Luis Anchordoqui
Lehman College
City University of New York

Thermodynamics and Statistical Mechanics

Kinetic Theory of Gases

9 October 2014

- **Basic assumptions of kinetic theory**
- **Molecular flux**
- **Energy equipartition**
- **Maxwell-Boltzmann distribution**
- **Effusion**

BASIC ASSUMPTIONS OF THE MOLECULAR THEORY

There are about 10^{19} molecules in $1\ \mathrm{cm}^3$ at normal conditions

Because of large number of particles
impacts of individual particles on walls merge into time-independent pressure

Characteristic distance between molecules largely exceeds molecular size
and typical radius of intermolecular forces

This assumption allows to consider gas as ideal
with internal energy dominated by kinetic energy of molecules

In describing equilibrium properties of ideal gas
collisions between molecules can be neglected

Molecules are uniformly distributed within container

Directions of velocities of molecules are also uniformly distributed

CHARACTERISTIC LENGTHS OF GAS

Concentration of molecules n is defined by

total number of molecules

$$n \equiv \frac{N}{V} \qquad (1)$$

volume of container

Characteristic distance r_0 between molecules can be estimated as

$$r_0 = \frac{1}{n^{\frac{1}{3}}} \qquad (2)$$

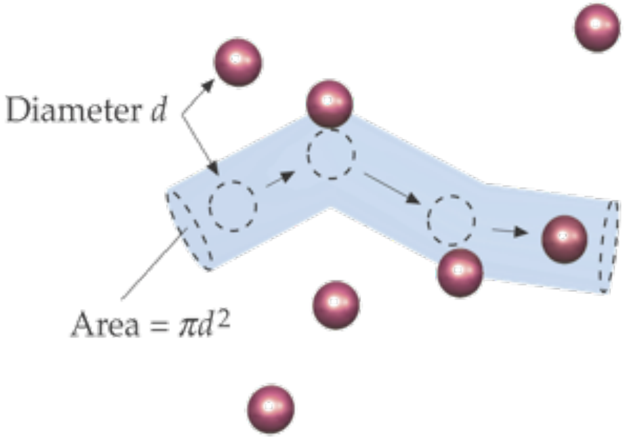
Let a be radius of molecule ☛ assumption (2) requires $a \ll r_0$

There are also long-range attractive forces between molecules
but they are weak and do not essentially deviate molecular trajectories
if temperature is high enough and gas is ideal

MEAN FREE PATH

mean free path ☛ typical distance l travel by molecules before colliding

Considering other molecules as non-moving ☛



molecule under consideration will hit (on average) other molecules

that are within cylinder of height l and cross-section $\sigma = \pi(2a)^2$

Volume σl of this cylinder ☛ volume per molecule $1/n$

$$l = \frac{1}{\sigma n} \sim \frac{1}{a^2 n} = \left(\frac{r_0}{a}\right)^2 r_0 \gg r_0 \gg a \qquad (3)$$

VELOCITY DISTRIBUTION FUNCTIONS

Distribution of molecules in space is practically uniform,

Distribution in space of velocities (v_x, v_y, v_z) is nontrivial

Introduce the distribution function $G\ (v_x, v_y, v_z)$ via

$$dN = NG(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z \qquad (4)$$

☟

number of molecules with velocities within elementary volume ☟

$$dv_x\, dv_y\, dv_z \equiv d^3v \equiv dv \ (5)$$

around velocity vector specified by its components ☛ (v_x, v_y, v_z)

Integration over the whole velocity space gives total number of molecules N

$G\ (v_x, v_y, v_z)$ ☛ satisfies normalization condition ☟

$$1 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_x\, dv_y\, dv_z\, G(v_x, v_y, v_z) \qquad (6)$$

DISTRIBUTION FUNCTION OF MOLECULAR SPEEDS

Since directions of molecular velocities are distributed uniformly

$G\ (v_z, v_y, v_z)$ depends only on absolute value of the velocity ☛ the speed

$$v = \sqrt{v_z^2 + v_y^2 + v_z^2} \quad (7)$$

Using expression for elementary volume in spherical coordinates

$$d^3v = dv \times v d\theta \times v \sin\theta d\varphi = v^2 dv \sin\theta d\theta d\varphi \quad (8)$$

(4) becomes ☛ $dN = N\,G\,(v) v^2\, dv d\Omega$ ☟ (9)

$$d\Omega \equiv \sin\theta d\theta d\varphi \quad (10)$$

Using area of a sphere of unit radius

$$\int_{\text{sphere}} d\Omega = \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi = 2\pi \int_{-1}^{1} dx = 4\pi \quad (11)$$

☟ $(x \equiv \cos\theta)$

number of molecules within spherical shell becomes

$$dN = NG(v)\, 4\pi v^2 dv = N\, f(v) dv \quad (12)$$

distribution function over molecular speeds ☛ $f(v) = 4\pi v^2 G(v)$ (13)

normalization ☛ $1 = \int_0^\infty dv\, f(v)$ (14)

AVERAGE, MEAN SQUARE AND RMS SPEEDS

(9) can be rewritten in terms of $f(v)$ as

$$dN = N\, f(v) dv\, \frac{d\Omega}{4\pi} \tag{15}$$

average speed

$$\bar{v} = \int_0^\infty dv\, v\, f(v) \tag{16}$$

mean square speed

$$\bar{v^2} = \int_0^\infty dv\, v^2\, f(v) \tag{17}$$

root mean square or **rms** speed

$$v_{\rm rms} = \sqrt{\bar{v^2}} \tag{18}$$

Luis Anchordoqui

MOLECULAR FLUX

Molecular flux Φ is defined as number of molecules dN crossing a unit surface in one direction during a unit of time

Molecular flux determines rate of molecules striking wall or exiting container through a small orifice in wall (effusion)

The expression for flux reads ☛

$$\Phi = \frac{dN}{dS\,dt} \qquad (19)$$

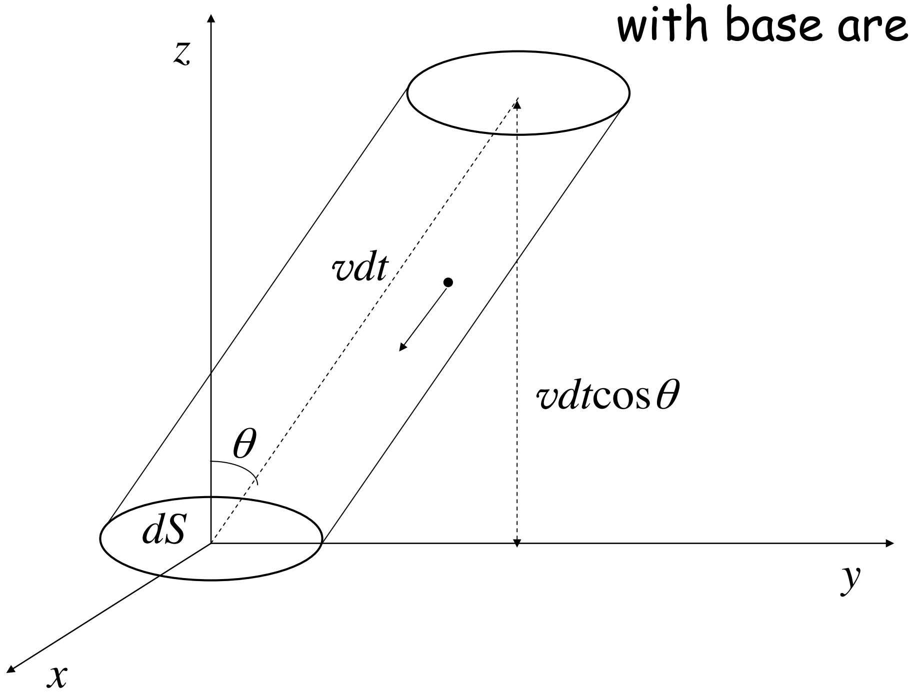
Molecules are approaching surface dS from all directions θ, φ of a hemisphere

Consider number of molecules $dN_{\theta,\varphi}$ coming from a particular direction θ, φ within solid angle $d\Omega$ around it

Single out molecules with speeds in interval dv around v ☛ $dN_{v,\theta,\varphi}$

MOLECULAR FLUX II

$dN_{v,\theta,\varphi}$ is number of molecules within slant cylinder with base area dS and height $v\,\cos\,\theta dt$



Cylinder volume ☛ $dV = dSv\,\cos\,\theta dt$

total number of molecules in it ☛ $dN_V = ndV$

From this total number of molecules dN_V pick up those within given velocity interval specified by v, θ, φ

MOLECULAR FLUX III

With help of (15) with $N \Rightarrow dN_V$

$$dN_{v,\theta,\varphi} = dN_V f(v) dv \frac{d\Omega}{4\pi} = ndSv \cos\theta dt f(v) dv \frac{\sin\theta d\theta d\varphi}{4\pi} \quad (20)$$

$$\Phi = \int \frac{dN_{v,\theta,\varphi}}{dSdt} = n \int_0^\infty dv\, v\, f(v)\, \frac{1}{4\pi} \int_0^{\pi/2} d\theta\, \sin\theta\, \cos\theta \int_0^{2\pi} d\varphi \quad (21)$$

Integrating over v, θ, φ using (19) and (16)

$$\Phi = \frac{1}{4} n\bar{v} \quad (22)$$

Upper limit $\pi/2$ in (21) corresponds to hemisphere

in contrast to π for whole sphere

GAS PRESURE ON THE WALLS

Gas pressure is due to impact of molecules on walls ☛ $P = dF/dS$

dF ☛ force acting upon surface dS from molecules

From Newton's second law ☛ $dp/dt = F$

p ☛ momentum of molecules that changes in time due to rebound from wall

Adopting this to our case yields ☛

$$P = \frac{dp}{dS dt} \qquad (23)$$

dp ☛ change of momentum of molecules within slant cylinder

GAS PRESURE ON THE WALLS II

Change of momentum of single molecule in collision with wall is not well defined

atomic level walls are rough ☛ incident molecule can rebound in different directions

Since P doesn't depend on orientation of elementary surfaces
dismiss effect of wall roughness

Inelasticity of molecule-wall collision further complicates model building
☟
due to energy exchange between molecules and atoms of the wall

If walls and gas have same temperatures and hence are at equilibrium
molecule-wall collisions average out to the elastic collision

Throughout we consider collisions of molecules with wall
as elastic collisions with a flat surface

GAS PRESURE ON THE WALLS III

Change of momentum of individual molecule in elastic collision

☟

$$mv\,\cos\,\theta - (-mv\,\cos\,\theta) = 2mv\,\cos\,\theta$$

Substituting ☟

$$P = \int 2mv\,\cos\,\theta\,\frac{dN_{v,\theta,\varphi}}{dSdt} = 2nm\int_0^\infty dv\,v^2\,f(v)\,\frac{1}{4\pi}\int_0^{\pi/2} d\theta\,\sin\,\theta\,\cos^2\,\theta\int_0^{2\pi} d\varphi$$

$$= 2nm \times \bar{v^2} \times \frac{1}{4\pi}\int_0^1 dx\,x^2 \times 2\pi \qquad (24)$$

It follows that ☛

$$P = \frac{1}{3}nm\bar{v^2} \qquad (25)$$

MOLECULAR INTERPRETATION OF TEMPERATURE

Rewriting (25) as $PV = (1/3)\, Nm\overline{v^2}$

and comparing this with equation of state ☛ $PV = Nk_BT$

$$k_BT = \frac{1}{3}m\overline{v^2} \qquad (26)$$

fundamental relation between temperature & average kinetic energy of molecule $\bar{\varepsilon}$

This relation can be rewritten in the form

$$\bar{\varepsilon} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT \qquad (27)$$

Since $\overline{v^2} = \overline{v^2}_x + \overline{v^2}_y + \overline{v^2}_z$ and by symmetry $\overline{v^2}_x = \overline{v^2}_y = \overline{v^2}_z = \overline{v^2}/3$

for kinetic energies corresponding to three **degrees of freedom** x, y, z

$$\bar{\varepsilon}_x = \bar{\varepsilon}_y = \bar{\varepsilon}_z = \frac{1}{2}k_BT \qquad (28)$$

Thermal energy per degree of freedom ☛ $(1/2)k_BT$

ENERGY EQUIPARTITION

This is a particular case of the equipartition of energy valid for classical systems:

There is thermal energy $(1/2)k_BT$ per each degree of freedom

If molecules of gas consist of more than one atom

in addition to three translational degrees of freedom

there are rotational and vibrational degrees of freedom

Vibrational degrees of freedom are counted twice

since there are both kinetic and potential energies involved

For diatomic molecules there are two rotational degrees of freedom

corresponding to rotations around axes perpendicular to axis connecting molecules

and one vibrational degree of freedom that is counted twice

Total number of degrees of freedom for diatomic molecules

$$f = 3 + 2 + 2 = 7 \tag{29}$$

ENERGY EQUIPARTITION II

For multi-atomic molecules with $\mathcal{N} > 2$ atoms that are not aligned
there are 3 translational and 3 rotational degrees of freedom

Number of vibrational degrees of freedom can be calculated
by subtracting 3 + 3 non-vibrational degrees of freedom
from the total $3\mathcal{N}$ degrees of freedom

That is ☛ $3\mathcal{N} - 6$ vibrational degrees of freedom that should be counted twice

Total number of degrees of freedom for multi-atomic molecules

$$f = 3 + 3 + 2\,(3\mathcal{N} - 6) = 6(\mathcal{N} - 1) \qquad (30)$$

for $\mathcal{N} = 3$ ☛ $f = 12$

HEAT CAPACITY OF THE IDEAL GAS

For monoatomic gas average energy per particle is given by (27)

Since there is no potential energy ☛ $$U = \frac{3}{2} N k_B T \qquad (31)$$

Heat capacity at constant volume ☛ $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B \qquad (32)$$

Using of Mayer's formula ☛ $$C_P = C_V + N k_B = = \frac{5}{2} N k_B \qquad (33)$$

that yields ☛ $\gamma = C_P/C_V = 5/3$

For multi-atomic molecules assuming equipartition ☛ $U = (f/2) N k_B T$

$$C_V = \frac{f}{2} N k_B \qquad C_P = \frac{f+2}{2} N k_B \qquad \gamma = 1 + \frac{2}{f} \qquad (34)$$

WHEN IDEAL IS NOT PERFECT

We have taken heat capacity as constant so that ideal gas is perfect gas

Vibrational degrees of freedom for multi-atomic gases
are affected by quantum effects at low temperatures

As a result ☛ these degrees of freedom are fully or partially frozen out
so that there is less thermal energy in them than equipartition would suggest

At high temperatures the vibrational modes behave classically

As a result ☛ heat capacities increase with temperature
making the ideal gas not a perfect gas

MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION

Motion of molecules of an ideal gas along different axes x, y, z is completely independent

Statistical independence of different velocity components ☛ $G(v)$ factorizes

$$G(v) = G\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right) = g(v_x)\, g(v_y)\, g(v_z) \qquad (35)$$

$$1 = \int_{-\infty}^{\infty} dv_x\, g(v_x) \qquad (36)$$

Each velocity component has its own distribution function g

Number of molecules within shell dv_x around v_x is obtained by integrating (4) over irrelevant v_y, v_z

$$dN = N\left[\int\int_{-\infty}^{\infty} dv_y\, dv_z\, G(v)\right] dv_x \qquad (37)$$

With help of (35) and (36) this becomes ☛ $dN = N\, g(v_x)\, dv_x$ (38)

that is ☛ $g(v_x)$ is distribution function of v_x

MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION II

Factorization of G and its spherical symmetry implemented in (35) already allows to find its functional form

Take logarithm of (35)

$$\ln G(v) = \ln g(v_x) + \ln g(v_y) + \ln g(v_z) \qquad (39)$$

and differentiate with respect to v_x

$$\frac{G'(v)}{G}\frac{\partial v}{\partial v_x} = \frac{G'(v)}{G}\frac{v_x}{v} = \frac{g'(v_x)}{g(v_x)} \qquad (40)$$

Rearranging and adding similar results for other components one obtains

$$\frac{1}{v}\frac{G'(v)}{G} = \frac{1}{v_x}\frac{g'(v_x)}{g(v_x)} = \frac{1}{v_y}\frac{g'(v_y)}{g(v_y)} = \frac{1}{v_z}\frac{g'(v_z)}{g(v_z)} \qquad (41)$$

MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION III

Different terms of (41) depend on different independent arguments

only possibility to satisfy equations is all terms being equal to same constant

$$\frac{1}{v}\,\frac{G'(v)}{G} = -2k \qquad \frac{1}{v_x}\,\frac{g'(v_x)}{g(v_x)} = -2k \tag{42}$$

Integrating ☛ $G(v) = Ae^{-kv^2}$ (43)

☟

integration constant

$G(v)$ factorizes and so ☛ $g(v_x) = A^{1/3}\,e^{-kv_z^2}$ (44)

k and A can be found from:

normalization condition (14) and condition for mean square speed (17)

taking into account (26)

MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION IV

$f(v)$ is related to $G(v)$ by (13)

$$f(v) = 4\pi v^2 \, A e^{-kv^2} \tag{45}$$

Using Gaussian integrals

$$\int_0^\infty dx \, x^2 \, e^{-kx^2} = \frac{\sqrt{\pi}}{4} k^{-3/2} \qquad \int_0^\infty dx \, x^4 \, e^{-kx^2} = \frac{3\sqrt{\pi}}{8} k^{-5/2} \tag{46}$$

obtained by successive differentiation of generic integral

$$\int_0^\infty dx \, e^{-kx^2} = \frac{\sqrt{\pi}}{2} k^{-1/2} \tag{47}$$

with respect to k

Normalization condition (14) works out as

$$1 = \int_0^\infty dv \, f(v) = 4\pi \, A \int_0^\infty dv \, v^2 \, e^{-kv^2} = \pi^{3/2} \, A k^{-3/2} \tag{48}$$

Luis Anchordoqui

MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION IV

Condition for mean square speed becomes

$$\frac{3k_BT}{m} = \bar{v^2} = \int_0^\infty dv\, v^2\, f(v) = 4\pi\, A \int_0^\infty dv\, v^4\, e^{-kv^2} = \frac{3\pi^{3/2}}{2}\, Ak^{-5/2} \qquad (49)$$

From (48) and (49)

$$k = \frac{m}{2k_BT} \qquad A = \left(\frac{k}{\pi}\right)^{3/2} = \left(\frac{m}{2\pi k_BT}\right)^{3/2} \qquad (50)$$

Let us now write down final results for distribution functions:

(45) becomes

$$f(v) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} \quad 4\pi v^2 \exp\left(-\frac{\varepsilon}{k_BT}\right) \qquad \varepsilon = \frac{mv^2}{2} \qquad (51)$$

and (44) becomes

$$g(v_x) = \left(\frac{m}{2\pi k_BT}\right)^{1/2} \quad \exp\left(-\frac{\varepsilon_x}{k_BT}\right) \qquad \varepsilon_x = \frac{mv_x^2}{2} \qquad (52)$$

CHARACTERISTIC SPEEDS OF GAS MOLECULES

rms speed can be immediately obtained from (49)

$$v_{\rm rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} \simeq 1.732\sqrt{\frac{k_BT}{m}} \qquad (53)$$

To calculate average speed ☛ use of Gaussian integral

$$\int_0^\infty dx\, x^{2n+1}\, e^{-kx^2} = \frac{n!}{2k^{n+1}} \qquad n = 0, 1, 2, \ldots \qquad (54)$$

with $n = 1$

Form (16) it follows that

$$\bar{v} = \int_0^\infty dv\, v\, f(v) = 4\pi\, A \int_0^\infty dv\, v^3\, e^{-kv^2} = 4\pi\, A\, \frac{1}{2k^2} = \frac{2\pi}{k^2}\left(\frac{k}{\pi}\right)^{3/2} = \frac{2}{\sqrt{\pi k}} = \sqrt{\frac{8k_BT}{\pi m}} \simeq 1.596\sqrt{\frac{k_BT}{m}} \qquad (55)$$

CHARACTERISTIC SPEEDS OF GAS MOLECULES

Third characteristic speed is most probable speed v_m

corresponding to maximum of $f(v)$

From

$$0 = \frac{d}{dv^2} v^2 e^{-kv^2} = e^{-kv^2} - v^2 k e^{-kv^2} \qquad (56)$$

it follows that

$$v_m = \frac{1}{\sqrt{k}} = \sqrt{\frac{2k_BT}{m}} \simeq 1.414 \sqrt{\frac{k_BT}{m}} \qquad (57)$$

smallest of three characteristic speeds

EFFUSION

If there is a small hole in the wall of the container

molecules will escape through this hole ☛ process called **effusion**

If hole is small enough it does not disturb gas in the container close to hole

and result for molecular flux given by (22) remains valid

Number of molecules leaving container per second is given by $\Phi\,\Delta S$

area of the hole

Speed distribution of escaping molecules is not Maxwell-Boltzmann distribution

Characteristic speeds of effusing molecules

are higher than speeds of molecules in the container

Faster molecules are approaching hole from inside container

and exit at a higher rate than slow molecules

EFFUSION (cont'd)

v

Speed distribution of effusing molecules

$$\Phi = \int_0^\infty dv\, \Phi_v \qquad (58)$$

$$\Phi_v = \frac{1}{4} n v\, f(v) \qquad (59)$$

defines speed distribution of effusing molecules

Because of additional v ☛ this distribution is shifted to higher speeds

Most probable speed of effusing molecules corresponds to maximum of Φ_v

$$0 = \frac{d}{dv} v^3\, e^{-kv^2} = 3v^2\, e^{-kv^2} - v^3\, 2kve^{-kv^2} \qquad (60)$$

$$v_{e,m} = \sqrt{\frac{3}{2k}} = \sqrt{\frac{3k_BT}{m}} \qquad (61)$$

It follows that ☛ $v_{e,m} > v_m$ given by (57)

similarly ☛ $v_{e,\rm rms} > v_{\rm rms}$ and $\bar{v}_e > \bar{v}$