PHYS641_Statistical mechanics

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PHYS641_Statistical Mechanics-Spring 2025

Class meeting: FMH405, Wednesdays, 6PM to 8:50PM

Jan 21 to May 7, 2026

Office Location & Hours

Wednesdays, 2PM to 3PM

Tiernan Hall 460

Course Materials Text (optional)

Keith Stowe, *An Introduction to Thermodynamics and Statistical Mechanics,*

Mehran Kardar, *Statistical Physics of Particles*

Kerson Huang, *Statistical Mechanics*.

Prerequisites:

Knowledge of thermodynamics and quantum mechanics at undergraduate level.

Final Grade Calculation:

The Weights for parts of the course are as follows:	
Class Participation	10%
Homework	30%
Research project and Oral presentation	10%
Mid Exam	20%
Final Exam	30%
Total	100%

Research project: oral presentation and text report.

Mid and Final exam: closed book, with formulas sheet.

> 85% A; >80 to 85 B+; >70 to 80 B; >65 to 70 C+; >55 to 65 C and <55 F

- Outline

Class 1 to 2: Basic concepts and laws (Keith Stowe)
Degree of freedom, Equipartition theorem
First Law, Second Law, and Third Law
Heat Capacity, Entropy, Free Energy, and Special Processes

Class 3 to 5: Classical Statistics (Mehran Kardar and Kerson Huang)

Ensembles: Micro-canonical, Canonical, Grand canonical,

Occupation number, Partition Functions, Maxwell-Boltzmann Statistics

Interaction and van der Waals gas

Class 6: Midterm Exam

Class 7 to 13: Quantum Statistics (Mehran Kardar and Kerson Huang)

Phonons, Photons,

Fermi statistics, Bose-Einstein statistics, Superfluids

Phase Transitions, Landau theory, Spins and Magnetism

Class 14: Oral presentation

PHYS641 is a graduate level course, NOT a review course for qualifying exam!

• Policies

[1] Class participation: sign the attendance sheet for every class.

[2] Overdue homework without any notices will get zero grade.
For any special cases (e.g., medical issues), send me an email 24 hrs before the deadline.
And provide the document approved by Dean's of Student (can be later).

[3] The homework solutions will be posted on Canvas after the due date. Zero grade for any homework submitted after I post the solutions.

[4] Make sure you submit the correct homework (your responsibilities). Wrong submission (such as wrong chapter or homework of electromagnetism) without corrections before due date will get zero grade.

[5] No make-up homework.

[6] No curved grade: 84.9 is B+, 54.9 is F.

[7] Meeting with me in my office hours (questions about lecture materials and homework problems) is highly recommended.

- # What Statistical Physics studies: Connecting the microscopic and macroscopic.

When a system is composed of a large number of identical elements, you can use the observed behavior of an individual element to predict the properties of the whole system, or conversely, you can use the observed properties of the entire system to deduce the probable behaviors of the individual elements.

P. W. Anderson's famous argument: More is different.
When you have a lot of elements in a system, the interactions between the elements at different scale will result in very different physics.

Examples: various quantum phenomena, such as superconductivity.

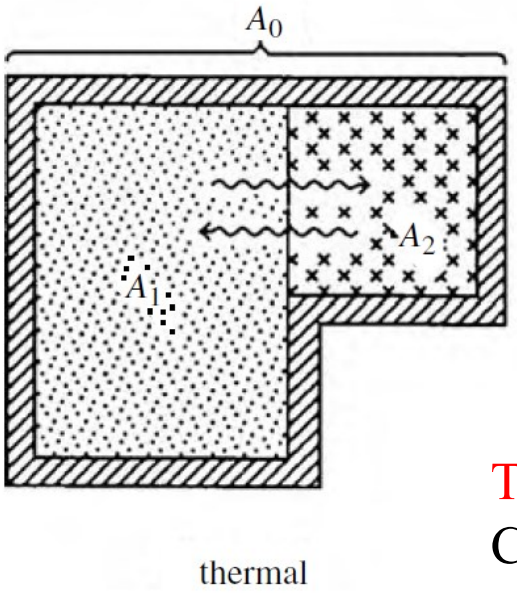
The most important physical quantity to consider: ***Energy***!

• Energy transfer at macroscopic level

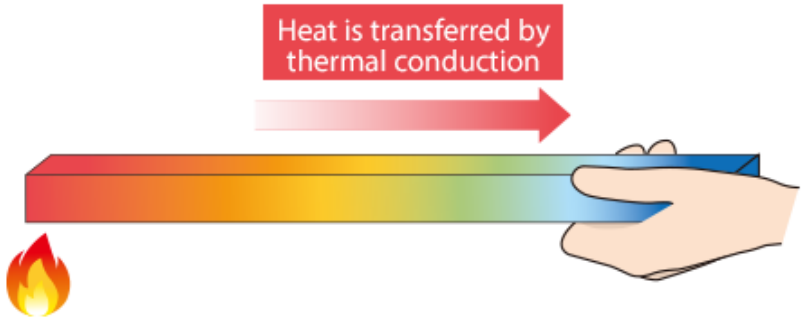
Energy can be transferred between systems by three mechanisms

- the transfer of heat Q;
- the transfer of work W (i.e., one system does work on another);
- the transfer of particles N.

These are called thermal, mechanical, and diffusive interactions, respectively.



thermal



Thermal interaction (heat Q):

Conduction involves particle collisions. On average, collisions transfer energy from more energetic particles to less energetic ones. Energy flows from hot to cold.

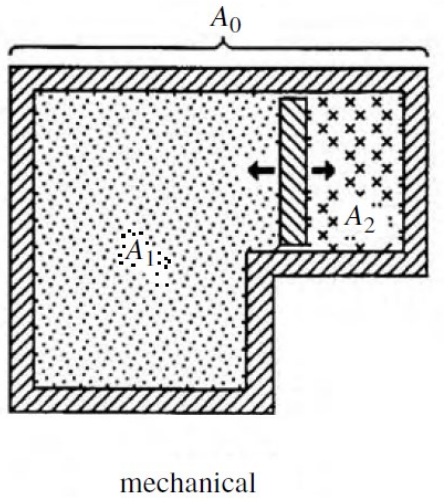
• Energy transfer at macroscopic level

Work: $dW = \boldsymbol{F}\cdot d\boldsymbol{s}$ (*an external force F pushing over a distance ds*)

$dW = pdV$ (*an external pressure p forcing a change in volume dV*)

$dW = -\boldsymbol{B}\cdot d\boldsymbol{\mu}$ (*a magnetic field* ***B*** *causing a change in magnetic moment* $\boldsymbol{\mu}$)

$dW = -\boldsymbol{E}\cdot d\boldsymbol{p}$ (*an electric field* ***E*** *causing a change in electric dipole moment* ***p***)



mechanical

Some sort of external force must cause a displacement of the system's particles.

Forces come in equal and opposite pairs, so

work done by the system =

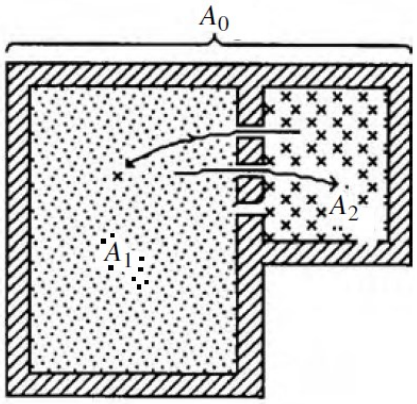
- work done on the system

$$\Delta E = \Delta Q - \Delta W \quad \text{(thermal and mechanical interactions)}$$

Q represents heat added, therefore increasing internal energy, W represents work done *by* the system, therefore decreasing internal energy.

• Energy transfer at macroscopic level

Diffusive interaction: the transfer of particles N.



diffusive

A particle goes from one system to another, it experiences a new environment and new interactions. This will change the energy of the system and the number of states accessible to the system.

Diffusive interaction is described by the "chemical potential" μ as follows.

When N particles enter a system, the energy delivered via this third mechanism is given by

$$\Delta E = \mu \Delta N \quad \text{(diffusive interaction only: no work or heat transfer)}$$

• The first law of thermodynamics

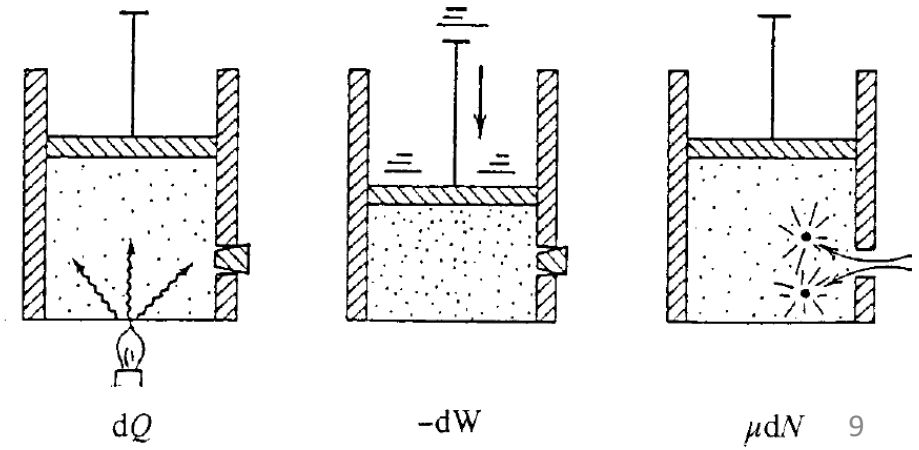
We examined each of the three ways by which the internal energy of a system may be changed: by transferring heat in or out of the system; by having work done on or by the system; by adding or removing particles from the system.

First law of thermodynamics: The change in internal energy of a system is given by

$$dE = dQ - dW + \mu dN$$

If more than one kind of work is being done, then dW must be replaced by a sum over different kinds of work dWj .
Similarly, if there are several kinds of particles in the system then the last term becomes $\sum_i \mu_i dN_i$ where the sum is over the different types of particle:

$$dE = dQ - \sum_j dW_j + \sum_i \mu_i \, dN_i$$



• Energy at the microscopic level

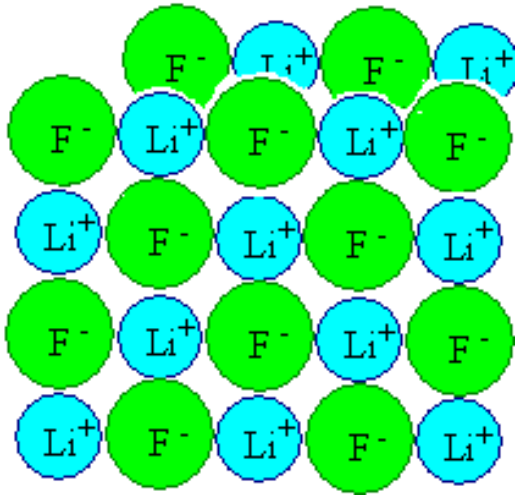
First, let's consider a solid. The individual atoms are held by EM interactions with neighboring atoms as if they were bound by tiny springs. Each atom vibrates in all three dimensions around its equilibrium position.

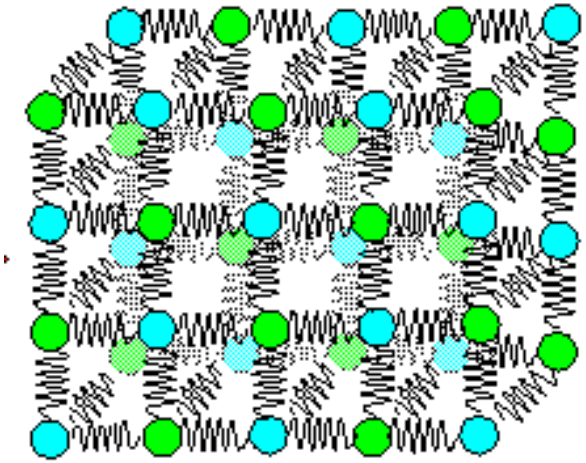
For one atom, its energy is given by

$$\varepsilon = \varepsilon_{\text{potential}} + \varepsilon_{\text{kinetic}} \quad \text{(Specific form ?)}$$

$$= \frac{1}{2}\kappa x^2 + \frac{1}{2}\kappa y^2 + \frac{1}{2}\kappa z^2$$

$$+ \frac{1}{2m}p_x^2 + \frac{1}{2m}p_y^2 + \frac{1}{2m}p_z^2$$





It is made up of two parts:
the potential energy and kinetic energy
If not isotropic, the constants κ could be different in different directions.

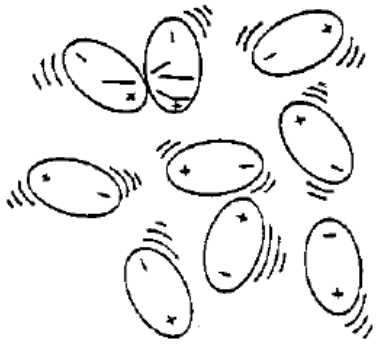
How about gas and liquid?

• Team Discussion: Gas and liquid

In **liquids**, the potential energies of the mobile molecules fluctuate rapidly as the configurations of the other molecules around them change. So the potential energy reference level u_0 is an average or "mean field" value, and the total energy of a liquid can be written as.

$$\varepsilon = \varepsilon_{\text{potential}} + \varepsilon_{\text{kinetic}}$$

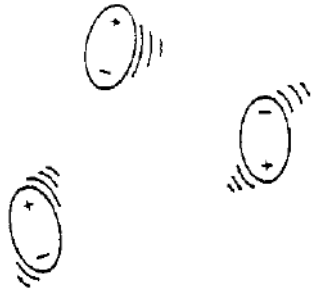
$$= u_0 + \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2$$



high concentration

In **gases**, neighboring particles are usually so far apart that interactions are negligible. So, for most cases, we can treat a particle's energy in gas as:

$$\varepsilon = \varepsilon_{\text{kinetic}} = \frac{1}{2m} p_x^2 + \frac{1}{2m} p_y^2 + \frac{1}{2m} p_z^2$$



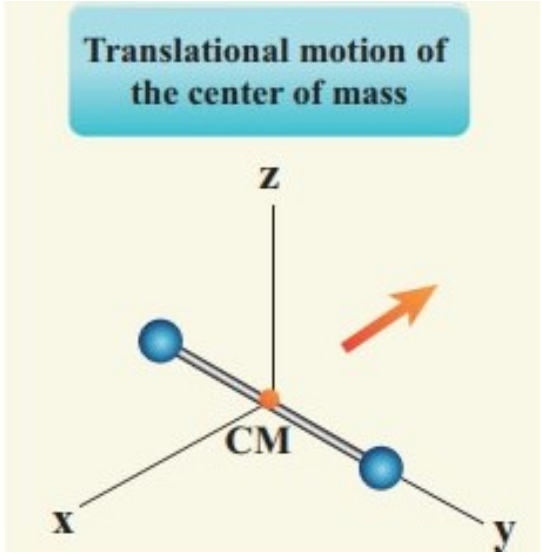
low concentration

• Team Discussion: Polyatomic gas

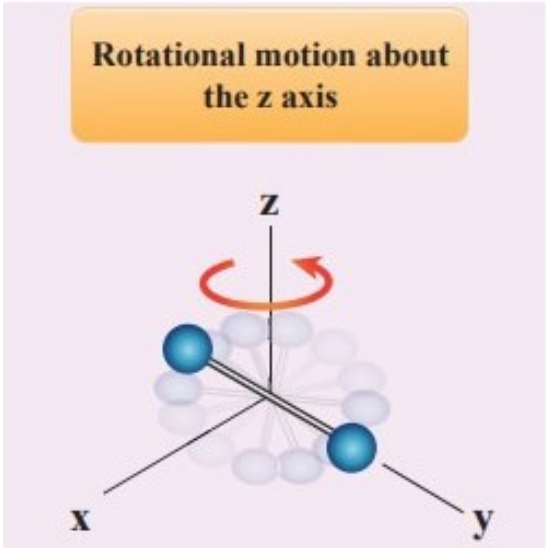
Collisions with other molecules might cause polyatomic molecules rotate and/or vibrate internally. This would provide additional modes of energy storage :

$$\varepsilon = \varepsilon_{\text{pot}} + \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{vib}$$

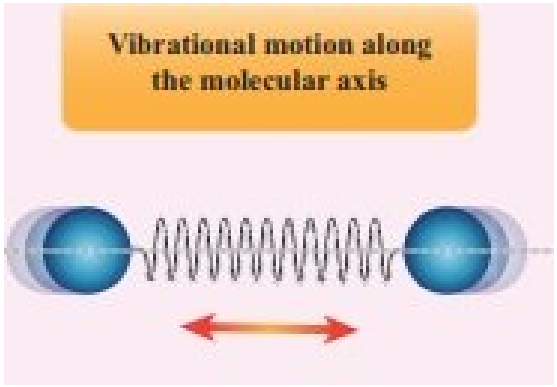
The diatomic molecules can have 3 degrees of freedom from translational motion, two from rotational motion, and two from vibrational motion.



$$\frac{1}{2M_{mole}}p_x^2 + \frac{1}{2M_{mole}}p_y^2 + \frac{1}{2M_{mole}}p_z^2$$



$$\frac{1}{2I_y}L_y^2 + \frac{1}{2I_x}L_x^2$$



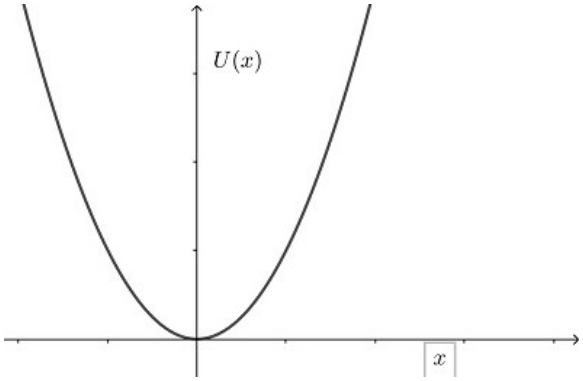
$$\frac{1}{2\mu}p_{relative}^2 + \frac{k}{2}x_{relative}^2$$

μ is reduced mass

• Energy: Quantum Effects

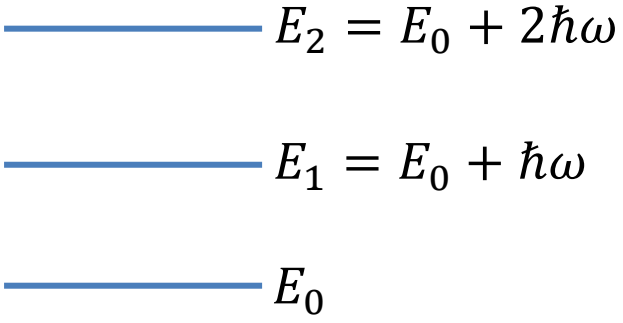
Vibrational: $E_{vib} = \frac{1}{2\mu} p_{rel}^2 + \frac{1}{2}\kappa x_{rel}^2$

Relative:
Position
Momentum



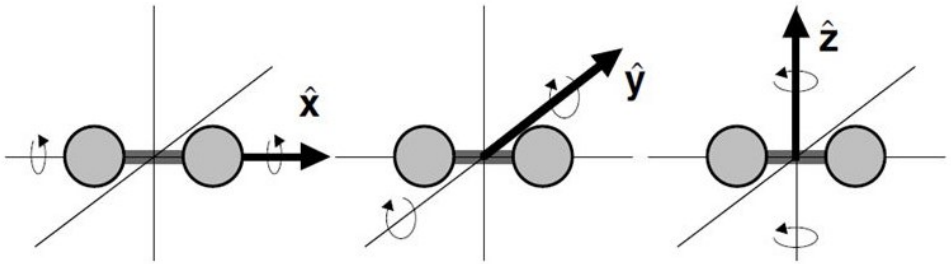
Small quantum spring

$E = n\hbar\omega + E_0 \quad n = 0,1,2,\ldots \quad \omega = \sqrt{\frac{\kappa}{m}}.$



Rotational: Kinetic energies for rotations around any axis are inversely related to the rotational inertia *I*. For rotations around the *i*th axis,

$$\varepsilon_{\text{rot}} = \frac{1}{2I_i} L_i^2,$$



Angular momentum *L* of small polyatomic molecules is also quantized.

$$L_i = (0, \pm 1, \pm 2 \ldots)\hbar$$

• Degree of freedom

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{\text{rot}} = \frac{1}{2m}p_x^2 + \frac{1}{2m}p_y^2 + \frac{1}{2m}p_z^2 + \frac{1}{2I_1}L_1^2 + \frac{1}{2I_2}L_2^2$$

$$\varepsilon = \varepsilon_{\text{potential}} + \varepsilon_{\text{kinetic}} = \frac{1}{2}\kappa x^2 + \frac{1}{2}\kappa y^2 + \frac{1}{2}\kappa z^2 + \frac{1}{2m}p_x^2 + \frac{1}{2m}p_y^2 + \frac{1}{2m}p_z^2$$

In all the examples above, the energies of individual particles are of the form

$$\varepsilon = \sum_i b_i \xi_i^2$$

where the b_i are constants (e.g., $\kappa/2$, $1/2m$, $1/2I$, etc.) and the ξ_i are position or momentum coordinates (x, p_x , L_1, etc.)

Each of these $b_i\ \xi^2_i$ terms represents a distinct way in which a particle can store energy, called a "**degree of freedom**."

Standard notation: υ represents the number of degrees of freedom per particle and N represents the number of particles in the system:

Degree of freedom per particle = υ
Degrees of freedom for a system of N particles = $N\upsilon$

• Microscopic to macroscopic: equipartition

Degrees of freedom are useful for consideration of (distribution of) energy!

(1) Potential $\kappa x^2/2$, and kinetic $p^2/2m$ carry equal energies when an average is taken (introductory physics courses).
(2) Motion in all three directions is equally likely.

The average kinetic or potential energies in the x, y, and z directions must all be equal.

Equipartition theorem: the *average energy* stored in each degree of freedom is the same.

$$\bar{\varepsilon} = \frac{1}{2}kT$$

where T is the temperature and k is Boltzmann's constant.

$$k = 1.381\times10^{-23}\ \text{J/K} = 8.63\times10^{-5}\ \text{eV/K}$$

Microscopic degree of freedom is connected to macroscopic temperature!

• Thermal energy and degree of freedom

The "thermal energy" of a system is the energy that does not include the potential energy reference level u_0. Generally, for an atom

$$\varepsilon = u_0 + \underbrace{\frac{1}{2}\kappa x^2 + \frac{1}{2}\kappa y^2 + \frac{1}{2}\kappa z^2 + \frac{1}{2m}p_x^2 + \frac{1}{2m}p_y^2 + \frac{1}{2m}p_z^2}_{\varepsilon_{\text{thermal}}}$$

Since each degree of freedom carries an average energy of $kT/2$,
the average thermal energy of an atom in a solid is $\varepsilon_{\text{thermal}} = 6kT/2 = 3kT$.

Q: What is the average thermal energy of a molecule in ideal gas?

Generally, the average energy of a particle in any system can be written as

$$\bar{\varepsilon} = u_0 + \frac{v}{2}kT, \qquad N \text{ particles (average)} \qquad E = N\bar{\varepsilon} = Nu_0 + \frac{Nv}{2}kT$$

$$E_{\text{therm}} = N\varepsilon_{\text{therm}} = \frac{Nv}{2}kT$$

thermal energy is stored in the various degrees of freedom, proportional to T.

$$\Delta E = N\Delta u_0 + \frac{Nv}{2}k\Delta T$$

Add energy to a N system

• Microscopic state of one particle: Phase space

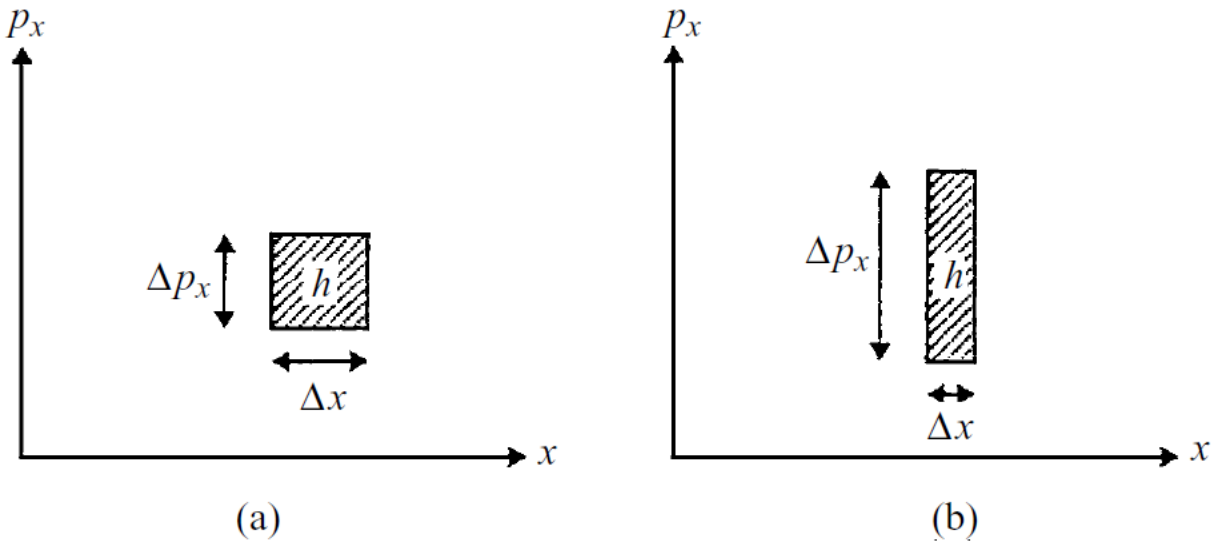
In order to understand the statistics, we need to know the "microscopic states".

Wave nature of particles $\lambda = \frac{h}{p} \quad \left(h = 6.626 \times 10^{-34}\ \mathrm{J\,s}\right)$

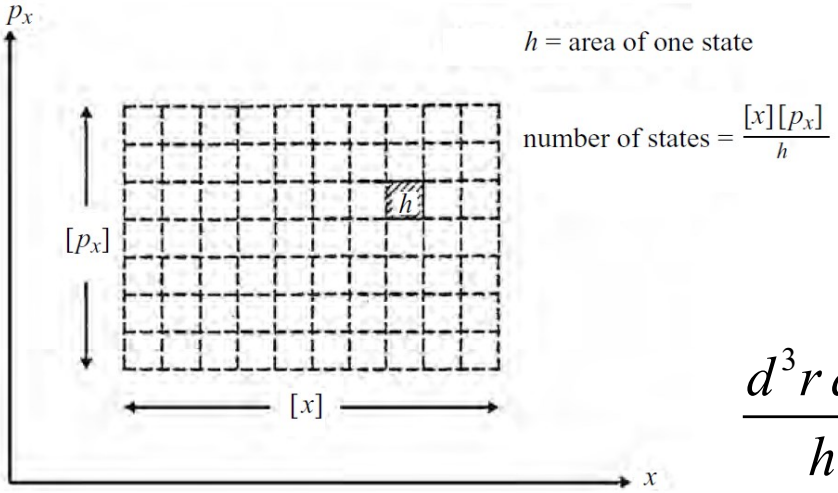
$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k \quad \left(\hbar = \frac{h}{2\pi}\right) \qquad \vec{p} = \hbar\vec{k},\ \varepsilon = \frac{\vec{p}^{\,2}}{2m} = \frac{\hbar^2\vec{k}^{\,2}}{2m}$$

Uncertainty principle

$\Delta x \Delta p_x = h$



• Microscopic states for a single particle



$$number\ of\ accessible\ states = \frac{V_r V_p}{h^3},$$

Number of states in a volume element of $\mathrm{d}^3 r\,\mathrm{d}^3 p$

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

More often used: $$\frac{d^3 r\, d^3 k}{(2\pi)^3} = \frac{dx\,dy\,dz\,dk_x\,dk_y\,dk_z}{(2\pi)^3} = \frac{dV}{(2\pi)^3}\,dk_x\,dk_y\,dk_z \qquad p = \frac{h}{2\pi}k$$

Integral: Total states for one particle (in N-particle system)

$$\omega = \int \frac{\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z}{h^3} = ?$$

Ideal gas: $$\omega = CV\left(\frac{E_{\mathrm{therm}}}{Nv}\right)^{v/2}$$

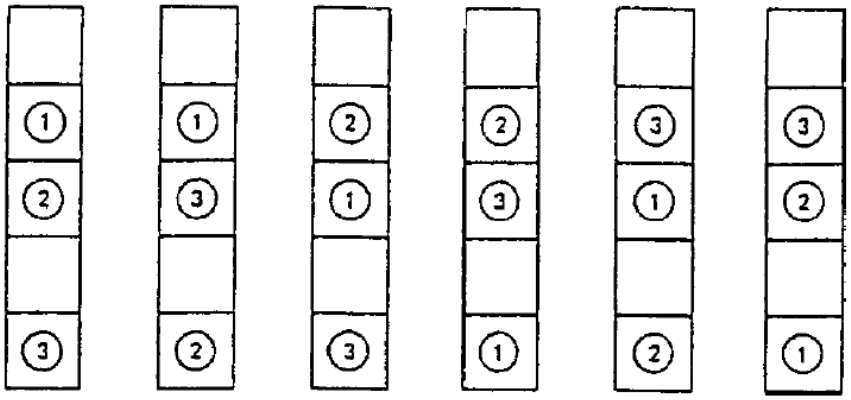
Equipartition theorem $$\overline{b\zeta^2} = \left(\frac{E_{\mathrm{therm}}}{Nv}\right) \Rightarrow \zeta_{\mathrm{rms}} = \left(\frac{E_{\mathrm{therm}}}{bNv}\right)^{1/2} \qquad \int \mathrm{d}\zeta \propto \left(\frac{E_{\mathrm{therm}}}{Nv}\right)^{1/2}$$

• Microscopic states: N particles

The N distinguishable particles and each particle has ω states, then the number of states for the total system is given by?

$$\Omega = \omega \times \omega \times \omega \times \cdots = \omega^N$$

If the particles are indistinguishable, however, the number of states is reduced by $1/N!$, $\Omega = \omega^N/N!$



5 states for 3 distinguishable particles: Total 5^3 microscopic states.

Indistinguishable particles: The left 3!=6 ways are identical

Note: $1/N!$ factor is only correct if there are many more states than particles, so that there is little likelihood that two or more particles will occupy the same state simultaneously.

• Microscopic states: N identical particles

For large N, use Stirling's approximation for $N!$, $N! \approx \sqrt{2\pi N}\left(\frac{N}{\mathrm{e}}\right)^N \approx \left(\frac{N}{\mathrm{e}}\right)^N$

we can get $\Omega = \frac{\omega^N}{N!} \approx \left(\frac{\mathrm{e}\omega}{N}\right)^N$

With this, we can get $\Omega = \omega_c^N$, where ω_c is the number of states per particle, "corrected" for the case of identical particles:

$$\omega_\mathrm{c} = \frac{\mathrm{e}\omega}{N} \quad \text{(corrected for identical particles)}$$

$$\omega_\mathrm{c} = \omega \quad \text{(distinguishable particles)}$$

We reduce the problem of finding the number of states for a large system of N particles to that of finding the number of states ω for one single particle.

For distinguishable particles (gas):

$$\omega = CV\left(\frac{E_\mathrm{therm}}{Nv}\right)^{v/2}$$

For identical particles (gas), the corrected number of states per particle:

$$\omega_\mathrm{c} = \frac{\mathrm{e}\omega}{N} = C\left(\frac{V}{N}\right)\left(\frac{E_\mathrm{therm}}{Nv}\right)^{v/2}$$

- # Team discussion: distinguishable vs identical

For distinguishable particles (gas):

$$\omega = CV\left(\frac{E_{\text{therm}}}{Nv}\right)^{v/2}$$

For identical particles (gas), the number of states per particle:

$$\omega_{\text{c}} = \frac{\text{e}\omega}{N} = C\left(\frac{V}{N}\right)\left(\frac{E_{\text{therm}}}{Nv}\right)^{v/2}$$

Q: Which one is more reasonable? Why?

• The role of Ω in statistical mechanics

Isolated system A_0 is composed of A_1 and A_2. The internal energies of the two subsystems may change as a result of their interaction, but the energy of the combined system is constant: $E_1 + E_2 = E_0 = \text{constant}$.

The number of states that are accessible to a system with Nv degrees of freedom is sensitive to its thermal energy:

$$\omega = C\left(\frac{V}{N}\right)\left(\frac{E_{\text{therm}}}{Nv}\right)^{v/2}$$

$$\Omega = \omega^N \propto E^{Nv/2}$$

The number of states for the combined system is?

$$\Omega_0 = \Omega_1\Omega_2 \propto E_1^{N_1v_1/2}E_2^{N_2v_2/2}$$

We will apply this result to an example, to show how the distribution of energy is most probably at the peaked optimum value.

• The role of Ω in statistical mechanics

First, we choose very small systems: A_1 has **6** degrees of freedom and A_2 has **10**. According to the above,

$$\Omega_1 = E_1^3 \qquad \Omega_2 = E_2^5$$

Suppose that the energy of combined system is an integer number **5**:

$$E_1 + E_2 = E_0 = 5.$$

Question 1: the of number of accessible states for A_1, A_2 and A_0?

E_1	E_2	$\Omega_1 = E_1^3$	$\Omega_2 = E_2^5$	$\Omega_0 = \Omega_1\Omega_2$
0	5	0	3125	0
1	4	1	1024	1024
2	3	8	243	1944
3	2	27	32	864
4	1	64	1	64
5	0	125	0	0

Question 2: What is the most probable energy distribution?

• The role of Ω in statistical mechanics

Now we consider that E_1 a *continuous* variable. Let's try to calculate the probabilities for *all* possible distributions of energy between two interacting systems. n_i is the total number of degrees of freedom of system *i*:

$$n_i = N_i \nu_i$$

The probability that system 1 has energy E_1 is proportional to the number of accessible states. We have,

$$\Omega_0(E_1) = E_1^{n_1/2} E_2^{n_2/2}, \text{ where } E_2 = E_0 - E_1$$

We will use the logarithm of the number of states:

$$f(E_1) \equiv \ln \Omega_0 = \ln C + \frac{n_1}{2} \ln E_1 + \frac{n_2}{2} \ln (E_0 - E_1),$$

We expand the logarithm of the number of states in a Taylor series around its maximum ($\overline{E_1}$).

$$f(E_1) = f(\bar{E}_1) + \left.\frac{\partial f}{\partial E_1}\right|_{\bar{E}_1} (E_1 - \bar{E}_1) + \frac{1}{2} \left.\frac{\partial^2 f}{\partial E_1^2}\right|_{\bar{E}_1} (E_1 - \bar{E}_1)^2 + \cdots$$

• The role of Ω in statistical mechanics

$$f\left(E_1\right) \equiv \ln \Omega_0 = \ln C + \frac{n_1}{2} \ln E_1 + \frac{n_2}{2} \ln\left(E_0 - E_1\right),$$

We assume a distribution sharply peaked at $\bar{E}_1$.
The first derivative is equal to zero (must be true at a function's maximum). We find the position of the peak and get equipartition as a by-product:

$$\left.\frac{\partial f}{\partial E_1}\right|_{\bar{E}_1} = 0 \quad \Rightarrow \quad \frac{\bar{E}_1}{\bar{E}_2} = \frac{n_1}{n_2}$$

That is, the energy is distributed in proportion to the number of degrees of freedom.

The second derivative is evaluated from equation $f(E_1)$, (Homework)

$$\left.\frac{\partial^2 f}{\partial E_1^2}\right|_{\bar{E}_1} = -\frac{n_0}{2\bar{E}_1\bar{E}_2}.$$

$$f\left(E_1\right) = f\left(\bar{E}_1\right) + 0 + \frac{1}{2}\left.\frac{\partial^2 f}{\partial E_1^2}\right|_{\bar{E}_1}\left(E_1 - \bar{E}_1\right)^2 + \cdots \approx -\frac{n_0}{4\bar{E}_1\bar{E}_2}\left(E_1 - \bar{E}_1\right)^2 = \ln \Omega_0$$

Now that we know the first and second derivatives, we can take the antilogarithm of the Taylor series and get $\Omega_0(E_1)$

- Ω gives rise to the most probable distribution

$$-\frac{n_0}{4\bar{E}_1\bar{E}_2}\left(E_1-\bar{E}_1\right)^2=\ln\Omega_0$$

$$\Omega_0\left(E_1\right)=\Omega_0\left(\bar{E}_1\right)e^{-\left(E_1-\bar{E}_1\right)^2/2\sigma^2},\ \text{with}\ \sigma^2=\frac{2\bar{E}_1\bar{E}_2}{n_0}=\frac{n_1n_2}{2n_0}(kT)^2$$

$$\text{we use}\ \overline{E_1}=\left(\frac{n_1}{2}\right)kT\ \text{in evaluating}\ \sigma^2\ \text{and}\ \ \frac{\bar{E}_1}{\bar{E}_2}=\frac{n_1}{n_2}$$

Because the probability is proportional to the number of states ($P \propto \Omega_0$), and the sum over all possible distributions gives a total probability of 1, the distribution is the familiar Gaussian form:

$$P\left(E_1\right)=\frac{1}{\sqrt{2\pi\sigma}}\mathrm{e}^{-\left(E_1-\bar{E}_1\right)^2/2\sigma^2}\qquad \bar{E}_1=\frac{n_1}{2}kT\qquad \text{and}\qquad \sigma=\sqrt{\frac{n_1n_2}{2n_0}kT}$$

- Ω gives rise to the most probable distribution

If A_2 is a relatively large system, i.e., a "reservoir," so that $n_1 \ll n_2 \approx n_0$, then the standard deviation and relative fluctuation become

$$\sigma = \sqrt{\frac{n_1 n_2}{2n_0}}kT \qquad \sigma \approx \sqrt{\frac{n_1}{2}}kT, \qquad \frac{\sigma}{\bar{E}_1} \approx \sqrt{\frac{2}{n_1}} \quad (A_2 \gg A_1).$$

$$\bar{E}_1 = \frac{n_1}{2}kT$$

$$n_1 = N_1 \nu_1$$

So, for a macroscopic system, having 10^{24} degrees of freedom (10×10^{23}), the relative fluctuation would be given by

$$\frac{\sigma}{\bar{E}_1} \approx 10^{-12} \quad (for\ 10^{24}\ degrees\ of\ freedom)$$

Interacting macroscopic systems in **equilibrium** will always be in a state with the one optimal distribution of energies between them. The chance of our seeing a different distribution of energies is infinitesimal.

When two interacting macroscopic systems are in **equilibrium**, the distribution of energy must be such that the number of states available to the combined system is a **maximum**.

Next week:

Third law, Second law and equilibrium,
Entropy and heat capacity,
Fluctuations,
Helmholtz/Gibbs free energy, Enthalpy
Maxwell's relations
van der Waals gas and equation of state
Isobaric/Isothermal/Adiabatic processes, Free expansion