

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$S = k_B (\ln \Omega - \beta \frac{\partial \ln \Omega}{\partial \beta}) = k_B (\ln \Omega + \beta \langle E \rangle) \quad \langle E \rangle = -\frac{\partial \ln \Omega}{\partial \beta}$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2; \quad \langle U \rangle \langle V \rangle \text{ for } U \perp V.$$

$$Pr[\epsilon] = \frac{1}{\Omega(E)} \text{ if } E_\epsilon = E$$

$$\text{Mayer Reln. } C_p - C_v = R$$

Heat is thermal energy in transit:

Monatomic Ideal Gas (Eq. posth.)

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v; \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

$$U = \frac{3}{2} RT, \quad C_v = \frac{3}{2} R, \quad C_p = \frac{5}{2} R$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Thermal Contact:

$$E = E_a + E_b \rightarrow \Omega(E) = \Omega_a(E_a) \Omega_b(E_b) \quad \text{Isothermal } \Delta T = 0. \text{ For ideal gas } \rightarrow dU = 0 \Rightarrow dQ = PdV$$

Most probable maximizes $\Omega(E)$:

$$\frac{\partial}{\partial E_a} \ln(\Omega_a(E_a)) = \frac{\partial}{\partial E_b} \ln(\Omega_b(E_b))$$

$$Q_{iso, rev} = \int_1^2 P dV = RT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \frac{1}{k_B T} = \frac{\partial}{\partial E} \ln(\Omega(E))$$

$$\text{Heat} = RT \ln\left(\frac{V_2}{V_1}\right)$$

Sys in thermal contact w/ reservoir:

$$E_{tot} = E_{sys} + E_{res} \text{ const.}$$

$$Pr[E_s] \propto \Omega_R(E_{tot} - E_s) \quad \text{Exp:}$$

$$\ln(\Omega_R(E_{tot} - E_s)) \approx \ln(\Omega_R(E_{tot})) - \frac{E_s}{k_B T}$$

$$\Rightarrow \Omega_R(E_{tot} - E_s) \propto \exp(-\beta E_s)$$

$$Pr[\epsilon] = \frac{\exp(-\beta E_\epsilon)}{Z} \text{ for } Z = \sum \exp(-\beta E_\epsilon)$$

Boltzmann Distr.

$$E = \frac{1}{2} mv^2 = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2)$$

$$Pr[v_x, v_y, v_z] = A \exp(-a v_x^2) \exp(-a v_y^2) \exp(-a v_z^2)$$

$$g(v_x^2) = C \exp(-a v_x^2), \quad C = \int \frac{a}{\pi} = \sqrt{\frac{m}{2\pi k_B T}}$$

Moments of one component:

$$\langle v_x \rangle = 0 \text{ (odd integrand)} \quad \langle v_x^2 \rangle = \frac{k_B T}{m}$$

$$\langle |v_x| \rangle = 2 \int_0^\infty v_x g(v_x) dv_x = \sqrt{\frac{2k_B T}{\pi m}}$$

$$\text{By indep. } Pr[v_x, v_y, v_z] = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right)$$

Speed Distr:

$$f(v) dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{3/2} v^2 dv \exp(-mv^2/2k_B T)$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad \langle v^2 \rangle = \frac{3k_B T}{m}$$

$$\text{Most Probable Speed } v_{mp} = \sqrt{\frac{2k_B T}{m}}$$

$$\sqrt{2} \langle v \rangle < v_{rms} \Rightarrow \sqrt{2} < \sqrt{\frac{8}{\pi}} < \sqrt{3}$$

$$\text{Energy: } \Delta U = \Delta Q + \Delta W \equiv dU = dQ + dW$$

$$dW = -PdV, \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_p$$

Ideal Gas: PV = RT per mole

$$S = k_B \ln \Omega$$

$$S = -k_B \sum P_i \ln P_i$$

$$E = \sum_i a_i x_i^2 \quad a_i > 0 \quad \langle E \rangle = \frac{1}{2} k_B T$$

Equipartition of Energy: For f DoF $U = \frac{f}{2} N k_B T, C_v = \frac{f}{2} N k_B$

Diatomic: H, N, O, F, Cl, Br, I
Monatomic: He, Ne, Ar, Kr, Xe

Core Formulas:

$$\Delta S_{sys} = \frac{Q_{rev}}{T}$$

$$\text{Isobaric (const } p) \quad W = P \Delta V$$

$$\text{Isochoric (const } V) \quad W = 0, Q = \Delta U$$

$$\text{Isothermal (const } T) \quad \Delta U = 0, W = nRT \ln \frac{V_f}{V_i}$$

$$\text{Adiabatic } PV^\gamma = \text{const}, Q = 0, \Delta U = -W$$

$$COP_H = \frac{Q_H}{W} = \frac{T_H}{T_H - T_C} \quad COP_R = \frac{Q_C}{W} = \frac{T_C}{T_H - T_C}$$

$$Q_{in} - Q_{out} = W, \text{ in equil. } Q_{in} = Q_{out}$$

$$\Delta U = Q - W \quad (Q = \text{heat added to sys, } W = \text{work done by sys})$$

$$2 + 273.15 = 300 \text{ K, For fixed mass of gas}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$m_a c_a (T_i - T_f) = m_b c_b (T_i - T_f)$$

$$\Delta S_{ai} = m_a c_a \ln\left(\frac{T_f}{T_i}\right) \quad \Delta S_{ht} = \sum \Delta S_i$$

$$COP_H \times W = Q_{in}, \quad COP_R \times W = Q_{out}$$

$$Q \text{ steady state } Q_{in} = Q_{out}$$

$$W = \int P dV \quad \eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H}$$

$$\text{Adiabatic: } T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{Reversible: } \Delta S = 0$$

$$\text{General } \Delta U = Q - W$$

$$C_p > C_v \quad \text{Ideal Gas Exp. into Vacuum}$$

$$Q = 0, U = 0, \Delta U = 0, T \text{ same}$$

$$\Delta S > 0$$

TdS = dE + PdV

Time Dependent Schrödinger Egn.

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t) \Psi(x,t)$$

Linear PDE \Rightarrow Superposition applies

Born Interpretation

$$\Psi(x,t) \in \mathbb{C}$$

$$Pr[x,t] = |\Psi(x,t)|^2$$

$$Pr[x \in (a,b)] = \int_a^b |\Psi(x,t)|^2 dx$$

Normalization: Only L^2 finite allowed (not $\Psi=0$).

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

If normalized at $t=0$, stays normalized

Expectation Values

For operator \hat{Q} :

$$\langle Q \rangle = \int \Psi^*(x,t) \hat{Q} \Psi(x,t) dx$$

Position: $\hat{x} = x \quad \langle x \rangle = \int x |\Psi|^2 dx$

Momentum: $\hat{p} = -i\hbar \frac{d}{dx} \quad \langle p \rangle = \int \Psi^* (-i\hbar \frac{d}{dx}) \Psi dx$

Kinetic Energy: $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$

Observables

Every observable \Leftrightarrow Hermitian operator

$$\hat{Q} \phi = q \phi \text{ Hermitian} \Rightarrow q \in \mathbb{R}$$

Time Independent Schrödinger Egn.

Assume $V(x) = V(x,t)$

Separation of Variables gives

$$\Psi(x,t) = \Psi(x) T(t)$$

$$T(t) = e^{-iEt/\hbar}$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + V(x) \Psi = E \Psi$$

Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$

Stationary States:

$$\text{Form } \Psi_n(x,t) = \Psi_n(x) e^{-iE_n t/\hbar}$$

$\Rightarrow |\Psi_n|^2 = |\Psi_n|^2$. All exp. vals are const in time. Energy is exact.

$$R+T=1; \Psi \text{ cont.}$$

Ψ' cont. except for spot.

Superposition

$$\Psi(x,t) = \sum_n c_n \Psi_n(x) e^{-iE_n t/\hbar}$$

where $c_n = \int \Psi_n^*(x) \Psi(x,0) dx$

$$Pr[E_n] = |c_n|^2 \text{ s.t. } \sum_n |c_n|^2 = 1$$

$$\langle H \rangle = \sum_n |c_n|^2 E_n$$

Infinite Square Well (0 to a)

$$V(x) = \begin{cases} 0 & x \in (0,a) \\ \infty & \text{else} \end{cases}$$

$$\Psi(0) = \Psi(a) = 0$$

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad n \in \mathbb{Z}_{>0}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad n-1 \text{ nodes inside well}$$

Harmonic Oscillator

$$V(x) = \frac{1}{2} m \omega^2 x^2$$

$$E_n = \hbar \omega (n + \frac{1}{2}), \quad n = \mathbb{Z}_{\geq 0}$$

$$\hat{a} = \frac{1}{\sqrt{2\hbar m \omega}} (m\omega x + i\hat{p})$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar m \omega}} (m\omega x - i\hat{p})$$

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$$

Uncertainty Principle

$$\sigma_A \sigma_B \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|$$

$$\Rightarrow \sigma_x \sigma_p \geq \frac{\hbar}{2}$$

Delta Function Barrier

$$V(x) = a \delta(x-a) \quad |a| \leq \sqrt{\frac{2mE}{\hbar^2}}$$

$$\Psi \text{ cont.} \Rightarrow \Psi(a^+) = \Psi(a^-) = \frac{2ma}{\hbar^2} \Psi(a)$$

$$T_r = \frac{1}{1 + \left(\frac{ma}{\hbar^2 k}\right)^2} \quad R_r = \frac{\left(\frac{ma}{\hbar^2 k}\right)^2}{1 + \left(\frac{ma}{\hbar^2 k}\right)^2}$$

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < a \\ Fe^{ikx}, & x > a \text{ (incidence)} \end{cases}$$

$$\Psi(a^+) = \Psi(a^-), \quad R_r = \frac{|B|^2}{|A|^2}, \quad T_r = \frac{|F|^2}{|A|^2}$$

Finite Sq. Well

$$V(x) = \begin{cases} -V_0 & |x| < a \\ 0 & |x| > a \end{cases} \quad k = \sqrt{\frac{2mE}{\hbar^2}}, \quad k_2 = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < -a \\ Ce^{ik_2 x} + De^{-ik_2 x} & -a < x < a \\ Fe^{ikx} & x > a \end{cases}$$

$$\Psi \text{ cont. @ } x = \pm a, \quad \Psi' \text{ cont. @ } x = \pm a$$

$$R_r = \frac{|B|^2}{|A|^2}, \quad T_r = \frac{|F|^2}{|A|^2}$$

$$E^2 = (pc)^2 + (mc^2)^2$$

Math

$$\ln n! \approx n \ln n - n$$

$$\left(\frac{\partial x}{\partial y}\right) \left(\frac{\partial y}{\partial z}\right) \left(\frac{\partial z}{\partial x}\right) = -1$$

$$\left(\frac{\partial x}{\partial y}\right) = \left[\left(\frac{\partial y}{\partial x}\right)^{-1}\right] \left(\frac{\partial x}{\partial z}\right) = \left(\frac{\partial x}{\partial y}\right) \left(\frac{\partial y}{\partial z}\right)$$

$$\sinh x = \frac{e^x - e^{-x}}{2} \quad \cosh x = \frac{e^x + e^{-x}}{2}$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad (1+x)^n \approx 1 + nx \text{ for } |x| \ll 1$$

$$S_n = a \frac{1-x^{n+1}}{1-x} \text{ for a finite geo sum; } S_\infty = \frac{a}{1-x}$$

$$\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \int_0^L \cos^2\left(\frac{n\pi x}{L}\right) dx = \frac{L}{2} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L}{2} - \frac{L}{4n\pi} \sin\left(\frac{2n\pi x}{L}\right) \Big|_0^L = \frac{L}{2}$$

$$\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L^2}{4} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L^2}{4} - \frac{L^2}{4n\pi} \sin\left(\frac{2n\pi x}{L}\right) \Big|_0^L = \frac{L^2}{4}$$

$$\int_0^\infty e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad \text{also } \int_0^\infty e^{-2kx} dx = \frac{1}{2k}$$

$$\text{Wavelength Stuff } \lambda = \frac{h}{ap} \quad p = \sqrt{2mk} \quad \hbar = \frac{h}{2\pi}$$

$$\text{Bragg Condition } 2d \sin \theta = n\lambda \quad \text{spacing b/w crystal planes}$$

$$\text{Photoelectric Effect } E_f = hf = \frac{hc}{\lambda} \quad hf = \phi + K_{\max}$$

At threshold, $\phi = hf_0 = \frac{hc}{\lambda_0}$ workfn of e^-

$$K_{\max} = hf - \phi = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) \quad eV_s = K_{\max} \quad \lambda > \lambda_0 \Rightarrow \text{no}$$

$$p = \hbar k, \quad E = \frac{\hbar^2 k^2}{2m} \quad \text{Photons } E = hf = \hbar \omega$$

$$v_{\text{phase}} = \frac{\omega}{k} \quad v_{\text{grp}} = \frac{d\omega}{dk} \quad v_{\text{phase}} = \frac{v_{\text{grp}}}{2} \text{ for free particle}$$

individual wave crests physical velocity

Rectangular Barrier

$$V(x) = \begin{cases} V_0 & 0 < x < a \\ 0 & \text{else} \end{cases} \quad k \geq \sqrt{\frac{2mE}{\hbar^2}}$$

$$\Psi_I = Ae^{ikx} + Be^{-ikx} \quad \Psi_{III} = Fe^{ikx} \quad \text{if } E > V_0: \quad T = \frac{2k(E-V_0)}{k^2 + 2k(E-V_0)}$$

$$\Psi_{II} = Ce^{ik_2 x} + De^{-ik_2 x} \quad \text{if } E < V_0: \quad K = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$$

$$\Psi_{II} = Ce^{Kx} + De^{-Kx}$$

Qualitative stuff: oscillatory \Leftrightarrow classically allowed

exponential \Leftrightarrow classically forbidden

Node: $\Psi=0$. nth bound state = n-1 nodes, more nodes \Rightarrow more E

Bound: $E < V$ scattering: $E > V$

For perfect transmission $E > V$, $qL = n\pi \quad q = \sqrt{\frac{2m(E-V)}{\hbar^2}}$

$$\text{Transmission } E > V_0 \quad T = \left(1 + \frac{V_0^2}{4E(E-V_0)} \sin^2(qL)\right)^{-1}$$

$$E < V_0 \quad T = \left(1 + \frac{V_0^2}{4E(V_0-E)} \sinh^2(KL)\right)^{-1}$$