



General Physics I

Lecture 24: Microscopic Model of Ideal Gases



Outline

How to relate macroscopic properties to microscopic properties?

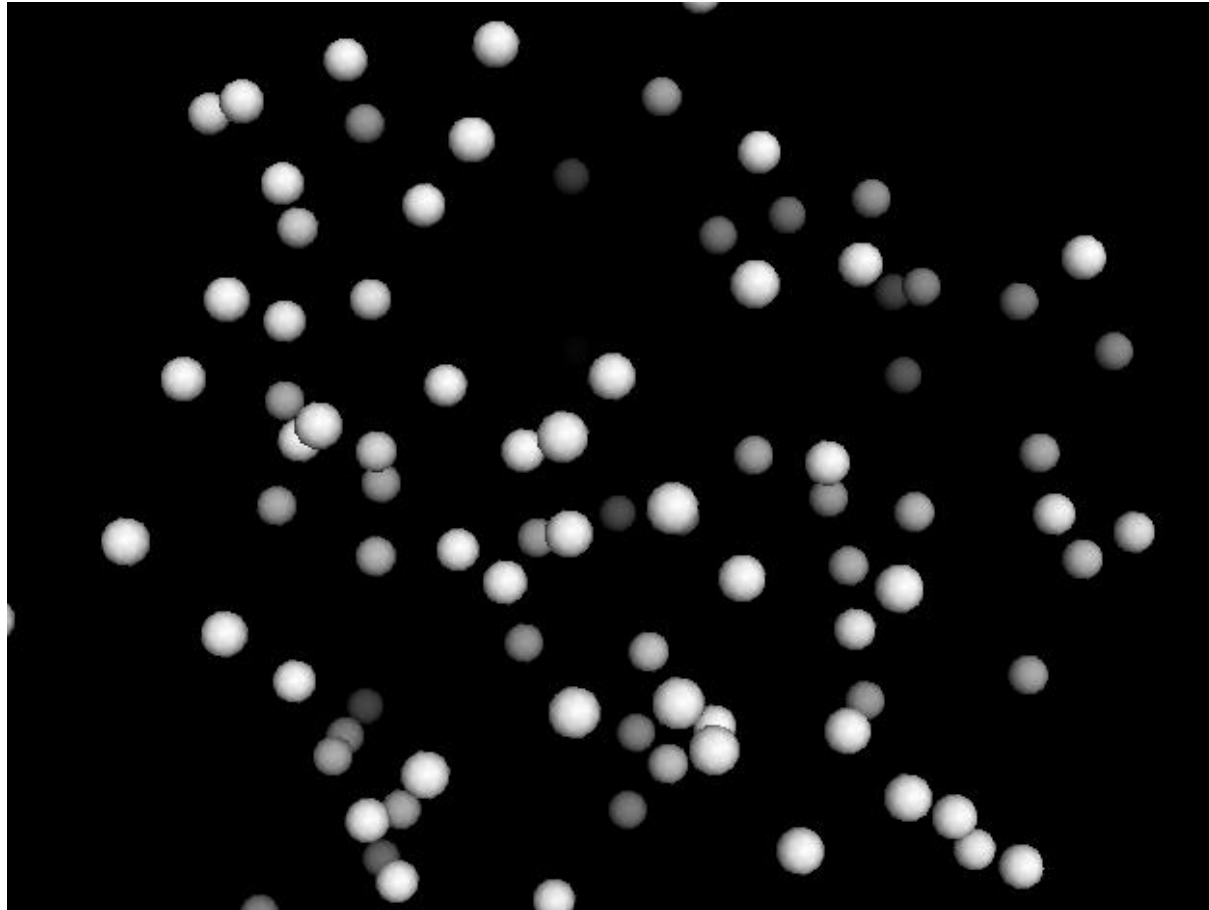
- Pressure, temperature, heat capacity

Statistical rules of a many-particle system

- Maxwell's distribution



What is an Ideal Gas?





Assumptions of the Ideal Gas Model

Large number of molecules and large average separation (molecular volume is negligible).

The molecules obey Newton's laws, but as a whole they move randomly with a time-independent distribution of speeds.

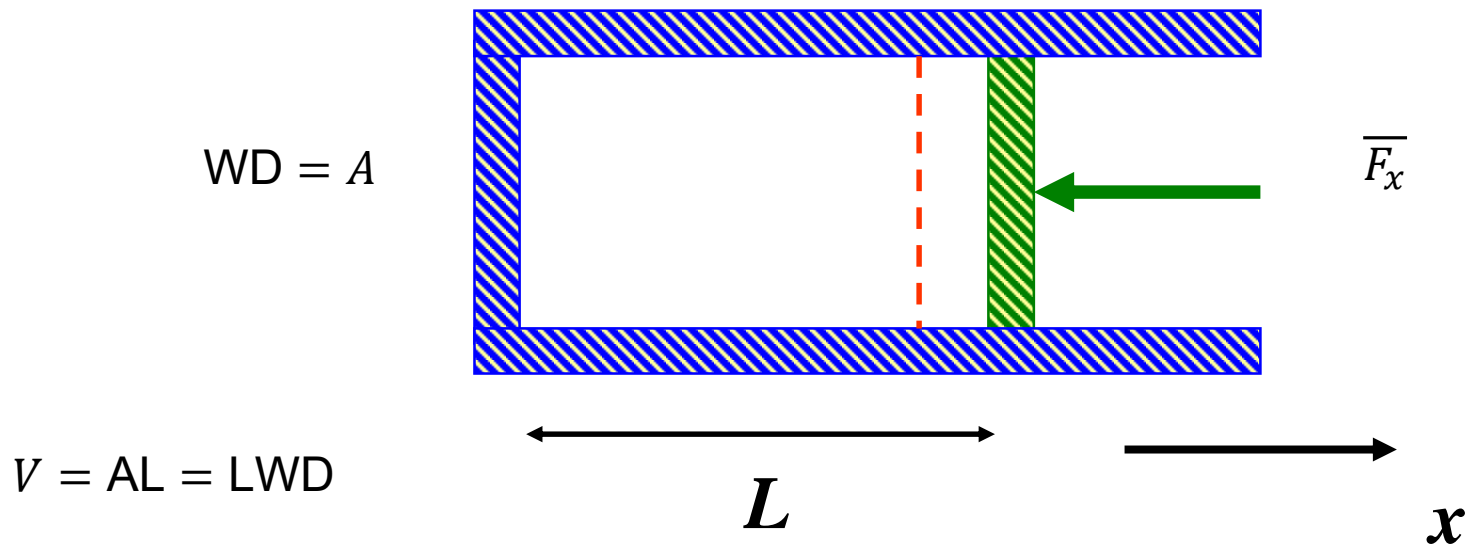
The molecules undergo elastic collisions with each other and with the walls of the container.

The forces between molecules are short-range, hence negligible except during a collision.

All of the gas molecules are identical.



The Microscopic Model



$$\bar{p} = \frac{\overline{F}_{x, \text{on piston}}}{A} = -\frac{\overline{F}_{x, \text{on molecules}}}{A} = -\frac{\overline{\sum (m\Delta v / \Delta t)}}{A}$$



Pressure, the Microscopic View

Pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls.

$$\overline{p}A\Delta t = -\overline{\sum m\Delta v} = 2m\overline{\sum v_x}$$

$$\sum \rightarrow A \cdot v_x \Delta t \cdot \rho \cdot \frac{1}{2} \Rightarrow \overline{p} = \rho \overline{mv_x^2} = \frac{\rho}{3} \overline{mv^2}$$

$$\rho = N / V$$

half of molecules
moving right



Applying the Ideal Gas Law

$$\bar{p}V = \frac{N}{3} \overline{mv^2} = \frac{nN_A}{3} \overline{mv^2}$$

$$\Rightarrow \overline{\frac{1}{2}mv^2} = \frac{3\bar{p}V}{2nN_A} \xrightarrow{\overline{pV = nRT}} \frac{3}{2}k_B T$$

**Boltzmann's
constant**

$$k_B = \frac{R}{N_A} = \frac{8.31 \text{ J}/(\text{mole} \cdot \text{K})}{6.02 \times 10^{23} \text{ (/mole)}} = 1.38 \times 10^{-23} \text{ J/K}$$



Temperature

Temperature is a measure of internal energy (k_B is the conversion factor). It measures the average energy per degree of freedom per molecule/atom.

$$\overline{\frac{1}{2}mv_x^2} = \overline{\frac{1}{2}mv_y^2} = \overline{\frac{1}{2}mv_z^2} = \frac{1}{2}k_B T$$

Equipartition theorem: can be generalized to rotational and vibrational degrees of freedom.



Heat Capacity at Constant V

We can detect the microscopic degrees of freedom by measuring heat capacity at constant volume.

Internal Energy $U = Nfk_B T/2$

Heat capacity

$$C_V = \left(\frac{\Delta U}{\Delta T} \right)_{\text{fixed } V} = \frac{f}{2} N k_B$$

degrees of freedom

Molar specific heat $c_V = (f/2)R$



Specific Heat at Constant V

表 2 - 3 0°C 下几种气体的摩尔定体热容量的实验值

单原子分子气体	He	Ne	Ar	Kr	Xe	单原子 N
C_V^{mol}/R	1.49	1.55	1.50	1.47	1.51	1.49
双原子分子气体	H ₂	O ₂	N ₂	CO	NO	Cl ₂
C_V^{mol}/R	2.53	2.55	2.49	2.49	2.57	3.02
多原子分子气体	CO ₂	H ₂ O	CH ₄	C ₂ H ₄	C ₃ H ₆	NH ₃
C_V^{mol}/R	3.24	3.01	3.16	4.01	6.17	3.42

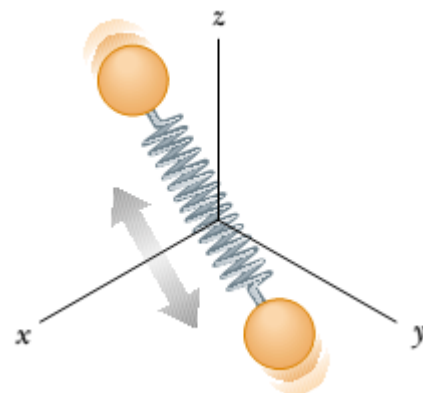
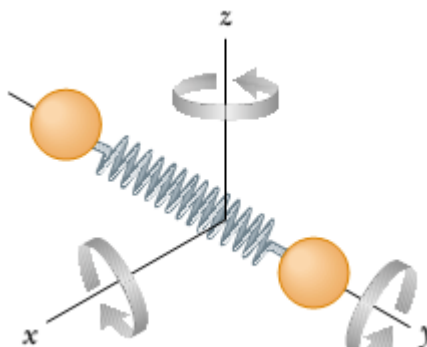
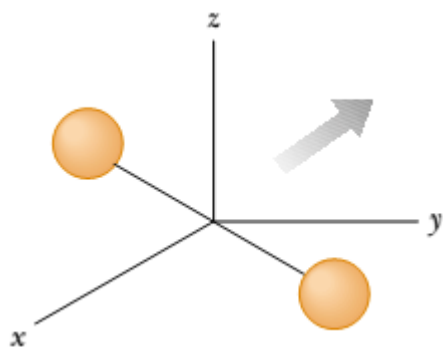
- Monoatomic gases has a ratio 3/2. Remember?
- Why do diatomic gases have the ratio 5/2?
- What about polyatomic gases?



Specific Heat at Constant V

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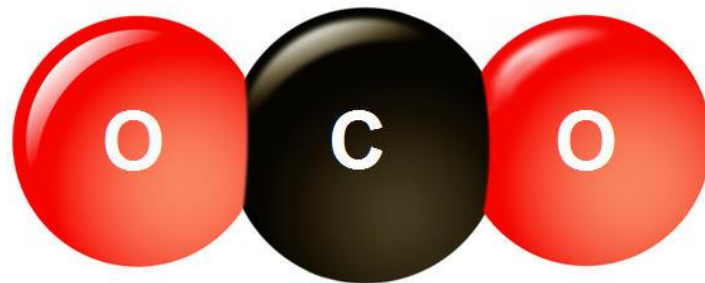




Mode Counting

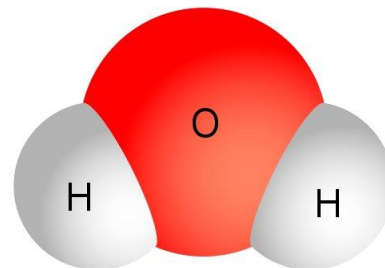
N-atom linear molecule

- Translation: 3
- Rotation: 2
- Vibration: $3N - 5$



N-atom (nonlinear) molecule

- Translation: 3
- Rotation: 3
- Vibration: $3N - 6$

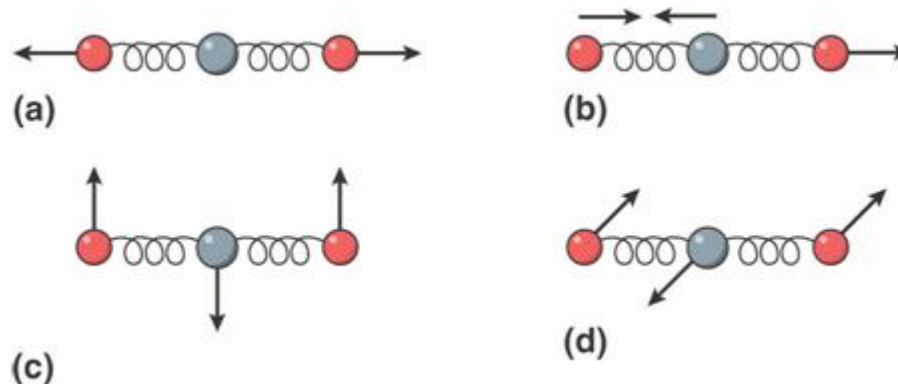




Vibrational Modes of CO₂

N = 3, linear

- **Translation: 3**
- **Rotation: 2**
- **Vibration: $3N - 3 - 2 = 4$**



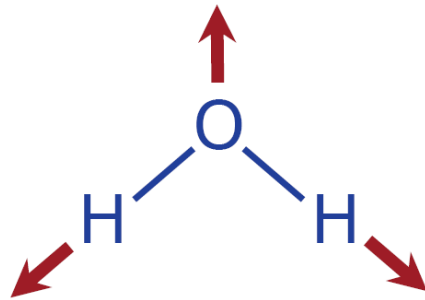


Vibrational Modes of H₂O

N = 3, planer

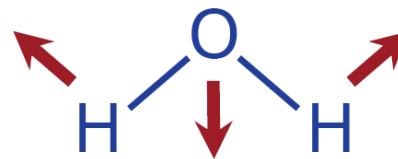
- **Translation: 3**
- **Rotation: 3**
- **Vibration: $3N - 3 - 3 = 3$**

**symmetric
stretching**



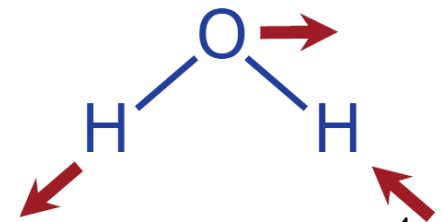
Free molecules: $\tilde{\nu} = 3657 \text{ cm}^{-1}$
Liquid: $\tilde{\nu} = 3400 \text{ cm}^{-1}$

**antisymmetric
stretching**



$\tilde{\nu} = 1595 \text{ cm}^{-1}$

bending



$\tilde{\nu} = 3756 \text{ cm}^{-1}$

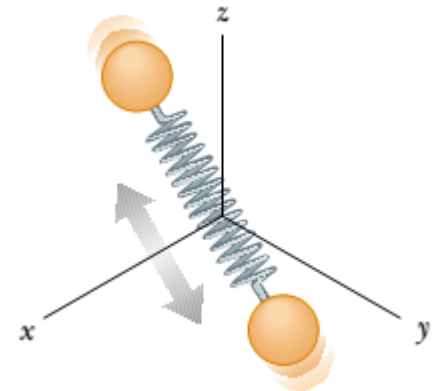
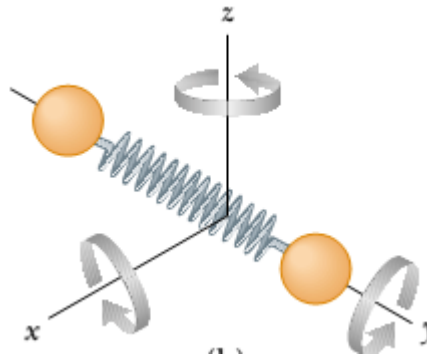
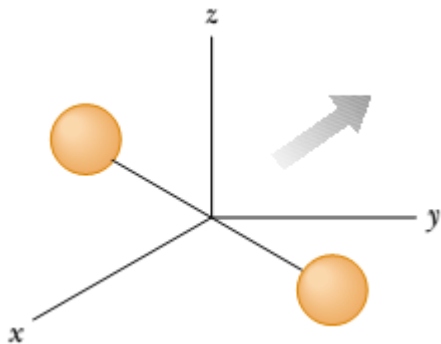


Contribution to Specific Heat

$$E = \sum_i \frac{p_i^2}{2m_i} + \sum_i \frac{1}{2} k_i q_i^2 + \dots$$

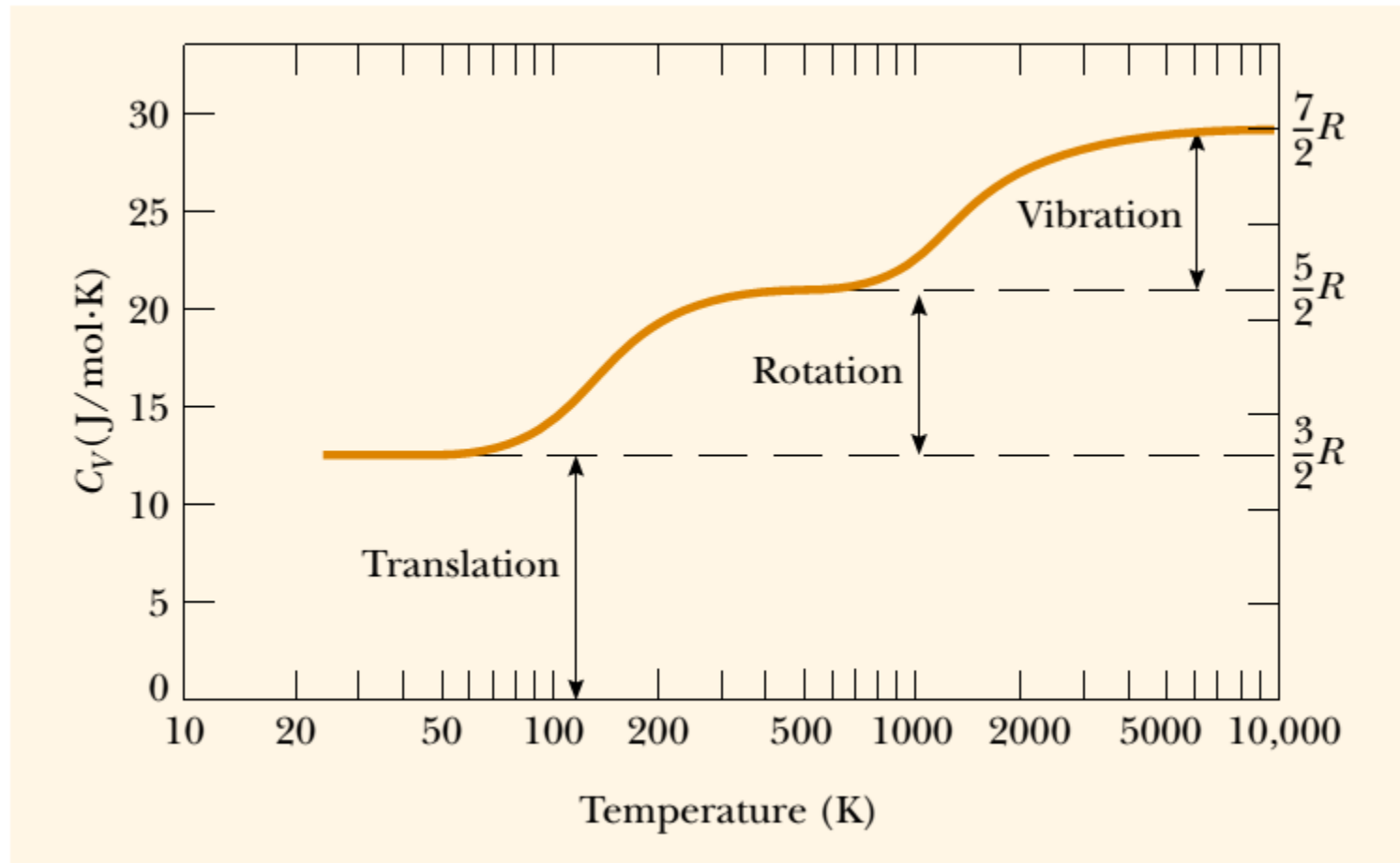
Equipartition theorem: The mean value of each independent quadratic term in the energy is equal to $k_B T/2$.

Vibration has both kinetic energy and potential energy, hence is counted as **two degrees of freedom.**





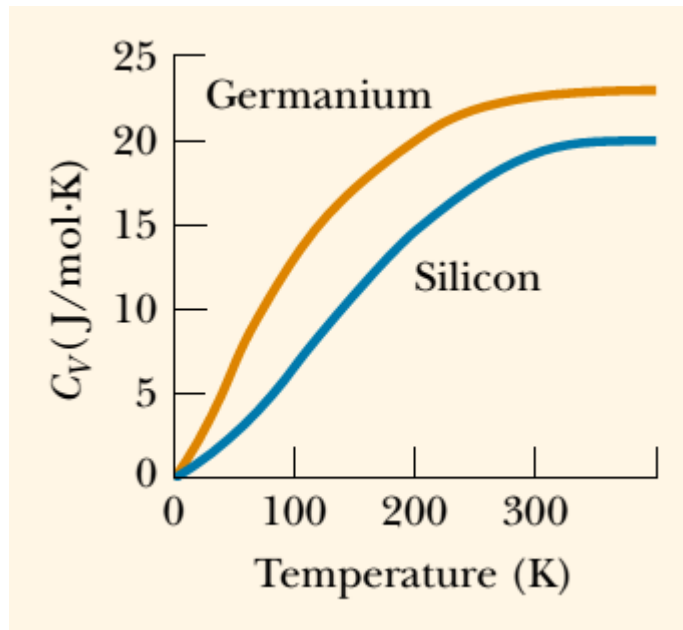
Specific Heat of H_2



Quantum mechanics is needed to explain this.



Specific Heat of Solids



DuLong – Petit law

$$U = 3Nk_B T = 3nRT$$

spatial
dimension

vibration
energy

Molar specific heat

$$c_V = \frac{1}{n} \left(\frac{dU}{dT} \right)_V = 3R$$

Again, quantum mechanics is needed.



Elementary Probability Theory

Assume the speeds of 10 particles are 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 m/s

$$\bar{v} = \frac{\sum v_i}{N} = \frac{0.0 + 1.0 + \dots + 9.0}{10} = 4.5 \text{ m/s}$$

$$v_{\text{rms}} = \sqrt{\frac{\sum v_i^2}{N}} = \sqrt{\frac{0.0^2 + 1.0^2 + \dots + 9.0^2}{10}} = 7.5 \text{ m/s}$$

When we have many particles, we may denote p_a the probability of finding their velocities in the interval $[v_a, v_{a+1}]$.



Elementary Probability Theory

Now, the averages become

$$\bar{v} = \sum v_a p_a, \text{ where } \sum_a p_a = 1 \quad v_{\text{rms}} = \sqrt{\sum v_a^2 p_a}$$

In the continuous version, we may denote $p(v)dv$ the probability of finding particles' velocities in the interval $[v, v+dv]$.

$$\bar{v} = \int_{-\infty}^{+\infty} vp(v)dv, \text{ where } \int_{-\infty}^{+\infty} p(v)dv = 1$$

$$v_{\text{rms}} = \sqrt{\int v^2 p(v)dv}$$



The Life and Death Game

Suppose a group of N people standing along a circle. At time t , each one of them either turn left or turn right, fire an armgun and kill the next person. What is the chance of survival?





The Life and Death Game

The lesson to learn here is that although we cannot predict the life or death of each individual, we are able to predict the collective outcome based on the probability theory.

We now demonstrated how to enumerate to solve the problem for $N = 4$.

[Project for those who are interested] Generalize it to the **large N limit. Use computers for help and try to prove the computer findings by analytical calculations or conjecture the analytical results, if you cannot prove them.**

Now what about molecules?



Small Systems & Conjecture

- 分析 N=3 的情况:

	A	B	C	0 : 0.25 1 : 0.75
1	→	→	→	
2	→	→	←	
3	→	←	→	
4	→	←	←	
5	←	→	→	
6	←	→	←	
7	←	←	→	
8	←	←	←	

此时存活人数期望为 0.75, 占总人数的 25%

- 当 N=5 时, 共 32 种情况, 不在此列举

了, 存活人数及概率, $P(0) = \frac{1}{16}$

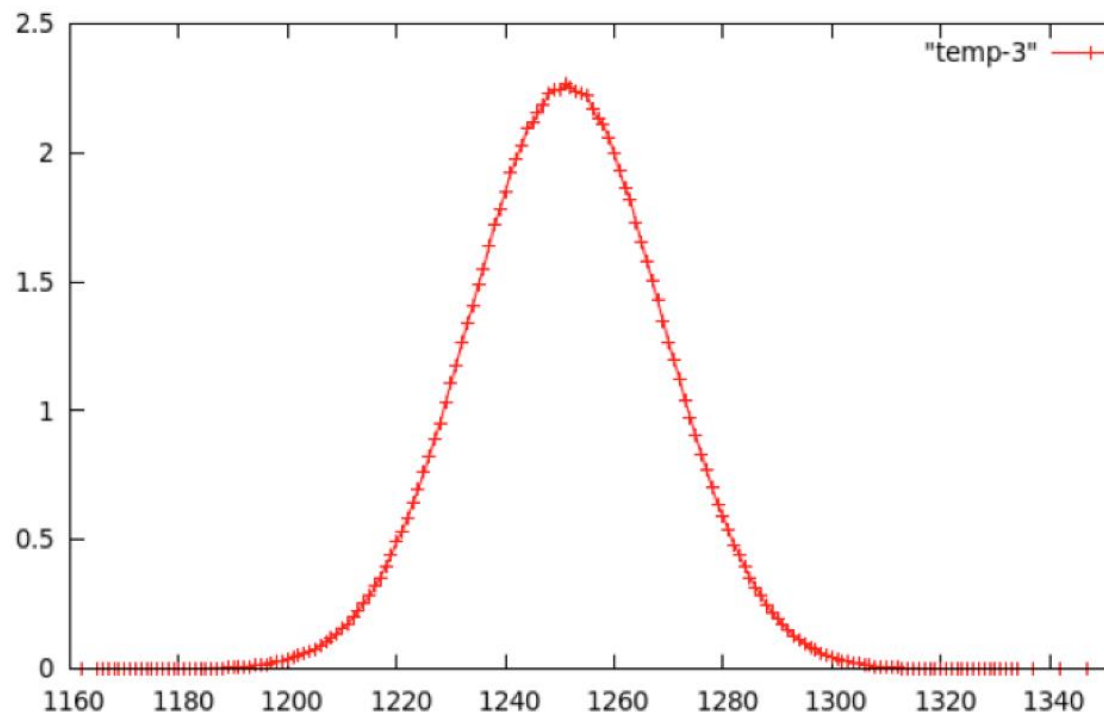
$$P(1) = \frac{5}{8} \quad P(2) = \frac{5}{16}$$

初步结论: 此时猜测存活人数期望所占比率为 25%, N=4 是一个比较特殊的情况, 其分布点比较对称, 猜测概率分布曲线也是对称的。由于数据大时枚举不合适, 此时想到用计算机编程来进行重复性操作, 并且可以来计算存活人数概率并画出概率分布曲线。



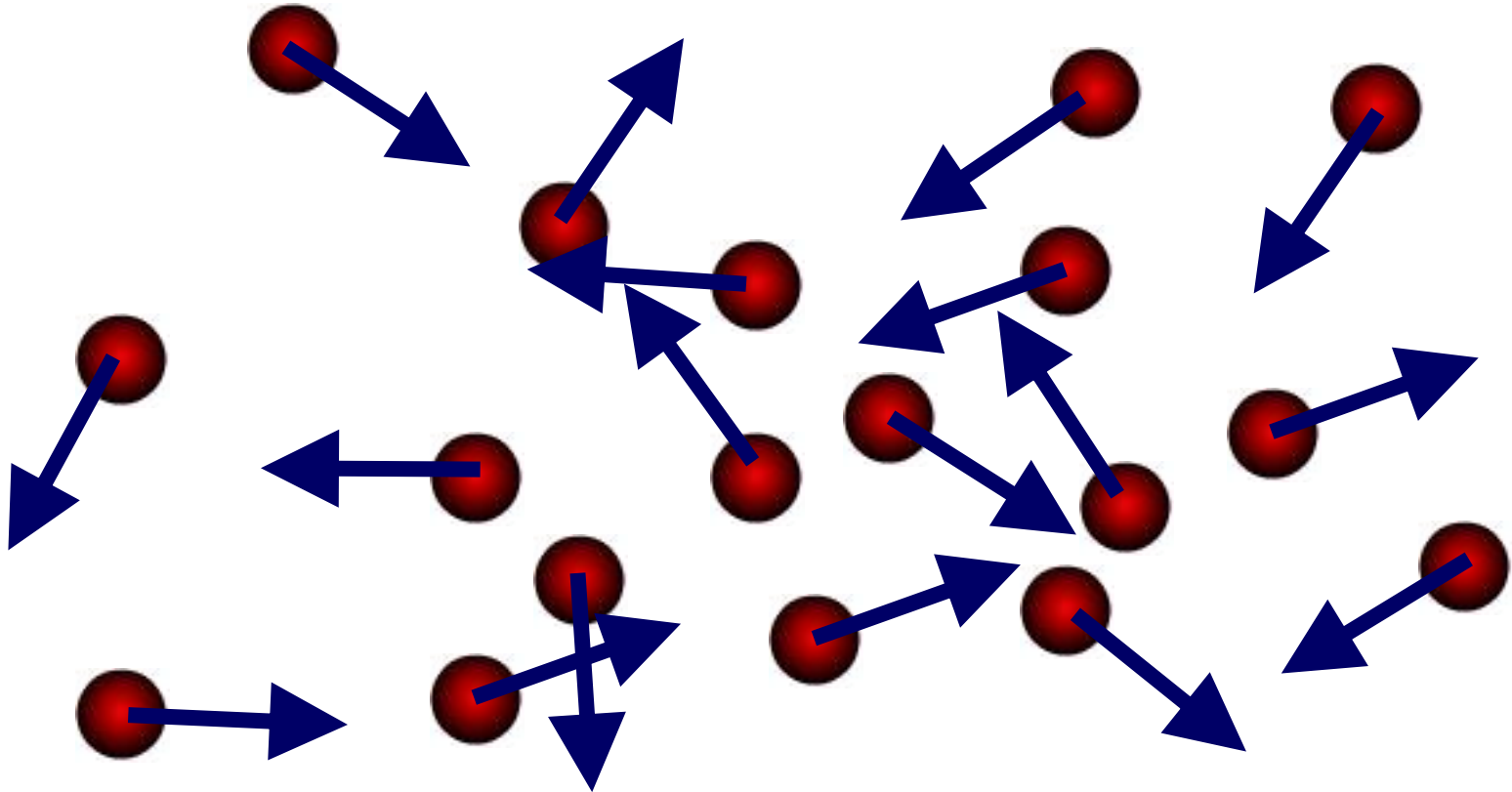
Computer Simulation

- 五千人重复五百万次：
(平均活下来 25.000026%的人)





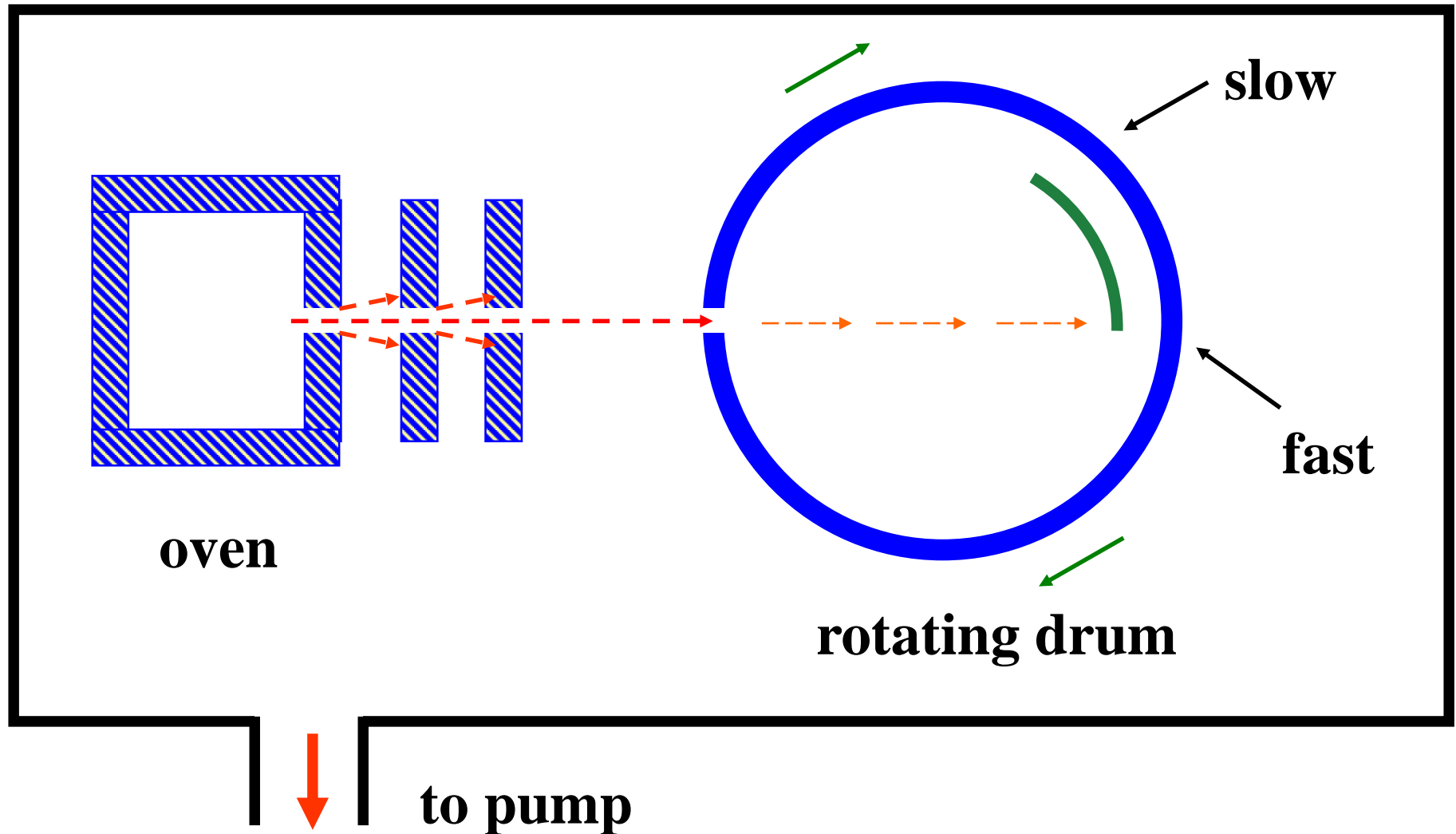
What Is the Speed Distribution?



We want to know how many molecules have a velocity between, for example, $[v, v+dv]$.



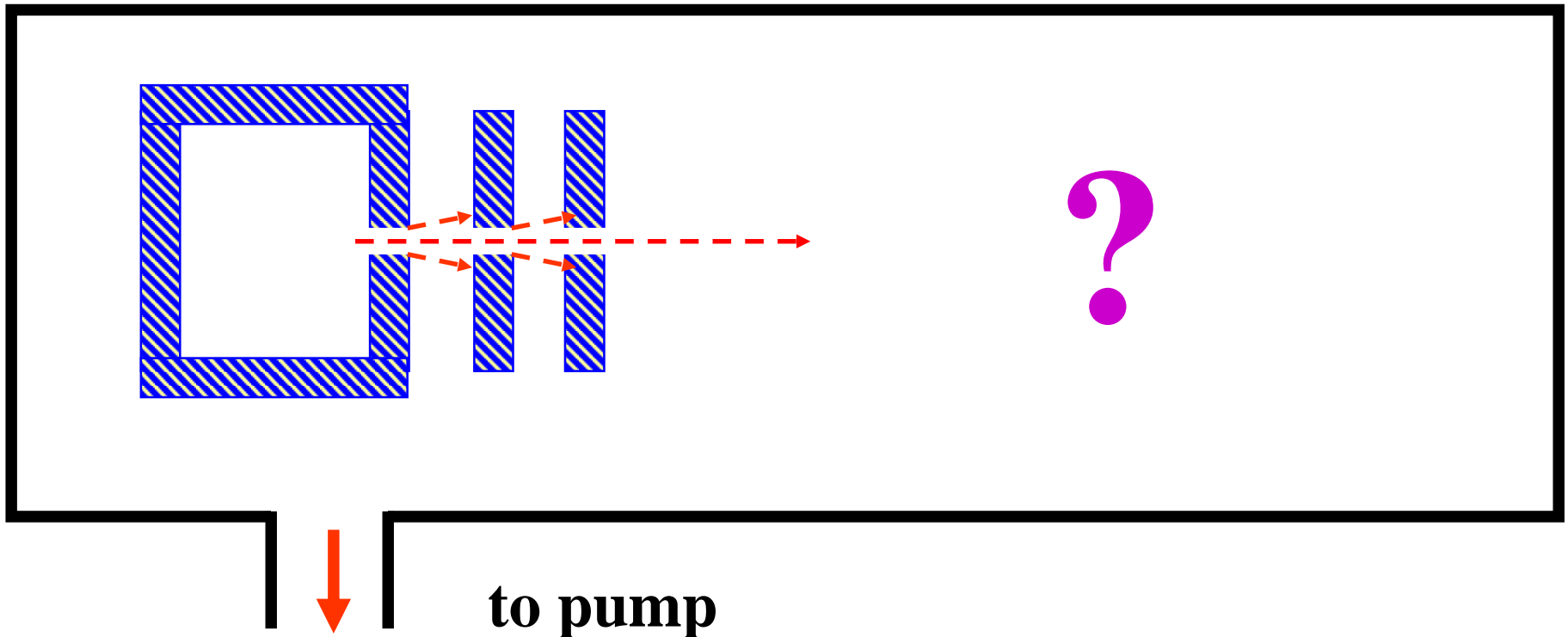
Distribution of Speed





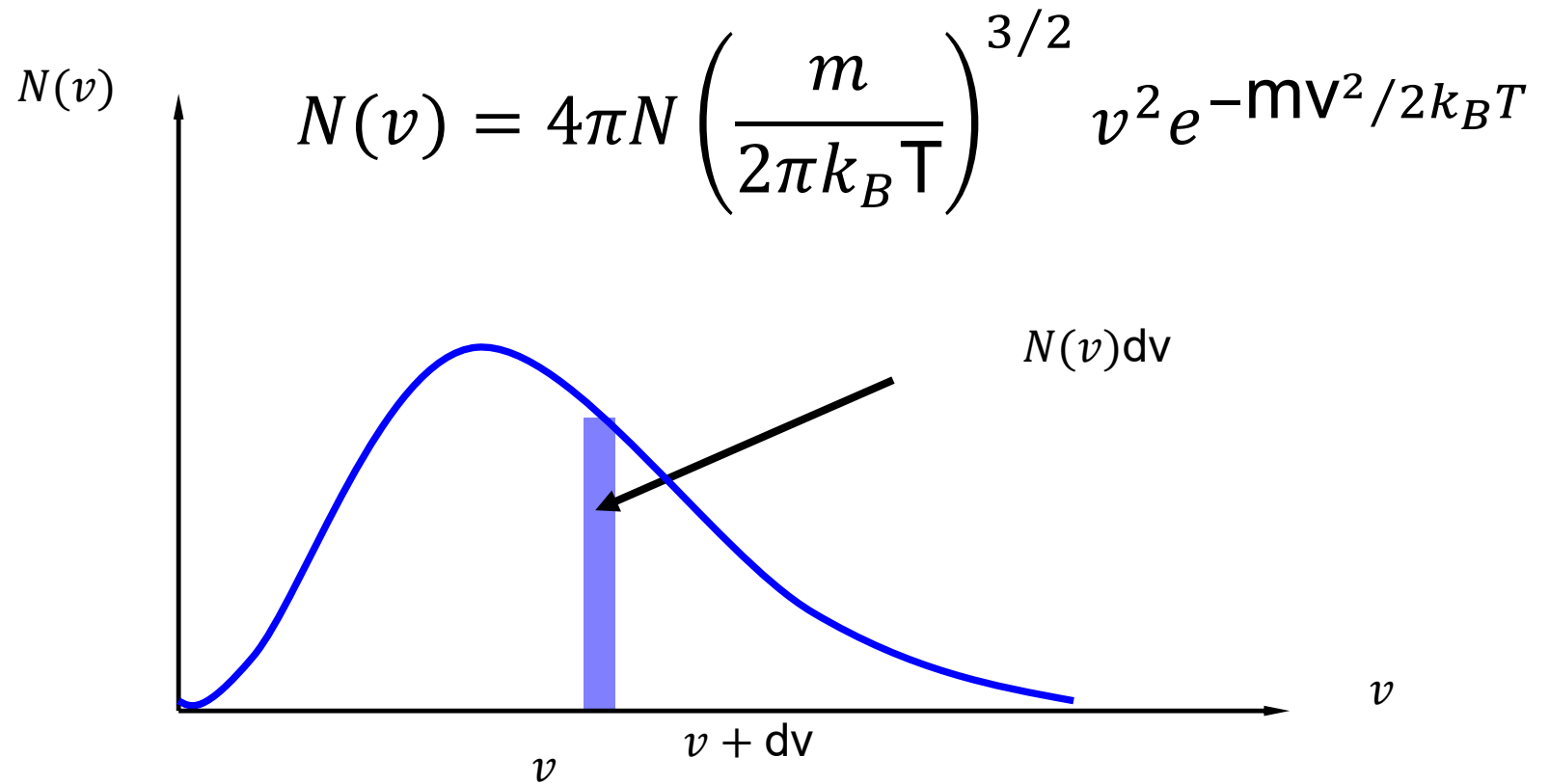
Speed Selection

Can you design an equipment to select gas molecules with a chosen speed?





Maxwell Distribution





Understanding Maxwell Distrib.

In real space

- Homogeneous: translational symmetry
- Isotropic: rotational symmetry

In velocity space

- Isotropic: $N(v) \sim N f(v)$

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$



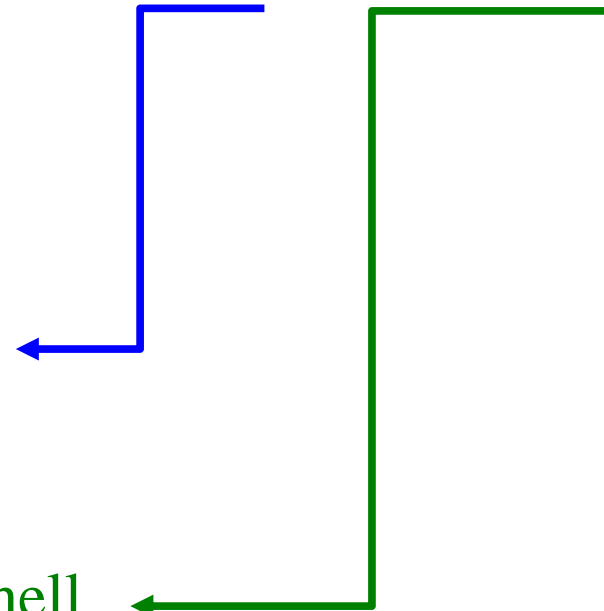
Understanding Maxwell Distrib.

$$N(v)dv = N \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} 4\pi v^2 dv$$

Normalization

Exponentially fewer particles
with higher energies

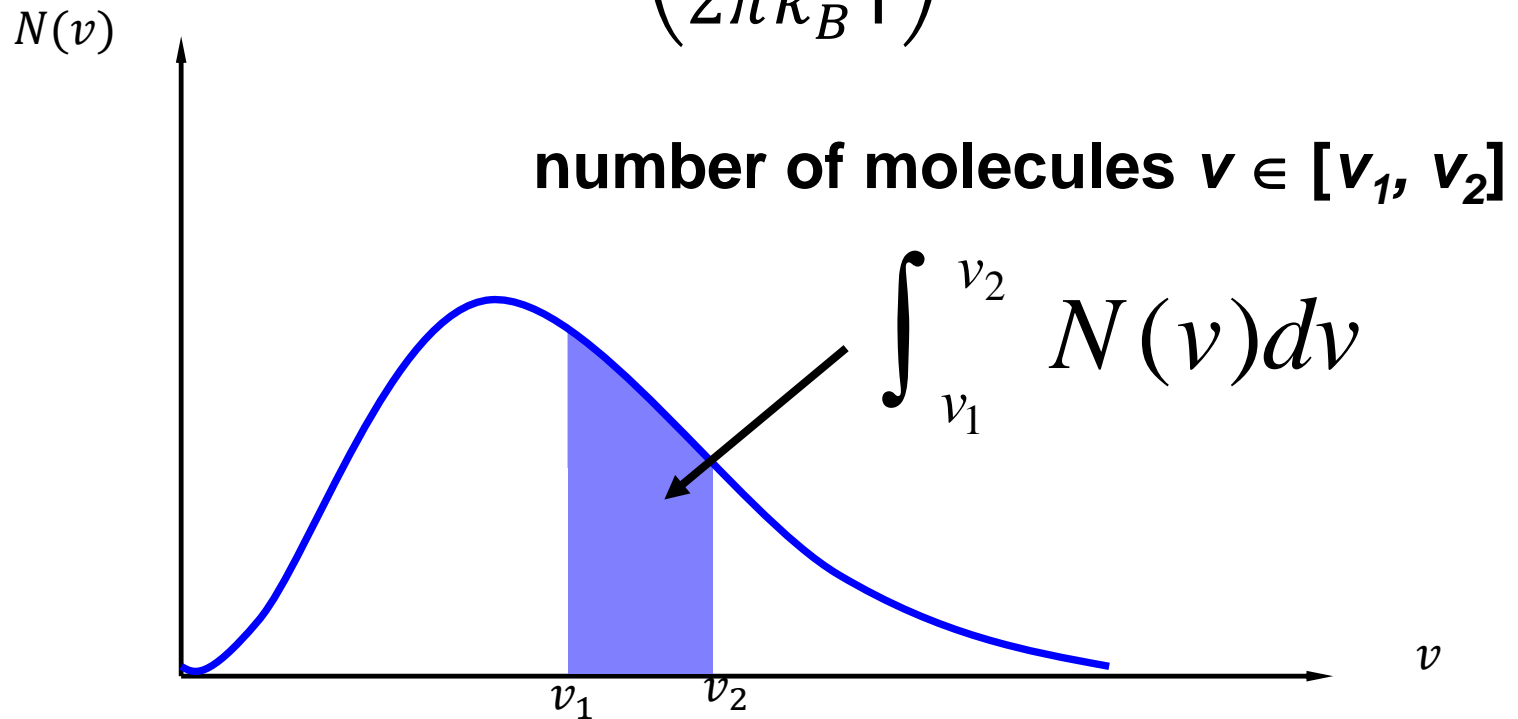
Volume of the equal-velocity shell





Maxwell Distribution

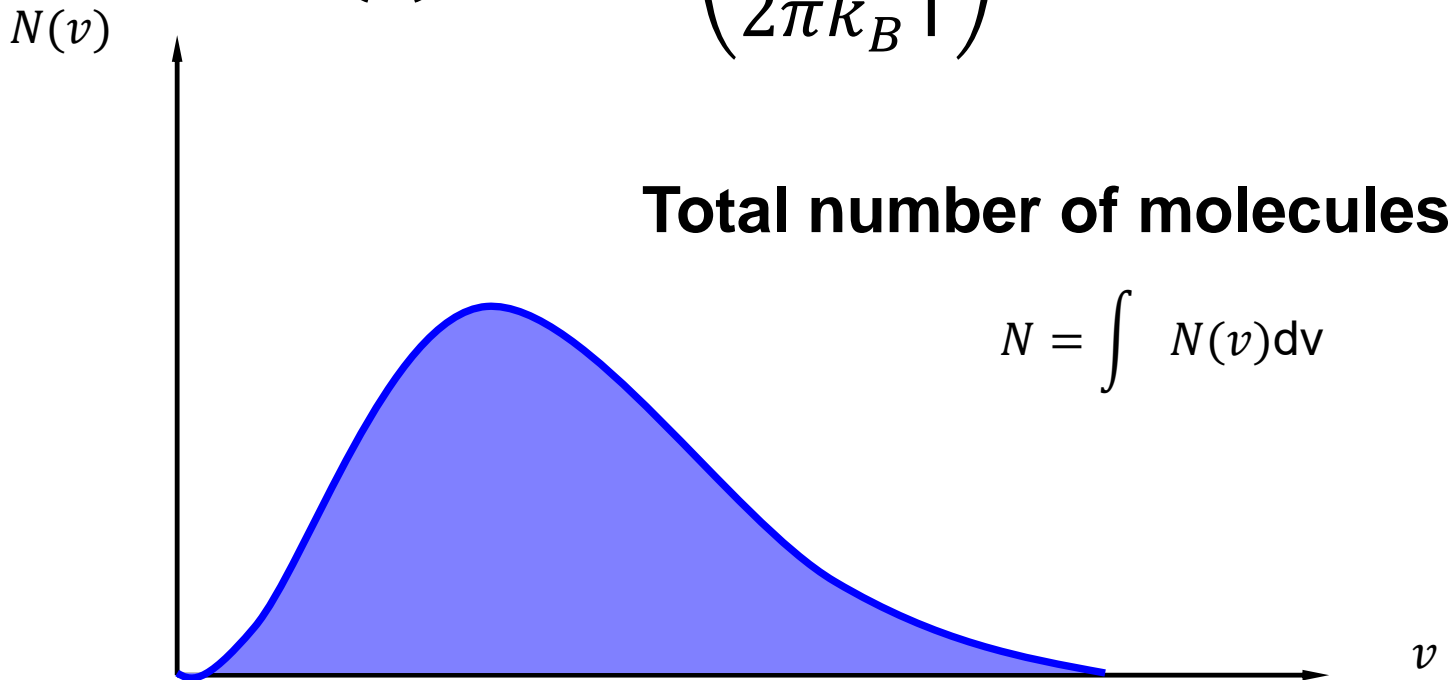
$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$





Maxwell Distribution

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$



You can find out how to calculate the integral in
Appendix I: Mathematical Formulas.



Gauss's Probability Integral

$$I_0 = \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad (\text{Gauss's probability integral})$$

$$I_1 = \int_0^{\infty} xe^{-ax^2} dx = \frac{1}{2a}$$

$$I_2 = \int_0^{\infty} x^2 e^{-ax^2} dx = -\frac{dI_0}{da} = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$$

$$I_3 = \int_0^{\infty} x^3 e^{-ax^2} dx = -\frac{dI_1}{da} = \frac{1}{2a^2}$$

$$I_4 = \int_0^{\infty} x^4 e^{-ax^2} dx = \frac{d^2 I_0}{da^2} = \frac{3}{8} \sqrt{\frac{\pi}{a^5}}$$

$$I_5 = \int_0^{\infty} x^5 e^{-ax^2} dx = \frac{d^2 I_1}{da^2} = \frac{1}{a^3}$$

$$I_{2n} = (-1)^n \frac{d^n}{da^n} I_0$$

$$I_{2n+1} = (-1)^n \frac{d^n}{da^n} I_1$$



Characteristic Speed

Most probable speed $\frac{dN(v)}{dv} = 0$

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

$$\Rightarrow 2ve^{-mv^2/2k_B T} - \frac{mv^3}{kT} e^{-mv^2/2k_B T} = 0$$

$$v_p = \sqrt{\frac{2k_B T}{m}}$$



Characteristic Speed

Root mean square speed

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

$$\overline{v^2} = \frac{\int_0^\infty v^2 N(v) dv}{N} = \int_0^\infty 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^4 e^{-mv^2/2k_B T} dv$$

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$



From Equipartition Theorem

root mean square speed

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

Estimate the root mean square speed of water molecules at room temperature.

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \approx 600 \text{ m/s}$$



Characteristic Speed

Average speed

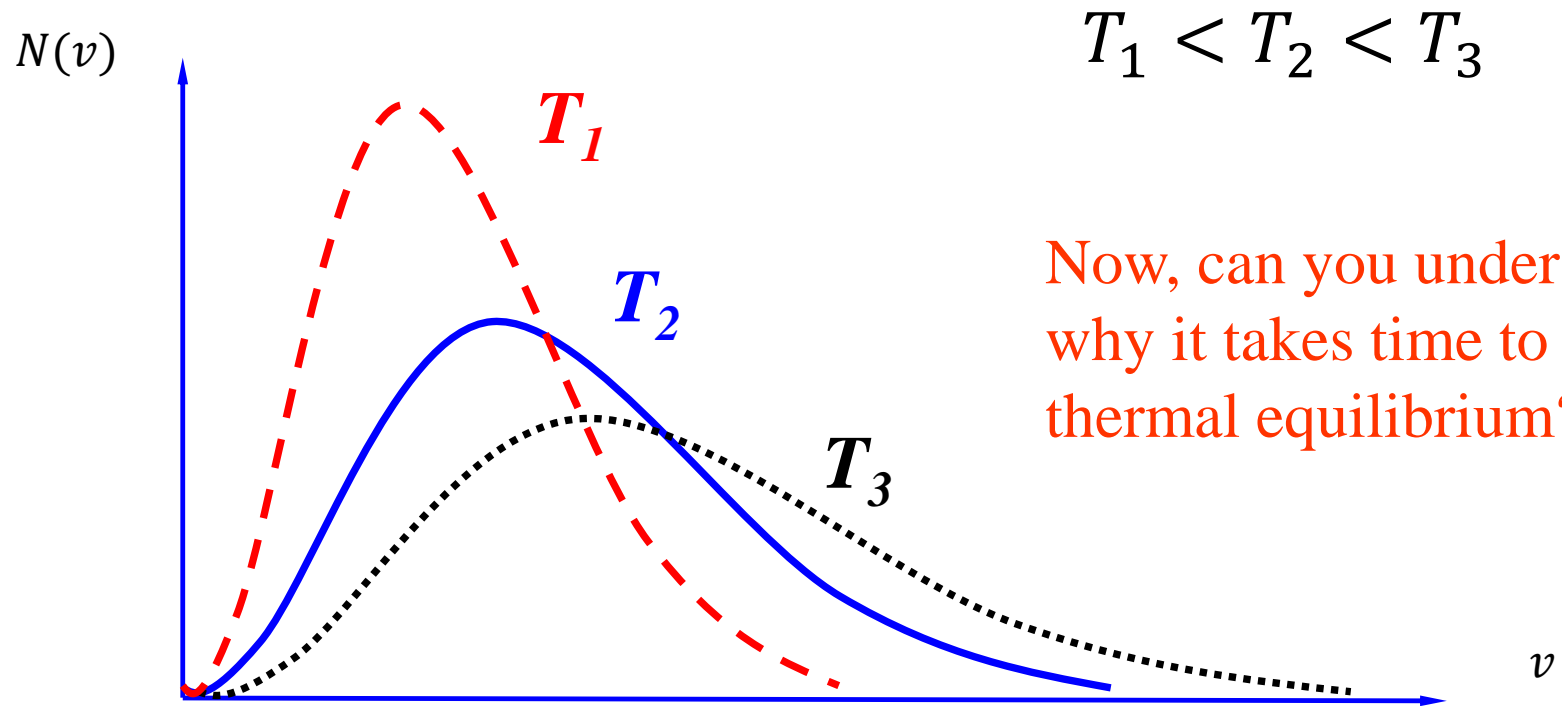
$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

$$\bar{v} = \frac{\int_0^\infty v N(v) dv}{N} = \int_0^\infty 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^3 e^{-mv^2/2k_B T} dv$$

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$$



Varying Temperature



$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$



Boltzmann Distribution

Continuing from fluid statics

potential energy

$$p = p_0 e^{-\rho_0 g h / p_0} \quad \overrightarrow{p = n_V k_B T} \quad n_V = n_0 e^{-mgy/k_B T}$$

The probability of finding the molecules in a particular energy state varies exponentially as the negative of the energy divided by $k_B T$.

$$n_V(v, h, \dots) = n_0 e^{-E(v, h, \dots)/k_B T}$$

Boltzmann distribution law



Derive the Speed Distribution

Thermal physics deals with collections of many particles. We are neither interested in nor capable of following the details of individual particles. We take a statistical point of view and ask what the probability is to find a gas atom/molecule with a speed between v and $v + dv$.

We define a one-dimensional normalized distribution function of a single velocity component, v_i , by

$$f(v_i) = \frac{1}{n} \frac{dn}{dv_i}, \quad (1)$$

where n is the density of the ideal gas and dn/dv_i represents the density of atoms with the velocity component between v_i and $v_i + dv_i$.



Continued

For any values of v_x and v_y , it is possible to define a rotation to a new set of coordinates, α and β , where $v_\alpha^2 = v_x^2 + v_y^2$ and $v_\beta^2 = 0$. Consequently, it follows that

$$f(v_\alpha)f(0) = f(v_x)f(v_y). \quad (2)$$

Differentiating the expression with respect to v_x gives

$$f'(v_x)f(v_y) = f'(v_\alpha)\frac{\partial v_\alpha}{\partial v_x}f(0). \quad (3)$$

Because of the relationship between v_α and v_x

$$\frac{\partial v_\alpha}{\partial v_x} = \frac{v_x}{v_\alpha}. \quad (4)$$

Plugging this into Eq. 3 and developing similar relationship for v_y give

$$f'(v_\alpha)f(0) = \frac{v_\alpha}{v_x}f'(v_x)f(v_y) = \frac{v_\alpha}{v_y}f(v_x)f'(v_y). \quad (5)$$

Dividing this expression by $f(v_x)f(v_y)$ gives

$$\frac{1}{v_x} \frac{f'(v_x)}{f(v_x)} = \frac{1}{v_y} \frac{f'(v_y)}{f(v_y)}. \quad (6)$$



Continued

Because each side of Eq. 6 is independent of the other, the only way the relation can be satisfied is if both sides are equal to the same constant, C . As a result we see that

$$f(v_{x,y}) = A \exp \left(-\frac{C}{2} v_{x,y}^2 \right). \quad (7)$$

If we require $f(v_{x,y})$ to be normalized, it follows that

$$1 \equiv \int_{-\infty}^{\infty} f(v_i) dv_i = A \sqrt{\frac{2}{C}} \int_{-\infty}^{\infty} \exp(-t^2) dt = A \sqrt{\frac{2\pi}{C}}, \quad (8)$$

so that

$$f(0) = A = \sqrt{\frac{C}{2\pi}}. \quad (9)$$

In three dimensions, the density of states with speed between v and $v+dv$ goes as $4\pi v^2 dv$. By analogy, in three dimensions,

$$\frac{dn}{dv} = 4\pi n v^2 f(v) f^2(0). \quad (10)$$



Continued

By definition, the average of the square of the speed is given by

$$\overline{v^2} = 4\pi f^2(0) \int_0^\infty v^4 f(v) dv = 4\pi \left(\frac{C}{2\pi}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{C}{2}v_{x,y}^2\right) dv. \quad (11)$$

The constant C can be determined by $m\overline{v^2}/2 = 3kT/2$ (the equipartition theorem), which gives

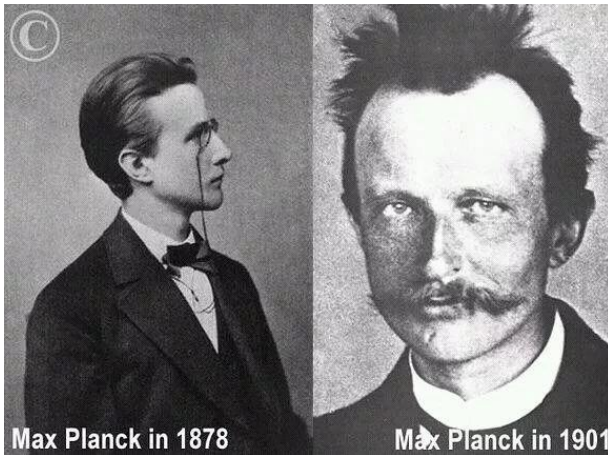
$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right), \quad (12)$$

which is the Maxwell speed distribution.

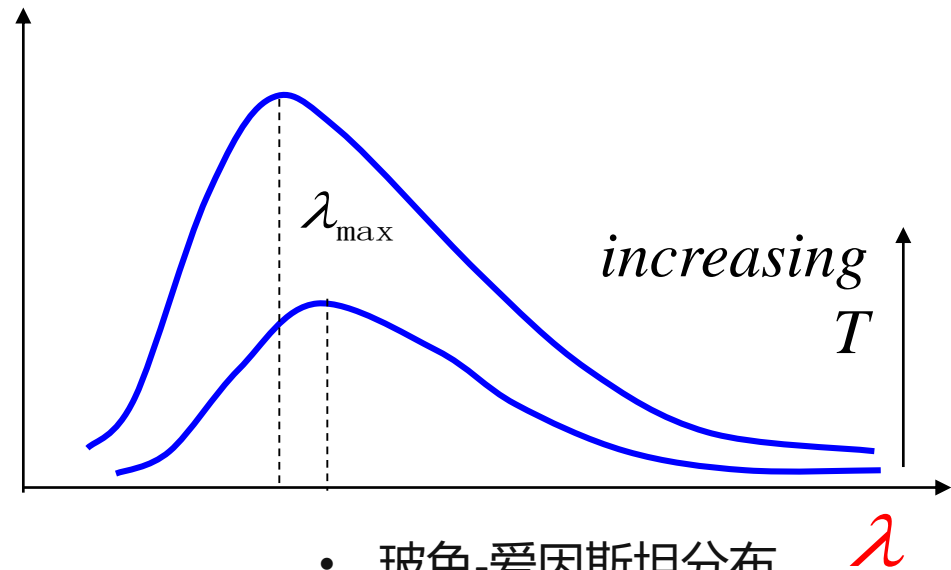


Black Body Radiation

► Planck's Law (1900):



$R(\lambda)$



- 玻色-爱因斯坦分布 λ

$$\bar{n}_{BE} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$$

- 费米-狄拉克分布

$$\bar{n}_{FD} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

$$R(\lambda, T) = \frac{2\pi hc^2}{\lambda^5 (e^{\frac{hc}{\lambda kT}} - 1)} = \frac{2\pi hc^2}{\lambda^5} \frac{1}{(e^{\frac{h\nu}{kT}} - 1)}$$

$$h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$$