Chapter 18: Thermal Properties of Matter

- What is “mole”; and what is “molar mass”?
- How to describe the status of a gas? And what is “ideal gas”?
- What is the origin of the “pressure”?
- How do we know the specific heat for ideal gas?
- Do all the air molecules move with the same speed?
- What is “phase diagram”?

Confusing Notations (don't be confused):

- *N*: number of molecules
- *n*: number of moles
- N_A : Avogadro's number: 6.02×10^{23} .
- *M*: molar mass (how much mass per mole)
- *m*: mass of “ONE” molecule
- m_{total}: total mass
- *p*: pressure
- *P*: momentum

What is “mole”; and what is “molar mass”?

- I have 2.5 dozens of identical coins with total weight of 300 g. How much weight does one dozen of coins have? How much weight does one coin have?
- I have 2.5 moles of identical molecules with total weight of 300 g. How much weight does one mole of molecules have? How much weight does one molecule have?

\# of dozens

- A “dozen” refers to “12” objects. $\$_{dozen} = 12\,\$_1$ $\$_{total} = n\,\$_{dozen}$
- A “mole” refers to “6.02 x 10^{23}“ objects (we use N_A to represent 6.02 x 10^{23})

\# of moles

$$M = N_A m \qquad m_{total} = n\,M$$

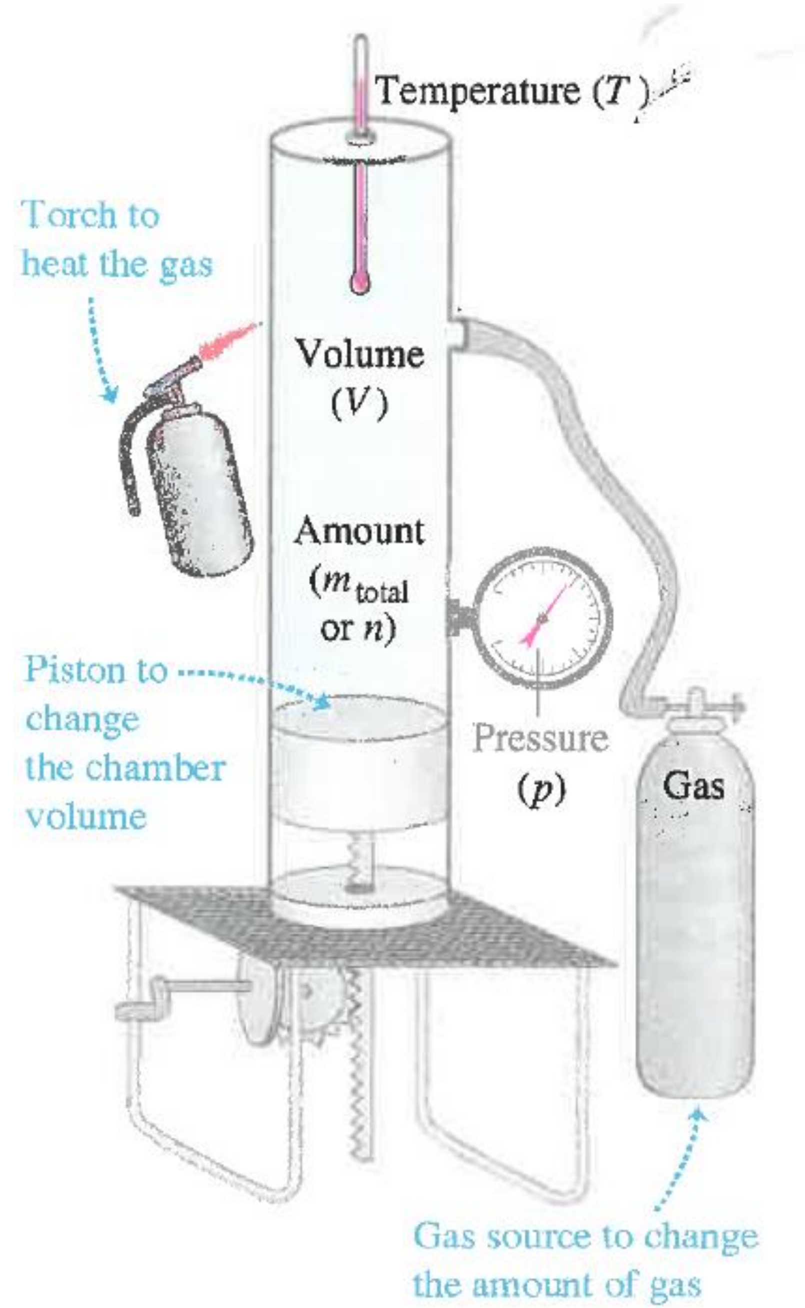
Molar mass

Single molecule mass

Equation of State

Parameters for describing a gas

- Volume
- Pressure
- Temperature
- Number of molecules (number of moles)



- Simplest model: Linear response model:

$$V = V_0\left[1+\beta(T-T_0)-k(p-p_0)\right]$$

Is this model good enough?

Equation of State

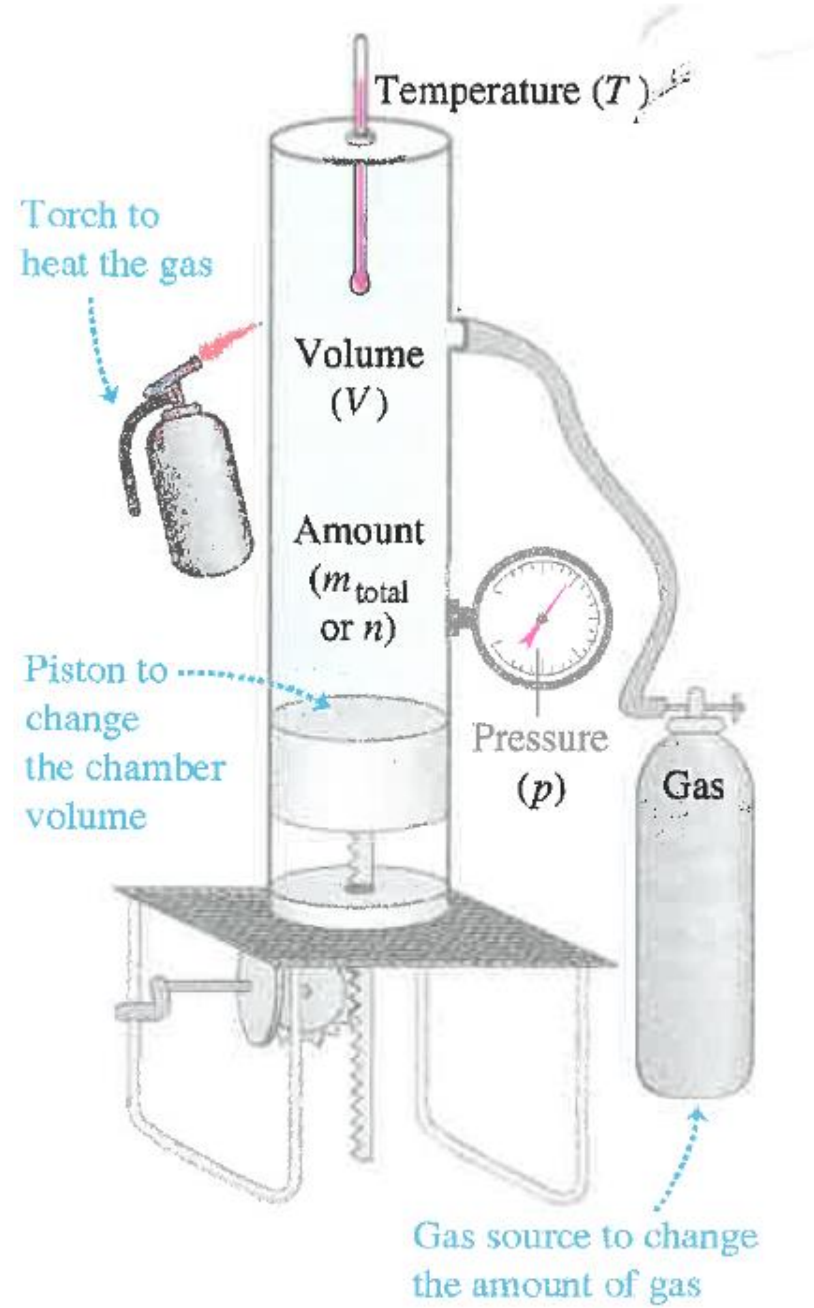
From experiments:

- *V* is proportional to *n*
- *V* is proportional to 1/*p*
- *p* is proportional to *T*

$$pV = nRT$$

$$R = 8.314472\, J/mol \cdot K$$

$$R = 0.08206\, \frac{L \cdot atm}{mol \cdot K}$$



$$pV = \frac{m_{total}}{M} RT$$

$$pM = \rho RT$$

Unit of Pressure

	Pascal (Pa)	Bar (bar)	Standard atmosphere (atm)	Torr (Torr)	Pounds per square inch (psi)
1 Pa	≡ 1 N/m^2	10^{-5}	9.8692×10^{-6}	7.5006×10^{-3}	1.450377×10^{-4}
1 bar	10^5	≡ 100 kPa≡ 10^6 dyn/cm^2	0.98692	750.06	14.50377
1 atm	1.01325×10^5	1.01325	1	≡ 760	14.69595
1 Torr	133.3224	1.333224×10^{-3}	≡ 1/760 ≈ 1.315789×10^{-3}	≡ 1 Torr≈ 1 mmHg	1.933678×10^{-2}
1 psi	6.8948×10^3	6.8948×10^{-2}	6.8046×10^{-2}	51.71493	≡ 1 lbf $/in^2$

Question

An “empty” aluminum scuba tank contains 11.0 L of air at 21 ºC and 1 atm. When the tank is filled rapidly from a compressor, the air temperature is 42 ºC and the gauge pressure is $2.1 \times 10^7\ Pa$. What mass of air was added? (Air has the average molar mass of 28.8 g/mol)

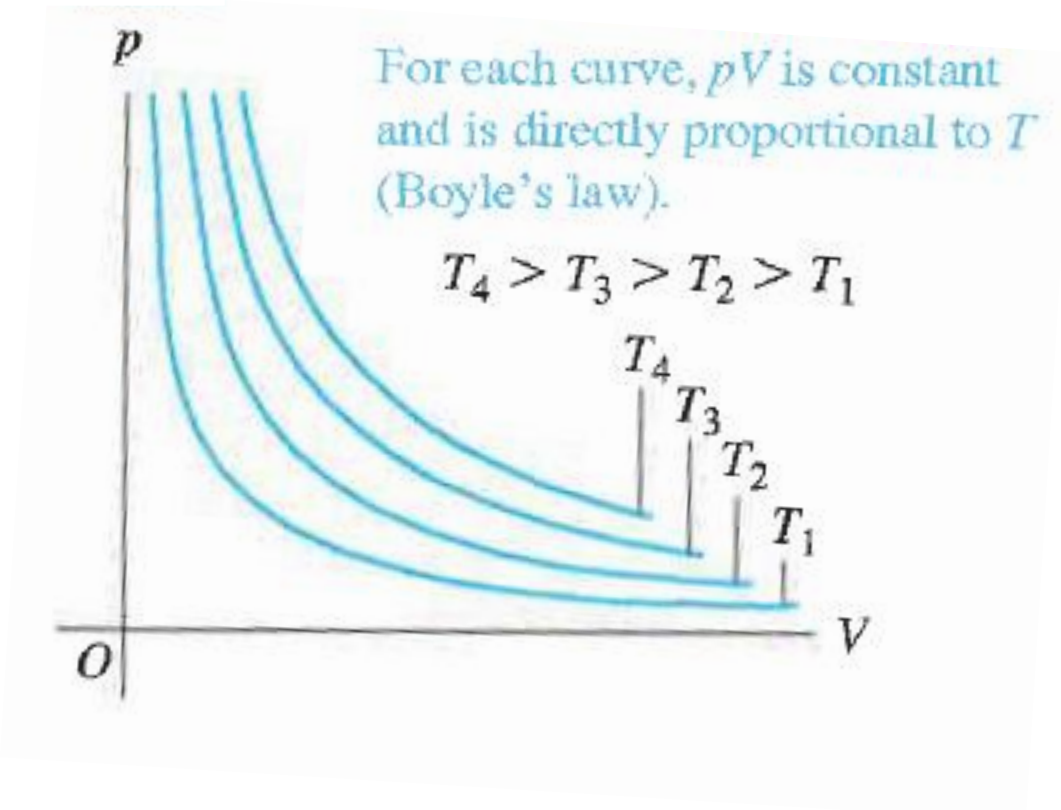
How to describe the status of a gas? And what is "ideal gas"?

- Ideal gas:
  - (1) no inter-molecular interactions (each gas molecule does not feel the others);
  - (2) no volume (each gas molecule is considered as a "point mass" particle)

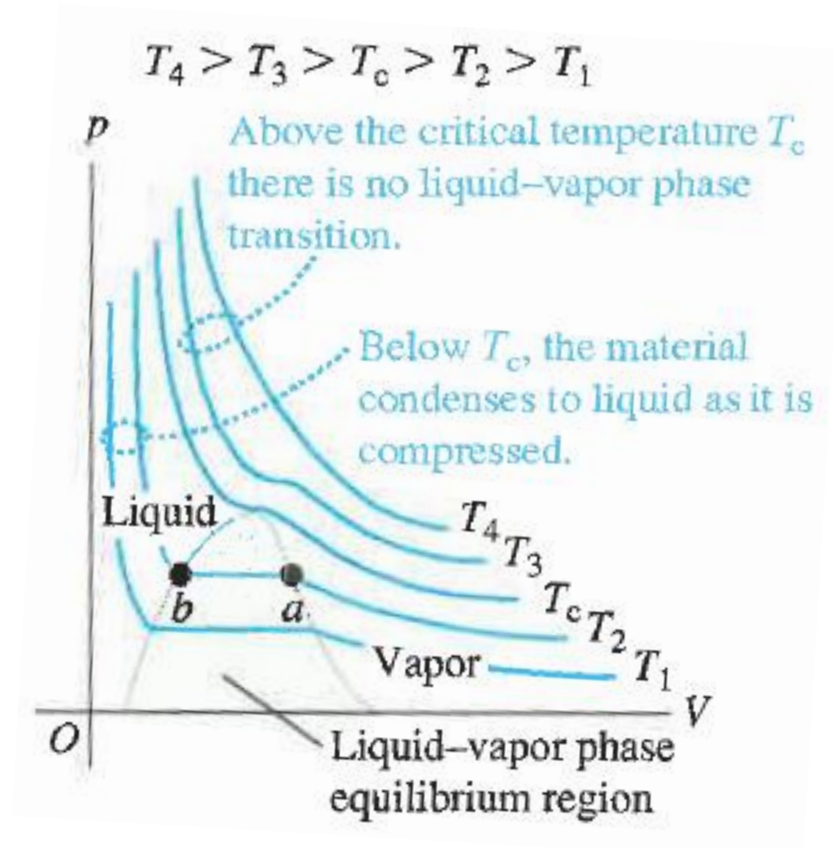
Corrections for non-ideal gas (van der Waals Equation):

$$\left(p+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

p-V diagram



Ideal Gas



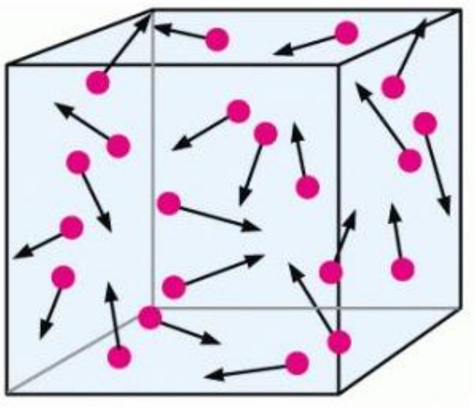
Non-Ideal Gas

What is the origin of the “pressure”?

- What is “pressure”?

$$p=\frac{F}{A}$$

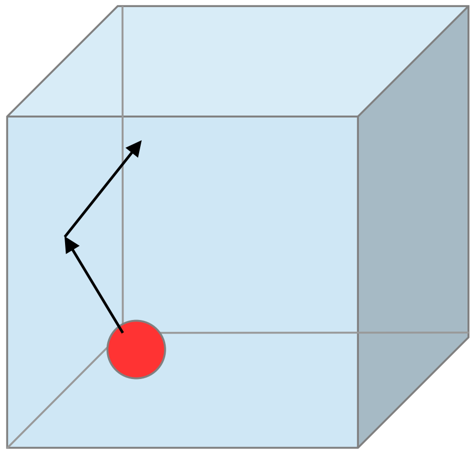
- Where does “Force” come from?



Air molecules hitting/bouncing the wall

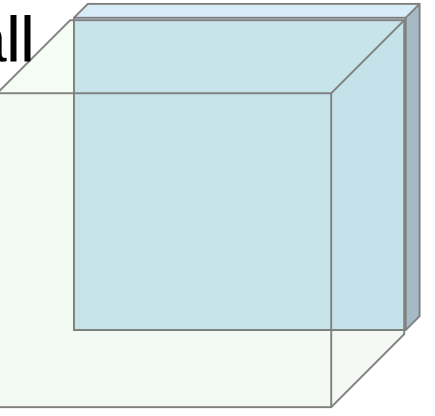
- Let's look at one molecule:

$$F_x=\frac{\Delta P_x}{\Delta t}$$



What is the origin of the “pressure”?

- How many molecules hitting the wall within a certain time period?
- Molecules with v_x within a volume could hit the wall



$$V_{hit} = A|v_x|\Delta t$$

- Numbers of molecules that hit the wall:

$$N_{hit} = \frac{1}{2}\frac{N}{V}V_{hit} = \frac{1}{2}\frac{N}{V}A|v_x|\Delta t$$

- Momentum change of one molecule that hit the wall

$$\Delta P_x = 2m|v_x|$$

- Sum of momentum changes of all molecules that hit the wall

$$\Delta P_{x,total} = N_{hit}\Delta P_x = 2m|v_x|\frac{1}{2}\frac{N}{V}A|v_x|\Delta t = m|v_x^2|\frac{N}{V}A\Delta t$$

What is the origin of the “pressure”?

- Total force due to the molecule collisions

$$F = \frac{\Delta P_{x,total}}{\Delta t} = m|v_x^2|\frac{N}{V}A$$

- Pressure on the wall

$$p = \frac{F}{A} = m|v_x^2|\frac{N}{V}$$

- Average v_x vs v

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$(v^2)_{av} = (v_x^2)_{av} + (v_y^2)_{av} + (v_z^2)_{av} = 3(v_x^2)_{av}$$

$$(v_x^2)_{av} = \frac{1}{3}(v^2)_{av}$$

What is the origin of the "pressure"?

- Pressure on the wall

$$p = m|v_x^2|\frac{N}{V} = m\frac{1}{3}|v^2|\frac{N}{V}$$

$$p = \frac{2}{3}\frac{1}{2}m|v^2|\frac{N}{V} = \frac{2}{3}E_k\frac{N}{V} = \frac{2}{3}\frac{K_{tr}}{V}$$

Average kinetic energy of ONE molecule (E_k)

Total kinetic energy of ALL molecules (K_{tr})

$$pV = \frac{2}{3}E_k N = \frac{2}{3}K_{tr} = nRT$$

$$K_{tr} = \frac{3}{2}nRT$$

$$E_k = \frac{3}{2}kT$$

$$n = \frac{N}{N_A}$$

$$k = \frac{R}{N_A}$$

Kinetic energy of molecules vs Temperature

$$K_{tr} = \frac{3}{2} nRT = N\, E_k$$

Total kinetic energy of all molecules

$$E_k = \frac{3}{2} kT = \frac{1}{2} m \left(v^2\right)_{av}$$

Average kinetic energy of one molecule

Root-mean-square speed (rms speed)

$$v_{rms} = \sqrt{(v^2)_{av}} \longrightarrow v_{rms}^2 = \left(v^2\right)_{av}$$

$$\frac{3}{2} kT = \frac{1}{2} m\, v_{rms}^2 \longrightarrow v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Summary

- Average kinetic energy of single molecule on depends on temperature

$$E_k = \frac{3}{2} kT$$

- Root-mean-square speed depends on both temperature and molecular mass

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Question

(a) What is the average translational kinetic energy of an ideal-gas molecule at 27 ºC?

(b) What is the total random translational kinetic energy of the molecules in 1 mole of this gas?

(c) What is the root-mean-square speed of oxygen molecules at this temperature?

How do we know the specific heat for ideal gas?

Recall from Ch 17: Molar heat capacity

$$C = \frac{1}{n}\frac{dQ}{dT} \quad \Rightarrow \quad \Delta Q = n C \Delta T$$

There are two types of Molar heat capacity

$$C_V = \frac{1}{n}\left(\frac{dQ}{dT}\right)_{constant\ volume}$$

$$C_p = \frac{1}{n}\left(\frac{dQ}{dT}\right)_{constant\ pressure}$$

How do we know the specific heat for ideal gas?

- For ideal gas, if you add heat into the system, where does the heat go?

$$\Delta Q = \Delta K_{tr}$$

$$\Delta Q = n C_V \Delta T \qquad K_{tr} = \frac{3}{2} nRT$$

$$\Delta Q = n C_V \Delta T = \frac{3}{2} nR \Delta T$$

$$C_V = \frac{3}{2} R$$

Equipartition of Energy principle

Where does this "3" come from?

$$C_V = \frac{3}{2} R \qquad\qquad \left(v_x^2\right)_{av} = \frac{1}{3}\left(v^2\right)_{av}$$

$$E_k = \frac{1}{2} m \left(v^2\right)_{av} = \frac{1}{2} m \left(\left(v_x^2\right)_{av} + \left(v_y^2\right)_{av} + \left(v_z^2\right)_{av}\right) = E_{k,x} + E_{k,y} + E_{k,z}$$

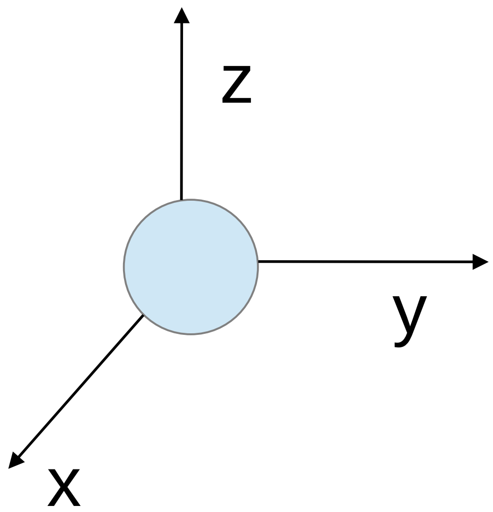
One **degree of freedom** gives one equipartition of energy

$$C_V = \frac{dof}{2} R$$

What is “degree of freedom”?

Monatomic vs Diatomic molecules

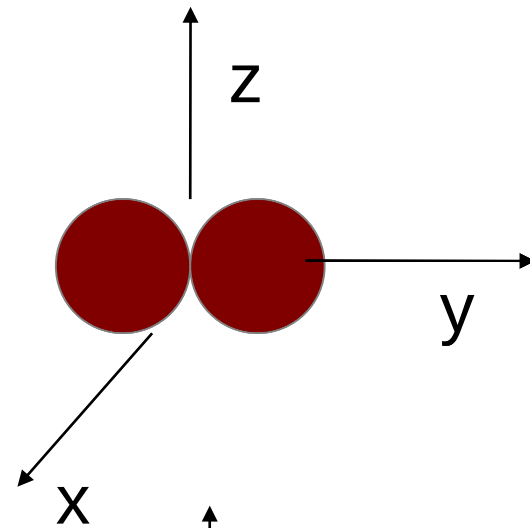
$$C_V = \frac{dof}{2} R$$

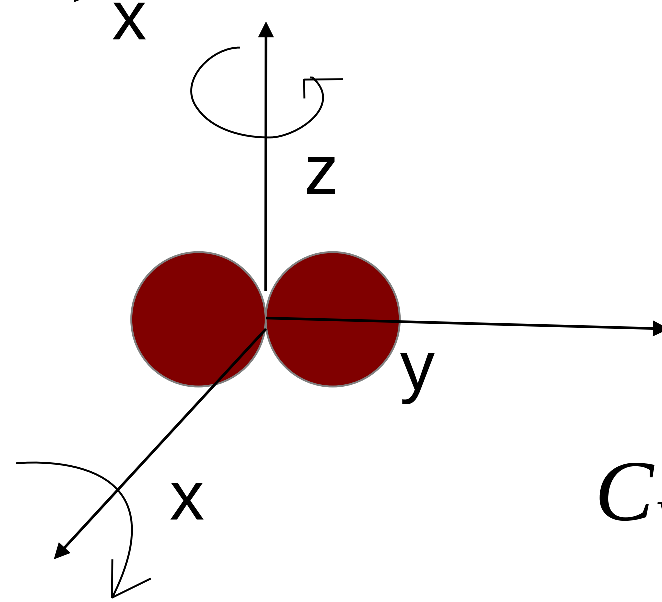


dof = 3

$$C_V = \frac{3}{2} R$$

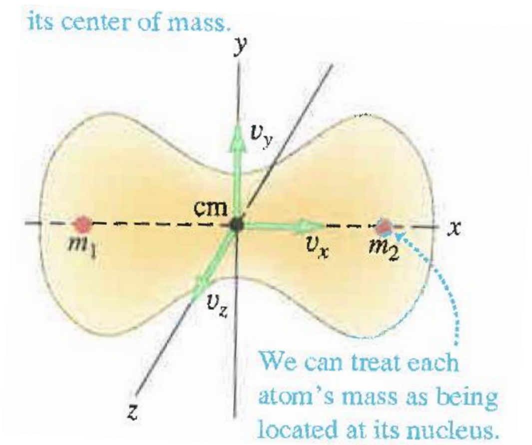
dof = 5



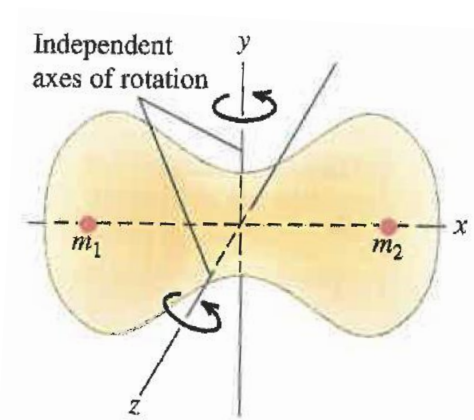


$$C_V = \frac{5}{2} R$$

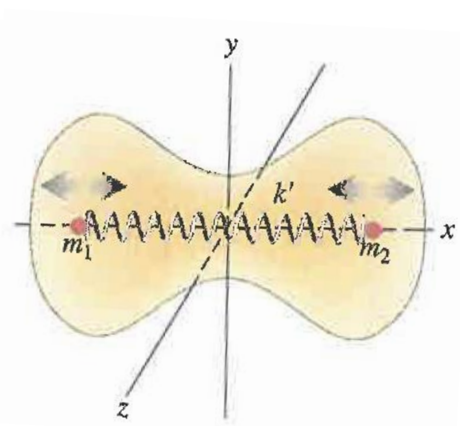
Degree of freedom vs C_V



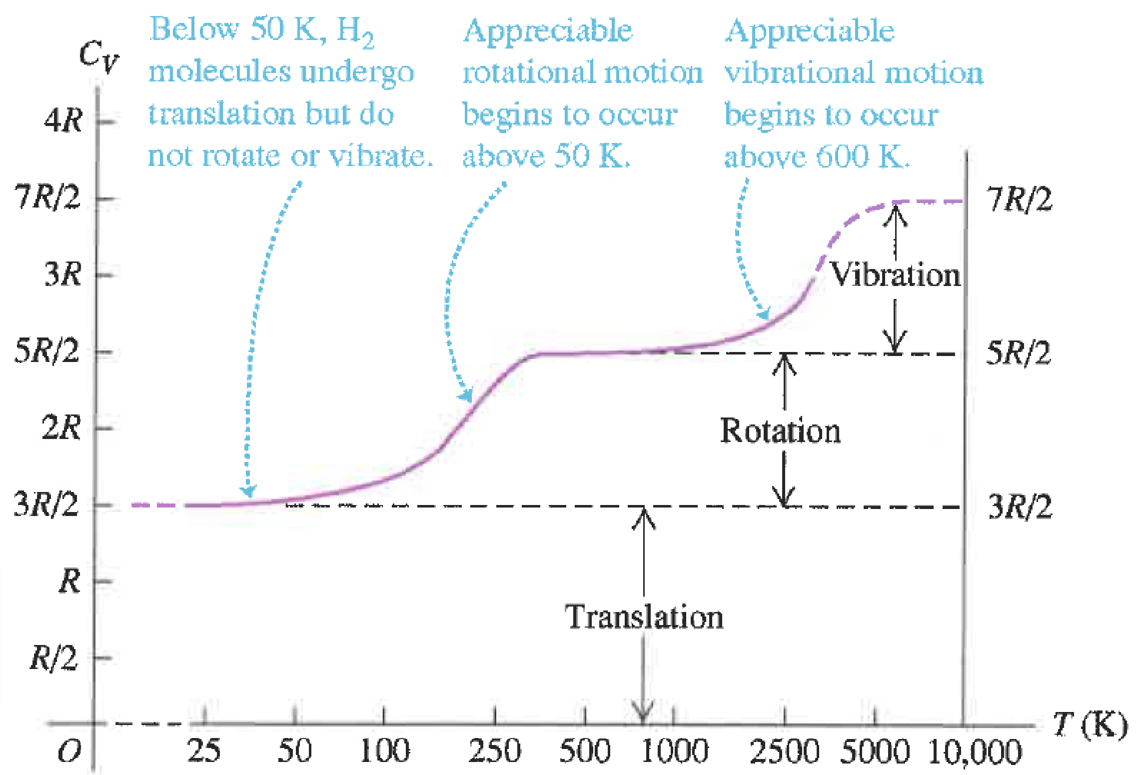
Translation: dof: 3



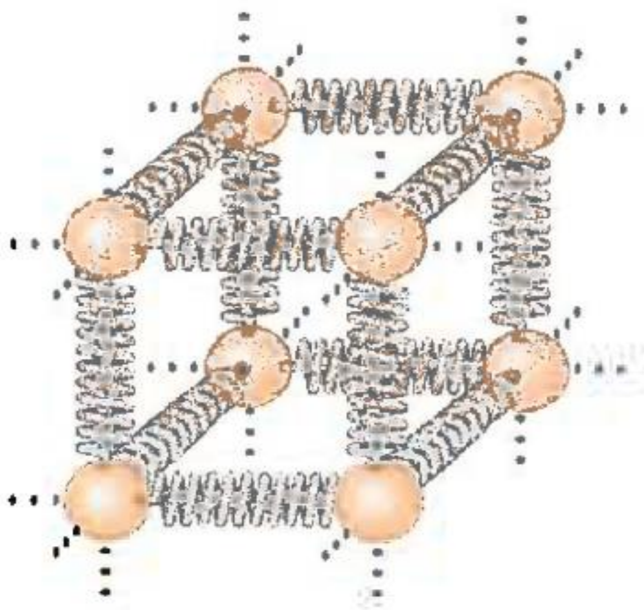
Rotation: dof: 2



Vibration: dof: 2



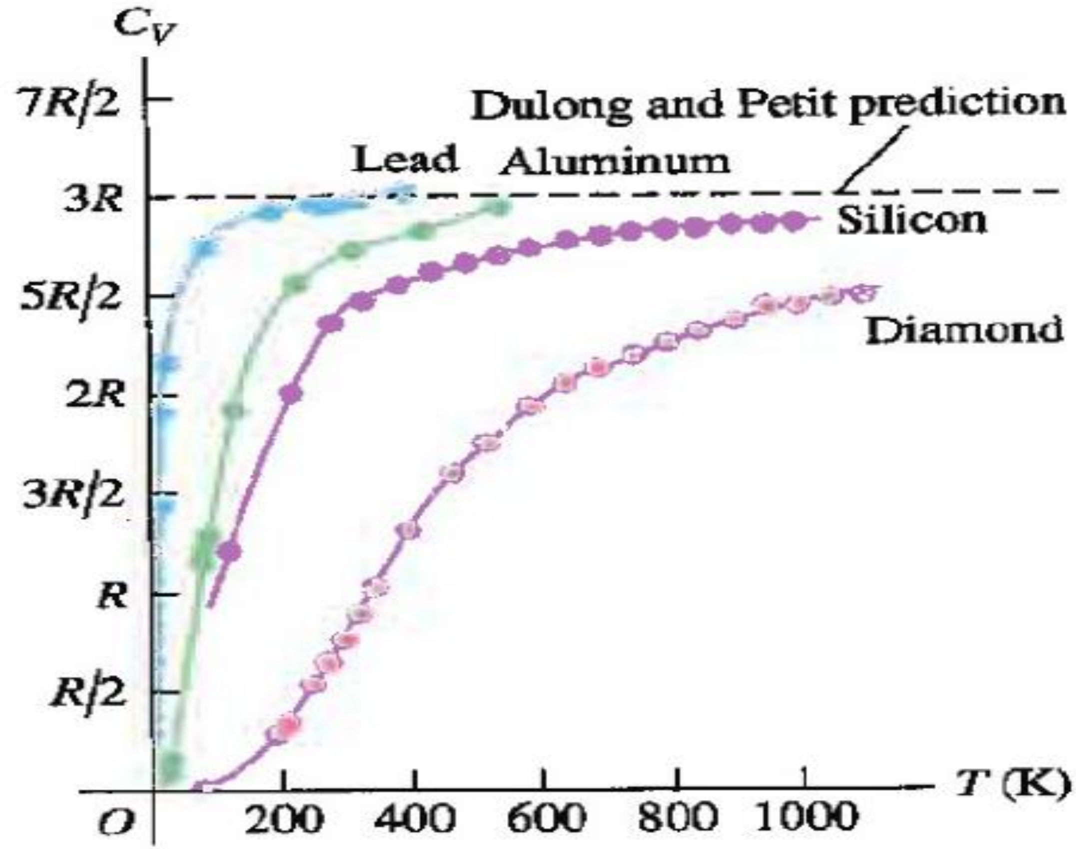
What is "degree of freedom"?



- Kinetic energy
  - *x*, *y*, and *z*
- Potential energy (vibration)
  - *x*, *y*, and *z*

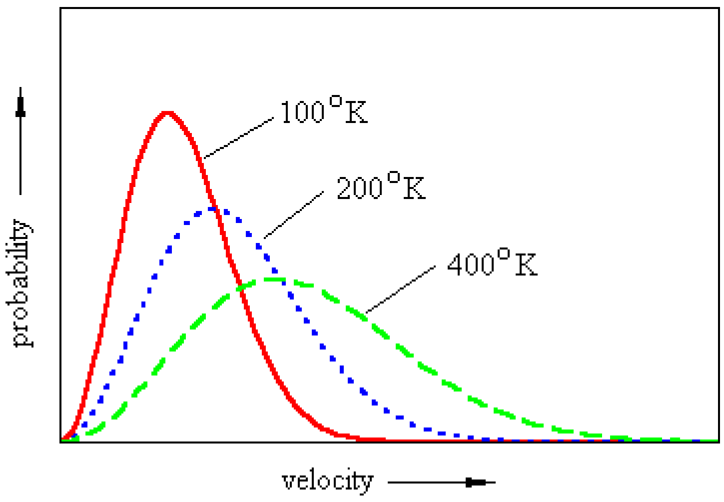
dof = 6

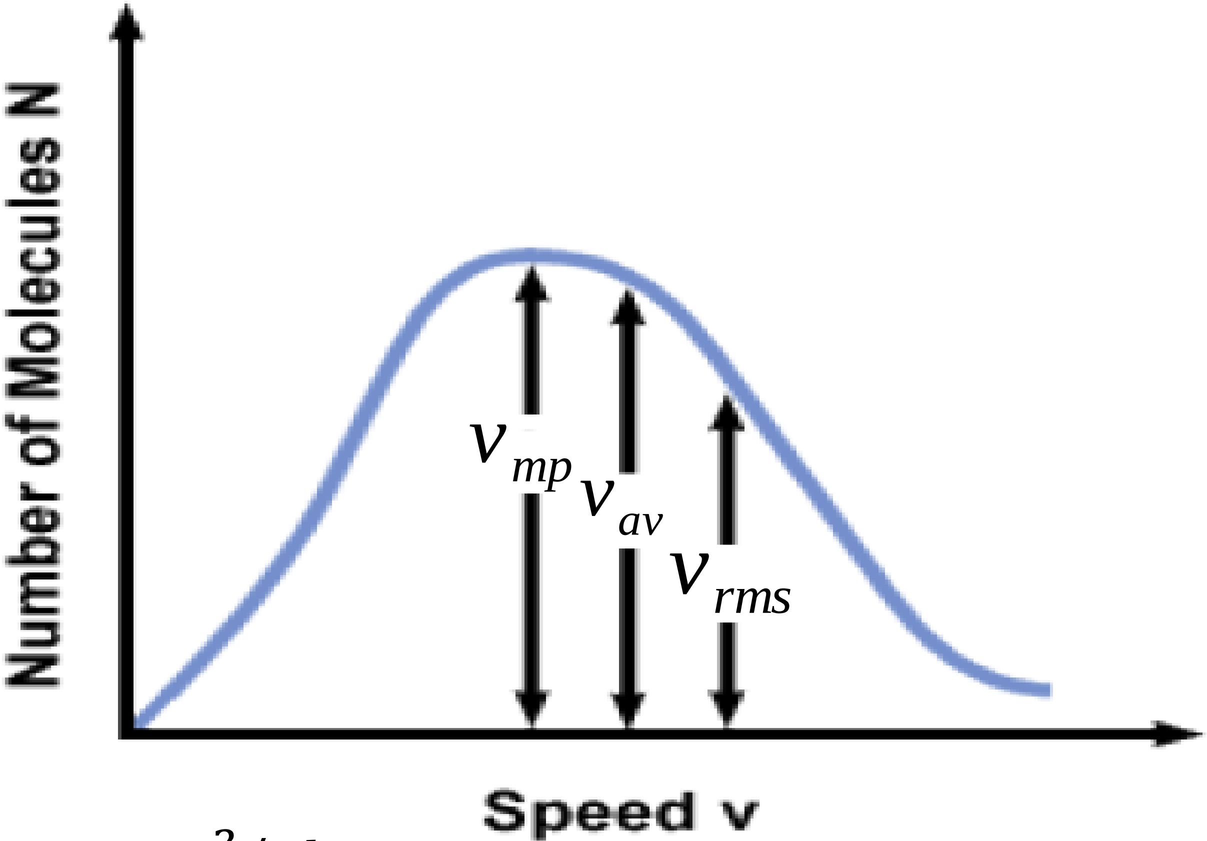
$$C_V = \frac{6}{2} R$$



- In general, the following could contribute to dof.
  - **Kinetic energy**
  - **Rotational energy**
  - **Vibration energy**

Do all the air molecules move with the same speed?





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

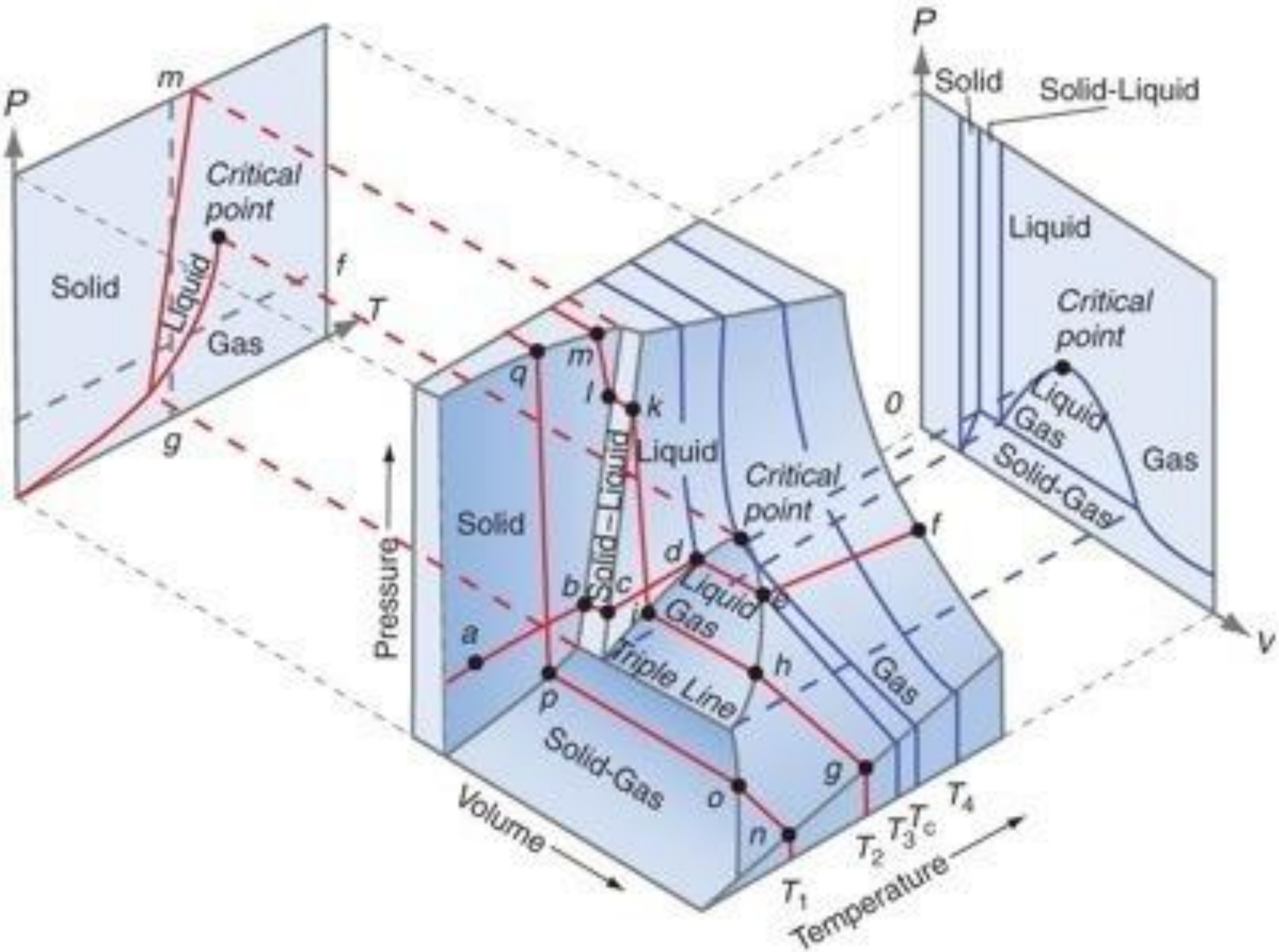
$$v_{mp} = \sqrt{\frac{2kT}{m}} \qquad v_{av} = \sqrt{\frac{8kT}{\pi m}} \qquad v_{rms} = \sqrt{\frac{3kT}{m}}$$

Speeds

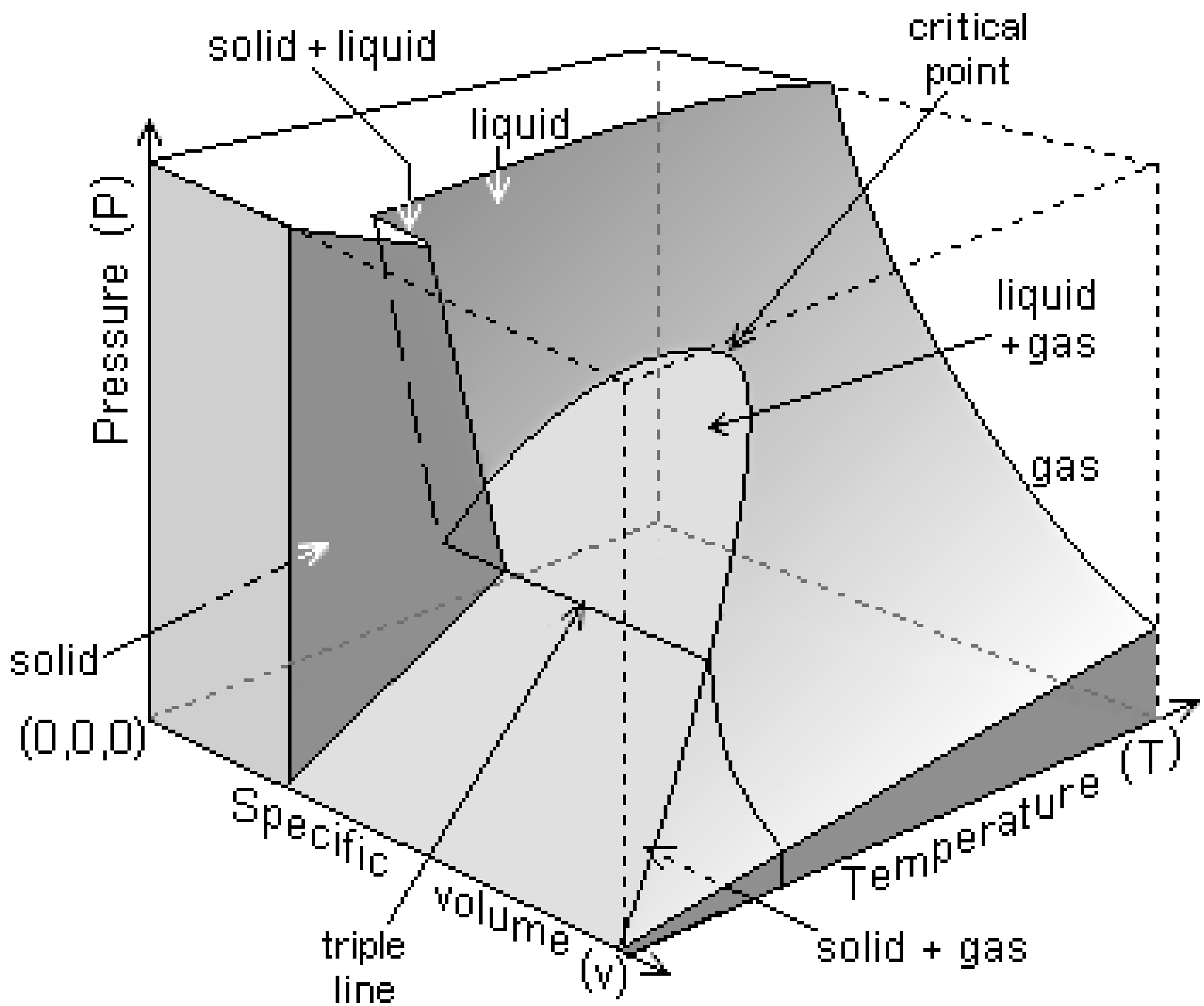
$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

- $\frac{df(v)}{dv} = 0$ Solve for v_{mp}
- $v_{av} = \int_0^\infty v f(v) dv$
- $v_{rms} = \sqrt{\int_0^\infty v^2 f(v) dv}$

What is “phase diagram”?



What is “phase diagram”?



What is "phase diagram"?