Physics 301 Fall 2020

Lec 1: Heat & Temperature

I. Heat & Work

heat(ing) is energy transfer to system by contact or radiation (e.g. microwaves) without changing system external parameters (e.g. volume, magnetic field). energy transfer by changing external parameters is called work.

heating is a process of energy transfer by conduction or radiation (not convection) "thermal contact"

II. Temperature measured with thermometer

heat flows from hot to cold unique ordering of direction of heat flow.

III. Zeroth law

Systems A, B are same temperature when no heat is transferred when put in thermal contact.

System A, B, C if $T_A = T_C$ and $T_B = T_C$

then $T_A = T_B$

for example C could be thermometer

<u>Ideal Gas Law</u> no interaction between molecules, molecular collisions <u>perfectly elastic</u>*.

Empirical law $PV = nRT = NkT$

$n = \frac{N}{N_A}$ "moles" Kelvin

$N_A = 6.022 \times 10^{23} \frac{\#}{mole}$ $\frac{\text{number}}{\text{mole "unit"}}$

Avogadro's number (pure number)

$k = 1.381 \times 10^{-23} \frac{J}{K}$ $\underline{K} \equiv$ Kelvin

$= 8.617 \times 10^{-5}$ eV/K

$R = 8.315 \frac{J}{(mole \cdot K)}$

* Excitation of hydrogen

$\Delta(E_2 - E_1) = 10.2 eV \gg k(298K)$

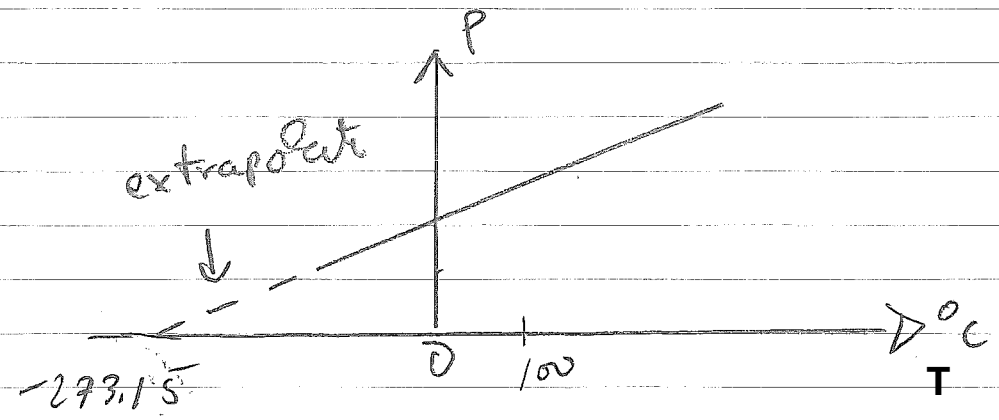
$k(298K) = \frac{1}{38.94}$ eV

<u>Thermometer</u> linearly related over some useful range to P of ideal gas at constant V.

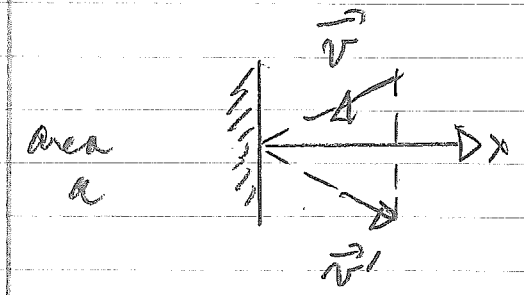
- expansion of liquid (mercury)
- expansion of metal (bi-metalic strip)
- thermocouple – 2 metals in thermal contact with T dependent on voltage

	Celcius	Kelvin
water freezes	0	273.15
water boils	100	373.15

at atmospheric pressure $P = 1.013$ bar
$= 1.013 \times 10^5 \ N/m^2 = 100 \ kPa$



<u>Some kinetic theory</u> ideal, monatomic gas



V_x changes sign in collision

$\Delta p_x = 2mV_x$ momentum change

$|\Delta x| = V_x \Delta t$

force exerted by molecule $f_x = \frac{\Delta p_x}{\Delta t} = \frac{2mV_x^2}{\Delta x}$

average force of gas with number density $\frac{N}{V}$

$$F = \left[\left(\frac{N}{V}\right) A \cdot \Delta x\right] \left(\frac{1}{2}\right)\left(\frac{2mV_x^2}{\Delta x}\right)$$

on average, $\frac{1}{2}$ move towards wall

$$\langle v^2 \rangle = \langle V_x^2 \rangle + \langle V_y^2 \rangle + \langle V_z^2 \rangle = 3 \langle V_x^2 \rangle$$ 3D motion

$$P = \frac{F}{A} = \left(\frac{N}{V}\right) \frac{m}{3} \langle v^2 \rangle$$

compare to empirical law

$$\frac{PV}{N} = kT = \frac{1}{3} m \langle v^2 \rangle = \frac{2}{3} \langle E \rangle$$

$$\langle E \rangle = \frac{3}{2} kT \quad \text{(monatomic)}$$

3 is # <u>degrees of freedom</u> (f) suggests generalizing

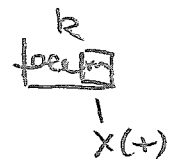
$$\langle E \rangle = \frac{f}{2} kT$$

<u>Degrees of freedom</u>

position, velocity enter as $\boxed{\text{quadratic terms}}$ in energy.

$$E = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) = \frac{1}{2} m |\vec{v}|^2 \qquad f = 3$$

mass on spring



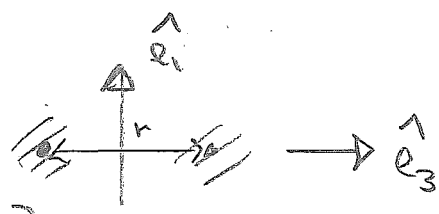
$$\omega = \sqrt{\frac{k}{m}}$$

$$x(t) = A \cos(\omega t - \delta)$$

$$E = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} m \cdot x^2$$

$f = 2$ for harmonic oscillator

diatomic molecule



$$E = \underbrace{\frac{1}{2} m |\vec{v}|^2}_{\text{translation}} + \underbrace{\frac{1}{2} \sum_{i=1}^{3} I_i \omega_i^2}_{\text{rotation}}$$

with $L_i = I_i \omega_i \qquad \vec{p} = m\vec{v}$

$$E = \frac{1}{2} \frac{|\vec{p}|^2}{m} + \frac{1}{2} \sum_{i=1}^{3} \frac{L_i^2}{I_i}$$

L_3 is example of thermally inaccessible or <u>frozen</u> degree of freedom.

Planck's constant / 2π

In Q.M. $L_i^2 = \hbar^2 l_i(l_i+1)$ $\quad l_i = 0, 1, 2, 3$

$$\Delta E^i_{rot} = \frac{1}{2}\frac{\hbar^2}{I_i}\left[(l_i+1)(l_i+2) - l_i(l_i+1)\right]$$

$$= \frac{l_i \hbar^2}{I_i}$$

minimum change is $\frac{\hbar^2}{I_i}$

$I_3 \ll I = I_2$ for diatomic molecule.

$\boxed{\text{frozen}}$

Vibrational energy ~~spacing~~ $\omega_{vib} = \sqrt{\frac{k}{m}}$

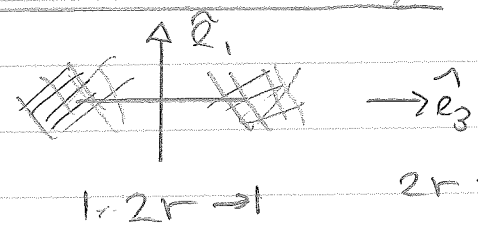
$$\Delta E_{vib} = \hbar\omega_{vib} = h f_{vib} \sim eV$$

$\boxed{\text{frozen at room temp}}$

diatomic molecule

$$f = 3 + 2 = 5$$

Ex. diatomic molecule H_2



$2r \simeq 0.1\,nm$

$$\boxed{\begin{aligned}\hbar c &= 197\ eV\cdot nm \\ &= 197\ MeV\cdot fm\end{aligned}}$$

$$I_1 = 2m_p r^2$$

$$\Delta E'_{min} = \frac{\hbar^2}{I_1} = \frac{\hbar^2 c^2}{2(m_p c^2) r^2}$$

$$m_p c^2 \simeq 10^9\ eV = 10^3\ MeV$$

$$\Delta E'_{min} = \frac{(200\ eV\cdot nm)^2}{2(10^9 eV)\left(\frac{1}{2}0.1\,nm\right)^2} = 8\times 10^{4-9+2}\ eV = 8\times 10^{-3}\ eV \ll kT\big|_{300K}$$

whereas, I_3

$2r = fm = 10^{-15}\,m$ proton size

$$\Delta E^3_{min} = \frac{(200\ MeV\cdot fm)^2}{2(10^3 MeV)\left(\frac{1}{2}fm\right)^2} = 80\ MeV \gg kT\big|_{300K}$$

$\Rightarrow$ frozen

therefore, diatomic molecule has $\boxed{f=5}$

Equipartition theorem $\boxed{\text{to be proved}}$
for isolated system
energy equally distributed between
accessible degrees of freedom f.

$$U_{th} = N\left(\frac{f}{2}kT\right)$$

$\boxed{\text{First Law}}$

$$\Delta U = Q + W$$

↑ total energy

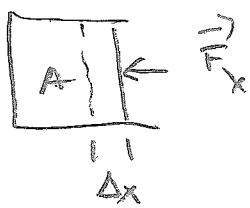
important convention

$$\boxed{\begin{array}{l} Q \equiv \text{heat added to system} \\ W \equiv \text{work done on system} \end{array}}$$

$\boxed{\text{note Baierlein defines } W \text{ as negative of this}}$

Example quasi-static* change in V of ideal gas at constant T.

$\boxed{\begin{array}{l} \text{* slow, through stages of equilibrium} \\ \text{slow compared to speed of sound in system.} \end{array}}$



$$\Delta V = -A\,\Delta x$$

volume decreases!

$$W = F_x\,\Delta x = PA\,\Delta x = -P\,\Delta V$$

generally, $W = \int \vec{F}\cdot d\vec{r}$

$d\vec{r}$ direction of displacement

$$W = -\int P\,dV$$

for ideal gas at constant T

$$p = \frac{NkT}{V}$$

$$W = -\int_1^2 p\,dV = -NkT\int_1^2 \frac{dV}{V}$$

$$= NkT \ln\left(\frac{V_1}{V_2}\right)$$

<u>Enthalpy H</u> "heat content" of system
typical chemical process occurs at const. T, P

$H = U + PV$ a type of <u>Legendre transformation</u>
dependence on $V \to P$

$\Delta H = \Delta U + P\Delta V + V\Delta P = Q + W_{other} + V\Delta P$
$\overset{*}{=} Q - P\Delta V + W_{other}$
$\underset{\text{const } P}{=} Q + W_{other}$

So for typical chemical process @ <u>const. P</u>
with $\underline{W_{other} = 0}$, $\Delta H = Q$ "heat content"

$\Delta H > 0$	absorbed heat	endothermic
$\Delta H < 0$	released heat	exothermic

H includes work done to put system with volume V into environment at constant P

Ex (1.52) $H + H \to H_2$ H = hydrogen

Table p. 404 <u>note</u> <u>H</u> is T, P dependent!

$\Delta_f H \left(\frac{kJ}{mole}\right) = 217.97 + 217.97 = 0$

formation

binding energy per molecule H_2: $\Delta H < 0$ exothermic (final − initial)

$$E_b = \frac{2(217.97)\ kJ/mole}{(6\times10^{23}\ \#/mole)(1.6\times10^{-19}\ J/eV)}$$

$$= \frac{2(217.92)}{6(1.6)}\ 10^{-1}\ \frac{eV}{\#} = 4.5\ eV/\#$$

latent heat.

from table p. 405

	$\Delta_f H$ kJ/mole
H_2O_l	-285.83
H_2O_g	-241.82
	$\Delta H = -44.01$ kJ/mole

$$H_f[H_2O_g] = H_f[H_2O_l] - \Delta H_f$$

Q absorbed > 0

Q absorbed changes phase not temperature.
called latent heat.

$$L_w = \frac{44 \text{ kJ/mole}}{(1.602\times10^{-19} \text{ J/eV})(6.022\times10^{23} \#/\text{mole})} = 0.456 \text{ eV}/\#$$

1 kg water is $n = \frac{10^3 g}{(2+16) g/mole} = 55.56$ mole

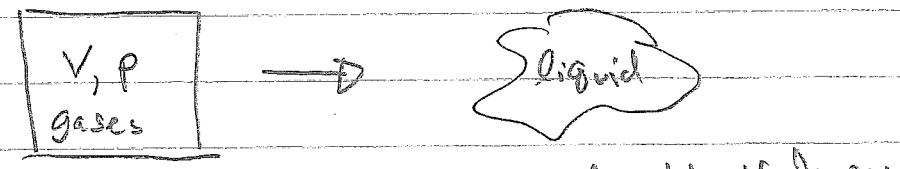
$$L_w = (44 \text{ kJ/mole})(55.56 \text{ mole/kg})$$

$$= 2444 \text{ kJ/kg}$$

note. $L_w = 2265$ kJ/kg @ 373.15 K boiling
typically quoted number

$\boxed{\text{Ex 1.49}}$ Combustion 1 mole H_2 + $\frac{1}{2}$ mole O_2 gas

What is total change in energy?



negligible volume

Δ Enthalpy:

$$H_2 + O_2 = H_2O$$

$\Delta_f H$ (kJ) 0 0 = −285.83 kJ (exothermic)

total heat released = 286 kJ

$$\Delta U = \Delta H - P\Delta V$$

Work P = sum of partial pressures kinetic theory

$$= (1 \text{ mole})\frac{RT}{V} + \left(\frac{1}{2} \text{ mole}\right)\frac{RT}{V} = \frac{3}{2}\frac{RT}{V}$$

$$\Delta \bar{V} = (0 - V) = -V$$

$$P\Delta V = -\frac{3}{2}RT = -3.7 \text{ kJ}$$

$$RT\Big|_{298K} = 2.478 \text{ kJ/mole}$$

$$\Delta U = (-286 + 4)\text{ kJ} = -282 \text{ kJ}$$

energy stored mostly in chemical bonding of H_2O

Heat Capacity

$$C_x \equiv \frac{Q}{\Delta T} \quad \text{or} \quad Q = C_x \Delta T$$

heat transferred in change of temperature under condition x = (P, V constant)

Constant volume, $Q = \Delta U$

$$C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

constant volume

U function of T

so $\Delta U = mC_v \Delta T$

with $U = N\frac{f}{2}k_B T$, $C_V = \frac{N f k_B}{2}$ (per #)

constant f.

= molecule

Heat capacity of ideal gas at constant P —

$$Q = \Delta U - W = \Delta U + P\Delta V = \Delta H$$

$$\boxed{C_p = \frac{\partial H}{\partial T}}$$

change of enthalpy with T

$P\Delta V = N k_B \Delta T$ so

constant pressure

so $\Delta H = mC_p \Delta T$

$$Q = N k_B \Delta T \left(1 + f/2\right)$$

$$C_p = N k_B \left(1 + f/2\right) = C_V + N k_B$$

or per mole,

$$C_p^{(m)} = C_V^{(m)} + R$$

heat capacity per mole

Return to Latent heat of water

$$C_p[H_2O_l] = 75.29\ J/K$$
$$C_p[H_2O_g] = 33.58\ J/K$$
$$\Delta C_p = 41.71\ J/K$$

from Table p. 405

to correct L_w from 25°C to 100°C,

$$(\Delta C_p)(100-25)K = 3.13\ kJ/mole$$

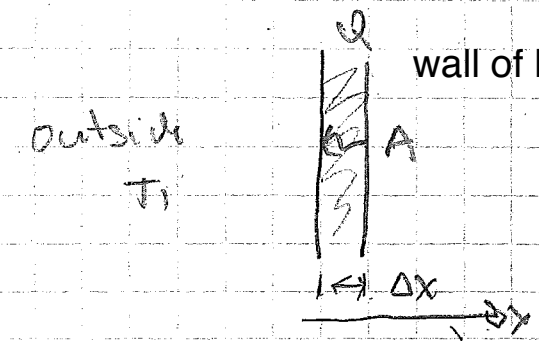
$$L_w^{100°C} = L_w^{25°C} - 3.13\ kJ/mole$$

$$= (44.01 - 3.13)\ kJ/mole = 40.88\ kJ/mole$$

from ΔH p. 11

or $L_w^{100°C} = (40.88\ kJ/mole)(55.56\ mole/kg) = 2270\ kJ/kg$

heat conduction



$$Q \propto \frac{A(\Delta T)\Delta t}{\Delta x}$$

rate $\boxed{\frac{Q}{\Delta t} = -k_t A\left(\frac{dT}{dx}\right)}$

→ k_t empirical constant $\left[\frac{J}{s}\cdot\frac{1}{m}\cdot\frac{1}{K}\right]$

air	0.026
glass	0.8

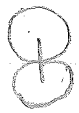
"Rvalue" $\frac{\Delta x}{k_T}$ $\boxed{\text{"thermal resistance"}}$

$$\frac{\text{Rate of heat loss}}{\text{unit area}} = \frac{\Delta T}{\text{Rvalue}}$$

See Baierlein Chapter on Transport Phenomena

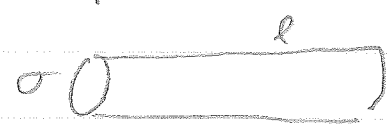
Conductivity for ideal gas

Separation for molecular collision $2r$



effective area $\sigma = \pi (2r)^2 = 4\pi r^2$

mean free path —



$$\boxed{\underbrace{\frac{N}{V}}_{\#\text{ density}} \underbrace{(\sigma \ell)}_{\text{Vol of cylinder}} = 1 \text{ collision}}$$

take $r = 0.15\,nm$ (N_2)

$$\sigma = 4\pi (0.15\,nm)^2 = 3 \times 10^{-19}\,m^2$$

at room Temperature $T = 25°C = 298K$, number density

$$\frac{N}{V} = \frac{P}{kT} = \frac{10^5\,N/m^2}{(1.38 \times 10^{-23}\,J/K)(300K)} = 0.24 \times 10^{26}\,\frac{\#}{m^3}$$

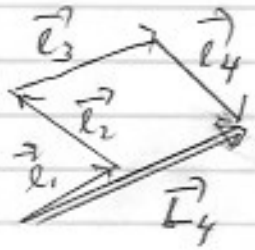
$$\ell = \left(\frac{1}{3 \times 10^{-19}\,m^2}\right)\left(\frac{1}{0.24 \times 10^{26}\,\frac{\#}{m^3}}\right) = 1.4 \times 10^{-7}\,m$$

mean time between collisions

$$\Delta t = \frac{\ell}{\bar{v}} = \frac{1.4 \times 10^{-7}}{500\,m/s} = 3 \times 10^{-10}\,s$$

so diffusion is very slow

Random walk



molecular collisions are isotropic

$$\vec{L}_N = \sum_{i=1}^{N} \vec{l}_i \qquad \text{vector sum}$$

Ave. displacement $\langle \vec{L}_N \rangle = \vec{0}$

root mean square displacement RMS

$$\langle \vec{L}_N \cdot \vec{L}_N \rangle^{1/2} = L_{rms} = c\, l \sqrt{N}$$

c ≈ one constant

if Δt is mean time between collisions

$\bar{v}$ mean molecular speed

$$l = \bar{v}\, \Delta t$$

total time $t = N \Delta t$, $N = \dfrac{\bar{v} t}{l}$

giving $L_{RMS} = l \sqrt{\dfrac{\bar{v} t}{l}} = \sqrt{\bar{v} l}\, \sqrt{t}$

increases like square root of time t

Physics 301: 3D Random Walk
August 14, 2020

Do a set of pseudo-experiments (random numbers) to show that in three dimensions, the **mean distance** traveled $\langle d_{end} \rangle$ after n steps is proportional to $\sqrt{n}$. Take $10 < n < 200$. Make a plot of $\langle d_{end} \rangle$ versus $\sqrt{n}$. Find the proportionality constant.

I did 20 tests with $10 < n < 200$. Each test consisted of 1000 trials of n steps each.

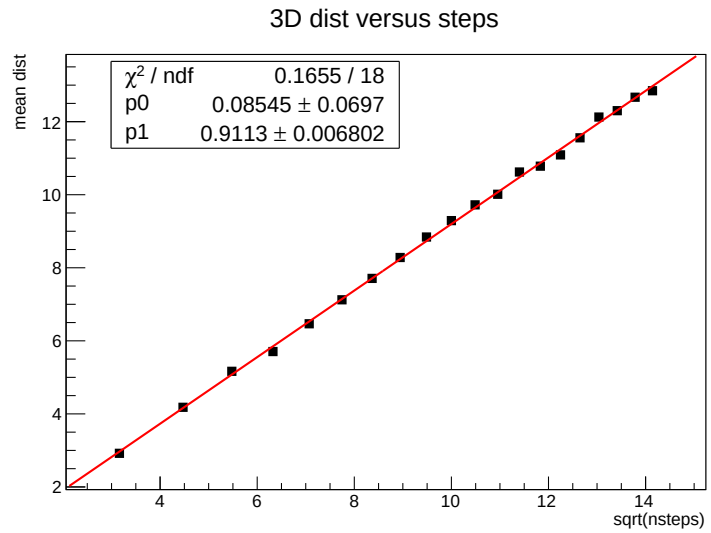
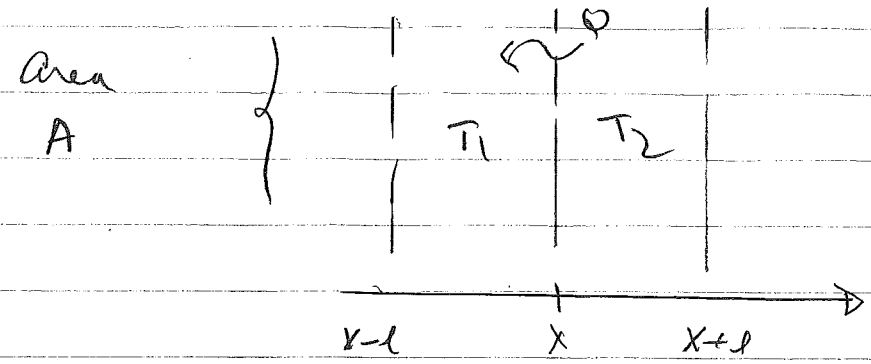


Figure 1: Mean distance $\langle d_{end} \rangle$ versus $\sqrt{n}$. The slope of the line is parameter $p_1 = 0.91$.

Rate of heat transfer for ideal gas



$$Q = \frac{1}{2}(U_2 - U_1) = -\frac{1}{2} C_v (T_2 - T_1)$$

$\frac{1}{2}$ moving in crossing direction

$$\frac{Q}{\Delta t} = -\frac{1}{2} C_v \frac{1}{\Delta t}\left[T(x+l) - T(x)\right]$$

$$T(x+l) = T(x) + l \left.\frac{dT}{dx}\right|_x$$

$$\frac{Q}{\Delta t} = -\frac{1}{2} C_v \left(\frac{l}{\Delta t}\right)\frac{dT}{dx} \equiv -k_t A \frac{dT}{dx}$$

def. of k_t

$$k_t = \frac{1}{2}\left(\frac{C_v}{Al}\right)\frac{l^2}{\Delta t} = \frac{1}{2}\left(\frac{C_v}{V}\right) l \bar{v} \qquad \bar{v} = \frac{l}{\Delta t}$$

Temp dependence of k_t:

$$\bar{E} = \frac{1}{2} m v^2 = \frac{f}{2} kT \Rightarrow \bar{v} = \sqrt{\frac{f}{m} kT}$$

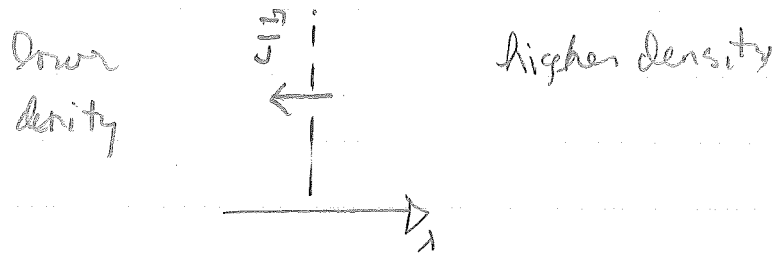
$$\frac{C_v}{V} = \frac{1}{V}\left(\frac{f}{2} Nk\right)$$

$l = \frac{N}{V}\frac{1}{\sigma}$ independent of temperature

$$k_T = \frac{1}{2}\left(\frac{f}{2}\frac{Nk}{V}\right)\left(\frac{N}{V}\frac{1}{\sigma}\right)\sqrt{\frac{fk}{m}}\sqrt{T} \propto \sqrt{T}$$

expect $k_T \propto \sqrt{T}$

Diffusion



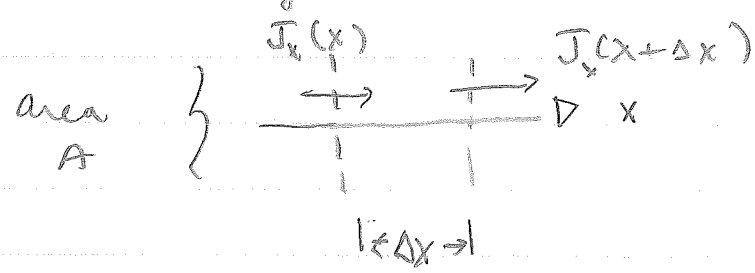
$J_x \equiv$ flux across boundary $\left[\frac{\#}{\text{area}\cdot\text{time}}\right]$

$$J_x = -D\frac{dn}{dx}$$

D is proportionality constant

$\boxed{\# \text{ density } n(x)}$

Conservation of molecules



$$\frac{dn}{dt} A\Delta x = A\left(J_x(x) - J_x(x+\Delta x)\right)$$

$$= -A\frac{dJ_x}{dx}\cdot\Delta x$$

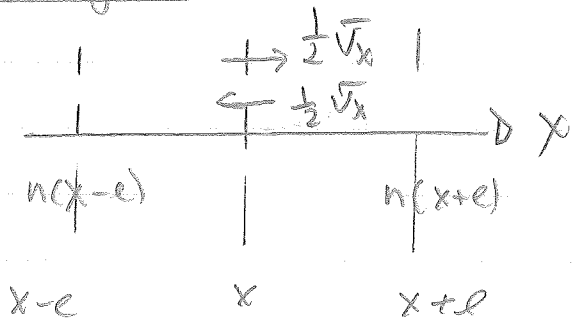
$$\frac{dn}{dt} = -\frac{dJ_x}{dx} = D\frac{d^2n}{dx^2}$$ diffusion equation.

these should be partial derivatives for n(x,t)

D for diluted gas

$$\boxed{\frac{\bar{v}}{6} = \frac{1}{2}\bar{v}_x}$$

n depends on x



$$J_x = \frac{1}{6}\bar{v}\, n(x-l) - \frac{1}{6}\bar{v}\, n(x+l)$$

Taylor expand $n(x \pm l) = n(x) \pm l \left.\frac{dn}{dx}\right|_x$

$$J_x = \frac{1}{6}\bar{v}\left(-2\frac{dn}{dx}l\right)$$

$$\boxed{D = \frac{1}{3}\bar{v}\, l}$$