Thermodynamics lectures

Phys 4230

Fall 2011

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Lecture Set 1

August 2, 2011

Introduction

1. Administrative details
   see class homepage:

http://www.colorado.edu/physics/phys4230/

2. Course overview

- $T, V, P, U, W, Q \longleftrightarrow \vec{r}_i, \vec{v}_i, \Psi_{k_i}, \{n_i\}, \ldots$
- equipartition "theorem": $U = \frac{f}{2} k_B T$
- ideal gas: $PV = N k_B T, \ldots$
- 1st law of thermodynamics: $U = W + Q$
- processes: isothermal, isochoric, isobaric, adiabatic
- statistical mechanics: microcanonical $\longrightarrow$ applicat's
- 2nd law of thermodynamics: $\Delta S_{tot} \geq 0$
- statistical mechanics: canonical & grand-canonical
- applications:
  - ideal gas
  - Maxwell-Boltzmann distibution
  - Bosons: black-body, BEC, ...
  - Fermions: metals

Thermodynamics Overview

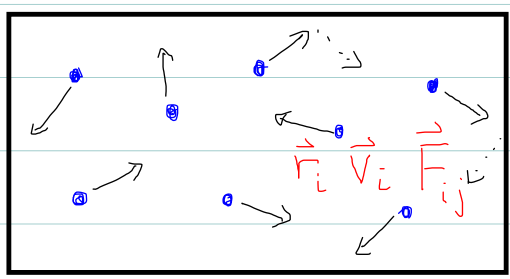
Thermodynamics:

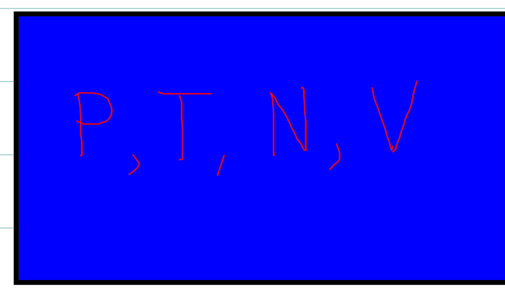
A set of principles (very general) underlying macroscopic (bulk) systems

ex's: air in the room, cup of coffee, rubber/plastic, piece of metal, superconductor, magnet, blackhole, ..

description:

microscopic vs macroscopic



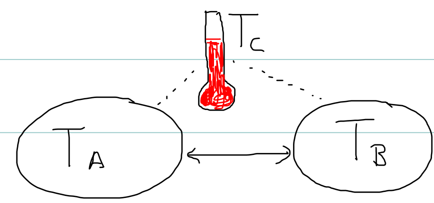


$$\left.\begin{aligned} m\vec{a}_1 &= \vec{F}_1 \\ m\vec{a}_2 &= \vec{F}_2 \\ &\vdots \\ m\vec{a}_N &= \vec{F}_N \end{aligned}\right\} \xrightarrow[\text{derives}]{} \underbrace{P, T, N, V, U, \ldots}_{\text{thermodynamics (relates these)}}$$

statistical mechanics $\longrightarrow$

0^{th} law of thermodynamics: $\underline{T \text{ exists}}$

- T – property of a bulk system, measured by a thermometer (many kinds)
- transitive:



$$T_A = T_c\,, \quad T_B = T_c \Rightarrow T_A = T_B$$

- measure via expansion, change in shape, color, resistance, … (calibrate)

- $T_F = \frac{9}{5} T_c + 32$: Fahreinheit vs Celsius

<u>absolute</u>/natural scale (all thermo. laws in terms of it: <u>Kelvin</u>

$T_c = T_K - 273.15$ (same unit size, just shifted up by 273°)

$T_K^{room} \simeq 300K$

$T_K^{lowest} = 0$

etc …

why lowest limiting T ?

T reflects (average) internal energy of the system

- $U \leftrightarrow T$ relation – function of state of system

Equipartition "theorem": $U = \frac{f}{2} k_B T$
(only valid for classical system w/ quadratic d.o.f.

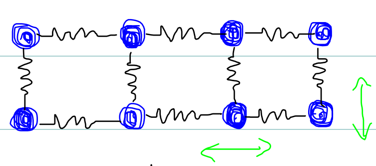
f – # of quadratic d.o.f.

- Ex's:

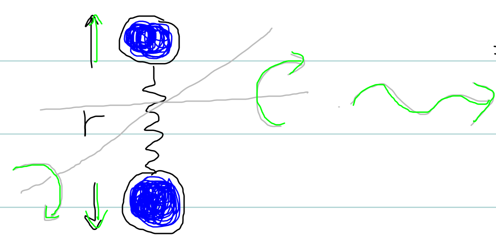
– 3d ideal (noninteracting) gas: $H = \frac{1}{2m} \underbrace{\sum_{i=1}^{N} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2)}_{3N = f}$
monotomic

– 1d harmonic oscillator: $H = \underbrace{\frac{p^2}{2m} + \frac{1}{2} k x^2}_{2 = f}$

– 3d diatomic molecule: $H = \underbrace{\frac{p^2}{2m}}_{3} + \underbrace{\frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y}}_{2} + \underbrace{\frac{p_r^2}{2\mu} + \frac{1}{2} k r^2}_{2}$



solid



$\Rightarrow$ $f = 7$

$k_B = 1.38 \times 10^{-23}$ J/K Boltzmann's constant ($E \leftrightarrow T$)

$U = \left\langle \sum_{i=1}^{N} \frac{p_i^2}{2m} \right\rangle = \frac{f}{2} k_B T \Rightarrow \begin{cases} \text{hot} \leftrightarrow \text{fast motion} \\ \text{cool} \leftrightarrow \text{slow motion} \\ T=0 \leftrightarrow \text{no motion} \rightarrow \text{can't be slower than 0} \end{cases}$

Equipartion Thm Applications

Ex's:

1. speed of gas molecules in the room:

$$\frac{1}{2} m v_{rms}^2 \simeq \frac{3 k_B T}{2}$$

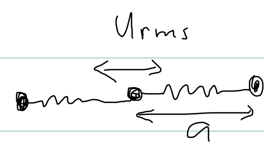
$$\Rightarrow v_{rms} = \sqrt{\frac{3 k_B T}{m}}$$

2. displacements of ions in a solid (phonons):

$$\frac{1}{2} \underbrace{m\omega_0^2}_{Y\text{ - modulus}} u^2 \simeq \frac{3 k_B T}{2}$$

Lindemann criterion:

$$\Rightarrow u_{rms} \simeq \sqrt{\frac{3 k_B T}{Y}} \rightarrow T_{melt} \text{ when } u_{rms} \approx a \text{ - lattice constant}$$



$$\Rightarrow \boxed{k_B T_m \approx \frac{a^2 Y}{3}}$$

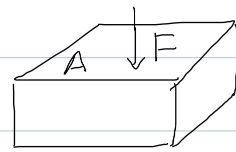
- ideal gas "equation of state": relation between T, P, V, N

$$PV = N k_B T \iff PV = nRT$$

$R = k_B N_A = 8.31 \frac{J}{mol \cdot K}$

n = # of moles $= \frac{N}{N_A}$, $N_A = 6.02 \times 10^{23}$ Avogadro's number

$P = \frac{\langle Force \rangle}{Area}$ – pressure



(dull vs sharp ice skate, knife, ...)

units:

Pressure, P: $1\ Atm \approx 10^5\ Pa \left(= \frac{Newtons}{m^2}\right) = 1\ bar$ (STP T_{room}, 1At)

Volume, V: $1\ liter = 10^{-3}\ m^3$ ($1\ ml = 1\ cm^3$)

molecules in a chunk of material: $1000\ N_A$

mass of 1 mole (N_A molecules) = total atomic mass in grams

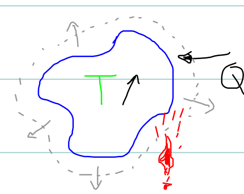
e.g. 1 H atom = 1 au $\rightarrow m^{H}_{1mole} = 1\,gram$, $m^{O_2}_{1mole} = 32\,g$

density, ρ: $\frac{N}{V} m$
(mass)

Q – heat = random kinetic (motion) energy

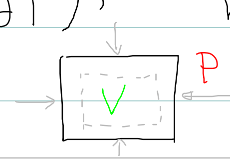
properties:

– thermal expansion coeff.: $\beta = \frac{1}{V}\frac{\partial V}{\partial T}$



– heat capacity: $C = \frac{Q}{\Delta T} \left(= \frac{\partial U}{\partial T}\right)$, $c = \frac{C}{m}$ (specific heat)

– compressibility: $\kappa = -\frac{1}{V}\frac{\partial V}{\partial P}$



• Equilibrium thermodynamics

– relax to thermal equilibrium after relaxation time τ

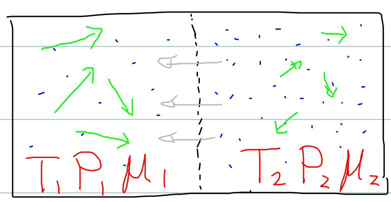
e.g. thermometer, cooling cup of coffee after T's equalize via Q transfer

– heat transfer via: conduction (touching), convection (bulk movement), radiation (light)

– thermal via energy U transfer same T

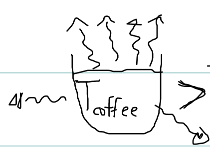
mechanical – volume V – pressure P

diffusive – particles N – chemical potential μ



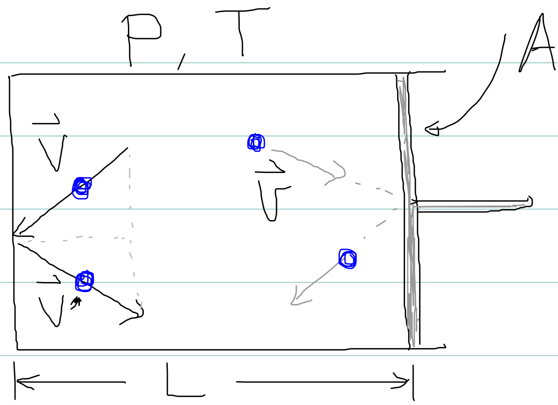
ex. osmosis in plants and cells via build up of osmotic pressure (due to ion concentration imbalance across a membrane) → drives water motion through a membrane.

heat/energy transfered from hot to cold



$T_{coffee} > T_{room}$

Ideal gas microscopics



$$\vec{p} = m\vec{v}$$

Newton: $\vec{F} = m\vec{a} = \frac{\Delta \vec{p}}{\Delta t}$

Pressure $P = \frac{\langle F_x \rangle}{A_x} = \left\langle \frac{p_x' - p_x}{A\Delta t} \right\rangle N = \left\langle \frac{2p_x}{A\, 2L/v_x} \right\rangle N$

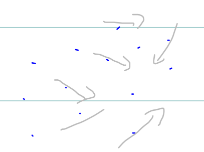
$$P = \frac{\langle p_x^2 \rangle}{m}\frac{N}{V} = \frac{1}{3}\frac{\langle \vec{p}^{\,2} \rangle}{m}\frac{N}{V} \underset{\substack{\text{equipartition} \\ (f=3)}}{=} k_B T\, N/V$$

$$U = \langle K.E \rangle = \frac{\langle p_x^2 + p_y^2 + p_z^2 \rangle}{2m}$$

$$\Rightarrow \boxed{PV = N k_B T}$$

$$\Leftrightarrow P = \rho\, k_B T$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \simeq 100\ m/s$$



- at same T more massive molecules are slower.
- nonideal gas: $P = k_B T \rho\left(1 + a_2\rho + a_3\rho^2 + \ldots\right)$
- $k_B T_{room} = 0.025\,eV \approx \frac{1}{40}\,eV$

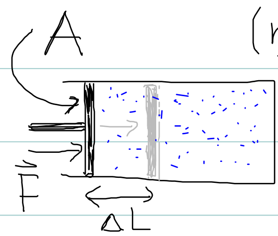
1^{st} law of thermodynamics

- heat Q – energy that flows spontaneously from hot $\xrightarrow[Q]{}$ cold (transferred, not inside syst.)

heat $Q < 0$ leaves the system (cup of coffee)
(positive when enters the system)

- work W – energy transferred deterministically (not fnc of state of syst.)

e.g.



$$W = -F\Delta L = -\underbrace{\int_{L_i}^{L_f} d\vec{x}\cdot\vec{F}}_{\text{usually path dependent}}$$

(quasistatic)

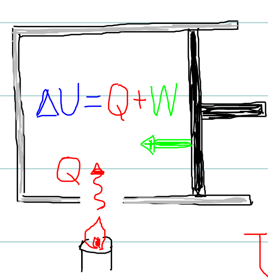
$$W = -F\Delta L = -\underbrace{\frac{F}{A}}_{P}\cdot\underbrace{A\Delta L}_{\Delta V}$$

$\longrightarrow \vec{F}$, $\longrightarrow d\vec{r}$ $(+)$ $\qquad$ $\longrightarrow \vec{F}$, $\longleftarrow d\vec{r}$ $(-)$

$= -P\Delta V$ compressional work (car pistons, pump tire) done on the system

1^{st} law: conservation of energy

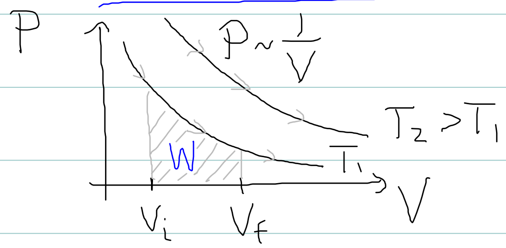
$$\underbrace{dU}_{\text{increase in energy of system}} = \underbrace{Q}_{\text{heat entering system}} + \underbrace{W}_{\text{work done on the system}}$$



U – fnc of state of the system (W, Q are NOT)

Processes that change system

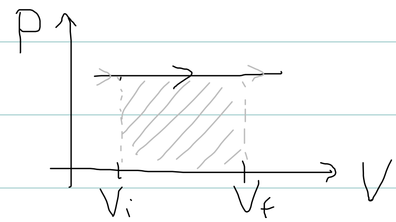
- isothermal (constant T, $\Delta T = 0$): $P = \dfrac{N k_B T}{V}$



$Q = -W$, to keep T const.

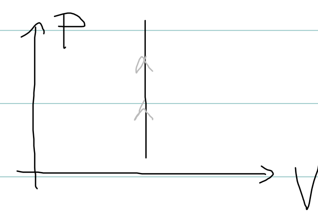
$$\boxed{W = -N k_B T \int_{V_i}^{V_f} \frac{dV}{V} = -N k_B T \ln \frac{V_f}{V_i}}$$

- isobaric (constant P, $\Delta P = 0$): $V \sim T$



$$W = -P(V_f - V_i)$$

- isochoric (constant V, $\Delta V = 0$): $P \sim T$

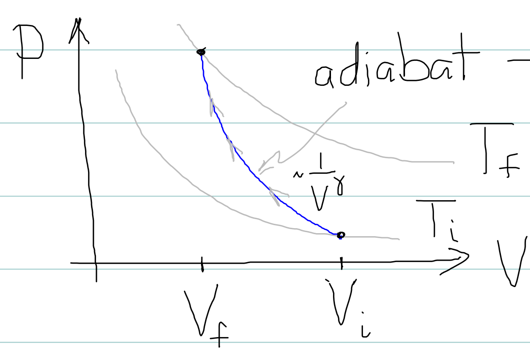


- adiabatic (fast $\Rightarrow$ no heat enters/leaves, $Q = 0$)

$$dU = \frac{f}{2} N k_B \, dT = -P\,dV \Rightarrow \frac{f}{2} \int \frac{dT}{T} = -\int \frac{dV}{V} = -\ln \frac{V_f}{V_i}$$

$$\Rightarrow \boxed{V T^{f/2} = \text{const.}} \xrightarrow[PV = N k_B T]{} \boxed{P V^{\gamma} = \text{const.}}, \quad \gamma = \frac{f+2}{f}$$

(adiabatic expon.)

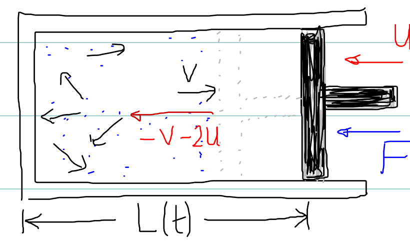


adiabat $\rightarrow$ T changes

- compressed adiabatically:
  - $U \uparrow \Rightarrow T \uparrow$
- expands adiabatically:
  - $U \searrow \Rightarrow T \searrow$ gas does work, $W < 0$

Microscopics of adiabatic process

1d (narrow piston)



$$v_i = v \ , \quad v_f = -v - 2u$$

every collision w/ moving wall speeds up by $2u$: $\quad v(t+\Delta t) = v(t) + 2u$

$$\Delta t = \frac{2L(t)}{v(t)} = \frac{2L_0 - 2ut}{v(t)} \Rightarrow \frac{dv}{dt} = \frac{2u}{\Delta t} = \left(\frac{u}{L_0 - ut}\right) v$$

$$\Rightarrow \int_{v_0}^{v} \frac{dv}{v} = \int_0^t \frac{dt}{L_0/u - t} \Rightarrow \ln \frac{v}{v_0} = \ln \frac{L_0}{L_0 - ut}$$

$$v(t) = v_0 \frac{L_0}{L_0 - ut} \Rightarrow U = \langle \tfrac{1}{2} m v^2 \rangle = U_0 \left(\frac{L_0}{L}\right)^2$$

$$\Rightarrow \boxed{T L^2 = \text{const.} \Leftrightarrow L T^{\frac{f}{2}} = \text{const.}, \ f = 1} \quad (\text{since } 1d)$$

Heat capacities

- $C \equiv \frac{Q}{\Delta T}$ – measures heat need per unit of temperature change

(as name implies, bigger body, bigger C)

- $c = \frac{C}{m}$ – specific heat $\left(\frac{J}{K \cdot kg}\right)$ e.g. $c^{p}_{H_2O} = 1 \frac{cal}{g \cdot {}^\circ C} = 4.2 \frac{J}{g \cdot {}^\circ C}$

- need to specify process, e.g.:
  - isochoric, $\Delta V = 0 = W$

$$\Rightarrow \boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \quad \left(= N \frac{f}{2} k_B \text{, for equip. syst.}\right)$$

Dulong & Petit

  - isobaric, $\Delta P = 0$

$$\Rightarrow C_p = \frac{\Delta U - (-P\Delta V)}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_p + \underbrace{P\left(\frac{\partial V}{\partial T}\right)_p}_{\text{small for solids, liquids}}$$

$$= C_V + N k_B = N\left(\frac{f}{2} + 1\right) k_B \quad \text{(ideal gas)}$$

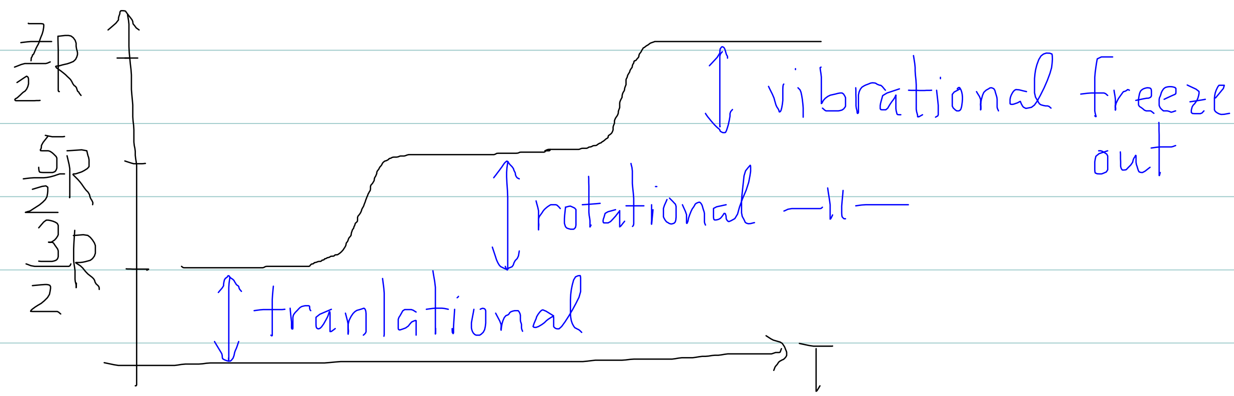
bigger because for C_p expands $\Rightarrow$ does work $W < 0$

$$\Rightarrow Q_p = \Delta U - \underbrace{W}_{\text{negative}} > \Delta U + 0 = Q_V$$

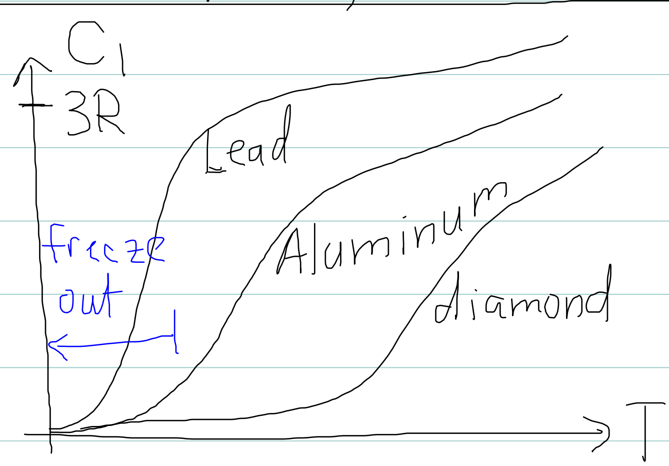
Quantum violation of equip. thm.

at low T, degrees of freedom (d.o.f.) freeze out
(we'll see how this happens via Q.M. later)

C_V for 1 mole of H_2:



Heat capacity of a solid:



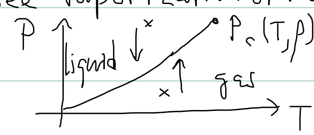
Latent heat

- amount of heat Q to melt & boil system

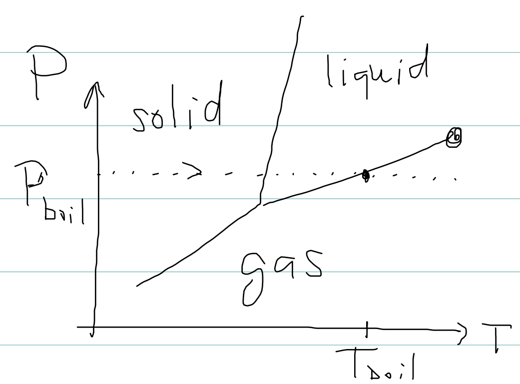
$$L = \frac{Q}{m}$$

- $L_{Ice}^{melt} = 333\,J/g = 80\,cal/g$ $\quad (1\,cal = 4.2\,J)$
  energy to raise 1 g of H_2O by 1 C°.
- $L_{H_2O}^{boil} = 2260\,J/g = 540\,\frac{cal}{g}$
- $C_p^{H_2O} = \frac{1\,cal}{1g \cdot K} \Rightarrow 100\,\frac{cal}{g}$ to raise H_2O from $T=0 \rightarrow T=100\,^\circ C$
- at boiling & melting phase transition (1^{st} order)
  $\Delta T = 0$, as all $Q \rightarrow$ phase transformation
  $\Rightarrow C_{at\ trans.} = \frac{Q}{0} = \infty$

(see vaporization of H_2O drop discussion,



ex:

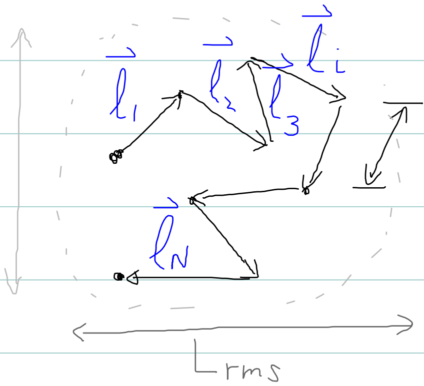


L – is why steam at 100°C is much more damaging that boiling water!

Diffusion

Heat (and other random processes) take place via diffusion (slow), where molecules execute "random walk"

Random walk:



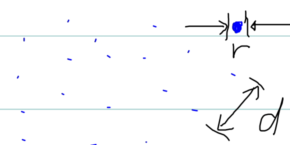
l = mean free path
= ave distance betw. collisions
= step length

N steps of length l

$$= \frac{1}{n\sigma}$$

σ ← crossection $4\pi r^2 = \sigma$, $r \sim 10\,\text{Å}$

n ← density $= \frac{N}{V} = \frac{1}{d^3}$, d ← distance between molecules.



$r \ll l \ll d$

$(l_{air} \sim 1500\,\text{Å})$

How far travels in N steps? $L_{rms} = \sqrt{\langle \vec{L}^2 \rangle}$

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots \vec{l}_N, \quad |\vec{l}_i| = l$$

$$L_{rms}^2 = \langle \vec{L}\cdot\vec{L} \rangle = \langle \sum_i \vec{l}_i \sum_j \vec{l}_j \rangle = \underbrace{\sum_{i=1}^{N} \langle l_i^2 \rangle}_{N l^2} + \underbrace{\sum_{i \neq j} \langle \vec{l}_i \cdot \vec{l}_j \rangle}_{0, \text{ since random}}$$

$$\underbrace{L_{rms} = l\sqrt{N} \sim \sqrt{N} \sim \sqrt{t}}_{\text{diffusive}} \ll t \text{ - ballistic}$$

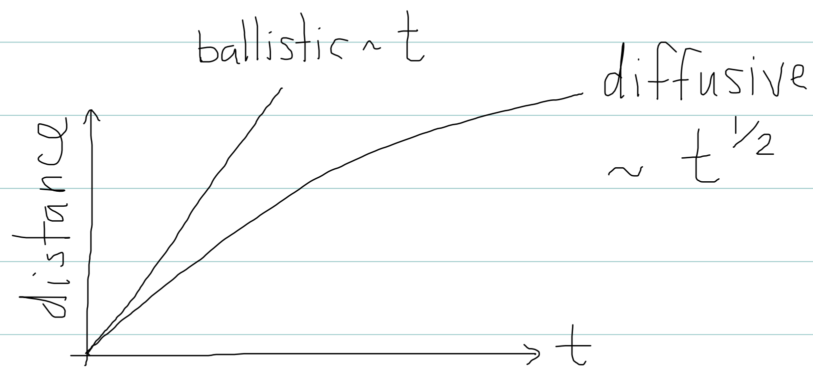
diffusive motion is slow qualitatively $\boxed{t^{1/2}}$
(e.g. heat, sugar in coffee, etc.)

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} \Rightarrow \tau = \frac{\ell}{v_{rms}}$$

$$\Rightarrow N = \#\,\text{steps} = \frac{t}{\tau} = \frac{\text{total time}}{\text{time per step}}$$

$$L_{rms} = \ell\sqrt{N} = \frac{\ell}{\sqrt{\tau}}\sqrt{\underbrace{N\tau}_{t}} = \sqrt{\underbrace{\frac{\ell}{\tau}}_{v_{rms}}\ell\, t}$$

$$\boxed{L_{rms} = \sqrt{Dt}\,, \quad D = v_{rms}\,\ell}$$ — diffusion coefficient



Fick's law:

$$J_n \simeq -D\frac{\partial n}{\partial x}$$

$$\Rightarrow \partial_t n = D\partial_x^2 n$$

for air at STP molecules move $V_{rms} \sim 100\,\frac{m}{s}$

time to diffuse across a room is days

to speed up:

- stir (convection)
- T-gradient: $\frac{Q}{\Delta t} = -\underset{\text{thermal conductivity}}{\kappa_t}\ \underset{\text{area}}{A}\ \underset{T\text{ gradient}}{\frac{\partial T}{\partial x}}$, $\kappa_t \simeq \frac{C_v}{V} D$