Statistical mechanics for molecular simulations. (2015)

Lecture 1
1/22/2015.

Fundamentals of statistical mechanics.

* ensemble theory
* two postulates of Stat. mech.
* microcanonical ensemble
* canonical ensemble.
* thermodynamic limit.

* Course description / details.

> first lecture!
> 1. list of attendances.
> 2. textbook / references
> 3. open / informal environment.
> 4. background check.
> 5. web resources & course details.

http://quantum.ch.ntu.edu.tw/ycclab/winter-short-course-2015

Molecular simulations have become invaluable tools for researchers in chemistry, physics, biology, & material science.
This short course aims to provide the basic theoretical background that should better prepare you to understand / interpretate the results of molecular simulations

timeless

Of course, we can only present a very brief introduction to the very fundamentals here. Two things I want to discuss in particular ⇒ entropy & Boltzman distribution.

⇒ but, yes, I want to teach you statistical thermodynamics in a week !!
✻ ensemble theory.

Modern stat. mech. is presented using ensemble theory as its foundation.

Macroscopic systems are too complicated, we can not track all microscopic/molecular motions of all particles in a bulk system ⇒ we can only consider "averaged" quantities.

thermodynamic state
Key ⇒ a macroscopic state actually is consist of many-many "microstates".

We define "ensemble" to describe macroscopic states. There are two "equivalent" views: Ensemble is:

① ~~ensemble~~ (microstate view) the collection of all microstates consistent with <u>the constraints</u> that characterize the macroscopic system.

e.g. : two spins : $\uparrow\uparrow$, $\downarrow\downarrow$, $\frac{1}{\sqrt{2}}(\uparrow\downarrow \pm \uparrow\downarrow)$

"full house" in a deck of cards ...

② (replica view) a collection of independent systems ($\sim 10^{23}$) that each can be in a different state <u>satisfying the constraints</u>.

e.g. : an ensemble of proteins in water. in an NMR tube
the ensemble of boys/girls in the classroom —

Note that these two views are the same.

☆ Ensemble is defined by "constraints" —

← we can calculate macroscopic
observables based on
"statistics" !!

* Statistical principle.

↑

Ensemble
postulate
of
Gibbs.

Now we "assume" that in equilibrium,

an ensemble exhibits a definite distribution

over microstates, so a thermodynamic variable.

ensemble average.   observed value when
                         system in the with
                         microstate.

$$X = \langle X \rangle = \sum_{\nu} P_{\nu} \cdot X_{\nu}$$

↑   ↖ prob. of the occurrence of ν-th
                                      microstate
└ over all microstates

So, the key is to figure out P_{ν} for

different ensembles.

How do we determine P_{ν}?

one can't be proven,
↙ "you can see that it is true
                    just lying
* The principle of equal "a priori" probabilities. on your
                                                     couch.

For an isolated system in thermal equilibrium,

all microstates with the same energy are

equally populated.

* actually we neglect the "ergodic hypothesis" here: ensemble average = time
                                                                         average.

time*less*

So, let's think about ensemble. (5)

* microcanonical ensemble : (E, V, n) fixed.

nature for Isolated systems, because the underlying "mechanics" is energy conserving.

Now we are ready to consider a particular ensemble. Let's start from the simplest case, with (E, V, n) fixed. This is called a microcanonical ensemble.

(E, V, n) fixed $\Rightarrow$ microcanonical.

It is clear that all states are equally populated, so

$$\langle X \rangle = \frac{1}{\Omega} \sum_{\nu} X_{\nu}$$

Ω: number of states on the microcanonical ensemble.

Ω is the key microscopic quantity of the ensemble !! $\quad \Omega = \Omega(E, V, n)$.

To determine the thermodynamic properties of this ensemble, we must calculate some thermodynamic functions, recognize.
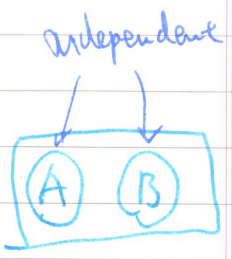
$$(E, V, n) \text{ fixed} \longrightarrow \text{entropy, } S$$

So S is the key thermodynamic function that describes the microscopic ensemble.

How can we determine S?

but this is the only reasonable one. ↗ ① We "postulate" that S is a function of Ω.

So, for a system A.

$$S_A(E, V, n) = f(\Omega_A(E, V, n)).$$

independent

② Entropy is additive., for independent systems A & B

$$S_{A+B} = S_A + S_B$$

note that the # of microstates for independent systems

← multiplication!!

$$\Omega_{A+B} = \Omega_A \times \Omega_B$$

It is Impossible to really understand "entropy" ⑦ without the microscopic formula.

∴ we need to find $f(\cdot)$ such that

$$f(\Omega_A \times \Omega_B) = f(\Omega_A) + f(\Omega_B)$$

clearly, this function is $\ln(\cdot)$.

The only physically reasonable ~~definition~~ relation between S & Ω is then

Boltzman's Tomb:

$$S = k log W$$

$$S_A = k_B \ln \Omega$$

This is Boltzman's microscopic definition of entropy.

We finally answer "What is entropy"

Entropy measures the number of accessible microstates in an microcanonical ensemble!!

※ third law

Now the third law is easy to see, because $\Omega \geqslant 1$

⇒ at $T=0$, system only occupy the ground state, $\Omega \geqslant 1$ ⇒ $S=0$!!

timeless

* Connection to thermodynamics

Now it is easy to calculate thermodynamic variables. Recall

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

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dn$$

It is straightforward to derive.

$$\boxed{\frac{1}{k_b T} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V,n}}$$

← highlight this, we will use this next time.

$$\frac{p}{k_b T} = \left(\frac{\partial \ln \Omega}{\partial V} \right)_{E,n}$$

$$\frac{\mu}{k_b T} = - \left(\frac{\partial \ln \Omega}{\partial N} \right)_{E,V}$$

all thermodynamic properties can be calculated once Ω is determined !!

All these can be formally derived...

The microcanonical ensemble does not have temperature. It is nature in simulation, but it is not very useful.

We must release some of the constraints to ②
≠ Canonical ensemble. study more general ensemble.

So we consider an ensemble with

fixed (T, V, n) $\Rightarrow$ canonical ensemble.

Again $\langle X \rangle = \sum\limits_{\nu} P_{\nu} X_{\nu}$, the key 为
to figure out P_{ν} !! A trick 为
to construct the canonical ensemble
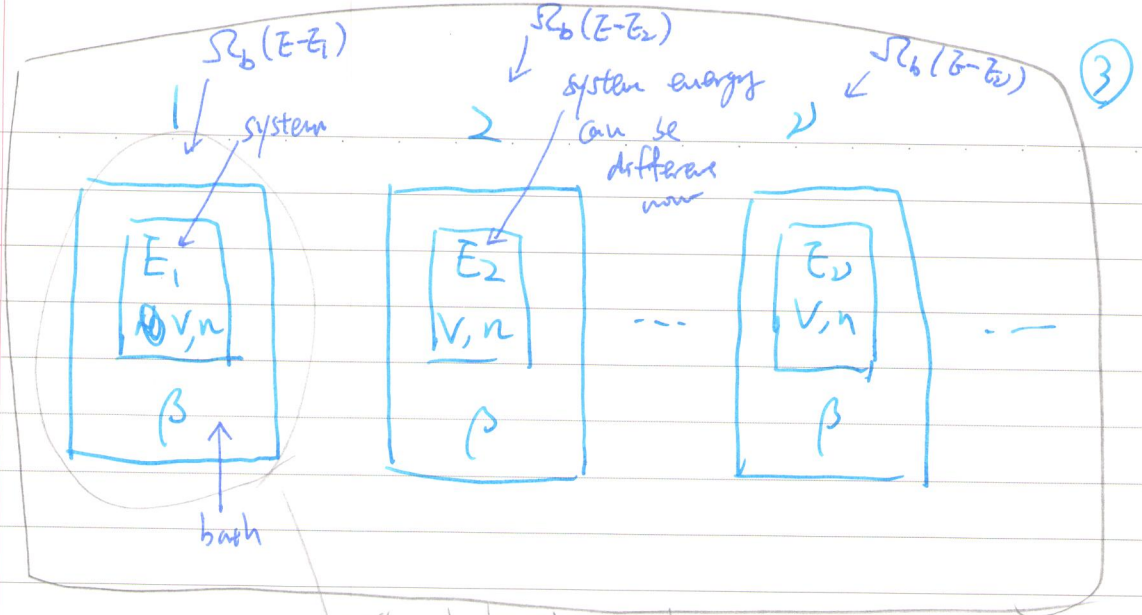
using composite microcanonical ensemble.

We picture an $\underset{\wedge}{\text{ensemble of}}$ isolated system + bath that

has a fixed total energy $E = E_{B} + E_{\nu}$.

$E_{B}:$ bath energy

$E_{\nu}:$ system energy

Notice that naturally $E_{B} \gg E_{\nu}$, because bath is
large.

$\Omega_b(E-E_1)$ $\Omega_b(E-E_2)$ $\Omega_b(E-E_\nu)$ ③

↓ system   ↓ system energy can be different now   ↓

1   2 ν

E_1 E_2 E_ν

V, n V, n - - - V, n - -

β β β

↑ bath

system + bath has the same energy
all microstates isolated with fixed (E, V, n) → microcanonical

Note that all these system + bath states ~~have~~

form a microcanonical ensemble, while all

the systems form a canonical ensemble.

Now, if we the system is in one

specific state ν with energy E_ν.

many microstates on the system + bath microcanonical

ensemble have system energy E_ν, because

the bath can exist in many different

states !!

The number of states with $E_S = E_\nu$ is

determined by the # of configurations in the

bath, i.e. number of bath states satisfying

$$E_B + E_\nu = E.$$

Mathematically:

# of bath states

$E_B = E - E_\nu$

$$\Omega_{STB}(\text{system energy} = E_\nu) = \Omega_b(E_B)$$

↳ # of states of
the total STB.

$$= \Omega_b(E - E_\nu)$$

Now, within such states in the system + bath

microcanonical ensemble → they have the same

total $E = E_B + E_\nu$

energy, so the probability is proportional

to the # of states.

$$P(E_\nu) \equiv P_\nu = \frac{\Omega_b(E - E_\nu)}{\sum_\nu \Omega_b(E - E_\nu)} \propto \Omega_b(E - E_\nu)$$

Let's now estimate $\Omega_b(E - E_\nu)$.

Notice that

$$\Omega_b(E - E_\nu) = \exp\{\ln \Omega_b(E - E_\nu)\}.$$

Since $E \gg E_\nu$, we can expand $\ln \Omega(E - E_\nu)$ as a Taylor series of E_ν:

Ω is a large number so only expansion on $\ln \Omega$ makes sense.

$$\ln \Omega(E - E_\nu) = \ln \Omega(E) - E_\nu \cdot \left(\frac{d \ln \Omega}{dE}\right)_{V,n} + \cdots$$

Now recall that $\left(\frac{d \ln \Omega}{dE}\right)_{V,n} = \frac{1}{k_b T} = \beta$

There fore

$$\Omega(E - E_\nu) \approx \Omega(E) \cdot e^{-\beta E_\nu} \qquad P_\nu \propto e^{-\beta E_\nu}$$

$\Omega(E - E_\nu) \approx \Omega(E) \cdot e^{-\beta E_\nu}$

that is, the number of of accessible states grows exponentially as a function of energy!!

This is the Canonical Boltzman distribution law !!

$$P_\nu = \frac{1}{Q} e^{-\beta E_\nu}$$

exp. for exp. growth of # of accessible states.

$$Q = Q(\beta, V, n) = \sum_\nu e^{-\beta E_\nu} \quad \text{is the}$$

normalization factor, and is called the Canonical partition function.

timeless

Note that we pay special attention

to the partition function because

it is the generating function of

various thermodynamic variables.

For example:

$$Q = \sum_{\nu} e^{-\beta E_\nu}$$

$$\therefore \left(\frac{\partial Q}{\partial \beta}\right) = \sum_{\nu} E_\nu \cdot e^{-\beta E_\nu}$$

$$-\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,n} = -\left[\frac{1}{Q} \cdot \left(\frac{\partial Q}{\partial \beta}\right)\right]_{V,n}$$

$dA = -SdT - pdV + \mu dn$

$\left(\frac{\partial A}{\partial T}\right)_{V,n} = -S$

$$= +\frac{1}{Q} \cdot \sum_{\nu} E_\nu \cdot e^{-\beta E_\nu}$$

internal energy !!

$$= \sum_{\nu} P_\nu \cdot E_\nu = \langle E \rangle = U$$

also

$A = U - TS$

at fixed T

$A = U + T \cdot \left(\frac{\partial A}{\partial T}\right)_{V,n}$

So $\quad U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,n} = -k_B \cdot \left(\frac{\partial \ln Q}{\partial (1/T)}\right)_{V,n}$

now realize:

$U = -T^2 \left[\frac{\partial (A/T)}{\partial T}\right]_{V,n}$

$= \left(\frac{\partial (A/T)}{\partial (1/T)}\right)_{V,n}$

$U = \left(\frac{\partial (A/T)}{\partial (1/T)}\right)_{V,n}$ from thermo.

$\Rightarrow \frac{A}{T} = -k_B \cdot \ln Q \Rightarrow A = -k_B T \cdot \ln Q.$

* Connection to thermodynamics.

So for the canonical ensemble, we calculate the <u>Helmholtz free energy</u> :

as expected!! fixed (T, V, n)

$$A = -k_B T \cdot \ln Q .$$

and then.

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V, n} = k_B \ln Q + k_B T \cdot \left(\frac{\partial \ln Q}{\partial T}\right)_{V, n}$$

$$p = k_B T \cdot \left(\frac{\partial \ln Q}{\partial V}\right)_{T, n}$$

$$\mu = -k_B T \cdot \left(\frac{\partial \ln Q}{\partial n}\right)_{T, V} .$$

$$E = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V, n} = k_B T^2 \cdot \left(\frac{\partial \ln Q}{\partial T}\right)_{V, n} .$$

practical prescription
of stat. mech.
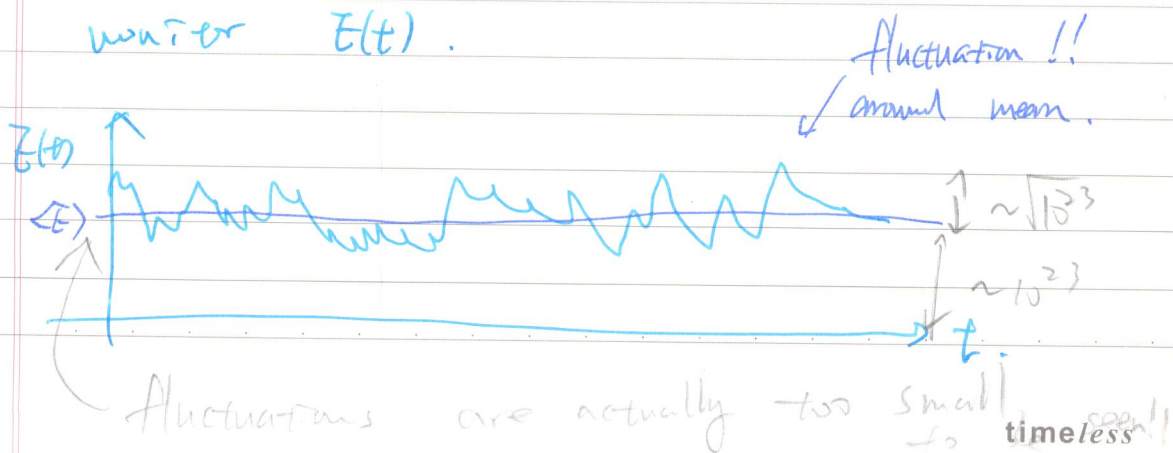calculations. { all thermodynamic properties can be calculated from Q.

$\Rightarrow$ basic principles of statistical thermodynamics are all here !!

* Thermodynamic limit.

As a final note, a departing gift, I want to come back to a sentence that I made at the first lecture.

Thermodynamics requires "macroscopic" bulk systems. Why?

Consider the ~~fluct~~ canonical ensemble, the system can be in any microstate at any time, and it is actually time dependent!! if one can monitor $E(t)$.

fluctuation!!
↙ around mean.

$E(t)$

$\langle E \rangle$

$\updownarrow \sim \sqrt{10^{23}}$

$\sim 10^{23}$

t.

Fluctuations are actually too small to **time**_less_!!

The essential question is that
why we do not observe the
fluctuations
variance of the energy (or any other
extensive
macroscopic ∧ observable) as a function of time ?

Let's calculate the ~~squa~~ amplitude of
fluctuations : Notice that

$$\langle E^2 \rangle = \sum_{\nu} p_{\nu} \cdot E_{\nu}^2$$

$$= \sum_{\nu} \frac{e^{-\beta Q}}{Q} E_{\nu}^2 = \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \beta^2}\right)_{V,n}$$

$\ln Q = -\beta A$

$$= \left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{V,n} + \langle E \rangle^2$$

$\beta = \frac{1}{k_B T}$ C_v

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

$\left(\frac{\partial \beta}{\partial T}\right) = -\frac{1}{k_B} \cdot \frac{1}{T^2}$

$\therefore \left(\frac{\partial T}{\partial \beta}\right) = -k_B \cdot T^2$

Therefore

$$\langle \delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{V,n}$$

$$= -\left(\frac{\partial^2 (\beta A)}{\partial \beta^2}\right)_{V,n} = -\frac{\partial}{\partial \beta}\left(\frac{\partial (\beta A)}{\partial (1/T)}\right)_{V,n} = -\left(\frac{\partial U}{\partial \beta}\right)_{V,n}$$

$$= k_B \cdot T^2 \cdot C_v$$

clearly, the amplitude of fluctuations

$$\sqrt{\langle \Delta E^2 \rangle} = \sqrt{\underset{\underset{\text{extensive}}{\uparrow}}{k_B \cdot C_V} \cdot \underset{\underset{\text{intensive}}{\uparrow}}{T^2} \cdot} \quad \sim \sqrt{N}$$

(const. over C_V)

The energy fluctuation depends on temperature and the heat capacity of the system. This is reasonable considering the random heat transfer is what actually leads to the fluctuations.

What is physically insightful is that when one looks at the "relative" amplitude of fluctuations.

E is extensive !!

Recall

$\langle E \rangle$ is extensive, so $\langle E \rangle \sim N$

C_v is extensive, so $C_v \sim N$

Therefore $\sqrt{\langle \delta E^2 \rangle} \sim \sqrt{N}$.

Therefore, the relative amplitude of fluctuation
to the mean energy is

$$\frac{\sqrt{\langle \delta E^2 \rangle}}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

given that $N \approx 10^{23}$,

What does this mean?

Ans: The fluctuations are so small
that they can't be detected !!

Now one can imagine that to
have a macroscopic system is important
to "supress" the fluctuations.
otherwise, stationary thermodynamic
thermal equilibrium can not be
established, the microscopic
system is
always in fluctuations !!

$\Rightarrow$ thermodynamics requires that $N \gg 1$.

$\Rightarrow$ thermodynamic limit !!

$\Rightarrow$ This ends our discussion on
thermodynamics, and I hope this course
is useful for you !!

timeless