

Draft

- Temperature (mathematically)
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- Heat Capacity
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- Heat Capacity & Ideal Gas
 - Equilibrium theorem
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- Phases of Matter
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- 1st Law of Thermodynamics: $\Delta Q = \Delta U + \Delta W$
- Internal Energy $U(p, V, T)$ path-ind.
- Work $W = P \cdot \Delta V$ path:
- Thermodynamic Processes
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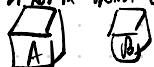
Thermodynamics

Temperature

Thermal eqm.

- A and B are always in thermal eqm
 - A and D are in thermal eqm \Rightarrow so are D and A
 - (3rd law of thermodynamics) A and B in thermal eqm; B and C in thermal eqm
 \Rightarrow A and C are in thermal eqm
- \Rightarrow equilibrium condition
 labelled by temperature T: measure of balance

If not in thermal eqm: excess flow from hot to cold object

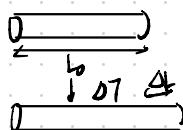


$$\frac{\text{heat/energy flow}}{T_A - T_B}$$

Temperature: Celsius Kelvin K
 SI Unit

Thermal Expansion

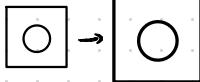
Low T High T



$$\frac{\Delta L}{L_0} = \alpha \Delta T$$

Fractional length change

α coefficient of linear expansion [K⁻¹]



$$\frac{\Delta V}{V_0} = \beta \Delta T$$

Fractional change in vol.

β coeff of vol. Δ

$$V_0 \rightarrow V_0 + \Delta V \\ L_0^3 \rightarrow (L_0 + \Delta L)^3 \approx L_0^3 + 3L_0^2 \Delta L \quad \beta = \frac{1}{V_0} \frac{\Delta V}{\Delta T} = \frac{1}{L_0^3} \frac{3L_0^2 \Delta L}{\Delta T} = 3\alpha$$

Heat Capacity

$$\Delta Q = C \Delta T$$

$$\frac{\Delta Q}{\Delta T} \text{ in heat } [Q] = L^2 M T^{-2} \text{ unit J}$$

$$C \text{ Heat capacity (of an object)} [C] = L^2 M T^{-1} \Omega^{-1} \text{ unit JK^{-1}}$$

Change in Temperature

$$\text{e.g. heat } C(T) = \alpha L^2 M T^2$$

$$dQ = C(T) dT$$

$$Q = \int C(T) dT$$

$$m \text{ mass of object}$$

$$f \text{ specific heat capacity (of a material)} [c] = L^2 T^{-1} \Omega^{-1}$$

$$dQ = m c dT$$

$$Q = m f c dT$$

Latent Heat

Phase changes from ice
solid, liquid, gas

$$\Delta Q = L \Delta m$$

$$L \text{ (latent heat)} [L] = L^2 T^{-1}$$

Heat Transfer

Conduction

$$(A) \xrightarrow{k} (B) \quad \dot{Q} = k A \frac{T_B - T_A}{L}$$

$$T_A \quad T_B$$

$$k \text{ thermal conductivity } [k] = ? \quad \text{W m^{-1} K^{-1}}$$

$$A \text{ cross-sectional area } [A] = L^2 \quad \text{m}^2$$

$$\frac{T_B - T_A}{L} \text{ temperature gradient } [\cdot] = \Theta L^{-1} \text{ K m^{-1}}$$

$$\begin{array}{c} \text{---} \\ k_1 A_1 L_1 \\ \parallel \\ k_2 A_2 L_2 \end{array}$$

$$\text{parallel} \quad \dot{Q} = \left(\frac{k_1 A_1}{L_1} + \frac{k_2 A_2}{L_2} \right) (T_B - T_A)$$

$$\text{series} \quad \begin{array}{c} \text{---} \\ k_1 A_1 L_1 \\ \parallel \\ k_2 A_2 L_2 \end{array} \quad \dot{Q} = \frac{k_1 A_1 (T_B - T_A)}{L_1} = \frac{k_2 A_2 (T_B - T_A)}{L_2}$$

Example: find T_A here \dot{Q}

Gauss's Law: heat equation

$$\frac{\partial T}{\partial x^2} = \alpha \frac{\partial T}{\partial t}$$

Conduction



$$Q = kA(T_1 - T_2)$$

expand: $\ln S/A$?

Radiation

$$\frac{1}{4\pi} \int_{4\pi} S \sigma T^4 d\Omega = \text{Stefan-Boltzmann Law } H = A \epsilon \sigma T^4$$

A surface area

ϵ emissivity

$$\sigma \text{ Stefan-Boltz law const} \approx 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$$

Example: find temperature of Earth



$$I \cdot \pi R_E^2 = 4\pi R_E^2 \sigma T_E^4$$

$$I = 0.7 \times 1370 \text{ W/m}^2 \text{ Solar intensity}$$

$$T_E \approx 255 \text{ K} = -18^\circ \text{C}$$

Greenhouse effect

$$\frac{P_A}{P_i} \quad P_A > P_i \quad P_A + P_i = 2P_i$$

$$T \sim P^2$$

$$T_E = 255 \cdot 2^2 = 303 \text{ K}$$

Equation of state

macroscopic \Rightarrow microscopic

$$P, V, T, n, N, \dots$$

$$f(p, V, T) = 0$$

e.g. ideal gas

gas particles are point masses (i.e. size=0)

no interacting Lennard-Jones

classical, relativistic, no collis.

$$PV = nRT$$

$$P \text{ Pressure } [P] = \text{L}^{-1} \text{ M}^{-2} \text{ Pa}$$

$$V \text{ Volume } [V] = \text{L}^3 \text{ m}^3$$

$$n \# \text{ atoms in gas } [n] = \text{mol} \quad N = nN_A, \quad N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \text{ Avogadro's constant}$$

$$R \text{ universal gas const } \approx 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T \text{ temperature } \text{K}$$

Two gas is ideal gas $\Rightarrow PV/n = kT$ or see

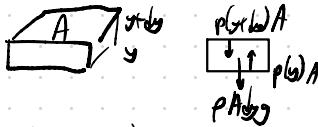
Consider a gas, $PV/T = nR$

$$M \text{ molar mass} \quad \text{kg mol}^{-1}$$

$$pV = \frac{m}{M} RT \Rightarrow p = \frac{f}{M} RT$$

Standard Temperature and Pressure $T=0^\circ\text{C}=273\text{ K}$, $p = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$

Example: Assume Temperature is constant, find $p(y)$, y is height from the ground. In terms of molar mass M , gravity g , universal gas constant R , temperature T



$$(p_0 + \rho g y) - p_0 = -\rho A dy g$$

$$\frac{dp}{dy} \cdot A = -\frac{\rho M}{R T} A dy g$$

$$\frac{dp}{dy} = -\frac{\rho M g}{R T}$$

$$\frac{dp}{y} = -\frac{M g}{R T} dy$$

$$\ln\left(\frac{p}{p_0}\right) = -\frac{M g}{R T} y$$

$$p = p_0 \exp\left(-\frac{M g y}{R T}\right)$$

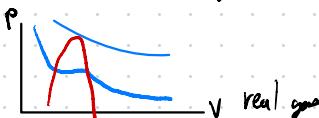
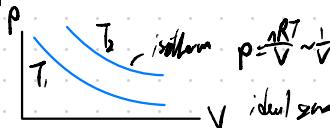
$$M = m_{\text{mol}}/n = N_m/n = m/N_A$$

$$R = N_A k_B$$

$$p = p_0 \exp\left(-\frac{m_{\text{mol}}}{k_B T}\right)$$

$$= p_0 \exp\left(-U/k_B T\right)$$

$p-V$ diagram



Kinetic Theory

$$K = \frac{1}{2} n R T = \frac{3}{2} M_k T = \sum_i \frac{1}{2} m_i v_i^2 = \frac{1}{2} N_m v_{\text{rms}}^2, v_{\text{rms}} = \sqrt{\frac{\sum_i v_i^2}{N}}$$

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

Equivalent Therm. $\propto K = \frac{3}{2} N k T$, $f = \text{degrees of freedom}$

$$\boxed{f=2} \quad \text{DOF}$$

Translation $\overset{\circ}{O} \rightarrow \overset{\circ}{O}$ d. Df
 Rotation $\overset{\circ}{O} \overset{\circ}{O}$ $k_B T \geq \hbar \omega_r$, $\omega_r = \hbar / I$
 Vibrat. $\overset{\circ}{O} \overset{\circ}{O}$ $2 \text{ Df } k_B T \geq \hbar \omega_v$, $\omega_v = \sqrt{k_B / \mu}$
 es rotation f=3 He, Ar
 diatomic f=5 $\text{N}_2, \text{O}_2, \dots$

Mean-free path

Assume particles have size a & spherical radius

$$\textcircled{1} \quad \frac{1}{2\pi a^2} \text{ collision rate} = \frac{\pi (2n)^2 v dt \cdot \frac{V}{dt}}{dt} = \frac{4\pi n^2 V}{d}$$

$$\text{Collision rate} = \text{actual collision rate} = \frac{4\pi n^2 v^2 N}{V}$$

$$\text{mean free path} = \frac{V}{4\pi n^2 N}, \text{ mean-free path} \lambda = \sqrt{\lambda_{\text{mean}}} = \frac{V}{4\pi n^2 N} = \frac{L}{4\pi n^2 N}$$

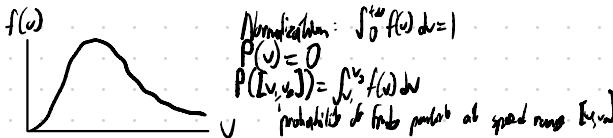
Heat capacity at constant volume

$$\text{constant volume} \quad dk = n(C_V) dT = dk = \frac{f}{2} R dT$$

molar heat capacity

$$C_V = \frac{f}{2} R \quad \text{molar heat capacity at const vol.}$$

Maxwell-Boltzmann Distribution



$$\text{Maxwell-Boltzmann distribution} \\ f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{1/2} v^2 e^{-mv^2/2kT}$$

Volume phase space

$$P(v) \sim \exp(-E/vT) dv = \exp(-mv^2/kT) dv$$

$$P(v) = 4\pi v^2 P(v) \\ = 4\pi v^2 \exp(-mv^2/kT) dv$$

$$\text{Exercise: find } \langle v \rangle = \int v P(v) dv = \int v \exp(-mv^2/kT) dv$$

$$\langle v \rangle = \frac{1}{2} \int v \exp(-\frac{mv^2}{kT}) dv$$

$$\text{Hence: } \int v^2 \exp(-\frac{mv^2}{kT}) dv = \int \frac{\pi}{\alpha} \frac{1}{4\pi} dv$$

$$\int v^2 e^{-\frac{mv^2}{kT}} dv = \sqrt{\frac{\pi}{\alpha}} \frac{1}{8\pi^2}$$

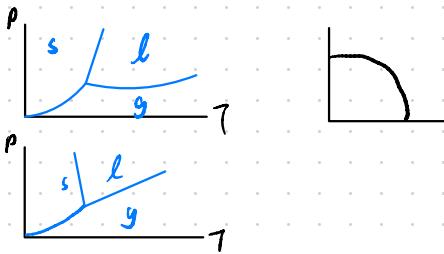
$$\begin{aligned} u &= v^2 \\ du &= 2v dv \\ u &= 1 \\ 0 &= \frac{1}{(mv^2/kT)} e^{-\frac{mv^2}{kT}} \\ 0 &= +(\frac{1}{m}) e^{-\frac{mv^2}{kT}} \end{aligned}$$

$$\langle v \rangle = 4\pi \left(\frac{m}{2kT}\right)^{\frac{1}{2}} \left(\frac{mkT}{m}\right)^2$$

$$\begin{aligned} \int_0^{\infty} v^2 f(v) dv &= 4\pi \left(\frac{m}{2kT}\right)^{\frac{1}{2}} \int_0^{\infty} v^4 e^{-\frac{mv^2}{2kT}} dv \quad w = \sqrt{\frac{m}{2kT}} v \\ &= 4\pi \left(\frac{m}{2kT}\right)^{\frac{1}{2}} \int_0^{\infty} \left(\frac{w^2}{m}\right)^2 v^4 e^{-w^2} \sqrt{\frac{m}{2kT}} dw \\ &= 4\pi \cdot \frac{2}{\pi^{\frac{1}{2}}} \cdot \frac{kT}{m} \int_0^{\infty} w^4 e^{-w^2} dw \\ &= \frac{8}{\pi kT} \frac{1}{m} \cdot \sqrt{\pi} \cdot 3! \\ &= \frac{3kT}{m} \end{aligned}$$

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

Phase of Matter



Implications: ice floats, icebergs

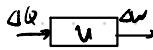
Clausius-Clapeyron Relation

$$\frac{dp}{dT} = \frac{1}{T \Delta V}, \quad V = V_f - V_i$$

Ideal Gas

1st Law of Thermodynamics: $dQ = dU + dW$

2nd Law (heat flow (>0 into, <0 out of))



3rd Law (ideal gases stick harder $\Delta U(pV, T)$)

4th Law (work done (>0 work due to the object))

$dQ = dU + dW$

$$dW = F \cdot dv = p \cdot dV$$

$$\begin{array}{c|c} \text{P} & T_2 \\ \hline T_1 & V \end{array} \quad \begin{array}{l} U = \frac{1}{2} n R T \\ \Delta W = \int_{V_1}^{V_2} p(V) dV \\ \Delta U = U + \Delta W \end{array}$$

$$\begin{aligned} &\text{In general suff. f. } p(V, T) ? \\ &W = \int p(V) dV = \int p(V) V'(V) dV \end{aligned}$$

Isobaric: p is constant

$$\begin{array}{c|c} \text{P} & V_2 \\ \hline V_1 & V_2 \end{array} \quad \begin{array}{l} \Delta W = \int_{V_1}^{V_2} p dV = p(V_2 - V_1) \\ \Delta U = \frac{1}{2} n R \Delta T = \frac{1}{2} p \Delta V = \frac{1}{2} p (V_2 - V_1) \\ \Delta U = \Delta H - \Delta W = \frac{1}{2} p (V_2 - V_1) \end{array}$$

Isochoric: V is const.

$$\begin{aligned} P & \downarrow \\ P_1 & \xrightarrow{\Delta V=0} P_2 \end{aligned}$$

$$\Delta U = \frac{f}{3} (P_2 - P_1) V = \Delta Q$$

Isothermal: T is const.

$$\begin{aligned} P & \downarrow \\ V & \uparrow \end{aligned}$$

$$\begin{aligned} \Delta W &= \int P dV \\ &= \int \frac{nRT}{V} dV \\ &= nRT \ln(V_2/V_1) = \Delta Q \end{aligned}$$

Free expansion

$$\begin{array}{|c|c|} \hline \text{out} & \text{in} \\ \hline P & ? \\ \hline \end{array}$$

$$\begin{aligned} \Delta W &= 0 \\ \Delta Q &= 0 \\ Q &= 0 \end{aligned}$$

Heat capacities & 2nd law

const! value / pressure

$$dU = nC_V dT$$

$$dQ_p = nC_p dT$$

$$dQ = dU + dW$$

$$nC_p dV = n(C_V dT + T dC_V)$$

$$\Rightarrow C_p = f + R$$

$$= \left(\frac{f+1}{2}\right)R$$

$$\text{adiabatic ratio } \gamma = (p/C_v)^{1/f}$$

Adiabatic process: $\Delta Q = 0$

$$dU = dQ = 0$$

$$d(Q_p V) + P_d V dQ = 0$$

$$\frac{f}{2} V dP + \frac{f}{2} P dV + P dV = 0$$

$$\frac{f}{2} P_d V_2 - \frac{f}{2} P_d V_1$$

$$\gamma \frac{P_2}{P_1} = \frac{V_1}{V_2}$$

$$\frac{P_2}{P_1} = \text{const.}$$

$$T_2 V_2^{\gamma-1} = \text{const.}$$

$$\frac{T_2}{T_1} = \text{const.}$$

$$\frac{P_2}{P_1} \sim \frac{T_2}{T_1}$$

$$\Delta U = \frac{f}{3} nR (T_2 - T_1)$$

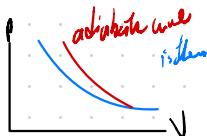
$$= \frac{f}{3} nR \left(\frac{P_2 V_2}{T_2} - \frac{P_1 V_1}{T_1} \right)$$

$$= (P_2 V_2 - P_1 V_1) / 2 f$$

$$= \frac{1}{f} (P_2 V_2 - P_1 V_1)$$

$$\Delta W = -\Delta U$$

$$= \frac{1}{f-1} (P_1 V_1 - P_2 V_2)$$



$$\begin{aligned} P_1 V_1^{\gamma} &= P_2 V_2^{\gamma} \\ P_1^{\frac{1}{\gamma}} &= V_2^{\frac{1}{\gamma}} \end{aligned}$$

$$T_2^{\frac{1}{\gamma-1}} = T_1$$

$$T_2 = T_1^{\frac{\gamma}{\gamma-1}}$$

$$P_2 = P_1 \cdot T_2^{\frac{1}{\gamma-1}}$$

$$= P_1 \cdot T_1^{\frac{1}{\gamma-1}}$$

$$= P_1 \cdot (P_1 V_1)^{\frac{1}{\gamma-1}}$$

$$= P_1^{\frac{\gamma}{\gamma-1}} V_1^{\frac{1}{\gamma-1}}$$

$$= P_1^{\frac{\gamma}{\gamma-1}} V_1^{\frac{1}{\gamma-1}}$$

Heat Engine

heat \rightarrow work

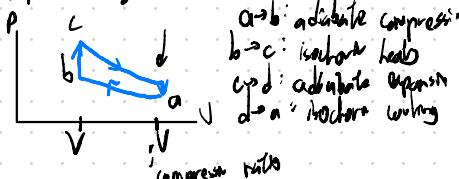
$$\int_{Q_{in}}^T \rightarrow W$$

Work

T_o

thermal efficiency $e = W/Q_{in}$

Example Otto cycle



Exercise: find thermal efficiency e in terms of r and other coeffs

$$a \rightarrow b: \Delta W = \frac{1}{r-1} (p_{atm}V_b - p_{atm}V_a)$$

$$pV^r = \text{const} \quad p_{atm} = p_{atm}^r \quad p_{atm}^r = p_b$$

$$\Delta W = \frac{1}{r-1} (p_{atm}V_b - p_{atm}V_a)$$

$$= \frac{r-1}{r} p_{atm} V$$

$$b \rightarrow c: \Delta Q = \frac{r}{r-1} R(T_c - T_b)$$

$$= \Delta Q_u$$

$$d \rightarrow a: Q_c = \Delta Q_u = \frac{r}{r-1} R(T_a - T_b)$$

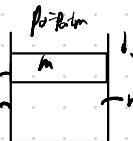
$$e = 1 - \frac{Q_c}{Q_{in}}$$

$$= 1 - \frac{Q_u + Q_c}{Q_{in}} \quad T_b^{r-1} = \text{const}$$

$$= 1 - \frac{T_b}{T_c - T_b}$$

$$= 1 - \frac{1}{r-1}$$

Exercise:



if v_0 is slightly displaced, find the period of oscillation
the state

$T = T_0$ of comp. $V = A_0 v_0$ of comp.

$$\text{Schalter} \quad p_{\text{ext}} = p_0 + mg/A$$

$$m\ddot{y} = (p - p_0)A - mg$$

adimension: $PV' = \text{const}$

$$\frac{dp}{p} + Y \frac{dy}{\sqrt{y}} = 0$$

$$dp/p + Y dy/y = 0$$

Assume shift dependent to y_0 (punkt)

$$dF = (dp)A$$

$$= -Y p \cdot \frac{dy}{y} A$$

$$= -Y \frac{p_0}{h_0} A \frac{dy}{y} \quad p_0 = \frac{nRT_0}{Ah_0}$$

$$= -Y \frac{nRT_0}{h_0} dy$$

$$k = Y \frac{nRT_0}{h_0}$$

$$T = 2\pi\sqrt{\frac{m}{k}} = 2\pi\sqrt{\frac{m h_0}{Y n R T_0}}$$