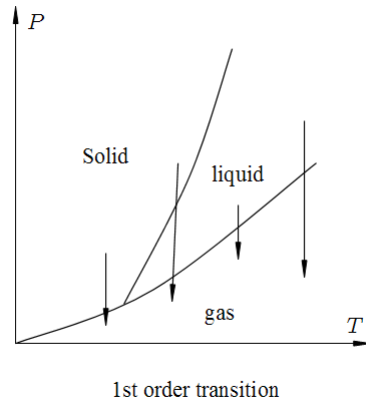$$V = Nn \quad n = \frac{N}{V} \qquad \frac{\partial}{\partial V} = \frac{\partial n}{\partial V}\frac{\partial}{\partial n} = -\frac{N}{V^2}\frac{\partial}{\partial n}$$

$$\kappa_T(n) = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = -\frac{1}{V}\frac{1}{\left.\frac{\partial P}{\partial V}\right|_T}$$

$$= -\frac{1}{V}\frac{1}{\left.\frac{\partial P}{\partial n}\right|_T\left(-\frac{N}{V^2}\right)} = \frac{1}{n}\frac{1}{\left.\frac{\partial P}{\partial n}\right|_T}$$

$$= \frac{1}{n\left(k_B T - bn + \frac{c}{2}n^2\right)}$$

For $n = n_c$

$$-bn_c + \frac{c}{2}n_c^2 = -k_B T_c$$

So

$$\kappa_T(n_c) = \frac{1}{n(T - T_c)} \xrightarrow[T \to T_c]{} \infty$$

$$\kappa_T(T) \propto (T - T_c)^{-\gamma}$$

experiment $\gamma = 1.3$.

2. Exponent δ with $(P - P_c) \propto (v - v_c)^\delta$

   at $T = T_c$

$$P - P_c = nk_B T_c - \frac{b}{2}n^2 + \frac{c}{6}n^3 - \frac{b^3}{6c^2}$$

$$= n\frac{b^2}{2c} - \frac{b}{2}n^2 + \frac{c}{6}n^3 - \frac{b^3}{6c^2}$$

$$= \frac{c}{6}\left(n^3 - 3\frac{b}{c}n^3 + 3\left(\frac{b}{c}\right)^2 n - \left(\frac{b}{c}\right)^3\right)$$

$$= \frac{c}{6}\left(n^3 - 3n_c n^2 + 3n_c^2 n - n_c^3\right)$$

$$= \frac{c}{6}(n - n_c)^3 \propto (v - v_c)^\delta$$

$$\delta = 3$$

experiment $\delta \approx 5.0$

3. Exponent β with $(n - n_c) \propto (T - T_c)^\beta$
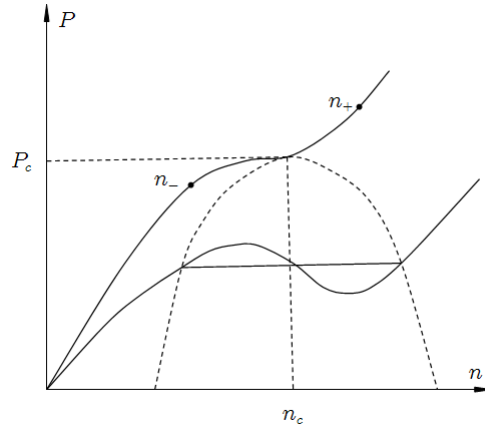
Maxwell-construction

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

$$G = \mu N \longrightarrow dG = \mu dN + Nd\mu$$

So

$$VdP - SdT - Nd\mu = 0 \qquad \text{(Gibbs-Duhem relation)}$$

isotherm process

$$dT = 0$$

$$Vdp - Nd\mu = 0$$

$$d\mu = \frac{V}{N}dP = \frac{dP}{n}$$

from n_- to n_+ $(n_\pm = n_c\,(1\pm\delta))$

$$0 = \mu\,(n_+) - \mu\,(n_-) = \int\limits_{n_c\,(1-\delta)}^{n_c\,(1+\delta)} \frac{dP}{n}$$

$$P = n k_B T - \frac{b}{2} n^2 + \frac{c}{6} n^3$$

$$= \int\limits_{n_c\,(1-\delta)}^{n_c\,(1+\delta)} \frac{k_B T - b n + \frac{c}{2} n^2}{n}\, dn$$

$$= k_B T \ln\left(\frac{1+\delta}{1-\delta}\right) - b n_c\,(2\delta) + \frac{c}{4}\left[(1+\delta)^2 - (1-\delta)^2\right] n_c^2$$

$$= k_B T \ln\left(\frac{1+\delta}{1-\delta}\right) - 2 k_B T_c \delta$$

$$= 2 k_B T \left(\delta + \delta^3\right) - 2 k_B T_c \delta$$

$$\delta = \frac{T}{T_c}\left(\delta + \delta^3\right) \qquad \left(1 - \frac{T_c}{T}\right)\delta = \frac{T}{T_c}\delta^3$$

$$\delta \approx \sqrt{1 - \frac{T_c}{T}} \sim \sqrt{T - T_c}$$

$$\delta \propto (T - T_c)^{\frac{1}{2}} \qquad \beta = 0.5$$

experiment $\beta = 0.3$

12 | QUANTUM STATISTICAL MECHANICS FOR INTERACTING SYSTEMS

12.1   COMPARISON OF CSM AND QSM

Classical SM
$$n_l = g_l e^{-\alpha - \beta \varepsilon_l}$$

Nointeracting System
(Nearly independent
system)

Bose - Einstein
distribution
$$n_l = \frac{g_l}{e^{\alpha + \beta \varepsilon_l} - 1}$$

Ideal Bose gas
(BEC, Superfluid)

Fermi - Dirac
distribution
$$n_l = \frac{g_l}{e^{\alpha + \beta \varepsilon_l} + 1}$$

Ideal Fermi gas
(Fermi liquid)

The most probable
distribution

Classical SM

Interacting
system

Ensemble Theory

Microcanonical / Canonical / Grand Canonical

Quantum statistical Mechanics

Comparison of CSM and QSM		
	Classical SM	Quantum SM
Microscopic Structure (Microstate)	microstate $(1)\ \Gamma_S = \{\vec{p}_i, \vec{q}_i\}_{i=1}^N$ $\qquad$ 6N-dim space Γ-Space $(2)\ H\,(\Gamma_S)$ $(3)\ \frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{q}_i}$ $\qquad \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i}$ For a mechanical system	microstate (1) wavefunction ψ $\qquad \langle \{\vec{q}_i\}\,|\psi\rangle = \psi\,(\{\vec{q}_i\})$ $(2)\ H\,(\{\vec{q}_i\})$ $(3)\ i\hbar \frac{\partial}{\partial t}\psi = H\psi$
		Physical quantities are represented by operator (In CM, states & physical quantities are described by $\{\vec{q}_i, \vec{p}_i\}_{i=1}^N$; $E_k = \sum \frac{\vec{p}_i^2}{2m},\quad U\,(\{\vec{q}_i\})$
Partition function build a bridge Connection microscopy & macroscopy	For statistical Mechanics system, We don't need to know the detailed states of a system. We just need to know the distribution of the system. $\rho\,(\Gamma_S) = \frac{e^{-\beta H(\Gamma_S)}}{\mathcal{Z}}$ $\begin{cases} \mathcal{Z} = \sum\limits_{\Gamma_S} H\,(\Gamma_S) = \frac{\int \prod\limits_{i=1}^N d\vec{p}_i\, d\vec{q}_i}{N! h^{3N}} e^{-\beta H} \\ \langle O \rangle = \sum\limits_{\Gamma_S} \rho\,(\Gamma_S)\, O\,(\Gamma_S) \end{cases}$ Nonequilibrium: $\frac{\partial \rho}{\partial t} = \{\rho, H\}$	Using density matrix $\rho = \sum\limits_n e^{-\beta \varepsilon_n} |\psi_n\rangle \langle \psi_n|$ $\mathcal{Z} = \text{Tr}\rho$ $\langle O \rangle = \text{Tr}\,(\rho O)$ $\frac{\partial \rho}{\partial t} = [\rho, H]$
Macroscopic properties	$F = -k_B T \ln \mathcal{Z} \qquad$ the same! $E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$ $\downarrow$ $P = -\frac{\partial F}{\partial V}$ $S = -\frac{\partial F}{\partial T}$	$F = -k_B T \ln \mathcal{Z}$ $E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$ $\downarrow$ $P = -\frac{\partial F}{\partial V}$ $S = -\frac{\partial F}{\partial T}$

12.2 SUMMARY OF QUANTUM MECHANICS

1. Microstate

The describption of any physical system can be divided into two categories: One is the states of a system. The other is the physical measured quantities of the system.

For a classical system. the state of the system is $\Gamma_S = \{\vec{p}_i, \vec{q}_i\}_{i=1}^N$.

The evolution of state is determined by $H\,(\Gamma_S) = H\,(\{\vec{p}_i, \vec{q}_i\})$.

$$\begin{cases} \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i} \\ \frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{q}_i} \end{cases}$$

The physical quantities such as:

Kinetic energy $\quad E_k = \sum\limits_i \frac{\vec{p}_i^2}{2m}$ is determined by $\{\vec{p}_i\}$

Potential energy $\quad U\,(\vec{q}_i)$ is determined by $\{\vec{q}_i\}$

But for QM, states are described by wave-function $|\psi\rangle$, and physical quantities are described by operators $\hat{O}$.

– States $|\psi\rangle$

wavefunction $|\psi\rangle$ is a "vector" in a ∞-dimensional Hilbert space.

It can be represented by a complete arthogonal basis

$$\sum_n |n\rangle\langle n| = 1$$

$$|1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \qquad \langle 1| = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \end{bmatrix}$$

$$|2\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \qquad \langle 2| = \begin{bmatrix} 0 & 1 & 0 & \cdots & 0 \end{bmatrix}$$

$$|1\rangle\langle1| + |2\rangle\langle2| = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \end{bmatrix} + \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & \cdots & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 0 \end{bmatrix}$$

$$\sum_n |n\rangle\langle n| = \mathbf{1}$$

$$|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle$$

$$= \sum_n \langle n|\psi\rangle|n\rangle$$

$$= \sum_n C_n |n\rangle$$

where C_n is the coefficience, $|n\rangle$ is the basis.

For continous case

$$\int d\{\bar{q}_i\} |\{\bar{q}_i\}\rangle\langle\{\bar{q}_i\}| = \mathbf{1}$$

$$\psi = \int d\{\bar{q}_i\} |\{\bar{q}_i\}\rangle\langle\{\bar{q}_i\}|\psi\rangle$$
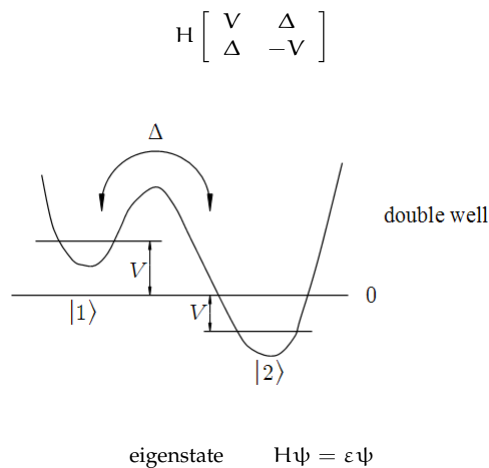
$$= \int d\{\bar{q}_i\} \psi\{\bar{q}_i\} |\{\bar{q}_i\}\rangle$$

where $\psi\{\bar{q}_i\}$ is many-body wavefunction.

$$1 = \langle\psi|\psi\rangle = \sum_n \langle\psi|n\rangle\langle n|\psi\rangle = \sum_n (\langle n|\psi\rangle)^* \langle n|\psi\rangle$$

$$= \sum_n |C_n|^2$$

– Evolution of States

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}H(t-t_0)}|\psi(t_0)\rangle$$

$$= U(t, t_0)|\psi(t_0)\rangle$$

12.3 QUANTUM MECHANICS OF TWO-LEVEL SYSTEMS

$$H\begin{bmatrix} V & \Delta \\ \Delta & -V \end{bmatrix}$$

double well

eigenstate $\quad H\psi = \varepsilon\psi$

$$E = \pm\sqrt{\Delta^2 + V^2}$$

$$E = +\sqrt{\Delta^2 + V^2}$$

$$\begin{bmatrix} V - \sqrt{\Delta^2 + V^2} & -\Delta \\ \Delta & -V - \sqrt{\Delta^2 + V^2} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0$$

$$\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} V + \sqrt{\Delta^2 + V^2} \\ \Delta \end{bmatrix} \propto \begin{bmatrix} V + \sqrt{\Delta^2 + V^2} \\ \Delta \end{bmatrix} \frac{1}{\sqrt{2\sqrt{\Delta^2 + V^2}\left(\sqrt{\Delta^2 + V^2} + V\right)}}$$

$$\equiv |+\rangle = \begin{bmatrix} \sqrt{\frac{V + \sqrt{\Delta^2 + V^2}}{2\sqrt{\Delta^2 + V^2}}} \\ \sqrt{\frac{\Delta}{2\sqrt{\Delta^2 + V^2}\left(\sqrt{\Delta^2 + V^2} + V\right)}} \end{bmatrix}$$

$$\equiv \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix}$$

where $\tan\theta = \frac{\Delta}{V + \sqrt{\Delta^2 + V^2}}$.

$$E = -\sqrt{\Delta^2 + V^2}$$

$$\begin{bmatrix} V + \sqrt{\Delta^2 + V^2} & \Delta \\ \Delta & -V + \sqrt{\Delta^2 + V^2} \end{bmatrix} \begin{bmatrix} c \\ d \end{bmatrix} = 0$$

$$\begin{bmatrix} c \\ d \end{bmatrix} = \begin{bmatrix} V - \sqrt{\Delta^2 + V^2} \\ \Delta \end{bmatrix} \propto \begin{bmatrix} V - \sqrt{\Delta^2 + V^2} \\ \Delta \end{bmatrix} \frac{1}{\sqrt{2\sqrt{\Delta^2 + V^2}\left(\sqrt{\Delta^2 + V^2} - V\right)}}$$

$$\equiv \quad |-\rangle \equiv \begin{bmatrix} -\sin\theta \\ \cos\theta \end{bmatrix}$$

– Physical quantities are represented by operator

Classical Mechanics

$$O = O\left(\{\vec{p}_i, \vec{q}_i\}\right)$$

a function defined on Γ-Space.

QM

$$O = \hat{O}\left(\{\vec{p}_i, \vec{q}_i\}\right)$$

an operator defined in Γ-Space.

$$\text{Hermit operator} \quad \hat{O}^+ = O$$

$$\vec{p}_i \rightarrow \hat{\vec{p}}, \qquad \vec{q}_i \rightarrow \hat{\vec{q}}$$

$$\left[\hat{\vec{p}}, \hat{\vec{q}}\right] = \hat{\vec{p}}\,\hat{\vec{q}} - \hat{\vec{q}}\,\hat{\vec{p}} = \frac{\hbar}{i}\delta_{jk}$$

in $|\{\vec{q}_i\}\rangle$ basis

$$\hat{\vec{p}} = \frac{\hbar}{i}\nabla \qquad \hat{\vec{q}} = \vec{q}_i$$

$$\hat{O}|n\rangle = d_n|n\rangle$$

$|n\rangle$ are the eigenstates of $\hat{O}$, they form a complete orthogonal basis. Usually, average values are used to represent a measured result.

$$\begin{aligned} \langle \hat{O} \rangle &= \langle \psi | \hat{O} | \psi \rangle \\ &= \sum_{m,n} \langle \psi | m \rangle \langle m | \hat{O} | n \rangle \langle n | \psi \rangle \end{aligned}$$

For example

$$|n\rangle = |\{\vec{q}_i\}\rangle$$

$$\langle U(\vec{q}) \rangle = \int \prod_i dq_i \psi^*(q_1, \cdots, q_N)\, U(\{\vec{q}_i\})\, \psi(q_1, \cdots, q_N)$$

$$\langle K(\vec{q}) \rangle = \int \prod_i dq_i \psi^*(q_1, \cdots, q_N)\, K\left(\left\{\frac{\hbar}{i}\frac{\partial}{\partial \vec{q}_i}\right\}\right) \psi(q_1, \cdots, q_N)$$

12.4 DENSITY MATRIX

2. Macrostates (Using density matrix)

– Classical SM

$$\Gamma_S = \{\vec{p}_i, \vec{q}_i\}_{i=1}^N$$

$\rho\,(\Gamma_S)$ probability that a system is in microstate Γ_S.

$O\,(\Gamma_S)$ physical quantities

$$\langle O \rangle_{Ensemble} = \sum_{\Gamma_S} \rho\,(\Gamma_S)\,O\,(\Gamma_S)$$

$$= \prod_{i=1}^N \int d^3\vec{p}_i d^3\vec{q}_i\, \rho\,(\{\vec{p}_i, \vec{q}_i\})\, O\,(\{\vec{p}_i, \vec{q}_i\})$$

where $\rho\,(\{\vec{p}_i, \vec{q}_i\})$ is the distribution in phase space (Γ-Space)

– QM

$$\langle O \rangle_{Ensemble} = \sum_{\alpha} P_\alpha \langle \psi_\alpha | \hat{O} | \psi_\alpha \rangle$$

$$= \sum_{\alpha m,n} P_\alpha \langle \psi_\alpha | m \rangle \langle m | \hat{O} | n \rangle \langle n | \psi_\alpha \rangle$$

$$= \sum_{\alpha} \langle n | \psi_\alpha \rangle P_\alpha \langle \psi_\alpha | m \rangle \langle m | \hat{O} | n \rangle$$

where P_α is the probability from ensemble, ψ_α is the probability from QM.

Define $\hat{\rho} = \sum_{\alpha} P_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|$ density matrix.

$$\langle O \rangle = \sum_{m,n} \langle n | \hat{\rho} | m \rangle \langle m | \hat{O} | n \rangle$$

$$= \sum_{m,n} \left[\quad \right]_{nm} \left[\quad \right]_{mn}$$

$$= \sum_{n} \left(\sum \left[\quad \right]_{nm} \left[\quad \right]_{mn} \right)$$

$$= \sum_{n} \left(\quad \right)_{nn}$$

$$= \mathrm{Tr}\,(\hat{\rho}\hat{O})$$

density matrix has the following properties.

a) Normalized

$$\mathrm{Tr}\rho = \sum_{n} \langle n | \rho | n \rangle$$

$$= \sum_{n,\alpha} \langle n | \psi_\alpha \rangle P_\alpha \langle \psi_\alpha | n \rangle$$

$$= \sum_{n,\alpha} |\langle n | \psi_\alpha \rangle|^2 P_\alpha$$

$$= \sum_{\alpha} P_\alpha = 1$$

b) Hermitian

$$\hat{\rho}^+ = \left(\sum_{\alpha} |\psi_\alpha\rangle\langle\psi_\alpha|P_\alpha \right)^+$$

$$= \sum_{\alpha} P_\alpha^+ |\psi_\alpha\rangle\langle\psi_\alpha|$$

$$= \hat{\rho}$$

where $P_\alpha \in$ real.

c) Positive defined

For $\forall \Phi$

$$
\begin{aligned}
\langle \Phi | \hat{\rho} | \Phi \rangle &= \sum_{\alpha} P_{\alpha} \langle \Phi | \psi_{\alpha} \rangle \langle \psi_{\alpha} | \Phi \rangle \\
&= \sum_{\alpha} P_{\alpha} | \langle \Phi | \psi_{\alpha} \rangle |^2 \\
&\geqslant 0
\end{aligned}
$$

d) Evolution of ρ

$$
\begin{aligned}
i\hbar \frac{\partial}{\partial t} &\sum_{\alpha} P_{,} | \psi_{\alpha}(t) \rangle \langle \psi_{\alpha}(t) | \\
&= \sum_{\alpha} P_{\alpha} \left[\left(i\hbar \frac{\partial}{\partial t} | \psi_{\alpha}(t) \rangle \right) \langle \psi_{\alpha}(t) | + | \psi_{\alpha}(t) \rangle \left(i\hbar \frac{\partial}{\partial t} \langle \psi_{\alpha}(t) | \right) \right] \\
&= \sum_{\alpha} P_{\alpha} \left[H | \psi_{\alpha}(t) \rangle \langle \psi_{\alpha}(t) | - | \psi_{\alpha}(t) \rangle \langle \psi_{\alpha}(t) | H \right] \\
&= H\rho - \rho H = [H, \rho]
\end{aligned}
$$

by using

$$
i\hbar \frac{\partial}{\partial t} | \psi_{\alpha}(t) \rangle = H | \psi_{\alpha}(t) \rangle \overset{\text{Hermit}}{\longrightarrow} -i\hbar \frac{\partial}{\partial t} \langle \psi_{\alpha}(t) | = \langle \psi_{\alpha}(t) | H^{+} = \langle \psi_{\alpha}(t) | H
$$

So

$$
i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]
$$

quantum version of Liouville's theorem.

12.5   QUANTUM ENSEMBLE THEORY (QET)

– Classical Microcanonical Ensemble

$$
\rho(\Gamma_S) = \frac{\delta(H(\Gamma_S) - E)}{\Omega(E)}
$$

– Quantum Microcanonical Ensemble

Using energy eigenstates

$$
\begin{aligned}
\langle n | \hat{\rho} | m \rangle &= \sum_{\alpha} P_{\alpha} \langle n | \psi_{\alpha} \rangle \langle \psi_{\alpha} | m \rangle \\
&= \begin{cases} \frac{1}{\Omega} & \text{if } \varepsilon_n = E \text{ and } m = n \\ 0 & \text{if } \varepsilon_n \neq E \text{ or } \varepsilon_n = E \text{ but } m \neq n \end{cases}
\end{aligned}
$$

$$
\text{tr}\rho = 1 \qquad \Omega(E) = \sum_{n} \delta(E - E_n)
$$

– Quantum Canonical Ensemble

$$
\rho(\beta) = \frac{e^{-\beta \hat{H}}}{\mathcal{Z}}
$$

$$
\text{tr}\rho = 1 = \frac{\text{Tr} e^{-\beta \hat{H}}}{\mathcal{Z}}
$$

$$
\mathcal{Z} = \text{tr} e^{-\beta \hat{H}}
$$

$$
H | n \rangle = \varepsilon_n | n \rangle
$$

$$
H = \sum_{n} \varepsilon_n | n \rangle \langle n |
$$

For example: $n = (0, 1, 2)$

$$e^{-\beta \hat{H}} = e^{-\beta \sum_n \varepsilon_n |n\rangle \langle n|}$$

$$= e^{-\beta (\varepsilon_1 |1\rangle \langle 1| + \varepsilon_2 |2\rangle \langle 2|)}$$

$$= \sum_{n=0}^{\infty} \frac{(-\beta)^n (\varepsilon_1 |1\rangle \langle 1| + \varepsilon_2 |2\rangle \langle 2|)^n}{n!}$$

$$= \sum_{n=0}^{\infty} \frac{(-\beta)^n \varepsilon_1^n}{n!} |1\rangle \langle 1| + \sum_{n=0}^{\infty} \frac{(-\beta)^n \varepsilon_2^n}{n!} |2\rangle \langle 2|$$

$$= e^{-\beta \varepsilon_1^n} |1\rangle \langle 1| + e^{-\beta \varepsilon_2^n} |2\rangle \langle 2|$$

$$(|1\rangle \langle 1|)^m = |1\rangle \langle 1|$$

$$(|1\rangle \langle 1|) (|2\rangle \langle 2|) = 0$$

or more generally

$$e^{-\beta \hat{H}} = \sum_n |n\rangle \langle n| e^{-\beta \varepsilon_n}$$

$$\mathcal{Z} = \text{tr} e^{-\beta \hat{H}} = \text{tr} \left(\sum_n |n\rangle \langle n| e^{-\beta \varepsilon_n} \right)$$

– Quantum Grand Canonical Ensemble

$$\rho (\beta, \mu) = \frac{e^{-\beta \hat{H} + \beta \mu \hat{N}}}{Q}$$

$$Q = \text{tr} \left(e^{-\beta \hat{H} + \beta \mu \hat{N}} \right)$$

Usually, we like to choose energy eigenstates as basis $\varepsilon_{\vec{k}}$, and assume occupation number are good quantum number $n_{\vec{k}}$.

$$\mathcal{Z}_N = \text{tr} e^{-\beta \hat{H}} = \sum_{\{k_\alpha\}} \exp \left(-\beta \sum_{\alpha=1}^{N} \varepsilon_{\vec{k}_\alpha} \right)$$

$$= \sideset{}{'}\sum_{\{n_{\vec{k}}\}} \exp \left(-\beta \sum_{\vec{k}} \varepsilon_{\vec{k}} n_{\vec{k}} \right)$$

$\sum_{\vec{k}} n_{\vec{k}} = N$ constraint for canonical, $\sum'$ mean with constraint.

For grand canonical

$$Q_\eta (T, \mu) = \sum_{N=0}^{\infty} e^{\beta \mu N} \sideset{}{'}\sum_{\{n_{\vec{k}}\}} \exp \left(-\beta \sum_{\vec{k}} \varepsilon_{\vec{k}} n_{\vec{k}} \right)$$

$$= \sum_{\{n_{\vec{k}}\}} \prod_{\vec{k}=1}^{\eta} \exp \left(-\beta \left(\varepsilon_{\vec{k}} - \mu \right) n_{\vec{k}} \right)$$

$\eta = \pm$, Boson, Fermion.

For boson $n_{\vec{k}} = 0, 1, 2, \cdots, \infty$

$$Q_+ = \prod_{\vec{k}} \sum_{\{n_k\}} \exp \left[-\beta \left(\varepsilon_{\vec{k}} - \mu \right) n_{\vec{k}} \right]$$

$$= \prod_{\vec{k}} \left[1 - \exp \left(\beta \mu - \beta \varepsilon_{\vec{k}} \right) \right]^{-1}$$

For fermion $n_{\vec{k}} = 0, 1$

$$Q_- = \prod_{\vec{k}} \sum_{\{n_k\}} \exp \left[-\beta \left(\varepsilon_{\vec{k}} - \mu \right) n_{\vec{k}} \right]$$

$$= \prod_{\vec{k}} \left[1 + \exp \left(\beta \mu - \beta \varepsilon_{\vec{k}} \right) \right]$$

So

$$Q_\eta = \prod_{\vec{k}} \left[1 - \eta \exp \left(\beta \mu - \beta \varepsilon_{\vec{k}} \right) \right]^{-\eta}$$

$$\ln Q_\eta = -\eta \sum_{\vec{k}} \ln \left[1 - \eta \exp \left(\beta \mu - \beta \varepsilon_{\vec{k}} \right) \right]$$

$$\langle n_{\vec{k}} \rangle_\eta = -\frac{\partial \ln Q_\eta}{\partial \left(\beta \varepsilon_{\vec{k}} \right)} = \frac{1}{z^{-1} e^{\beta \varepsilon_{\vec{k}}} - \eta}$$

It is FD distribution and BE distribution,
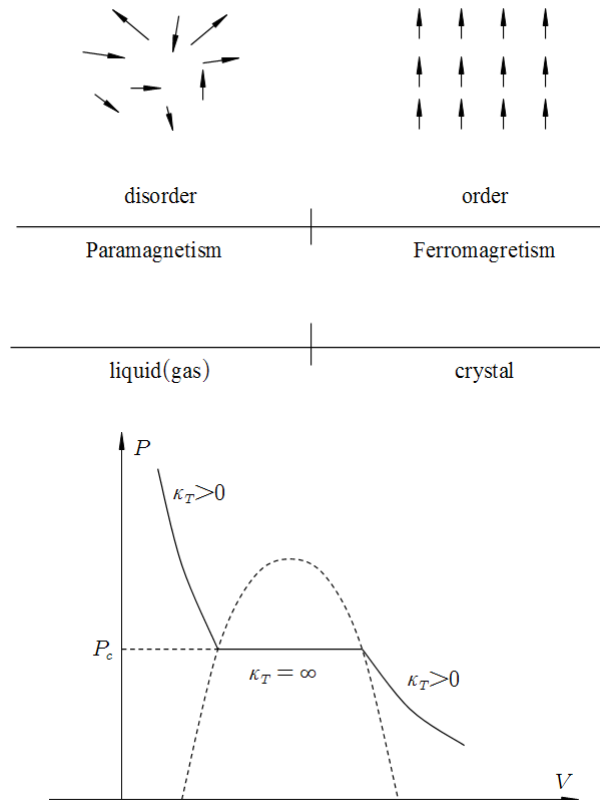
$$\text{or} \; = \frac{\partial \ln Q}{\partial \left(\beta \mu \right)}$$

13 | CONTINOUS PHASE TRANSITION

- less "ordered" phase $\xleftrightarrow{\text{PT}}$ "ordered" phase.

  PT: "Change in order"

  Ex:

disorder	order
Paramagnetism	Ferromagretism

liquid(gas)	crystal

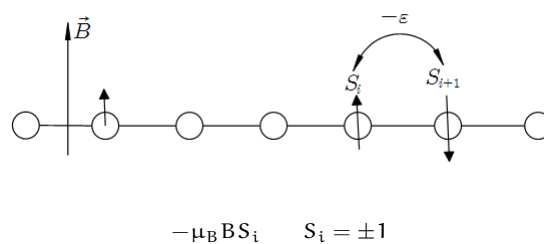
At transition point, free energy F is continous, $P = -\frac{\partial F}{\partial V}$ is continous, but

$$\frac{\partial^2 F}{\partial^2 V} = \frac{1}{V}\left(-V\frac{\partial P}{\partial V}\right) = \frac{1}{V}\frac{1}{\kappa_T} \qquad \kappa_T = \frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T$$

divergent at $P = P_c$, $\exists$ latent heat $\longrightarrow$ 1st order PT.

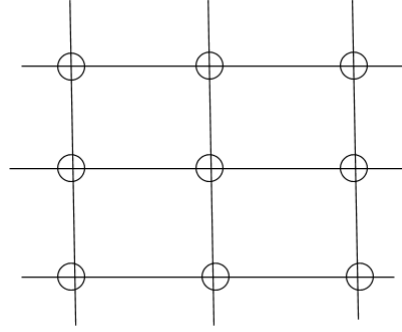Let us take a look at some special model and see whether there exist PT.

13.2 1D ISING MODEL

$$-\mu_B B S_i \qquad S_i = \pm 1$$

Each lattice site has two state $S_i = \pm 1$. Spin up/down.

$\uparrow -\mu_B B S_i$ Zeeman energy

$-\varepsilon S_i S_j$ exchange energy

$$H = -\beta \mu_B B \sum_i S_i - \beta \varepsilon \sum_{\langle i,j \rangle} S_i \cdot S_j$$

$$\mathcal{Z} = \sum_{\{S_i\}} e^{\beta \mu_B B \sum S_i + \beta \varepsilon \sum S_i \cdot S_j}$$

For 1D

$$\mathcal{Z} = \sum_{\{S_i = \pm 1\}} e^{\beta \mu_B B \sum_i S_i + \beta \varepsilon \sum_i S_i S_{i+1}}$$

$$= \sum_{\{S_1 = \pm 1, S_2 = \pm 1, \cdots\}} \prod_{i=1}^{\infty} e^{\beta \mu_B S_i + \beta \varepsilon S_i S_{i+1}}$$

$$= \sum \prod_i e^{\frac{1}{2} \beta \mu_B (S_i + S_{i+1}) + \beta \varepsilon S_i S_{i+1}}$$

Define transfer matrix

$$T_{i,i+1} = \begin{bmatrix} e^{\frac{1}{2}\beta\mu_B(+1+1)+\beta\varepsilon(+1)(+1)} & e^{\frac{1}{2}\beta\mu_B(+1-1)+\beta\varepsilon(+1)(-1)} \\ e^{\frac{1}{2}\beta\mu_B(-1+1)+\beta\varepsilon(-1)(+1)} & e^{\frac{1}{2}\beta\mu_B(-1-1)+\beta\varepsilon(-1)(-1)} \end{bmatrix} \begin{matrix} S_i = +1 \\ S_i = -1 \end{matrix}$$

$$\qquad\qquad S_{i+1} = +1 \qquad\qquad\qquad S_{i+1} = +1$$

$$= \begin{bmatrix} e^{\beta\mu_B+\beta\varepsilon} & e^{-\beta\varepsilon} \\ e^{-\beta\varepsilon} & e^{-\beta\mu_B+\beta\varepsilon} \end{bmatrix}$$

$$\{T\}_{S_i,S_{i+1}} = e^{\frac{1}{2}\beta\mu_B(S_i+S_{i+1})+\beta\varepsilon(S_i S_{i+1})}$$

$$\mathcal{Z} = \sum \{T\}_{S_1,S_2} \{T\}_{S_2,S_3} \cdots \{T\}_{S_N,S_1}$$
$$= \mathrm{Tr} T^N$$

Diagonalize T

$$\det|T - \lambda I| = \det \begin{bmatrix} e^{\beta\mu_B+\beta\varepsilon} & e^{-\beta\varepsilon} \\ e^{-\beta\varepsilon} & e^{-\beta\mu_B+\beta\varepsilon} \end{bmatrix}$$
$$= \lambda^2 - \left(e^{\beta\mu_B} + e^{-\beta\mu_B}\right) e^{\beta\varepsilon} \lambda + \left(e^{2\beta\varepsilon} - e^{-2\beta\varepsilon}\right)$$
$$= 0$$

$$\lambda = \frac{1}{2}\left[\left(e^{\beta\mu_B} + e^{-\beta\mu_B}\right) e^{\beta\varepsilon} \pm \sqrt{\left(e^{\beta\mu_B} + e^{-\beta\mu_B}\right)^2 e^{2\beta\varepsilon} - 4\left(e^{2\beta\varepsilon} - e^{-2\beta\varepsilon}\right)}\right]$$

$$= \cosh\beta\mu_B e^{\beta\varepsilon} \pm \frac{1}{2}\sqrt{\left(e^{\beta\mu_B} + e^{-\beta\mu_B}\right)^2 e^{2\beta\varepsilon} + 4e^{-2\beta\varepsilon}}$$

$$= \cosh\beta\mu_B e^{\beta\varepsilon} \pm \sqrt{\sinh\beta\mu_B e^{2\beta\varepsilon} + 4e^{-2\beta\varepsilon}}$$

$$= \lambda_\pm$$

$$\mathrm{Tr} T^N = \mathrm{Tr}\begin{bmatrix} \lambda_+ & \\ & \lambda_- \end{bmatrix}^N = \mathrm{Tr}\begin{bmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{bmatrix}$$

$$\mathcal{Z} = \lambda_+^N + \lambda_-^N \approx \lambda_+^N$$

$$F = -k_B T \ln \mathcal{Z} = -k_B T N \ln \left[\cosh \beta \mu_B \, e^{\beta \varepsilon} + \sqrt{\sinh \beta \mu_B \, e^{2\beta \varepsilon} + 4 e^{-2\beta \varepsilon}} \right]$$
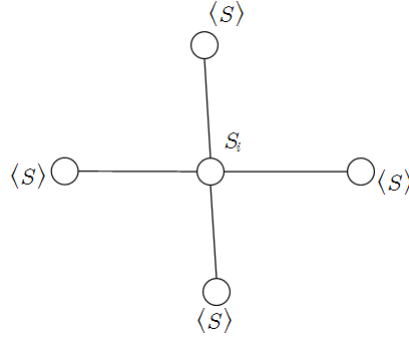
$$M = -\frac{\partial F}{\partial B} = N k_B T \, \frac{\sinh \beta \mu B e^{\beta \varepsilon} \beta \mu + \frac{\cosh \beta \mu B e^{2\beta \varepsilon}}{2\sqrt{\sinh \beta \mu B e^{2\beta \varepsilon} + 4 e^{-2\beta \varepsilon}}} \beta \mu}{\cosh \beta \mu B e^{\beta \varepsilon} + \sqrt{\sinh \beta \mu B e^{2\beta \varepsilon} + 4 e^{-2\beta \varepsilon}}}$$

No phase transition in 1D.

13.3 2D ISING MODEL AND MEAN FIELD THEORY

Onsager give the exact solution of 2D Ising model, we give the solution by MFT

$$H = -\beta \mu_B B \sum_i S_i - \beta \varepsilon \sum_{\langle i,j \rangle} S_i \cdot S_j$$
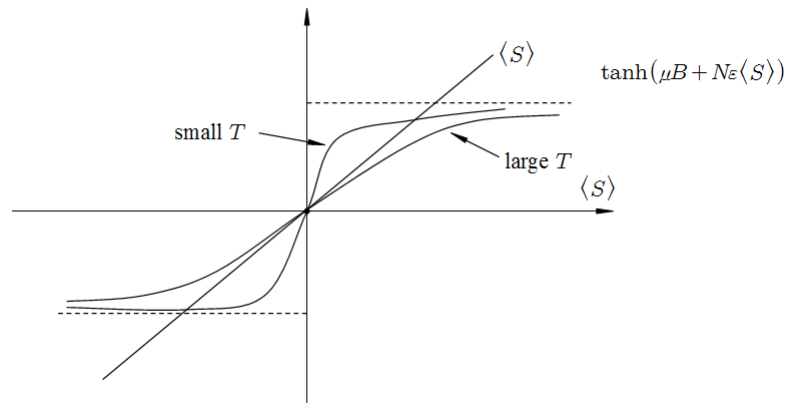

$$\mathcal{Z} = \sum_{\{S_i\}} e^{\beta \mu B S_i + \beta \varepsilon N \langle S \rangle S_i}$$

$$= \left(e^{\beta \mu B + \beta \varepsilon N \langle S \rangle} + e^{-\beta \mu B - \beta \varepsilon N \langle S \rangle} \right)^N$$

$$= 2^N \left[\cosh \left(\beta \mu B + \beta \varepsilon N \langle S \rangle \right) \right]^N$$

$$F = -k_B T \ln \mathcal{Z} \qquad M = -\frac{\partial F}{\partial B}$$

magnetization

$$\langle M \rangle = N \mu \langle S_i \rangle = N \mu \langle S \rangle$$

$$= \frac{\partial k_B T \ln \mathcal{Z}}{\partial B}$$

$$= \frac{N k_B T \partial \ln \cosh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)}{\partial B}$$

$$= N k_B T \frac{\sinh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)}{\cosh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)} \cdot \beta \mu$$

$$= N \mu \tanh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)$$

$$= N \mu \langle S \rangle$$

So

$$\langle S \rangle = \tanh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)$$

So

$$E = \frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{N \partial \ln \cosh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)}{\partial \beta}$$

$$= N \left(\mu B + \varepsilon N \langle S \rangle \right) \tanh \left(\beta \mu B + \beta N \varepsilon \langle S \rangle \right)$$

$$C_V = \frac{dE}{dT}$$

13.4   NEAR THE TRANSITION POINT AND CRITICAL EXPONENT

Near the critical point T_c

$$\frac{M}{N\mu} = \sqrt{\left(1 - \frac{T}{T_c} \right)}$$

more generally

$$\tau = 1 - \frac{T}{T_c} \qquad \frac{1}{\tau} \xrightarrow{T \to T_c} \infty$$

i. Specific heat

$$C_1 = \begin{cases} A_+ |\tau|^{-\alpha_+} & T \to T_c^+ \\ A_- |\tau|^{-\alpha_-} & T \to T_c^- \end{cases}$$

$$\alpha_+ = \alpha_- = 0 \qquad \text{for Ising model (2D)}$$

ii. Magnetization

$$M \propto \tau^\beta \qquad \beta = \frac{1}{2}$$
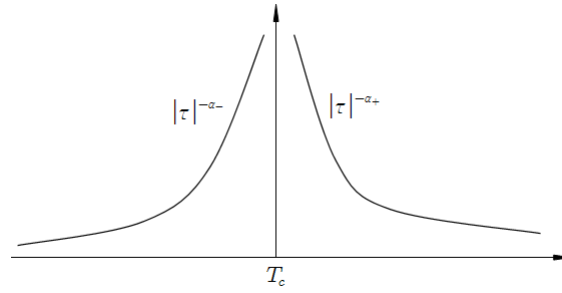
iii. Spin susciptibility

$$\chi = \left(\frac{\partial M}{\partial B} \right)_{B=0} \propto \begin{cases} |\tau|^{-\gamma_+} & T \to T_c^+ \\ |\tau|^{-\gamma_-} & T \to T_c^- \end{cases}$$

$$\gamma_+ = \gamma_- = 1$$

iv. Critical magnetic field

$$B \propto M^\delta \qquad \delta = 3$$

13.5 SECOND ORDER PHASE TRANSITION AND LANDAU–GINSUBURG THEORY

If a system go through a phase transition and don't absorb or emit heat (Lattern heat), it is a second order phase transition.

$$\left. \begin{array}{l} \text{Liquid-gas} \\ \text{Solid-liquid} \end{array} \right\} \text{1st PT}$$

FM-PM 2nd order PT

2nd order PT is related to a change of symmetry.

In PM phase, $S_i = \pm 1$ with equal probability (symmetry)

When $T < T_c$, (FM phase) $S_i = \pm 1$ has high probability than $S_i = -1$, or $S_i = -1$ —————— $S_i = +1$

($S_i = \pm 1$ symmetry is broken) Spontanous Symmetry Breaking.

We can describe such phase transition using Landau-Ginsuburg Theory:

1st, we use a order parameter to characterize the system $\phi \neq 0$ (ordered phase), $\phi = 0$ (disordered phase)

The free energy of 2D Ising model is

$$\mathcal{L} = \frac{1}{2} \alpha(T) M^2 + \frac{1}{4} \beta(T) M^4$$

($\phi = M$ order parameter is this case)

When at equilibrium

$$0 = \frac{\partial \mathcal{L}}{\partial m} = \alpha(T) M + \beta(T) M^3$$
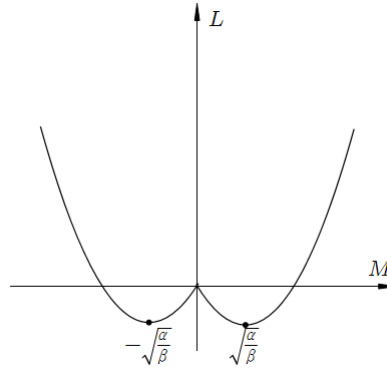$$= M \left(\alpha(T) + \beta(T) M^2 \right)$$

so

$$M = 0 \text{ or } M = \pm \sqrt{\frac{\alpha}{\beta}}$$

$\beta > 0$ for the system to be stable. α can be positive or negative.

when $\alpha > 0$, $M = 0$ is the only solution
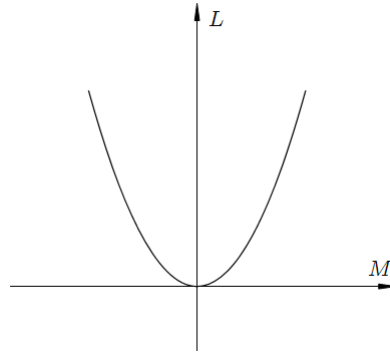
when $\alpha \leqslant 0$, $M = \pm\sqrt{\frac{\alpha}{\beta}}$ are the two degenerated solution

But which state will the system choose?

either one is fine. (randomly chosen, spontanous symmetry breaking)

SSB (2nd PT)

Include

  i. PM-FM (SU(2)sym, Time Reversal Sym)

  ii. Superconductor-Metal transition (U(1) Sym)

  iii. Charge-density-wave-metal transition (translation Sym)

  iv. quasi-crystal-liquid (rotational Sym)

    ....

In those case, M is replaced by other "function" which is called order parameter Φ

$$\begin{cases} \Phi = 0 & \text{trivial phase} \\ \Phi \neq 0 & \text{SSB phase} \end{cases}$$

$$\alpha = \alpha_0 (T - T_c)$$

i.

$$m = \begin{cases} 0 & T > T_c \ (\alpha > 0) \\ \sqrt{\frac{-\partial(T)}{\beta(T)}} \propto \sqrt{T_c - T} & (\alpha < 0) \end{cases}$$

$$m \propto (\tau)^\beta \qquad \beta = \frac{1}{2}$$

ii.

$$\mathcal{L} = \frac{1}{2}\alpha(T) M^2 + \frac{1}{4}\beta(T) M^4 + hM \qquad \text{(free energy)}$$

$$\frac{\partial \mathcal{L}}{\partial M} = \alpha(T) M + \beta(T) M^3 + h = 0$$

$$\frac{d}{dM} X \text{ and } h = h(M)$$

$$\frac{dh}{dM} + \alpha + 3\beta M^2 = 0$$

near $T = T_c$, $\alpha \sim 0$, $M \sim \sqrt[3]{\frac{h}{\beta}} \sim h^{\frac{1}{3}} = h^{\frac{1}{\delta}}$, $\delta = 3$.

and at $h \to 0$

$$M \left(\alpha + \beta M^2 \right) = 0$$

$$\frac{dh}{dm} + \alpha + 3 \left(-\alpha \right) = 0$$

$$\frac{dh}{dM} \Big|_{h \to 0} = 2\alpha = 2\alpha_0 \left(T - T_c \right)$$

$$\chi = \frac{dM}{dh} \Big|_{h \to 0} = \frac{1}{2\alpha_0} \frac{1}{\left(T - T_c \right)} \sim \tau^{-\gamma} \qquad \gamma = 1$$

iii.

$$\mathcal{L} = F = \frac{1}{2} \alpha \left(T \right) M^2 + \frac{1}{4} \beta \left(T \right) M^4$$

$$\frac{\partial F}{\partial M} = 0 = \alpha M + \beta M^3 = M \left(\alpha + \beta M^2 \right)$$

when $M = \pm \sqrt{-\frac{\alpha}{\beta}}$

$$F = \frac{1}{2} \alpha \left(-\frac{\alpha}{\beta} \right) + \frac{1}{4} \beta \left(-\frac{\alpha}{\beta} \right)^2$$

$$= -\frac{1}{2} \frac{\alpha^2}{\beta} + \frac{1}{4} \frac{\alpha^2}{\beta}$$

$$= -\frac{1}{4} \frac{\alpha^2}{\beta}$$

$$C = \frac{\partial E}{\partial T} = \frac{\partial \left(F + TS \right)}{\partial T}$$

$$= \frac{\partial F}{\partial T} + S + T \frac{\partial F}{\partial T}$$

$$= -S + S + T \left(\frac{\partial}{\partial T} \right) \left(-\frac{\partial F}{\partial T} \right)$$

$$= \frac{\partial^2 F}{\partial T^2}$$

$$= -T \frac{\partial^2}{\partial T^2} \left(-\frac{1}{4} \frac{\alpha_0 \left(T - T_c \right)^2}{\beta} \right)$$

$$= T_c \frac{\alpha_0^2}{2\beta} = \text{const} \qquad \left(\text{at } T = T_c \right)$$

To higher order

$$\mathcal{L} = \frac{1}{2} \alpha M^2 + \frac{1}{6} \gamma M^6$$

$$0 = \frac{\partial \mathcal{L}}{\partial M} = \alpha M + \gamma M^5 = \left(\alpha + \gamma M^4 \right) M$$

$$M = \left(-\frac{\alpha}{\gamma} \right)^{\frac{1}{4}}$$

$$\mathcal{L} = \frac{1}{2} \alpha \left(-\frac{\alpha}{\gamma} \right) + \frac{1}{6} \gamma \left(-\frac{\alpha}{\gamma} \right)^{\frac{3}{2}} = \frac{2}{3} \gamma \left(-\frac{\alpha}{\gamma} \right)^{\frac{3}{2}}$$

$$C = -T_c \frac{d^2}{dT^2} \left[\frac{2}{3} \gamma \left(-\frac{\alpha_0 \left(T - T_c \right)}{\gamma} \right)^{\frac{3}{2}} \right] = T_c \gamma \left(-\frac{\alpha \left(T - T_c \right)}{\gamma} \right)^{-\frac{1}{2}} \qquad \delta = \frac{1}{2}$$

We can get the same critical exponents as MFT of 2D Ising model.

This is related to a new subject: the statistical physics of field

The microstates described by a field $\phi \left(\vec{x} \right)$

$$\mathcal{L} = \mathcal{L} \left[\phi \left(\vec{x} \right) \right]$$

$$\mathcal{Z} = \int e^{-\beta \mathcal{F} \left[\phi \left(\vec{x} \right) \right]} d\phi \left(\vec{x} \right)$$

and so on.

Transition	Materials	α	β	γ
Ferromagnets $(n = 3)$ $\vec{M} = (M_x, M_y, M_z)$	Fe, N	-0.1	0.4	1.3
Superfluid $(n = 2)$ $\phi = \phi_1 + i\phi_2$	He^4	0	0.3	1.3
Liquid-gas $n = (0, 1)$	CO_2, Xe	0.1	0.3	1.2
MFT		0	$\frac{1}{2}$	1

The values of critical exponents doesnot depend on the details of the system. And it is universal for many system.

It is obout universality.

– Universality and Correlation length

The above G-L theory does not take spacial variance of ϕ into account, we consider the case $\phi = \phi(x)$ and define the correlation function of $\phi(x)$

$$G(\vec{x} - \vec{y}) = \langle \phi(\vec{x})\phi(\vec{y}) \rangle - \langle \phi(\vec{x}) \rangle \langle \phi(\vec{y}) \rangle$$

without spacial correlation $G(\vec{x} - \vec{y}) = 0$

If with correlation $G \neq 0$, normally, the correlation will decay with $|\vec{x} - \vec{y}|$, so we expect $|\vec{x} - \vec{y}| \longrightarrow$ large

$$G(\vec{x} - \vec{y}) = \exp\left(-\frac{|\vec{x} - \vec{y}|}{\xi}\right)$$

Let us consider a new version of G-L theory, with a point charge like external field $h = h_0 \delta^D(\vec{x})$ and a spacial variance of ϕ, $\phi(\vec{x})$

$$\mathcal{L} = \int d^D x \left[|\nabla\phi(\vec{x})|^2 + \frac{\alpha}{2}\phi^2(\vec{x}) + \frac{1}{4}\beta\phi^4(\vec{x}) + h(x)\phi(\vec{x}) \right]$$

replace $\phi \longrightarrow \phi + \delta\phi$ and

$$0 = \frac{\partial \mathcal{L}}{\partial \delta\phi} = \nabla^2\phi(\vec{x}) + \alpha\phi(\vec{x}) + \beta\phi^3(\vec{x}) + h(x)$$

Nonlinear Shrödinger Equation.

ignore higher order term m^2, we get

$$-\nabla^2\phi(x) + \alpha m^2 = h_0 \delta^D(x)$$

Taking Fourier transform of both sides

$$\left(\vec{k}^2 + \alpha\right)\tilde{\phi}\left(\vec{k}\right) = h_0$$

$$\tilde{\phi}\left(\vec{k}\right) = \int e^{-i\vec{k}\cdot\vec{x}}\phi(\vec{x})\, d^D\vec{x}$$

so

$$\tilde{\phi}\left(\vec{k}\right) = \frac{h_0}{\vec{k}^2 + \alpha}$$

$$\phi(x) = h_0 \int \frac{d^D\vec{k}}{(2\pi)^D}\frac{e^{-i\vec{k}\cdot\vec{x}}}{\vec{k}^2 + \alpha^2}$$

$$\cong C_0|\vec{x}|^{2-D}\exp\left(-\frac{|\vec{x}|}{\xi}\right)$$

where $D > 2$,

$$\xi = \alpha_0^{-\frac{1}{2}} \propto (T - T_c)^{-\frac{1}{2}}$$

$$\sim (T - T_c)^{-V} \qquad V = \frac{1}{2}$$

or we can rewrite $(T - T_c) \propto \xi^{-2}$, so all the other divergent physical quantities can be writen as a power law of ξ, and at $T \to T_c$, $\xi \to \infty$.

ξ means that the physical system organize itself into more or less uniform blocks of size ξ. We can not resolve spacial structure on a finer scale than ξ.

So when $\xi \to \infty$, $(T - T_c)$ all details of the system are lost. So many systems with different details show the same behavior, that si the "universality" of the phase transition and the cooresponding order phase.

A systematic way to calculate critical exponents beyond MFT is the Renormalization Group methods.

Part IV

Nonequilibrium Statistical Mechanics

14 | KINETIC THEORY

– Mechanics

microstates (Γ-Space)

$$\Gamma_S = \{\vec{q}_i, \vec{p}_i\}_{i=1}^N = \{\vec{q}_1, \vec{q}_2, \cdots, \vec{q}_N, \vec{p}_1, \vec{p}_2, \cdots, \vec{p}_N\}$$

$H(\Gamma_S)$

evolution

$$\begin{cases} \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i} \\ \frac{d\vec{p}_1}{dt} = -\frac{\partial H}{\partial \vec{q}_i} + \text{initial condition} \end{cases}$$

obserables $O(\Gamma_S)$

$$\begin{aligned} K(\{\Gamma_S\}) &= \sum \frac{\vec{p}_i}{2m} \\ U(\{\Gamma_S\}) &= \sum_i U(\vec{q}_i) + \sum_{i<j} V(\vec{q}_i - \vec{q}_j) \end{aligned}$$

– Statistical Mechanics

SM don't focus on one specific microstates

i. Assuming

$$\rho(\Gamma_S) = \frac{e^{-\beta H(\Gamma_S)}}{Z} \qquad \text{Ensemble Theory}$$

The probability of which the system is in microstate Γ_S

$$\langle O \rangle = \int \rho(\Gamma_S) O(\Gamma_S) d\Gamma_S$$

We prove that in midterm

$$\frac{d\rho(\Gamma_S)}{dt} = \{\rho, H\} = 0$$

It is equilibrium state.

ii. Liouville's Equation

$$\begin{aligned} \frac{d\rho(\Gamma_S, t)}{dt} &= \{\rho(\Gamma_S, t), H\} \\ &= \sum_i \left\{ \frac{\partial \rho}{\partial \vec{p}_i} \frac{\partial H}{\partial \vec{q}_i} - \frac{\partial H}{\partial \vec{p}_i} \frac{\partial \rho}{\partial \vec{q}_i} \right\} + \rho(\Gamma_S, t_0) \quad \text{intitial condition} \end{aligned}$$

Solve for $\rho(\Gamma_S, t)$.

That is the main idea of Kinetic Theory.—— solve dynamical Equation.

$$\begin{aligned} dP'_\alpha &= dP_\alpha + \frac{d\left(\frac{dP_\alpha \delta t}{dt}\right)}{dP_\alpha} \delta P_\alpha \\ &= dP_\alpha + \frac{d\dot{P}_\alpha}{dP_\alpha} \delta t \delta P_\alpha \end{aligned}$$

$$\begin{aligned} dP'_\alpha dQ'_\alpha &\cong dP_\alpha \left[1 + \frac{d\dot{P}_\alpha}{dP_\alpha} \delta t\right] dQ_\alpha \left[1 + \frac{d\dot{Q}_\alpha}{dQ_\alpha} \delta t\right] \\ &= dP_\alpha dQ_\alpha \left[1 + \left(\frac{d\dot{P}_\alpha}{dP_\alpha} + \frac{d\dot{Q}_\alpha}{dQ_\alpha}\right) \delta t + O\left(\delta t^2\right)\right] \end{aligned}$$

$$\begin{aligned} \frac{\partial \dot{Q}_\alpha}{\partial Q_\alpha} &= \frac{\partial}{\partial Q_\alpha}\left(\frac{\partial H}{\partial P_\alpha}\right) = \frac{\partial^2 H}{\partial Q_\alpha \partial P_\alpha} \\ \frac{\partial \dot{P}_\alpha}{\partial P_\alpha} &= \frac{\partial}{\partial P_\alpha}\left(-\frac{\partial H}{\partial Q_\alpha}\right) = -\frac{\partial^2 H}{\partial P_\alpha \partial Q_\alpha} \end{aligned}$$

So

$$dP'_\alpha dQ'_\alpha = dP_\alpha dQ_\alpha \left[1 + O\left(\delta t^2\right)\right]$$

$$\cong dP_\alpha dQ_\alpha$$

$$d\Gamma = d\Gamma'$$

ρ behaves like the density of an incompressible fluid.

$$\rho\left(P', Q', t + \delta t\right) = \rho\left(P, Q, t\right)$$

(distribution function for microstate P, Q)

$$0 = \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{dp_\alpha}{dt} + \frac{\partial \rho}{\partial q_\alpha} \frac{dq_\alpha}{dt}\right)$$

$$= \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left[\frac{\partial \rho}{\partial p_\alpha}\left(-\frac{\partial H}{\partial q_\alpha}\right) + \frac{\partial \rho}{\partial q_\alpha}\left(\frac{\partial H}{\partial p_\alpha}\right)\right]$$

$$= \frac{\partial \rho}{\partial t} + \sum_{\partial=1}^{3N} \left[\frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial H}{\partial q_\alpha} \frac{\partial \rho}{\partial p_\alpha}\right]$$

$$= \frac{\partial \rho}{\partial t} + \{\rho, H\}$$

So

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}$$

It's the Louville's Equation, where the "{}" is the Poisson bracket.

initial state $\rho\left(\Gamma_S, t = t_0\right) \longrightarrow$ assumption.

But it is impossible to solve $\rho\left(\Gamma_S, t\right)$ for $N \sim 10^{19}$. (for $N \leqslant$ a few particles. It is possible!)

14.1 BBGKY–REDUCE DEGREE OF FREEDOM

– 1 particle density (unconditional probability)

$$f_1\left(\vec{p}, \vec{q}, t\right) = \langle \sum_{i=1}^{N} \delta^3\left(\vec{p} - \vec{p}_1\right) \delta^3\left(\vec{q} - \vec{q}_1\right)\rangle$$

$$= N \int \prod_{i=2}^{N} \rho\left(\vec{p}_1 = \vec{p}, \vec{q}_1 = \vec{q}, \vec{p}_2, \vec{q}_2, \cdots, \vec{p}_N, \vec{q}_N\right) d^3\vec{p}_i d^3\vec{q}_i$$
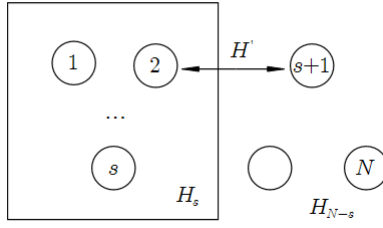
– 2-particle density

$$f_2\left(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t\right) = N\left(N-1\right) \int \prod_{i=3}^{N} \rho\left(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, \cdots, \vec{p}_N, \vec{q}_N\right) d^3\vec{p}_i d^3\vec{q}_i$$

– s-particle density

$$f_S\left(\vec{p}_1 \cdots \vec{p}_s, \vec{q}_1 \cdots \vec{q}_s, t\right) = \frac{N!}{(N-s)!} \int \prod_{i=s+1}^{N} \rho\left(\vec{p}, \vec{q}, t\right) dV_i$$

$$\equiv \frac{N!}{(N-s)!} \rho_s\left(\vec{p}_1 \cdots \vec{p}_s, \vec{q}_1 \cdots \vec{q}_s, t\right)$$

– Simplification of the dynamics

$$H\left(\vec{p},\vec{q}\right) = \sum_{i=1}^{N}\left[\frac{\vec{p}_1^2}{2m} + U\left(\vec{q}_1\right)\right] + \frac{1}{2}\sum_{i,j=1}^{N} V\left(\vec{q}_i - \vec{q}_j\right)$$

$$= H_s + H_{N-s} + H^{'}$$

$$H_s = \sum_{i=1}^{s}\left[\frac{\vec{p}_i^2}{2m} + U\left(\vec{q}_i\right)\right] + \frac{1}{2}\sum_{i,j=1}^{s} V\left(\vec{q}_i - \vec{q}_j\right)$$

$$H_{N-s} = \sum_{i=s+1}^{N}\left[\frac{\vec{p}_i^2}{2m} + U\left(\vec{q}_1\right)\right] + \frac{1}{2}\sum_{i,j=s+1}^{N} V\left(\vec{q}_i - \vec{q}_j\right)$$

$$H^{'} = \sum_{n=1}^{s}\sum_{i=s+1}^{N} V\left(\vec{q}_n - \vec{q}_i\right)$$

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=s+1}^{N}\frac{\partial \rho}{\partial t}dV_i$$

$$= -\int \prod_{i=1}^{N}\left\{\rho, H_s + H_{N-s} + H^{'}\right\}$$

$$\int \prod_{i=s+1}^{N} dV_i\left\{\rho, H_s\right\} = \left\{\int \prod_{i=s+1}^{N} dV_i, H_s\right\} = \left\{\rho_s, H_s\right\}$$

$$\int \prod_{i=s+1}^{N} dV_i\left\{\rho, H_{N-s}\right\}$$

$$= \int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N}\left[\frac{\partial \rho}{\partial \vec{p}_j}\frac{\partial H_{N-s}}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j}\frac{\partial H_{N-s}}{\partial \vec{p}_j}\right]$$

$$= \int \prod_{i=s+1}^{N} dV_i \sum_{j=s+1}^{N}\frac{\partial \rho}{\partial \vec{p}_j}\left(\frac{\partial U\left(\vec{q}_j\right)}{\partial \vec{q}_j} + \frac{1}{2}\sum_{k=s+1}^{N}\frac{\partial V\left(\vec{q}_j - \vec{q}_k\right)}{\partial \vec{q}_j}\right) - \frac{\partial \rho}{\partial \vec{q}_j}\frac{\vec{p}_j}{m}$$

$$= 0$$

$$\int dq_j dp_j \frac{\partial \rho}{\partial p_j}\left(U\left(q_j\right)\right)$$

$$= dq_j d\rho\left(p_j, q_j\right) U\left(q_j\right)$$

$$= q_j \rho U\left(q\right)|_{\text{Boundary}} - dq_j \rho \frac{dU\left(q_j\right)}{dp_j}$$

$$= 0$$

$$\int dq_j dp_j \frac{\partial \rho}{\partial q_j}\vec{p}_j$$

$$= p_j d\rho dp_j$$

$$= \rho p_j p_j - \int dp_j \rho \frac{\partial p_j}{\partial q_j}$$

$$= 0$$

$$\int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \frac{\partial H'}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \frac{\partial H'}{\partial \vec{p}_j} \right]$$

$$= \int \prod_{i=s+1}^{N} dV_i \left[\sum_{j=1}^{s} \frac{\partial \rho}{\partial \vec{p}_j} \sum_{k=s+1}^{N} \frac{\partial V(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_j} + \sum_{j=s+1}^{N} \frac{\partial \rho}{\partial \vec{p}_j} \sum_{k=1}^{s} \frac{\partial V(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_j} \right]$$

$$= (N-s) \int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{s} \frac{\partial V(\vec{q}_j - \vec{q}_{s+1})}{\partial \vec{q}_j} \frac{\partial \rho}{\partial \vec{p}_j}$$

$$= (N-s) \sum_{j=1}^{s} \int dV_{s+1} \frac{\partial V(\vec{q}_j - \vec{q}_{s+1})}{\partial \vec{q}_j} \int \prod_{i=s+2}^{N} \frac{\partial \rho}{\partial \vec{p}_j}$$

$$= (N-s) \sum_{j=1}^{s} \int dV_{s+1} \frac{\partial V(\vec{q}_j - \vec{q}_{s+1})}{\partial \vec{q}_j} \frac{\partial}{\partial \vec{p}_j} \left[\int \prod_{i=s+2}^{N} dV_i \rho \right]$$

So

$$\frac{\partial \rho_s}{\partial t} - \{H_s, \rho_s\} = (N-s) \sum_{j=1}^{s} \int dV_{s+1} \frac{\partial V(\vec{q}_j - \vec{q}_{s+1})}{\partial \vec{q}_j} \frac{\partial \rho_{s+1}}{\partial \vec{p}_j}$$

$$f_s = \frac{N!}{(N-s)!} \rho_s$$

$$\frac{\partial f_s}{\partial t} - \{H_s, f_s\} = \sum_{j=1}^{s} \int dV_{s+1} \frac{\partial V(\vec{q}_j - \vec{q}_{s+1})}{\partial \vec{q}_j} \frac{\partial f_{s+1}}{\partial \vec{p}_j}$$

$$f_1 \longrightarrow f_2 \longrightarrow \cdots \longrightarrow f_{s-1} \longrightarrow f_s$$
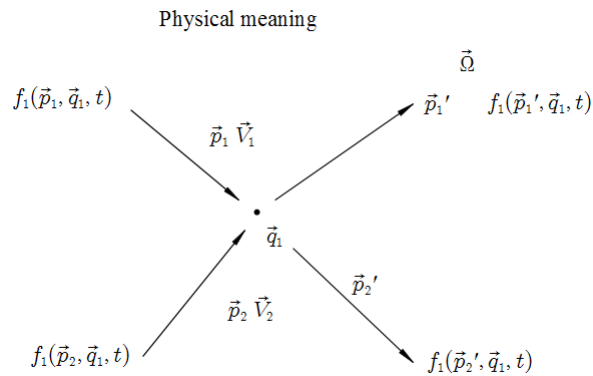
It is another form of

$$\frac{\partial \rho}{\partial t} - \{H, \rho\} = 0$$

But we can make some assumptions to truncate it!

14.2 BOLTZMAN EQUATION

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} \right] f_1(\vec{p}_1, \vec{q}_1, t)$$

$$= - \int d^3\vec{p}_2 d^2\Omega \left| \frac{d\sigma}{d\Omega} \right| |\vec{V}_1 - \vec{V}_2| \left[f_1(\vec{p}_1, \vec{q}_1, t) f_1(\vec{p}_2, \vec{q}_1, t) - f_1(\vec{p}_1', \vec{q}_1, t) f_1(\vec{p}_2, \vec{q}_1, t) \right]$$

How to get it from BBGKY?

Physical meaning

$$\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2' \qquad \text{Four particles collide on } \vec{q}_1.$$

$\frac{d\sigma}{d\Omega}$ differential cross-section

$|\vec{V}_1 - \vec{V}_2|$ flux of incident particles.

$$f(p_1, p_2) = f(p_1) f(p_2)$$

$f(\vec{p}_1) f(\vec{p}_2)$ joint probability of two particles at $(\vec{p}_1, \vec{p}_2)$.

$f(\vec{p}_1') f(\vec{p}_1')$ joint probability of two particles at $(\vec{p}_1', \vec{p}_2')$.

$\vec{p}_1, \vec{p}_2 \longrightarrow \vec{p}_1', \vec{p}_2'$ decrease $f(\vec{p}_1)$.

$\vec{p}_1, \vec{p}_2 \longleftarrow \vec{p}_1', \vec{p}_2'$ increase $f(\vec{p}_1)$.

consider f_1, f_2

$$\begin{cases} H_1 = \frac{\vec{p}_1^2}{2m} + U(\vec{q}_1), & H_1' = V(\vec{q}_1 - \vec{q}_2) \\ H_2 = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} + U(\vec{q}_1) + U(\vec{q}_2) + V(\vec{q}_1 - \vec{q}_2), & H_2' = V(\vec{q}_1 - \vec{q}_3) + V(\vec{q}_2 - \vec{q}_3) \end{cases}$$

$$\{H_1, f_1\} = \frac{\partial H_1}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\partial H}{\partial \vec{p}_1} \frac{\partial f_1}{\partial \vec{q}_1}$$
$$= \frac{\partial U}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\vec{p}_1}{m} \frac{\partial f_1}{\partial \vec{q}_1}$$

$$\frac{\partial f_1}{\partial t} - \{H_1, f_1\} = \int dV_2 \frac{\partial V(q_1 - q_2)}{\partial q_1} \frac{\partial f_2}{\partial \vec{p}_1}$$

$$\left[\frac{\partial}{\partial t} \left(-\frac{\partial U}{\partial \vec{q}_1} \frac{\partial}{\partial \vec{p}_1} \right) + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} \right] f_1 = \int dV_2 \frac{\partial V(q_1 - q_2)}{\partial \vec{q}_1} \frac{\partial f_2}{\partial \vec{p}_1} \qquad \text{---- (A)}$$

$$\frac{\partial f_2}{\partial t} - \{H_2, f_2\} = \sum_{s=1}^{2} \int dV_3 \frac{\partial V(q_s - q_3)}{\partial \vec{q}_s} \frac{\partial f_3}{\partial \vec{p}_s}$$

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \frac{\partial}{\partial \vec{p}_1} - \frac{\partial U}{\partial \vec{q}_2} \frac{\partial}{\partial \vec{p}_2} + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} - \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \frac{\partial}{\partial p_1} - \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_2} \frac{\partial}{\partial \vec{p}_2} \right] f_2$$
$$= \int dV_3 \left[\frac{\partial V(\vec{q}_1 - \vec{q}_3)}{\partial \vec{q}_1} \frac{\partial}{\partial \vec{p}_1} + \frac{\partial V(\vec{q}_2 - \vec{q}_s)}{\partial \vec{q}_2} \frac{\partial}{\partial \vec{p}_2} \right] f_3 \qquad \text{----(B)}$$

i.

$$\int dV_3 \left[\frac{\partial V(q_1 - q_3)}{\partial q_1} \frac{\partial}{\partial p_1} + \frac{\partial V(q_2 - q_3)}{\partial q_2} \frac{\partial}{\partial p_2} \right] f_3 = 0$$

mean free time $\tau_x \approx 10^{-8}$s.

ii.

$$\left[\frac{\partial V(q_1 - q_2)}{\partial q_1} \frac{\partial}{\partial \vec{p}_2} \right] f_2 \approx \frac{f_2}{\tau_c}$$
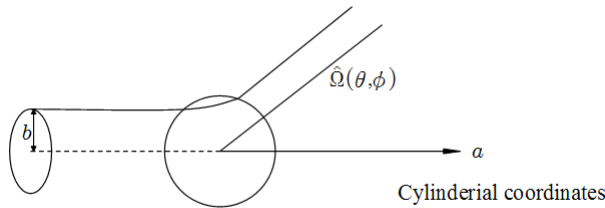
collision duration time $\tau_c \approx 10^{-12}$s

iii.

$$\left[\frac{\partial U(q_1)}{\partial q_1} \frac{\partial}{\partial p_1} \right] f_1$$

extrinsic time scale $\tau_u \sim 10^{-5}$.

Substitate 1 into (B) and then simplify (A)

(A) can be simplified to (ignore the process)

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} \right] f_1 = \int dV_2 \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right) f_2$$
$$\approx \int d^3 p_3 d^3 q \left(\frac{\vec{p}_1 - \vec{p}_2}{m} \right) \frac{\partial}{\partial \vec{q}} f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}; t)$$

$$\vec{q} = \vec{q}_2 - \vec{q}_1$$

Cylinderial coordinates

$$\frac{df_1}{dt}\bigg|_{\text{coll}} \approx \int d^3 \vec{p}_2 d^3 \vec{q} \left(\frac{\vec{p}_1 - \vec{p}_2}{m} \right) \frac{\partial}{\partial q} f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}, t)$$

$$\int d^3\vec{q}\left(\frac{\vec{p}_1 - \vec{p}_2}{m}\right)\frac{\partial}{\partial\vec{q}} = \int d^2\vec{b}\int da|\vec{V}_1 - \vec{V}_2|(0,1)\left(\frac{\partial}{\partial b}\cdot\frac{\partial}{\partial a}\right)$$

$$= \int d^2b|V_1 - V_2|\int\limits_{-\infty}^{+\infty}da\frac{\partial}{\partial a}$$

$$\left.\frac{df_1}{dt}\right|_{coll} = \int d^3\vec{p}_2 d^2b|\vec{V}_1 - \vec{V}_2|\left[f_2\left(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},+;t\right) - f_2\left(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},-;t\right)\right]$$

$$(\vec{p}_1,\vec{p}_2)\longrightarrow(\vec{p}_1',\vec{p}_2')\overset{\text{time reversal}}{\longrightarrow}(\vec{p}_1',\vec{p}_2')\longrightarrow(\vec{p}_1,\vec{p}_2)$$

$$f_2\left(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},+;t\right) = f_2\left(\vec{p}_1',\vec{q}_1,\vec{p}_2',\vec{b},-;t\right)$$

$$\left.\frac{df_1}{dt}\right|_{coll} = \int d^3\vec{p}_2 d^2b|\vec{V}_1 - \vec{V}_2|\left[f_2\left(\vec{p}_1',\vec{q}_1,\vec{p}_2',\vec{b},-;t\right) - f_2\left(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},-;t\right)\right]$$
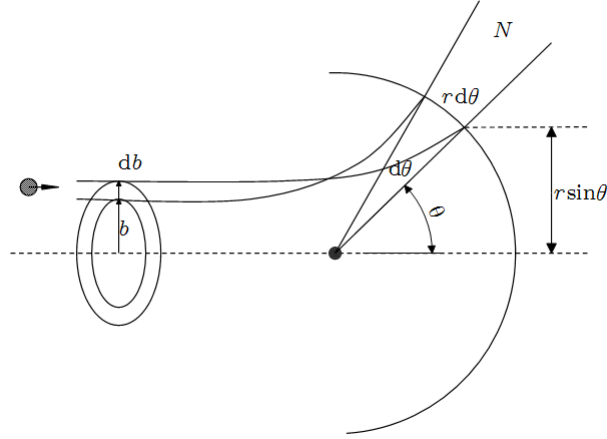
N Number of particles scattered into direction (θ,ϕ) per unit time per unit solid angle.

Number of incident particles per unit time per unit area.

$\vec{b}$ determine (θ,ϕ), $(b\longrightarrow b+db)\longrightarrow(\theta\longrightarrow\theta+d\theta)$.

$$2\pi bdb\qquad d\Omega = 2\pi\sin\theta d\theta\qquad j\times 2\pi bdb = Nd\Omega\qquad \frac{N}{j} = \frac{bdb}{\sin\theta d\theta}\qquad \frac{N}{j}\equiv\frac{d\sigma}{d\Omega}.$$

So

$$d^2\vec{b} = 2\pi bd\theta = 2\pi\frac{d\sigma}{d\Omega}\sin\theta d\theta = \frac{d\sigma}{d\Omega}d^2\Omega$$

$$\left.\frac{\partial f_1}{\partial t}\right|_{coll} = \int d^3\vec{p}d^2\Omega\frac{d\sigma}{d\Omega}|\vec{V}_1 - \vec{V}_2|\left[f_2\left(\vec{p}_1',\vec{q}_1,\vec{p}_2',\Omega,-;t\right) - f_2\left(\vec{p}_1,\vec{q}_1,\vec{p}_2,\Omega,-;t\right)\right]$$

$$f_2\left(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},-;t\right) = f_1\left(\vec{p}_1,\vec{q}_1,t\right)f_1\left(\vec{p}_2,\vec{q},t\right)\qquad\text{molecular chaos}$$

$$\left[\frac{\partial f}{\partial t} - \frac{\partial U}{\partial\vec{q}_1}\frac{\partial}{\partial\vec{p}_1} + \frac{\vec{p}_1}{m}\frac{\partial}{\partial\vec{q}_1}\right]f_1\left(\vec{p}_1,\vec{q}_1,t\right)$$

$$= -\int d^3\vec{p}_2 d^2\Omega\left|\frac{d\sigma}{d\Omega}\right||\vec{V}_1 - \vec{V}_2|\left[f_1\left(\vec{p}_1,\vec{q}_1,t\right)f_1\left(\vec{p}_2,\vec{q},t\right) - f_1\left(\vec{p}_1',\vec{q}_1,t\right)f_1\left(\vec{p}_2',\vec{q},t\right)\right]$$

Another way to derive Boltzman Equation

$$f_1\left(\vec{p}_1,\vec{q}_1,t\right)\qquad H_1 = \frac{\vec{p}_1^2}{2m} + U\left(\vec{q}_1\right)$$

$$\frac{df_1}{dt} = \frac{\partial f_1}{\partial t} + \frac{d\vec{p}_1}{dt}\frac{\partial f_1}{\partial\vec{p}_1} + \frac{d\vec{q}_1}{dt}\frac{\partial f_1}{\partial\vec{q}_1}$$

$$= \frac{\partial f_1}{\partial t} - \frac{\partial H_1}{\partial\vec{q}_1}\frac{\partial f_1}{\partial\vec{p}_1} + \frac{\partial H_1}{\partial\vec{p}_1}\frac{\partial f_1}{\partial\vec{q}_1}$$

$$= \frac{\partial f_1}{\partial t} - \frac{\partial U\left(\vec{q}_1\right)}{\partial\vec{q}_1}\frac{\partial f_1}{\partial\vec{p}_1} + \frac{\vec{p}_1}{m}\frac{\partial f}{\partial\vec{q}_1}$$

Stream term

$$\left.\frac{df_1\left(\vec{p}_1,\vec{q}_1,t\right)}{dt}\right|_{stream} = \left.\frac{df_1}{dt}\right|_{collidsion}$$

j = incidenting particles, per unit time, per unit area;

N = Number of particles scattered into direction (θ, ϕ), per unit time, per unit sdid angle.

$$j \cdot 2\pi b db = N \sin\theta d\theta d\phi \qquad N_{in} = N_{out}$$

$$\frac{N}{j} \equiv \frac{d\sigma}{d\Omega} = \frac{N_{in} \cdot \text{unit time} \cdot \text{unit area}}{N_{out} \cdot \text{unit time} \cdot \text{unit solid angle}}$$

$$= \frac{\text{unit area}}{\text{unit solid angle}} = \left(\frac{d\sigma}{d\Omega}\right)$$

So probability/unit time for a pair of particle from $(\vec{p}_1, \vec{p}_2)$ state to $\left(\vec{p}_1', \vec{p}_2'\right)$ state is

$$\int d^2\Omega \left(\frac{d\sigma}{d\Omega}\right) \vec{j} = \int d^2\Omega \left(\frac{d\sigma}{d\Omega}\right) f(\vec{p}_2, \vec{q}, t) |\vec{V}_1 - \vec{V}_2|$$

$$j = n\nu$$

this change $f_1(\vec{p}_1, \vec{q}_1, t)$ per unit time

$$-\int d^3\vec{p}_1 f_1(\vec{p}_1, \vec{q}_1, t) \times \left[\int d^2\Omega \left(\frac{d\sigma}{d\Omega}\right) f(\vec{p}_2, \vec{q}, t) |\vec{V}_1 - \vec{V}_2|\right]$$

on the other hand, $\left(\vec{p}_1', \vec{p}_2'\right)$ state will change to $(\vec{p}_1, \vec{p}_2)$ state by

$$\int d\vec{p}_1 f_1\left(\vec{p}_1', \vec{q}, t\right) \left[\int d^2\Omega \left(\frac{d\sigma}{d\Omega}\right) f(\vec{p}_2, \vec{q}, t) |\vec{V}_1' - \vec{V}_2'|\right]$$

$$\frac{\partial f_1(\vec{p}_1, \vec{q}, t)}{\partial t} = -\int d^3\vec{p}_2 d^2\Omega \left(\frac{d\sigma}{d\Omega}\right) |\vec{V}_1 - \vec{V}_2| \left[f_1(\vec{p}_1, \vec{q}, t) f_1(\vec{p}_2, \vec{q}, t) - f_1\left(\vec{p}_1', \vec{q}, t\right) f_1\left(\vec{p}_2', \vec{q}, t\right)\right]$$

14.3 H–THEOREM (PROVE THAT SYSTEM WILL APPROACH EQUILIBRIUM)

$$H(t) = \int f_1(\vec{p}, \vec{q}, t) \ln f_1(\vec{p}, \vec{q}, t) d^3\vec{p} d^3 q$$

$$H = -\frac{S}{k_B} \qquad S \text{ "entropy"}$$

$$\frac{dH}{dt} \leqslant 0$$

$$\frac{dH}{dt} = \int d\omega \left[\frac{\partial f_1}{\partial t} \ln f_1 + f_1 \frac{1}{f_1} \frac{\partial f_1}{\partial t}\right]$$

$$= \int d\omega \left[1 + \ln f(p_1)\right] \frac{\partial f(p_1)}{\partial t}$$

$$= \int d\omega \left[1 + \ln f(p_1)\right] \left\{\frac{\partial U}{\partial q_1} \frac{\partial f(p_1)}{\partial p_1} + \frac{\vec{p}_1}{m} \frac{\partial f(\vec{p}_1, \vec{q}_1)}{\partial \vec{q}_1} - \int d^3 p_2 d^2\Omega \left|\frac{d\sigma}{d\Omega}\right|\right.$$

$$\left. |\vec{V}_1 - \vec{V}_2| \left[f(\vec{p}_1) f(\vec{p}_2) - f\left(\vec{p}_1'\right) f\left(\vec{p}_2'\right)\right]\right\}$$

$\frac{\partial U}{\partial \vec{q}}$ is indept of $\vec{p}$

$$\int dp dq \frac{\partial U}{\partial q} \frac{\partial f(\vec{p}_1, \vec{q}_1)}{\partial \vec{p}_1}$$

$$= \int dq \frac{\partial U}{\partial q} df$$

$$= \frac{\partial U}{\partial q} f\Big|_{Boundary} - \int f \frac{d}{d\vec{p}}\left(\frac{\partial U}{\partial \vec{q}}\right) dq$$

$$= 0$$

and

$$\int d\omega \frac{\vec{p}_1}{m} \frac{\partial f}{\partial \vec{q}_1} = 0$$

$$\frac{dH}{dt} = \int d\omega \, [1 + \ln f(p_1)] \int d^3p_2 d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2| \left[f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2')\right]$$

$$= \int dq \int dp_1 dp_2 d^2\Omega \, [1 + \ln f(p_1)] \left[f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2')\right] \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2| \qquad \text{—(a)}$$

$$\vec{V}_1 \longleftrightarrow \vec{V}_2 \qquad (\vec{p}_1 \longleftrightarrow \vec{p}_2)$$

$$\frac{dH}{dt} = \int dq \int dp_2 dp_1 d^2\Omega \, [1 + \ln f(p_2)] \left[f(\vec{p}_2) f(\vec{p}_1) - f(\vec{p}_2') f(\vec{p}_1')\right] \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2|$$

$$= \int dq \int dp_1 dp_2 d^2\Omega \, [1 + \ln f(p_2)] \left[f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2')\right] \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2| \qquad \text{—(b)}$$

$$\frac{(a) + (b)}{2}$$

$$\frac{dH}{dt} = -\frac{1}{2} \int dq \int dp_1 dp_2 d^2\Omega \, [2 + \ln f(\vec{p}_1) f(\vec{p}_2)] \left[f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2')\right]$$

$$\times \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2| \qquad \text{———(c)}$$

$$\vec{p}_1 \longleftrightarrow \vec{p}_1' \qquad \vec{p}_2 \longleftrightarrow \vec{p}_2'$$

$$\frac{dH}{dt} = -\frac{1}{2} \int dq \int dp_1' dp_2' d^2\Omega \, \left[2 + \ln f(\vec{p}_1') f(\vec{p}_2')\right] \left[f(\vec{p}_1') f(\vec{p}_2') - f(\vec{p}_1) f(\vec{p}_2)\right]$$

$$\times \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1' - \vec{V}_2'| \qquad \text{———(d)}$$

$$|\vec{V}_1' - \vec{V}_2'| = |\vec{V}_1 - \vec{V}_2|$$

$$\int dp_1' dp_2' = \int dp_1 dp_2 \qquad \vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$$

determine each other.

(d) $\longrightarrow$

$$\frac{dH}{dt} = -\frac{1}{2} \int dq \int dp_1 dp_2 d^2\Omega \, \left[2 + \ln f(\vec{p}_1') f(\vec{p}_2')\right] \left[f(\vec{p}_1') f(\vec{p}_2') - f(\vec{p}_1) f(\vec{p}_2)\right] \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2|$$

$$\frac{(a) + (e)}{2}$$

$$\frac{dH}{dt} = -\frac{1}{4} \int dq \int dp_1 dp_2 d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{V}_1 - \vec{V}_2| \left[\ln f(\vec{p}_1) f(\vec{p}_2) - \ln f(\vec{p}_1') f(\vec{p}_2')\right]$$

$$\times \left[f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2')\right]$$

If $f(\vec{p}_1) f(\vec{p}_2) > f(\vec{p}_1') f(\vec{p}_2')$

$$\begin{cases} \ln f(\vec{p}_1) f(\vec{p}_2) - \ln f(\vec{p}_1') f(\vec{p}_2') > 0 \\ f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2') > 0 \end{cases}$$

$$\Longrightarrow \frac{dH}{dt} \leqslant 0$$

and if $f(\vec{p}_1) f(\vec{p}_2) < f(\vec{p}_1') f(\vec{p}_2')$

$$\begin{cases} \ln f(\vec{p}_1) f(\vec{p}_2) - \ln f(\vec{p}_1') f(\vec{p}_2') < 0 \\ f(\vec{p}_1) f(\vec{p}_2) - f(\vec{p}_1') f(\vec{p}_2') < 0 \end{cases}$$

$$\Longrightarrow \frac{dH}{dt} \leqslant 0$$

so

$$\frac{dH}{dt} \leqslant 0$$

$$\frac{dS}{dt} = \frac{d(-k_B H)}{dt} \geqslant 0$$

entropy won't decrease. When at equilibrium,

$$\frac{dH}{dt} = 0$$

14.4 PROPERTIES OF EQUILIBRIUM SYSTEM & NEAR EQUILIBRIUM

14.4.1 Distribution at equilibrium

At Equilibrium $\frac{dH}{dt} = 0$, so

$$f(\vec{p}_1) f(\vec{p}_2) = f\left(\vec{p}_1'\right) f\left(\vec{p}_2'\right)$$

and we know

$$\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2' \quad \text{(momentum conseration)} \text{——(a)}$$

$$\varepsilon(\vec{p}_1) + \varepsilon(\vec{p}_2) = \varepsilon\left(\vec{p}_1'\right) + \varepsilon\left(\vec{p}_2'\right) \quad \text{(energy conservation)} \text{——(b)}$$

$$1 + 1 = 1 + 1 \quad \text{(particle number conservation)} \text{——(c)}$$

$$\ln f_1(\vec{p}_1) + \ln f_1(\vec{p}_2) = \ln f_1\left(\vec{p}_1'\right) + \ln f_1\left(\vec{p}_2'\right) \quad \text{——(d)}$$

So

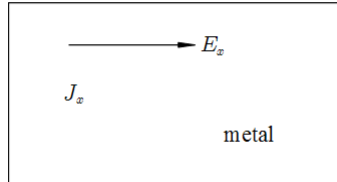$$\ln f_1(\vec{p}) = \alpha_0 + \alpha_i p_i + \beta\left(\frac{\vec{p}^2}{2m}\right)$$

$$f_1(\vec{p}, \vec{q}) = n\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} \exp\left[-\frac{\beta(\vec{p} - \vec{p}_0)^2}{2m}\right]$$

or more generally

$$f_1(\vec{p}, \vec{q}) = N(\vec{q}) \exp\left[-\vec{\alpha}(\vec{q}) \cdot \vec{p} - \beta(\vec{q})\left(\frac{\vec{p}^2}{2m} + U(\vec{q})\right)\right]$$

local equilibrium.

14.4.2 Electric Conductivity

$$J_z = \sigma E_z \quad \text{(Ohm's law)}$$

We can simplify the collision term

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \frac{\partial f}{\partial \vec{q}} + \frac{\partial U(\vec{q})}{\partial \vec{q}} \frac{\partial f}{\partial \vec{p}} = -\frac{f - f^{(0)}}{\tau_0}$$

For stationary states

$$\frac{\partial f}{\partial t} = 0$$

$$\frac{\vec{p}}{m} \frac{\partial f}{\partial \vec{q}} + \frac{\partial U(\vec{q})}{\partial \vec{q}} \frac{\partial f}{\partial \vec{p}} = -\frac{f - f^{(0)}}{\tau_0}$$

$$J_x = -e\bar{v}_x n$$

$$= -2e \int \frac{d^3p \, d^3q}{h^3} f(\vec{p}, \vec{q}) v_x$$

where "$-2e$" means electron has two spin state.

For

$$f(\vec{p}, \vec{q}) = n\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} \exp\left(-\beta \frac{\vec{p}^2}{2m}\right)$$

without external field

$$J_x = 0$$

If an external field is presented

$$\frac{\partial U(\vec{q})}{\partial \vec{q}} = (-eE_x)$$

Solve

$$-eE_x \frac{\partial f}{\partial p_x} = -\frac{f - f^{(0)}}{\tau_0}$$

For weak field

$$f = f^{(0)} + f^{(1)}$$

$$eE_x \frac{\partial f^{(0)}}{\partial p_x} = \frac{f^{(1)}}{\tau_0}$$

$$f = f^{(0)} + eE_x \tau_0 \frac{\partial f^{(0)}}{\partial p_x}$$

$$J_x = (-e) \int \frac{d^3p\, d^3q}{h^3} eE_x \tau_0 \frac{\partial f^{(0)}}{\partial p_x} v_x$$

$$= -\frac{e^2 E_x \tau_0}{m} \int \frac{d^3p\, d^3q}{h^3} \frac{\partial f^{(0)}}{\partial p_x} \cdot p_x$$

$$\int dp_x \frac{\partial f^{(0)}}{\partial p_x} p_x$$

$$= \int df^{(0)} p_x$$

$$= f^{(0)} p_x \Big|_{-\infty}^{+\infty} - \int f^{(0)} dp_x$$

$$= \frac{e^2 E_x \tau}{m} \int \frac{d^3p\, d^3q}{h^3} f^{(0)} (\vec{p} \cdot \vec{q})$$

$$= \frac{e^2 n \tau}{m} E_x$$

so

$$\sigma = \frac{e^2 n \tau}{m} \qquad \text{Drude formula}$$

e) Kerson Huang, "Introduction to Statistical Mechanics" *Wieley*

f) Marah Kardar, "Statistical Mechanics of Particles", McGraw-Hill, New York, 1962.

g) Liang X. X. , "Introduction to Statistical Mechanics"