Thermal Equilibrium - when objects have been in contact and macroscopic coordinates have stopped changing

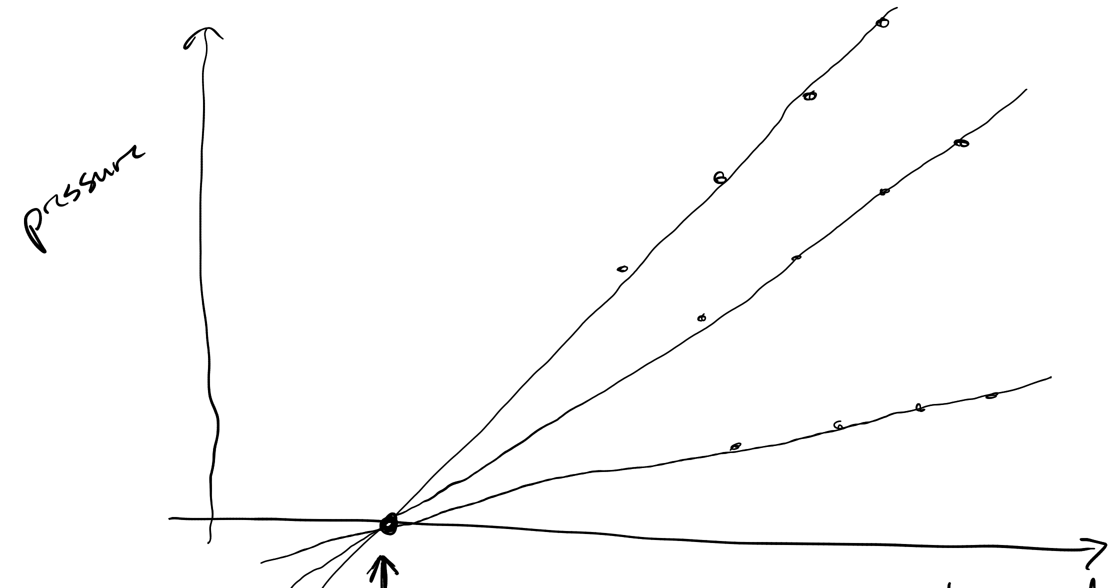
→ involves an exchange of energy between two object, or an object + its surrounding

→ volume (constant pressure) → mercury/alcohol

- pressure

- electrical resistance

- radiation/thermal emf



"absolute zero"

$0K = -273.15°C$

1) $C_1 = 0°C$ $\quad C_2 = 100°C$

$F_1 = 32°F$ $\quad F_2 = 212°F$

$C = mF + b$

1.2 Ideal Gas Law → Equation of State → relates all of the state variables together

$$pV = N k_B T$$

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

$[Pa] = \left[\frac{N}{m^2}\right]$

N ↳ number of particles

k_B: Boltzmann's constant

$k_B = 1.38 \cdot 10^{-23}\ J/K$

T → K

$$pV = nRT$$

n ↳ number of moles

R → universal gas constant

$R = 8.31\ J/mol \cdot K$?

$$N k_B = nR$$

$$6.022 \cdot \cancel{10^{23}} \cdot 1.38 \cdot \cancel{10^{-23}} = R$$

$$8.31\ J/mol\,K = R$$

Number, moles, molar, density

1 mole of things = $6.022 \cdot 10^{23}$ things

particle
atom
molecule

C^{12}
↳ 6 proton
6 neutrons

C^{14}
↳ 6 protons
↳ 8 neutrons

1 mole is 1 gram of protons + neutrons

Ex: mass of one proton in kg?

mass of one proton × number of proton = mass of the collection

$$m \times N = M$$

$$m = \frac{1g}{N_A} = \frac{1}{6.022 \cdot 10^{23}} = 1.7 \cdot 10^{-24} \text{ grams} = 1.7 \cdot 10^{-27} \text{ kg}$$

What about N_2?

$$1 \text{ mole of } N_2 = 2\left(14 \tfrac{g}{mol}\right) = 28 \text{ g/mol}$$

Volume of 1 mole of air at room temp and atmospheric pressure?

↳ $1 \text{ atm} = 1.013 \cdot 10^5 \text{ Pa}$

$$V = \frac{nRT}{P} = \frac{1 \text{ mol} \cdot 8.31 \text{ J/K·mol} \cdot 300\text{K}}{10^5 \text{ Pa}} = 0.0249 \text{ m}^3$$

$$V_{cube} = s^3$$

$$s = 0.292\ m \sim 30\ cm \sim 1\ ft$$

1.17

$$PV = nRT\left(1 + \frac{B(T)}{V/n}\right)$$

a)

$$PV = nRT\left(1 + \frac{n}{V} \cdot B(T)\right)$$

at atmospheric pressure $P = 10^5\ Pa$

solve for $\frac{n}{V}$

$$P = \frac{n}{V} RT\left(1 + \frac{n}{V} B(T)\right)$$

$$0 = \frac{n}{V} RT + \left(\frac{n}{V}\right)^2 \cdot RT \cdot B(T) - P$$

T	$B(T)$	$\frac{n}{V}$	$\frac{n}{V} \cdot B(T)$
100	-160		
200	-35		
300	-4.2		
400	9.0		
500	16.9		
600	21.3		

b) $PV = nRT\left(1 + \frac{B(T)}{V/n}\right)$ if

c) $\rightarrow PV = nRT\left(1 + \frac{B(T)}{V/n} + \frac{C(T)}{(V/n)^2}\right)$

want: B + C in terms of a + b

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

$$\left(P + \frac{an^2}{V^2}\right)V\left(1 - \frac{nb}{V}\right) = nRT$$

$$\left(P + \frac{an^2}{V^2}\right)V = nRT\left(1 - \frac{nb}{V}\right)^{-1}$$

$$PV + \frac{an^2}{V} = nRT\left(1 - \frac{nb}{V}\right)^{-1}$$

$$PV = nRT\underbrace{\left(1-\frac{nb}{V}\right)^{-1}}_{\text{use our approx.}} - \frac{an^2}{V}$$

$$(1+x)^p \approx 1 + px + \frac{1}{2}p(p-1)x^2 \qquad px \ll 1$$

$$\left(1+\left(-\frac{nb}{V}\right)\right)^{-1} \approx 1 + (-1)\left(-\frac{nb}{V}\right) + \frac{1}{2}(-1)\overbrace{(-1-1)}^{-2}\left(-\frac{nb}{V}\right)^2$$

$$\approx \underbrace{1 + \frac{nb}{V} + \left(\frac{nb}{V}\right)^2}$$

$$PV = nRT\left(1 + \frac{nb}{V} + \left(\frac{nb}{V}\right)^2\right) - \frac{an^2}{V}\left(\frac{nRT}{nRT}\right) \longleftrightarrow PV = nRT\left(1 + \frac{n}{V}\cdot B(T) + \left(\frac{n}{V}\right)^2\cdot C(T)\right)$$

$$PV = nRT\left(1 + \frac{nb}{V} + \left(\frac{nb}{V}\right)^2 - \frac{a\cancel{n}^{2}}{V\cdot\cancel{n}RT}\right) = nRT\left[1 + \frac{n}{V}\underbrace{\left(b - \frac{a}{RT}\right)}_{B(T)} + \left(\frac{n}{V}\right)^2\cdot\underbrace{b^2}_{C(T)}\right]$$

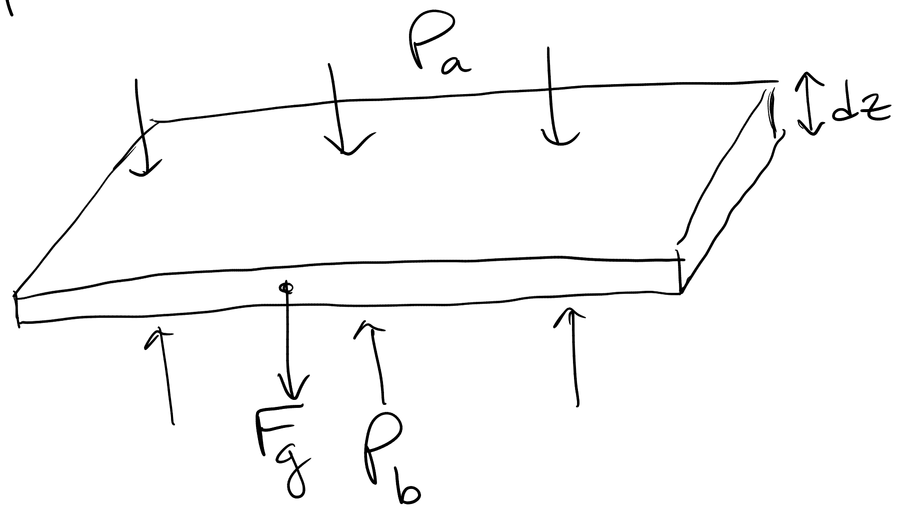
d) → plot data from that table

→ plot $B(T) = b - \frac{a}{RT}$ choose b, a

$\boxed{1.16}$

$\rho = \frac{M}{V}$

"rho"
volumetric
mass
density



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

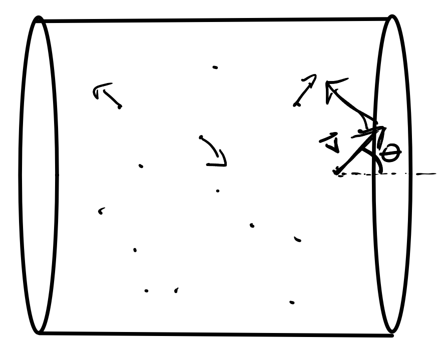
$+P_b \cdot A - P_a \cdot A - M \cdot g = 0$

$$\frac{dP}{dz} = \underbrace{\qquad\qquad}_{\rho}$$

1.2b Kinetic Theory and Equipartion of Energy

pressure $\longleftrightarrow$ kinetic energy $\longleftrightarrow$ temperature

$$\underbrace{\text{pressure}}_{\text{collision}} = \frac{F}{A} = \frac{\Delta p}{A \Delta t} \quad \Delta p = \underbrace{2mv\cos\theta}$$



$$d(\text{pressure}) = \frac{2mv\cos\theta}{dA \cdot dt} \cdot \underbrace{\begin{array}{c}\text{number of particles hitting area } dA \\ \text{w/ velocity } v \text{ in } dt \text{ amount of time}\end{array}}$$ } integrate over all velocities and over θ

number of atoms traveling in a particular direction w/ a particular speed $\cdot$ fraction of them that are within striking distance of the surface dA

Probability

$$P(x) = \frac{\text{desired outcomes}}{\text{total outcomes}}$$

$N(x) \leftarrow$ number of desired outcomes

$$N = \sum_{x=0}^{\infty} N(x)$$

total outcomes

$$P(x) = \frac{N(x)}{N}$$

rearrange

$$N(x) = P(x) \cdot N$$

normalized probabilities

$$\sum_{x=0}^{\infty} P(x) = 1$$

$$\langle x \rangle = \underbrace{\sum_{x=0}^{\infty} x \cdot P(x)}$$

- average value
- expectation value

$\rightarrow$ weighted average by probability

$$\langle x^2 \rangle = \sum_{x=0}^{\infty} x^2 \cdot P(x)$$

$$\langle f(x) \rangle = \sum_{x=0}^{\infty} f(x) \cdot P(x)$$

Example (Blundell 3.3)

a. $P(x) = \frac{e^{-m} m^x}{x!}$; show $\sum_{x=0}^{\infty} P(x) = 1$

Looked up Taylor Series:
$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

$$\sum_{x=0}^{\infty} \frac{e^{-m} m^x}{x!} \stackrel{?}{=} 1$$

$$e^{-m} \cdot \sum_{x=0}^{\infty} \frac{m^x}{x!} \stackrel{?}{=} 1$$

$$\sum_{x=0}^{\infty} \frac{m^x}{x!} \stackrel{?}{=} e^m \checkmark$$

b. Show $\langle x \rangle = \sum_{x=0}^{\infty} x \cdot P(x) \stackrel{?}{=} m$

$$= \sum_{x=0}^{\infty} x \cdot \frac{e^{-m} m^x}{x!} \stackrel{?}{=} m$$

$$= e^{-m} \sum_{x=0}^{\infty} \frac{x \cdot m^x}{x!} \stackrel{?}{=} m$$

$$\underbrace{\sum_{x=0}^{\infty} \frac{x \cdot m^x}{x!}}_{} \stackrel{?}{=} m e^m$$

$x \cdot (x-1) \cdot (x-2)(x-3) \cdots 1$

$$\cancel{\frac{0 \cdot m^0}{0!}}^{\,0} + \frac{1 \cdot m^1}{1!} + \frac{2m^2}{2!} + \ldots$$

$$\sum_{x=1}^{\infty} \frac{x\, m^x}{x!} = \sum_{x=1}^{\infty} \frac{m^x}{(x-1)!} = \sum_{x=1}^{\infty} \frac{m^{x+1-1}}{(x-1)!} = \sum_{x=1}^{\infty} \frac{m \cdot m^{x-1}}{(x-1)!}$$

$x \cdot (x-1) \cdot (x-2) \ldots$

$x' = x - 1$

$x = x' + 1$

$$m \cdot \sum_{x'=0}^{\infty} \frac{m^{x'}}{x'!}$$

drop the primes!

c. $\langle x \rangle = \sum_{x=0}^{\infty} x \cdot P(x)$

$$= 0 \cdot \frac{109}{200} + 1 \cdot \frac{65}{200} + 2 \cdot \frac{22}{200} + 3 \cdot \frac{3}{200} + 4 \cdot \frac{1}{100} + 5 \cdot \frac{0}{200}$$

$$= \underline{\underline{0.61}} = \frac{122}{200}$$

$$P(x) = \frac{e^{-0.61}\, 0.61^x}{x!}$$

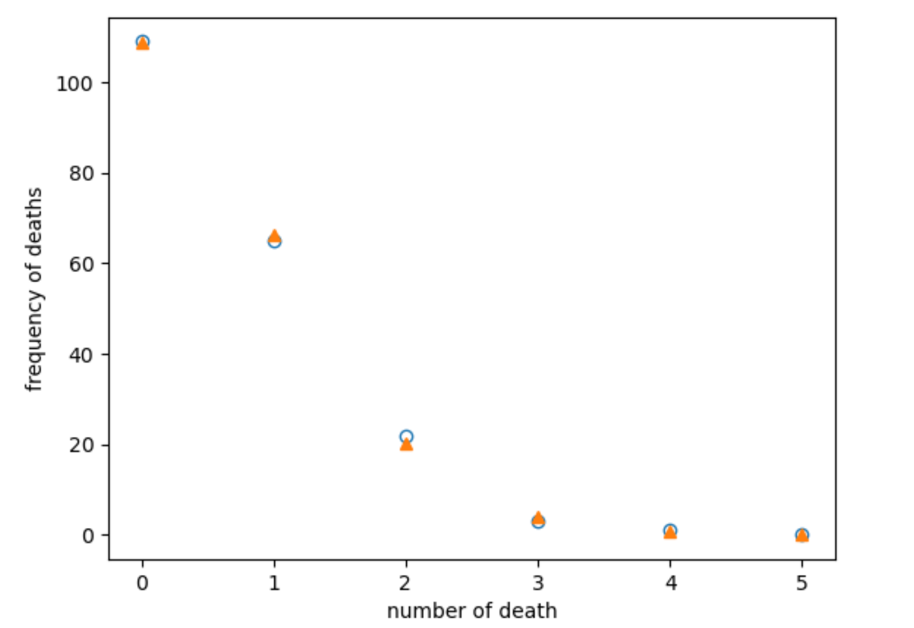
$$m \cdot \underbrace{\sum_{x=0}^{\infty} \frac{m^x}{x!}}_{= e^m}$$

$$m e^m \overset{?}{=} m e^m$$

$$\langle x \rangle = m$$

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.special import factorial

x = [0,1,2,3,4,5]
y = [109, 65, 22, 3, 1, 0]

fig, ax = plt.subplots()
ax.plot(x, y, 'o', mfc='none')
ax.set_xlabel('number of death')
ax.set_ylabel('frequency of deaths')

def deaths(number):
    return(np.exp(-0.61)*np.power(0.61, number)/factorial(number))

ax.plot(x, deaths(x)*200, '^')
```

→

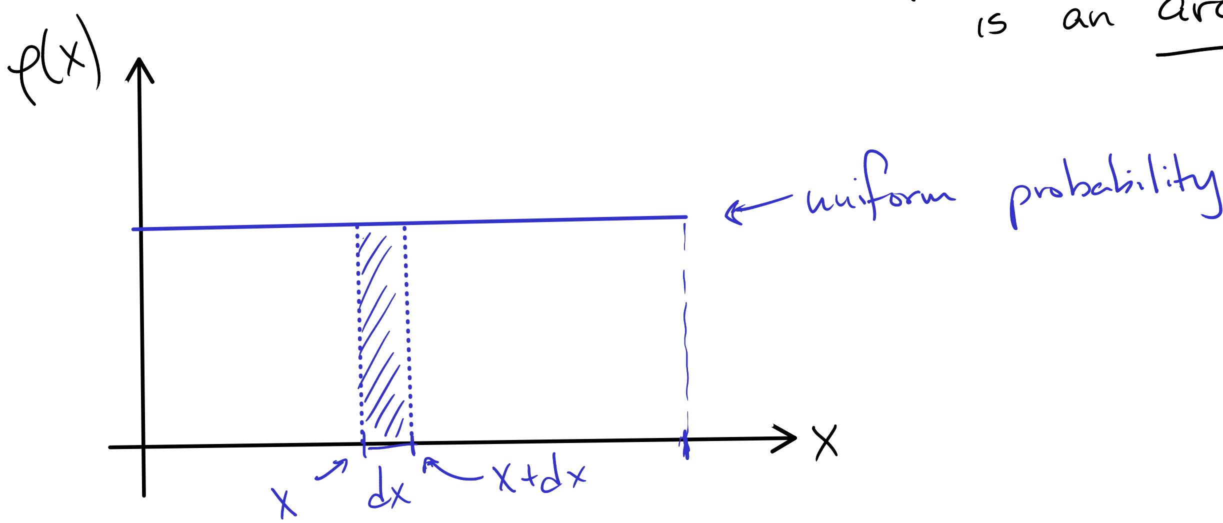


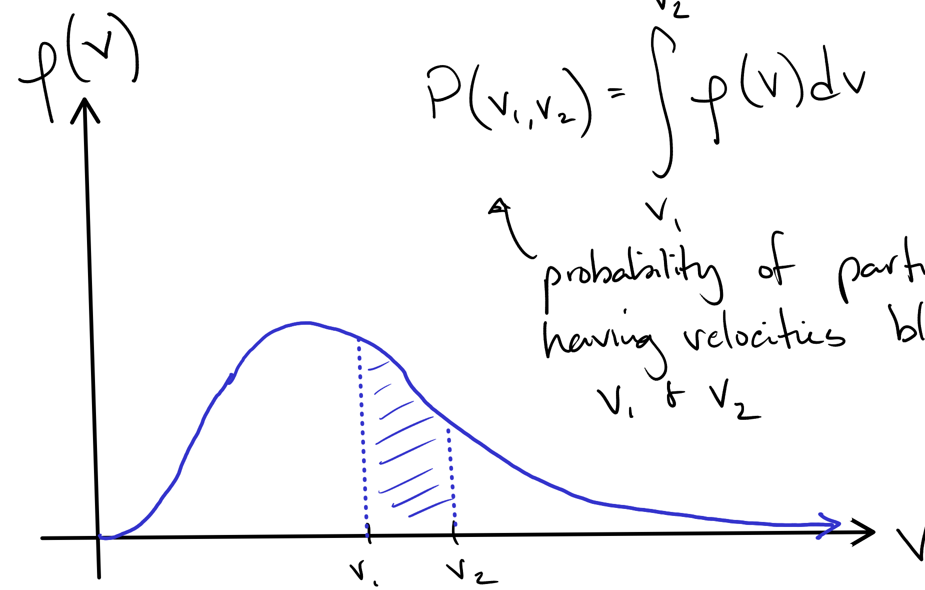
The continuous variable case follows by analogy but w/ some clarifications

$$\left\{\begin{array}{l}\text{probability of choosing}\\ \text{a value of random}\\ \text{between } x \text{ and } x+dx\end{array}\right\} = \rho(x)\cdot dx$$

$\rho(x)$ → distribution function

probability itself is an area.





$$P(v_1,v_2) = \int_{v_1}^{v_2} \rho(v)\,dv$$

probability of particles having velocities b/t v_1 & v_2

Normalized

$$\int_{-\infty}^{\infty} \rho(v)\,dv = 1$$

Since we will be dealing w/ such large numbers

$$\left\{\begin{matrix}\text{probability that a}\\ \text{particle has a}\\ \text{velocity between}\\ v \text{ and } v+dv\end{matrix}\right\} = \left\{\begin{matrix}\text{fraction of particles}\\ \text{having a velocity}\\ \text{between } v + v+dv\end{matrix}\right\}$$

Also mean

$$\langle v\rangle = \int_{-\infty}^{\infty} v\cdot \rho(v)\,dv$$

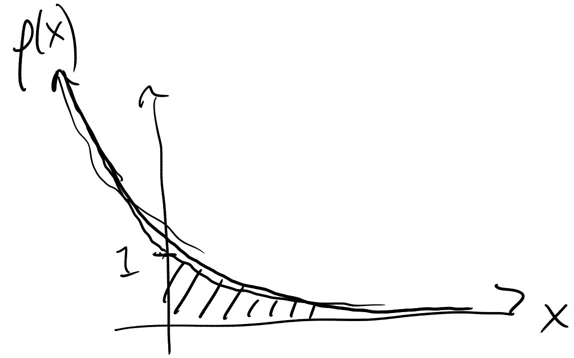
or

$$\langle v^2\rangle = \int_{-\infty}^{\infty} v^2\cdot \rho(v)\,dv$$

or

$$\langle f(v)\rangle = \int_{-\infty}^{\infty} f(v)\cdot \rho(v)\,dv$$

<u>Example:</u> (Blundell 3.4)



$$\rho(x)\,dx = Ae^{-x/\lambda}\,dx$$

a) Find A so that

$$\int_0^\infty \rho(x)\,dx = 1$$

$$\int_0^\infty Ae^{-x/\lambda}\,dx = 1$$

$$A(-\lambda)e^{-x/\lambda}\Big|_0^\infty = 1$$

$$A(-\lambda)(0 - -1) = 1 \qquad A\lambda = 1 \Rightarrow \boxed{A = \frac{1}{\lambda}}$$

$$uv\Big|_0^\infty - \int_0^\infty v\,du$$

$$u = x \qquad dv = e^{-x/\lambda}dx$$

$$du = dx \qquad v = -\lambda e^{-x/\lambda}$$

b) $$\langle x\rangle = \int_0^\infty x\,\rho(x)\,dx = \lambda$$

$$\int_0^\infty x\cdot\frac{1}{\lambda}e^{-x/\lambda}\,dx \overset{?}{=} \lambda$$

$$\frac{1}{\lambda}\left(-\lambda x e^{-x/\lambda}\Big|_0^\infty - (-\lambda)\int_0^\infty e^{-x/\lambda}\,dx\right)$$

$$\lambda = \langle x \rangle \checkmark$$

c) $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

$\sigma \Rightarrow$ standard deviation

$\sigma^2 \Rightarrow$ variance

$$\langle x \rangle = \lambda$$

$$\langle x \rangle^2 = \lambda^2$$

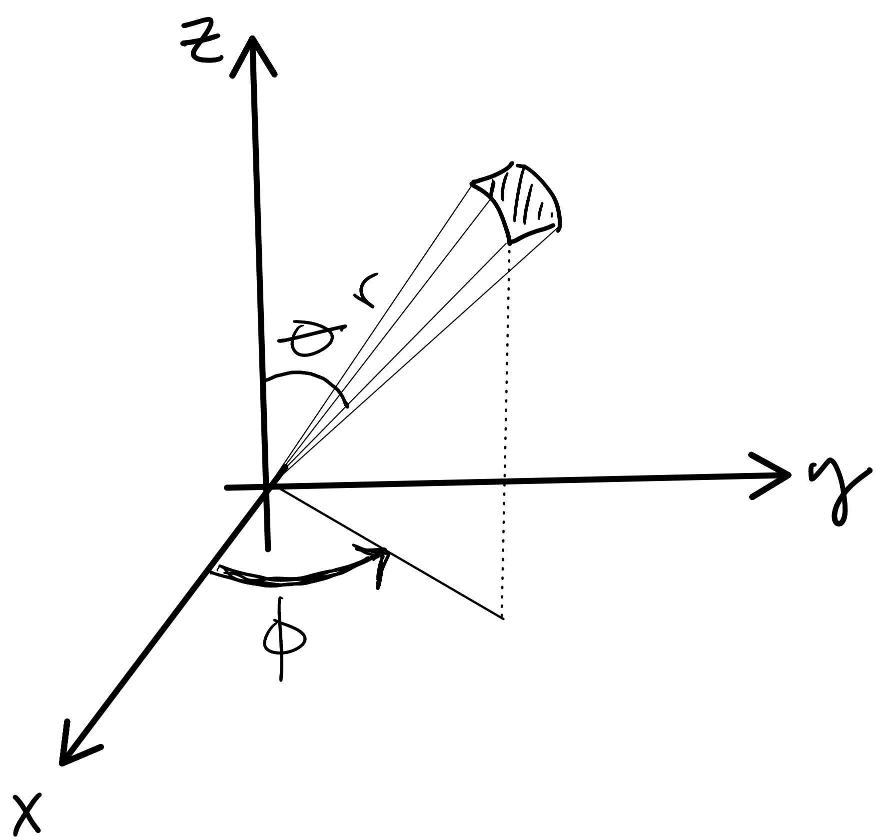
$$\langle x^2 \rangle = \int_0^\infty x^2 \cdot \frac{1}{\lambda} \cdot e^{-x/\lambda} \, dx$$

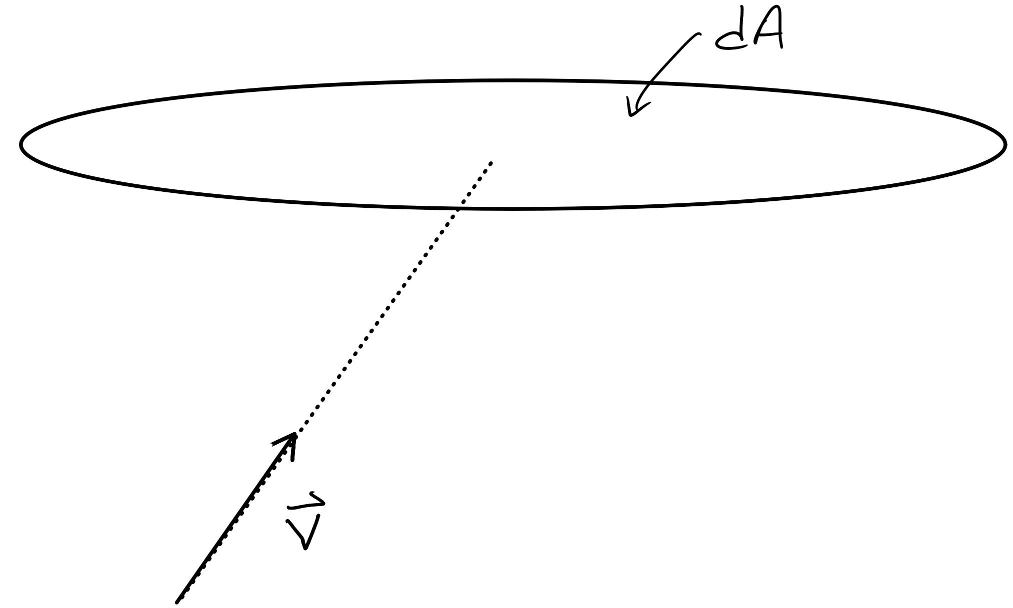
$\hookrightarrow$ LOOK IT UP!

$$\langle x^2 \rangle = 2\lambda^2$$

$\sigma^2 = 2\lambda^2 - \lambda^2 = \lambda^2 \leftarrow$ variance

$\sigma = \lambda \leftarrow$ standard deviation number of particles traveling in a particular direction w/ a particular speed





$$\boxed{U = \frac{3}{2} N k_B T}$$

internal energy

$$U = N\langle K \rangle$$

avg of kinetic energy

$$\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle$$

$$= \frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle$$

average of a sum is the sum of averages

$$= \frac{1}{2} m \left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right)$$

$$= \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle$$

$$\frac{3}{2} k_B T = \frac{3}{2} m \langle v_x^2 \rangle$$

$$\frac{1}{2} k_B T = \frac{1}{2} m \langle v_x^2 \rangle$$

Equipartition Theorem

$$U_{thermal} = N \cdot f \cdot \frac{1}{2} k_B T$$

f → degree of freedom (quadratic)

$\frac{1}{2}mv_x^2$, $\frac{1}{2}mv_y^2$, $\frac{1}{2}mv_z^2$, $\frac{1}{2}I\omega_x^2$, $\frac{1}{2}k_s x^2$

$f = 3 \leftarrow$ monatomic gas

$f = 5 \leftarrow$ diatomic gas near room temp

$f = 6 \leftarrow$ solid

1.23

$V = 1\ \text{liter} = 0.001\ m^3 = 10^{-3}\ m^3$

$p = 1.01 \cdot 10^5\ Pa = 10^5\ Pa$

$T = 293\ K$

monoatomic → $U = \frac{3}{2} N k_B T$ (f) $pV = N k_B T$

$U = \frac{3}{2} pV = \frac{3}{2} (10^5\ Pa)(10^{-3}\ m^3)$

$= 1.5 \cdot 10^2\ J = \underline{150\ J}$

diatomic

$U = \frac{5}{2} N k_B T = \frac{5}{2} pV$

$= 2.5 \cdot 10^2 = \underline{250\ J}$

$pV = nRT$

$\frac{10^5 Pa \cdot 10^{-3} m^3}{8.31 \cdot 293} = \underline{\underline{0.04\ mol}}$

1.24

$f = 6$

$U = \frac{6}{2} N k_B T$

$U = 3 N k_B T$

1g of Pb

$207\ \frac{g}{mol}$

$\frac{1\ gr}{207\ gr/mol} = \underline{\underline{0.0048}}\ \cancel{mol} \cdot \frac{6.022 \cdot 10^{23}\ \text{atoms}}{1\ \cancel{mol}}$

$U = 3 n_m R T = 3 \cdot 0.0048\ mol \cdot 8.31\ J/K\,mol \cdot 293 = \underline{35\ J}$

1.4 Heat and Work

Heat: spontaneous flow of energy due to a difference in temperature

Work:
- force applied over distance
- energy through resistor

Equation: $dU = \text{đ}Q + \text{đ}W$

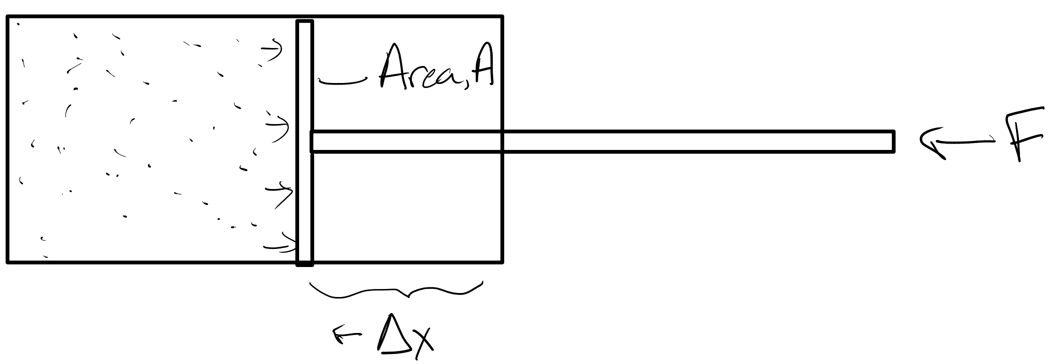
small amount

NOT a small change in amount

$\delta Q + \delta W \;|\; Q + W$

Compressive Work

$$\text{đ}W = \vec{F}\cdot d\vec{r} = \vec{F}\cdot\Delta\vec{x} = P\cdot \underbrace{A\cdot\Delta x}_{-\Delta V}$$

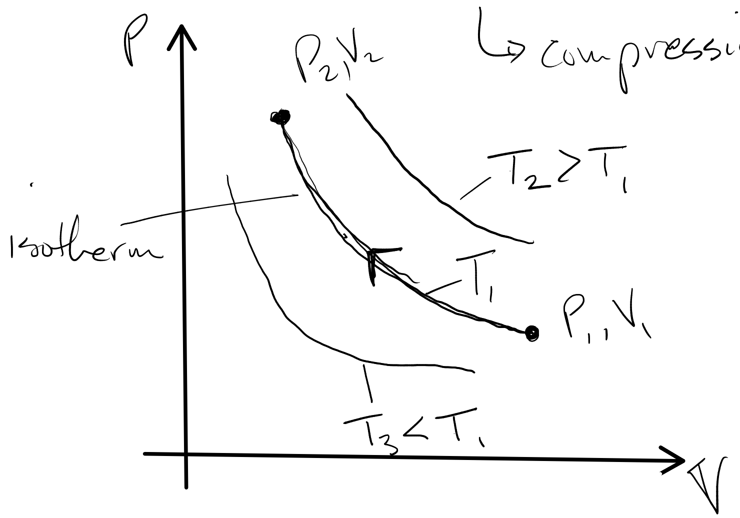


quasistatic, static-ish

$$\text{đ}W = -P\,dV = -P\,\Delta V$$

$$\text{đ}W = -P(V)\,dV$$

Isothermal process (constant temperature)



$$PV = \underline{\underline{Nk_BT}}$$

all constant

$$\boxed{P = \frac{Nk_BT}{V}} \leftarrow \text{hyperbola}$$

$$W = -\int p\,dV = -\underbrace{Nk_BT}_{\text{constants in this case}} \int_{V_i}^{V_f} \frac{1}{V}\,dV$$

$$W = -Nk_BT \ln\left(\frac{V_f}{V_i}\right) \qquad \ln\left[\left(\frac{V_f}{V_i}\right)^{-1}\right]$$

$$W = Nk_BT \ln\left(\frac{V_i}{V_f}\right)$$

$$\cancel{dU}^{\,0} = đQ + đW$$

$$0 = đQ + đW$$

$$đQ = -đW \leftarrow \text{isothermal}$$

$$Q = -Nk_BT \ln\left(\frac{V_i}{V_f}\right)$$

$$Q = Nk_BT \ln\left(\frac{V_f}{V_i}\right)$$

$$U = \frac{f}{2} Nk_BT$$

$$\Delta U = \frac{f}{2} Nk_B \Delta T$$

$$dU = \frac{f}{2} Nk_B dT$$

$$dT = 0 \therefore dU = 0$$

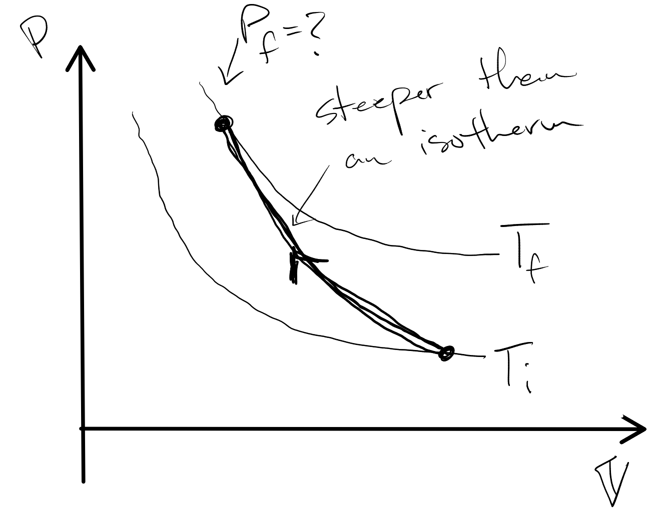
Adiabatic process (Isentropic process) (no heat)

↳ compression

first law → $dU = \cancel{đQ}^{\,0} + đW$

$dU = đW$ for an ideal gas: $U = \frac{f}{2} N k_B T$

$dU = \frac{f}{2} N k_B dT$



$$\frac{f}{2} N k_B dT = đW$$

$$\frac{f}{2} N k_B dT = -p\,dV$$

$$\frac{f}{2} \cancel{N k_B} dT = -\frac{\cancel{N k_B} T}{V} dV$$

$$\frac{f}{2} dT = -\frac{T}{V} dV$$

$$\frac{f}{2} \frac{dT}{T} = -\frac{dV}{V}$$

$$\frac{f}{2} \ln\left(\frac{T_f}{T_i}\right) = -\ln\left(\frac{V_f}{V_i}\right)$$

$$\rightarrow \frac{f}{2} \ln\left(\frac{T_f}{T_i}\right) = \ln\left(\frac{V_i}{V_f}\right)$$

$$\rightarrow \left(\frac{T_f}{T_i}\right)^{\frac{f}{2}} = \frac{V_i}{V_f} \rightarrow V \propto \frac{1}{T^{f/2}}$$

$$\downarrow$$

$$V \propto T^{-f/2}$$

$$T_f^{f/2} \cdot V_f = T_i^{f/2} \cdot V_i \rightarrow V \cdot T^{f/2} = \text{constant of proportionality}$$

HW: 32, 33, 35