ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 1. Introduction

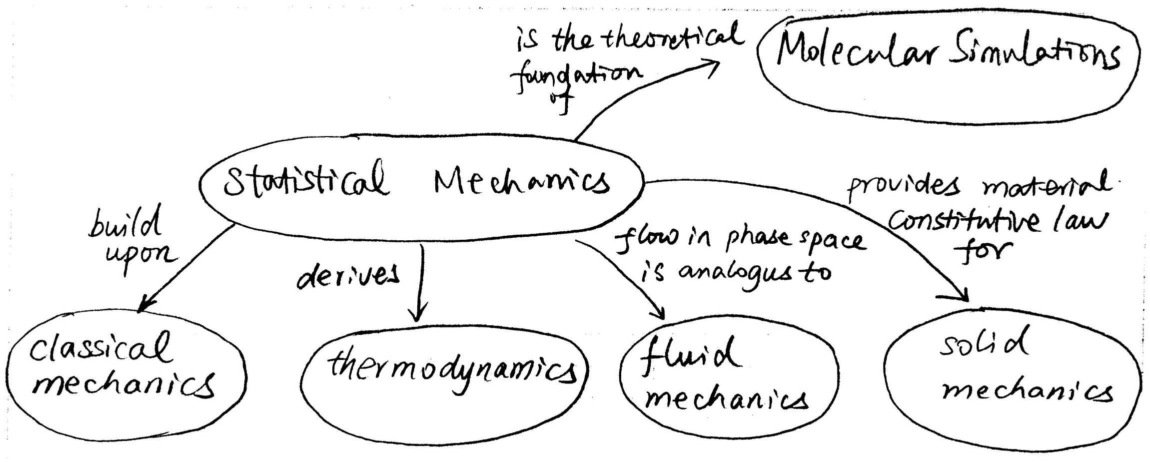
January 7, 2011

Statistical Mechanics

- is the theory with which we analyze the behavior of natural or spontaneous fluctuations — Chandler “Introduction to Modern Statistical Mechanics” (1987)
- provides a set of tools for understanding simple behavior that emerges from underlying complexity — Sethna “Statistical Mechanics” (2007)
- provides the basic tools for analyzing the behavior of complex systems in thermal equilibrium — Sachs, Sen and Sexten “Elements of Statistical Mechanics” (2006)
- involves systems with a larger number of degrees of freedom than we can conveniently follow explicitly in experiment, theory or simulation — Halley “Statistical Mechanics” (2007).

The **main purpose** of this course is to provide enough statistical mechanics background to the Molecular Simulation courses (ME 346 B and C), including fundamental concepts such as ensemble, entropy, free energy, etc.

We also try to identify the connection between statistical mechanics and all major branches of “Mechanics” taught in the Mechanical Engineering department.



Textbook

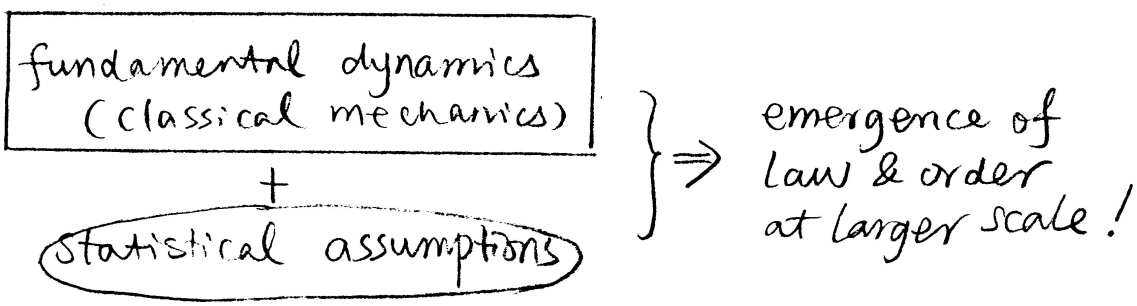
- Frederick Reif, "Fundamentals of Statistical and Thermal Physics", (McGraw-Hill, 1965). (required) $67.30 on Amazon, paperback. Available at bookstore. Several copies on reserve in Physics library.
- James P. Sethna, "Statistical Mechanics: Entropy, Order Parameters, and Complexity", (Claredon Press, Oxford). Suggested reading. PDF file available from Web (free!) `http://pages.physics.cornell.edu/sethna/StatMech/`.

First Reading Assignment

- Reif § 1.1-1.9 (by next class, Monday Jan 10).
- Sethna Chap. 1 and Chap. 2

What will be covered in this class: (Sethna Chapters 1 to 6)

- classical, equilibrium, statistical mechanics



- some numerical exercises (computer simulations)

What will be touched upon in this class:

- non-equilibrium statistical mechanics (phase transition, nucleation)

What will NOT be covered in this class:

- quantum statistical mechanics

Acknowledgement

I would like to thank Seunghwa Ryu for helping convert the earlier hand-written version of these notes to electronic (Latex) form.

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Handout 2. Diffusion

January 7, 2011

Contents

1 What is diffusion?

<u>Diffusion</u> is the process by which molecules spread from areas of high concentration to areas of low concentration.

It is a spontaneous, natural process that has also been widely used in technology, such as

- doping of semiconductors by impurities (to create P-N junction and transistor)
- diffusional bonding (between two metals)
- transdermal drug delivery (patches)
- $\cdots$ (can you think of other examples of diffusion?)

Here we use diffusion to illustrate many aspects of statistical mechanics

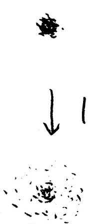
- the concept of "ensemble"
- the emergence of simple laws at the larger scale from complex dynamics at the smaller scale
- the "Boltzmann" distribution
- the Einstein relation
- the relationship between random walk and diffusion equation is analogous to that between Hamiltonian dynamics (classical mechanics) and Liouville's theorem (flow in phase space)

[A Demo of Diffusion]

a drop of ink in water

color ↔ concentration of ink molecules

$c(\underset{\sim}{x}, t)$ (number per unit volume) ← (Sethna uses ρ instead of c)



You can watch an on-line demo "Hot water diffusion" (with sound effects) from a link in the Materials/Media section on coursework. (Unfortunately, this is not a purely diffusive process. We can clearly see convection and gravity playing a role here.)

You can read more about diffusion from many classic books, such as The Mathematics of Diffusion, by John Crank, whose Section 1.1 reads,

> “Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. It is usually illustrated by the classical experiment in which a tall cylindrical vessel has its lower part filled with iodine solution, for example, and a column of clear water is poured on top, carefully and slowly, so that no convection currents are set up.$\cdots$”
>
> “This picture of random molecular motions, in which no molecule has a preferred direction of motion, has to be reconciled with the fact that a transfer of iodine molecules from the region of higher to that of lower concentration is nevertheless observed.$\cdots$”

2 The diffusion equation

Diffusion equation in 1-dimension:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

where D is the diffusion coefficient.

Diffusion equation in 3-dimension:

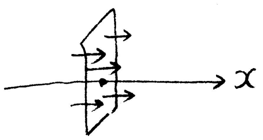
$$\frac{\partial C(\mathbf{x},t)}{\partial t} = D\nabla^2 C(\mathbf{x},t) \equiv D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \tag{2}$$

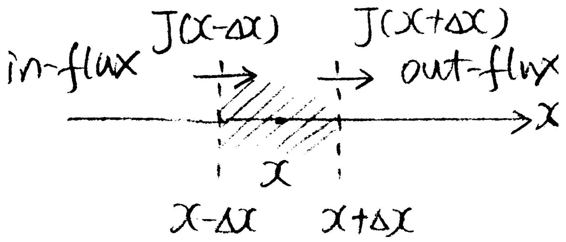
where $\mathbf{x} = (x, y, z)$: position vector in 3-D space.

The diffusion equation is the consequence of two “laws” :

1. **Conservation of Mass**: (no ink molecules are destroyed; they can only move from one place to another.)

   Let $J(x,t)$ be the flux of ink molecules (number per unit area per unit time).





Conservation of mass in 1-D means (equation of continuity):

$$\frac{\partial}{\partial t}C(x,t) = -\frac{\partial}{\partial x}J(x,t) \tag{3}$$

Equation of continuity in 3-D:

$$\frac{\partial}{\partial t}C(x,t) = -\nabla \cdot J(\mathbf{x},t) \equiv -\left(\frac{\partial}{\partial x}J_x + \frac{\partial}{\partial y}J_y + \frac{\partial}{\partial z}J_z\right) \tag{4}$$

Physical interpretation: change of concentration = accumulation due to net influx.

2. **Fick's Law**:
   In 1-D:

$$J(x,t) = -D\frac{\partial}{\partial x}C(x,t) \tag{5}$$

   In 3-D

$$\mathbf{J}(\mathbf{x},t) = -D\nabla C(x,t) = -D\left(\frac{\partial}{\partial x}C, \frac{\partial}{\partial y}C, \frac{\partial}{\partial z}C\right) \tag{6}$$

   Physical interpretation: flux always points in the direction from high concentration to low concentration.

Combining 1 and 2, we get the following partial differential equation (PDE) in 1-D:

$$\frac{\partial}{\partial t}C = -\frac{\partial}{\partial x}J = -\frac{\partial}{\partial x}\left(-D\frac{\partial}{\partial x}C\right) = D\frac{\partial}{\partial x^2}C \tag{7}$$

(if D is a constant).

3 Useful solutions of the diffusion equation

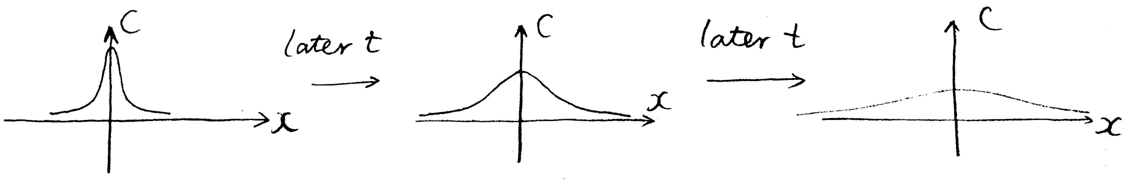
Consider the 1-D diffusion equation

$$\frac{\partial}{\partial t}C = D\frac{\partial^2 C}{\partial x^2}, \tag{8}$$

A useful solution in the infinite domain ($-\infty < x < \infty$) with the initial condition $C(x,0) = \delta(x)$ is

$$C(x,t) = \frac{1}{\sqrt{4\pi Dt}}e^{-\frac{x^2}{4Dt}} \equiv G(x,t) \tag{9}$$

where $G(x,t)$ is the Green function for diffusion equation in the infinite domain. This solution describes the spread of "ink" molecules from a concentrated source.



We can plot this solution as a function of x at different t in Matlab and observe the shape change.

4 Physical origin of the diffusion equation

Q: How can we explain the diffuion equation?

A: Diffusion equation comes from (1) the conservation of mass and (2) Fick's law. Conservation of mass is obvious. But Fick's law is based on empirical observation similar to Fourier's law for heat conduction that "Heat always goes from regions of high temperature to regions of low temperature". So what is the physical origin of Fick's law?

Q: Does the ink molecule know where is the region of low concentration and is smart enough to go there by itself?

A:

Q: Is the diffusion equation a consequence of a particular type of interaction between ink and water molecules?

A: No. The diffusion equation can be used to describe a wide range of material pairs - metals, semiconductors, liquids, $\cdots$ — in which the nature of interatomic interaction is very different from one another.

⇒ **Hypothesis:** The diffusion equation emerges when we consider a large ensemble (i.e. a large collection) of ink molecules, and the diffusion equation is insensitive to the exact nature of their interactions. On the other hand, the value of diffusion coefficient D depends on the nature of interatomic interactions. For example,

- A bigger ink molecule should have smaller D
- Diffusion coefficient of different impurities in silicon can differ by more than 10 orders of magnitude.

Q: How can we test this hypothesis?

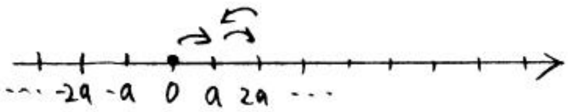
A: We will construct a very simple (toy) model for ink molecules and see whether the diffusion equation jumps out when we consider many ink molecules

— Now, this is the spirit of the statistical mechanics!

5 Random walk model

For simplicity, we will consider a one-dimensional model. First, consider only one ink molecule. Let's specify the rules that it must move.

The random walk model:



Rule 1: The molecule can only occupy positions $x = 0$, ± a, ± 2a,$\cdots$

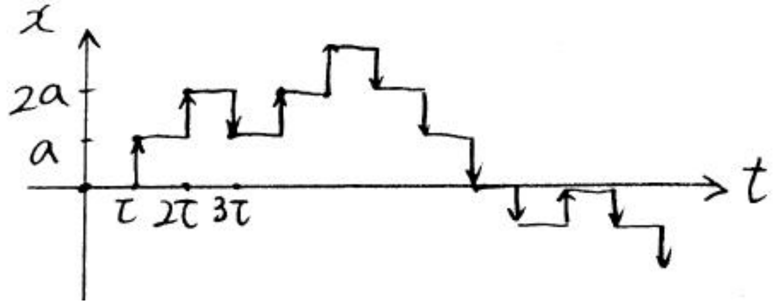
Rule 2: The molecule can only jumps at times $t = \tau$, 2τ,$\cdots$

Rule 3: At each jump, the molecule moves either to the left or to the right with equal probability.

$$x(t+\tau) = \begin{cases} x(t) + a & \text{prob} = \frac{1}{2} \\ x(t) - a & \text{prob} = \frac{1}{2} \end{cases} \tag{10}$$

This model is very different from the "real picture" of an ink molecule being bombarded by water molecules from all directions. In fact, it is more similar to the diffusion of impurity atoms in a crystalline solid. However, since our hypothesis is that "the details should not matter", let's continue on with this simple model.

Trajectory of one random walker:



It is easy to generate a sample trajectory of a random walker.

Suppose the walker starts at $x = 0$ when $t = 0$.

Q: Where is the average position of the walker at a later time t, where $t = n\tau$?

A: $x(t) = x(0) + l_1 + l_2 + l_3 + \ldots + l_n$, where l_i is the jump distance at step i ($i = 1, \ldots, n$)

$$l_i \text{ is a random variable, } \quad l_i = \begin{cases} +a & \text{prob} = \frac{1}{2} \\ -a & \text{prob} = \frac{1}{2} \end{cases} \tag{11}$$

l_i is independent of l_j (for $i \neq j$)
since $x(0) = 0$,

$$\langle x(t) \rangle = \langle \sum_i l_i \rangle = \sum_i \langle l_i \rangle = 0 \tag{12}$$

because $\langle l_i \rangle = (+a) \cdot (\frac{1}{2}) + (-a) \cdot (\frac{1}{2}) = 0$.
On the average, the molecule is not going anywhere!

Q: What is the variance and standard deviation of x(t)?

A: variance:

$$\begin{aligned} \langle x^2(t) \rangle &= \langle (\sum_i l_i)^2 \rangle \\ = \langle \sum_i (l_i^2) + \sum_{i \neq j} (l_i l_j) \rangle &= \sum_i \langle l_i^2 \rangle + \sum_{i \neq j} \langle l_i l_j \rangle \\ \langle l_i^2 \rangle &= (+a)^2 \cdot \frac{1}{2} + (-a)^2 \cdot \frac{1}{2} = a^2 \\ \langle l_i l_j \rangle &= \langle l_i \rangle \langle l_j \rangle = 0 \\ \langle x^2(t) \rangle &= \sum_i \langle l_i^2 \rangle = n a^2 \end{aligned} \tag{13}$$

standard deviation:

$$\sigma_{x(t)} = \sqrt{\langle x^2(t) \rangle} = \sqrt{n} a \tag{14}$$

These are the statements we can make for a single ink molecule.

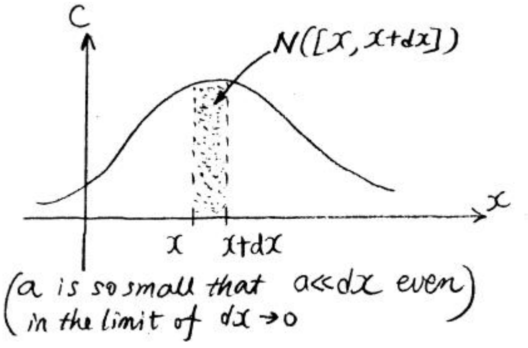
To obtain the diffusion equation, we need to go to the "continuum limit", where we need to consider a large number of ink molecules.

There are so many ink molecules that

(1) in any interval $[x, x + dx]$ where dx is very small, the number of molecules inside is still very large $N([x, x + dx]) \gg 1$

(2) we can define $C(x) \equiv \lim_{dx \to 0} N([x, x + dx])/dx$ as a density function.

(3) $C(x)$ is a smooth function.



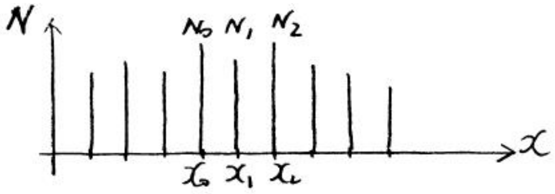
The number of molecules has to be very large for the continuum limit to make sense. This condition is usually satisfied in practice, because the number of molecules in (1 cm^3) is on the order of 10^{23}.

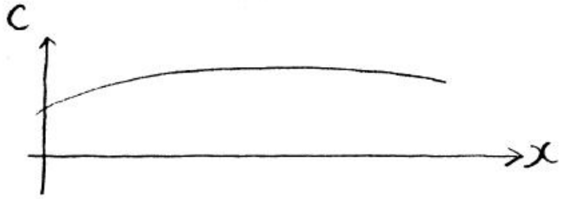
Suppose each ink molecule is just doing independent, “mindless” random walk,

Q: how does the density function evolve with time?

Q: can we derive the equation of motion for $C(x,t)$ based on the random-walk model?

First, we need to establish a “correspondence” between the discrete and continuum variables.





discrete: N_i = number of molecules at $x = x_i = i \cdot a$.

continuum: $C(x)$ = number density at x.

Hence

$$C(x_i) = \frac{\langle N_i \rangle}{a} \tag{15}$$

Notice that average $\langle\rangle$ is required because N_i is a random variable whereas $C(x)$ is a normal variable (no randomness).

6 From random walk to diffusion equation

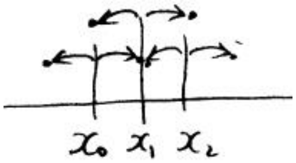
6.1 Method I

At present time, the number of molecules at x_0, x_1, x_2 are N_0, N_1, N_2.

What is the number of molecules at time τ later?

- all molecules originally on x_1 will leave x_1

- on the average, half of molecules on x_0 will jump right to x_1.
- on the average, half of molecules on x_2 will jump left to x_1.

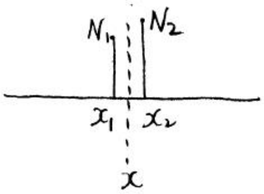


therefore,

$$\begin{aligned}
\langle N_1^{new}\rangle &= \frac{1}{2}\langle N_0\rangle + \frac{1}{2}\langle N_2\rangle \\
\frac{\partial C(x_1)}{\partial t} &= \frac{\langle N_1^{new}\rangle - \langle N_1\rangle}{a\tau} = \frac{1}{2a\tau}(\langle N_0\rangle + \langle N_2\rangle - 2\langle N_1\rangle) \\
&= \frac{1}{2\tau}[C(x_0) + C(x_2) - 2C(x_1)] \\
&= \frac{a^2}{2\tau}\frac{C(x_1 - a) + C(x_1 + a) - 2C(x_1)}{a^2} \qquad (16) \\
\text{in the limit of} a \to 0 & \\
&= \frac{a^2}{2\tau}\frac{\partial^2}{\partial x^2}C(x) \qquad (17) \\
\frac{\partial C}{\partial t} &= D\frac{\partial^2}{\partial x^2}C \qquad (18)
\end{aligned}$$

A brief discussion on the numerical derivative of a function is given in the Appendix.

6.2 Method II



Via Fick's Law, after time τ, on the average half of molecules from x_1 will jump to the right, half of molecules from x_2 will jump to the left. Next flux to the right across the dashed line:

$$\begin{aligned}
J(x) &= \frac{\frac{1}{2}\langle N_1\rangle - \frac{1}{2}\langle N_2\rangle}{\tau} \\
&= \frac{a}{2\tau}[C(x_1) - C(x_2)] \\
&= \frac{a^2}{2\tau}\frac{C(x_1) - C(x_2)}{a}
\end{aligned}$$

$$= -\frac{a^2}{2\tau}\frac{\partial C}{\partial x} \tag{19}$$

in the limit of a → 0

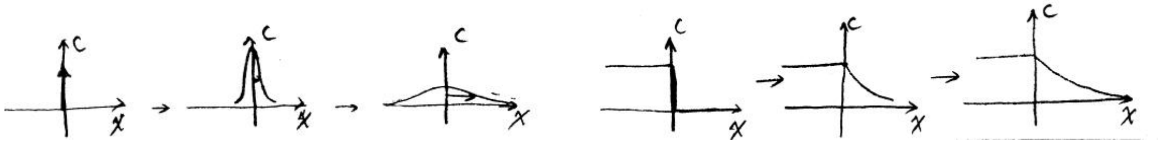
$$J(x) = -D\frac{\partial C}{\partial x} \tag{20}$$

Diffusion equation follows by combining with equation of continuity.

A third way to derive the diffusion equation is given by Sethna (p.20). It is a more formal approach.

7 Two interpretations of the diffusion coefficient D

⇒ Two ways to measure/compute D



(1) Continuum (PDE)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{21}$$

$$\text{solution for} \quad C(x,t) = \frac{N}{\sqrt{4\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right) \tag{22}$$

(2) Discrete (Random Walk)

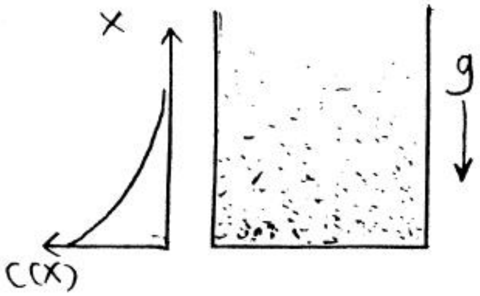
$$X(t) - X(0) = \sum_{i=1}^{n} l_i \tag{23}$$

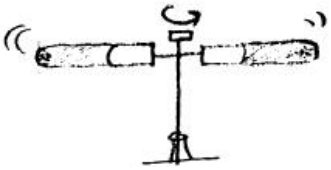
$$\langle X(t) - X(0)\rangle = 0 \tag{24}$$

$$\langle (X(t) - X(0))^2\rangle = \sum_{i=1}^{n}\langle l_i^2\rangle = na^2 = \frac{t}{\tau}a^2 = 2Dt \tag{25}$$

$\langle (X(t) - X(0))^2\rangle$ is called "Mean Square Displacement" (MSD) — a widely used way to compute D from molecular simulations.

8 Diffusion under external potential field





example a: sedimentation of fine sand particles under gravity (or centrifuge) The equilibrium concentration $C_{\text{eq}}(x)$ is not uniform.

example b: why oxygen density is lower on high mountain ⇒ breathing equipment.

Q: Are the molecules staying at their altitude when the equilibrium density is reached?

A:

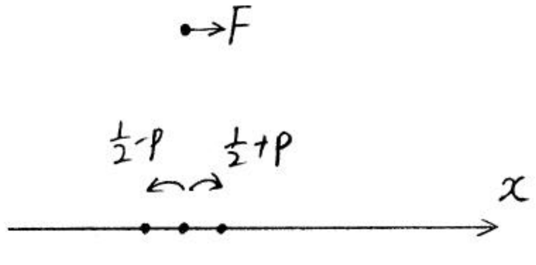
We will

(1) Modify the random-walk-model to model this process at the microscopic scale

(2) Obtain the modified diffusion equation by going to the continuum limit

(3) Make some important "discoveries" as Einstein did in 1905!

(4) Look at the history of Brownian motion and Einstein's original paper (1905) on coursework. (This paper is fun to read!)



Let us assume that the molecule is subjected to a force F.
(in the sedimentation example, $F = -mg$)
that bias the jump toward one direction

$$l_i = \begin{cases} +a & \text{prob} = \frac{1}{2} + p \quad \text{jump to right} \\ -a & \text{prob} = \frac{1}{2} - p \quad \text{jump to left} \end{cases} \tag{26}$$

So the walk is not completely random now.

$$\begin{aligned} \langle X(t) - X(0) \rangle &= \sum_{i=1}^{n} \langle l_i \rangle, \quad \langle l_i \rangle = a(1/2+p) + (-a)(1/2-p) & (27) \\ &= n \cdot 2ap & (28) \\ &= \frac{2ap}{\tau} t & (29) \\ \langle v \rangle &= \frac{2ap}{\tau}, \text{ average velocity of molecule} & (30) \end{aligned}$$

Define mobility $\mu = \frac{\langle v \rangle}{F}$, $\langle v \rangle = \mu F$, which leads

$$\mu = \frac{2ap}{\tau F} \tag{31}$$

or

$$p = \frac{\mu \tau F}{2a} \tag{32}$$

i.e. our bias probability p is linked to the mobility μ and force F on the molecule.

Q: what is the variance of $X(t) - X(0)$?

A:

$$\begin{aligned} V(X(t) - X(0)) &= \langle (X(t) - X(0)^2 \rangle - \langle X(t) - X(0) \rangle^2 & (33) \\ &= \langle (\sum_i l_i)^2 \rangle - (\sum_i \langle l_i \rangle)^2 & (34) \\ &= \langle \sum l_i^2 \rangle + \sum_{i \neq j} \langle l_i l_j \rangle - \sum_i \langle l_i \rangle^2 - \sum_{i \neq j} \langle l_i \rangle \langle l_j \rangle & (35) \end{aligned}$$

but $\langle l_i l_j \rangle = \langle l_i \rangle \langle l_j \rangle$ for $i \neq j$.

$$V(X(t) - X(0)) = \sum_i \langle l_i^2 \rangle - \langle l_i \rangle^2 = \sum_i V(l_i) \tag{36}$$

$$\langle l_i^2 \rangle = a^2(1/2 + p)+) + (-a)^2(1/2 - p) = a^2 \tag{37}$$

$$V(l_i) = \langle l_i^2 \rangle - \langle l_i \rangle^2 = a^2 - (2ap)^2 = a^2(1 - 4p^2) \tag{38}$$

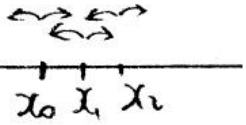
$$V(X(t) - X(0)) = na^2(1 - 4p^2) = \frac{a^2 t}{\tau}(1 - 4p^2) \tag{39}$$

Again, based on the central limit theorem, we expect $X(t) - X(0)$ to satisfy Gaussian distribution with

$$\begin{aligned}
\text{mean} &= \frac{2ap}{\tau} = \mu F t \\
\text{variance} &= \frac{a^2(1 - 4p^2)}{\tau} t \\
&\approx \frac{a^2}{\tau} t \quad (\text{if } p \ll 1) && (40) \\
&= 2Dt \quad \left(\text{define } D = \frac{a^2}{2\tau} \right) && (41) \\
f_x(x,t) &= \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - \mu F t)^2}{4Dt} \right] && (42) \\
C(x,t) &= \frac{N}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - \mu F t)^2}{4Dt} \right] && (43)
\end{aligned}$$

This is the modified diffusion equation.

Derivation of Continuum PDE for $C(x,t)$ from discrete model.



$$\begin{aligned}
\langle N_1^{new} \rangle &= (1/2 + p)\langle N_0 \rangle + (1/2 - p)\langle N_2 \rangle && (44) \\
\frac{\partial C(x_1)}{\partial t} &= \frac{\langle N_1^{new} \rangle - \langle N_1 \rangle}{a\tau} && (45) \\
&= \frac{1}{2a\tau}[(1 + 2p)\langle N_0 \rangle + (1 - 2p)\langle N_2 \rangle - 2\langle N_1 \rangle] && (46) \\
&= \frac{1}{2\tau}[C(x_0) + C(x_2) - 2C(x_1) + 2p(C(x_0) - C(x_2))] && (47) \\
&= \frac{a^2}{2\tau} \frac{C(x_0) + C(x_2) - 2C(x_1)}{a^2} + \frac{2ap}{\tau} \frac{C(x_0) - C(x_2)}{2a} && (48) \\
&= \frac{a^2}{2\tau} C''(x_1) - \frac{2ap}{\tau} C'(x_1) && (49)
\end{aligned}$$

Notice: $\frac{a^2}{2\tau} = D$, $\frac{2ap}{\tau} = \mu F$. Finally, we obtain the following PDE for $C(x,t)$,

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2}{\partial x^2}C(x,t) - \mu F\frac{\partial}{\partial x}C(x,t) \tag{50}$$

First term in the right hand side corresponds to diffusion, while second term corresponds to drift.

We can rewrite the equation into:

(1) mass conservation: $\frac{\partial C(x,t)}{\partial t} = -\frac{\partial}{\partial x}J(x,t)$

(2) Fick's law: $J(x,t) = -D\frac{\partial}{\partial x}C(x,t) + \mu F C(x,t)$

Molecules are constantly at motion even at equilibrium. Diffusional and drift flows balance each others to give zero flux J.

The above discussion can be further generalized to let external force F be non-uniform, but depend on x.

We may assume that $F(x)$ is the negative gradient of a potential function $\phi(x)$, such that

$$F(x) = -\frac{\partial \phi(x)}{\partial x} \tag{51}$$

The variation of F is smooth at the macroscopic scale. We will ignore the difference of F at neighboring microscopic sites, i.e. $F(x_0) \approx F(x_1) \approx F(x_2)$.

$$J(x,t) = -D\frac{\partial}{\partial x}C(x,t) + \mu F(x)C(x,t) \tag{52}$$

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2}{\partial x^2}C(x,t) - \mu\frac{\partial}{\partial x}[F(x)C(x,t)] \tag{53}$$

9 Einstein's relation

At equilibrium, we expect net flux to be zero.

$$C(x,t) = C_{\text{eq}}(x), \quad J(x) = 0 = -D\frac{\partial}{\partial x}C_{eq}(x) + \mu F(x)C_{eq}(x) \tag{54}$$

$$\frac{\partial}{\partial x}C_{eq}(x) = \frac{\mu F(x)}{D}C_{eq}(x) = -\frac{\mu}{D}\frac{\partial \phi(x)}{\partial x}C_{eq}(x) \tag{55}$$

Solution: $C_{\text{eq}}(x) = A\,\mathrm{e}^{-\frac{\mu\phi(x)}{D}}$ where A is normalization constant giving $\int_{-\infty}^{+\infty} C_{eq}(x) = N$. Compare with Boltzman's distribution $C_{\text{eq}}(x) = A\,\mathrm{e}^{-\frac{\phi(x)}{k_B T}}$ where T is absolute temperature and k_B is Boltzmann constant. This leads to Einstein's relation

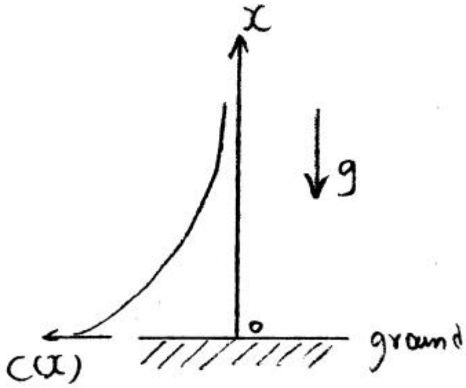
$$\mu = \frac{D}{k_B T} \tag{56}$$

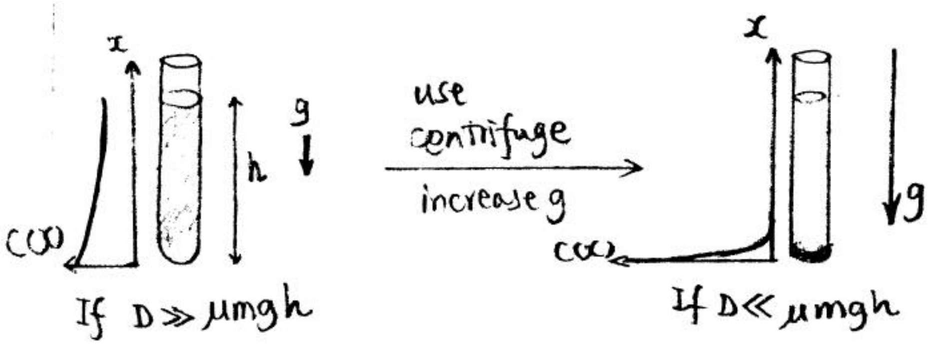
Interpretation of equilibrium distribution

$$C_{eq}(x) = Ae^{-\frac{\mu}{D}\phi(x)} = Ae^{-\frac{1}{k_B T}\phi(x)} \tag{57}$$

Example: under gravitational field $\phi(x) = mgx$, the number density will be

$$C_{eq}(x) = Ae^{-\frac{\mu mgx}{D}} = Ae^{-\frac{mgx}{k_B T}} \tag{58}$$





μ, D, T can be measured by 3 different kinds of experiments.

Einstein's relation $\mu = \frac{D}{k_B T}$ says that they are not independent. μ, the response of a system to external stimulus and D, the spontaneous fluctuation of the system without external stimulus are related to each other. ⇒ More details on the relations will be dealt with by the Fluctuation-Dissipation Theorem.

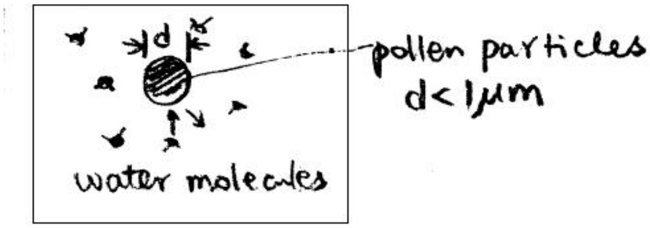
History and Significance of Einstein's Relation

3 Landmark papers published by Einstein in 1905 as a clerk in a patent office in Bern, Switzerland

- special theory of relativity
- photoelectric effect (Nobel Prize 1921)
- Brownian motion ($\mu = \frac{D}{k_B T}$)

History of Brownian Motion

- 1827 British Botanist Robert Brown: Using light microscope, he noticed pollen grains suspended in water perform a chaotic and endless dance



- It took many years before it was realized that Brownian motion reconcile an apparent paradox between thermodynamics (irreversible) and Newtonian mechanics (reversible). Einstein played a key role in this understanding (1905)
- Einstein's work allowed Jean Perrir and others to prove the physical reality of molecules and atoms.
- "We see the existence of invisible molecules ($d < 1$ nm) through their effects on the visible pollen particles ($d < 1\mu$m)."
- Einstein laid the ground work for precision measurements to reveal the reality of atoms.

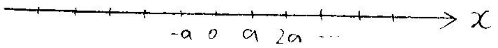
10 Random walk model exercise

ME346A | Random Walk | Cai

Reading Assignment: Reif §1.1-1.4, 1.7, 1.9

Diffusion equation $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$ —— continuum

Random walk model —— discrete



$x(0)=0$ $\qquad$ $x(t+\tau) = \begin{cases} x(t)+a & \text{prob} = \frac{1}{2} \\ x(t)-a & \text{prob} = \frac{1}{2} \end{cases}$

Q: what are the possible values of .

$x(\tau) = \begin{cases} a & \frac{1}{2} \\ -a & \frac{1}{2} \end{cases}$ prob, $\quad x(2\tau) = \{$ prob, $\quad x(3\tau) = \{$ prob

$x(n\tau) = \{$

$x(n\tau) = l_1 + l_2 + l_3 + \cdots + l_n$ $\qquad$ $l_i = \begin{cases} a & \text{prob} = \frac{1}{2} \\ -a & \text{prob} = \frac{1}{2} \end{cases}$

↑ random number $\qquad$ ↑ random number

$P(l_i = a) = \frac{1}{2}, \qquad P(l_i = -a) = \frac{1}{2}$

average value (mean) of l_i: $\langle l_i \rangle = a \cdot P(l_i = a) + (-a)\cdot P(l_i = -a)$

$= \frac{a}{2} + \frac{-a}{2} = 0$

Q: average value of l_i^2: $\langle l_i^2 \rangle =$

Q: average value of l_i^3: $\langle l_i^3 \rangle =$

Q: averge value of l_i^n: $\langle l_i^n \rangle =$

Fact: if X and Y are two random variables (may or may not be independent)
then $\langle X+Y \rangle = \langle X \rangle + \langle Y \rangle$.

Q: $\langle l_i + l_j \rangle =$ ______________

$\langle x(n\tau) \rangle =$ ______________________

Q: what is the average value of $l_i l_j$? $(i \neq j)$

4 possibilities

$l_i = a$	$l_j = a$	prob =	$l_i l_j =$
$l_i = a$	$l_j = -a$	prob =	$l_i l_j =$
$l_i = -a$	$l_j = a$	prob =	$l_i l_j =$
$l_i = -a$	$l_j = -a$	prob =	$l_i l_j =$

$\langle l_i l_j \rangle =$ ______________ $i \neq j$

Fact: if X and Y are <u>independent</u> random variables
then $\langle XY \rangle = \langle X \rangle \langle Y \rangle$

$\langle l_i l_j \rangle = \langle l_i \rangle \langle l_j \rangle =$ ________ $i \neq j$

Q: what is $\langle l_i l_j \rangle$ when $i = j$?

$\langle l_i l_j \rangle =$ ____________

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$

Q. what is $\langle x^2(n\tau) \rangle = \langle (l_1 + l_2 + \cdots + l_n)^2 \rangle$?

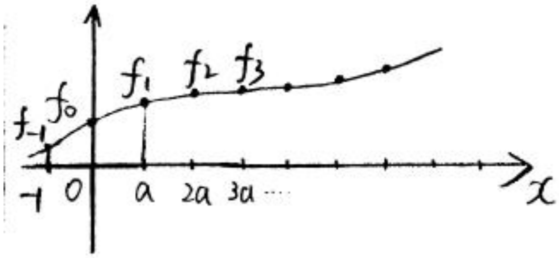
variance: $\langle x^2(n\tau) \rangle - \langle x(n\tau) \rangle^2 =$ ________________

Standard deviation. $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} =$ ________________

A Numerical derivatives of a function $f(x)$

We discretize a continuous function $f(x)$ by storing its value on a discrete set of points.

$f_i = f(x_i)$, $x_i = i \cdot a$, a is the grid spacing.



There are several ways to compute $f'(x)$ at some point x.

(1) $f'_0 = \frac{f_1 - f_0}{a}$ $f'_0 \cong f'(x=0)$

(2) $f'_0 = \frac{f_1 - f_{-1}}{a}$ $f'_0 \cong f'(x=0)$

(3) $f'_{1/2} = \frac{f_1 - f_0}{a}$ $f'_{1/2} \cong f'(x=\frac{a}{2})$

$f'_{-1/2} = \frac{f_0 - f_{-1}}{a}$ $f'_{-1/2} \cong f'(x=-\frac{a}{2})$

Notice that Scheme (1) is not centered (bigger error) schemes (2) and (3) are centered (smaller error, preferred).

By the same approach, we can approximate $f''(x)$ by centered difference.

$$f''_0 = \frac{f'_{1/2} - f'_{-1/2}}{a} = \frac{\frac{f_1 - f_0}{a} - \frac{f_0 - f_{-1}}{a}}{a} = \frac{f_1 + f_{-1} - 2f_0}{a^2} \tag{59}$$

$$f''_0 = f''(x=0) \tag{60}$$

This topic will be discussed in detail in ME300B (CME204) "Partial Differential Equations".

References

1. The Mathematics of Diffusion, John Crank, 2nd Ed., Clarendon Press, Oxford, 1975. (You can read Section 1.1 *The Diffusion Process* from Google books.)
2. Fundamentals of statistical and thermal physics, F. Reif, McGraw-Hill, 1976. § 1.1-1.4, § 1.7, § 1.9.
3. Statistical Mechanics: Entropy, Order Parameters and Complexity, J. P. Sethna, Clarendon Press, Oxford, 2008. § 2.1-2.3.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 3. Probability

January 7, 2011

Contents

Statistical mechanics is an inherently probabilistic description of the system. Familiarity with manipulations of probability is an important prerequisite – M. Kadar, "Statistical Mechanics of Particles".

1 Definitions

The Sample Space Ω is the set of all logically possible outcomes from same experiment $\Omega = \{w_1, w_2, w_3, \cdots\}$ where w_i is referred to each sample point or outcome.

The outcomes can be discrete as in a dice throw

$$\Omega = \{1, 2, 3, 4, 5, 6\} \tag{1}$$

or continuous

$$\Omega = \{-\infty < x < +\infty\} \tag{2}$$

An Event E is any subset of outcomes $E \subseteq \Omega$ (For example, $E = \{w_1, w_2\}$ means outcome is either w_1 or w_2) and is assigned a probability $p(E)$, [1] e.g. $p_{dice}(\{1\}) = \frac{1}{6}$, $p_{dice}(\{1, 3\}) = \frac{1}{3}$.

The Probabilities must satisfy the following conditions:

i) Positivity $p(E) \geq 0$

ii) Additivity $p(A \text{ or } B) = p(A) + p(B)$ if A and B are disconnected events.

iii) Normalization $p(\Omega) = 1$

Example 1.

Equally likely probability function p defined on a finite sample space

$$\Omega = \{w_1, w_2, \cdots, w_N\} \tag{3}$$

assigns the same probability

$$p(w_i) = \frac{1}{N} \tag{4}$$

to each sample point.[2]

When $E = \{w_1, w_2, \cdots, w_k\}$ (interpretation: the outcome is any one from $w_1, \cdots, w_k$), then $p(E) = k/N$.

---

[1] p is called a probability measure (or probability function). It is a mapping from a set E to real numbers between 0 and 1.

[2] This is an important assumption in the statistical mechanics, as we will see in the micromechanical ensemble.

Example 2.

Consider a party with 40 people in a ball room. Suddenly one guy declares that there are at least two people in this room with the same birthday. Do you think he is crazy? Would you bet money with him that he is wrong?

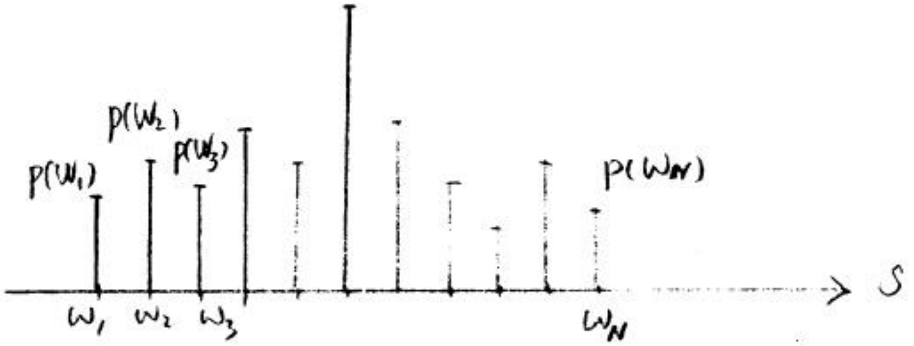
2 Interpretations of probability

Frequency interpretation of probability

When an experiment is repeated n times, with n a very large numbers, we expect the relative frequency with which event E occurs to be approximately equal to $p(E)$.

$$\lim_{n\to\infty} \frac{\text{number of occurrence of event } E}{n} = p(E) \tag{5}$$

The probability function on discrete sample space can be visualized by 'stem-plots'. $\Omega = \{\omega_1, \omega_2, \cdots, \omega_N\}$, $\sum_{i=1}^{N} p(\omega_i) = 1$.



Two possible approaches to assign probability values:

Objective Probabilities

Perform a lot of experiments, record the number of times event E is observed N_E.

$$p_E = \lim_{n \to \infty} \frac{N_E}{N} \tag{6}$$

Subjective Probabilities

Theoretical estimate based on the uncertainty related to lack of precise knowledge of outcomes (e.g. dice throw).

- all assignment of probability in statistical mechanics is subjectively based (e.g. uniform distribution if no information is available)
- information theory interpretation of Entropy
- whether or not the theoretical estimate is correct can be checked by comparing its prescriptions on macroscopic properties such as thermodynamical quantities with experiments. (Isn't this true for all science?)
- theoretical estimate of probability may need to be modified if more information become available

Example 3. Binomial distribution

Let X denote the number of heads in n tosses of a coin. Each toss has probability p for heads. Then the probability function of X is

$$p(X = x) = C_n^x \, p^x \, (1-p)^{n-x} \tag{7}$$

where $C_n^x = \binom{n}{x} = \frac{n!}{x!(n-x)!}$. C_n^k is called the number of combinations of k objects taken from n objects. For example, consider a set $S = \{a, b, c\}$ (n=3). There are 3 ways to take 2 objects ($K = 2$) from S.

$$\{a, b\}, \ \{b, c\}, \ \{a, c\} \tag{8}$$

In fact, $C_3^2 = \frac{3!}{2!(3-2)!} = 3$.

Example 4. Random walk

Consider a random walker that jumps either to the left or to the right, with equal probability, after every unit of time.

$$X(n+1) = \begin{cases} X(n)+1, & \text{prob} = 1/2 \\ X(n)-1, & \text{prob} = 1/2 \end{cases} \tag{9}$$

What is the probability $p(X(n)=x)$ that after n steps the random walker arrives at x?

3 Probability rules

1) Additive rule: If A and B are two events, then

$$p(A \cup B) = p(A) + p(B) - p(A \cap B) \tag{10}$$

($A \cup B$ means A or B, $A \cap B$ means A and B.)

2) If A and B are mutually exclusive (disconnected), then

$$p(A \cup B) = p(A) + p(B) \tag{11}$$

(Mutually exclusive means $A \cap B = \phi$, where ϕ is the empty set. $p(\phi) = 0$.)

3) Conditional probability: The conditional probability of B, given A is defined as,

$$p(B|A) = \frac{p(A \cap B)}{p(A)} \quad \text{provided} \quad p(A) > 0 \tag{12}$$

4) Events A and B are **independent** if

$$p(B|A) = p(B) \tag{13}$$

5) Multiplicative rule:

$$p(A \cap B) = p(B|A)\,p(A) \tag{14}$$

6) If two events A and B are independent, then

$$p(A \cap B) = p(A)\,p(B) \tag{15}$$

Example 5. Dice throw.

The sample space of a dice throw is $\Omega = \{1, 2, 3, 4, 5, 6\}$.

The event of getting an even number is $A =$ ________________. $p(A) =$ ________________.

The event of getting an odd number is $B =$ ________________. $p(B) =$ ________________.

The event of getting a prime number is $C =$ ________________. $p(C) =$ ________________.

The event of getting a number greater than 4 is $D =$ ________________. $p(D) =$ ________________.

The probability of getting a prime number given that the number is even is

$$p(C|A) = \underline{\hspace{4cm}} \tag{16}$$

The probability of getting a prime number given that the number is greater than 4

$$p(C|D) = \underline{\hspace{4cm}} \tag{17}$$

The probability of getting a number greater than 4 given that the number is a prime number is

$$p(D|C) = \underline{\hspace{4cm}} \tag{18}$$

4 Discrete random variable

For example: X could be the number of heads observed in throwing a coin 3 times. The event $\{X = x\}$ has a probability $p(X = x)$, which is also written as $f_X(x)$, and is called probability mass function.

The Expected Value of a random variable X is

$$\langle X \rangle = \sum_x x\, p(X = x) = \sum_x x\, f_X(x) \tag{19}$$

The k-th Moment of random variable X is

$$\mu_k = \langle X^k \rangle \tag{20}$$

The Variance of random variable X is

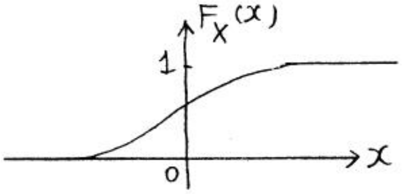
$$V(X) = \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2 = \mu_2 - (\mu_1)^2 \tag{21}$$

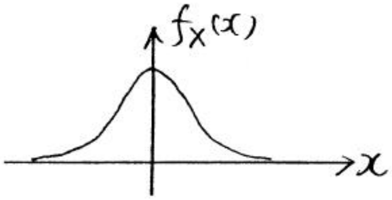
The Standard Deviation is defined as

$$\sigma(X) = \sqrt{V(X)} \tag{22}$$

5 Continuous random variable

The event $\{X \leq x\}$ has probability $p(X \leq x) = F_X(x)$, which is called cumulative probability function (CPF).





The event $\{x_1 \leq X \leq x_2\}$ has probability $F_X(x_2) - F_X(x_1)$. $f_X(t) = \frac{dF_X(x)}{dx}$ (if it exists) is called the probability density function (PDF).

In the limit of $\delta x \to 0$, the event $\{x \leq X \leq x + \delta x\}$ has probability $f_X(x) \cdot \delta x$. (We will omit X in the following.)

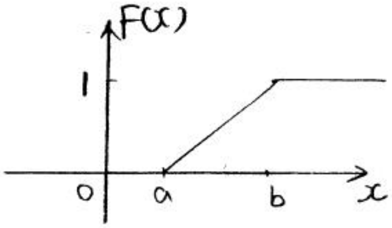
Obviously,

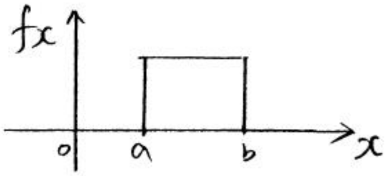
$$\lim_{x \to -\infty} F(x) = 0 \tag{23}$$

$$\lim_{x \to +\infty} F(x) = 1 \tag{24}$$

$$\int_{-\infty}^{+\infty} f(x)\, dx = 1 \quad \text{(normalization)} \tag{25}$$

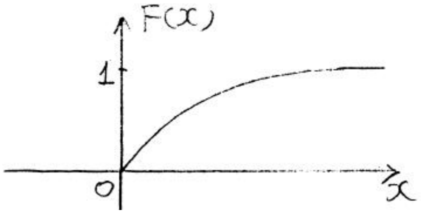
Example 6. Uniform distribution on interval $[a, b]$

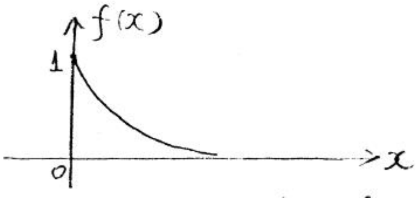




$$f(x) = \begin{cases} \frac{1}{b-a} & a < x < b \\ 0 & \text{elsewhere} \end{cases} \tag{26}$$

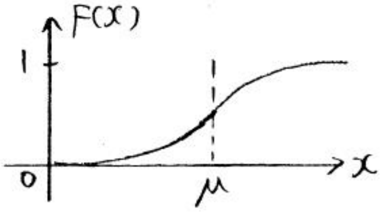
Example 7. Exponential distribution

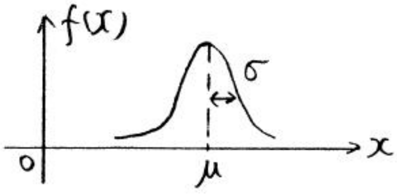




$$f(x) = \begin{cases} \lambda\, e^{-\lambda x} & 0 < x < \infty \\ 0 & x < 0 \end{cases} \tag{27}$$

Example 8. Gaussian distribution





$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(X-\mu)^2}{2\sigma^2}\right]. \tag{28}$$

6 Multivariate probability distributions

If random variables X and Y are independent, then

$p(X = x, Y = y) = p(X = x) \cdot p(Y = y)$ for discrete case, and

$f_{XY}(x, y) = f_X(x) \cdot f_Y(y)$ for continuum case.

Additive Rule

$$\langle aX + bY \rangle = a\langle X \rangle + b\langle Y \rangle \tag{29}$$

This rule is satisfied regardless of whether or not X, Y are independent.

Covariance

$$\begin{aligned} \mathrm{Cov}(X, Y) &= \langle (X - \mu_X)(Y - \mu_Y) \rangle = \langle XY \rangle - \mu_X \mu_Y && (30) \\ \mathrm{Cov}(X, X) &= V(X) && (31) \end{aligned}$$

If X and Y are independent, then $\langle XY \rangle = \langle X \rangle \langle Y \rangle \rightarrow$ If X and Y are independent, then $\mathrm{Cov}(X, Y) = 0$.

Correlation function is defined by $\rho(X, Y) = \frac{\mathrm{Cov}(X,Y)}{\sigma_X \sigma_Y}$ and $-1 \leq \rho(X, Y) \leq 1$.

Example 9. Average of n independent random variables $X_1, X_2, \cdots, X_N$ with identical distributions (i.i.d.) is

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

Suppose $\langle X_i \rangle = \mu$ and $V(X_i) = \sigma^2$, then

$$\langle \overline{X} \rangle = \mu$$

$$V(X) = \frac{\sigma^2}{n}$$

and the standard deviation of the average is

$$\sigma(\overline{X}) = \sqrt{V(X)} = \frac{\sigma}{\sqrt{n}}$$

7 Useful theorems

Central Limit Theorem (CLT)

Let $X_1, X_2, \cdots, X_n$ be a random sample from an arbitrary distribution with mean μ and variance σ^2. Then for n sufficiently large, the distribution of the average $\overline{X}$ is approximately a Gaussian distribution with mean μ and standard deviation $\sigma(\overline{X}) = \frac{\sigma}{\sqrt{n}}$.

Stirling's Formula

$$\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N) + O\left(\frac{1}{N}\right) \tag{32}$$

or

$$N! \approx \sqrt{2\pi N} \left(\frac{N}{e}\right)^N \qquad \text{for large N} \tag{33}$$

For a numerical verification of Stirling's formula, visit `http://micro.stanford.edu/∼caiwei/Download/factorial.php`. In this page we compute $N!$ to arbitrary precision (using unlimited number of digits to represent an integer) and then compute its logarithm, and compare it with Stirling's formula.

References

1. M. Kadar, "Statistical Mechanics of Particles", Cambridge University Press (2007). Chapter 2.

2. W. Rosenkrantz, "Introduction to Probability and Statistics for Scientists and Engineers", McGraw-Hill (1997).

3. R. Walpole, Rj. H. Myers, S. L. Myers and K. Ye, "Probability and Statistics for Engineers and Scientists", 3rd ed., Pearson Prentice Hall, 2007.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 4. Classical Mechanics

January 19, 2011

Contents

(The task of Statistical Mechanics

What we have done	What we will do next
Einstein's relation	Fluctuation-dissipation theorem
$\mu = \frac{D}{K_B T}$	$(\Delta E)^2 = K_B T^2 C_V$ (handout 8)
Diffusion equation (with drift)	Thermodynamics
$\frac{\partial}{\partial t} C(x,t) = \frac{\partial}{\partial x}\left(D(x)\frac{\partial}{\partial x} C\right) - \mu \frac{\partial}{\partial x}(F(x) \cdot C)$	$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}, \cdots$ (handout 6)
↑	↑
Random walk (with bias)	Classical mechanics
$x(t+\tau) = x(t) + \begin{cases} +a & prob = \frac{1}{2}+p \\ -a & prob = \frac{1}{2}-p \end{cases}$	$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$

In this lecture, we will discuss

1. Hamilton's equation of motion

   ↓

2. System's trajectory as flow in phase space

   ↓

3. Ensemble of points flow in phase space as an incompressible fluid

   ↓

4. Evolution equation for density function in phase space (Liouville's Theorem)

The path from *Hamilton's equation of motion* to *density evolution in phase space* is analogous to the path we took from the *random walk model* to *diffusion equation.*

Reading Assignment

- Landau and Lifshitz, Mechanics, Chapters 1, 2 and 7

Reading Assignment:

1 Lagrangian and Hamiltonian

In statistical mechanics, we usually consider a system of a large collection of particles (e.g. gas molecules) as the model for a macroscopic system (e.g. a gas tank).

The equation of motion of these particles are accurately described by classical mechanics, which is, basically,

$$\mathbf{F} = m\,\mathbf{a} \tag{1}$$

In principle, we can use classical mechanics to follow the exact trajectories of these particles, (just as we can follow the trajectories fo planets and stars) which becomes the method of Molecular Dynamics, if you use a computer to solve the equation of motion numerically.

In this section, we review the fundamental "machinery" (math) of classical mechanics. We will discuss

- Hamiltonian and Lagrangian formulations of equation of motion.
- Legendre transform that links Lagrangian ↔ Hamiltonian. We will use Legendre transformation again in both thermodynamics and statistical mechanics, as well as in classical mechanics.
- The conserved quantities and other symmetries in the classical equation of motion. They form the basis of the statistical assumption.

1.1 Notation

Consider a system of N particles whose positions are $(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = (q_1, q_2, \cdots, q_{3N})$, where $\mathbf{r}_1 = (q_1, q_2, q_3), \mathbf{r}_2 = (q_4, q_5, q_6), \cdots$.

The dynamics of the system is completely specified by trajectories, $q_i(t)$, $i = 1, 2, \cdots, 3N$.

The velocities are: $v_i = \dot{q}_i \equiv \frac{dq}{dt}$.

The accelerations are: $a_i = \ddot{q}_i \equiv \frac{d^2q}{dt^2}$

For simplicity, assume all particles have the same mass m. The interaction between particles is described by a potential function $U(q_1, \cdots, q_{3N})$ (such as the gravitation potential between planets and stars).

The equation of motion for the system was given by Newton:

$$F_i = m a_i \tag{2}$$

where $F_i = -\partial U / \partial q_i$ and $a_i \equiv \ddot{q}_i$, which leads to

$$\ddot{q}_i = -\frac{1}{m}\frac{\partial U}{\partial q_i} \qquad i = 1, \cdots, 3N \tag{3}$$

The trajectory can be solved from the above ordinary differential equation (ODE) given the initial condition $q_i(t=0)$, $\dot{q}_i(t=0)$, $i = 1, \cdots, 3N$.

All these should look familiar and straightforward. But we can also write into more "odd-looking" ways in terms of Hamiltonian and Lagrangian. But why? Why create more work for ourselves?

Reasons for Hamiltonian/Lagrangian of classical Mechanics:

1. Give you something to brag about after you have learned it. (Though I have to admit that the formulation is beautiful and personally appealing.)
2. Hamiltonian formulation connects well with Quantum Mechanics.
3. Lagrangian formulation connects well with Optics.
4. Provides the language to discuss conserved quantities and symmetries in phase space. i.e. the symplectic form (and symplectic integrators in molecular simulations).
5. Allows derivation of equation of motion when q_i's are not cartesian coordinates.

1.2 Lagrangian formulation

At the most fundamental level of classical mechanics is the Lagrangian Formulation.

Lagrangian is a function of q_i (position) and $\dot{q}_i$ (velocity), and is kinetic energy K minus potential energy U.

$$L(\{q_i\}, \{\dot{q}_i\}) = K - U \tag{4}$$

when q_i's are cartesian coordinates of particles,

$$L(\{q_i\}, \{\dot{q}_i\}) = \sum_{i=1}^{3N} \frac{1}{2} m \dot{q}_i^2 - U(\{q_i\}) \tag{5}$$

Lagrange's equation of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \left(\frac{\partial L}{\partial q_i}\right) = 0 \quad \text{for every } i = 1, \cdots, 3N \tag{6}$$

Equivalence between Lagrange's equation of motion and Newton's can be shown by

$$\begin{aligned} \frac{\partial L}{\partial \dot{q}_i} &= m\dot{q}_i \equiv p_i && (7) \\ \frac{\partial L}{\partial q_i} &= -\frac{\partial U}{\partial q_i} && (8) \\ \frac{d}{dt}(m\dot{q}_i) - \left(-\frac{\partial U}{\partial q_i}\right) &= 0 && (9) \\ \Rightarrow \quad \ddot{q}_i &= -\frac{1}{m}\frac{\partial U}{\partial q_i} && (10) \end{aligned}$$

Note that L is a function of q_i and $\dot{q}_i$. This means that

$$dL = \sum_i \frac{\partial L}{\partial q_i} dq_i + \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i$$

How does L change with time?

$$\begin{aligned} \frac{dL}{dt} &= \sum_i \frac{\partial L}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial L}{\partial \dot{q}_i}\frac{d\dot{q}_i}{dt} \\ &= \sum_i \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)\dot{q}_i + \frac{\partial L}{\partial \dot{q}_i}\frac{d}{dt}\left(\dot{q}_i\right) \\ &= \frac{d}{dt}\sum_i \frac{\partial L}{\partial \dot{q}_i}\dot{q}_i \qquad (11) \end{aligned}$$

Hence L is not a conserved quantity, but

$$\frac{d}{dt}\left(\sum_i \frac{\partial L}{\partial \dot{q}_i}\dot{q}_i - L\right) = 0 \qquad (12)$$

In other words,

$$H = \sum_i \frac{\partial L}{\partial \dot{q}_i}\,\dot{q}_i - L \qquad (13)$$

is a conserved quantity, i.e.

$$\frac{dH}{dt} = 0 \qquad (14)$$

1.3 Legendre transform

The above expression can be rewritten (simplified) using the definition of momentum

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i} \qquad (15)$$

Using the Lagrange's equation of motion

$$\frac{\partial L}{\partial q_i} = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = \frac{d}{dt}p_i = \dot{p}_i \qquad (16)$$

we have

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i} \qquad (17)$$

$$\dot{p}_i \equiv \frac{\partial L}{\partial q_i} \qquad (18)$$

Using the new variable p_i, the change of Lagrangian L can be expressed as,

$$\begin{aligned} dL &= \sum_i \frac{\partial L}{\partial q_i} dq_i + \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i = \sum_i \dot{p}_i dq_i + p_i d\dot{q}_i & (19) \\ \frac{dL}{dt} &= \sum_i \dot{p}_i \frac{dq_i}{dt} + p_i \frac{d\dot{q}_i}{dt} = \sum_i \frac{dp_i}{dt}\dot{q}_i + p_i \frac{d\dot{q}_i}{dt} \\ &= \frac{d}{dt}\left(\sum_i p_i \dot{q}_i\right) & (20) \end{aligned}$$

$$\frac{d}{dt}(\sum_i p_i \dot{q}_i - L) = 0 \tag{21}$$

Hence $H = \sum_i p_i \dot{q}_i - L$ is a conserved quantity.

The transformation from L to H is a Legendre transform.

Notice what happened when going from L to H:

1. $L(\{q_i\}, \{\dot{q}_i\}) \Rightarrow L$ is a function of q_i and $\dot{q}_i$.
2. $p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$
3. $H \equiv \sum_i p_i \dot{q}_i - L$

We notice that $dH = \sum_i -\dot{p}_i dq_i + \dot{q}_i dp_i$, which means H is a function of q_i and p_i, no longer a function of q_i and $\dot{q}_i$. This is an important property of the Legendre transform.

Example 1.

To help illustrate the point, we can perform Legendre transform on a one-dimensional function $f(x)$. Notice that

$$df = \frac{\partial f}{\partial x} dx \tag{22}$$

Define $p \equiv \partial f/\partial x$, then $df = p\,dx$. The Legendre transform of $f(x)$ is $g(p) = p\,x - f$. Notice that,

$$dg = p\,dx + x\,dp - p\,dx = x\,dp \tag{23}$$

This means that g is a function of p and $x = \partial g/\partial p$.

Find the Legendre transform of $f(x) = x^3$.

1.4 Hamiltonian formulation

Because H is a function of q_i and p_i, (i.e., we will treat q_i and p_i as independent variables when discussing H).

We expect

$$dH = \sum_i \frac{\partial H}{\partial q_i} dq_i + \frac{\partial H}{\partial \dot{q}_i} d\dot{q}_i \tag{24}$$

Comparing with the previous equation ($dH = \sum_i -\dot{p}_i dq_i + \dot{q}_i dp_i$), we get the

Hamilton's equation of motion

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{25}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \tag{26}$$

$*$ In principle, classical mechanics can also be formulated, starting from a Hamiltonian $H(\{q_i\},\{p_i\})$ and the Lagrangian L can be obtained from Legendre transform. But it is conceptually easier to start with $L(q_i,\dot{q}_i) = K - U$. It is easy to make mistakes when trying to identify the correct (q_i, p_i) pair when q_i is not a Cartesian coordinate.

Example 2.

When q_i is the Cartesian coordinate of particles,

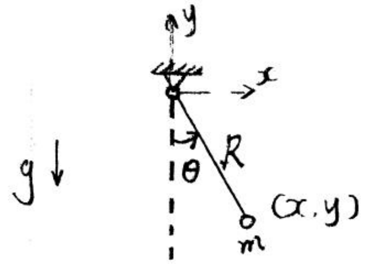
$$\begin{aligned}
L(\{q_i\},\{\dot{q}_i\}) &= \sum_i \frac{1}{2} m \dot{q}_i{}^2 - U(\{q_i\}) && (27)\\
p_i &= \frac{\partial L}{\partial \dot{q}_i} = m\dot{q}_i && (28)\\
H &= \sum_i p_i \dot{q}_i - L = \sum_i m\dot{q}_i{}^2 - \frac{1}{2} m \dot{q}_i{}^2 + U(\{q_i\}) \\
&= \sum_i \frac{1}{2} m \dot{q}_i{}^2 + U(\{q_i\}) \\
&= \sum_i \frac{p_i^2}{2m} + U(\{q_i\}) && (29)\\
H &= K + U && (30)
\end{aligned}$$

where K, U correspond to kinetic energy and potential energy, respectively.

$dH/dt = 0$ means conservation of energy.

Example 3. Pendulum (motion in 2D)

Consider a mass m attached to rigid rode of length R.



The coordinate (x, y) must satisfy the constraint $\sqrt{x^2+y^2} = R$. If we write the equation in terms of x, y then, we need to worry about the constraint. Alternatively, we can deal with a single variable θ and forget about the constraint. Then what is the equation of motion in terms of θ? This is when the Lagrangian formulation becomes handy.

Here are the 4 steps to derive the equation of motion for a generalized (i.e. non-cartesian) coordinate. (The direction of y-axis is opposite to that of Landau and Lifshitz "Mechanics", p.11.)

1. Write down $L(\theta, \dot{\theta}) = K - U$.

$$\begin{aligned} K &= \frac{1}{2}m(\dot{x}^2+\dot{y}^2) \\ &= \frac{1}{2}m(R^2\cos^2\theta + R^2\sin^2\theta)\dot{\theta}^2 \\ &= \frac{1}{2}mR^2\dot{\theta}^2 && (31) \\ U &= mgy = -mgR\,\cos\theta && (32) \end{aligned}$$

$$\Rightarrow \quad L(\theta, \dot{\theta}) = \frac{1}{2}mR^2\dot{\theta}^2 + mgR\cos\theta \tag{33}$$

2. Write down Lagrangian equation of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) - \frac{\partial L}{\partial \theta} = 0 \tag{34}$$

$$\frac{\partial L}{\partial \dot{\theta}} = mR^2\dot{\theta}\,, \quad \frac{\partial L}{\partial \theta} = -mgR\sin\theta \tag{35}$$

$$\frac{d}{dt}(mR^2\dot{\theta}) + mgR\sin\theta = 0 \tag{36}$$

$$\Rightarrow \quad \ddot{\theta} = -\frac{g}{R}\sin\theta \tag{37}$$

3. Find Hamiltonian by Legendre transformation, starting with the momentum

$$p_\theta \equiv \frac{\partial L}{\partial \dot\theta} = mR^2\dot\theta \tag{38}$$

Notice that $p_\theta \neq mR\dot\theta$, as might have been guessed naively. This is why it's always a good idea to start from the Lagrangian.

The Hamiltonian is

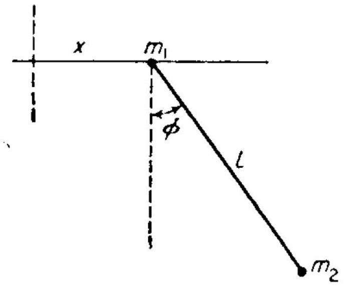
$$\begin{aligned} H &= p_\theta\dot\theta - L \\ &= mR^2\dot\theta^2 - \frac{1}{2}mR^2\dot\theta^2 - mgR\cos\theta \\ &= \frac{1}{2}mR^2\dot\theta^2 - mgR\cos\theta & (39) \\ H(\theta, p_\theta) &= \frac{p_\theta^2}{2mR^2} - mgR\cos\theta & (40) \end{aligned}$$

4. Double check by writing down Hamiltonian's equation of motion

$$\dot{p_\theta} = -\frac{\partial H}{\partial \theta} \quad \dot\theta = \frac{\partial H}{\partial p_\theta} \tag{41}$$

Example 4. Pendulum with moving support (from Landau & Lifshitz, p.11)

Write down the Lagrangian for the following system. A simple pendulum of mass m_2, with a mass m_1 at the point of support which can move on a horizontal line lying in the plane in which m_2 moves.



2 Phase space

The instantaneous state of a system of N particles is completely specified by a $6N$-dimensional vector,

$$\boldsymbol{\mu} = (q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N})$$

Given $\boldsymbol{\mu}(0)$ (initial condition), the entire trajectory $\boldsymbol{\mu}(t)$ is completely specified by Hamiltonian's equation of motion.

$$\left[\begin{array}{l} \dot{q}_i = \frac{\partial H}{\partial p_i} \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} \end{array}\right] \quad \Longleftrightarrow \quad \dot{\boldsymbol{\mu}} = \left[\begin{array}{cc} 0 & I_{3N\times 3N} \\ -I_{3N\times 3N} & 0 \end{array}\right] \frac{\partial H}{\partial \boldsymbol{\mu}} \quad \text{(in matrix form)} \tag{42}$$

Equation of motion in phase space can be written as

$$\dot{\boldsymbol{\mu}} = \omega \, \frac{\partial H}{\partial \boldsymbol{\mu}} \tag{43}$$

where

$$\omega \equiv \left[\begin{array}{cc} 0 & I_{3N\times 3N} \\ -I_{3N\times 3N} & 0 \end{array}\right] \tag{44}$$

This seems deceivingly simple.

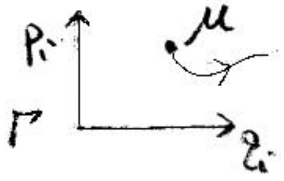
The trajectories of all N-particles are equivalent to the motion of a point ($\boldsymbol{\mu}(t)$) in $6N$-dimensional space, which is called the <u>phase space</u> (Γ).

$*$ The $3N$-dimensional space of all the positions q_i is called the <u>configurational space</u>.

A system of N particles

$\{q_i\}$, $\{p_i\}$, $i = 1, 2, \cdots, 3N$.

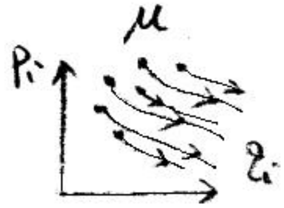
$\Longleftrightarrow$



An ensemble of systems,

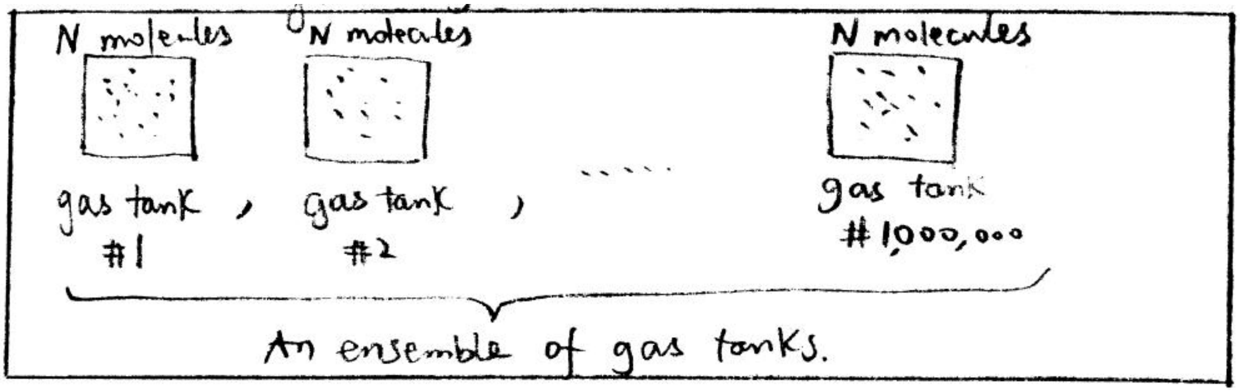
each containing N particles.

$\Longleftrightarrow$



How do we imagine "an ensemble of systems, each consisting a large number N of particles"?

Let's say each system is a gas tank containing $N = 10^9$ particles. Now imagine 10^6 gas tanks $\rightarrow$ that's 10^{15} particles.

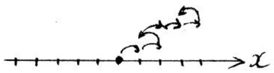
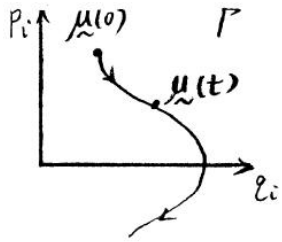
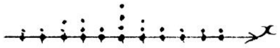
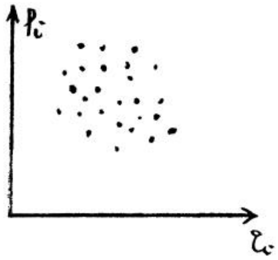


1. That's a lot of molecules to think about!

   Fortunately, the 1,000,000 gas tanks only exist in our imagination (which has ∞ capacity). We do not need to really create 1,000,000 gas tanks and do experiments on them to test the predictions of statistical mechanics .

2. Ok, so the other 999,999 gas tanks are not real. That's great, because I only have one gas tank in my lab. But why do I need to even imagine those "ghost" gas tanks?

   – They form the concept of "microcanonical" ensemble from which all laws of thermodynamics can be derived. The price we pay is to imagine many-many gas tanks — I'd say it's a good deal!

	From Random Walk to Diffusion Equation	From Classical Mechanics to Thermodynamics
Step 1	 one particle jump on a lattice (random)	 one point move in $6N$-dimensional phase space (deterministic)
Step 2	 many independent particles (random walkers) on a lattice – an ensemble of random walkers – so many that a density function $C(x)$ makes sense	 many copies of the system (gas tanks) corresponding to many points in the $6N$-dimensional phase space – an ensemble of gas tanks – so many that a density function $\rho(\{q_i\},\{p_i\})$ in Γ make sense
Step 3	$X(t) = X(0) + \sum_i l_i$ going to the continuum limit → Diffusion equation $\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$ PDE for $C(x,t)$	$\dot{\boldsymbol{\mu}} = \omega \frac{\partial H}{\partial \boldsymbol{\mu}}$ going to the continuum limit → Liouville's theorem $\frac{d\rho}{dt} \equiv D\frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i}\dot{q}_i + \sum_i \frac{\partial \rho}{\partial p_i}\dot{p}_i = 0$ PDE for $\rho(\{q_i\},\{p_i\},t)$ (incompressible flow in Γ)

3 Liouville's theorem

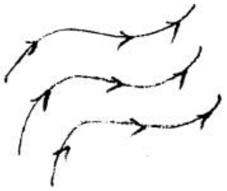
Liouville's theorem states that the phase space density $\rho(\boldsymbol{\mu}, t)$ behaves like an incompressible fluid.

So, after going to the continuum limit, instead of the diffusion equation, we get an equation in fluid mechanics.

How can we prove it?

3.1 Flow of incompressible fluid in 3D

Let's first familiarize ourselves with the equations in fluid mechanics. Imagine a fluid consisting of a large number of particles with density $\rho(\mathbf{x}, t) \equiv \rho(x, y, z, t)$. Imagine that the particles follow a deterministic (no diffusion) flow field $\mathbf{v}(\mathbf{x})$, i.e. $v_x(x, y, z)$, $v_y(x, y, z)$, $v_z(x, y, z)$ (velocity of the particle only depends on their current location). This tells us how to follow the trajectory of one particle.



How do we obtain the equation for $\rho(\mathbf{x}, t)$ from the flow field $\mathbf{v}(\mathbf{x})$?

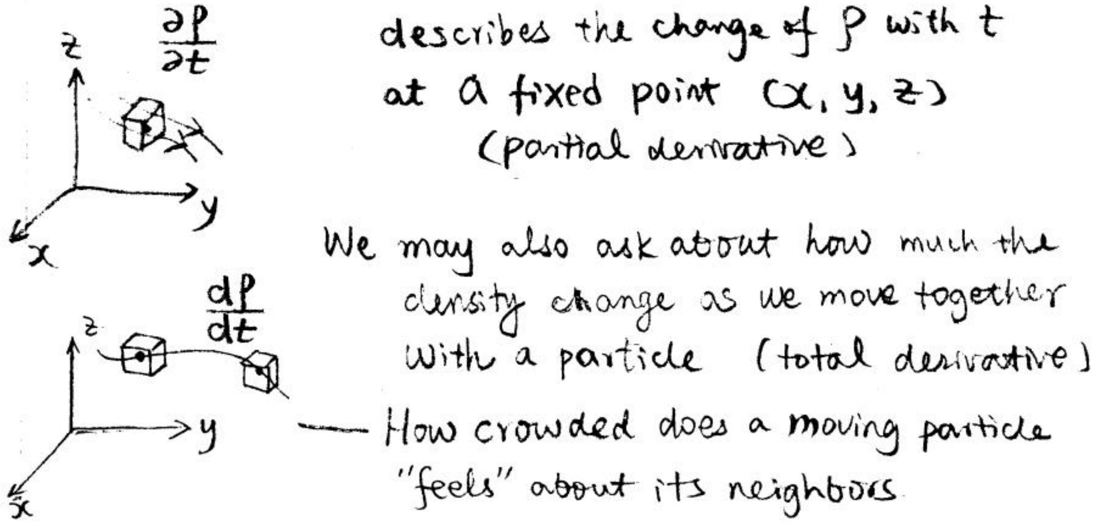
1. mass conservation (equation of continuity)

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} = -\boldsymbol{\nabla} \cdot \mathbf{J} = -\left(\frac{\partial}{\partial x} J_x + \frac{\partial}{\partial y} J_y + \frac{\partial}{\partial z} J_z\right). \tag{45}$$

2. flux for deterministic flow $\mathbf{J}(\mathbf{x}) = \rho(\mathbf{x})\, \mathbf{v}(\mathbf{x})$

$$\begin{aligned}\frac{\partial \rho(\mathbf{x}, t)}{\partial t} &= -\boldsymbol{\nabla} \cdot (\rho(\mathbf{x})\, \mathbf{v}(\mathbf{x})) \\ &= -\left[\frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z)\right] \\ &= -\left[\left(\frac{\partial}{\partial x}\rho\right) v_x + \left(\frac{\partial}{\partial y}\rho\right) v_y + \left(\frac{\partial}{\partial z}\rho\right) v_z\right] + \\ &\quad \left[\rho\left(\frac{\partial}{\partial x} v_x\right) + \rho\left(\frac{\partial}{\partial y} v_y\right) + \rho\left(\frac{\partial}{\partial z} v_z\right)\right] \qquad (46) \\ \frac{\partial \rho}{\partial t} &= -(\boldsymbol{\nabla}\rho) \cdot \mathbf{v} - \rho\, (\boldsymbol{\nabla} \cdot \mathbf{v}) \qquad (47)\end{aligned}$$

$\partial\rho(x,y,z,t)/\partial t$ describes the change of ρ with it at a fixed point (x,y,z).



describes the change of ρ with t at a fixed point (x, y, z) (partial derivative)

We may also ask about how much the density change as we move together with a particle (total derivative)

— How crowded does a moving particle "feels" about its neighbors.

We may also ask about how much the density changes as we move together with a particle, i.e., or how crowded a moving particle "feels" about its neighborhood. This is measured by the <u>total derivative</u>,

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + (\boldsymbol{\nabla}\rho)\cdot\mathbf{v} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x}v_x + \frac{\partial \rho}{\partial y}v_y + \frac{\partial \rho}{\partial z}v_z \tag{48}$$

Hence the density evolution equation can also be expressed as

$$\frac{d\rho}{dt} = -\rho\,(\boldsymbol{\nabla}\cdot\mathbf{v}) \tag{49}$$

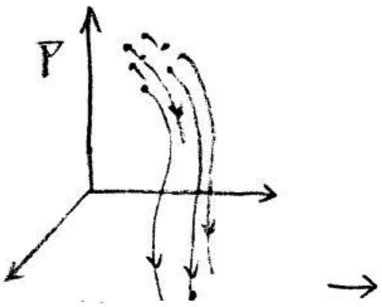
For incompressible flow,

$$\frac{d\rho}{dt} = 0\,, \quad \boldsymbol{\nabla}\cdot\mathbf{v} = 0 \tag{50}$$

a particle always feels the same level of "crowdedness".

3.2 Flow in phase space

Why do we say the collective trajectories of an ensemble of points following Hamiltonian dynamics can be described by incompressible flow in phase space?



each point
follow a
deterministic
trajectory $\underset{\sim}{\mu}(t)$

all points considered together
follows incompressible flow.

a point always find same # of
neighbors per unit volume as it moves
ahead with time.

All points considered together follows incompressible flow. A point always find the same numbers of neighbors per unit volume as it moves ahead with time.

real flow in 3D	flow in $6N$-D phase space
x, y, z	$q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N}$
$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$	$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \cdots, \frac{\partial}{\partial q_{3N}}, \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \cdots, \frac{\partial}{\partial p_{3N}}\right)$
$\mathbf{v} = (\dot{x}, \dot{y}, \dot{z})$	$\mathbf{v} = (\dot{q}_1, \dot{q}_2, \cdots, \dot{q}_{3N}, \dot{p}_1, \dot{p}_2, \cdots, \dot{p}_{3N})$
$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla}(\rho\mathbf{v})$ $= -(\boldsymbol{\nabla}\rho)\mathbf{v} - \rho(\boldsymbol{\nabla}\cdot\mathbf{v})$	$\frac{\partial \rho}{\partial t} = -\left[\sum_{i=1}^{3N} \frac{\partial}{\partial q_i}(\rho\dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\dot{p}_i)\right]$ $= -\left[\sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] - \left[\sum_{i=1}^{3N} \rho\frac{\partial \dot{q}_i}{\partial q_i} + \rho\frac{\partial \dot{p}_i}{\partial p_i}\right]$
$\frac{d\rho}{dt} \equiv= \frac{\partial \rho}{\partial t} + (\boldsymbol{\nabla}\rho)\cdot\mathbf{v} = -\rho(\boldsymbol{\nabla}\cdot\mathbf{v})$	$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i = -\rho\left[\sum_{i=1}^{3N} \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right]$
flow is incompressible if $\boldsymbol{\nabla}\cdot\mathbf{v} = 0$	flow is incompressible if $\sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$ (is this true?)

Proof of Liouville's theorem $(d\rho/dt = 0)$

Start from Hamilton's equation of motion

$$\begin{aligned} \dot{q}_i = \frac{\partial H}{\partial p_i} \qquad &\rightarrow \quad \frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial p_i \partial q_i} &(51)\\ \dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad &\rightarrow \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial q_i} &(52)\\ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \quad &= \quad \frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0 &(53) \end{aligned}$$

Therefore, we obtain

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i}\,\dot{q}_i + \frac{\partial \rho}{\partial p_i}\,\dot{p}_i = 0 \tag{54}$$

which is Liouville's theorem.

Using Liouville's theorem, the equation of evolution for the density function $\rho(\{q_i\}, \{p_i\}, t)$ can be written as

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\sum_i \left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i \right) \\ &= -\sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right) \end{aligned} \tag{55}$$

This can be written concisely using Poisson's bracket,

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\} \tag{56}$$

Poisson's bracket

$$\{A, B\} \equiv \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i} \right) \tag{57}$$

Obviously, $\{A, B\} = -\{B, A\}$ and $\{A, A\} = 0$.

Not so obviously, $\{A, A^2\} = 0$, and $\{A, B\} = 0$ if B is a function of A, i.e. $B = f(A)$.

4 Ensemble

An ensemble is a large number of points in the phase space that can be described by a density function $\rho(\{q_i\},\{p_i\})$.

$\rho(\{q_i\},\{p_i\})$ is like a probability density function (PDF) — the probability of picking any particular point out of the entire ensemble.

Now, consider an arbitrary function $A(\{q_i\},\{p_i\})$ which takes different value at different points in phase space, such as the kinetic energy

$$E_{\text{kin}} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

What is the average value for A among all these points?

The ensemble average can be written as

$$\langle A \rangle \equiv \int_\Gamma \prod_{i=1}^{3N} dq_i\, dp_i\, A(\{q_i\},\{p_i\})\, \rho(\{q_i\},\{p_i\}) \tag{58}$$

This is same as expectation value if we interpret $\rho(\{q_i\},\{p_i\})$ as PDF.

Notice that $A(\{q_i\},\{p_i\})$ is not an explicit function of time. It is a function defined on the phase space. But the ensemble average will depend on time t if ρ evolves with time.

$$\langle A \rangle(t) \equiv \int_\Gamma \prod_{i=1}^{3N} dq_i\, dp_i\, A(\{q_i\},\{p_i\})\, \rho(\{q_i\},\{p_i\},t) \tag{59}$$

How does the ensemble average evolve with time?

$$\begin{aligned}
\frac{d\langle A \rangle(t)}{dt} &\equiv \int_\Gamma \prod_{i=1}^{3N} dq_i dp_i A(\{q_i\},\{p_i\}) \frac{\partial}{\partial t}\rho(\{q_i\},\{p_i\},t) \\
&= \int_\Gamma \prod_{i=1}^{3N} dq_i dp_i A(\{q_i\},\{p_i\}) \sum_{j=1}^{3N} \left(\frac{\partial \rho}{\partial p_j}\frac{\partial H}{\partial q_j} - \frac{\partial \rho}{\partial q_j}\frac{\partial H}{\partial p_j} \right) \\
&= -\int_\Gamma \prod_{i=1}^{3N} dq_i dp_i \sum_{j=1}^{3N} \left(\frac{\partial A}{\partial p_j}\frac{\partial H}{\partial q_j} - \frac{\partial A}{\partial q_j}\frac{\partial H}{\partial p_j} \right) \cdot \rho(\{q_i\},\{p_i\},t) \\
&= \int_\Gamma \prod_{i=1}^{3N} dq_i dp_i \{A, H\} \cdot \rho(\{q_i\},\{p_i\},t) && (60) \\
\frac{d\langle A \rangle}{dt} &= \langle \{A, H\} \rangle && (61)
\end{aligned}$$

(Very similar equation appears in quantum mechanics!)

For example, average total energy among all points in the ensemble

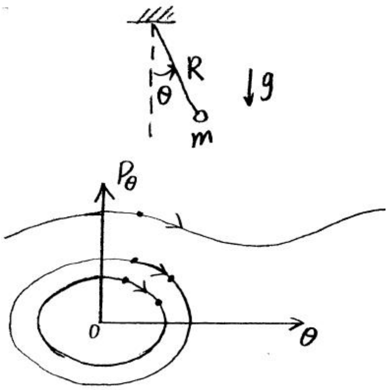
$$E_{\text{tot}} \equiv \langle H \rangle \tag{62}$$

$$\frac{dE_{tot}}{dt} = \frac{d\langle H \rangle}{dt} = \langle \{H, H\} \rangle = 0 \tag{63}$$

This is an obvious result, because the total energy of each point is conserved as they move through the phase space. As a result, the average total energy also stays constant.

Example 5. Pendulum with Hamiltonian

$$H(\theta, p_\theta) = \frac{p_\theta^2}{2mR^2} + mgR\cos\theta$$



Phase space is only 2-dimensional (θ, p_θ).

Equilibrium motion of one point in phase space is

$$\dot{\theta} = \frac{\partial H}{\partial p_\theta} \quad \dot{p_\theta} = -\frac{\partial H}{\partial \theta} \tag{64}$$

Now consider a large number of points in the (θ, p_θ) space. $p(\theta, p_\theta, t)$ describes their density distribution at time t.

What is the evolution equation for ρ?

$$\begin{aligned} \frac{\partial p(\theta, p_\theta, t)}{\partial t} &= -\frac{\partial \rho}{\partial \theta}\dot{\theta} - \frac{\partial \rho}{\partial p_\theta}\dot{p_\theta} \\ &= -\frac{\partial \rho}{\partial \theta}\frac{\partial H}{\partial p_\theta} + \frac{\partial \rho}{\partial p_\theta}\frac{\partial H}{\partial \theta} \equiv -\{\rho, H\} \end{aligned} \tag{65}$$

From $\frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{mR^2}$, $\frac{\partial H}{\partial \theta} = -mgR\sin\theta$

$$\Rightarrow \frac{\partial \rho}{\partial t} = -\frac{\partial \rho}{\partial \theta}\frac{p_\theta}{mR^2} - \frac{\partial \rho}{\partial p_\theta} mgR\sin\theta \tag{66}$$

Suppose $A = \theta^2$, the ensemble average of A is

$$\langle A \rangle = \int d\theta dp_\theta \, \theta^2 \, \rho(\theta, p_\theta, t) \tag{67}$$

How does $\langle A \rangle$ changes with time?

$$\frac{d\langle A \rangle}{dt} = \langle \{A, H\} \rangle \tag{68}$$

$$\{A, H\} = \frac{\partial \theta^2}{\partial \theta}\frac{\partial H}{\partial p_\theta} - \frac{\partial \theta^2}{\partial p_\theta}\frac{\partial H}{\partial \theta} = 2\theta(-mgR\sin\theta) \tag{69}$$

$$\Rightarrow \frac{d\langle A \rangle}{dt} = \frac{d\langle \theta^2 \rangle}{dt} = -2mgR \, \langle \theta \sin\theta \rangle \tag{70}$$

Example 6. Consider an ensemble of pendulums described in Example 5. At $t = 0$, the density distribution in the ensemble is,

$$\rho(\theta, p_\theta, t = 0) = \frac{1}{2\pi}\frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{p_\theta^2}{2\sigma^2}\right] \tag{71}$$

where $-\pi \le \theta < \pi$, $-\infty < p_\theta < \infty$.

(a) Verify that $\rho(\theta, p_\theta, t = 0)$ is properly normalized.

(b) What is $\partial\rho/\partial t|_{t=0}$? Mark regions in phase space where $\partial\rho/\partial t|_{t=0} > 0$ and regions where $\partial\rho/\partial t|_{t=0} < 0$.

(c) How can we change $\rho(\theta, p_\theta, t = 0)$ to make $\partial\rho/\partial t = 0$?

5 Summary

By the end of this lecture, you should:

- be able to derive the equations of motion of a mechanical system by constructing a Lagrangian, and obtain the Hamitonian through Legendre transform. (This is important for Molecular Simulations.)
- agree with me that the flow of an ensemble of points in phase space, each following the Hamilton's equation of motion, is the flow of an incompressible fluid.
- be able to write down the relation between partial derivative and total derivative of $\rho(\{q_i\}, \{p_i\}, t)$.
- be able to write down the equation of Liovielle's theorem (close book, of course).
- be able to express the ensemble average of any quantity as an integral over phase space, and to write down the time evolution of the ensemble average (be ware of the minus sign!)

The material in this lecture forms (part of) the foundation of statistical mechanics.

As an introductory course, we will spend more time on how to use statistical mechanics.

A full appreciation of the foundation itself will only come gradually with experience.

Nonetheless, I think an exposure to the theoretical foundation from the very beginning is a good idea.

References

1. Landau and Lifshitz, Mechanics, 3rd. ed., Elsevier, 1976. Chapter I, II, VII.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 5. Microcanonical Ensemble

January 19, 2011

Contents

The purpose of this lecture is

1. To justify the "uniform" probability assumption in the microcanonical ensemble.
2. To derive the momentum distribution of one particle in an ideal gas (in a container).
3. To obtain the entropy expression in microcanonical ensemble, using ideal gas as an example.

Reading Assignment: Sethna § 3.1, § 3.2.

1 Properties of flow in phase space

1.1 Trajectories in phase space

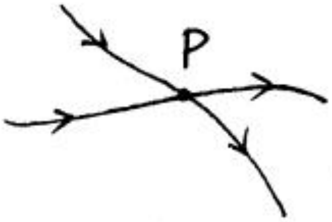
Q: What can we say about the trajectories in phase space based on classical mechanics?

A:

1. Flow line (trajectory) is completely deterministic

$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} \end{cases} \tag{1}$$

   Hence two trajectories <u>never cross</u> in phase space.



   This should <u>never</u> happen, otherwise the flow direction of point P is not determined.

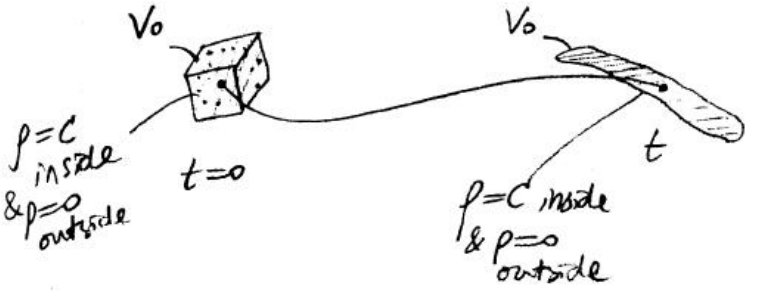
2. Liouville's theorem

$$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \tag{2}$$

   So there are <u>no attractors</u> in phase space.

This should <u>never</u> happen, otherwise $d\rho/dt > 0$. Attractor is the place where many trajectories will converge to. The local density will increase as a set of trajectories converge to an attractor.

3. Consider a little "cube" in phase space. (You can imagine many copies of the system with very similar initial conditions. The cube is formed all the points representing the initial conditions in phase space.) Let the initial density of the points in the cube be uniformly distributed. This can be represented by a density field $\rho(\boldsymbol{\mu}, t = 0)$ that is uniform inside the cube and zero outside.



As every point inside the cube flows to a different location at a later time, the cube is transformed to a different shape at a different location.

Due to Liouville's theorem, the density ρ remain $\rho = c$ (the same constant) inside the new shape and $\rho = 0$ outside. Hence the volume of the new shape remains constant (V_0).

1.2 One trajectory over long time

Q: Can a trajectory from on point $\boldsymbol{\mu}_1$ in phase space always reach any other point $\boldsymbol{\mu}_2$, given sufficiently long time?

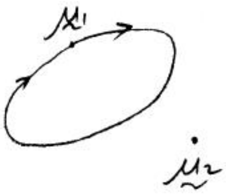
A: We can imagine the following possibilities:

1. We know that the Hamiltonian H (total energy) is conserved along a trajectory.

   So, there is no hope for a trajectory to link $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ if $H(\boldsymbol{\mu}_1) \neq H(\boldsymbol{\mu}_2)$.

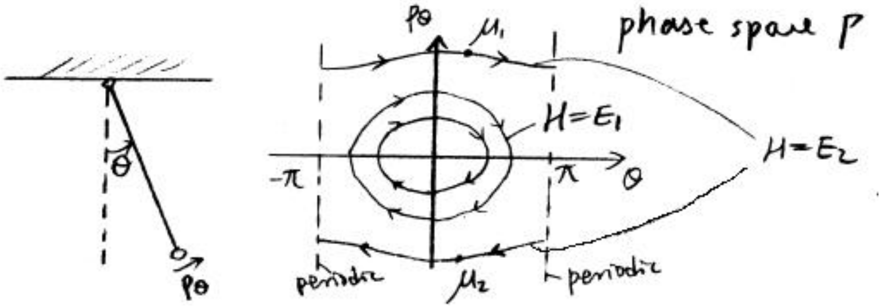
   Hence, in the following discussion we will assume $H(\boldsymbol{\mu}_1) = H(\boldsymbol{\mu}_2)$, i.e. $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ lie on the same constant energy surface: $H(\boldsymbol{\mu}) = E$. This is a $(6N-1)$-dimensional hyper-surface in the $6N$-dimensional phase space.

2. The trajectory may form a loop. Then the trajectory will never reach $\boldsymbol{\mu}_2$ if $\boldsymbol{\mu}_2$ is not in the loop.

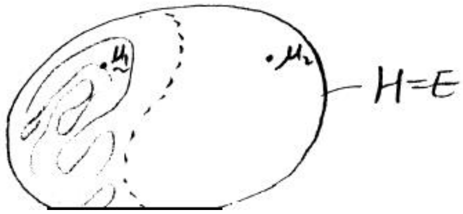


3. The constant energy surface may break into several disjoint regions. If $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are in different regions, a trajectory originated from $\boldsymbol{\mu}_1$ will never reach $\boldsymbol{\mu}_2$.

   Example: pendulum



4. Suppose the trajectory does not form a loop and the constant energy surface is one continuous surface. The constant energy surface may still separate into regions where trajectories originated from one region never visit the other region.



— This type of system is called non-ergodic.

5. If <u>**none**</u> of the above (1-4) is happening, the system is called <u>Ergodic</u>. In an ergodic system, we still cannot guarantee that a trajectory starting from $\boldsymbol{\mu}_1$ will exactly go through any other part $\boldsymbol{\mu}_2$ in phase space. (This is because the dimension of the phase space is so high, hence there are too many points in the phase space. One trajectory, no matter how long, is a one-dimensional object, and can "get lost" in the phase space, i.e. not "dense enough" to sample all points in the phase space.)

   But the trajectory can get <u>arbitrarily close</u> to $\boldsymbol{\mu}_2$.

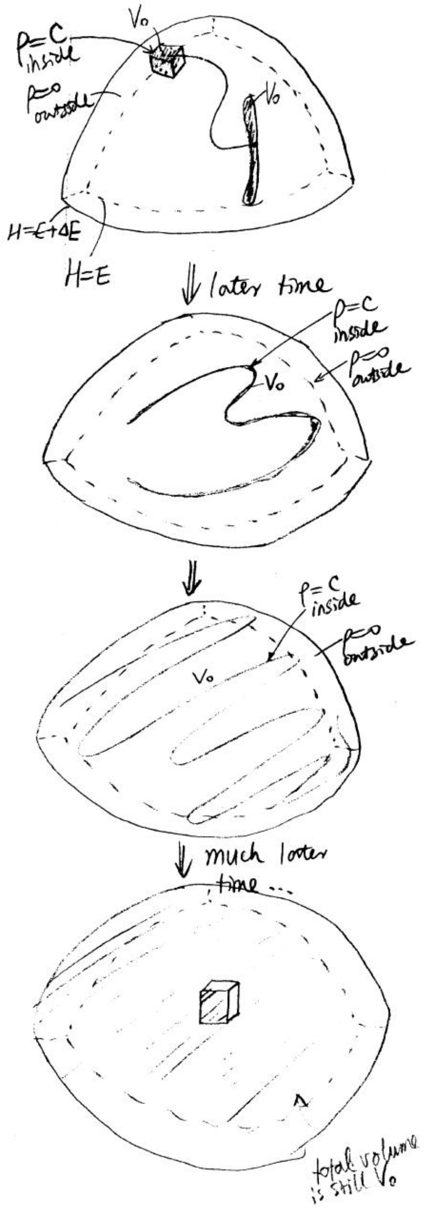
   "At time t_1, the trajectory can pass by the neighborhood of $\boldsymbol{\mu}_2$. At a later time t_2, the trajectory passes by $\boldsymbol{\mu}_2$ at an even smaller distance..."

   After a sufficiently long time, a single trajectory will visit <u>the neighborhood of every point</u> in the constant energy surface.

   — This is the property of an <u>ergodic</u> system. Ergodicity is ultimately an assumption, because mathematically it is very difficult to prove that a given system (specified by its Hamiltonian) is ergodic.

1.3 An ensemble of points flowing in phase space

Now imagine a small cube (page 1) contained between two constant-energy surfaces $H = E$, $H = E + \Delta E$.



As all points in the cube flows in phase space. The cube transforms into a different shape but its volume remains V_0.

The trajectories of many non-linear systems with many degrees of freedom is chaotic, i.e. two trajectories with very similar initial conditions will diverge exponentially with time.

Q. How can the volume V_0 remain constant while all points in the original cube will have to be very far apart from each other as time increases?

A: The shape of V_0 will become very complex, e.g. it may consists of many thin fibers distributed almost every where between the two constant energy surface.

At a very late time t, $\rho(\boldsymbol{\mu}, t)$ still has the form of

$$\rho(\boldsymbol{\mu}, t) = \begin{cases} C & \boldsymbol{\mu} \in V_0 \\ 0 & \boldsymbol{\mu} \notin V_0 \end{cases} \qquad (3)$$

except that the shape of V_0 is distributed almost every where between constant energy surface.

A density function $\rho(\boldsymbol{\mu}, t)$ corresponds to an ensemble of points in phase space. Suppose we have a function $A(\boldsymbol{\mu})$ defined in phase space. (In the pendulum example, we have considered $A = \theta^2$.)

The average of function $A(\boldsymbol{\mu})$ over all points in the ensemble is called the <u>ensemble average</u>.

If ρ changes with time, then the ensemble average is time dependent

$$\langle A \rangle(t) \equiv \int d^{6N}\boldsymbol{\mu}\, A(\boldsymbol{\mu})\, \rho(\boldsymbol{\mu}, t) \tag{4}$$

From experience, we know that many system will reach an equilibrium state if left alone for a long time. Hence we expect the following limit to exist:

$$\lim_{t\to\infty} \langle A \rangle(t) = \langle A \rangle_{\mathrm{eq}} \tag{5}$$

$\langle A \rangle_{\mathrm{eq}}$ is the "equilibrium" ensemble average.

Q: Does this mean that

$$\lim_{t\to\infty} \rho(\boldsymbol{\mu}, t) = \rho_{eq}(\boldsymbol{\mu})? \tag{6}$$

No. In previous example, no matter how large t is,

$$\rho(\boldsymbol{\mu}, t) = \begin{cases} C & \boldsymbol{\mu} \in V_0 \\ 0 & \boldsymbol{\mu} \notin V_0 \end{cases} \tag{7}$$

The only thing that changes with t is the shape of V_0. The shape continues to transform with time, becoming thinner and thinner but visiting the neighborhood of more and more points in phase space.

So, $\lim_{t\to\infty} \rho(\boldsymbol{\mu}, t)$ **DOES NOT EXIST!**

What's going on?

2 Microcanonical Ensemble

2.1 Uniform density assumption

In Statistical Mechanics, an ensemble (microcanonical ensemble, canonical ensemble, grand canonical ensemble, ...) usually refers to an <u>equilibrium</u> density distribution $\rho_{eq}(\boldsymbol{\mu})$ that does not change with time.

The macroscopically measurable quantities is <u>assumed</u> to be an ensemble average over $\rho_{eq}(\boldsymbol{\mu})$.

$$\langle A \rangle_{\mathrm{eq}} \equiv \int d^{6N}\boldsymbol{\mu}\, A(\boldsymbol{\mu})\, \rho_{\mathrm{eq}}(\boldsymbol{\mu}) \tag{8}$$

In the <u>microcanonical ensemble</u>, we assume $\rho_{\rm eq}$ to be uniform inside the entire region between the two constant energy surfaces, i.e.

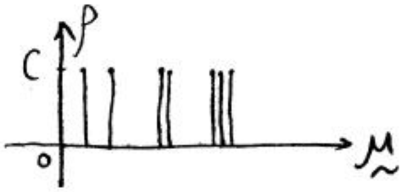
$$\rho_{\rm eq}(\boldsymbol{\mu}) = \rho_{\rm mc}(\boldsymbol{\mu}) = \begin{cases} C' & E \le H(\boldsymbol{\mu}) \le E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{9}$$

There is nothing "micro" in the microcanonical ensemble. It's just a name with an obscure historical origin.

Q: How do we justify the validity of the microcanonical ensemble assumption, given that $\lim_{t\to\infty} \rho(\boldsymbol{\mu}, t) \neq \rho_{\rm mc}(\boldsymbol{\mu})$ (recall previous section)?

A:

1. As t increases, $\rho(\boldsymbol{\mu}, t)$ becomes a highly oscillatory function changing volume rapidly between C and 0, depending on whether $\boldsymbol{\mu}$ is inside volume V_0 or not.



   But if function $A(\boldsymbol{\mu})$ is smooth function, as is usually the case, then it is reasonable to expect

$$\lim_{t\to\infty} \int d^{6N}\boldsymbol{\mu}\, A(\boldsymbol{\mu})\, \rho(\boldsymbol{\mu}, t) = \int d^{6N}\boldsymbol{\mu}\, A(\boldsymbol{\mu})\, \rho_{\rm mc}(\boldsymbol{\mu}) \tag{10}$$

   In other words, $\lim_{t\to\infty} \rho(\boldsymbol{\mu}, t)$ and $\rho_{\rm eq}(\boldsymbol{\mu})$ give the same ensemble averages.

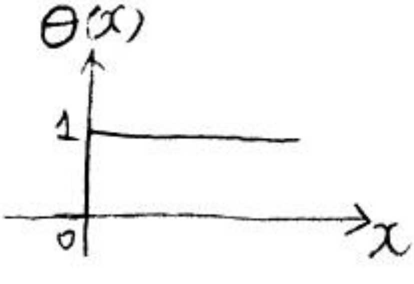
2. A reasonable assumption for $\rho_{eq}(\boldsymbol{\mu})$ must be time stationary, i.e.

$$\frac{\partial \rho_{\rm eq}}{\partial t} = -\{\rho_{\rm eq}, H\} = 0 \tag{11}$$

   Notice that

$$\rho_{\rm mc}(\boldsymbol{\mu}) = [\Theta(H(\boldsymbol{\mu}) - E) - \Theta(H(\boldsymbol{\mu}) - E - \Delta E)] \cdot C' \tag{12}$$

   where $\Theta(x)$ is the step function.



Because ρ_{mc} is a function of $H \Rightarrow \{\rho_{mc}, H\} = 0$.

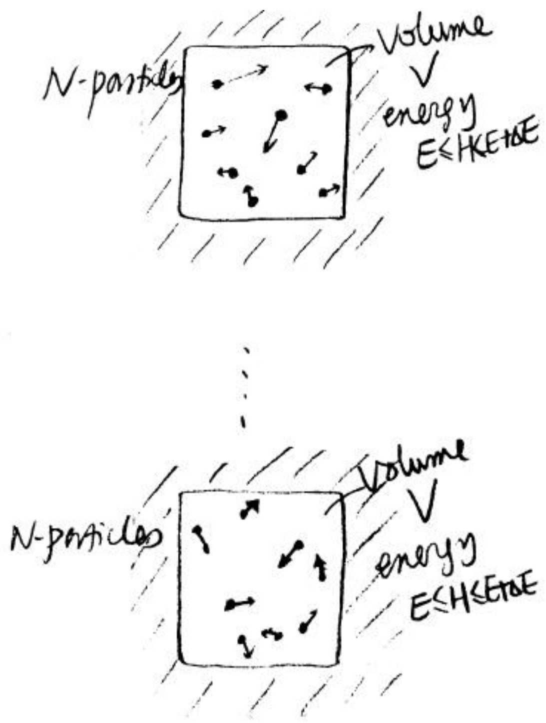
Hence

$$\frac{\partial \rho_{\mathrm{mc}}}{\partial t} = 0 \tag{13}$$

The microcanonical ensemble distribution ρ_{mc} is stationary!.

3. The microcanonical ensemble assumption is consistent with the subjective probability assignment. If all we know about the system is that its total energy H (which should be conserved) is somewhere between E and $E + \Delta E$, then we would like to assign equal probability to all microscopic microstate $\boldsymbol{\mu}$ that is consistent with the constraint $E \leq H(\boldsymbol{\mu}) \leq E + \Delta E$.

2.2 Ideal Gas



(ensemble of containers each having N ideal gas molecules)

Ideal gas is an important model in statistical mechanics and thermodynamics. It refers to N molecules in a container. The interaction between the particles is sufficiently weak so that it will be ignored in many calculations. But conceptually, the interaction cannot be exactly zero, otherwise the system would no longer be ergodic — a particle would never be able to transfer energy to another particle and to reach equilibrium when there were no interactions at all.

Consider an ensemble of gas containers containing ideal gas particles (mono-atomic molecules) that can be described by the microcanonical ensemble.

Q: What is the velocity distribution of on gas particle?

The Hamiltonian of N-ideal gas molecules:

$$H(\{q_i\}, \{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \phi(\mathbf{x}_i) \tag{14}$$

where $\phi(\mathbf{x})$ is the potential function to represent the effect of the gas container

$$\phi(\mathbf{x}) = \begin{cases} 0 & \text{if} \quad \mathbf{x} \in V \ \text{(volume of the container)} \\ \infty & \text{if} \quad \mathbf{x} \notin V \end{cases} \tag{15}$$

This basically means that $\mathbf{x}_i$ has to stay within volume V and when this is the case, we can neglect the potential energy completely.

$$H(\{q_i\}, \{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \tag{16}$$

The constant energy surface $H(\{q_i\}, \{p_i\}) = E$ is a sphere in $3N$-dimensional space, i.e.,

$$\sum_{i=1}^{3N} p_i^2 = 2mE = R^2 \tag{17}$$

with radius $R = \sqrt{2mE}$.

Let's first figure out the constant C' in the microcanonical ensemble,

$$\rho_{\text{mc}}(\boldsymbol{\mu}) = \begin{cases} C' & E \le H(\boldsymbol{\mu}) \le E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{18}$$

Normalization condition:

$$1 = \int d^{6N}\boldsymbol{\mu}\, \rho_{\text{mc}}(\boldsymbol{\mu}) = \int_{E \le H(\boldsymbol{\mu}) \le E+\Delta E} d^{6N}\boldsymbol{\mu} C' = \left[\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)\right] \cdot C' \tag{19}$$

where $\tilde{\Omega}(E)$ is the phase space volume of region $H(\boldsymbol{\mu}) \le E$ and $\tilde{\Omega}(E + \Delta E)$ is the phase space volume of region $H(\boldsymbol{\mu}) \le E + \Delta E$. This leads to

$$C' = \frac{1}{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)} \tag{20}$$

How big is $\tilde{\Omega}(E)$?

$$\tilde{\Omega}(E) = \int_{H(\boldsymbol{\mu}) \le E} d^{6N}\boldsymbol{\mu} \quad = \quad V^N \cdot \int_{\sum_{i=1}^{3N} p_i^2 \le 2mE} dp_1 \cdots dp_N \tag{21}$$

Here we need to invoke an important mathematical formula. The volume of a sphere of radius R in d-dimensional space is,[1]

$$\mathcal{V}_{\text{sp}}(R, d) = \frac{\pi^{d/2}\, R^d}{(d/2)!} \tag{22}$$

---

[1] It may seem strange to have the factorial of a half-integer, i.e. $(d/2)!$. The mathematically rigorous expression here is $\Gamma(d/2 + 1)$, where $\Gamma(x)$ is the Gamma function. It is defined as $\Gamma(x) \equiv \int_0^\infty t^{x-1}\, \mathrm{e}^{-t}\, dt$. When x is a positive integer, $\Gamma(x) = (x-1)!$. When x is not an integer, we still have $\Gamma(x+1) = x\,\Gamma(x)$. $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$. Hence $\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$, $\Gamma\left(\frac{5}{2}\right) = \frac{3}{4}\sqrt{\pi}$, etc. We can easily verify that $\mathcal{V}_{\text{sp}}(R, 3) = \frac{4}{3}\,\pi\, R^3$ and $\mathcal{V}_{\text{sp}}(R, 2) = \pi\, R^2$.

The term behind V^N is the volume of a sphere of radius $R = \sqrt{2mE}$ in $d = 3N$ dimensional space. Hence,

$$\tilde{\Omega}(E) = V^N \cdot \frac{\pi^{3N/2} R^{3N}}{(3N/2)!} \tag{23}$$

$$\begin{aligned} \lim_{\Delta E \to 0} \frac{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)}{\Delta E} &= \frac{\partial \tilde{\Omega}(E)}{\partial E} \\ &= \frac{3N}{2} \frac{1}{E} \frac{(2\pi m E)^{3N/2}}{(3N/2)!} V^N \\ &= \frac{(2\pi m)^{3N/2} \, E^{3N/2-1} \, V^N}{(3N/2-1)!} \end{aligned} \tag{24}$$

In the limit of $\Delta E \to 0$, we can write

$$\begin{aligned} C' &= \frac{1}{\Delta E} \cdot \frac{\Delta E}{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)} \\ &= \frac{1}{\Delta E} \cdot \frac{(3N/2-1)!}{(2\pi m)^{3N/2} \, E^{3N/2-1} \, V^N} \end{aligned} \tag{25}$$

Q: What is the probability distribution of p_1 — the momentum of molecule $i = 1$ in the x-direction?

A: The probability distribution function for p_1 is obtained by integrating the joint distribution function $\rho_{\mathrm{mc}}(q_1, \cdots, q_{3N}, p_1, \cdots, p_{3N})$ over all the variables except p_1.

$$\begin{aligned} f(p_1) &= \int dp_2 \cdots dp_{3N} \cdot dq_1 dq_2 \cdots dq_{3N} \, \rho_{\mathrm{mc}}(q_1, \cdots, q_{3N}, p_1, \cdots, p_{3N}) \\ &= \int_{2mE \,\le\, \sum_{i=1}^{3N} p_i^2 \,\le\, 2m(E+\Delta E)} dp_2 \cdots dp_{3N} \, V^N C' \\ &= \int_{2mE - p_1^2 \,\le\, \sum_{i=2}^{3N} p_i^2 \,\le\, 2m(E+\Delta E) - p_1^2} dp_2 \cdots dp_{3N} \, V^N C' \\ &= \left[\mathcal{V}_{\mathrm{sp}}\left(\sqrt{2m(E+\Delta E) - p_1^2}, 3N-1 \right) - \mathcal{V}_{\mathrm{sp}}\left(\sqrt{2mE - p_1^2}, 3N-1 \right) \right] V^N C' \end{aligned} \tag{26}$$

In the limit of $\Delta E \to 0$,

$$\begin{aligned}
&\frac{\mathcal{V}_{\rm sp}\left(\sqrt{2m(E+\Delta E)-p_1^2}, 3N-1\right) - \mathcal{V}_{\rm sp}\left(\sqrt{2mE-p_1^2}, 3N-1\right)}{\Delta E} \\
= \ & \frac{\partial}{\partial E}\,\mathcal{V}_{\rm sp}\left(\sqrt{2mE-p_1^2}, 3N-1\right) \\
= \ & \frac{\partial}{\partial E}\left[\frac{\pi^{(3N-1)/2}(2mE-p_1^2)^{(3N-1)/2}}{\left(\frac{3N-1}{2}\right)!}\right] \\
= \ & \frac{3N-1}{2}\,\frac{2m}{2mE-p_1^2}\,\frac{\pi^{(3N-1)/2}(2mE-p_1^2)^{(3N-1)/2}}{\left(\frac{3N-1}{2}\right)!} \\
= \ & 2m\,\frac{\pi^{(3N-1)/2}(2mE-p_1^2)^{3(N-1)/2}}{\left(\frac{3(N-1)}{2}\right)!}
\end{aligned} \tag{27}$$

Returning to $f(p_1)$, and only keep the terms that depend on p_1,

$$f(p_1) \propto \left(2mE - p_1^2\right)^{\frac{3(N-1)}{2}} \propto \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3(N-1)}{2}} \tag{28}$$

Notice the identity

$$\lim_{n\to\infty}\left(1+\frac{x}{n}\right)^n = \mathrm{e}^x \tag{29}$$

and that $N \approx N-1$ in the limit of large N. Hence, as $N \to \infty$,

$$f(p_1) \propto \left(1 - \frac{2}{3N}\,\frac{3N}{2E}\,\frac{p_1^2}{2m}\right)^{3N/2} \to \exp\left(-\frac{p_1^2}{2m}\,\frac{3N}{2E}\right) \tag{30}$$

Using the normalization condition

$$\int_{-\infty}^{\infty} dp_1\, f(p_1) = 1 \tag{31}$$

we have,

$$f(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}}\,\exp\left(-\frac{p_1^2}{2m}\,\frac{3N}{2E}\right) \tag{32}$$

Later on we will show that for an ideal gas (in the limit of large N),

$$E = \frac{3}{2}\,N\,k_B\,T \tag{33}$$

where T is temperature and k_B is Boltzmann's constant. Hence

$$f(p_1) = \frac{1}{\sqrt{2\pi m k_B T}}\,\exp\left(-\frac{p_1^2/2m}{k_B T}\right) \tag{34}$$

Notice that $p_1^2/2m$ is the kinetic energy associated with p_1. Hence $f(p_1)$ is equivalent to Boltzmann's distribution that will be derived later (in canonical ensemble).

2.3 Entropy

Entropy is a key concept in both thermodynamics and statistical mechanics, as well as in information theory (a measure of uncertainty or lack of information). In information theory, if an experiment has N possible outcomes with equal probability, then the entropy is

$$S = k_B \log N \tag{35}$$

In microcanonical ensemble,

$$S(N,V,E) = k_B \log \left[\begin{array}{l} \text{number of microscopic states between} \\ \text{the constant energy surfaces:} \\ E \le H(\boldsymbol{\mu}) \le E + \Delta E \end{array} \right] \tag{36}$$

For an ideal gas,

$$S(N,V,E) = k_B \log \frac{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)}{N!\, h^{3N}} \tag{37}$$

The numerator inside the log is the volume of the phase space between the two constant energy surfaces. h is Planck's constant, which is the fundamental constant from quantum mechanics.

Yes, even though we only discuss classical equilibrium statistical mechanics, a bare minimum of quantum mechanical concepts is required to fix some problems in classical mechanics.

We can view this as another evidence that classical mechanics is really just an approximation and quantum mechanics is a more accurate description of our physical world. Fortunately, these two terms can be intuitively understandable without working with quantum mechanics equations. The following are the justifications of the two terms in the denominator.

1. $N!$ term: Quantum mechanics says that the gas molecules are all identical or indistinguishable. Even though we would like to label molecules as $1, 2, ..., N$ there is really no way for us to tell which one is which! Therefore, two molecular structures with coordinates: $\mathbf{x}_1 = (1,2,3)$, $\mathbf{x}_2 = (4,5,6)$ and $\mathbf{x}_1 = (4,5,6)$, $\mathbf{x}_2 = (1,2,3)$ are indistinguishable from each other.

   Swapping the location between two molecules does not give a new microscopic state.

2. h^{3N} term: $h = 6.626 \times 10^{-34}$ J·s is Planck's constant.

   The numerator, $\tilde{\Omega}(E)$, is the phase space volume and has the unit of (momentum · distance)^{3N}.

   The term inside log has to be dimensionless, otherwise, the magnitude of entropy would depend on our choices for the units of length, time, mass, and etc, which would be clearly absurd.

   h has the unit of momentum · distance. Therefore h^{3N} has exactly the right unit to make the entire term inside the log dimensionless.

> The uncertainty principle in quantum mechanics states that we cannot measure both the position and the momentum of any particle to infinite accuracy. Instead, their error bar must satisfy the relation:
>
> $$\Delta q_i \cdot \Delta p_i \geq h \quad \text{for any} \quad i = 1, \cdots, 3N \tag{38}$$
>
> Therefore, $\tilde{\Omega}(E)/(N!\, h^{3N})$ gives us the number of distinguishable states contained inside a phase space volume of $\Omega(\tilde{E})$.

We can show that the entropy expression for the ideal gas in microcanonical ensemble is

$$S(N, V, E) \quad = \quad N k_B \left[\log \left(\frac{V}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad \text{(Sackur-Tetrode formula)} \tag{39}$$

We will derive the Sackur-Tetrode formula later. (Stirling's formula is used to derive it.)

Define number density $\rho = \frac{N}{V}$, and de Broglie wavelength

$$\lambda = \frac{h}{\sqrt{4\pi m E / 3N}} \left(= \frac{h}{\sqrt{2\pi m k_B T}} \right) \tag{40}$$

then

$$S(N, V, E) = N k_B \left[\frac{5}{2} - \log(\rho \lambda^3) \right] \tag{41}$$

In molecular simulations, the microcanonical ensemble is usually referred to as the NVE ensemble.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 6. Thermodynamics

January 26, 2011

Contents

In the 1st lecture, we will discuss the concepts of thermodynamics, namely its 4 laws. The most important concepts are the second law and the notion of Entropy.

(reading assignment: Reif § 3.10, 3.11)

In the 2nd lecture, We will discuss the mathematics of thermodynamics, i.e. the machinery to make quantitative predictions. We will deal with partial derivatives and Legendre transforms.

(reading assignment: Reif § 4.1-4.7, 5.1-5.12)

1 Laws of thermodynamics

Thermodynamics is a branch of science connected with the nature of heat and its conversion to mechanical, electrical and chemical energy. (The Webster pocket dictionary defines, Thermodynamics: physics of heat.)

Historically, it grew out of efforts to construct more efficient heat engines — devices for extracting useful work from expanding hot gases (http://www.answers.com/thermodynamics).

Sethna says "Thermodynamics is a zoo of partial derivatives, transformations and relations".

Thermodynamics is summarized by its Four laws, which are established upon a large number of empirical observations.

These laws describes what you cannot do, if you are in the business (or game) of converting heat into work.

- Zeroth law: you CANNOT ignore the temperature of your heat engine.
- First law: you CANNOT win, the best you can do is to break even. Here "winning" means you extract MORE work than your net in-take of heat.
- Second law: you CANNOT break even, unless you can reach zero temperature.
- Third law: you CANNOT reach zero temperature in your life time.

What is the conclusion on your prospect in this game?

1.1 The zeroth law

The zeroth law of thermodynamics established the existence of temperature in macroscopic systems.

Temperature is a state quantity which is unknown in classical mechanics. It is specially introduced for thermodynamics. — Greiner.

Zeroth law — "transitivity of thermodynamic equilibrium"

> If systems A and B are in thermal equilibrium,
> and systems B and C are in thermal equilibrium,
> then systems A and C are in thermal equilibrium.

Q: What does thermal equilibrium mean?

A: If a closed system is left alone for a long time, it will automatically reach an equilibrium state and its macroscopic state quantities will no longer change with time.

Suppose system A and B have individually reached equilibrium.

If we bring A and B in thermal contact with each other, i.e. allowing them to exchange heat, then the state quantities of A and B (generally speaking) will change until the combined system A + B reaches equilibrium again.

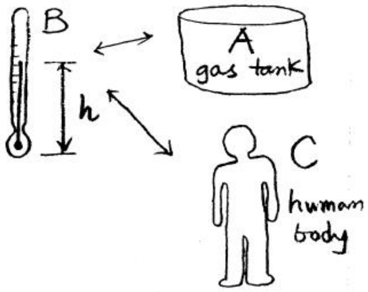
System A and B are said to be in thermal equilibrium if none of the state quantities change when they are brought in thermal contact with each other. Hence, systems which are in thermal equilibrium with each other have a common (intensive) quantity, called temperature.

An extensive property scales linearly with the size of the system, e.g. number of molecules N, volume V, energy E, entropy S.

An intensive property is independent of the system size. e.g. pressure p, temperature T.

In other words, if we bring two identical copies of a system together to form a new system, all the extensive properties will double, while all the intensive properties will remain unchanged.

Notice that the zeroth law applies to any system, so we can let system B be a thermometer.



The height of the liquid h can be used to define the temperature values of all other systems (e.g. A and C) that it can be in thermal contact with.

It is often reasonable to speak of thermodynamic equilibrium even if the state quantities still change very slowly. Any living organism cannot be in a state of complete equilibrium, yet the doctor still wants to know your temperature. — You wouldn't tell the doctor your temperature is not well defined since you are still alive.

1.2 The first law

The first law of thermodynamics establishes the total energy as a state variable.

Heat is nothing but a special form of energy — Mayer (1842)

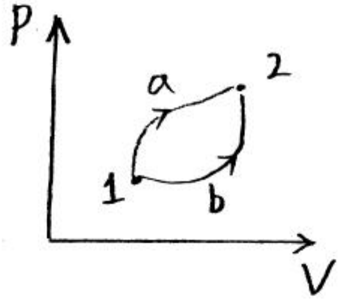
First law — "conservation of energy"

Statement 1: you can change the total energy of the system by doing work $đW$ to it, and/or giving it heat $đQ$. The change of total energy is

$$dE = đW + đQ \tag{1}$$

dE is a complete differential (path independent).

$đW$ and $đQ$ are not complete differentials (they are path dependent).



Suppose we want to transform the system from an equilibrium state 1 to another equilibrium state 2. There are infinite number of paths (ways) to do this.

The intermediate states along the path do not even need to be equilibrium states! Although it is often convenient to imagine a path that goes through a sequence of equilibrium states.

$E_2 - E_1 = \Delta E = \int_a dE = \int_b dE$ is independent of the path.

$\Delta W_a = \int_a đW \neq \Delta W_b = \int_b đW$ and
$\Delta Q_a = \int_a đQ \neq \Delta Q_b = \int_b đQ$ are dependent on path chosen.

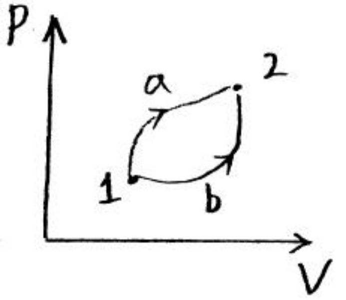
$\Rightarrow$ Energy is a state property, whereas work and heat are not.

Statement 2: you can never "gain energy". $\oint dE = 0 = \oint đW + đQ$.

1.3 The second law

The second law of thermodynamics establishes the entropy as a state variable.

Consider two arbitrary reversible paths from state 1 to state 2.



From the first law, we know that $\Delta Q_a = \int_a đQ_{rev} \neq \Delta Q_b = \int_b đQ_{rev}$, i.e. the total heat deposited into the system depends on the chosen path.

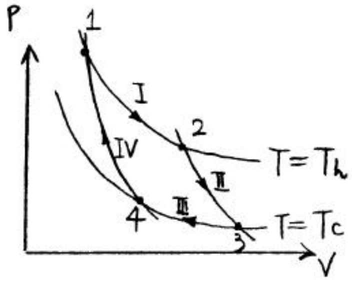
However, experiments confirm that $dS = \frac{đQ}{T}$ is an exact differential, i.e.

$$S_2 - S_1 = \Delta S = \int_a dS = \int_a \frac{đQ_{\text{rev}}}{T} = \int_b dS = \int_b \frac{đQ_{\text{rev}}}{T} \tag{2}$$

S is thus a state property called Entropy. We can think of $\frac{1}{T}$ as the factor to convert the incomplete differential $đQ_{\text{rev}}$ to a complete differential $dS = \frac{đQ_{\text{rev}}}{T}$.

1.3.1 Efficiency of Carnot engine

Entropy is usually discussed together with the Carnot cycle — A heat engine using ideal gas and operating between two temperatures.



Step I: isothermal expansion at higher temperature T_h. volume from V_1 to V_2. engine take in heat $\Delta Q_I > 0$ and produce work.

Step II: adiabatic expansion $\Delta Q_{II} = 0$. T drops to lower temperature T_c. volume from V_2 to V_3.

Step III: isothermal compression at low temperature T_c. volume from V_3 to V_4. engine release heat $\Delta Q_{III} < 0$.

Step IV: adiabatic compression $\Delta Q_{IV} = 0$.

After the Carnot engine has completed one cycle, it returns to state 1. Hence total energy change $\Delta E = \Delta Q + \Delta W = 0$. Since $\Delta Q_{II} = \Delta Q_{IV} = 0$ (adiabatic steps, no heat exchange by definition), the total heat intake for the entire cycle is,

$$\Delta Q = \Delta Q_I + \Delta Q_{III} \tag{3}$$

Notice that $\Delta Q_I > 0$ (ΔQ_I is the heat absorbed from high temperature reservoir T_h) and $\Delta Q_{III} < 0$ ($|\Delta Q_{III}|$ is the heat dumped to low temperature reservoir T_c).

$$\Delta W = -\Delta Q = -\Delta Q_I - \Delta Q_{III} < 0 \tag{4}$$

Since $\Delta Q_{III} < 0$, $|\Delta W| < \Delta Q_I$ not all heat absorbed from T_h can be converted to useful work, some of them $|\Delta Q_{III}|$ are wasted and has to be dumped to T_c. Hence the efficiency of the Carnot engine is,

$$\eta = \frac{|\Delta W|}{\Delta Q_I} = 1 + \frac{\Delta Q_{III}}{\Delta Q_I} < 1 \tag{5}$$

The efficiency η can be obtained using the fact that entropy S is a state property.

After the Carnot engine has completed one cycle $\Delta S = 0$.

Since $\Delta Q_{II} = \Delta Q_{IV} = 0$, $\Delta S = \Delta S_I + \Delta S_{III} = 0$,

$$\frac{\Delta Q_I}{T_h} + \frac{\Delta Q_{III}}{T_c} = 0 \quad \rightarrow \quad \Delta Q_{III} = -\frac{T_c}{T_h}\Delta Q_I \tag{6}$$

$$\eta = 1 - \frac{T_c}{T_h} \tag{7}$$

Hence, you break even ($\eta = 1$) only if $T_c = 0$ (or $T_h \rightarrow \infty$).

1.3.2 Alternative statements of the second law

The second law has many equivalent statements:

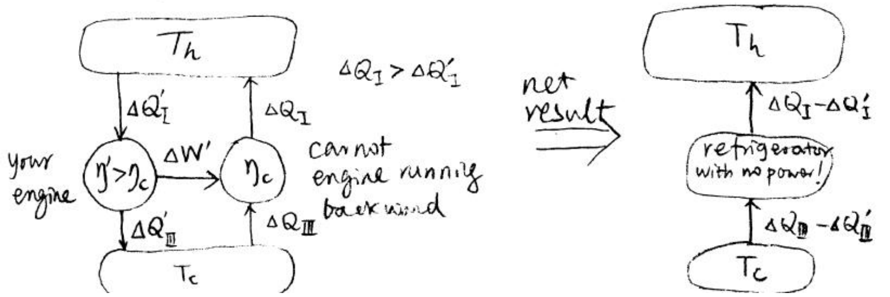
1. The entropy of an isolated system never decreases.
2. A system in contact with one thermal reservoir cannot produce positive work in a cycle (Kelvin's statement).
3. A system operates in a cycle cannot produce heat flow from a colder body to a hotter body — unless it consumes work (Clausius statement).

   — i.e. heat never flows from a low temperature to a high temperature place unless you have a refrigerator (e.g. a Carnot engine running backward).

Statement 3 is probably the most intuitive.

We all experience spontaneous heat flow from high T to low T but never the opposite. This also means the Carnot engine, being a reversible engine, is the most efficient heat engine between T_h and T_c. Otherwise, if you have another engine that is more efficient than the Carnot engine. Then we could give the work produced by this engine to the Carnot engine which now runs backwards - consuming work and carry heat from T_c to T_h without consuming external work.

— The two engines together form a refrigerator that requires no power!



One can use similar ideas to show that statements 1 and 2 are both equivalent to statement 3.

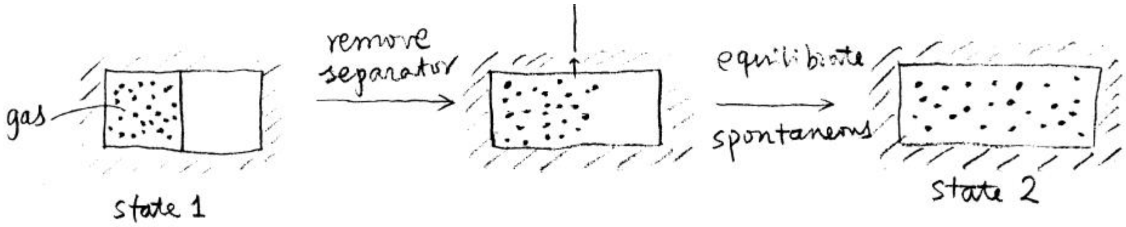
For example, according to statement 1, having absorbed heat ΔQ_I, the engine has increased its own entropy. It has to dump this entropy somewhere else (to T_c) before it can start a new cycle. Therefore, the Carnot engine cannot have $\eta = 100\%$ efficiency.

If there is a "magic stone" that can spontaneously decrease its entropy, an engine coupled to this "magic stone" will no longer need to find another heat reservoir to dump entropy through heat exchange. It's efficiency (work output / heat intake) can then achieve 100%.

This "magic heat engine" coupled with a Carnot engine running in reverse, would lead to refrigerator requiring no power.

Any system, when left alone, will go to equilibrium. In other words, going to equilibrium is a spontaneous process. Hence entropy only increases during equilibration and reaches maximum at equilibrium.

In an adiabatic ($\Delta Q = 0$) irreversible process, entropy only increases.



During this process, there is no external work and no heat exchange. The process is irreversible. Hence $S_2 > S_1$.

1.4 The third law

The third law of thermodynamics is an axiom of nature regarding entropy and the impossibility of reaching absolute zero of temperature.

Third law: "As a system approaches absolute zero temperature, all processes cease and the entropy of the system approaches an minimum value" (which can be defined as zero) — also known as Nernst's theorem.

Alternative statement: "It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations."

(Unfortunately, showing the equivalence between the above two statements of this third law is beyond this class.)

> Since $S = k_B \ln \Omega$, entropy is related to the number of microscopic states consistent with macroscopic states variables. Third low states that at zero temperature, there is only one microscopic state, i.e., the system can only occupy the ground state at $T = 0$.

Here we list some world records of reaching down to zero K.
Doug Osheroff, a Cornell graduate student, discovered (in 1970's) superfluid phase of helium-3 at 0.002K. (Osheroff is currently a physics professor at Stanford. He won the 1996 Nobel Prize for this discovery.)

NIST (1994) $T = 7 \times 10^{-7}$K.

MIT (2003) $T = 4.5 \times 10^{-10}$K

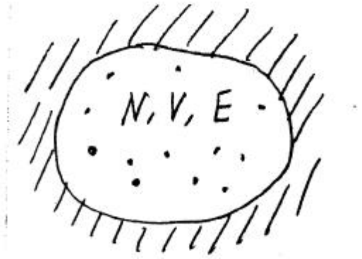
2 Mathematics of thermodynamics

In this lecture, we will go through the mathematics of thermodynamics.

2.1 Equation of state

Let's start by considering an isolated system — A gas tank of volume V, containing N gas molecules, the total energy of the gas molecules is E.

If the gas tank is left alone for a time, it should go to a thermal equilibrium state, and N, V, E stay constant.



For a given type of gas, the three variables (N, V, E) will completely specify the state of this (pure) gas.

From 2nd law of thermodynamics, we also know that every equilibrium state has a well defined entropy S. Therefore, S must be a function of N, V, E i.e. $S(N, V, E)$ — This function is specific to the type of material (gas) that we are studying and can be considered as an "equation of state".

Notice that S, N, V, E are all extensive state functions. Any three of them uniquely specifies a state. The fourth one then has to be a function of these three.

For example, the equation of state of ideal gas can be written as

$$S(N, V, E) = N k_B \left[\log \left(\frac{V}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{8}$$

(See "microcanonical ensemble" notes. We will derive it later.)

Now let's start taking partial derivatives!

Because S, N, V, E are all state functions, dS, dN, dV, dE are all complete differentials.

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV \tag{9}$$

— be careful which variables we keep fixed while taking the derivatives.

The above equation is valid for an arbitrary differential change of a equilibrium state.

Let us now consider a more specific change, where we pass heat $đQ$ to the gas tank while keeping N, V fixed. In this case

$$dN = 0, \quad dV = 0, \quad dE = đQ \tag{10}$$

we also know $dS = \frac{1}{T}đQ$, which leads to $\frac{đQ}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} đQ$. Hence

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \tag{11}$$

We can consider this as the definition of temperature — from the equation of state $S(N, V, E)$.

It is perhaps more convenient to rewrite the equation of state as $E(S, V, N)$.

Then

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN \tag{12}$$

Thus,

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N} \tag{13}$$

Let us now consider a different (reversible) change of state.

Suppose we do mechanical work $đW$ to the gas tank by changing its volume (dV). The work will be done adiabatically ($đQ = 0$). Hence,

$$dS = 0, \quad dN = 0, \quad dE = dW$$

We also know that $dW = -p\,dV$, so $-p\,dV = \left(\frac{\partial E}{\partial V}\right)_{S,N} dV$.

Hence we arrive at the definition of pressure.

$$p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N} \tag{14}$$

We can also do “chemical work” to the gas tank by injecting more gas molecules (dN).

In this case, $dW = \mu\, dN$, μ is called chemical potential. Again,

$$dS = 0, \quad dN = 0, \quad dE = dW$$

So, $\mu\, dN = \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$.

Hence we arrive at the definition of chemical potential.

$$\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V} \tag{15}$$

Therefore,

$$dE = T\, dS - p\, dV + \mu\, dN \tag{16}$$

Summary: Equation of state $E(S, V, N)$ — material specific

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V} \tag{17}$$

E, S, V, N are extensive variables. T, p, μ are intensive variables.

$$dE = T\, dS - p\, dV + \mu\, dN \tag{18}$$

2.2 Gibbs-Duhem relation

Let’s prove some mathematical identities now!

2.2.1 Homogeneous function

Suppose we collect λ gas tanks, each having energy E, entropy S, volume V, and number of molecule N, and put them together to form a big gas tank. The result is a system that should have energy λE, entropy λS, volume λV and number of molecule λN. This means that the equation of state function $E(S, V, N)$ should have the following property.

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N) \tag{19}$$

This means $E(S, V, N)$ is a “homogeneous function of 1st order”.

Next we will apply Virial theorem (Euler’s theorem) to show some “surprising” properties.

2.2.2 Virial theorem / Euler theorem

Consider function $f(x_1, x_2, \cdots, x_n)$ which is homogeneous of 1st order.

Define $u_i = \lambda x_i$,

$$f(u_1, u_2, \cdots, u_n) = \lambda f(x_1, x_2, \cdots, x_n) \tag{20}$$

therefore

$$\frac{\partial}{\partial \lambda} f(u_1, u_2, \cdots, u_n) = f(x_1, x_2, \cdots, x_n) \tag{21}$$

At the same time,

$$\frac{\partial}{\partial \lambda} f(u_1, u_2, \cdots, u_n) = \sum_{i=1}^{n} \frac{\partial f}{\partial u_i} \cdot \frac{\partial u_i}{\partial \lambda} = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} \cdot x_i \tag{22}$$

Take $\lambda = 1$, we get

$$f(x_1, x_2, \cdots, x_n) = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} x_i \tag{23}$$

This is the <u>Virial Theorem</u>: for a homogenous function of 1st order, $f(x_1, x_2, \cdots, x_n)$,

$$f(x_1, x_2, \cdots, x_n) = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} \cdot x_i \tag{24}$$

Applying this theorem to function $E(S, V, N)$,

$$E(S, V, N) \ = \ \left(\frac{\partial E}{\partial S}\right)_{V,N} \cdot S + \left(\frac{\partial E}{\partial V}\right)_{S,N} \cdot V + \left(\frac{\partial E}{\partial N}\right)_{S,V} \cdot N \tag{25}$$

In other words,

$$E(S, V, N) \ = \ T \cdot S - p \cdot V + \mu \cdot N \tag{26}$$

Recall that

$$dE \ = \ T \cdot dS - p \cdot dV + \mu \cdot dN \tag{27}$$

(Both the above two equations are true!)

Let's push the math one step further!

$$E(S, V, N) \ = \ \left(\frac{\partial E}{\partial S}\right)_{V,N} \cdot S + \left(\frac{\partial E}{\partial V}\right)_{S,N} \cdot V + \left(\frac{\partial E}{\partial N}\right)_{S,V} \cdot N \tag{28}$$

$$\Rightarrow \ dE \ = \ T\,dS + S\,dT - p\,dV - V\,dp + \mu\,dN + N\,d\mu \tag{29}$$

But

$$dE = T\,dS - p\,dV + \mu\,dN$$

This leads to the Gibbs-Duhem relation

$$S\,dT - V\,dp + N\,d\mu = 0 \tag{30}$$

Consequence of the Gibbs-Duhem relation: It is impossible to vary all the intensive variables freely. This is contrary to extensive variables (N, V, E), which can be changed freely.

If you vary T and p, then μ will change in a predictable manner.

2.3 Maxwell relations

Mathematical identity 1:

Consider a function $f(x, y)$,

$$df = a\,dx + b\,dy, \quad a \equiv \left(\frac{\partial f}{\partial x}\right)_y, \quad b \equiv \left(\frac{\partial f}{\partial y}\right)_x \tag{31}$$

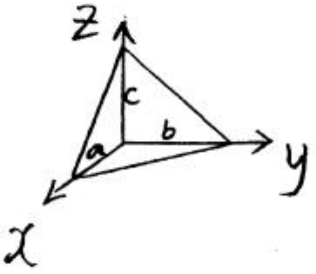
then, we get

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \tag{32}$$

because they both equal to $\frac{\partial^2 f}{\partial x \partial y}$.

Mathematical identity 2:

Consider a function $z(x, y)$



This function defines a relation between x, y, z, i.e. a 2D surface in 3D space. The same relation can also be expressed by $x(y, z)$ and $y(x, z)$.

Then

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \tag{33}$$

(Shouldn't be confused with the chain rule! Note the minus sign!)

Equivalently, we can write

$$\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{34}$$

This is because

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{a}{b},\ \left(\frac{\partial y}{\partial z}\right)_x = -\frac{b}{c},\ \left(\frac{\partial z}{\partial x}\right)_y = -\frac{c}{a} \tag{35}$$

An alternative, algebraic way to prove this identity is the following.

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy & (36) \\ dx &= \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz & (37) \end{aligned}$$

Plug the second equation into the first, we obtain,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y \cdot \left[\left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz\right] + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{38}$$

The dz term cancel and we have

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial z}{\partial y}\right)_x dy = 0 \tag{39}$$

Because this has to be true for arbitrary dy, we have proved the identity of interest.

We can now apply these two identities to function $E(S, V, N)$. Because,

$$dE = TdS - pdV + \mu dN \tag{40}$$

the first identity leads to the following Maxwell's relations.

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_{S,N} &= -\left(\frac{\partial p}{\partial S}\right)_{V,N} & (41) \\ \left(\frac{\partial T}{\partial N}\right)_{S,V} &= \left(\frac{\partial \mu}{\partial S}\right)_{V,N} & (42) \\ \left(\frac{\partial p}{\partial N}\right)_{S,V} &= -\left(\frac{\partial \mu}{\partial V}\right)_{S,N} & (43) \end{aligned}$$

Let's fix N, then $E(V, S)$ is similar to $x(y, z)$. The second identity leads to the following Maxwell's relation.

$$\left(\frac{\partial E}{\partial V}\right)_{S,N} = -\left(\frac{\partial E}{\partial S}\right)_{V,N} \cdot \left(\frac{\partial S}{\partial V}\right)_{E,N} \quad \text{i.e.} \quad -p = -T \cdot \left(\frac{\partial S}{\partial V}\right)_{E,N} \tag{44}$$

Similarly, we can fix S, and consider $E(V, N)$ as $x(y, z)$. The following Maxwell relation appears.

$$\left(\frac{\partial E}{\partial V}\right)_{N,S} = -\left(\frac{\partial E}{\partial N}\right)_{V,S} \cdot \left(\frac{\partial N}{\partial V}\right)_{E,S} \tag{45}$$

All of these Maxwell relations are mathematically true. But the physical meaning of some of them is not obvious. So some of them are not very useful.

2.4 Legendre transform

The equation of state $E(S,V,N)$ is not convenient to work with. This is because we usually do not do experiments at adiabatic conditions ($đQ = 0$).

Very often, experiments are performed at constant temperature T. The sample is allowed to exchange heat with a thermostat at temperature T.

The Legendre transform allows us to work with a different equation of state $A(T,V,N)$ where A is called the Helmholtz free energy — another very important concept in thermodynamics and statistical mechanics (as important as entropy S)

Recall the same Legendre transformation in classical mechanics

$$L(q,\dot{q}) \rightarrow H(q,p), \quad p \equiv \frac{\partial L}{\partial \dot{q}} \tag{46}$$

Notice that as we change variable $\dot{q}$ to its conjugate variable p, the Lagrangian L is transformed to Hamiltonian H.

Here, we want the following Legendre transformation,

$$E(S,V,N) \rightarrow A(T,V,N), \quad T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N} \tag{47}$$

As we change variable S to its conjugate variable T, the energy E is transformed to Helmholtz free energy A.

Start with $E(S,V,N)$, we know $dE = TdS - pdV + \mu dN$

Define

$$A = E - TS \tag{48}$$

What is A a function of?

$$\begin{aligned} dA &= dE - d(TS) = dE - TdS - SdT \\ &= TdS - pdV + \mu dN - TdS - SdT \\ &= -SdT - pdV + \mu dN \end{aligned}$$

So A is a function of T, V, N!

$$A(T,V,N) \tag{49}$$

$$dA = -SdT - pdV + \mu dN \tag{50}$$

The equation of state $A(T, V, N)$ is convenent to use when experimental condition is at constant temperature T, volume V and number of particles N (e.g. gas tank at room temperature).

We can also formulate thermodynamics starting from $A(T, V, N)$ and define $S,\ p,\ \mu$ as

$$S \equiv -\left(\frac{\partial A}{\partial T}\right)_{V,N}, \quad p \equiv -\left(\frac{\partial A}{\partial V}\right)_{T,N}, \quad \mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V} \tag{51}$$

these definitions are completely consistent with earlier equations.

Notice here that p and μ are defined as derivatives with T fixed! — this is easier to do in experiments than to keep S fixed.

2.5 Thermodynamic potentials

Both $E(S, V, N)$ and $A(T, V, N)$ are thermodynamic potentials. Recall Euler's theorem: $E = TS - pV + \mu N$, and the definition $A \equiv E - TS$, we have

$$\begin{aligned} \Rightarrow \qquad A &= -pV + \mu N & (52) \\ \text{together with} \qquad dA &= -SdT - pdV + \mu dN & (53) \end{aligned}$$

From $A(T, V, N)$, we can obtain another set of Maxwell relations, e.g.

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T,N} &= \left(\frac{\partial p}{\partial T}\right)_{V,N} & (54) \\ &\cdots \\ &\cdots \end{aligned}$$

This Legendre transform is fun!

We can continue the Legendre transform with other variables, e.g. V and N, and we will get more and more mathematical identities.

What a harvest!

Suppose we no longer keep our gas tank at constant volume. Instead, we would like to allow volume to adjust automatically but want to keep the pressure p as well as temperature T constant.

In thermodynamics, this correspond to another Legendre transform

$$A(T, V, N) \to G(T, p, N), \ p \equiv -\left(\frac{\partial A}{\partial V}\right)_{T,N} \tag{55}$$

Legendre transform again:

$$A(T, V, N) \tag{56}$$

$$dA = -SdT - pdV + \mu dN \tag{57}$$

Define

$$G = A + pV = E - TS + pV \tag{58}$$

$$\begin{aligned} dG &= dA + d(pV) && (59)\\ &= -SdT - pdV + \mu dN + pdV + Vdp && (60)\\ &= -SdT + Vdp + \mu dN && (61) \end{aligned}$$

G is a function of $T,\ p,\ N$!

$$G(T, p, N) \tag{62}$$

$$dG = -SdT + Vdp + \mu dN \tag{63}$$

$G(T, p, N)$ is an equation of state useful at constant $T,\ p,\ N$.

We can also formulate thermodynamics starting from $G(T, p, N)$ and define $S,\ V,\ \mu$ as

$$S \equiv -\left(\frac{\partial G}{\partial T}\right)_{p,N},\ V \equiv \left(\frac{\partial G}{\partial p}\right)_{T,N},\ \mu \equiv \left(\frac{\partial G}{\partial N}\right)_{T,p} \tag{64}$$

> This seems a little bit of a stretch, because the volume V doesn't require such an obscure definition — "It is obvious what is the volume of my gas tank!" But these definitions are mathematically exact and completely consistent with the previous definitions.

Recall: $E = TS - pV + \mu N$ and $A = -pV + \mu N$

Now $G = A + pV$, therefore

$$G = \mu N \tag{65}$$

Hence,

$$\mu = \frac{G}{N} \tag{66}$$

Therefore, chemical potential is the same as Gibb's free energy per particle!

Recall

$$\mu \equiv \left(\frac{\partial G}{\partial N}\right)_{T,p} \tag{67}$$

(both the above two expressions for μ are true)

From $G(T,p,N)$, we can derive more Maxwell relations!

Another Legendre transform

$$H = E + pV \tag{68}$$

$$H(S,p,N) \tag{69}$$

H is called enthalpy and is good for constant S (adiabatic) and constant p, N conditions.

$$\begin{aligned}
H &= TS - \mu N && (70)\\
dH &= TdS + Vdp + \mu dN && (71)\\
T &\equiv \left(\frac{\partial H}{\partial S}\right)_{p,N}, \cdots && (72)
\end{aligned}$$

more Maxwell relations!

The four thermodynamic potentials consider above: E, A, H, G form a square.

$$\begin{tikzcd}
\begin{array}{c} E(S,V,N) \\ = TS - pV + \mu N \end{array} \arrow[r, "-TS"] \arrow[d, "+pV"] & \begin{array}{c} A(T,V,N) \\ = -pV + \mu N \end{array} \arrow[d, "+pV"] \\
\begin{array}{c} H(S,p,N) \\ = TS + \mu N \end{array} \arrow[r, "-TS"] & \begin{array}{c} G(T,p,N) \\ = \mu N \end{array}
\end{tikzcd}$$

Here we have always kept N fixed.

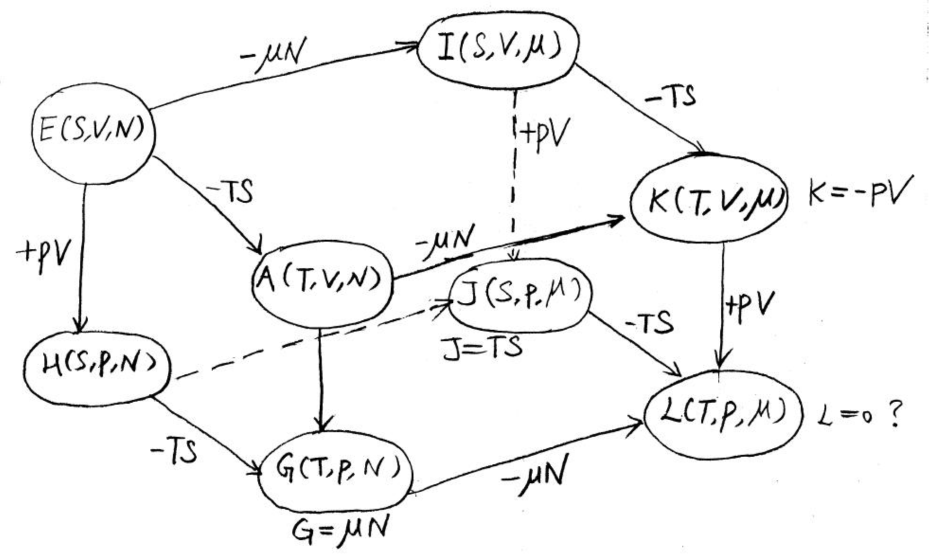
As a result, G, μ seem special, because they are the only ones for which we can write

$$G = \mu N, \qquad \mu = \frac{G}{N} \tag{73}$$

But it does not have to be that way.

Let's get really "energetic" about the Legendre transform and consider ...

The "thermodynamic-potential Cube"!



The thermodynamic potentials $I(S,V,\mu)$, $J(S,p,\mu)$, and $K(T,V,\mu)$ do not have names (that I know of), because nobody uses them (yet). — Hey, you can get more Maxwell relations out of them.

Notice that

$$\mu = \frac{G}{N}, \quad T = \frac{J}{S}, \quad p = -\frac{K}{V} \tag{74}$$

So μ and G are not that special after all! Well.... except that nobody uses J and K...

What happened to $L(T,p,\mu)$? It is zero!

So, it is not a useful thermodynamic potential, e.g. we can't get any Maxwell relation out of it.

Recall the Gibbs-Duhem relation $SdT - Vdp + Nd\mu = 0$, you cannot specify all 3 intensive variables as free variables. That's why $L(T,p,\mu)$ has no meaning!

3 Worked examples

3.1 Thermodynamic potentials and Maxwell's relation

Consider a gas tank of volume V containing N gas molecules with total energy E. For all 7 thermodynamic potentials,

$$E(S, V, N) \tag{75}$$
$$A(T, V, N) \tag{76}$$
$$H(S, p, N) \tag{77}$$
$$G(T, p, N) \tag{78}$$
$$I(S, V, \mu) \tag{79}$$
$$J(S, p, \mu) \tag{80}$$
$$K(T, V, \mu) \tag{81}$$

write down the corresponding 3 conjugate variables. For example, for $E(S, V, N)$, they are the definitions of T, p, and μ. Also write down 3 Maxwell relations for each thermodynamic potential. There should be $7 \times (3 + 3) = 42$ equations in total.

Solution

Energy: E(S,V,N)

$$dE = TdS - pdV + \mu dN$$

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N}, \qquad p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \qquad \mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

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

Helmoltz Free Energy: A(T,V,N)

$$\begin{aligned} A &= E - TS \\ dA &= dE - TdS - SdT = -SdT - pdV + \mu dN \end{aligned}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}, \qquad p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}, \qquad \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

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

Enthalpy: H(S,p,N)

$$\begin{aligned} H &= E + pV \\ dH &= dE + pdV + Vdp = TdS + Vdp + \mu dN \end{aligned}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{p,N}, \qquad V = \left(\frac{\partial H}{\partial p}\right)_{S,N}, \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,p}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}, \qquad \left(\frac{\partial T}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{p,N}, \quad \left(\frac{\partial V}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial p}\right)_{S,N}$$

Gibbs Free Energy: G(T,p,N)

$$\begin{aligned} G &= A + pV \\ dG &= dA + pdV + Vdp = -SdT + Vdp + \mu dN \end{aligned}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,N}, \qquad V = \left(\frac{\partial G}{\partial p}\right)_{T,N}, \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

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

I(S,V,μ)

$$\begin{aligned} I &= E - \mu N \\ dI &= dE - \mu dN - Nd\mu = TdS - pdV - Nd\mu \end{aligned}$$

$$T = \left(\frac{\partial I}{\partial S}\right)_{V,\mu}, \qquad p = -\left(\frac{\partial I}{\partial V}\right)_{S,\mu}, \qquad N = -\left(\frac{\partial I}{\partial \mu}\right)_{S,V}$$

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

J(S,p,μ)

$$\begin{aligned} J &= H - \mu N \\ dJ &= dH - \mu dN - Nd\mu = TdS + Vdp - Nd\mu \end{aligned}$$

$$T = \left(\frac{\partial J}{\partial S}\right)_{p,\mu}, \qquad V = \left(\frac{\partial J}{\partial p}\right)_{S,\mu}, \qquad N = -\left(\frac{\partial J}{\partial \mu}\right)_{S,p}$$

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

K(T,V,μ)

$$\begin{aligned} K &= A - \mu N \\ dK &= dA - \mu dN - N d\mu = -SdT - pdV - Nd\mu \end{aligned}$$

$$S = -\left(\frac{\partial K}{\partial T}\right)_{V,\mu}, \qquad p = -\left(\frac{\partial K}{\partial V}\right)_{T,\mu}, \qquad N = -\left(\frac{\partial K}{\partial \mu}\right)_{T,V}$$

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

3.2 Properties of ideal gas

The Sackur-Tetrode equation gives the analytic expression for the entropy of an ideal gas,

$$S = k_B N \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{82}$$

(a) Invert this equation to obtain $E(S, V, N)$. Derive the expression for T, p, and μ. Verify the ideal gas law $pV = Nk_BT$.

(b) Obtain $A(T, V, N)$ and recompute S from $A(T, V, N)$.

(c) Obtain $G(T, p, N)$ and compare it with $\mu\, N$.

(d) Compute the heat capacity at constant volume C_V, heat capacity at constant pressure C_p, coefficient of thermal expansion α and compressibility β, which are defined as follows

$$\begin{aligned} C_V &= \left(\frac{đQ}{dT} \right)_{V,N} && (83) \\ C_p &= \left(\frac{đQ}{dT} \right)_{p,N} && (84) \\ \alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N} && (85) \\ \beta &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} && (86) \end{aligned}$$

Verify that $C_p - C_V = \alpha^2 VT/\beta$ (this relation is valid for arbitrary thermodynamic system).

Solution

(a) At fixed S, V, N, the property thermodynamic potential is $E(S, V, N)$.

$$E(S, V, N) = \frac{3Nh^2}{4\pi m} \left(\frac{N}{V} \right)^{2/3} \exp \left[\frac{2S}{3Nk_B} - \frac{5}{3} \right]$$

$$\begin{aligned} T &= \left(\frac{\partial E}{\partial S} \right)_{V,N} = E \, \frac{2}{3Nk_B} \quad \Rightarrow \quad E = \frac{3Nk_BT}{2} \\ p &= -\left(\frac{\partial E}{\partial V} \right)_{S,N} = E \, \frac{2}{3V} = \frac{Nk_BT}{V} \quad \Rightarrow \quad pV = Nk_BT \end{aligned}$$

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} = \frac{E}{N} \left[\frac{5}{3} - \frac{2S}{3Nk_B} \right]$$

(b) At fixed T, V, N, the property thermodynamic potential is $A(T,V,N)$. Recall that $A = E - TS$. But we need to be careful about rewriting everything in terms of T, V, N now.

$$\begin{aligned}
E &= \frac{3}{2}Nk_BT \\
S &= Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)+\frac{5}{2}\right] \qquad (87)\\
A(T,V,N) &= E - TS = \frac{3Nk_BT}{2} - Nk_BT\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)+\frac{5}{2}\right] \\
&= -Nk_BT\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)+1\right] \\
S &= -\left(\frac{\partial A}{\partial T}\right)_{V,N} = -\frac{A}{T} + Nk_BT\frac{3}{2T} = -\frac{A}{T} + \frac{3Nk_B}{2} \\
&= Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)+\frac{5}{2}\right]
\end{aligned}$$

which reproduces Eq. (87).

(c) At fixed T, p, N, the property thermodynamic potential is $G(T,p,N)$. Recall that $G = A + pV$. But we need to be careful about rewriting everything in terms of T, p, N now.

$$\begin{aligned}
A &= -Nk_BT\left[\ln\left(\frac{k_BT}{p}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)+1\right] \\
pV &= Nk_BT \\
G &= A + pV \\
&= -Nk_BT\left[\ln\left(\frac{k_BT}{p}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)\right] \qquad (88)
\end{aligned}$$

At the same time, Eq. (87) leads to

$$\begin{aligned}
\mu N &= E\left[\frac{5}{3} - \frac{2S}{3Nk_B}\right] = \frac{5Nk_BT}{2} - TS \\
&= \frac{5Nk_BT}{2} - Nk_BT\left[\ln\left(\frac{k_BT}{p}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)+\frac{5}{2}\right] \\
&= -Nk_BT\left[\ln\left(\frac{k_BT}{p}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right)\right] \qquad (89)
\end{aligned}$$

Comparing Eqs. (88) and (89), we have

$$G = \mu N$$

(d) To compute heat capacity at constant volume, C_V, the proper thermodynamic potential to consider is $A(T, V, N)$, with

$$\begin{aligned} S &= -\left(\frac{\partial A}{\partial T}\right)_{V,N} \\ C_V &= \left(\frac{đQ}{dT}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} \end{aligned}$$

Recall that

$$S(T, V, N) = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

we have

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B$$

To compute heat capacity at constant pressure, C_p, the proper thermodynamic potential to consider is $G(T, p, N)$, with

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{p,N} \\ C_p &= \left(\frac{đQ}{dT}\right)_{p,N} = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} \end{aligned}$$

From

$$S(T, p, N) = Nk_B\left[\ln\left(\frac{k_B T}{p}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

we have

$$\begin{aligned} C_p &= T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{5}{2}Nk_B \\ C_p - C_V &= Nk_B \end{aligned}$$

To compute coefficient of thermal expansion, α, the proper thermodynamic potential to consider is $G(T, p, N)$, with

$$\begin{aligned} V &= \left(\frac{\partial G}{\partial p}\right)_{T,N} = \frac{Nk_B T}{p} \\ \alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{1}{V}\frac{\partial^2 G}{\partial p\,\partial T} \end{aligned}$$

Therefore

$$\alpha \;=\; \frac{p}{Nk_BT}\frac{Nk_B}{p} = \frac{1}{T}$$

To compute compressibility, β, the proper thermodynamic potential to consider is also $G(T,p,N)$, with

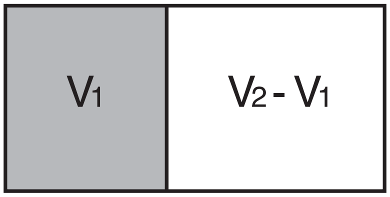
$$\beta \;=\; -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,n} = -\frac{1}{V}\frac{\partial^2 G}{\partial\, p^2}$$

Therefore

$$\begin{aligned} \beta &= -\frac{p}{Nk_BT}\frac{Nk_BT}{-p^2} = \frac{1}{p} \\ \frac{\alpha^2 VT}{\beta} &= \frac{1}{T^2}\,V\,T\,p = N\,k_B = C_p - C_V \end{aligned}$$

3.3 Gas expansion

Consider an insulated container of volume V_2. N idea gas molecules are initially confined within volume V_1 by a piston and the remaining volume $V_2 - V_1$ is in vacuum. Let T_1, p_1, E_1, S_1 A_1, H_1, G_1 be the temperature, pressure, energy, entropy, Helmholtz free energy, enthalpy, and Gibbs free energy of the ideal gas at this state, respectively.



(a) Imagine that the piston is suddenly removed so that the gas has volume V_2. After some time the system settles down to equilibrium again. What are the temperature T_2, pressure p_2, energy E_2, entropy S_2, Helmholtz free energy A_2, enthalpy H_2, and Gibbs free energy G_2 in the new equilibrium state? Mark the initial and final states in the p-V plot and the T-S plot.

(b) Suppose we move the piston infinitely slowly (a reversible process) to let the gas expand to the full volume V_2. The gas container is thermally insulated during this process. What is the work done ΔW to the system? What are T_2, p_2, E_2, A_2, H_2, G_2 in the final equilibrium state? Express them in terms of the thermodynamic functions of state 1 and V_2/V_1. Mark the initial and final states in the p-V plot and the T-S plot.

Solution:

(a) Because there is no heat flow or work done to the system during the free expansion, the change of total energy is zero,

$$E_2 = E_1$$

From the Sackur-Tetrode equation for the entropy of ideal gas

$$S = k_B N \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{90}$$

Hence

$$S_2 = S_1 + k_B N \ln \frac{V_2}{V_1}$$

Because temperature is defined as

$$T = \left(\frac{\partial S}{\partial E} \right)^{-1}_{V,N} = \frac{2\,E}{3Nk_B}$$

we have,

$$T_2 = T_1 = \frac{2E_1}{3Nk_B}$$

Because $p\,V = N\,k_B\,T$, we have

$$p_2 = \frac{Nk_BT_2}{V_2} = \frac{p_1\,V_1}{V_2}$$

Change of Helmholtz free energy,

$$\begin{aligned} A_2 - A_1 &= (E_2 - T_2S_2) - (E_1 - T_1S_1) \\ &= -T_1(S_2 - S_1) \\ A_2 &= A_1 - N\,k_B\,T_1\,\ln\frac{V_2}{V_1} \end{aligned}$$

Enthalpy,

$$H_2 = E_2 + p_2V_2 = \frac{5}{2}Nk_BT_1 = H_1$$

Change of Gibbs free energy,

$$\begin{aligned} G_2 - G_1 &= (H_2 - T_2S_2) - (H_1 - T_1S_1) \\ &= -T_1(S_2 - S_1) \\ G_2 &= G_1 - N\,k_B\,T_1\,\ln\frac{V_2}{V_1} \end{aligned}$$

Table 1: Change of thermodynamic properties if the piston suddenly disappears and the gas settle down to the new equilibrium state with volume V_2.

$T_2 - T_1$	0
$p_2 - p_1$	$p_1(V_1/V_2 - 1)$
$E_2 - E_1$	0
$S_2 - S_1$	$N\,k_B\ln(V_2/V_1)$
$A_2 - A_1$	$-N\,k_B\,T\ln(V_2/V_1)$
$H_2 - H_1$	0
$G_2 - G_1$	$-N\,k_B\,T\ln(V_2/V_1)$

(b) Here the piston expansion is a reversible and adiabatic (no heat flow) process. Hence the entropy change should be zero,

$$S_2 = S_1$$

From Eq. (90),

$$\begin{aligned} V_1\,E_1^{3/2} &= V_2\,E_2^{3/2} \\ E_2 &= \left(\frac{V_1}{V_2}\right)^{2/3} E_1 \end{aligned}$$

Because $E = \frac{3}{2}Nk_BT$,

$$T_2 = \left(\frac{V_1}{V_2}\right)^{2/3} T_1 \tag{91}$$

Eq. (91) can also be obtained from the ideal gas law, $p\,V = Nk_BT$. During the expansion process, the energy change corresponding to a differential change of volume dV is,

$$dE = đW = -p\,dV = -\frac{Nk_BT}{V}\,dV$$

At the same time, $E = \frac{3}{2}Nk_BT$, therefore $dE = \frac{3}{2}Nk_BdT$, so that,

$$\begin{aligned} \frac{3}{2}Nk_BdT &= -\frac{Nk_BT}{V}dV \\ \frac{3}{2}\frac{dT}{T} &= -\frac{dV}{V} \\ \frac{3}{2}\int_{T_1}^{T_2}\frac{dT}{T} &= -\int_{V_1}^{V_2}\frac{dV}{V} \\ \frac{3}{2}\ln\frac{T_2}{T_1} &= -\ln\frac{V_2}{V_1} \\ T_2 &= \left(\frac{V_1}{V_2}\right)^{2/3} T_1 \end{aligned}$$

Because

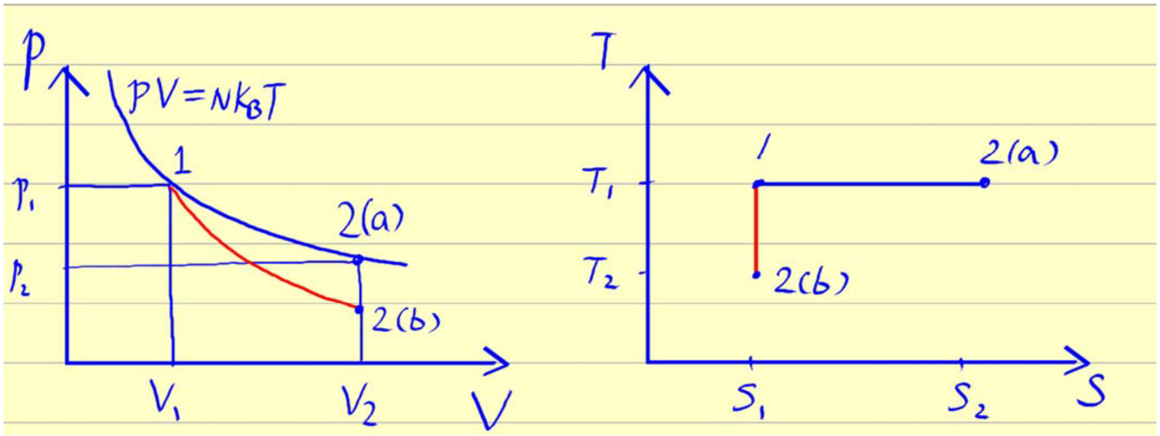
$$\begin{aligned} p_2\,V_2 &= N\,k_B\,T_2 = \left(\frac{V_1}{V_2}\right)^{2/3} p_1\,V_1 \\ p_2 &= \left(\frac{V_1}{V_2}\right)^{5/3} p_1 \end{aligned}$$

Helmholtz free energy, enthalpy and Gibbs free energy,

$$\begin{aligned}
A_2 &= E_2 - T_2 S_2 = \left(\frac{V_1}{V_2}\right)^{2/3} E_1 - \left(\frac{V_1}{V_2}\right)^{2/3} T_1 S_1 \\
&= \left(\frac{V_1}{V_2}\right)^{2/3} A_1 \\
H_2 &= E_2 + p_2 V_2 = \frac{3}{2} N k_B T_2 + N k_B T_2 \\
&= \frac{5}{2} N k_B T_2 = \left(\frac{V_1}{V_2}\right)^{2/3} \frac{5}{2} N k_B T_1 \\
&= \left(\frac{V_1}{V_2}\right)^{2/3} H_1 \\
G_2 &= A_2 + p_2 (V_1 + V_2) = A_2 + N k_B T_2 \\
&= \left(\frac{V_1}{V_2}\right)^{2/3} (A_1 + N k_B T_1) \\
&= \left(\frac{V_1}{V_2}\right)^{2/3} G_1
\end{aligned}$$

Table 2: Change of thermodynamic properties if the piston moves very slowly and adiabatically expand the volume to V_2.

T_2/T_1	$(V_1/V_2)^{2/3}$
p_2/p_1	$(V_1/V_2)^{5/3}$
E_2/E_1	$(V_1/V_2)^{2/3}$
S_2/S_1	1
A_2/A_1	$(V_1/V_2)^{2/3}$
H_2/H_1	$(V_1/V_2)^{2/3}$
G_2/G_1	$(V_1/V_2)^{2/3}$



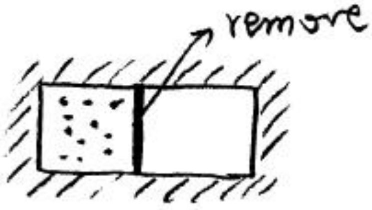
4 Irreversible processes

4.1 Entropy and irreversibility

Second Law: The entropy of an isolated system never decreases.

Interpretation:

> When a system is in a thermal equilibrium state A, it has a definite entropy S_A, which is a function of $N,\ V,\ E$. If certain constraint is removed in the system, e.g. consider the sudden removal of a separator between the gas and the rest of the container.



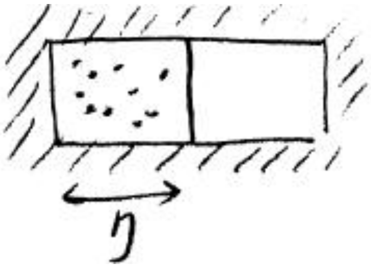
> The system will (irreversibly) reach a new equilibrium state B, which has entropy S_B.
>
> The second law says: $S_B \geq S_A$.

In the above example, the process is adiabatic (no heat exchanges). We can make the following statement about the entropy depending on whether heat is exchanged, or whether the process is reversible.

> For an adiabatic process, $S_B \geq S_A$.
>
> For an adiabatic and reversible process, $S_B = S_A$.
>
> For a non-adiabatic and reversible process $S_B = S_A + \int đQ_{\text{rev}}/T$, $dS = đQ_{\text{rev}}/T$.
>
> For a non-adiabatic, non-reversible process, $dS > đQ/T$

In summary, entropy is related to both heat and irreversibility.

4.2 Variational statement of second law



Let η represent an internal constraint, e.g., the position of the separator.

Let $S(E,V,N;\eta)$ be the entropy of the system subjected to constraint η.

$S(E,V,N)$ is the entropy when the constraint is removed and is the global maximum of $S(E,V,N;\eta)$.

$$S(E,V,N) = \max_{\eta} S(E,V,N;\eta) \tag{92}$$

Since $\left(\frac{\partial S}{\partial E}\right)_{V,N} > 0$, we have the following minimum principle for the entropy function $E(S,V,N)$.

$$E(S,V,N) = \min_{\eta} E(S,V,N;\eta) \tag{93}$$

Care must be taken to interpret the physical meaning of this equation. Usually, when we remove a constraint, E remains constant while S will spontaneously increase. However, it if we want to restore entropy S to its original value, we must extract heat from the system, which will lead to a decrease of energy.

The minimum energy principle becomes much easier to use and to interpret after Legendre transform to $A(T,V,N)$

$$A(T,V,N) = \min_{\eta} A(T,V,N;\eta) \tag{94}$$

In the following we will prove this and other minimum principles.

First, let us recall some relations:

For a reversible process: $dS = đQ_{\text{rev}}/T$

For a irreversible process: $dS > đQ/T, đQ < TdS$.

From first law,

$$\begin{aligned} dE &= đQ + đW \\ &= đQ - pdV + \mu dN \\ dE &< TdS - pdV + \mu dN \quad \text{(for irreversible processes)} \end{aligned}$$

Therefore, for irreversible processes, we can write

$$đZ \equiv dE - TdS + pdV - \mu dN < 0 \tag{95}$$

whereas

$$đZ = 0 \tag{96}$$

for reversible processes.

The above two equations can be used as a general criteria for irreversible processes.

- If we can keep S, V, N constant, then $dZ = dE$, then for an irreversible process $dE < 0$. i.e. $E(S,V,N) = \min_\eta E(S,V,N;\eta)$. (We noted earlier that it is quite different to keep S constant in an irreversible process).
- If we keep T, V, N constant, the proper thermodynamic potential to use is the Helmholtz free energy $A(T,V,N)$.

  $$\begin{aligned} A &= E - TS \\ dA &= dE - TdS - SdT \\ dE &= dA + TdS + SdT \\ đZ &= dA + SdT + pdV - \mu dN = dA \end{aligned} \tag{97}$$

  Hence, for an irreversible process, $dA < 0$,

  $$\Rightarrow A(T,V,N) = \min_\eta A(T,V,N;\eta) \quad \text{(minimum Helmholtz free energy principle)} \tag{98}$$

- If we can keep S, p, N constant, ($đZ = dH$), then for an irreversible process $dH < 0$,

  $$\Rightarrow H(S,p,N) = \min_\eta H(S,p,N;\eta) \quad \text{(minimum enthalpy principle)} \tag{99}$$

  This one is not easy to use, because it is difficult to keep S constant in an irreversible process.

- If we keep T, p, N constant, ($đZ = dG$), then for an irreversible process $dG < 0$,

  $$\Rightarrow G(T,p,N) = \min_\eta G(T,p,N;\eta) \quad \text{(minimum Gibbs free energy principle)} \tag{100}$$

Summary:

> A system (when given a chance) will evolve toward minimizing its Helmholtz/Gibbs free energy at constant $(T,V,N)/(T,p,N)$ conditions.
>
> When equilibrium is reached, its Helmholtz/Gibbs free energy will be at a global minimum.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 7. Entropy

January 26, 2011

Contents

In this lecture, we will first discuss the relation between entropy and irreversibility. Then we will derive the entropy formula for ideal gas,

$$S(N,V,E) = N k_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (1)$$

from the microcanonical (NVE) ensemble. To do so, we will

1. Establish Boltzmann's entropy expression

$$S = k_B \ln \Omega(N,V,E) \quad (2)$$

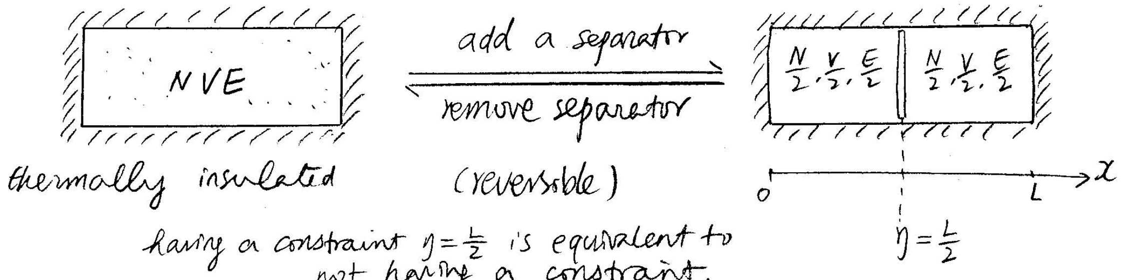
   where Ω is the number of microscopic states consistent with macroscopic state (N,V,E). This is a special case of entropy defined in the <u>information theory</u> $S = \sum_{i=1}^{n} p_i \ln p_i$ when $p_i = \frac{1}{\Omega}$ for all i.

2. Count the number of microscopic state $\Omega(N,V,E)$, carefully.

Reading Assignment, Reif §3.1-3.10.

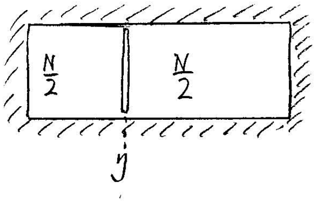
1 Reaching equilibrium after removal of constraint

First let us consider a specific example of irreversible process caused by the removal of a constraint on a thermodynamic system (see Lecture Note 6.4. Irreversible processes).



having a constraint $\eta = \frac{L}{2}$ is equivalent to not having a constraint.

now imagine a general situation (with constraint) with arbitrary η.



Imagine the separator is thermally conducting

Let the system settle down to an equilibrium state **under the constraint** η. In this state, the two sides should have the same temperature T. Given the ideal gas equation of state $PV = Nk_BT$, the two sides will not have the same pressure, unless $\eta = L/2$. This means that, in general, force must be applied on the separator to maintain the constraint η.

Let $S(N, V, E; \eta)$ be the entropy of the system in this state (with constraint η).

Now imagine removing the constraint η, by allowing the separator to slide in response to the pressure difference between the two sides.

Initially the separator may oscillate due to inertia effects. Imagine there is friction between the gas tank wall and the separator. Then the oscillation will eventually die down. Mechanical motion is converted to heat in the process, while the total energy remains constant (assuming the system is isolated from the rest of the world).

Entropy S will increase in this process.

When the system eventually settle down to the new equilibrium state (without constraint η), the new entropy is

$$S(N, V, E) = \max_\eta S(N, V, E; \eta) \tag{3}$$

If the system is in contact with a thermostat at temperature T, then N, V, T remain constants during the irreversible process. One can show that the Helmholtz free energy decreases in the process (heat generated by friction flows to the thermostat). The Helmholtz free energy in the new equilibrium state is

$$A(N,V,T) = \min_{\eta} A(N,V,T;\eta) \tag{4}$$

2 Entropy and irreversibility

2.1 Birth of entropy

Entropy is first defined by German physicist Clasius, “On various forms of the laws of thermodynamics that are convenient for applications”, (1865).

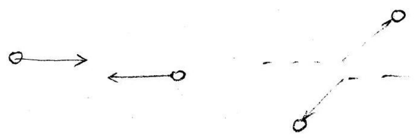
Entropy is the Greek word for “transformation” — Hans C. von Baeyer, “Maxwell’s Demon”, (1998), p.61.

Entropy — stays constant in reversible processes.

Entropy — always increases in irreversible processes.

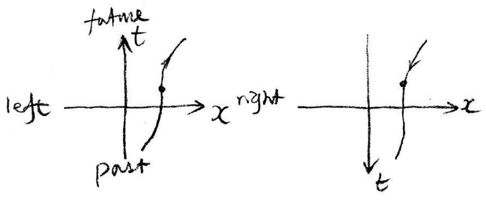
2.2 Entropy increase defines arrow of time

This should be <u>very puzzling</u> for everybody, because all microscopic theories of nature (e.g. classical mechanics, electromagnetism, relativity, quantum mechanics) are time reversible.



In classical mechanics, the trajectories of individual particles are completely reversible. One cannot tell whether the movies is playing forward or backward.

Einstein was very puzzled by the arrow of time.



In the theory of relativity, time is just one of the axes of the 4-dimension “space-time”.

Past-v.s.-future is not so different from left-v.s.-right.

Einstein remarked “... this separation between part, present and future is <u>an illusion</u>, albeit a stubborn one.” — “Maxwell’s Demon” p.129.

Indeed the illusion of "the arrow of time" is a very stubborn one. It is one of the most fundamental aspect of human experience.

Obviously, we remembers the past, but are usually not so good at predicting the future.

Why cannot we "remember" the future?

Clausius stated that: Entropy always increases as we move into the future.

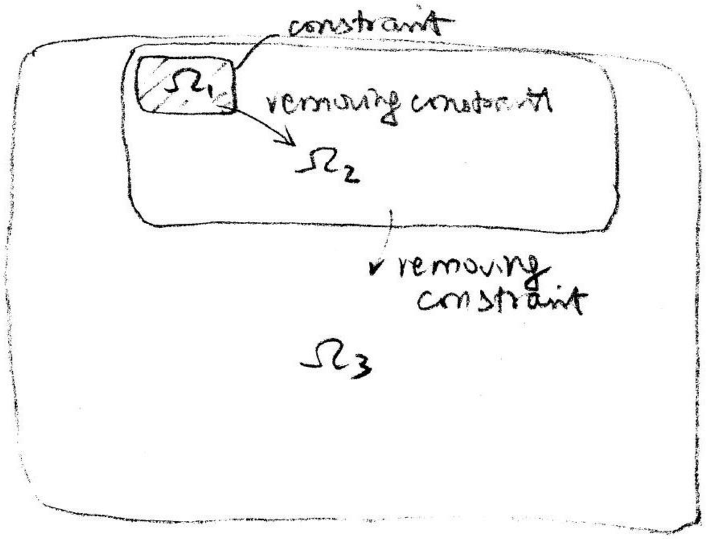
What is this entropy anyway? How can we explain it in terms of the microscopic particles (atoms)?

Why does it always increase with time?

2.3 Boltzmann's entropy expression

$$S = k_B \ln \Omega \tag{5}$$

where Ω is the number of microscopic states consistent with the macroscopic state, e.g. (N, V, E).



Phase space

- As we remove some internal constraint on the system, it "diffuses" out of its original volume in the phase space into a much larger volume in phase space: $\Omega_1 \to \Omega_2$.
- Microscopic dynamics is reversible. It does not prevent the system from spontaneously moving back into region Ω_1 — but to see that happen you will have to wait a LONG time.
- The waiting time easily exceeds the age of the universe, which has been only 14 billion years anyway. The age of the earth is about 4.5 billion years.

- If you want to reverse the change in your (very limited) life time, you will have to spend work.

- Hence irreversibility is connection to the finite span of our existence (yes, mortality, alas). — After all, God (being immortal) may not see irreversibility.

- Entropy increases because the system's initial condition has lower entropy than the equilibrium state. No irreversibility can be observed if the system is already in thermal equilibrium.

- Almost all irreversible processes (e.g. life) on earth are fuelled (ultimately) by sun light. The evolution of stars obeys thermodynamics, i.e. entropy always increases in a burning star. This means entropy is increasing everywhere in the universe.

- Future — will it be the "heat death of the universe"? Maybe. But not so eminent. I suggest we don't worry about it.

- Past — If the entropy has been always increasing, then the universe must have a beginning. The initial state of the universe must have very low entropy.

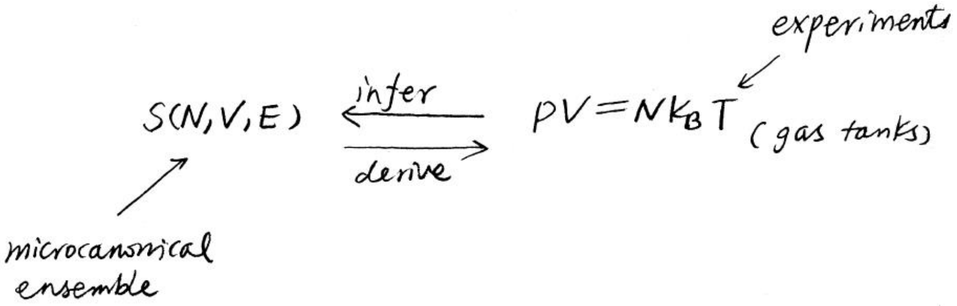
- "Big bang" — 14 billion years ago, all energy/mass of the universe is concentrated at one point (smaller than one atom). This initial state has very low entropy. Boltzmann (1844-1906) already realized that!

3 Boltzmann's entropy expression

S, V, N, E are all state functions in thermodynamics.

Furthermore, S is a function of (N, V, E). $S(N, V, E)$ is a material specific equation of state from which all thermodynamic relations of this material can be derived.

In thermodynamics, the equation of state is obtained from experiments:



In statistical mechanics, we can derive $S(N, V, E)$ from fundamental dynamics of the microscopic particles. Other equation of state (e.g. $pV = Nk_BT$) can be derived from this fundamental relation.

Statistical Mechanics	Thermodynamics
Microcanonical (N, V, E) ensemble. There are many microscopic states $\{q_i, p_i\}$ consistent with (N, V, E). Suppose the number of such microscopic states is Ω.	Macroscopic variables: $S,\ N,\ V,\ E$

Boltzmann proposes:

$$S = k_B \ln \Omega \tag{6}$$

where $k_B = 1.38 \times 10^{-23}$ J·K^{-1} is Boltzmann's constant.

Boltzmann's tombstone in Vienna reads: $S = K \log W$.

4 Shannon's entropy and information theory

Later on, people realize that Boltzmann's entropy formula is a special case of the entropy expression in Shannon's information theory.

$$S = -K \sum_{i=1}^{n} p_i \log(p_i) \tag{7}$$

This expression is called Shannon Entropy or Information Entropy.

Unfortunately, in the information theory, the symbol for entropy is H and the constant k_B is absent. We have changed their notation to avoid confusion.

4.1 How to understand Shannon's information entropy

Entropy measures the degree of our lack of information about a system. Suppose you throw a coin, which may land either with head up or tail up, each with probability $\frac{1}{2}$. Then we have some uncertainty about the outcome of each "experiment". The uncertainty can be quantified by a positive number S.

Now suppose you modified the coin (somehow) that you know for sure that each time you throw it, it will always land with head up (i.e. probability = 1). Then there is no uncertainty about the possible outcome of each "experiment". The information entropy should be $S = 0$.

In general, consider an experiment with n possible outcomes, each with probability p_i, $i = 1, \cdots, n$ with normalization condition $\sum_{i=1}^{n} p_i = 1$.

We are looking for a general formula $S(p_1, p_2, \cdots, p_n)$ that can characterize the uncertainty in all these experiments.

Intuitively, we expect

(1) $S(p_1 = 1/n, p_2 = 1/n, \cdots, p_n = 1/n)$ should be the maximum among all values $S(p_1, \cdots, p_n)$ with a fixed n.

(2) $S(p_1 = 0, p_2 = 1, \cdots, p_n = 0) = 0$ should be the minimum (no uncertainty).

But to develop a general formula for arbitrary $\{p_i\}$ seems impossible!

That's why Shannon is so smart. He did it!

4.2 Derivation of Shannon entropy

Shannon showed that if we assume the entropy function should satisfy a set of reasonable properties then there is only one possible expression for it!

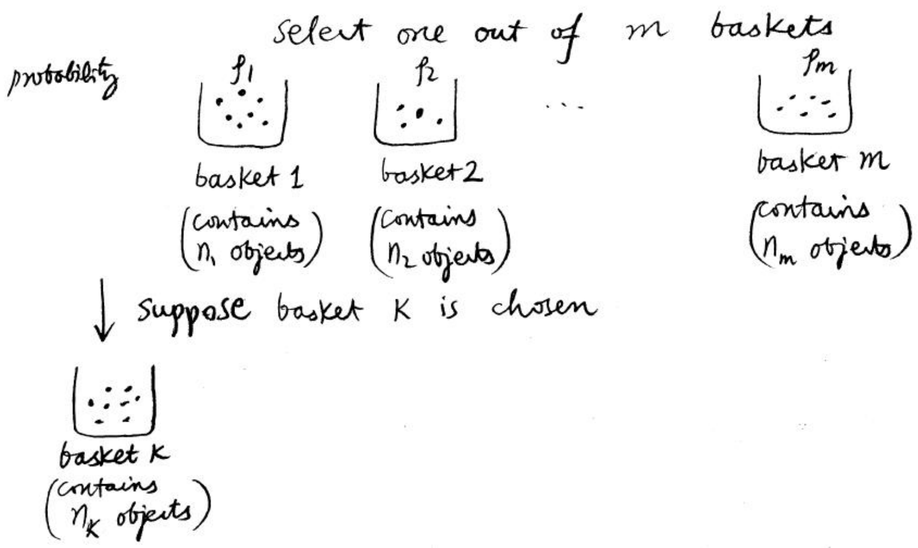
These conditions are:

(1) $S(p_1, p_2, \cdots, p_n)$ is a continuous function.

(2) $f(n) \equiv S(1/n, 1/n, \cdots, 1/n)$ is a monotonically increasing function of n.

(3) Composition law for compound experiments:

$$S(AB) = S(A) + \sum_{k=1}^{m} p_k \, S(B|A) \tag{8}$$



To understand the composition law, consider the following compound experiment AB.

Experiment A: Select one out of m baskets. (Suppose basket k is selected.)

Experiment B: Select one out of n_k objects from basket k.

In the end, all we did was to select one object from $N = \sum_{k=1}^{m} n_k$ objects.

Let the total uncertainty of the compound experiment be $S(AB)$.

The composition law states that we should be able to quantify the uncertainty at each step and add them together.

The uncertainty in 1st step is simply $S(A) = S(p_1, \cdots, p_n)$.

The uncertainty in 2nd step depends on the outcome of the 1st step. When basket k is selected, let the uncertainty of 2nd step be $S(B|A_k)$.

The expected value of the uncertainty in 2nd step is $\sum_{k=1}^{m} p_k S(B|A_k)$.

Hence we expect $S(AB) = S(A) + \sum_{k=1}^{m} p_k \, S(B|A_k)$

To show Shannon's entropy is the only expression that satisfy these three conditions, we design a special compound experiment.

Consider an experiment in which we randomly pick 1 object out of N objects. The probability of picking any object is $1/N$. The uncertainty of this experiment is

$$S(1/N, 1/N, \cdots, 1/N) \equiv f(N) \tag{9}$$

Now imagine that we artificially break down the experiment into two steps. Imagine that we divide the N objects into m groups.

Each group k contains n_k objects and k runs from 1 to m, i.e. $\sum_{k=1}^{m} n_k = N$. In the first step, we randomly pick one of the m groups, the probability of picking group k is

$$p_k = \frac{n_k}{N} \tag{10}$$

In the second step, we pick one object from the selected group. Suppose group k is selected in the first step, then the probability of selecting one object in the second step is $1/n_k$.

The uncertainty in the first step is $S(p_1, \cdots, p_m)$.

The expected value for the uncertainty in the second step is $\sum_{k=1}^{m} p_k f(n_k)$. Hence

$$f(N) = S(p_1, \cdots, p_m) + \sum_{k=1}^{m} p_k f(n_k) \tag{11}$$

Now consider a special case of $n_1 = n_2 = \cdots = n_m = n$, $p_k = 1/m$ for all k.

Every group has n objects, $n \cdot m = N$.

$$\begin{aligned} f(N) &= S(1/m, \cdots, 1/m) + \sum_{k=1}^{m} \frac{1}{m} f(n) \qquad (12) \\ f(mn) &= f(m) + f(n), \quad \text{for arbitrary } m,\ n \qquad (13) \end{aligned}$$

Thus

$$f(m) = K \log m \tag{14}$$

where K is arbitrary positive constant.

Plug it back to the general case

$$K \log N = S(p_1, \cdots, p_m) + \sum_{k=1}^{m} p_k K \log n_k \tag{15}$$

$$\begin{aligned} S(p_1, \cdots, p_m) &= K \log N - \sum_{k=1}^{m} p_k K \log n_k \\ &= K \sum_{k=1}^{m} p_k \log N - K \sum_{k=1}^{m} p_k \log n_k \\ &= K \sum_{k=1}^{m} p_k \log \frac{N}{n_k} \\ &= -K \sum_{k=1}^{m} p_k \log p_k \qquad (16) \end{aligned}$$

Of course, in the special case of $p_k = 1/\Omega,\ k = 1, 2, \cdots, \Omega$, we get back to Boltzmann's entropy expression

$$\begin{aligned} S &= -K \sum_{k=1}^{\Omega} (1/\Omega) \log(1/\Omega) \\ &= K \log \Omega \end{aligned} \tag{17}$$

5 Entropy of ideal gas

Now, let's count how many (Ω) microscopic states are consistent with macroscopic state variables N, V, E.

In the microcanonical ensemble, all microstates with $E \le H(\{q_i\}, \{p_i\}) \le E + \Delta E$ have equal probability density. (Yes, we need to talk about probability density because q_i and p_i are continuous variables).

From Lecture Notes "Microcanonical ensemble"

$$\Omega = \frac{\tilde{\Omega}(E + \Delta E) - \tilde{\Omega}(E)}{N!\, h^{3N}} \tag{18}$$

$\tilde{\Omega}(E)$ is the phase space volume occupied by all micro states with $H(\{q_i\}, \{p_i\}) \le E$. $N!$, h^{3N} are correction factors from quantum mechanics.

For an ideal gas, $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$, $\tilde{\Omega}(E)$ is the volume of $3N$-dimensional sphere ($R = \sqrt{2mE}$) times V^N.

$$\tilde{\Omega} = \frac{(2\pi m E)^{3N/2}}{(\frac{3N}{2})!} \cdot V^N \tag{19}$$

$$\begin{aligned} \Omega &= \frac{1}{N!\, h^{3N}} \cdot \frac{\partial \tilde{\Omega}(E)}{\partial E} \cdot \Delta E \\ &= \frac{1}{N!\, h^{3N}} \cdot \frac{(2\pi m)^{3N/2} \cdot E^{3N/2-1}}{(3N/2-1)!} \cdot V^N \cdot \Delta E \end{aligned} \tag{20}$$

$$\begin{aligned} \log \Omega = & -\log N! - 3N \log h + (3N/2) \log(2\pi m) \\ & + (3N/2 - 1) \log E - \log(3N/2 - 1)! + N \log V + \log \Delta E \end{aligned} \tag{21}$$

Apply stirling's formula, and only keep terms of the order N,

$$\begin{aligned}
\log \Omega &\approx -N \log N + N - N \log h^3 + N \log(2\pi m E)^{3/2} \\
&\quad -(3N/2)\log(3N/2) + 3N/2 + N \log V \\
&= N[-\log N + 1 - \log h^3 + \log(2\pi m E)^{3/2} \\
&\quad - \log(3N/2)^{3/2} + 3/2 + \log V] \\
&= N\left[\log \frac{(2\pi m E)^{3/2} V}{N h^3 (3N/2)^{3/2}} + 5/2\right] \\
&= N\left[\log\left(\frac{V}{N}\left(\frac{4\pi m E}{3N h^2}\right)^{3/2}\right) + \frac{5}{2}\right] \qquad (22)
\end{aligned}$$

Notice that Planck's constant h remains in the final expression, but ΔE does not, because the latter does not contribute a term of the order N.

Given the fundamental equation of state $S(E, V, N)$, we can derive all other properties of the ideal gas (Handout 6. Thermodynamics §3.2).

The statistical distribution of momentum of one particle in ideal gas in the microcanonical ensemble has been derived in Handout 5. Microcanonical Ensemble §2.2.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 8. Canonical Ensemble

January 26, 2011

Contents

Outline

- In this chapter, we will establish the equilibrium statistical distribution for systems maintained at a constant temperature T, through thermal contact with a heat bath.
- The resulting distribution is also called Boltzmann's distribution.
- The canonical distribution also leads to definition of the partition function and an expression for Helmholtz free energy, analogous to Boltzmann's Entropy formula.
- We will study energy fluctuation at constant temperature, and witness another fluctuation-dissipation theorem (FDT) and finally establish the equivalence of micro canonical ensemble and canonical ensemble in the thermodynamic limit. (We first met a manifestation of FDT in diffusion as Einstein's relation.)

Reading Assignment: Reif §6.1-6.7, §6.10

1 Temperature

For an isolated system, with fixed N – number of particles, V – volume, E – total energy, it is most conveniently described by the microcanonical (NVE) ensemble, which is a uniform distribution between two constant energy surfaces.

$$\rho_{\mathrm{mc}}(\{q_i\},\{p_i\}) = \begin{cases} \text{const} & E \le H(\{q_i\},\{p_i\}) \le E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{1}$$

Statistical mechanics also provides the expression for entropy $S(N,V,E) = k_B \ln \Omega$.

In thermodynamics, $S(N,V,E)$ can be transformed to a more convenient form (by Legendre transform) of Helmholtz free energy $A(N,V,T)$, which correspond to a system with constant N, V and temperature T.

Q: Does the transformation from N, V, E to N, V, T have a meaning in statistical mechanics?

A: The ensemble of systems all at constant N, V, T is called the canonical NVT ensemble.

Q: What is the probability distribution function for the canonical ensemble? Is it uniform?

A: The distribution is not uniform. It is called Boltzmann's distribution, which we will develop below.

Q: How do we define temperature in statistical mechanics?

A: In thermodynamics, temperature is established through the zeroth law — transitivity of thermal equilibrium.

This means that temperature is a property that emerges in the thermodynamic limit, $N \to \infty$, where N is the number of particles. — The existence of temperature is independent of the type of the material (e.g. gas, liquid, or solid).

On the other hand, a system with say, $N < 10$, particles does not have a well defined temperature (in the usual thermodynamic sense), unless it is in thermal contact with another system, i.e., a thermostat, which has a large number of particles and a well-defined temperature.

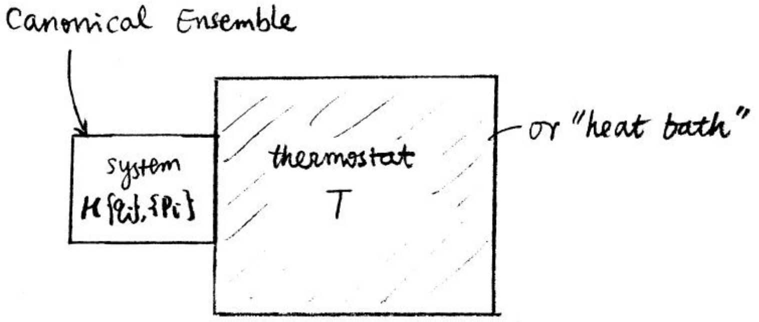
The thermostat is considered to be many many times larger than the system of interest, so that the heat exchange with the system has a negligible effect on the energy per particle and temperature of the thermostat.

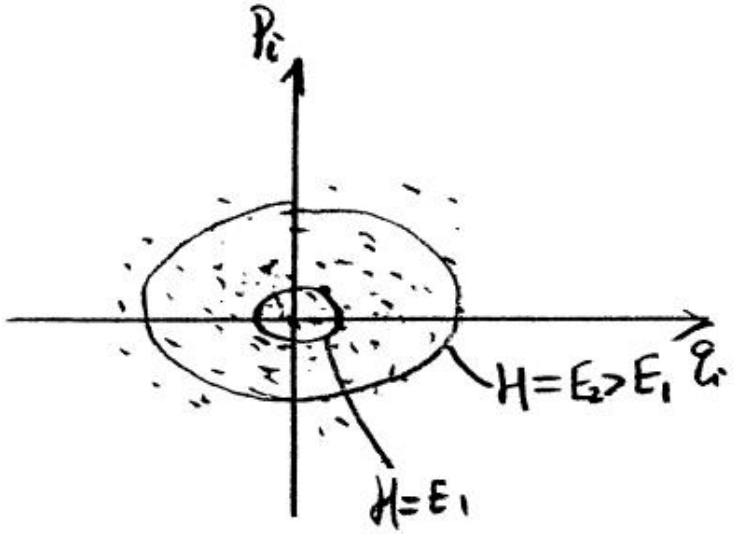
Through thermal contact with the thermostat, the system will eventually settle down to an equilibrium state with temperature equal to that of the thermostat.

The only requirement for the thermostat is that it is much larger than the system of interest. — You could imagine the rest of the universe as the thermostat. The only problem there is that the universe is not in thermal equilibrium.

For convenience, the ideal gas is usually used as a model for the thermostat (because its analytic expression for $S(N, V, E)$ is known). But this is not necessary. The property of the system of interest will not change if we use a different type of thermostat.

2 Boltzmann's distribution





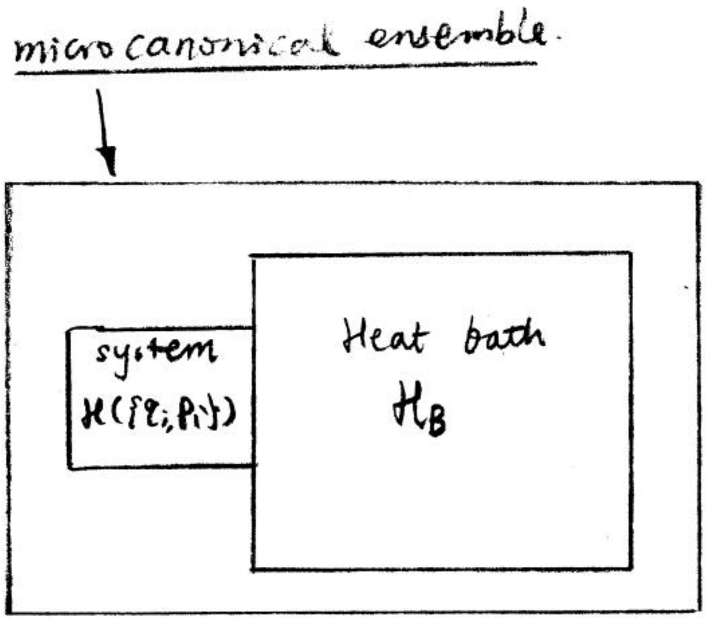
Because the system can exchange heat with the thermostat, its total energy is no longer conserved. Hence, we should no longer expect its energy to be confined as

$$E \leq H(\{q_i\}, \{p_i\}) \leq E + \Delta E$$

Instead, any energy is allowed.

Q: How can we obtain the equilibrium density distribution $\rho_c(\{q_i\}, \{p_i\})$ for the canonical ensemble?

A: The key idea is that, the (system + thermostat) can be considered an isolated system, and can be described by the microcanonical ensemble.



Let H be the Hamiltonian of the system and H_B be the Hamiltonian of the heat bath.

$H + H_B = \hat{E}$ is conserved. Hence the system and heat bath together can be described by the microcanonical ensemble when they have reached thermal equilibrium.

$$\rho_{\rm mc}(\{q_i\},\{p_i\};\{q_i^B\},\{p_i^B\}) = \begin{cases} \text{const} & \hat{E} \le H(\{q_i\},\{p_i\}) + H_B(\{q_i^B\},\{p_i^B\}) \le \hat{E} + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

where $\{q_i\}, \{p_i\}$ represent the system's degrees of freedom, and $\{q_i^B\}, \{p_i^B\}$ represent the heat bath's degrees of freedom. If we only want to know the statistical distribution concerning the system's degrees of freedom, all we need to do is to integrate out the degrees of freedom corresponding to the heat bath.

$$\rho_{\rm c}(\{q_i\},\{p_i\}) = \int \prod_{j=1}^{3N_B} dq_j^B \, dp_j^B \, \rho_{\rm mc}(\{q_i\},\{p_i\},\{q_i^B\},\{p_i^B\}) \tag{3}$$

This is very similar to the study of momentum distribution of one gas molecule in a gas tank of N molecules (see "Microcanonical ensemble" notes).

$\therefore$ $\rho(\{q_i\},\{p_i\})$ is proportional to the number of ways the thermostat molecules can rearrange themselves such that $\hat{E} \le H(\{q_i\},\{p_i\}) + H_B(\{q_i^B\},\{p_i^B\}) \le \hat{E} + \Delta E$.

$$\rho_{\rm c}(\{q_i\},\{p_i\}) = \text{const} \cdot \Omega_B(\hat{E} - H(\{q_i\},\{p_i\})) \tag{4}$$

Recall that the entropy S_B of the heat bath is a function of its energy E_B.

$$S_B(E_B) = k_B \ln \Omega_B(E_B) \qquad E_B = \hat{E} - H(\{q_i\}, \{p_i\}) \tag{5}$$

Also notice that $\hat{E}$, $E_B \gg E = H(\{q_i\}, \{p_i\})$. Hence we can do a Taylor expansion of S_B around $E = 0$.

$$S_B(E_B) \approx S_B(\hat{E}) - \left(\frac{\partial S_B}{\partial E_B}\right) \cdot H(\{q_i\}, \{p_i\}) \tag{6}$$

The higher order terms are neglected.

We recognize that $\frac{1}{T} \equiv \left(\frac{\partial S_B}{\partial E_B}\right)$, where T is the temperature of the thermostat. T must also be the temperature of the system at thermal equilibrium. Therefore,

$$\begin{aligned} S_B(E_B) &= \text{const} - \frac{H(\{q_i\}, \{p_i\})}{T} && (7) \\ \Omega_B(E_B) &= \exp\left(\frac{S_B(E_B)}{k_B}\right) = \text{const} \cdot \exp\left(-\frac{H(\{q_i\}, \{p_i\})}{k_B T}\right) && (8) \\ \rho_c(\{q_i\}, \{p_i\}) &= \text{const} \cdot \exp\left(-\frac{H(\{q_i\}, \{p_i\})}{k_B T}\right) && (9) \end{aligned}$$

This is the canonical distribution, also called Boltzmann's distribution or Boltzmann's law.

$$\rho_c(\{q_i\}, \{p_i\}) = \frac{1}{\tilde{Z}} \exp\left(-\frac{H(\{q_i\}, \{p_i\})}{k_B T}\right) \tag{10}$$

The term in the exponential is called Boltzmann's factor.

$\tilde{Z}$ is a normalization factor

$$\tilde{Z} \equiv \int \prod_{i=1}^{3N} dq_i\, dp_i\, \exp\left(-\frac{H(\{q_i\}, \{p_i\})}{k_B T}\right) \tag{11}$$

We can compare this result with the momentum distribution of one gas molecule in the microcanonical ensemble (see "Microcanonical ensemble" notes).

3 Helmholtz free energy

Do not say "it's *just* a normalization factor". We will see that $\tilde{Z}$ is actually very important.

In the miocrocanonical ensemble, we also have a nomalization constant $\tilde{\Omega}$ (volume of phase space)

$$\rho_{\text{mc}}(\{q_i\}, \{p_i\}) = \frac{1}{\tilde{\Omega}} \begin{cases} 1 & E \le H(\{q_i\}, \{p_i\}) \le E + \Delta E \\ 0 & \text{otherwise} \end{cases} \tag{12}$$

$\tilde{\Omega}$ is eventually connected to entropy

$$S(N,V,E) = k_B \ln \frac{\tilde{\Omega}}{N! h^{3N}} \tag{13}$$

In other words,

$$S = k_B \ln \Omega, \qquad \Omega \equiv \frac{\tilde{\Omega}}{N! h^{3N}} \tag{14}$$

Q: What's the meaning of the normalization constant Z in the canonical ensemble?

Q: What is entropy in the canonical ensemble?

A: Use Shannon's entropy formula,

$$\begin{aligned} S &= -k_B \sum_{i=1} p_i \ln p_i \\ &= -k_B \int_\Gamma dq\, dp \, \frac{1}{Z} \exp\left(-\frac{H}{k_B T}\right) \cdot \left(-\frac{H}{k_B T} - \ln \tilde{Z}\right) \\ &= \frac{1}{T} \int_\Gamma dq\, dp\, \rho_c(q,p)\, H(q,p) + k_B \ln \tilde{Z} \end{aligned} \tag{15}$$

where $\int_\Gamma$ means integration over the entire phase space.

Notice that the first term simply contains the ensemble average of energy.

$$E \equiv \langle H \rangle \equiv \int_\Gamma dq\, dp\, \rho_c(q,p)\, H(q,p) \tag{16}$$

$$\therefore \quad S = \frac{E}{T} + k_B \ln \tilde{Z}, \qquad k_B T \ln \tilde{Z} = TS - E \tag{17}$$

Recall in thermodynamics, the Helmholtz free energy is defined as $A \equiv E - TS$. Therefore,

$$A = -k_B T \ln \tilde{Z} \tag{18}$$

Adding quantum corrections

$$A(N,V,T) = -k_B T \ln \frac{\tilde{Z}}{N!\, h^{3N}} \tag{19}$$

$Z \equiv \frac{\tilde{Z}!}{N! h^{3N}}$ is called the partition function.

Notice that energy E is the ensemble average of the Hamiltonian. But the free energy A *cannot be written* as an ensemble average. A is proportional to the log of the normalization constant $A = -k_B \ln Z$. (Analogous to Boltzmann's entropy expression for the canonical ensemble $S = k_B \ln \Omega$.)

4 Fluctuation-dissipation theorem on energy

In the canonical ensemble, the system acquire a temperature by having a thermal contact with a thermostat (heat bath) with temperature T. Thus the system is no longer isolated any more. Its total energy, i.e., Hamiltonian $H(\{q_i\},\{p_i\})$ is no longer conserved. In other words, we should expect some fluctuation of total energy in the canonical ensemble.

On the other hand, fluctuations are not considered in thermodynamics. At constant N, V, T, the appropriate thermodynamics potential is $A(N,V,T)$, from which we can compute a definite value for energy $E = A + TS$, with $S \equiv -\left(\partial A/\partial T\right)_{N,V}$.

Hence, in thermodynamics, we expect the system to simultaneously have a definite temperature T and total energy E. In statistical mechanics, if the system have a well defined temperature, its total energy E must fluctuate.

Q: How do we reconcile this difference between statistical mechanics and thermodynamics?

A: (1) The total energy in thermodynamics should be identified as the ensemble average of the Hamiltonian in statistical mechanics.

$$E = \langle H \rangle \equiv \frac{1}{\tilde{Z}} \int \prod_{i=1}^{3N} dq_i\, dp_i\, \exp(-\beta H(\{q_i\},\{p_i\})) \cdot H(\{q_i\},\{p_i\}), \qquad \beta \equiv \frac{1}{k_B T} \tag{20}$$

(2) We expect the statistical fluctuation of the Hamiltonian to diminish in the thermodynamic limit ($N \to \infty$). Q: Can we show this?

Define ΔE as the standard deviation of the Hamiltonian in the canonical ensemble, where

$$(\Delta E)^2 \equiv \langle H^2 \rangle - \langle H \rangle^2 \tag{21}$$

We would like to compare the magnitude of ΔE with $E \equiv \langle H \rangle$ itself.

To proceed, we need to introduce a widely used technique (or trick) in statistical mechanics, which involves the all-important partition function (or normalization factor).

$$\tilde{Z} \equiv \int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})} \tag{22}$$

$$\frac{\partial \tilde{Z}}{\partial \beta} = -\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})}\, H(\{q_i\},\{p_i\}) \tag{23}$$

$$\therefore \quad E \equiv \langle H \rangle = -\frac{1}{\tilde{Z}} \frac{\partial \tilde{Z}}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln \tilde{Z} \tag{24}$$

In fact, many other thermodynamic properties can be expressed in terms of derivatives of $\tilde{Z}$.

Since

$$
\begin{aligned}
\frac{\partial \tilde{Z}}{\partial \beta} &= -\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})}\, H(\{q_i\},\{p_i\}) && (25)\\
\frac{\partial^2 \tilde{Z}}{\partial \beta^2} &= -\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})}\, H(\{q_i\},\{p_i\})^2 && (26)
\end{aligned}
$$

$$
\begin{aligned}
\langle H^2\rangle &= \frac{1}{\tilde{Z}}\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H}\, H^2 = \frac{1}{\tilde{Z}}\cdot\frac{\partial^2 \tilde{Z}}{\partial \beta^2} && (27)\\
\langle H^2\rangle - \langle H\rangle^2 &= \frac{1}{\tilde{Z}}\frac{\partial^2 \tilde{Z}}{\partial \beta^2} - \left(\frac{1}{\tilde{Z}}\frac{\partial \tilde{Z}}{\partial \beta}\right)^2 \\
&= \frac{1}{\tilde{Z}}\frac{\partial}{\partial \beta}\left(\frac{\partial \tilde{Z}}{\partial \beta}\right) + \frac{\partial}{\partial \beta}\left(\frac{1}{\tilde{Z}}\right)\frac{\partial \tilde{Z}}{\partial \beta} = \frac{\partial}{\partial \beta}\left(\frac{1}{\tilde{Z}}\frac{\partial \tilde{Z}}{\partial \beta}\right) \\
\therefore \quad \langle H^2\rangle - \langle H\rangle^2 &= -\frac{\partial}{\partial \beta}\langle H\rangle && (28)\\
(\Delta E)^2 &= \langle H^2\rangle - \langle H\rangle^2 = -\frac{\partial}{\partial \beta}E = k_B T^2\left(\frac{\partial E}{\partial T}\right) && (29)
\end{aligned}
$$

Notice that $C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V}$ is the heat capacity — an extensive quantity.

$C_V = N\cdot c_V$, where c_V is the specific heat – an intensive quantity

$$(\Delta E)^2 = k_B\, T^2\, C_V = N\, k_B\, T^2\, c_V \tag{30}$$

$$\Delta E = \sqrt{N k_B T^2 c_V} \tag{31}$$

$$\therefore \quad \Delta E \propto \sqrt{N} \quad \text{as} \quad N \to \infty \tag{32}$$

On the other hand, we expect as an extensive quantity

$$E \propto N \quad \text{as} \quad N \to \infty \tag{33}$$

$$\therefore \quad \frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}} \to 0 \quad \text{as} \quad N \to \infty \tag{34}$$

Therefore, the relative energy fluctuation diminishes in the thermodynamic limit. In this limit, the difference between canonical and microcanonical ensemble vanishes!

Notice that the variance of H, $(\Delta E)^2 \equiv \langle H^2\rangle - \langle H\rangle^2$, is a measure of the energy fluctuation of the system.

At the same time, the heat capacity $C_V \equiv \frac{\partial E}{\partial T}$ measures the response of the system to external stimuli — How much energy is needed if we want to raise the temperature by one degree.

Thus $(\Delta E)^2 = k_B T^2 C_V$ is an example of the fluctuation-dissipation theorem (FDT). Spontaneous fluctuations at thermal equilibrium and response to external stimuli are *not independent* of each other.

We have encountered another fluctuation-dissipation theorem ($\mu = \frac{D}{k_B T}$) in the "Diffusion" chapter.

Other fluctuation-dissipation theorems can be derived similarly. For example, the spontaneous volume fluctuation at constant pressure is related to compressibility — see future notes on the "(N, P, T) ensemble".

Because $(\Delta E)^2 = k_B T^2 C_V$, $(\Delta E)^2 \geq 0$, and $k_B T^2 \geq 0$, we must have $C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{N,V} \geq 0$. Hence the heat capacity is *always positive.*

5 Examples

5.1 Ideal Gas

Let's obtain the explicit expression for $A(T, V, N)$ from $A = -k_B T \ln Z$ and compare it with the results from the microcanonical ensemble + Legendre transform.

$$Z = \frac{1}{N!\, h^{3N}} \int \prod_{i=1}^{3N} dq_i\, dp_i \, \exp\left(-\frac{H(\{q_i\}, \{p_i\})}{k_B T}\right) \tag{35}$$

$$H(\{q_i\}, \{p_i\}) = \sum_i \frac{|p_i|^2}{2m} + U(\{q_i\}) \tag{36}$$

$$Z = \frac{V^N}{N!\, h^{3N}} \left[\int_{-\infty}^{\infty} dp \, \exp\left(-\frac{p^2}{2mk_B T}\right)\right]^{3N} = \frac{V^N}{N!\, h^{3N}} (2\pi m k_B T)^{3N/2} \tag{37}$$

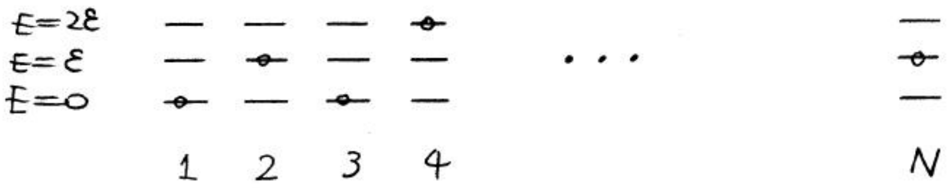
$$A(T, V, N) = -k_B T \ln Z = -k_B T N \left[\ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + 1\right] \tag{38}$$

Same as in the previous chapter on "Thermodynamics".

5.2 Molecules with three energy levels

Consider N molecules, each can be in one of the three energy states, $E = 0,\ \varepsilon,\ 2\varepsilon$.

- Q: What is the Helmholtz free energy, energy and the entropy of the system at the temperature T?
- Q: What is the heat capacity C_V?



The degree of freedom in this problem is $\{n_i\}$, $i = 1, \cdots, N$.

The energy of molecule i is $(n_i \cdot \varepsilon)$, $n_i = 0, 1, 2$.

This problem would be a nightmare if you have to solve it using the microcanonical ensemble in your midterm. But algebra is fairly easy if we use the canonical ensemble. The results must be the same. This is why people like to use canonical ensemble in derivations.

The first step is to find the partition function

$$Z = \sum_{\{n_i\}} \exp(-\beta H), \text{ where } H = \sum_{i=1}^{N} n_i \cdot \varepsilon \tag{39}$$

notice the $\frac{1}{N!h^{3N}}$ correction is no longer needed because the problem is already discrete and molecules are distinguishable.

The sum $\sum_{\{n_i\}}$ over all possible combinations seems impossible to obtain. But it can be transformed to a much simpler form.

$$\begin{aligned} \mathrm{e}^{-\beta H} &= \exp\left(-\beta\varepsilon \sum_{i=1}^{N} n_i\right) = \prod_{i=1}^{N} \mathrm{e}^{-\beta\varepsilon n_i} & (40) \\ Z &= \sum_{\{n_i\}} \prod_{i=1}^{N} \mathrm{e}^{-\beta\varepsilon n_i} = \prod_{i=1}^{N} \left(\sum_{n_i=0,1,2} \mathrm{e}^{-\beta\varepsilon n_i} \right) \\ &= \left(1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}\right)^N & (41) \end{aligned}$$

Helmholtz free energy $A = -k_B T \ln Z$

$$\begin{aligned} A &= -N k_B T \ln(1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}) & (42) \\ S &= -\frac{\partial A}{\partial T} = N k_B T \ln\left(1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}\right) + N k_B T \frac{\mathrm{e}^{-\beta\varepsilon} \frac{\varepsilon}{k_B T^2} + \mathrm{e}^{-2\beta\varepsilon} \frac{2\varepsilon}{k_B T^2}}{1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}} & (43) \\ E &= A + TS = N\varepsilon \frac{\mathrm{e}^{-\beta\varepsilon} + 2\mathrm{e}^{-2\beta\varepsilon}}{1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}} & (44) \end{aligned}$$

Alternative, we can obtain E from

$$\begin{aligned} E &= -\frac{\partial}{\partial\beta}(\ln Z) = -\frac{\partial}{\partial\beta}\left[N \ln(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon})\right] \\ &= N\varepsilon \frac{\mathrm{e}^{-\beta\varepsilon} + 2\mathrm{e}^{-2\beta\varepsilon}}{1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}} & (45) \end{aligned}$$

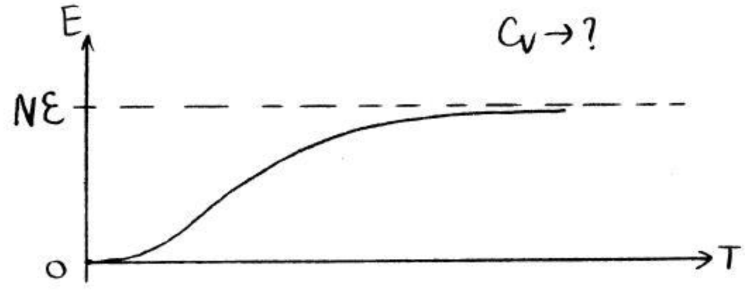
The heat capacity

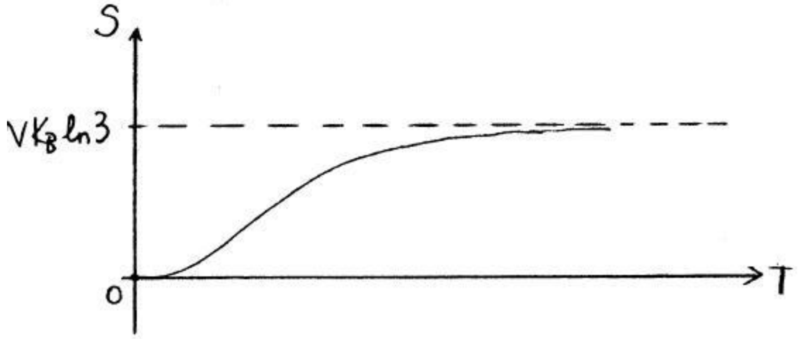
$$C_V = \left(\frac{\partial E}{\partial T}\right)_N \tag{46}$$

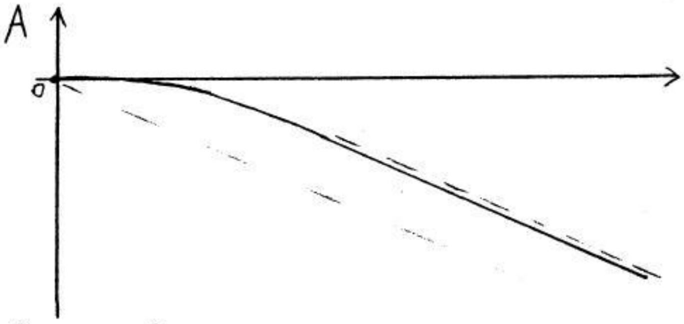
has a very long expression. But the main point here is that its analytic expression exists.

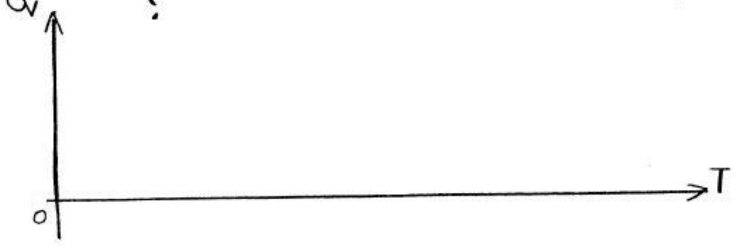
As $T \to 0$, $\mathrm{e}^{-\frac{\varepsilon}{k_B T}} \to 0$, $E \to 0$, $S \to 0$ (third law), $A \to 0$, $C_V \to ?$

As $T \to \infty$, $\mathrm{e}^{-\frac{\varepsilon}{k_B T}} \to 1$, $E \to N\varepsilon$ (is this reasonable?), $S \to Nk_B \ln 3$ (is this reasonable?), $A \to -Nk_B T \ln 3 + N\varepsilon$, $C_V \to ?$









ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 9. NPT and Grand Canonical Ensembles

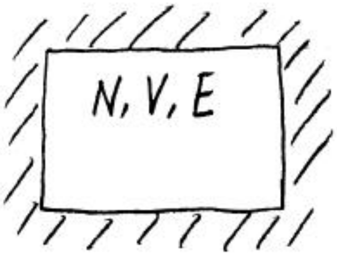
January 26, 2011

Contents

Reading Assignment: Reif §6.9.

1 Summary of NVE and NVT ensembles

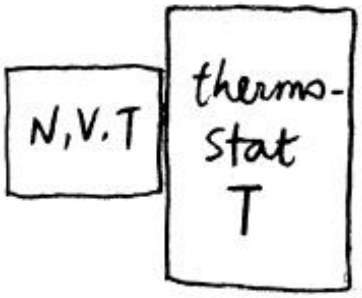
Let us start with a quick summary of the microcanonical (NVE) ensemble. It describes isolated systems with fixed number of particles N, volume V and energy E.



- The microcanonical ensemble is described by a uniform distribution with two constant energy shells.
- The connection with thermodynamics is made through Boltzmann's entropy formula: $S = k_B \ln \Omega$, where Ω is the number of microscopic states consistent with thermodynamic (macroscopic) variables $N,\ V,\ E$.
- Inverting $S(N, V, E)$ we can obtain $E(S, V, N)$. The other thermodynamic quantities are defined through partial derivatives.

  temperature $T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N}$, pressure $p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N}$, chemical potential $\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V}$

Next, a quick summary of the canonical (NVT) ensemble. It describes systems in contact with a thermostat at temperature T. As a result, the energy of the system no longer remain constant. The number of particles N and volume V remain fixed.



- The canonical ensemble is described by Boltzmann's distribution.

$$\rho(\{q_i\}, \{p_i\}) = \frac{1}{\tilde{Z}} \mathrm{e}^{-\beta H(\{p_i\},\{q_i\})} \tag{1}$$

$$\tilde{Z} = \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta H(\{p_i\},\{q_i\})} \tag{2}$$

- The connection with thermodynamics is made through the expression of Helmholtz free energy $A(N,V,T)$ through the partition function Z,

$$A = -k_B T \ln Z\,, \qquad Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H(\{p_i\},\{q_i\})} \tag{3}$$

- The other thermodynamic quantities are defined through partial derivatives.

  entropy $S \equiv \left(\frac{\partial A}{\partial T}\right)_{V,N}$, pressure $p \equiv -\left(\frac{\partial A}{\partial V}\right)_{T,N}$, chemical potential $\mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V}$

- The energy (Hamiltonian) of system is no longer conserved, but fluctuate around its average value.

$$E \equiv \langle H \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z \tag{4}$$

$$(\Delta E)^2 \equiv \langle H^2 \rangle - \langle H \rangle^2 = -\frac{\partial E}{\partial \beta} = k_B T^2 C_v = N k_B T^2 c_v \tag{5}$$

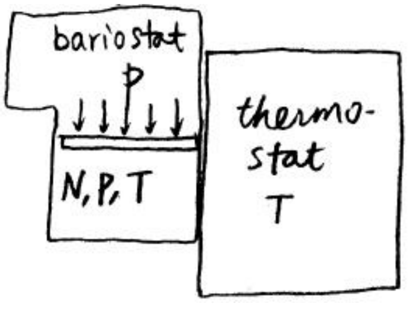
  Hence in the thermodynamic limit $N \to \infty$,

$$\Delta E = \sqrt{N k_B T^2 c_v} \qquad \frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}} \to 0 \tag{6}$$

  The difference between microcanonical (NVE) ensemble and canonical (NVT) ensemble vanishes.

2 NPT ensemble

The NPT ensemble is also called the **isothermal-isobaric** ensemble. It describes systems in contact with a thermostat at temperature T and a bariostat at pressure p. The system not only exchanges heat with the thermostat, it also exchange volume (and work) with the bariostat. The total number of particles N remains fixed. But the total energy E and volume V fluctuate at thermal equilibrium.



Q: What is the statistical distribution $\rho(\{q_i\},\{p_i\})$ at thermal equilibrium?

Q: What is the microscopic expression for the thermodynamic potential?

Approach: Consider system of interest + thermostat + bariostat all together as a closed system, which can be described using the microcanonical ensemble.

2.1 Equilibrium distribution

Notice that in the (NPT) ensemble, the probability distribution function must also include V as its variable, because the volume can (in principle) take any value at thermal equilibrium.

$\rho(\{q_i\},\{p_i\},V) \propto$ number of ways $(\tilde{\Omega})$ the thermostat and the bariostat can rearrange themselves to allow the system to have energy $E = H(\{q_i\},\{p_i\})$ and volume V.

Let $\tilde{S}$ be the entropy of the thermostat + bariostat, then

$$\tilde{\Omega} = \exp\left(\frac{\tilde{S}}{k_B}\right) \tag{7}$$

Let V_0 and E_0 be the total volume and total energy of the thermostat + bariostat + system of interest. Let V and E be the volume and energy of the system of interest. Then the volume and energy left for the thermostat + bariostat are, $V_0 - V$ and $E_0 - E$, respectively.

$$\tilde{S}(\tilde{N}, V_0 - V, E_0 - E) = \tilde{S}(\tilde{N}, V_0, E_0) - \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_{N,E} V - \left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)_{N,V} E \tag{8}$$

We recognize $\left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)_{N,V} \equiv \frac{1}{T}$ where T is the temperature of the thermostat.

But what is $\left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_{N,E}$?

This is the time to use the second type of Maxwell's relationship.

$$\left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)_{V,N} \cdot \left(\frac{\partial \tilde{E}}{\partial \tilde{V}}\right)_{S,N} \cdot \left(\frac{\partial \tilde{V}}{\partial \tilde{S}}\right)_{E,N} = -1 \tag{9}$$

$$\frac{1}{T} \cdot (-p) \cdot \left(\frac{\partial \tilde{V}}{\partial \tilde{S}}\right)_{E,N} = -1 \tag{10}$$

$$\Longrightarrow \qquad \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_{N,E} = \frac{p}{T} \tag{11}$$

where p is the pressure of the bariostat. Therefore,

$$\tilde{S}(\tilde{N}, \tilde{V}, \tilde{E}) = \tilde{S}(\tilde{N}, V_0, E_0) - \frac{p}{T} V - \frac{1}{T} E \tag{12}$$

$$\tilde{\Omega} = \text{const} \cdot \exp\left(-\frac{E + pV}{k_B T}\right) \tag{13}$$

Therefore, the equilibrium distribution of the isothermal-isobaric (NPT) ensemble is,

$$\rho(\{q_i\},\{p_i\},V) = \frac{1}{\Xi} \mathrm{e}^{-\beta[H(\{q_i\},\{p_i\})+pV]} \tag{14}$$

$$\Xi = \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta[H(\{q_i\},\{p_i\})+pV]} \tag{15}$$

2.2 Thermodynamic potential

By now, we would expect the normalization factor Ξ should be interpreted as a kind of partition function that will reveal us the fundamental equation of state.

To find out the precise expression, we start with the Shanon entropy expression. (Notice here that V is an internal degree of freedom to be integrated over and p is an external variable.)

$$\begin{align}
S &= -k_B \sum_i p_i \ln p_i \notag \\
&= -k_B \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i \, dp_i \, \rho(\{q_i\},\{p_i\},V) \cdot \left[\frac{H(\{q_i\},\{p_i\}) + pV}{-k_B T} - \ln \tilde{\Xi} \right] \notag \\
&= \frac{1}{T}(\langle H \rangle + p\langle V \rangle) + k_B \ln \tilde{\Xi} \tag{16} \\
&= \frac{1}{T}(E + pV_{\mathrm{avg}}) + k_B \ln \tilde{\Xi} \tag{17}
\end{align}$$

Hence

$$-k_B T \ln \tilde{\Xi} = E - TS + pV_{avg} \equiv G(N,T,P) \tag{18}$$

This is the Gibbs free energy, which is the appropriate thermodynamic potential as a function of N, T, P ! So everything falls into the right places nicely. We just need to careful that the volume in thermodynamics is the ensemble average $V_{\mathrm{avg}} \equiv \langle V \rangle$, because in (N, T, P) ensemble, V is not a constant.

Of course, we still need to put in the quantum corrections $1/(N!h^{3N})$, just as before. So the final expression for the Gibbs free energy and chemical potential μ is,

$$\begin{align}
\mu N &= G(T,p,N) = -k_B T \ln \Xi \tag{19} \\
\Xi(T,p,N) &= \frac{1}{N!h^{3N}} \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i \, dp_i \, p_i \mathrm{e}^{-\beta[H(\{q_i\},\{p_i\})+pV]} \tag{20} \\
\Xi(T,p,N) &= \int_0^\infty dV \, Z(T,V,N) \, \mathrm{e}^{-\beta pV} \tag{21}
\end{align}$$

Therefore, $\Xi(T,p,N)$ is the **Laplace transform** of the partition function $Z(T,V,N)$ of the canonical ensemble!

2.3 Volume fluctuations

To obtain the average of volume V and its higher moments, we can use the same trick as in the canonical ensemble and take derivatives of Ξ with respect to p.

$$
\begin{aligned}
\langle V \rangle &= -k_B T \, \frac{1}{\Xi} \, \frac{\partial \Xi}{\partial p} \\
\langle V^2 \rangle &= (k_B T)^2 \, \frac{1}{\Xi} \, \frac{\partial^2 \Xi}{\partial p^2} \\
-\frac{\partial V}{\partial p} &= k_B T \, \frac{\partial}{\partial p} \left(\frac{1}{\Xi} \, \frac{\partial \Xi}{\partial p} \right) = k_B T \left[\frac{1}{\Xi} \, \frac{\partial^2 \Xi}{\partial p^2} - \frac{1}{\Xi^2} \left(\frac{\partial \Xi}{\partial p} \right)^2 \right] \\
&= \frac{1}{k_B T} \left[(k_B T)^2 \, \frac{1}{\Xi} \, \frac{\partial^2 \Xi}{\partial p^2} - \left(k_B T \, \frac{1}{\Xi} \, \frac{\partial \Xi}{\partial p} \right)^2 \right] \\
&= \frac{1}{k_B T} \left(\langle V^2 \rangle - \langle V \rangle^2 \right) \\
&\equiv \frac{1}{k_B T} \, (\Delta V)^2 \qquad (22)
\end{aligned}
$$

Define compressibility[1]

$$\beta_c \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{(\Delta V)^2}{k_B T V} \qquad (23)$$

Then we have,

$$(\Delta V)^2 = k_B T \beta_c V \qquad (24)$$

$$\Delta V = \sqrt{k_B T \beta_c V} \qquad (25)$$

$$\frac{\Delta V}{V} \propto \frac{1}{\sqrt{V}} \to 0 \qquad \text{as V} \ \to \ \infty \qquad (26)$$

In other words, in the thermodynamic limit ($V \to \infty$), the relative fluctuation of volume is negligible and the difference between (NPT) ensemble and (NVT) ensemble vanishes.

2.4 Ideal gas example

To describe ideal gas in the (NPT) ensemble, in which the volume V can fluctuate, we introduce a potential function $U(\mathbf{r}, V)$, which confines the partical position r within the volume V. Specifically, $U(\mathbf{r}, V) = 0$ if $\mathbf{r}$ lies inside volume V and $U(\mathbf{r}, V) = +\infty$ if $\mathbf{r}$ lies outside volume V.

The Hamiltonian of the ideal gas can be written as,

$$H(\{q_i\}, \{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{j=1}^{N} U(\mathbf{r}_i, V) \qquad (27)$$

---

[1] Not to be confused with $\beta \equiv 1/(k_B T)$.

Recall the ideal gas partition function in the (NVT) ensemble.

$$Z(T,V,N) = \frac{V^N}{N!h^{3N}}(2\pi m k_B T)^{3N/2} = \frac{V^N}{N!\Lambda^{3N}} \tag{28}$$

where $\Lambda \equiv h/\sqrt{2\pi m k_B T}$ is the thermal **de Broglie wavelength**.

$$\begin{aligned}
\Xi(T,p,N) &= \int_0^\infty dV \cdot Z(T,V,N) \cdot \mathrm{e}^{-\beta p V} \\
&= \frac{1}{N!\lambda^{3N}} \int_0^\infty dV \cdot V^N \cdot \mathrm{e}^{-\beta p V} \\
&= \frac{1}{N!\lambda^{3N}} \frac{1}{(\beta p)^{N+1}} \int_0^\infty dx \cdot x^N \cdot \mathrm{e}^{-x} \\
&= \frac{1}{N!\lambda^{3N}} \frac{1}{(\beta p)^{N+1}} N! \\
&= \left(\frac{k_B T}{p}\right)^{N+1} \frac{1}{\Lambda^{3N}} \qquad (29)
\end{aligned}$$

In the limit of $N \to \infty$,

$$\Xi(T,p,N) \approx \left(\frac{k_B T}{p}\right)^N \cdot \frac{(2\pi m k_B T)^{3N/2}}{h^{3N}} \tag{30}$$

The Gibbs free energy is

$$G(T,p,N) = -k_B \ln \Xi = -N k_B T \ln\left[\left(\frac{k_B T}{p}\right) \cdot \frac{(2\pi m k_B T)^{3/2}}{h^3}\right] \tag{31}$$

This is consistent with Lecture Notes 6 Thermodynamics §3.2,

$$\mu = \frac{G}{N} = -k_B T \ln\left[\left(\frac{k_B T}{p}\right) \cdot \frac{(2\pi m k_B T)^{3/2}}{h^3}\right] \tag{32}$$

3 Grand canonical ensemble

The grand canonical ensemble is also called the μVT ensemble. It describes systems in contact with a thermostat at temperature T and a particle reservoir that maintains the chemical potential μ. The system not only exchanges heat with the thermostat, it also exchange particles with the reservoir. The volume V remains fixed.[2] But the number of particles N and energy E fluctuate at thermal equilibrium.

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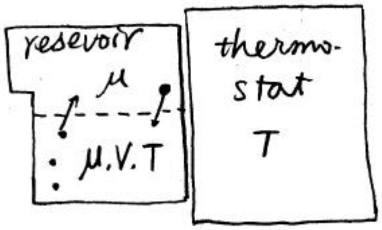
[2] Remember the Gibbs-Duhem relation. We cannot specify all three variables T, p, μ simultaneously.



Q: What is the statistical distribution $\rho(\{q_i\},\{p_i\})$ at thermal equilibrium?

Q: What is the microscopic expression for the thermodynamic potential?

Approach: Consider system of interest + thermostat + particle reservoir all together as a closed system, which can be described using the microcanonical ensemble.

3.1 Equilibrium distribution

Notice that int the grand canonical (μVT) ensemble, the probability distribution function must also include N as its variable, because the number of particle can (in principle) be any non-negative integer at thermal equilibrium.

Following the same approach as in the (NPT) ensemble, we obtain the equilibrium distribution of the grand canonical (μVT) ensemble as the following.

$$\rho(\{q_i\},\{p_i\},N) = \frac{1}{\tilde{\mathcal{Z}}}\,\mathrm{e}^{-\beta(H(\{q_i\},\{p_i\})-\mu N)} \tag{33}$$

where

$$\tilde{\mathcal{Z}} = \sum_{N=0}^{\infty}\int\prod_{i=1}^{3N} dq_i\,dp_i\,\mathrm{e}^{-\beta(H(\{q_i\},\{p_i\})-\mu N)} \tag{34}$$

$$= \sum_{N=0}^{\infty}\mathrm{e}^{\beta\mu N}\tilde{Z}(N,V,T) \tag{35}$$

ρ is grand canonical distribution and $\tilde{Z}(N,V,T)$ is the normalization factor in the canonical ensemble for N particles.

3.2 Thermodynamic potential

Again, we should expect the normalization factor to give us the thermodynamic potential for μ, V, T, which is the **Grand potential**, or Landau potential.[3]

$$\Phi(\mu,V,T) = E - TS - \mu N = -pV \tag{36}$$

---

[3] We called it K in Lecture Notes 6 Thermodynamics.

Starting from Shanon's entropy expression, we can show that

$$\Phi(\mu, V, T) = -k_B T \ln \mathcal{Z} \ , \quad pV = k_B T \ln \mathcal{Z} \tag{37}$$

where $\mathcal{Z}$ is the **grand partition function**,

$$\begin{aligned} \mathcal{Z} &= \sum_{N=0}^{\infty} \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta(H(\{q_i\},\{p_i\})-\mu N)} && (38) \\ &= \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Z(N, V, T) && (39) \end{aligned}$$

where $Z(N, V, T)$ is the partition function of the canonical ensemble. Notice that we have removed the $\tilde{}$ sign, meaning that we have applied the quantum correction $1/(N! h^{3N})$.

Define **fugacity** $z \equiv \mathrm{e}^{\beta\mu}$ (so that $\mu = k_B T \ln z$) we can write,

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \, Z(N, V, T) \tag{40}$$

Therefore, the grand partition function $\mathcal{Z}(\mu, V, T)$ is the **unilateral Z-transform** of the partition function $Z(N, V, T)$ of the canonical ensemble.[4]

3.3 Number of particles fluctuations

Average number of particles

$$\begin{aligned} \langle N \rangle &= k_B T \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = k_B T \frac{\partial}{\partial \mu} (\ln \mathcal{Z}) = z \frac{\partial}{\partial z} (\ln \mathcal{Z}) && (41) \\ \langle N^2 \rangle &= (k_B T)^2 \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} && (42) \\ \frac{\partial \langle N \rangle}{\partial \mu} &= \frac{1}{k_B T} (\langle N^2 \rangle - \langle N \rangle^2) = \frac{(\Delta N)^2}{k_B T} && (43) \end{aligned}$$

Define density $\rho \equiv \frac{\langle N \rangle}{V}$, $\langle N \rangle = \rho V$

$$\begin{aligned} V \cdot \frac{\partial \rho}{\partial \mu} &= \frac{(\Delta N)^2}{k_B T} && (44) \\ (\Delta N)^2 &= k_B T (\partial \rho / \partial \mu) V && (45) \\ \Delta N &= \sqrt{k_B T (\partial \rho / \partial \mu) V} && (46) \\ \frac{\Delta N}{\langle N \rangle} &= \frac{\sqrt{k_B T (\partial \rho / \partial \mu) V}}{\rho V} \propto \frac{1}{\sqrt{V}} \to 0 \quad (\text{as } V \to \infty) && (47) \end{aligned}$$

---

[4] No wonder it is called the Z-transform. See `http://en.wikipedia.org/wiki/Z-transform` for properties of the Z-transform.

3.4 Ideal gas example

Recall the ideal partition function in the canonical ensemble,

$$Z(N,V,T) = \frac{V^N}{N!h^{3N}}(2\pi m k_B T)^{3N/2} = \frac{V^N}{N!\Lambda^{3N}} \tag{48}$$

$$\tag{49}$$

From this we obtain the grand partition function,

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{V^N}{N!\Lambda^{3N}} = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{zV}{\Lambda^3}\right)^N \tag{50}$$

$$\mathcal{Z} = \exp\left(\frac{zV}{\Lambda^3}\right) \tag{51}$$

Next the grand potential $\Phi = -pV$,

$$pV = k_B T \ln \mathcal{Z} = k_B T\,\frac{zV}{\Lambda^3} \tag{52}$$

$$p = k_B T \frac{z}{\Lambda^3}, \quad z = \frac{p}{k_B T}\Lambda^3 \tag{53}$$

$$\mathrm{e}^{\beta\mu} = \frac{p}{k_B T}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} \tag{54}$$

$$\mu = k_B T \ln\left[\left(\frac{p}{k_B T}\right)\cdot\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right] \tag{55}$$

This is consistent with the results from the NPT ensemble, as it should!

We now can obtain an explicit expression of the **density fluctuation** of the ideal gas.

$$\langle N\rangle = z\frac{\partial}{\partial z}\ln\mathcal{Z} = z\frac{\partial}{\partial z}\left(\frac{zV}{\Lambda^3}\right) = \frac{zV}{\Lambda^3} = \ln Z = \frac{pV}{k_B T} \tag{56}$$

$$\langle N\rangle = \frac{e^{\beta\mu}V}{\Lambda^3} \tag{57}$$

$$\frac{\partial\langle N\rangle}{\partial\mu} = \frac{\mathrm{e}^{\beta\mu}\beta V}{\Lambda^3} = \beta\cdot\langle N\rangle = \frac{pV}{(k_B T)^2} \tag{58}$$

$$(\Delta N)^2 = k_B T\,\frac{\partial\langle N\rangle}{\partial\mu} = \frac{pV}{k_B T} = \langle N\rangle \tag{59}$$

$$\tag{60}$$

Hence the variance of N equals the expectation value of N. The standard deviation of N is

$$\Delta N = \sqrt{\langle N\rangle} \tag{61}$$

The relative fluctuation of N is

$$\frac{\Delta N}{N} = \frac{1}{\sqrt{\langle N \rangle}} \tag{62}$$

From the above we also obtain how density $\rho = N/V$ changes with the chemical potential,

$$\frac{\partial \rho}{\partial \mu} = \frac{1}{V}\frac{\partial \langle N \rangle}{\partial \mu} = \frac{p}{(k_B T)^2} \tag{63}$$

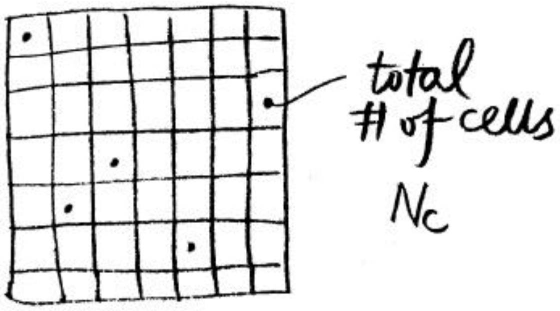
3.5 Lattice gas model

From the previous sections, we see

$$\Delta N = \langle N \rangle \tag{64}$$

Q: Is this result reasonable?

Ideal gas means no correlation between molecules. Hence we can build a lattice gas model as a further simplification to the ideal gas model.



Imagine we divide the volume V into N_c cells. Each cell can have either 1 molecule or 0 molecule.

Assume $N_c \gg \langle N \rangle$, so that we can ignore the possibility that two molecules occupy the same cell.

Define a random variable for each cell,

$$n_i = \begin{cases} 1 & \text{cell } i \text{ contains 1 molecule, probability } p \\ 0 & \text{cell } i \text{ contains 0 molecule, probability } (1-p) \end{cases} \tag{65}$$

n_i and n_j are independent of each other (for $i \neq j$)

The total number of molecules in volume V is

$$N = \sum_{i=1}^{N_c} n_i, \tag{66}$$

The average number of molecules is

$$\langle N \rangle = \sum_{i=1}^{N_c} \langle n_i \rangle = \langle n_i \rangle \cdot N_c \tag{67}$$

Notice that

$$\begin{aligned} \langle n_i \rangle &= p &(68)\\ \langle n_i^2 \rangle &= p &(69)\\ \langle n_i^2 \rangle - \langle n_i \rangle^2 &= p - p^2 = p\,(1-p) &(70) \end{aligned}$$

Hence

$$\begin{aligned} \langle N \rangle &= N_c\, p &(71)\\ \langle N^2 \rangle - \langle N \rangle^2 &= N_c\, p\,(1-p) = \langle N \rangle \left(1 - \frac{\langle N \rangle}{N_c}\right) &(72) \end{aligned}$$

In the limit of $N_c \gg \langle N \rangle$,[5]

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle \tag{73}$$

This is consistent with the prediction from the grand canonical ensemble.

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[5] N_c can be arbitrarily large and hence much larger than N.

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 10. Applications to Solids

February 23, 2011

Contents

We have considered a number of models that can be solved analytically in statistical mechanics, such as ideal gas, 2-level molecules, 3-level molecules, N-harmonic oscillators. They are all non-interacting models. In the canonical ensemble, the partition function of N identical but non-interacting particles is simply the N-th power of the partition function of a single particle.

If we want to go beyond the ideal gas systems, we need to account for interactions between molecules. Finding the partition function for systems with interactions is generally difficult (if not impossible). However, solids at low temperatures can be approximated by a connected set of harmonic oscillators. Through a coordinate transformation, the system can be rewritten as a set of independent harmonic oscillators, so that we can use the results from the non-interacting models again.

Reading assignment: Reif §7.1-7.7, §10.1-10.2.

1 Average kinetic and potential energy

Let us start with some general discussion that is applicable to a wide range of systems, which can be either solid, liquid, or gas. Consider a Hamiltonian of an N-particle system

$$H(\{q_i\},\{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{q_i\}) \tag{1}$$

where the first term on the right hand side is the kinetic energy and the second term is the potential energy.

In the canonical (N,V,T) ensemble, the partition function is

$$Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i\, dp_i\ \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})} \equiv \mathrm{e}^{-\beta A} \tag{2}$$

where A is the Helmholtz free energy.

The average energy is

$$E \equiv \langle H \rangle = \frac{\int \prod_{i=1}^{3N} dq_i\, dp_i\ \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})} H(\{q_i\},\{p_i\})}{\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H(\{q_i\},\{p_i\})}} \tag{3}$$

The average energy is the sum of the average kinetic energy and the average potential energy. The average kinetic energy is easy to evaluate,

$$\begin{aligned}
E_{kin} &= \left\langle \sum_{i=1}^{3N} \frac{p_i^2}{2m} \right\rangle = \frac{\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H} \left(\sum_{i=1}^{3N} \frac{p_i^2}{2m}\right)}{\int \prod_{i=1}^{3N} dq_i\, dp_i\, \mathrm{e}^{-\beta H}} \\
&= \sum_{i=1}^{3N} \frac{\int dp_i \mathrm{e}^{-\frac{p_i^2}{2mk_BT}} \frac{p_i^2}{2m}}{\int dp_i e^{-\frac{p_i^2}{2mk_BT}}} \\
&= \sum_{i=1}^{3N} \frac{mk_BT}{2m} \\
&= \frac{3}{2} N k_B T
\end{aligned} \tag{4}$$

Notice that the result does not depend on m. This means the result is $\frac{3}{2}Nk_BT$ as long as the kinetic energy is a quadratic function of p_i.

If the potential energy is also a quadratic function of q_i, i.e. the case of $3N$-independent harmonic oscillator,

$$U(\{q_i\}) = \sum_{i=1}^{3N} \frac{1}{2} k\, q_i^2 \tag{5}$$

then using the same derivation as above we will find that the average potential energy is also $\langle U \rangle = \frac{3}{2} N k_B T$. In this case, the average total energy is equally divided between the average kinetic energy and average potential energy (i.e. equipartition). But a system of independent harmonic oscillators is not a good (enough) model of a solid. Nonetheless, the average potential energy of a solid (at low temperature) is still $\langle U \rangle = \frac{3}{2} N k_B T$. We will explain the reason using Virial theorem.

At low temperature, atoms in solids vibrates around its equilibrium position $\{q_i^0\}$. Hence we can do a Taylor expansion of $U(\{q_i\})$ around the equilibrium position,

$$U(\{q_i\}) = U(\{q_i^0\}) + \sum_{i=1}^{3N} \left. \frac{\partial U}{\partial q_i} \right|_{q_i = q_i^0} \cdot (q_i - q_i^0) + \frac{1}{2} \sum_{i,j=1}^{3N} \left. \frac{\partial^2 U}{\partial q_i \partial q_j} \right|_{q_i = q_i^0} (q_i - q_i^0)(q_j - q_j^0) + \cdots \quad (6)$$

Define $U(\{q_i^0\}) = E_0 = -N E_{\text{coh}}$, where E_{coh} is called the cohesive energy. Because $\{q_i^0\}$ are equilibrium positions, by definition

$$\left. \frac{\partial U}{\partial q_i} \right|_{q_i = q_i^0} = 0 \quad (7)$$

Define $K_{ij} \equiv \frac{\partial^2 U}{\partial q_i \partial q_j}$. Matrix $\mathbf{K} \equiv \{K_{ij}\}$ is called the Hessian matrix.

At low temperature ($T < T_m/2$) where T_m is the melting temperature of the solid, $(q_i - q_i^0)$ is relatively small (compared with the distance between neighboring atoms), so that terms above the second order can be neglected, i.e.,

$$U(\{q_i\}) \approx -N E_{\text{coh}} + \frac{1}{2} \sum_{i,j=1}^{3N} K_{ij} (q_i - q_i^0)(q_j - q_j^0) \quad (8)$$

Therefore, the solid can be approximated as a set of $\underline{\text{coupled}}$ harmonic oscillators. Notice that in this approximation, and if we redefine the energy reference to make $E_{\text{coh}} = 0$, then $U(\{q_i\})$ is a homogeneous function of order 2, i.e.,

$$U(\{\lambda\, q_i\}) = \lambda^2\, U(\{q_i\}) \quad (9)$$

We will be using this property soon after the Virial theorem is derived.

2 Virial theorem

For an arbitrary potential energy function $U(\{q_i\})$, it is difficult to say anything general about its average $\langle U \rangle$. However, we can still say something very general about the **Virial**, which (for each $i = 1, \cdots, 3N$) is defined as

$$\frac{\partial U}{\partial q_i} q_i$$

and has the same dimension (unit) as the potential energy. Notice that the force on q_i is $f_i \equiv -\partial U / \partial q_i$. Thus the Virial is simply (minus) "force" times "position",

$$-f_i \, q_i$$

In fact, the average of every term in the summation can be obtained analytically.

$$\begin{aligned}
\left\langle \frac{\partial U}{\partial q_i} \, q_i \right\rangle &= \frac{\int \prod_{i=1}^{3N} \, dq_i \, \mathrm{e}^{-\beta U(\{q_j\})} \frac{\partial U}{\partial q_j} q_j}{\int \prod_{i=1}^{3N} \, dq_i \, \mathrm{e}^{-\beta U(\{q_i\})}} \\
&= \frac{\int dq_1 \cdots dq_{i-1} dq_{i+1} \cdots dq_{3N} \left(\frac{d}{dq_i} e^{-\beta U(\{q_j\})} dq_i \right) q_i (-k_B T)}{\int d^{3N} q_j \mathrm{e}^{-\beta U(\{q_j\})}} \\
&= \frac{-\int \prod_{i=1}^{3N} \, dq_j \mathrm{e}^{-\beta U(\{q_j\})}}{\int \prod_{i=1}^{3N} \, dq_j \mathrm{e}^{-\beta U(\{q_j\})}} (-k_B T) \\
&= k_B T
\end{aligned} \tag{10}$$

This is the **Virial Theorem**, which states that the ensemble average of the Virial is

$$\langle -f_i \cdot q_i \rangle = k_B T \tag{11}$$

If we sum over all $i = 1, \cdots, 3N$, we get,

$$\left\langle \sum_{i=1}^{3N} \frac{\partial U}{\partial q_i} \, q_i \right\rangle = 3N k_B T \tag{12}$$

which is twice the average kinetic energy!

3 Equipartition theorem

Suppose potential energy $U(\{q_i\})$ is a homogeneous function of order α, i.e.

$$U(\lambda q_1, \lambda q_2, \cdots, \lambda q_{3N}) = \lambda^\alpha U(q_1, q_2, \cdots, q_{3N}) \tag{13}$$

An example is the potential energy of solids at low temperature, where $U(\{q_i\})$ is a homogeneous function of order $\alpha = 2$, see Eq. (9).

For this class of potential energy functions, Euler's theorem tells us that the sum of Virial is proportional to the potential energy itself![1]

$$\sum_{i=1}^{3N} \frac{\partial U}{\partial q_i} \, q_i = \alpha \, U \tag{14}$$

---

[1] This can be shown by taking derivative of $U(\{\lambda \, q_i\})$ with respect to λ and evaluate it at $\lambda = 1$. On the one hand, from chain rule, $\frac{\partial U}{\partial \lambda}\big|_{\lambda=1} = \sum_{i=1}^{3N} \frac{\partial U}{\partial q_i} \, q_i$. On the other hand, $\frac{\partial \lambda^\alpha}{\partial \lambda}\big|_{\lambda=1} U = \alpha \, U$. For more discussions, see lecture note 6 "Thermodynamics", Section 2.2.2. "Virial theorem / Euler theorem".

Therefore, when Virial theorem is applied to a potential energy function $U(\{q_i\})$ that is a homogeneous function of order α, we get

$$\alpha\, U = \sum_{i=1}^{3N} \frac{\partial U}{\partial q_i}\, q_i \quad = \quad 3Nk_BT = 2\, E_{\rm kin} \tag{15}$$

For solids at low temperature (coupled harmonic oscillators), $\alpha = 2$. Hence

$$\langle U \rangle = E_{kin} = \frac{3}{2} N k_B T \tag{16}$$

which means the average total energy is equally divided between average potential energy and average kinetic energy. This is the energy **equipartition theorem** for solids.

Q: What is the prediction of the heat capacity from this expression?

As temperature increases and approaches the melting temperature, the fraction of the potential energy in the total energy will drop below 50%. In the limit of $T \to \infty$, everything will go to the ideal gas limit, in which case the fraction of the potential energy in the total energy goes to 0.

There are other systems whose potential energy is a homogeneous function of order $\alpha = -1$. An example is the gravitational interaction of matter in a galaxy,

$$U(\{\mathbf{r}_i\}) = \sum_{i,j} \frac{G m_i m_j}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{17}$$

Another example is the Coulomb interaction in a plasma,

$$U(\{\mathbf{r}_i\}) = \sum_{i,j} \frac{Q_i Q_j}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{18}$$

For these systems, both average potential energy and average total energy are negative. The average total energy is the negative of the average kinetic energy.[2]

$$\begin{array}{rrcl} & \alpha & = & -1 \\ & \langle U \rangle & = & -2E_{kin} \\ & E & = & \langle U \rangle + E_{kin} = -E_{kin} \\ \Rightarrow & E_{kin} & = & -E \\ \Rightarrow & \langle U \rangle & = & 2E \end{array} \tag{19}$$

---

[2] This holds even for systems not in thermal equilibrium, such as a satellite orbiting around the earth.

4 Free energy of solids

Even though Virial theorem gives us the average energy of solids at low temperature (coupled harmonic oscillators), it does not give us the Helmholtz free energy, for which we still need to evaluate the integrals in the partition function Z.

Recall that we have simplified the potential function to the following form,

$$U(\{q_i\}) = -N\,E_{\rm coh} + \frac{1}{2}\sum_{i,j=1}^{3N} K_{ij}(q_i - q_i^0)(q_j - q_j^0) \tag{20}$$

The harmonic oscillators can be decoupled by diagonalizing matrix $\mathbf{K} = \{K_{ij}\}$. For example, this can be done in Matlab by the following command,

$$[\mathbf{V}, \mathbf{D}] = \mathrm{eig}(\mathbf{K})$$

This gives a unitary matrix $\mathbf{V}$ and a diagonal matrix $\mathbf{D}$ such that[3]

$$\mathbf{K} = \mathbf{V}\,\mathbf{D}\,\mathbf{V}^T$$

The diagonal entries of $\mathbf{D}$ are eigenvalues ($\lambda_i = D_{ii}$) of matrix $\mathbf{K}$ and the columns of matrix $\mathbf{V}$ are the corresponding eigenvectors. Using matrix $\mathbf{V}$, we can define a coordinate transform

$$\tilde{q}_i = \sum_{j=1}^{3N} V_{ji}(q_j - q_j^0)\,, \quad \tilde{p}_i = \sum_{j=1}^{3N} V_{ji}p_j \tag{21}$$

The fact that $\mathbf{V}$ is a unitary matrix ensures that $\tilde{p}_i$ is still the conjugate momentum of $\tilde{q}_i$. The Hamiltonian can be rewritten in terms of the new variables, (for more details see Appendix A),

$$H(\{\tilde{q}_i\},\{\tilde{p}_i\}) = -N\,E_{\rm coh} + \sum_{i=1}^{3N} \frac{1}{2}\lambda_i \tilde{q}_i^{\,2} + \frac{\tilde{p}_i^{\,2}}{2m} \tag{22}$$

Now the Hamiltonian is identical to that of a set of independent harmonic oscillators (each with a different spring constant λ_i and vibration frequency ω_i). The distribution of vibration frequencies give rise to the "density of states" of a solid (see Reif p.410, Fig.10.1.1.). The partition function can be integrated analytically to give the Helmholtz free energy,[4]

$$A = -NE_{\rm coh} - k_BT\sum_{i=1}^{3N} \ln\frac{k_BT}{\hbar\omega_i}\,, \quad \text{where} \quad \omega_i \equiv \sqrt{\frac{\lambda_i}{m}} \tag{23}$$

Q: There are three modes (oscillators) with $\lambda_i = 0$, and hence $w_i = 0$. Why? What shall we do with them?

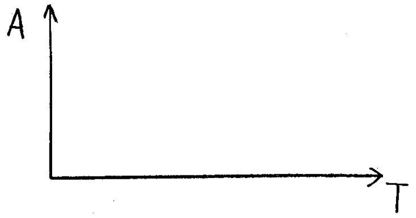
---

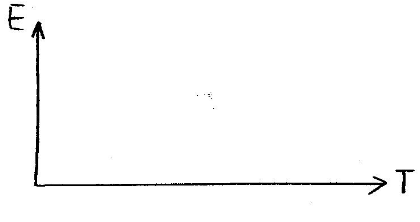
[3] A unitary matrix has the property that $\mathbf{V}^T = \mathbf{V}^{-1}$. A diagnoal matrix has the property that $D_{ij} = 0$ if $i \neq j$.

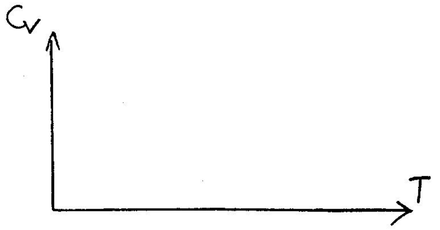
[4] When quantum effects are included, this model (independent oscillators with a distribution of vibration frequencies) gives a better description of the specific heat c_v of solid as a function of temperature T in the low T limit than the Einstein model (independent oscillators all having the same frequency). See Reif. p.416, Fig.10.2.2.

Heat capacity of Solids

Reif 10.1-10.2







$$U(\{q_i\}) = -NE_{coh} + \frac{1}{2}\sum_{ij} K_{ij}(q_i - q_i^0)(q_j - q_j^0) + \cdots$$

diagonalize Hessian matrix K

$$K = VDV^T \qquad D = \begin{pmatrix} \lambda_1 & & 0 \\ & \ddots & \\ 0 & & \lambda_{3N} \end{pmatrix}$$

$$\hat{q}_i = \sum V_{ij}(q_j - q_j^0), \quad \hat{p}_i = \sum V_{ij} p_j$$

$$H(\hat{q}_i, \hat{p}_i) = -NE_{coh} + \sum_{i=1}^{3N} \frac{1}{2}\lambda_i \hat{q}_i^2 + \frac{\hat{p}_i^2}{2m}$$

$$A = -NE_{coh} - k_B T \sum_{i=1}^{3N} \ln \frac{k_B T}{\hbar \omega_i}$$

(* typo in Lecture note 10. Eq.(23))

$$\hbar = \frac{h}{2\pi}. \quad \omega_i = \sqrt{\frac{\lambda_i}{m}} \quad \text{(angular frequency)}$$

$$\nu_i = \frac{\omega_i}{2\pi}$$

$$\hbar\omega_i = h\nu_i$$

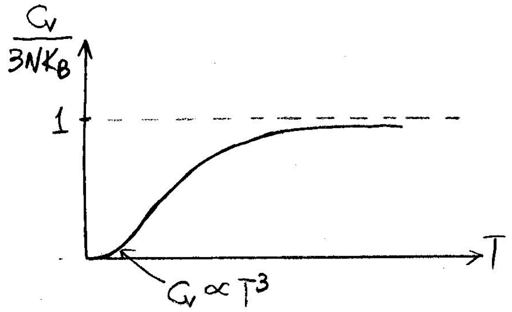
$dA = -SdT - pdV + \mu dN$

$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} =$ ____________

$E = A + TS =$ ____________

$E = \langle H \rangle =$ ____________

$C_V = \frac{\partial E}{\partial T} =$ ____________

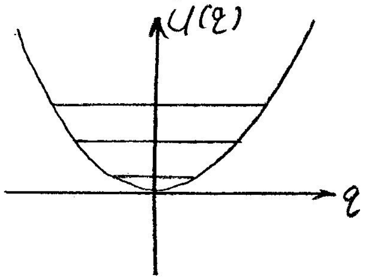


experimental data of heat capacity

what went wrong?

Quantum mechanics:

energy of a harmonic oscillator is quantized.



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

$$\varepsilon_n = \left(n+\tfrac{1}{2}\right)\hbar\omega \qquad \omega = \sqrt{\frac{K}{m}}$$

$$n = 0, 1, 2, \cdots$$

$\varepsilon_0 = \frac{1}{2}\hbar\omega$: zeropoint energy

classical mechanics

$$Z = \frac{1}{h}\int dq\,dp\; e^{-\beta\left(\frac{p^2}{2m}+\frac{1}{2}Kq^2\right)}$$

$$= \frac{1}{h}\sqrt{2\pi m k_B T}\cdot\sqrt{\frac{2\pi k_B T}{K}}$$

$$= \frac{2\pi}{h}k_B T\cdot\sqrt{\frac{m}{K}}$$

$$= \frac{k_B T}{\hbar\omega} \qquad \omega \equiv \sqrt{\frac{K}{m}}$$

$$A = -k_B T \ln Z$$

$$= -k_B T \ln\frac{k_B T}{\hbar\omega}$$

$E =$

____

$C_v =$

____

Quantum mechanics

$$Z = \sum_{n=0,1,2,\cdots} e^{-\beta\varepsilon_n}$$

$$= \sum_n e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

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

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

$$A = -k_B T \ln Z$$

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

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

In the limit of $T\to\infty$, $\beta\to 0$, $e^{-\beta\hbar\omega} \approx 1 - \frac{\hbar\omega}{k_B T}$

$$A \to \underset{\substack{\uparrow \\ \text{zero point} \\ \text{energy}}}{\frac{\hbar\omega}{2}} + k_B T\ln\frac{\hbar\omega}{k_B T} \approx A^{\text{classical}}$$

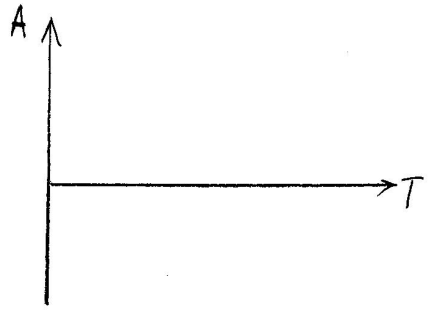
$$E = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\left(-\frac{1}{2}\beta\hbar\omega - \ln(1-e^{-\beta\hbar\omega})\right)$$

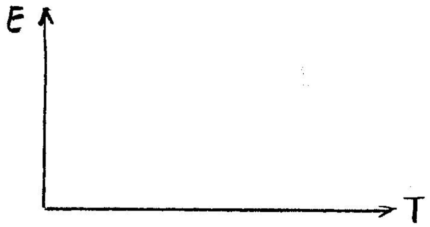
$=$

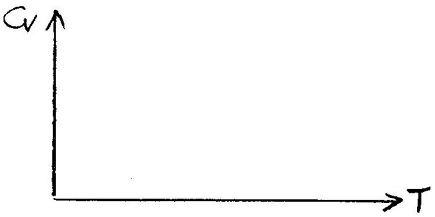
____

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = -k_B\beta^2\left(\frac{\partial E}{\partial\beta}\right)_v =$$

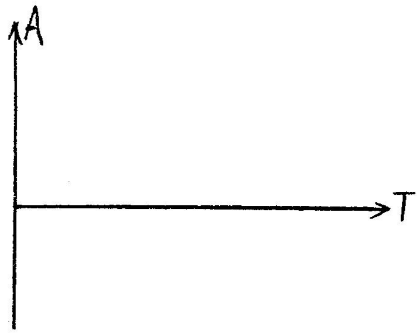
Classical mechanics

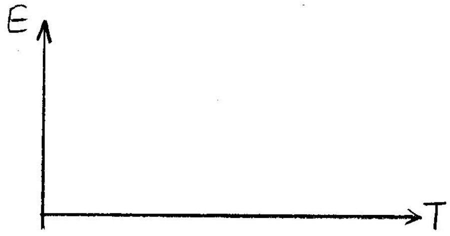


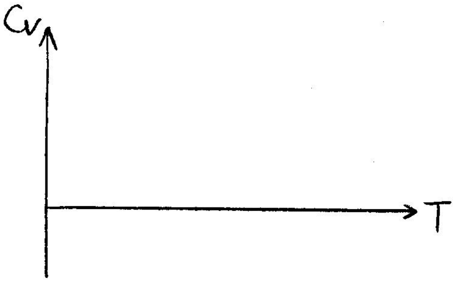




Quantum mechanics







Einstein model for solids.

3N harmonic oscillators all having the same frequency ω_E

$A =$ ________________ (Q.M.)

$E =$ ________________

$C_V =$ ________________

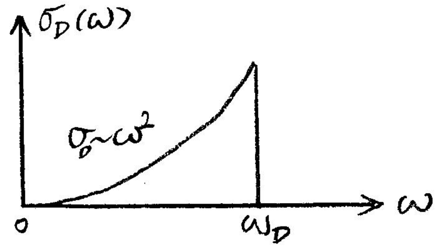
captures qualitative trend of $C_V \to 0$ at $T \to 0$

but $C_V \to 0$ too fast (exponential, instead of T^3).

what's wrong?

Debye model

vibrations in solid do not all have the same frequency.



density of states

$$\sigma_D = \begin{cases} \frac{3V}{2\pi^2 c_s^3}\,\omega^2 & \omega < \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

Debye frequency $\omega_D = \underset{\substack{\uparrow \\ \text{sound} \\ \text{velocity}}}{c_s} \left(6\pi^2 \frac{N}{V}\right)^{1/2}$

$$C_V = \int_0^{\omega_D} \sigma_D(\omega) \cdot C_V(\omega)\, d\omega$$

$$= \int_0^{\omega_D} \frac{3V}{2\pi^2 c_s^3} \cdot \omega^2 \cdot \underline{\qquad\qquad}\ d\omega$$

$\propto T^3$ $(T \to 0)$

A Decoupling of harmonic oscillators

In this appendix, we prove that the diagonalization of matrix $\mathbf{K}$ indeed leads a set of decoupled harmonic oscillators by coordinate transformation. In component forms, the relation $\mathbf{K} = \mathbf{V}\mathbf{D}\mathbf{V}^T$ can be written as,

$$K_{ij} = \sum_{k=1}^{3N} V_{ik}\, \lambda_k\, V_{jk} \tag{24}$$

Substitute that into Eq. (20), we obtain,

$$U(\{q_i\}) \;=\; -N\,E_{\text{coh}} + \frac{1}{2}\sum_{i,j=1}^{3N}\sum_{k=1}^{3N} V_{ik}\,\lambda_k\,V_{jk}(q_i - q_i^0)(q_j - q_j^0) \tag{25}$$

Define

$$\tilde{q}_k \equiv \sum_{i=1}^{3N} V_{ik}\,(q_i - q_i^0) \tag{26}$$

then

$$U(\{q_i\}) \;=\; -N\,E_{\text{coh}} + \frac{1}{2}\sum_{k=1}^{3N} \tilde{q}_k\,\lambda_k\,\tilde{q}_k \tag{27}$$

which is equivalent to the potential energy part of Eq. (22).

To evaluate the kinetic energy in the new coordinates, we notice that $\mathbf{V}$ is a unitary matrix, i.e. $\mathbf{V}^T\mathbf{V} = \mathbf{I}$. In component form, this means,

$$\sum_{k=1}^{3N} V_{ik}\, V_{jk} = \delta_{ij} \tag{28}$$

where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$. Hence the kinetic energy is

$$E_{\rm kin} \;=\; \sum_{i,j=1}^{3N} \frac{p_i\, p_j\, \delta_{ij}}{2m} = \frac{1}{2m} \sum_{i,j=1}^{3N} \sum_{k=1}^{3N} p_i\, V_{ik}\, V_{jk}\, p_j$$

Define

$$\tilde{p}_k \equiv \sum_{i=1}^{3N} V_{ik}\, p_i \tag{29}$$

then

$$E_{\rm kin} \;=\; \frac{1}{2m} \sum_{k=1}^{3N} \tilde{p}_k\, \tilde{p}_k \tag{30}$$

which is equivalent to the kinetic energy part of Eq. (22).

References

1. G. Marc and M. G. McMillian, *The Virial Theorem*, Adv. Chem. Phys. **58**, 209-361 (1985).
2. Barker, Leonard, Pompe, *Fifth Virial Coefficient*, J. Chem. Phys. **44**, 4206 (1964).

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 11. Applications to Fluids

February 23, 2011

Contents

In this lecture, we will discuss fluids beyond the ideal gas limit. This means we need to account for interactions between molecules. Unlike the case of solid, we cannot remove the interactions between different degrees of freedom simply from a coordinate transformation. Instead, techniques have been developed to account for the interactions as a perturbation to the non-interacting system.

Reading assignment: Reif §10.3-10.5.

1 Ideal gas model review

In the limit of temperature going to infinity and density goes to zero, all gases can be well described by the ideal gas model with the well-known equation of state,

$$pV = Nk_BT \tag{1}$$

For simplicity, we are considering mono-atomic gas molecules and N is the total number of gas molecules. Eq. (1) is not the most fundamental form of the equation of state, in the sense that from it we cannot derive all thermodynamic properties of the ideal gas.

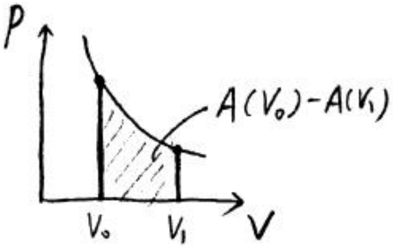
One of the fundamental form of the equation of state is,

$$A(T,V,N) = -Nk_BT\left[\ln\left(\frac{V}{N\Lambda^3}\right)+1\right] = Nk_BT\left[\ln\left(\rho\Lambda^3\right)-1\right] \tag{2}$$

where $\Lambda \equiv h/\sqrt{2\pi m k_B T}$ is the de Broglie wavelength at temperature T and $\rho \equiv N/V$ is the density. From Eq. (2) we can derive Eq. (1) easily by following the definition of pressure,

$$p \equiv -\left(\frac{\partial A}{\partial V}\right)_{N,T} = -\frac{Nk_BT}{V} \tag{3}$$

However, it is impossible to derive Eq. (2) from Eq. (1) alone.



We can give it a try by writing,

$$A(T,V_1,N) - A(T,V_0,N) = \int_{V_0}^{V_1}\frac{\partial A}{\partial V}\,dV = -\int_{V_0}^{V_1} p\,dV \tag{4}$$

Using Eq. (1) we have

$$A(T,V_1,N) - A(T,V_0,N) = -Nk_BT\int_{V_0}^{V_1}\frac{1}{V}dV = -Nk_BT\ln\frac{V_1}{V_0} \tag{5}$$

In other words,

$$A(T,V,N) = -Nk_BT\ln\frac{V}{h(N,T)} \tag{6}$$

where h is some arbitrary function of N and T. Hence the result is consistent with Eq. (2), but more information (such as heat capacity) is needed to uniquely determine the function $h(N,T)$.

2 Van der Waals model

With decreasing temperature and increasing density, all gases exhibit deviation from the ideal gas model. The Van der Waals model is an interesting phenomenological model that tries to capture the main physical effects responsible for the deviation from the ideal gas model. It tries to capture two main features of the interactions between two gas molecules. First, two molecules repel each other strongly when they get too close to each other. (This is mainly caused by the electrons on both molecules that are forbidden to take the same quantum state according to the Pauli's exclusion principle.) Hence we can think of molecules as tiny solid spheres each having a non-zero exclusion volume. Second, two molecules attract each other when they are far apart. (This is caused by the fluctuating electric dipole moment of each molecule. The interaction is called Van der Waals interaction and interaction energy scales as r^{-6} where r is the distance between two molecules.)

The p-V relation of the Van der Waals model of a non-ideal gas is,

$$\left(p + \frac{N^2\,a}{V^2}\right)(V - N\,b) = N\,k_B\,T \tag{7}$$

where $a > 0$ and $b > 0$ are two empirical constants. Equivalently, we have

$$p = \frac{Nk_BT}{V - Nb} - \frac{N^2a}{V^2} \tag{8}$$

b can be thought of as the exclusion volume of each gas molecule, so that the available volume for the gas molecules to wiggle around is reduced to $V - Nb$. a is supposed to capture the mutual attraction between the molecules, which should reduce the pressure exerted on the wall of the gas tank. Because the attraction is between every pair of molecules, the reduction of the pressure should be proportional to the square of density (in the limit of low density), hence the term $-N^2a/V^2$.

A fundamental form of the equation of state of the Van der Waals model is

$$A(T, V, N) = -Nk_BT\left[\ln\left(\frac{V - Nb}{N\Lambda^3}\right) + 1\right] - \frac{N^2\,a}{V} \tag{9}$$

Again, we can derive Eq. (8) from Eq. (9) but not vice versa.

3 Virial expansion

The Van der Waals model captures several important physical aspects of a real fluid (such as the transition between the liquid and vapor phases below a critical temperature, to be discussed later). However, the behavior of a real fluid is not necessarily described very accurately by the (two-parameter) Van der Waals model. The Virial expansion is a more systematic approach to describe the deviation of a real gas from an ideal gas. Define particle density $\rho \equiv N/V$, then the ideal gas satisfies the relation

$$\frac{p}{k_B T} = \rho \tag{10}$$

One way to generalize this (ideal gas) law is to add higher order terms of ρ to the right hand side. The resulting expression is called the **Virial expansion**.

$$\frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots \tag{11}$$

where $B_2(T), B_3(T), \cdots$ are called **Virial coefficients**. In the limit of $\rho \to 0$, the leading term (ρ) dominates the right hand side, and the ideal gas is recovered, as it should.

The Van der Waals equation of state, Eq. (8) can be rewritten in the form of Virial expansion.

$$\begin{aligned}
p &= \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2} \\
\frac{p}{k_B T} &= \frac{N}{V - Nb} - \frac{N^2 a}{V^2 k_B T} \\
&= \frac{\rho}{1 - b\rho} - \frac{a}{k_B T}\rho^2 \\
&= \rho\,(1 + b\rho + b^2\rho^2 + b^3\rho^3 + \cdots) - \frac{a}{k_B T}\rho^2 \\
&= \rho + \left(b - \frac{a}{k_B T}\right)\rho^2 + b^2\rho^3 + b^3\rho^4 + \cdots \qquad (12)
\end{aligned}$$

Hence

$$\begin{aligned}
B_2(T) &= b - \frac{a}{k_B T} \qquad (13) \\
B_3(T) &= b^2 \qquad (14) \\
B_4(T) &= b^3 \qquad (15) \\
&\cdots
\end{aligned}$$

Of course, the Virial coefficients of a real gas does not need to have the same form as above, which only holds for the Van der Waals model.

Q: Can we find the Helmholtz free energy $A(N, V, T)$ (i.e. the fundamental equation of state) of a non-ideal gas given its Virial expansion coefficients?

A: The answer is yes. This may sound strange because in the previous two sections we said that from the p-V relation alone it is impossible to completely determine the $A(N, V, T)$

function. However, now that the $A(N,V,T)$ function for an ideal gas is already known, we can use it to our advantage to determine the $A(N,V,T)$ function for an non-ideal gas.

All we need to do is to determine the Helmholtz free energy difference between the non-ideal (real) gas and the ideal gas, i.e.,

$$\Delta A(N,V,T) \equiv A^{\mathrm{real.gas}}(N,V,T) - A^{\mathrm{ideal.gas}}(N,V,T) \tag{16}$$

$$\begin{aligned}
\Delta A(T,V_1,N) - \Delta A(T,V_0,N) &= -\int_{V_0}^{V_1} (p^{real.gas} - p^{ideal.gas}) dV \\
&= -\int_{V_0}^{V_1} k_B T \left(\frac{B_2 N^2}{V^2} + \frac{B_3 N^3}{V^3} + \cdots \right) dV \\
&= \int_{V_1}^{V_0} k_B T \left(\frac{B_2 N^2}{V^2} + \frac{B_3 N^3}{V^3} + \cdots \right) dV
\end{aligned} \tag{17}$$

Notice that at constant N and T, a real gas goes to the ideal gas limit as $V \to \infty$. Hence

$$\lim_{V\to\infty} \Delta A(T,V,N) = 0 \tag{18}$$

$$\begin{aligned}
\Delta A(T,V_1,N) &= \int_{V_1}^{\infty} k_B T \left(\frac{B_2 N^2}{V^2} + \frac{B_3 N^3}{V^3} + \cdots \right) dV \qquad (19) \\
&= k_B T \left(\frac{B_2 N^2}{V_1} + \frac{B_3 N^3}{2V_1^2} + \cdots \right) \\
\Delta A(T,V,N) &= N k_B T \left(\frac{B_2 N}{V} + \frac{B_3 N^2}{2V^2} + \frac{B_4 N^3}{3V^3} + \cdots \right) \qquad (20) \\
&= N k_B T \left(B_2\, \rho + \frac{1}{2} B_3\, \rho^2 + \frac{1}{3} B_4\, \rho^3 + \cdots \right) \qquad (21)
\end{aligned}$$

Hence the Helmholtz free energy of a real gas described by the Virial coefficients $B_2(T), B_3(T), \cdots$ is,

$$A(T,V,N) = N k_B T \left[\ln\left(\rho \Lambda^3\right) - 1 + B_2(T)\, \rho + \frac{1}{2} B_3(T)\, \rho^2 + \frac{1}{3} B_4(T)\, \rho^3 + \cdots \right] \tag{22}$$

Adding this to the ideal gas Helmholtz free energy, we obtain the Helmholtz free energy of a real gas in terms of Virial expansion coefficients.

Q: What is the energy E of the gas? [Hint: $S \equiv -\left(\frac{\partial A}{\partial T}\right)_{V,N}$, $E = A + TS$.]

Q: What is the chemical potential of the gas?

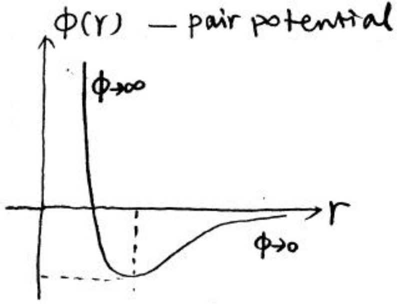
4 Virial coefficients from molecular interactions

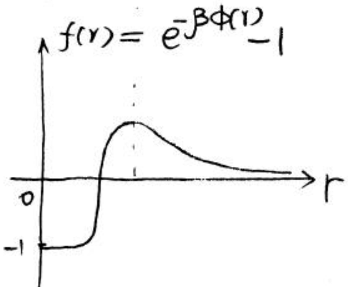
So far all of our discussions are still phenomenological. For example, we can consider the Virial coefficients $B_2(T), B_3(T), \cdots$ as empirical functions to characterize the experimental p-V curves of a non-ideal gas. However, to gain a fundamental understanding of the behavior of a non-ideal gas, we would like to be able to derive the Virial coefficients from the interaction potentials between the gas molecules.

We can often assume that the potential energy of a (non-ideal) gas can be written as a sum over all pair-wise interactions between the gas molecules

$$U^{\text{int}}(\{\mathbf{r}_i\}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(r_{ij}) \,, \tag{23}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between molecules i and j. The function $\phi(r)$ describes the interaction energy between two molecules as a function of their separation distance r. Typically, $\phi \to +\infty$ as $r \to 0$, $\phi \to 0$ as $r \to \infty$, and ϕ exhibits a minimum between these two limits, as shown below.





In this section, we will show that the Virial coefficients can indeed be expressed in terms of function $\phi(r)$. Specifically, the second Virial coefficient is

$$B_2(T) = -2\pi \int_0^\infty \left[\mathrm{e}^{-\beta\phi(r)} - 1 \right] r^2 \, \mathrm{d}r \tag{24}$$

Higher order Virial coefficient can also be derived (Barker 1964).

This means that the p-V curve measurements can tell us something about the inter-molecular interaction and vice versa.

First, we can write down the explicit expression of the Hamiltonian for a tank of gas with inter-molecular potential function $\phi(r)$,

$$\begin{aligned} H(\{q_i\},\{p_i\}) &= \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{\mathbf{r}_i\}) \\ &= \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N} U^{\mathrm{ext}}(\mathbf{r}_i) \end{aligned} \tag{25}$$

where $U^{\mathrm{ext}}(\mathbf{r}_i)$ is introduced to describe the confining effect of the gas container.

In order to derive the second Virial coefficient B_2 (or for anything else really), we start with the partition function in the canonical ensemble.

$$Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta\left(\sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{\mathbf{r}_i\})\right)}$$

The integrals over the momenta can be performed analytically (just in the case of the ideal gas), so that,

$$Z = \frac{1}{N! \Lambda^{3N}} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \, \mathrm{e}^{-\beta U(\{\mathbf{r}_i\})} \tag{26}$$

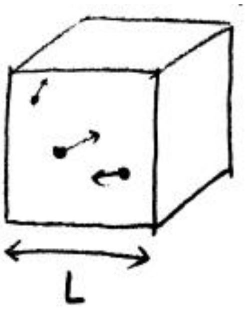
Define

$$Z_u \equiv \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \, \mathrm{e}^{-\beta U(\{\mathbf{r}_i\})}$$

then

$$Z = \frac{Z_u}{N! \Lambda^{3N}} \tag{27}$$

Recall that for an ideal gas, $Z_u = V^N$, hence $Z = \frac{V^N}{N!\Lambda^{3N}}$, leading to Eq. (2).



To get rid of the inconvenient potential from the container $U^{\mathrm{ext}}(r)$, we can assume the gas molecules are subjected to the periodic boundary conditions (PBC) in a cube of length L

$$V = L^3 \tag{28}$$

When there is no interaction between atoms, this directly give us $Z_u = V^N$. When there is pair interaction between gas molecules

$$U(\{\mathbf{r}_i\}) = \sum_{i<j} \phi(r_{ij}) \,, \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \tag{29}$$

Therefore

$$Z_u = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \exp(-\beta U) \tag{30}$$

$$\exp(-\beta U) = \prod_{i<j} \exp(-\beta\phi(r_{ij})) \tag{31}$$

$$= \prod_{i<j} (1 + f(r_{ij})) \tag{32}$$

where we have defined $f(r_{ij}) \equiv \mathrm{e}^{-\beta\phi(r_{ij})} - 1$.

Next we expand the product and write down all the terms...

$$\prod_{1\le i<j\le N} (1+f(r_{ij})) = 1 + \sum_{i<j} f(r_{ij}) + \sum_{i<j}\sum_{k<l} f(r_{ij}) f(r_{kl}) + \cdots$$

$$\frac{Z_u}{V^N} = \frac{1}{V^N} \int d^3\underset{\sim}{r_1} \cdots d^3\underset{\sim}{r_N} \cdot 1$$

$$+ \frac{1}{V^N} \int d^3\underset{\sim}{r_1} \cdots d^3\underset{\sim}{r_N} \cdot \sum_{i<j} f(r_{ij})$$

$$+ \frac{1}{V^N} \int d^3\underset{\sim}{r_1} \cdots d^3\underset{\sim}{r_N} \cdot \sum_{i<j}\sum_{k<l} f(r_{ij}) f(r_{kl})$$

$$+ \cdots$$

(# of pairs $(i,j) = \frac{N(N-1)}{2}$

$$\frac{Z_u}{V^N} = 1 + \frac{N(N-1)}{2V^2}\int d^3\underset{\sim}{r_1}\, d^3\underset{\sim}{r_2}\, f(r_{12}) + \cdots$$

$$= 1 + \frac{N(N-1)}{2V}\int d^3\underset{\sim}{r}\, f(r) + \cdots \qquad r = |\underset{\sim}{r}|$$

$$= 1 + \frac{N(N-1)}{2V}\int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots$$

$$Z = \frac{Z_u}{N!\Lambda^3} = \frac{V^N}{N!\Lambda^3}\left(1 + \frac{N(N-1)}{2V}\int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots\right)$$

$$= Z^{\text{ideal.gas}} \cdot \left(1 + \frac{N(N-1)}{2V}\int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots\right)$$

$$A = -k_B T \ln Z$$

$$\Delta A = A - A^{\text{ideal.gas}} = -k_B T \ln\left(1 + \frac{N(N-1)}{2V}\int_0^\infty dr\, 4\pi r^2 f(r) + \cdots\right)$$

$$= -\frac{N k_B T (N-1)}{2V}\int_0^\infty dr\, 4\pi r^2 f(r) + \cdots$$

$$\approx -N k_B T \rho \int_0^\infty dr\, 2\pi r^2 f(r) + \cdots \qquad (N-1 \simeq N \text{ as } N \to \infty)$$

Compare this with earlier expression

$$\Delta A(T, V, N) = N k_B T \left(B_2(T)\,\rho + \frac{1}{2} B_3(T) \rho^2 + \cdots \right) \tag{33}$$

We have

$$\begin{aligned} B_2(T) &= -2\pi \int_0^\infty f(r)\, r^2 dr \\ &= -2\pi \int_0^\infty [\mathrm{e}^{-\beta\phi(r)} - 1]\, r^2 dr \end{aligned} \tag{34}$$

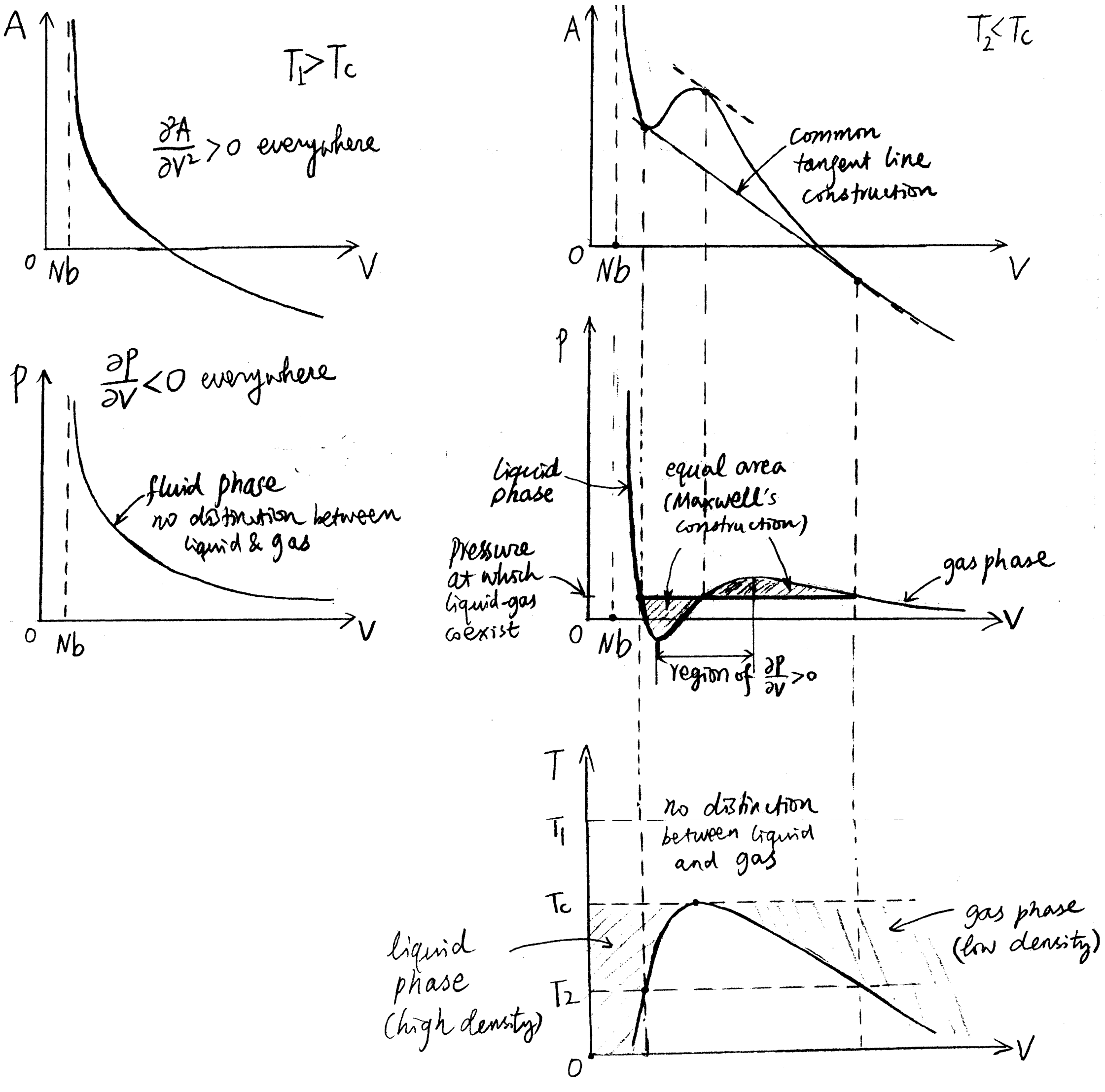
Higher order Virial coefficient can be obtained similarly — the approach is called cluster expansion. The math will become horrendous by the time you get to the 5th Virial coefficient but it can be done [2].

5 Liquid-gas phase transition

The Van der Waals model is important because it is a simple model that captures the transition between the liquid and gas phases (vaporization and condensation). This can be seen by plotting the Helmhotz free energy and pressure of the Van der Waals model as a function of V at constant T. (Download `plotvanderwaals.m` from coursework.)

$$\begin{aligned} A(T,V,N) &= -Nk_BT\left[\ln\left(\frac{(V-Nb)}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right)+1\right]-\frac{N^2a}{V} \\ p &= -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V-Nb}-\frac{N^2a}{V^2} \end{aligned}$$

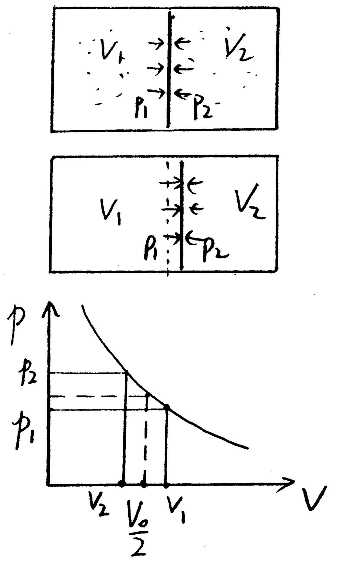
The model exhibits two different behaviors when T is above or below a critical temperature T_c, where $k_BT_c = \frac{8a}{27b}$. When $T > T_c$, the Van der Waals model behaves like one homogeneous fluid. When $T < T_c$, the model exhibits a distinction between two phases: a gas phase at large V and a liquid phase at small V, and a phase transition between the two.



Observations: There exist a critical temperature T_c.

- When $T > T_c$, the $A(V)$ curve is convex ($\frac{\partial^2 A}{\partial V^2} > 0$) everywhere. Correspondingly, the $p(V)$ curve has negative slope everywhere.
- When $T < T_c$, the $A(V)$ curve has concave regions ($\frac{\partial^2 A}{\partial V^2} < 0$). Correspondingly, the $p(V)$ curve has positive slope there.

A <u>convex</u> free energy is required for the <u>stability</u> of a homogeneous phase.



Consider a tank of gas with volume V_0 that has reached thermal equilibrium.

Now let us introduce a piston that separate the gas tank into two halves.

The gases on both sides of the piston can be described by the same $p(V)$ curve.

Initially, both of them have the same volume $V_1 = V_2 = V_0/2$.

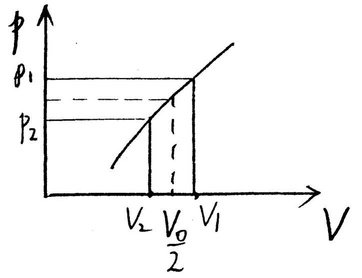
Hence they have the same pressure $p_1 = p_2$.

Now imagine a small perturbation on the position of the piston, such that

$$V_1 = \frac{V_0}{2} + \delta V\,, \quad V_2 = \frac{V_0}{2} - \delta V\,, \quad \delta V > 0$$

If $\frac{\partial^2 A}{\partial V^2} > 0$, $\frac{\partial p}{\partial V} < 0$, then $p_1 < p_2$. Therefore, there is a net force to the left, which pushes the piston <u>back</u> to its original position. In this case, we say that the system is <u>stable</u> against the perturbation.

What happens if $\frac{\partial^2 A}{\partial V^2} < 0$, $\frac{\partial p}{\partial V} > 0$?

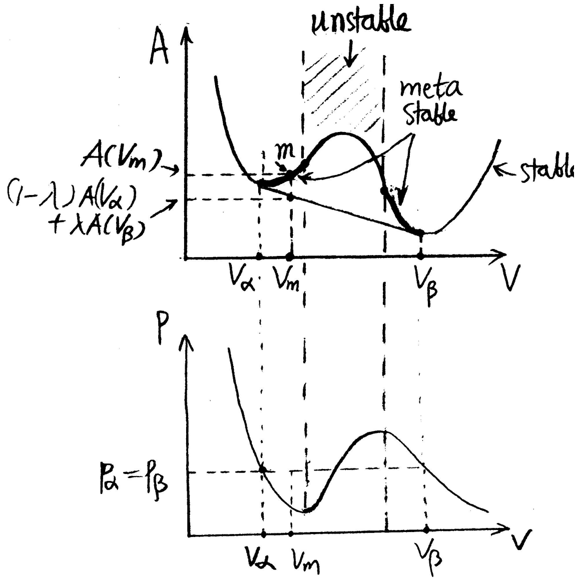


Then we will have $p_1 > p_2$. There is a net force to the right, pushing the piston <u>further away</u> from its original positions.

In this case, the system is <u>unstable</u> against the perturbation.

Q: Is this really bad if the position of the piston is unstable?

Yes! The piston is only imaginary. If $\frac{\partial p}{\partial V} > 0$, then a spontaneous density fluctuation somewhere inside the gas tank will always get amplified. The denser region will get even denser, the more dilute region will get even more dilute. In other words, the original homogeneous phase is <u>unstable</u> against spontaneous separation into <u>two phases</u> — a denser liquid phase and a more dilute gas phase.



Even if locally $\frac{\partial^2 A}{\partial V^2} > 0$, the phase is not necessarily stable.

For example, consider point m, whose voluem is V_m. According to the $A(V)$ curve, the free energy at V_m is $A(V_m)$.

Now consider a common tangent line touching the $A(V)$ curve at V_α and V_β. Let $V_m = (1-\lambda)V_\alpha + \lambda V_\beta$ ($\lambda > 0$).

Claim: A gas at volume V_m (density $\rho_m = N/V_m$) is thermodynamically unstable against separation into two phases: one phase having density $\rho_\alpha = N/V_\alpha$, the other phase having density $\rho_\beta = N/V_\beta$.

From Eq. (9), the Helmholtz free energy per molecule of the Van der Waals model can be expressed as a function of density $\rho = N/V$,

$$\frac{A(T,V,N)}{N} = -k_B T \left[\ln\left(\frac{1}{\rho\Lambda^3} - \frac{b}{\Lambda^3} \right) + 1 \right] - \rho\, a \tag{35}$$

Let us compute the free energy of a mixture of two phases (at density ρ_α and ρ_β) and compare it with the free energy of a homogeneous phase (at density ρ_m).

Let $\tilde{N}_\alpha$, $\tilde{N}_\beta$ be the number of molecules in phase α, β.

Let $\tilde{V}_\alpha$, $\tilde{V}_\beta$ be the volume occupied by phase α, β.

$$\begin{aligned}
\tilde{N}_\alpha + \tilde{N}_\beta &= N \\
\tilde{V}_\alpha + \tilde{V}_\beta &= V_m \\
\frac{\tilde{N}_\alpha}{\tilde{V}_\alpha} = \frac{N_\alpha}{V_\alpha} &= \rho_\alpha \\
\frac{\tilde{N}_\beta}{\tilde{V}_\beta} = \frac{N_\beta}{V_\beta} &= \rho_\beta
\end{aligned}$$

Hence

$$\begin{aligned}
\tilde{N}_\alpha &= (1-\lambda)\,N \\
\tilde{V}_\alpha &= (1-\lambda)\,V_\alpha \\
\tilde{N}_\beta &= \lambda\,N \\
\tilde{V}_\beta &= \lambda\,V_\beta
\end{aligned} \tag{36}$$

The Helmholtz free energy of the two phase mixture is

$$\begin{aligned}
& A(T,\tilde{V}_\alpha,\tilde{N}_\alpha) + A(T,\tilde{V}_\beta,\tilde{N}_\beta) \\
= \;& (1-\lambda)\,A(T,V_\alpha,N) + \lambda\,A(T,V_\beta,N) \\
< \;& A(T,V_m,N) \quad \text{(free energy of the homogeneous phase)}
\end{aligned} \tag{37}$$

Hence the fluid (starting from a homogenous phase at density ρ_m) can lower its Helmholtz free energy by breaking into two phases (with densities ρ_α and ρ_β). From second law of Thermodynamics, this shall happen spontaneously and is a irreversible process.

Hence for $T < T_c$, the Van der Waals fluid consists of a single phase only if $V \leq V_\alpha$ (liquid) or $V \geq V_\beta$ (gas). It is a mixture of two phases if $V_\alpha < V < V_\beta$.

For $T > T_c$, the Van der Waals fluid consists of a single phase at all volume (or density).

References

1. Barker, Leonard, Pompe, *Fifth Virial Coefficient*, J. Chem. Phys. **44**, 4206 (1964).

ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011

Handout 12. Ising Model

February 25, 2011

Contents

A major topic of interest in statistical mechanics (and in physics in general) is the understanding of phase transitions (e.g. freezing of water to form ice), which requires the study of interacting models.

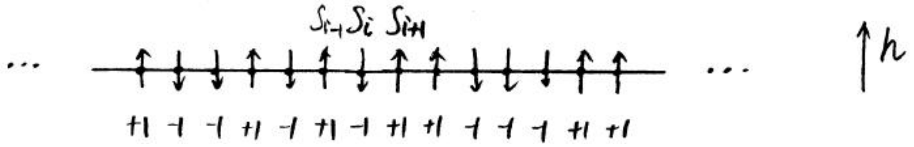
The 2-dimensional (2D) Ising model (see front page image on coursework) is one of the few interacting models that have been solved analytically (by Onsager, who found the expression of its partition function). It turns out that the 2D Ising model exhibits a phase transition. The analytic and numerical solutions of the Ising model are important landmarks in the field of statistical mechanics. They have significantly influenced our understanding of phase transitions.

We will first discuss the simpler 1-dimensional (1D) Ising model, whose analytic solution is easier to obtain. This will pave the road to the discussion of the 2D Ising model which comes next.

Reading assignment: Sethna p.163-165. Reif Chapter 10.

1 Definition of Ising model

Ising (Z. Physik, 31, 253, 1925) introduced a model consisting of a lattice of "spin" variables s_i, which can only take the values $+1$ ($\uparrow$) and -1 ($\downarrow$). Every spin interacts with its nearest neighbors (2 in 1D) as well as with an external magnetic field h.



The Hamiltonian[1] of the Ising model is

$$H(\{s_i\}) = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i \tag{1}$$

The sum $\langle i,j \rangle$ is over nearest neighbors ($j = i \pm 1$ in 1D).

J is a constant specifying the strength of interaction. The Ising model is usually studied in the canonical ensemble. (It would be a nightmare to do it in the microcanonical ensemble.)

In the canonical ensemble, the probability of finding a particular spin configuration $\{s_i\}$ is,

$$p(\{s_i\}) = \frac{1}{Z} \exp(-\beta H(\{s_i\})), \quad \beta \equiv \frac{1}{k_B T} \tag{2}$$

where $Z = \sum_{\{s_i\}} \exp(-\beta H(\{s_i\}))$ is the partition function. Due to the Boltzmann factor, $e^{-\beta H}$, spin configurations with lower energies will be favored.

We can now discuss the effect of J and h on the behavior of the spins.

- when $h > 0$, $s_i = +1$ is favored.
- when $h < 0$, $s_i = -1$ is favored.

This means that the spins wants to align with the direction of h.

---

[1] Here the Hamiltonian is no longer a function of coordinate q_i and momentum p_i, as in the case of classical mechanics. We still call H the Hamiltonian because it represents the total energy of the Ising model.

- when $J > 0$, neighboring spins prefer to be parallel, e.g. $s_i = +1$ and $s_{i+1} = +1$, or $s_i = -1$ and $s_{i+1} = -1$. (This is called the *ferromagnetic model.*)
- when $J < 0$, neighboring spins prefer to be anti-parallel, e.g. $s_i = +1$ and $s_{i+1} = -1$, or $s_i = -1$ and $s_{i+1} = +1$. (This is called the *anti-ferromagnetic model.*)

At low enough temperature, all spins in the 2D Ising model will “cooperate” and spontaneously align themselves (e.g. most spins become +1) even in the absence of the external field ($h = 0$). This phenomenon is called *spontaneous magnetization.*

At high enough temperatures, the spontaneous magnetization is destroyed by thermal fluctuation. Hence the 2D Ising model has a critical temperature T_c, below which there is spontaneous magnetization and above which there isn’t. In other words, there is a phase transition at T_c.

Unfortunately this doesn’t occur in the 1D Ising model. The 1D Ising model *does not* have a phase transition. We are discussing it here just to “warm up” for the discussion of the 2D Ising model.

The term “spin” and “magnetic field” in the Ising model originate from its initial application to the phenomenon of *spontaneous magnetization* in ferromagnetic materials such as iron. Each iron atom has a unpaired electron and hence a net spin (or magnetic moment). At low temperature, the spins spontaneously align giving rise to a non-zero macroscopic magnetic moment. The macroscopic magnetic moment disappears when the temperature exceeds the Curie temperature (1043 K for iron). (See `http://en.wikipedia.org/wiki/Ferromagnetic` for more details.) As we will see later, the Ising model can be applied to many other problems beyond magnetism, such as phase separation in binary alloys and crystal growth.

2 Solving the 1D Ising model

Q: What do we mean by solving the Ising model?

A: We are really after the partition function Z, as a function of J and h. If we have the analytic expression for Z, we can easily obtain all thermodynamic properties of the Ising model.

2.1 Non-interacting model ($J = 0$)

Let us first consider the simpler case of $J = 0$ ($h \neq 0$). This is a non-interacting model. It is the same as the two-level systems we have considered in the canonical ensemble section!

$$\begin{aligned} Z &= \sum_{\{s_i\}} e^{\beta h \sum_i s_i} = \sum_{\{s_i\}} \prod_{i=1}^{N} e^{\beta h s_i} = \prod_{i=1}^{N} \sum_{\{s_i = \pm 1\}} e^{\beta h s_i} \\ &= \left(\mathrm{e}^{\beta h} + e^{-\beta h}\right)^N = (2\cosh\beta h)^N \end{aligned} \tag{3}$$

Q: What thermodynamic quantities are we interested in?

A: Helmholtz free energy $A(N, T, h)$, energy E, entropy S, and average magnetization $M(N, T, h) \equiv \left\langle \sum_{i=1}^{N} s_i \right\rangle$.

Hyperbolic functions

$$\begin{aligned} \cosh x &= \frac{\mathrm{e}^x + \mathrm{e}^{-x}}{2} \\ \sinh x &= \frac{\mathrm{e}^x - \mathrm{e}^{-x}}{2} \\ \frac{d}{dx}\cosh x &= \sinh x \\ \frac{d}{dx}\sinh x &= \cosh x \\ \tanh x &= \frac{\sinh x}{\cosh x} \\ \frac{d}{dx}\tanh x &= 1 - (\tanh x)^2 \end{aligned}$$

(See `http://en.wikipedia.org/wiki/Hyperbolic_function` for more details.)

$$A = -k_B T \ln Z = -N k_B T \ln(2\cosh\beta h) \tag{4}$$

$$E = -\frac{\partial}{\partial\beta}\ln Z = -Nh\tanh\beta h \tag{5}$$

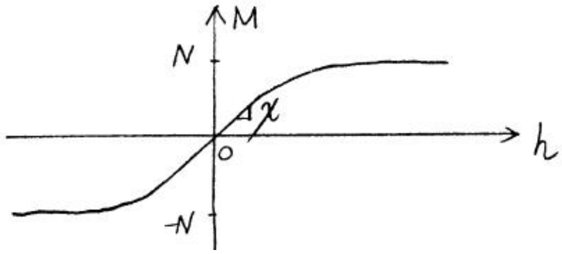
In this special case ($J = 0$), $H = -h \sum_i s_i$. Therefore,

$$E \equiv \langle H \rangle = -h \cdot M \tag{6}$$

$$M = -\frac{E}{h} = N \tanh \beta h \tag{7}$$

The *magnetic susceptibility*[2] is

$$\chi \equiv \frac{1}{N} \left(\frac{\partial M}{\partial h} \right)_T = (1 - \tanh^2 \beta h)\, \beta \tag{8}$$



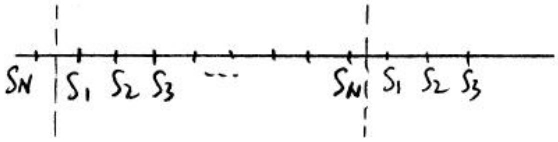
2.2 Ising model at zero field ($h = 0$)

For the first time, we are discussing an interacting model.

$$H(\{s_i\}) = -J \sum_{\langle i,j \rangle} s_i s_j = -J \sum_i s_i s_{i+1} \tag{9}$$

The interaction makes the derivation of the partition function more difficult. It is not surprising that we will try some coordinate transformations to turn it into an equivalent non-interacting model. After all, that's all we know how to solve at this point!

Before we proceed, we need to be more specific about the the boundary conditions (B.C.). A widely used B.C. is the periodic boundary condition (PBC). The advantage is that no spin is different from the others.



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[2] The magnetic susceptibility is a response function of the material. It describes how much does the magnetization M changes when the external field h is changed. It is analogous to the specific heat, $c_V \equiv \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_h$, which describes how much heat the system absorbs when the temperature T is changed.

PBC states that $s_{N+1} = s_1$. Therefore the Hamiltonian can be written as,

$$H = -J(s_1 s_2 + s_2 s_3 + \cdots + s_{N-1} s_N + s_N s_1) \tag{10}$$

Alternatively, we can use the "free-end" B.C.

$$H = -J \sum_{i=1}^{N-1} s_i s_{i+1} = -J(s_1 s_2 + s_2 s_3 + \cdots + s_{N-1} s_N) \tag{11}$$

The difference between different B.C. should vanish in the thermodynamic limit ($N \to \infty$).

Under free-end B.C., the partition function can be easily evaluated through a coordinate transformation.

$$\{s_1, s_2, \cdots, s_N\} \to \{s_1, p_2, \cdots, p_N\} \tag{12}$$

where $p_2 = s_1 s_2$, $p_3 = s_2 s_3$, $\cdots$, $p_N = s_{N-1} s_N$.

Since $s_i = \pm 1$, $p_i = \pm 1$, p_i describes whether the spin flips from i to $i + 1$.

The inverse transform can be written as

$$s_2 = s_1 p_2, \;\; s_3 = s_1 p_2 p_3, \;\; s_N = s_1 p_1 \cdots p_N \tag{13}$$

Hence there is a one to one correspondence between

$$\{s_1, s_2, \cdots, s_N\} \quad \text{and} \quad \{s_1, p_2, \cdots, p_N\} \tag{14}$$

- For free-end B.C., $H = -J\left(p_2 + p_3 + \cdots + p_N\right)$. Hence the partition function is

$$\begin{aligned} Z &= \sum_{\{s_1, p_2, \cdots, p_N\}} \mathrm{e}^{\beta J (p_2 + p_3 + \cdots + p_N)} \\ &= 2 \prod_{i=2}^{N} \sum_{p_i = \pm 1} \mathrm{e}^{\beta J p_i} \\ Z &= 2\left(2 \cosh \beta J\right)^{N-1} \end{aligned} \tag{15}$$

- One can show that under PBC

$$Z = (2 \cosh \beta J)^N \cdot [1 + (\tanh \beta J)^N] \tag{16}$$

We see that here J is taking the place of h in the previous section.

Given the partition function Z, we can easily obtain A, E, S, M, as well as specific heat c_V.

2.3 The general case ($J \neq 0$, $h \neq 0$)

To obtain the magnetic susceptibility χ at non-zero J, we need to consider the case of $J \neq 0$, $h \neq 0$, which is a true interacting model.

The partition function is usually expressed in terms of the trace of a matrix.

The trace is the sum of the diagonal elements of a matrix

$$\mathrm{Tr}(B) = B_{11} + B_{22} + \cdots + B_{nn} \tag{17}$$

$$\text{where} \quad B = \left(\begin{array}{cccc} B_{11} & B_{12} & \cdots & B_{1n} \\ B_{21} & B_{22} & \cdots & B_{2n} \\ \vdots & \vdots & \ddots & \\ B_{n1} & B_{n2} & \cdots & B_{nn} \end{array} \right) \tag{18}$$

For example, for an Ising model with one spin, $H = -h\, s_1$, the partition function is

$$Z = \mathrm{Tr} \left(\begin{array}{cc} e^{\beta h} & 0 \\ 0 & e^{-\beta h} \end{array} \right) = e^{\beta h} + e^{-\beta h} \tag{19}$$

Now consider two spins, under periodic B.C.,

$$H(s_1, s_2) = -J s_1 s_2 - J s_2 s_1 - h s_1 - h s_2 \tag{20}$$

Define matrix

$$P \equiv \left(\begin{array}{cc} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} \end{array} \right) \tag{21}$$

then,

$$Z = \sum_{\{s_1 s_2\}} e^{-\beta H} = \mathrm{Tr}(P \cdot P) \tag{22}$$

Q: Why?

A: Notice that P is a 2×2 matrix.

Let the 1st row (column) correspond to $s = +1$, and let the 2nd row(column) correspond to $s = -1$, e.g.,

$$\begin{array}{llll} P_{+1,+1} & = e^{\beta(J+h)}, & P_{+1,-1} & = e^{-\beta J}, \\ P_{-1,+1} & = e^{-\beta J}, & P_{-1,-1} & = e^{\beta(J-h)}, \end{array}$$

$$P_{s_1 s_2} = e^{\beta\left(J s_1 s_2 + \frac{h}{2} s_1 + \frac{h}{2} s_2\right)} \tag{23}$$

$$\mathrm{Tr}(P \cdot P) = \sum_{s_1} (P \cdot P)_{s_1, s_1} = \sum_{s_1, s_2} P_{s_1, s_2} P_{s_2, s_1} \tag{24}$$

$$\begin{aligned}\therefore\quad \mathrm{Tr}(P\cdot P) &= \sum_{s_1,s_2} \mathrm{e}^{\beta(Js_1s_2+\frac{h}{2}s_1+\frac{h}{2}s_2)}\cdot \mathrm{e}^{\beta(Js_2s_1+\frac{h}{2}s_2+\frac{h}{2}s_1)} \\ &= \sum_{s_1,s_2} \mathrm{e}^{-\beta H(s_1,s_2)} \\ &= Z \qquad (25)\end{aligned}$$

In general, for N spins forming a linear chain under PBC, the partition function is

$$\begin{aligned} Z &= \sum_{\{s_i\}} \mathrm{e}^{-\beta H(\{s_i\})} \\ &= \sum_{\{s_i\}} \mathrm{e}^{\beta\left(Js_1s_2+\frac{h}{2}s_1+\frac{h}{2}s_2\right)}\cdot \mathrm{e}^{\beta\left(Js_2s_3+\frac{h}{2}s_2+\frac{h}{2}s_3\right)}\cdots \\ &\quad\ \mathrm{e}^{\beta\left(Js_{N-1}s_N+\frac{h}{2}s_{N-1}+\frac{h}{2}s_N\right)}\cdot \mathrm{e}^{\beta\left(Js_Ns_1+\frac{h}{2}s_N+\frac{h}{2}s_1\right)} \\ &= \mathrm{Tr}\left(P^N\right) \qquad (26)\end{aligned}$$

Now we have obtained a concise formal expression for the partition function. But to compute matrix P^N, it requires a lot of calculations. Fortunately, we don't need P^N. we just need $\mathrm{Tr}(P^N)$. This is the time we need to introduce a little more matrix theory, concerning the properties of the trace.

1. Every symmetric (real) matrix can be diagonalized,

   $$P = U\cdot D\cdot U^T \qquad (27)$$

   where U is a unitary matrix ($U\cdot U^T = I$), and D is a diagonal matrix. For 2×2 matrices, define $\lambda_+ \equiv D_{11}$, $\lambda_- \equiv D_{22}$ ($D_{12} = D_{21} = 0$). $\lambda_\pm$ are the eigenvalues of matrix P.

2. Trace is unchanged after diagonalization

   $$\mathrm{Tr(P)} = \mathrm{Tr(D)} = \lambda_+ + \lambda_- \qquad (28)$$

   Hence the trace equals the sum of the eigenvalues.

3. The same matrix U that diagonalizes P also diagonalizes P^N, because

   $$P^N = \left(U\cdot D\cdot U^T\right)\cdot\left(U\cdot D\cdot U^T\right)\cdots\left(U\cdot D\cdot U^T\right) = U\cdot D^N\cdot U^T \qquad (29)$$

4. Notice that

   $$D^N = \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix} \qquad (30)$$

   We have

   $$\mathrm{Tr}(P^N) = \mathrm{Tr}(D^N) = \lambda_+^N + \lambda_-^N \qquad (31)$$

Thus, all we need to do is to diagonalize P. We can do this using Matlab (or Maple, Mathematica, etc). The result is

$$\begin{aligned}
\lambda_{\pm} &= \mathrm{e}^{\beta J}\left[\cosh\beta h \pm \sqrt{\sinh^2\beta h + \mathrm{e}^{-4\beta J}}\right] && (32)\\
U &= \begin{bmatrix} -\mathrm{e}^{\beta J}\left(\mathrm{e}^{\beta(J-h)-\lambda_+}\right) & 1 \\ 1 & -\mathrm{e}^{\beta J}\left(\mathrm{e}^{\beta(J+h)-\lambda_-}\right) \end{bmatrix} && (33)\\
\mathrm{Tr}(P) &= \lambda_+ + \lambda_- = 2\,\mathrm{e}^{\beta J}\cosh\beta h && (34)
\end{aligned}$$

$$\begin{aligned}
Z &= \mathrm{Tr}(P^N) = \lambda_+^N + \lambda_-^N \\
&= \mathrm{e}^{N\beta J}\left\{\left[\cosh\beta h + \sqrt{\sinh^2\beta h + \mathrm{e}^{-4\beta J}}\right]^N\right. \\
&\qquad \left. + \left[\cosh\beta h - \sqrt{\sinh^2\beta h + \mathrm{e}^{-4\beta J}}\right]^N\right\} && (35)
\end{aligned}$$

In the special case of $h = 0$,

$$\begin{aligned}
Z &= \mathrm{Tr}(P^N) \\
&= \mathrm{e}^{N\beta J}\left[\left(1+\mathrm{e}^{-2\beta J}\right)^N + \left(1-\mathrm{e}^{-2\beta J}\right)^N\right] \\
&= \left(\mathrm{e}^{\beta J}+\mathrm{e}^{-\beta J}\right)^N + \left(\mathrm{e}^{\beta J}-\mathrm{e}^{-\beta J}\right)^N \\
&= (2\cosh\beta J)^N + (2\sinh\beta J)^N \\
Z &= (2\cosh\beta J)^N\left[1+(\tanh\beta J)^N\right] && (36)
\end{aligned}$$

Given the general expression for $Z(N,T,J,h)$, we can obtain analytic expressions for

- Magnetization

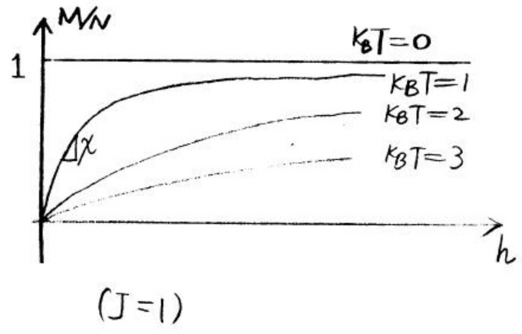
$$M(N,T,h) = \left\langle \sum_{i=1}^{N} s_i \right\rangle = k_B T \frac{1}{Z}\frac{\partial Z}{\partial h} = k_B T \frac{\partial \ln Z}{\partial h} = -\frac{\partial A}{\partial h} \tag{37}$$

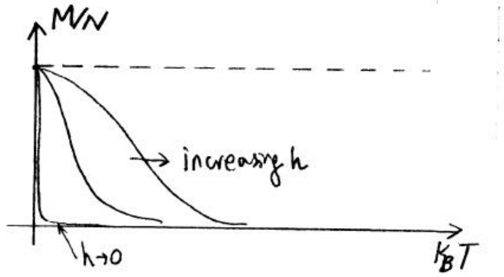
- Magnetic susceptibility

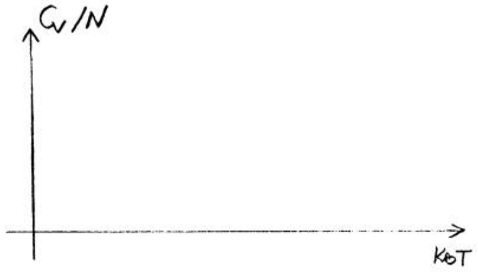
$$\chi \equiv \frac{1}{N}\left(\frac{\partial M}{\partial h}\right)_T = \frac{k_B T}{N}\frac{\partial^2 \ln Z}{\partial h^2} \tag{38}$$

In the thermodynamic limit ($N \to \infty$), notice that $\lambda_+ > \lambda_-$, we have,

$$\begin{aligned}
\ln Z \approx N \ln \lambda_+ &= N\,\ln\left\{ e^{\beta J}\cdot\left[\cosh\beta h + \left(\sinh^2\beta h + e^{-4\beta J}\right)^{1/2}\right]\right\} \\
&= N\beta J + N\ln\left[\cosh\beta h + \left(\sinh^2\beta h + e^{-4\beta J}\right)^{1/2}\right] && (39) \\
A &= -k_B T\,\ln Z \\
&= -NJ - N\,k_B T\,\ln\left[\cosh\beta h + \left(\sinh^2\beta h + e^{-4\beta J}\right)^{1/2}\right] && (40) \\
E &= \cdots \\
C_V &= \frac{\partial E}{\partial T} = \cdots \\
M &= k_B T\frac{\partial \ln Z}{\partial h} = -\frac{\partial A}{\partial h} = \cdots \\
\chi &= \frac{1}{N}\frac{\partial M}{\partial h} = -\frac{1}{N}\frac{\partial^2 A}{\partial h^2} = \cdots && (41)
\end{aligned}$$







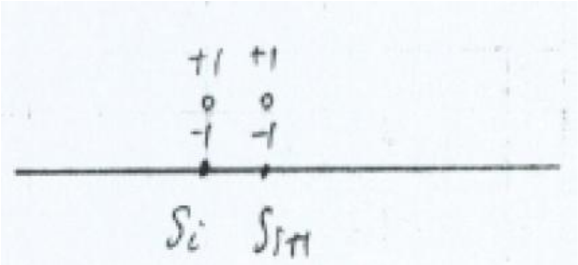
3 Generalized 1D Ising model

3.1 Spins with more than two states

The **transfer matrix method** can be applied to generalized Ising models. For example, we can consider a Hamiltonian similar to the one considered above,

$$H(\{s_i\}) = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i \tag{42}$$

except that each spin can take three possible values, $s_i = -1, 0, +1$.[3]



The partition function can be written as

$$Z = \sum_{\{s_i\}} \mathrm{e}^{-\beta H(\{s_i\})} = \mathrm{Tr}\left(P^N\right) \tag{43}$$

where P is now a 3 × 3 matrix,

$$P = \begin{array}{c} \\ S_i = 1 \\ S_i = 0 \\ S_i = -1 \end{array} \begin{array}{c} \begin{array}{ccc} S_j = 1 & S_j = 0 & S_j = -1 \end{array} \\ \left(\begin{array}{c|c|c} e^{\beta(J+h)} & e^{\frac{\beta}{2}h} & e^{-\beta J} \\ \hline e^{\frac{\beta}{2}h} & 1 & e^{-\frac{\beta}{2}h} \\ \hline e^{-\beta J} & e^{-\frac{\beta}{2}h} & e^{\beta(J-h)} \end{array} \right) \end{array}$$

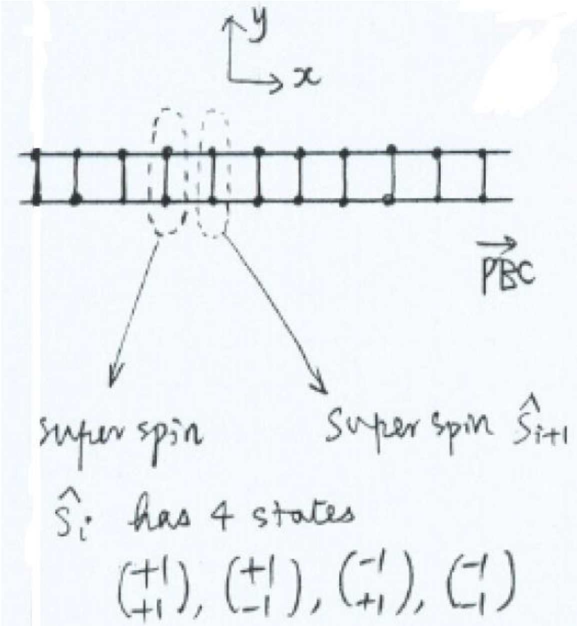
$$\begin{aligned} Z &= \lambda_+^N + \lambda_0^N + \lambda_-^N \\ &\approx \lambda_+^N \qquad (N \to \infty) \end{aligned} \tag{44}$$

---

[3] This is similar to the Potts model (`http://en.wikipedia.org/wiki/Potts_model`).

3.2 More than one row of spins

Another generalization of the 1D Ising model is to consider two rows of spins interacting with their nearest neighbors.[4]



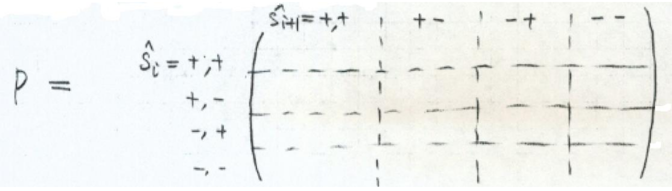
Apply periodic boundary condition in x-direction and free-end boundary condition in y-direction. In this case, each spin has 3 nearest neighbors. The Hamiltonian and partition function can still be written in the same way as before,

$$\begin{aligned} H(\{s_i\}) &= -J\sum_{\langle i,j\rangle} s_i s_j - h\sum_i s_i \\ Z &= \sum_{\{s_i\}} \mathrm{e}^{-\beta H(\{s_i\})} = \mathrm{Tr}\left(P^N\right) \end{aligned}$$

To apply the transfer matrix method, let us consider the two rows of spins as one row of "super-spins", $\hat{s}_i$. Each "super-spin" represents the 2 spins in each column, and hence has 4 different states: $(+,+)$, $(+,-)$, $(-,+)$, $(-,-)$. Hence we can still write,

$$Z = \mathrm{Tr}\left(P^N\right) \tag{45}$$

where P is a 4×4 matrix, N is the size of the Ising model in the x-direction.



Let $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ be the four eigenvalues of matrix P ($\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4$). Then,

$$Z = \lambda_1^N + \lambda_2^N + \lambda_3^N + \lambda_4^N \approx \lambda_1^N \qquad (N \to \infty) \tag{46}$$

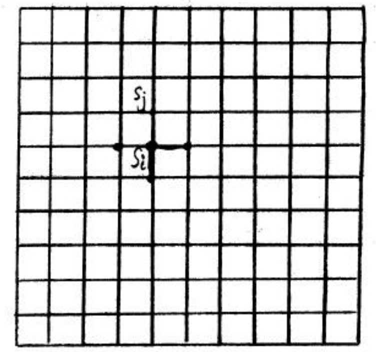
---

[4] We can consider this as a baby 2D model. As the number of rows increases, we gradually go to the 2D Ising model.

4 2D Ising model

4.1 Analytic solution

Consider the $2D$ Ising model defined over a square lattice of N spins under periodic boundary conditions. Again, the Hamiltonian can be written as



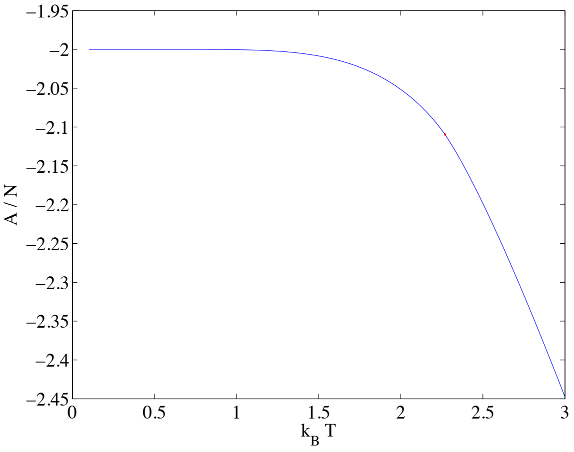
$$H(\{s_i\}) = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i \qquad (47)$$

J describes the strength of interaction, h is external magnetic field, and the sum $\sum_{\langle i,j \rangle}$ is over all nearest neighbor pairs. Each spin has 4 nearest neighbors.

Onsager's solution in the absence of magnetic field $h = 0$ in the thermodynamic limit is [4]

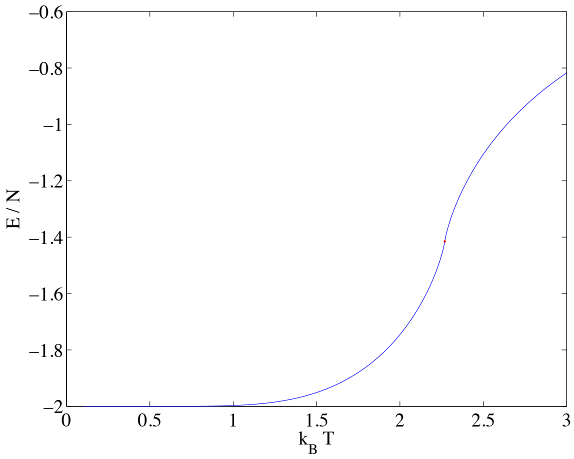
$$\begin{aligned} A &= -k_B T \, \ln Z \\ Z &= \lambda^N \\ \ln \lambda &= \ln(2 \cosh 2\beta J) + \frac{1}{\pi} \int_0^{\frac{\pi}{2}} dw \, \ln \left[\frac{1}{2} \left\{ 1 + (1 - K^2 \sin^2 w)^{1/2} \right\} \right] \\ K &= \frac{2 \sinh 2\beta J}{(\cosh 2\beta J)^2} \end{aligned} \qquad (48)$$

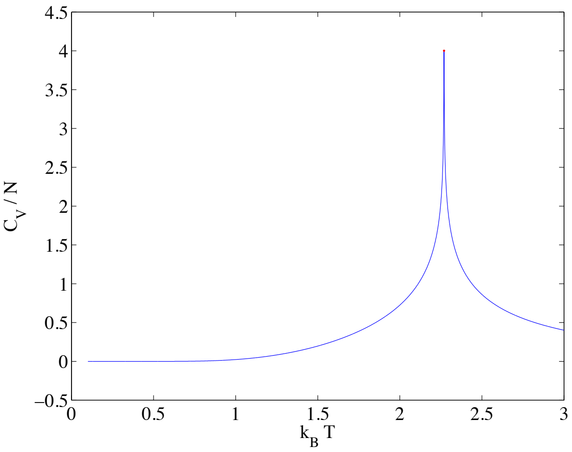
Onsager's original solution used the transfer matrix method, and was very complicated (Phys. Rev. 65, 117, 1943). Nine years later, Kac and Ward (Phys. Rev. 88, 1332, 1952) re-derived the result using a much simpler graphical/combinatorial approach. The combinatorial approach was also explained in Feynman's book on Statistical Mechanics (Ref. 2). While Onsager was well known for his exact solution of the 2D Ising model, he won the 1968 Nobel Prize in Chemistry (not in Physics) for his reciprocal relations in non-equilibrium thermodynamics.



$$k_B T_c = \frac{2J}{\ln(1+\sqrt{2})} = 2.269 \cdots J \qquad (49)$$

Onsager's solution predicts a phase transition at $T = T_c$. From Monte Carlo simulation (below), we will see that $\underline{T < T_c}$ is the <u>ordered phase</u>; $\underline{T > T_c}$ is the <u>disordered phase</u>. T_c of Ising model is analogous to the Curie Temperature of magnetic materials (e.g. Fe). The spontaneous magnetization disappears if $T > T_c$.





From Eq. (48) we can obtain the energy E of the 2D Ising model and its heat capacity.

$$E = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln \lambda}{\partial \beta} \tag{50}$$

$$C_V = \frac{\partial E}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial E}{\partial \beta} = \frac{N}{k_B T^2}\frac{\partial^2 \ln \lambda}{\partial \beta^2} \tag{51}$$

In the above, we plot A, E and C_V for the 2D Ising model as a function of k_BT (with $J = 1$). (Download `plot_Onsager_solution.m` and try it yourself.) We see that C_V becomes singular as $T \to T_c$. (It has been shown that $C_V \propto \ln|T - T_c|$ as $T \to T_c$.) This means that the slope of the $E(T)$ curve becomes infinite as $T \to T_c$. The second derivative of the $\ln \lambda(\beta)$ curve becomes infinite as $T \to T_c$. In other words, the second derivative of the integral with respect to β in Eq. (48) becomes infinite at $T = T_c$ ($K = 1$). The integral itself and its first derivative with respect to β remain finite at $T = T_c$ ($K = 1$).

4.2 Monte Carlo simulation

The Metropolis algorithm is a simple and widely used approach to generate the canonical ensemble. It is especially convenient to explain (and to implement) for an Ising model. The algorithm has the following steps.

0. Start with some spin configuration $\{s_i\}$.
1. Randomly choose a spin s_i
2. Attempt to flip it, i.e. $s_i := -s_i$ (trial).
3. Compute the energy change ΔE due to this flip.
4. If $\Delta E < 0$, accept the trial.
5. If $\Delta E > 0$, accept the trial with probability $p^{\text{acc}} = e^{-\beta \Delta E}$.

6. If trial is rejected, put the spin back, i.e. $s_i := -s_i$.
7. Go to 1, unless maximum number of iterations is reached.

* More details about this algorithm will be discussed later.

Numerical exercise: run `ising2d.m` for $N = 80 \times 80$, starting from random initial conditions, with $J = 1$, at $k_B T = 0.5, 1, 1.5, 2, 2.269, 3$. Write down your observations.

$k_B T = 0.5$	$k_B T = 2.269$	$k_B T = 3$

Q: Why does the Metropolis algorithm generate the canonical distribution?

To simplify the notation, let A, B represent arbitrary spin configurations $\{s_i\}$. Our goal is to prove that when the MC simulation has reached equilibrium, the probability of sampling state A is

$$p_A = \frac{1}{Z}\, \mathrm{e}^{-\beta H(A)} \tag{52}$$

where

$$Z = \sum_A \mathrm{e}^{-\beta H(A)} \tag{53}$$

— the sum is over all possible (2^N) spin configurations.

Monte Carlo simulation follows a Markov Chain, which is completely specified by a transition probability matrix π_{AB} — the probability of jumping to state B in the next step if the current state is A.

For an Ising model with N spins, there are 2^N spin configurations (states). So π_{AB} is a $2^N \times 2^N$ matrix. However, most entries in π_{AB} are zeros.

$\pi_{AB} \neq 0$ only if there is no more than one spin that is different (flipped) between A and B. For example,

$$\begin{aligned} \text{if } A &= \{+1,+1,+1,+1,+1,+1\} \quad \text{then} \\ \text{for } B &= \{+1,-1,+1,+1,+1,+1\}, \quad \pi_{AB} > 0 \\ \text{but for } B &= \{-1,-1,+1,+1,+1,+1\}, \quad \pi_{AB} = 0 \end{aligned}$$

To prove the Metropolis algorithm generates the canonical ensemble:

(1) transition matrix can be written as

$$\pi_{AB} = \alpha_{AB} \cdot p^{\text{acc}}_{AB}, \quad \text{for } B \neq A \tag{54}$$

$$\pi_{AA} = 1 - \sum_{B \neq A} \pi_{AB} \tag{55}$$

where α_{AB} is the trial probability that satisfies

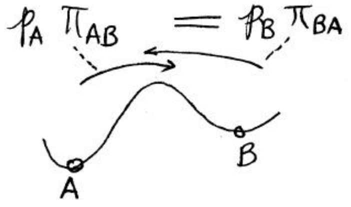
$$\alpha_{AB} = \alpha_{BA} \tag{56}$$

and p^{acc}_{AB} is the acceptance probability.

without loss of generality, let's assume $E_B > E_A$, then

$$\begin{cases} p^{acc}_{AB} = \exp\left(-\frac{E_B - E_A}{k_B T}\right) \\ p^{acc}_{BA} = 1 \end{cases} \quad \Longrightarrow \quad \frac{\pi_{AB}}{\pi_{BA}} = \frac{\alpha_{AB}}{\alpha_{BA}} \frac{p^{acc}_{AB}}{p^{acc}_{BA}} = \exp\left(-\frac{E_B - E_A}{k_B T}\right) \tag{57}$$

(2) If the equilibrium distribution is reached, with p_A being the probability of sampling state A, then we expect the following balance of fluxes.



$$\begin{aligned} \therefore \quad p_A \, \pi_{AB} &= p_B \, \pi_{BA} \\ \frac{p_A}{p_B} &= \frac{\pi_{BA}}{\pi_{AB}} = \mathrm{e}^{\frac{E_B - E_A}{k_B T}} \\ \Longrightarrow \quad p_A &= \text{const} \cdot \mathrm{e}^{-\frac{E_A}{k_B T}} \quad \text{for all } A \end{aligned} \tag{58}$$

The normalization of p_A, $\sum_A p_A = 1$, requires that

$$p_A = \frac{1}{Z} \mathrm{e}^{-\frac{E_A}{k_B T}}, \qquad Z = \sum_A \mathrm{e}^{-\frac{E_A}{k_B T}} \tag{59}$$

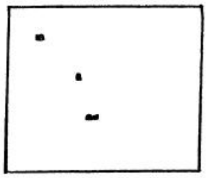
(end of proof)

4.3 Qualitative behavior

Observations from MC simulation at $h=0$

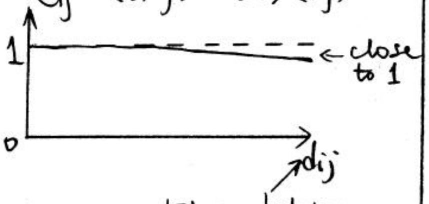
$T<T_c$

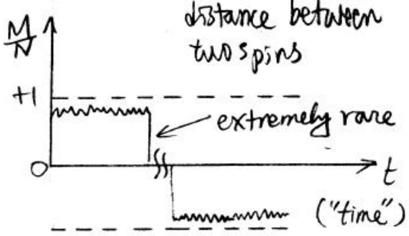
low temperature phase

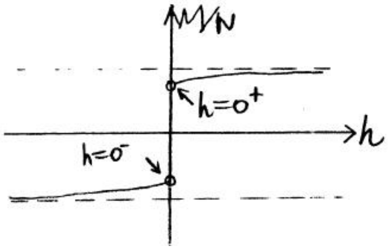


1. Dominance of one spin (e.g. $S_i=+1$) with fluctuations of the other spin (e.g. $S_i=-1$) as isolated clusters
2. Number & size of clusters increase as T↑
3. long range correlation

$C_{ij} = \langle S_iS_j\rangle - \langle S_i\rangle\langle S_j\rangle$



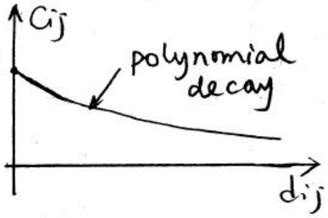


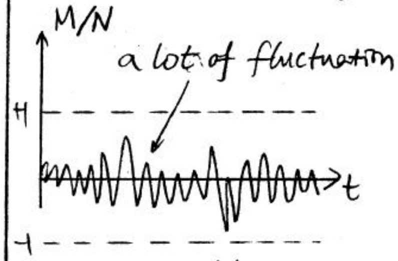


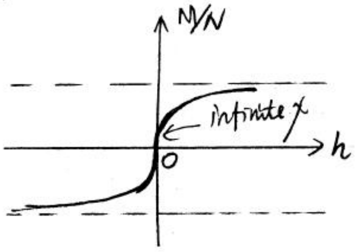
$T=T_c$

critical temperature

1. fluctuation at all scales
2. no clear dominance of one spin
3. Long range correlation



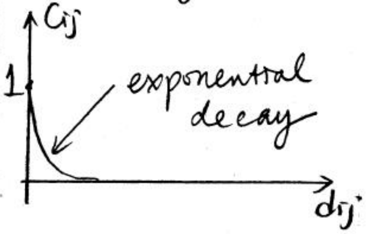


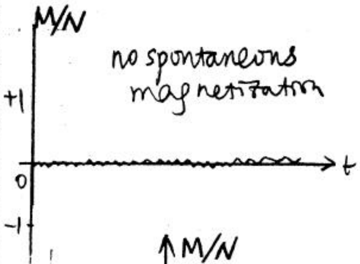


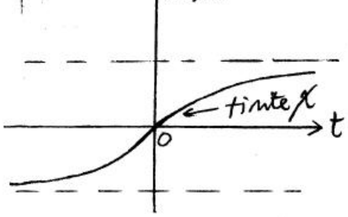
$T>T_c$

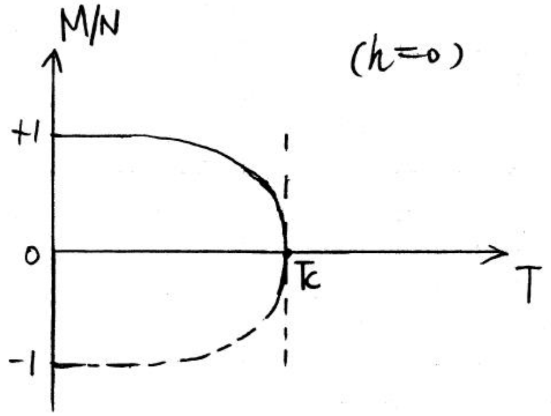
high temperature phase

1. no dominance of either spin
2. no obvious patterns
3. Short range correlation







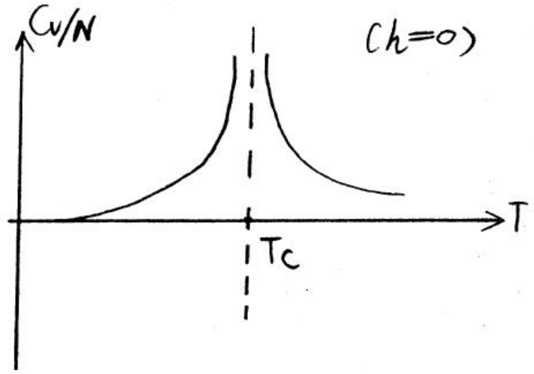


$$\frac{M}{N} \propto (T_c - T)^{\beta} \qquad T < T_c$$

critical exponent $\beta = \frac{1}{8}$ (2D)

$\beta \approx 0.313$ (3D)

(not to be confused with reciprocal temperature $\beta \equiv \frac{1}{k_B T}$)



$$\frac{C_V}{N} \propto \frac{8k_B}{\pi}\left(\frac{J}{k_B T}\right)^2 \ln\left|\frac{1}{T-T_c}\right| \quad (2D)$$

$$\frac{C_V}{N} \propto |T-T_c|^{-\alpha} \qquad \alpha \approx 0.125 \ (3D)$$

There is a problem with the top plot M/N vs T.

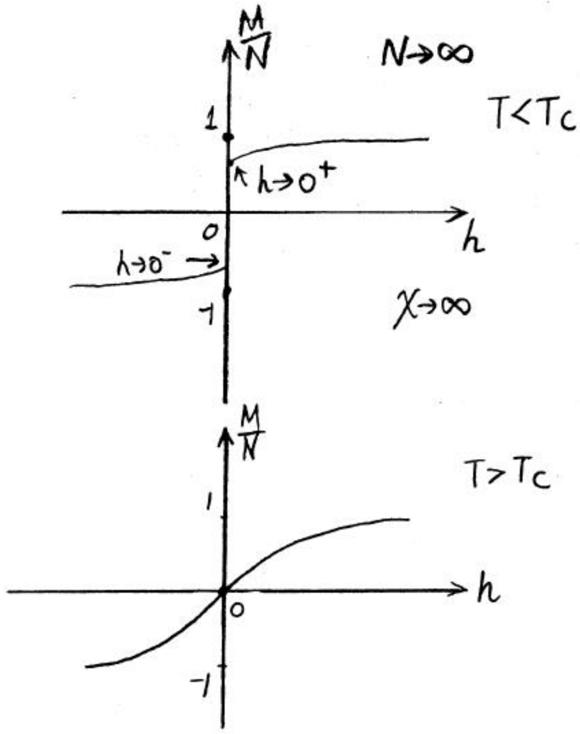
If we define $M \equiv \left\langle \sum_{i=1}^{N} s_i \right\rangle$, then if $h = 0$, we should always have $M = 0$ by symmetry.

Why do we claim that there is a difference between low temperature regime ($T < T_c$) and high temperature regime ($T > T_c$)?

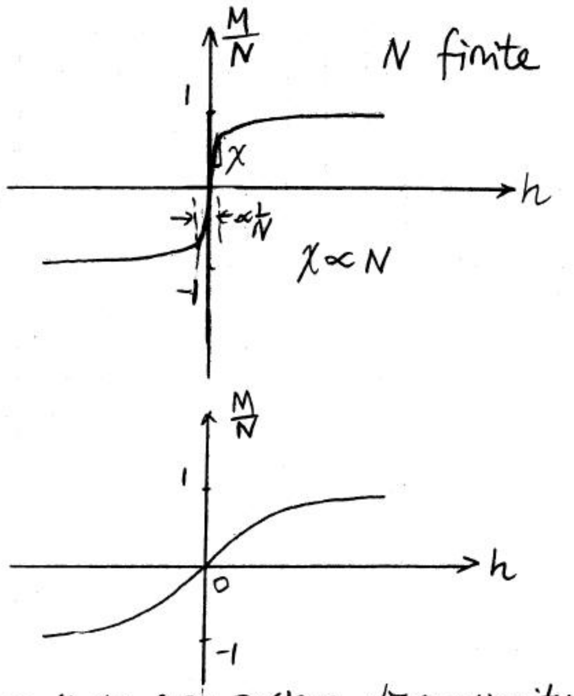
To reduce this paradox, we need to imagine the magnetic field h is a very small but positive number. $h \to 0^+$.

In this case, only the upper branch of the $\frac{M}{N}(T)$ curve will be selected, when $T < T_c$. The value remains positive as $h \to 0^+$ when $T > T_c$. The magnetization $\frac{M}{N} \to 0^+$ as $h \to 0^+$.

This is too complicate to do in a numerical simulation. So we need a different way to compute magnetic susceptibility χ, especially near $h \to 0$.



(Thermodynamic limit)



For a finite-size system, discontinuity does not occur. But χ at $h=0$ scales as N as $N\to\infty$ $(T<T_c)$

We expect the susceptibility $\chi \equiv \frac{1}{N}\frac{\partial M}{\partial N}$ to diverge if $T < T_c$ and $N \to \infty$.

Fluctuation-Dissipation Theorem

$$\chi = \frac{1}{N}\frac{\partial M}{\partial h} = \frac{1}{Nk_BT}\left(\langle \tilde{M}^2\rangle - \langle \tilde{M}\rangle^2\right) \tag{60}$$

where $\tilde{M} \equiv \sum_{i=1}^{N} s_i$

$$\begin{aligned} M &\equiv \langle \tilde{M}\rangle = \left\langle \sum_{i=1}^{N} s_i \right\rangle, \quad \langle \tilde{M}^2\rangle = \left\langle \left(\sum_{i=1}^{N} s_i\right)^2 \right\rangle. \\ \chi &= \frac{1}{Nk_BT}\sum_{i,j=1}^{N} \langle s_i s_j\rangle - \langle s_i\rangle\langle s_j\rangle \end{aligned} \tag{61}$$

Therefore, we arrived at another of fluctuation-dissipation theorem (FDT),

$$\chi = \frac{1}{k_BT}\sum_{j=1}^{N} C_{ij} \qquad \text{(the right hand side does not depend on } i\text{)} \tag{62}$$

where

$$C_{ij} \equiv \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle \tag{63}$$

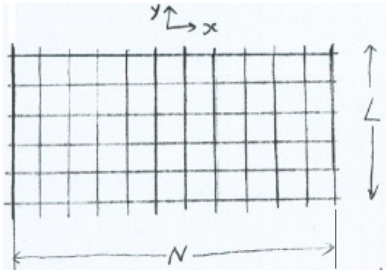
is the correlation function between spins i and j. When $T < T_c$, $\chi \to \infty$, corresponding to long range correlation, $\sum_{j=1}^{N} C_{ij} \propto N$. (unbounded as $N \to \infty$).

Proof of Eq. (60)

$$\begin{aligned}
Z &= \sum_{\{s_i\}} \mathrm{e}^{-\beta H(\{s_i\})} = \sum_{\{s_i\}} \exp\left[\beta J \sum_{\langle i,j \rangle} s_i s_j + \beta h \sum_i s_i\right] \\
\frac{\partial Z}{\partial h} &= \sum_{\{s_i\}} \mathrm{e}^{-\beta H(\{s_i\})} \, \beta \, \tilde{M} && (64) \\
M &= k_B T \, \frac{1}{Z} \frac{\partial Z}{\partial h} && (65) \\
\frac{\partial M}{\partial h} &= k_B T \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial h^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial h}\right)^2\right] \\
&= k_B T \left[\beta^2 \langle \tilde{M}^2 \rangle - \beta^2 \langle \tilde{M} \rangle^2\right] \\
&= \frac{1}{k_B T} \left[\langle \tilde{M}^2 \rangle - \langle \tilde{M} \rangle^2\right] && (66)
\end{aligned}$$

4.4 Sketch of derivations of partition function in 2D

Consider a 2D array of spins with dimension $N \times L$ under periodic boundary conditions in both directions.



We can follow the approach in Section 3.2 and define "super-spins" for each column of spins. The system then becomes a linear chain of N "super-spins". But each "super-spin" has 2^L states. This means the transfer matrix P is a $2^L \times 2^L$ matrix. Let λ_1 be the largest eigenvalue of matrix P. Then,

$$Z = Tr(P^N) \approx \lambda_1^N \qquad (N \to \infty) \tag{67}$$

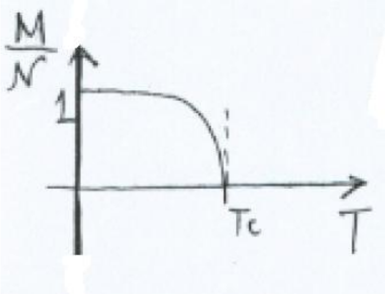
If L is not too large, this problem can be solved numerically using Matlab.

This is the approach Onsager took (1943) to find the analytic solution for Z in the limit of $N \to \infty$, $L \to \infty$.[5]

Onsager used some very advanced mathematical techniques to solve this problem. His solution predicts a critical temperature of $k_B T_c = \frac{2J}{\ln(1+\sqrt{2})} = 2.269\,J$. Onsager also stated the zero-field magnetization should be

$$\frac{M}{\mathcal{N}} = \left[1 - \sinh^{-4}(2\beta\,J)\right]^{1/8} \tag{68}$$

for $T < T_c$, but **did not give a proof** (Onsager 1943)! Finally, C. N. Yang (1952) was able to proof this (again) using a very difficult derivation.



In 1952, Kac and Ward found a much simpler approach to re-derive Onsager's result, using a graphical/combinatorial approach, which is what we will describe below.

The new idea is to rewrite the partition function as a multiplication and expand all the terms.

$$\begin{aligned} Z &= \sum_{\{s_i\}} \mathrm{e}^{\beta\,J\,\sum_{\langle i,j\rangle} s_i\,s_j} \\ &= \sum_{\{s_i\}} \prod_{\langle i,j\rangle} \mathrm{e}^{\beta\,J\,s_i\,s_j} \end{aligned} \tag{69}$$

Notice that $s_i\,s_j = \pm 1$, hence

$$\begin{aligned} \mathrm{e}^{\beta\,J\,s_i\,s_j} &= \frac{\mathrm{e}^{\beta\,J} + \mathrm{e}^{-\beta\,J}}{2} + \frac{\mathrm{e}^{\beta\,J} - \mathrm{e}^{-\beta\,J}}{2}\,s_i\,s_j \\ &= (\cosh\,\beta J) + (\sinh\,\beta J)\,s_i\,s_j \\ &= \cosh\,\beta J\,(1 + t\cdot s_i\,s_j) \end{aligned} \tag{70}$$

where $t \equiv \tanh\,\beta J$. Therefore,

$$Z = (\cosh\,\beta J)^N \sum_{\{s_i\}} \prod_{\langle i,j\rangle} (1 + t\cdot s_i\,s_j) \tag{71}$$

The key is to find the term following $(\cosh\,\beta J)^N$.

---

[5] Onsager obtained the solution for the case of $h = 0$. No analytic solution has been found for $h \neq 0$.

$$Z' = \sum_{\{S_i\}} \prod_{\langle ij \rangle} (1+tS_iS_j)$$

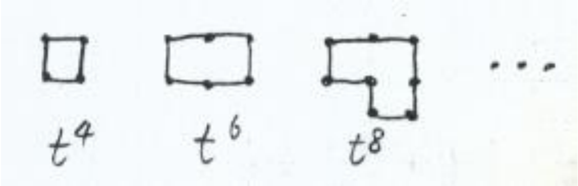
$$= \sum_{\{S_i\}} \underbrace{(1+tS_1S_2)\cdot(1+tS_1S_3)\cdot(1+tS_1S_4)\cdot\cdots}_{\#\text{ of terms } = \#\text{ of bonds.}}$$

$$= \sum_{\{S_i\}} 1 + \underbrace{tS_1S_2 + t^2 S_1S_2S_1S_3 + \cdots}_{} \longrightarrow \text{contribute } 0$$

$$+\, t^4 \underbrace{S_1S_2S_2S_6S_6S_3S_3S_1}_{} \longrightarrow \text{contribute non-zero}$$

$$+ \cdots$$

It turns out that Z' can be obtained by summing over all polygons that can be drawn on a square lattice, each one contributes t^n, where n is the number of lattice points on the polygon. For example,



It also turns out that there is a "simple" way to sum over all the graphs (need to use Fourier transform).

The entire derivation was explained by Richard Feynman [2] in 14 pages. So it is not so "easy". But all we need to do is to "count carefully". There is no need to master the theory of Group and Group Representations, which are used in Onsager's original proof.

References

1. B. M. McCoy and T. T. Wu, "The Two-Dimensional Ising Model", Harvard University Press (1973).

2. R. P. Feynman, "Statistical Mechanics: A Set of Lectures", W. A. Benjamin, Inc. (1972).

3. L. Onsager, "Crystal Statistics. I. A Two-Dimensional Model with an Order-Disorder Transition", Physical Review, 65, 117 (1944).

4. C. K. Majumdar, "Analytic Properties of the Onsager Solution of the Ising Model", Physical Review, 145, 158 (1966).

Today's goal:

Part A • free energy of a subspace ← *This lecture note only addresses Part A.

Part B • generalization of 1D Ising model ← Notes for part B can be fund in Handout 12 "Ising Model".

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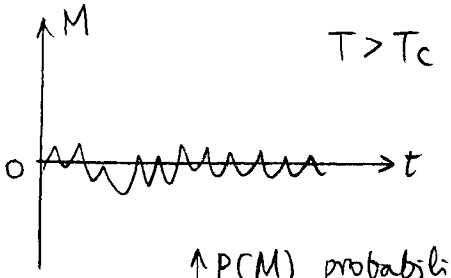
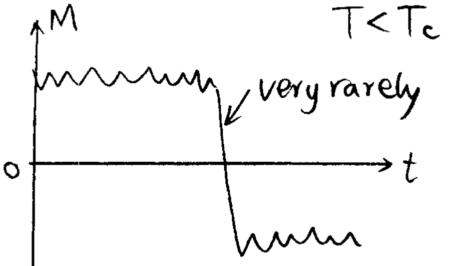
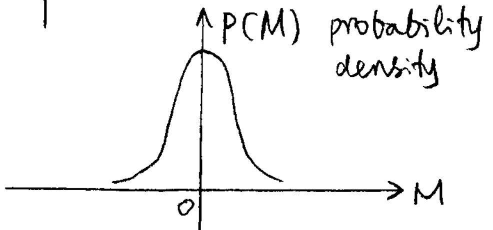
1. Motivation

HW8.3 2D Ising model, instantaneous magnetization $M = \frac{1}{N}\sum_i S_i$

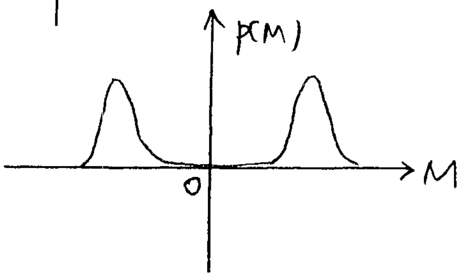
observations from Monte Carlo simulations





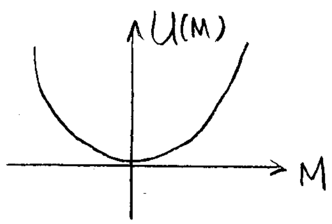


can be obtained from histogram with proper normalization: $\int_{-1}^{1} p(M)\,dM = 1$



Suppose we want to develop a coarse-grained model for M

e.g. $\ddot{M} = -k \frac{\partial U(M)}{\partial M} - \gamma \dot{M} + f^{\text{rand}}(t)$



We may consider M(t) as motion inside a one-dimensional potential U(M) subjected to random noise

For consistency, at thermal equilibrium, the *probability density* of observing a particular value of M is

$p(M) = \frac{1}{Z} e^{-\beta U(M)}$ U(M): effective potential, or potential of mean force

We will show that it is the same as the free energy A(M) defined below.

We can obtain $U(M)$ (up to a constant) from $p(M)$:

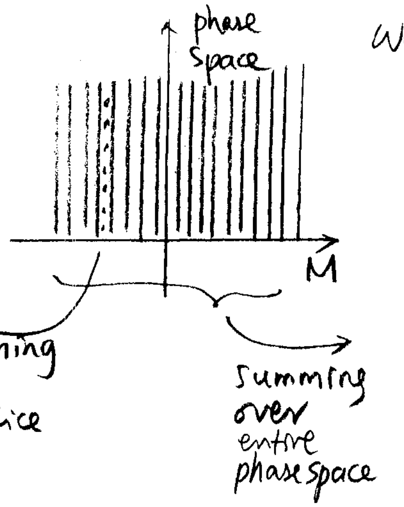
$$U(M) = -k_B T \ln p(M) \underbrace{- k_B T \ln \hat{Z}}_{\text{unknown constant}}$$

2. Ising model with a constraint

with constraint

$$Z(M,T) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} e^{-\beta H(\{S_i\})}$$

(note the phase space is partitioned into many slices. Perhaps this is why Z is called the partition function.)



Without constraint

$$Z(T) = \sum_{\{S_i\}} e^{-\beta H(\{S_i\})}$$

$$= \sum_M \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} e^{-\beta H(\{S_i\})}$$

$$= \sum_M Z(M,T)$$

$$e^{-\beta A(M,T)} = Z(M,T)$$

$$A(M,T) = -k_B T \ln Z(M,T)$$

is the Helmholtz free energy of the Ising model under constraint M.

$$e^{-\beta A(T)} = Z(T)$$

$$A(T) = -k_B T \ln Z(T)$$

is the Helmholtz free energy of the unconstrained Ising model

note: $Z(M,T) < Z(T)$

$A(M,T) > A(T)$, $e^{-\beta A(T)} = \sum_M e^{-\beta A(M,T)}$

All other thermodynamic quantities are similarly defined in the constrained and unconstrained Ising model, e.g.

$$E(M,T) = -\frac{\partial}{\partial\beta} \ln Z(M,T) \qquad E(T) = -\frac{\partial}{\partial\beta} \ln Z(T)$$

$$S(M,T) = \frac{1}{T}[E(M,T) - A(M,T)] \qquad S(T) = \frac{1}{T}[E(T) - A(T)]$$

$A(M,T)$ is also called the free energy landscape.

3. Proof of $U(M) = A(M,T)$

i.e. the "effective potential" is the same as the "free energy landscape", and as such, should in general depend on temperature.

Recall that

$U(M)$ is defined through:

$$p(M) = \frac{1}{\hat{Z}} e^{-\beta U(M)}$$

$\uparrow$

Probability of observing M in unconstrained model

$A(M,T)$ is defined through:

$$Z(M,T) = e^{-\beta A(M,T)}$$

$\uparrow$

partition function of a constrained model

For the unconstrained model, the probability of observing a particular spin configuration (one point in phase space) is

$$p(\{S_i\}) = \frac{1}{Z(T)} e^{-\beta \mathcal{H}(\{S_i\})}$$

The probability of observing a specific value of M is

$$p(M) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} p(\{S_i\}) = \frac{1}{Z(T)} \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} e^{-\beta \mathcal{H}(\{S_i\})} = \frac{Z(M,T)}{Z(T)} = \frac{e^{-\beta A(M,T)}}{e^{-\beta A(T)}}$$

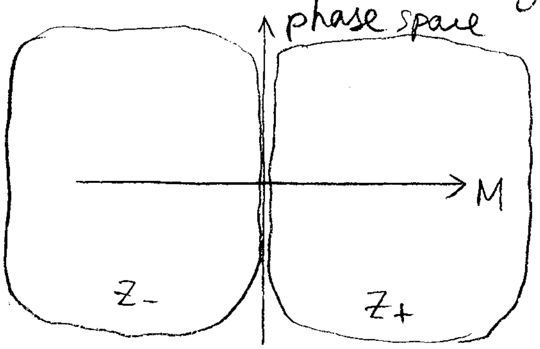
The ratio of the probabilities of observing two values of M is

$$\frac{p(M_1)}{p(M_2)} = \frac{e^{-\beta A(M_1,T)}}{e^{-\beta A(M_2,T)}} = \exp[-\beta(A(M_1,T) - A(M_2,T))]$$

The above results can be generalized into many other situations.

First, we do not have to divide the phase space into infinite number of slices.

e.g. we can divide it into two parts for the Ising model which naturally corresponds to the two phases at low T.



$$Z_+(T) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \sum_i S_i > 0}} e^{-\beta H(\{S_i\})}, \quad A_+(T) = -k_B T \ln Z_+(T)$$

$$Z_-(T) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \sum_i S_i < 0}} e^{-\beta H(\{S_i\})}, \quad A_-(T) = -k_B T \ln Z_-(T)$$

$$A_+(T) = A_-(T) \quad \text{if} \quad h = 0$$

$$A_+(T) < A_-(T) \quad \text{if} \quad h > 0$$

We can also talk about the free energy of different states of a protein

natural (folded) state

denaturalized (unfolded) state

$$A_n(T) = -k_B T \ln Z_n(T)$$

$$Z_n(T) = \int_{\substack{\text{phase space} \\ \text{region for the} \\ \text{folded state}}} \prod_{i=1}^{3N} dp_i\, dq_i\, e^{-\beta H(\{p_i\},\{q_i\})}$$

$$A_d(T) = -k_B T \ln Z_d(T)$$

$$Z_d(T) = \int_{\substack{\text{phase space} \\ \text{region for the} \\ \text{unfolded state}}} \prod_{i=1}^{3N} dp_i\, dq_i\, e^{-\beta H(\{p_i\},\{q_i\})}$$

When we compare the free energies of the solid phase and the liquid phase, they are again defined through partition functions that are integrated over subspaces of the entire phase space.