Equations of Physics 224 – Thermal Physics

You should know or be able to derive without guidance the highlighted equations.

Ideal gas: $pV = NkT = nRT$ Internal energy $U = Nf\frac{kT}{2}$ $U(p,V,N,T\ldots)$ = function of state

1st Law: $\Delta U = Q + W$: Q and W are *not* functions of state, but path dependent

Compressibility $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\left(\frac{\partial \ln V}{\partial p}\right)_T$ Equipartition $\langle E(1\text{ d.o.f.})\rangle = \frac{1}{2}kT$ so: $\langle\frac{1}{2}mv^2\rangle = \frac{3}{2}kT$

For compression, $W = -\int p dV$ Adiabatic: $\Delta Q = 0$ For ideal gas: pV^γ = const $\gamma = 1 + \frac{2}{f}$

$c_v = \frac{Q}{n\Delta T}\Big|_V = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_V$ $c_p = \frac{Q}{n\Delta T}\Big|_p = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_p + \frac{p}{n}\left(\frac{\partial V}{\partial T}\right)_p$ For ideal gas: $c_v = \frac{fR}{2}$ $c_p = c_v + R = \gamma c_v$

$L = \frac{Q}{m}\Big|_p$ $H = U + pV$ $c_p = \frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_p$ For reaction with p and T unchanged, $\Delta H = Q + W_{other}$

Fourier: $\mathbf{J} = -k_t\nabla T$ (in 1D, $J = -k_t\frac{dT}{dx}$) Cons. of energy: $\nabla.\mathbf{J} = w - C\frac{\partial T}{\partial t}$ (in 1D $\frac{\partial J}{\partial x} = w - C\frac{\partial T}{\partial t}$)

Heat equation: $\nabla^2 T = \frac{C}{k_t}\frac{\partial T}{\partial t}$ (in 1D $\frac{\partial^2 T}{\partial x^2} = \frac{C}{k_t}\frac{\partial T}{\partial t}$) Relaxation time $\tau = \frac{C}{k_t}L^2$ Ideal gas: $k_t = \frac{1}{2}Cl\bar{v}$

Probability distribution for scattering: $p(x) = \frac{1}{l}e^{-\frac{x}{l}} = -\frac{dP}{dx}$ $\langle x\rangle = l$ Mean free path $l = \frac{V}{\sqrt{2}N\sigma}$

Fick: $\mathbf{J}_\mathrm{p} = -D\nabla n$ $\nabla.\mathbf{J}_\mathrm{p} = \frac{\partial n}{\partial t}$ (or $J_p = -D\frac{dn}{dx}$) Diffusion equation $D\nabla^2 n = \frac{\partial n}{\partial T}$ $\tau = \frac{L^2}{D}$ L = system size

Two-state paramagnet: $E = q\Delta$ Multiplicity $\Omega(q) = \binom{N}{q} = \frac{N!}{q!(N-q)!}$ Probability $p(q) = \frac{\Omega(q)}{2^N}$

Einstein solid: $E = q\hbar\omega$ $q = \sum_{i=1}^N n_i$ $\Omega(q) = \binom{N+q-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \approx \left(\frac{eq}{N}\right)^N$ for $q \gg N \gg 1$

[Width of peak in $\Omega(q)$] / [range of possible values of q] $\approx 1/\sqrt{N}$ Systems A and B in contact: $\Omega = \Omega_A\Omega_B$

2nd Law: Entropy never decreases. All microstates equally probably in equilibrium. $S = k\ln\Omega \approx k\ln\Omega_{\max}$

Ideal gas: $\Omega(N,V,U) = \frac{1}{\mathrm{N}!}\frac{\mathrm{V^N}}{\mathrm{h^{3N}}}\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}(2\mathrm{mU})^{\frac{3N}{2}} = \mathrm{f(N)V^N U^{\frac{3N}{2}}}$ $S = Nk\left[\ln\left\{\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right]$

Free expansion of ideal gas: $\Delta S = Nk\ln\frac{V_f}{V_i}$ $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$ $p = T\left(\frac{\partial S}{\partial V}\right)_{U,N}$ $\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

$dU = TdS - pdV + \mu dN$ and so $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$ $\mu = p\left(\frac{\partial V}{\partial N}\right)_{U,S}$ $p = -\left(\frac{\partial U}{\partial V}\right)_{N,S}$

Quasistatic process: $TdS = Q$ $-p\,dV = W$ $S_2 - S_1 = \int_1^2\frac{CdT}{T}$ 3rd Law: Heat capacities vanish as $T\to 0$.

Heat engine: $\Delta S = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} \geq 0$ $\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$ efficiency $e \equiv \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h}$

Refrigerator: $\Delta S = \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \geq 0$ $\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$ $\mathrm{COP} \equiv \frac{Q_c}{W} = \left(\frac{Q_h}{Q_c} - 1\right)^{-1} \leq \left(\frac{T_h}{T_c} - 1\right)^{-1}$

Throttling: $\Delta H = 0$, cools if $\left(\frac{\partial T}{\partial p}\right)_H = 0$ $F = U - TS$ $dF = SdT - pdV + \mu dN$ $G = U - TS + pV$

$W_{other} \geq \Delta G$ $W_{useful} \leq -\Delta G$ $V_{cell} = -\frac{\Delta G\text{ per electron}}{e}$ efficiency $\frac{\mathrm{W_{useful}}}{\mathrm{Q}} \leq \frac{\Delta\mathrm{G}}{\Delta\mathrm{H}}$

$dG = -SdT + Vdp + \mu dN$ $S = -\left(\frac{\partial G}{\partial T}\right)_{p,N}$ $V = \left(\frac{\partial G}{\partial p}\right)_{T,N}$ $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$ $G = N\mu$

Spontaneous process at constant p, T: $\Delta G \leq 0$ ie $\Delta(S_{system} + S_{reservoir}) \geq 0$

Maxwell relations: $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

In phase equilibrium $G_A = G_B$ Clausius Clapeyron: $\left(\frac{\partial p}{\partial T}\right)_{phase\ boundary} = \frac{\mathrm{S_A - S_B}}{\mathrm{V_A - V_B}} = \frac{L}{T\Delta V}$

Boltzmann: $P(s) = \frac{1}{Z}e^{-\frac{E(s)}{kT}}$ Partition function $Z = \sum_s e^{-\frac{E(s)}{kT}}$ Continuous case: $Z = C\int e^{-E(s)/kT}ds$

$U = -\frac{\partial}{\partial\beta}(\ln Z)$ $\beta = 1/kT$ $F = -kT\ln Z$