Cycles

Carnot Engine

1) Isothermal compression at $T_c = T_1 = T_2$
2) Adiabatic compression
3) Isothermal expansion at $T_H = T_3 = T_4$
4) Adiabatic expansion

$$\eta_{carnot} = 1 - \frac{T_C}{T_H}$$

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

Otto Cycle: $\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{T_1}{T_2}$

Heat Engine Efficiency:

$$\eta^{rev}{}_{engine} = \frac{W_e}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{what\ you\ get}{what\ you\ pay}$$

η is always less than 1.

Pump Efficiency: $\eta^{rev}{}_{pump} = \frac{Q_H}{W} = \frac{1}{n^{rev}{}_{engine}}$

This is greater than 1 by definition

Refrigerator Efficiency:

$$\eta^{rev}{}_{fridge} = \frac{Q_C}{W_e} = \frac{Q_C}{Q_H - Q_C} = \frac{what\ you\ pay}{what\ you\ get}$$

This is usually greater than 1.

Expansions

Adiabatic:

$$PV^{\gamma} = const$$
$$TV^{\gamma-1} = const$$
$$T^{\gamma}P^{(1-\gamma)} = const$$

Isothermal

Constant temperature:

$$W = -nrT\int_{V_1}^{V_2} \frac{dV}{V}$$

$$PV = const$$

Isothermal Compressability: $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Energies

Energy: $\langle E\rangle = \frac{\partial}{\partial\beta}\left(\frac{F}{k_B T}\right) = -\left(\frac{\partial \ln Z}{\partial\beta}\right)_{V,N}$

Internal Energy per molecule/particle:

$$U = \frac{n}{2}kT = \langle E_{kin}\rangle$$

Helmholtz Free Energy:

$$F = E - TS$$
$$dF = -SdT - PdV + \mu dN$$
$$\langle F\rangle = -k_B T\ln Z$$

Gibbs Free Energy:

Specific Gibbs Free Energy when $g = \frac{G}{m}$, where m is the mass:

$$G = E - TS + PV$$
$$dG = -SdT + VdP + \mu dN$$

Chemical Potential

Can be seen as the Gibbs Free Energy per molecule:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{P,T} = g$$

Enthalpy:

$$H = E + PV$$
$$dH = dU + PdV + VdP$$
$$= dQ + VdP$$
$$= TdS + VdP$$
$$H(T) = H(T_0) + \int_{T_0}^{T} C_p(T)\,dT$$

Entropy

If not isothermal, consider the start and end states to obtain ΔS

$$\Delta S = \int \frac{dQ}{T} = \int \frac{ncdT}{T}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$S = k_B \ln\Omega$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}$$

Sackur-Tetrode Equation

$$S = Nx_B\left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T\,\frac{3}{2}\ln\left(\frac{Mk_B}{2\pi\hbar^2}\right) + \frac{5}{2}\right]$$

Heat Capacities

C is the overall capacity, while c is the specific heat capacity, and is per mole or kg

$$c = \frac{đQ^{rev}}{dT}$$

$$c_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$c_v = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{n}{2}R \approx \frac{1}{T^2}$$

$$c_p - c_v = nR = VT\frac{\alpha^2}{\kappa_T} > 0$$

$$\frac{c_p}{c_v} = \gamma = \frac{5}{3}(monatomic) = \frac{7}{3}(diatomic)$$

Low-temperature specific heat:

$$c = \gamma T + \varepsilon T^{3/2} + \beta T^3$$

Terms from: electron gas, disturbances in magnetic order, and Debye model

Availability

$$A = (E - T_o S + P_o V) \le 0$$

This is maximized in equilibrium

Maxwell Relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

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

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P$$

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

Gases

Clausius-Clapeyron Equation

L is the Latent heat

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

$$\frac{dp}{dT} = \frac{S_L - S_S}{V_L - V_S}$$

Conduction: $\kappa = \frac{1}{3} n_d c_v \bar{v}\lambda$

Density of State: $D(k) = \frac{Vk^2}{2\pi^2}$

Effusion: $\left(\frac{n_1}{n_2}\right)_{after} = \left(\frac{n_1}{n_2}\right)_{before} \underbrace{\sqrt{\frac{m_2}{m_1}}}_{\text{Enrichment Factor}}$

Gibb's Phase Law: $F = C - P + 2$

$F =$ # of degrees of freedom

$C =$ # of components

$P =$ # of phases

Heat flow: $\underline{j} = -k\underline{\nabla}T$

Diffusion equation: $\nabla^2 T = \frac{1}{D}\frac{\partial T}{\partial t}$

Thermal diffusivity: $D = \frac{k}{C_p}$

$$D = \frac{1}{2}\bar{v}\lambda$$

Ideal Gas Law: $PV = nRT = Nk_BT$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$$

$Z = \frac{PV_m}{RT} = 1$ for ideal gas

Ideal Gas Pressure: $P = \frac{1}{3}mn_d\overline{v^2} = \frac{1}{3}\rho\overline{v^2}$

Isobaric Thermal Expansivity: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Mean Free Path: $\lambda = \frac{1}{\sqrt{2}n_d\pi d^2}$

Quantum Concentration

λ_T is the de Broglie wavelength for a particle with thermal energy k_BT and mass m

$$n_Q = \frac{1}{\lambda_T{}^3}$$

$$\lambda_T = \frac{h}{\sqrt{2\pi M k_B T}}$$

Speed (Mean): $v_{mean} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$

Speed (Most probable):

$$v_{probable} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

Speed (RMS): $v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$

Van der Waal's Law:

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

Lenard-Jones Potential (for Van der Waal's solids):

$$U(r) = 4\varepsilon\left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^6\right]$$

Viscosity: $\nu = \frac{1}{3}n_d m\bar{v}\lambda$

Work: $W = \int \underline{F}\cdot\underline{dx} = \int pdV$

Thermal (volume) expansion coefficient:

$$\alpha \equiv \left(\frac{dV}{dT}\right)_p \frac{1}{V}\left[k^{-1}\right]$$

Compressibility:

$$X \equiv -\left(\frac{dV}{dp}\right)_T \frac{1}{V}\ \left[Pa^{-1}, bar^{-1}\right] = \frac{1}{B}$$

($B =$ bulk modulus)

Tension coefficient: $\beta \equiv \left(\frac{dP}{dT}\right)_V \frac{1}{P}$

Fluids

Bernoulli's Equation (conservation of flow along a pipe):

$$p_1 + \rho g h_1 + \frac{1}{2}\rho {v_1}^2 = p_2 + \rho g h_2 + \frac{1}{2}\rho {v_2}^2$$

Poiseuille's equation (flow of fluid in a pipe):

$$\frac{dV}{dt} = \frac{\pi}{8}\left(\frac{R^4}{\eta}\right)\left(\frac{P_a - P_b}{L}\right)$$

Stoke's Law (laminar flow):

$= 6\pi\eta r v$

Solids

Typical equation of state for a solid:

$$V = V_0\left(1 + \beta(T - T_0) - \kappa(P - P_0)\right)$$

Solid State Physics

Number of states:

$$g(\varepsilon)d\varepsilon = \rho(k)dk$$

$$g(\varepsilon) = \rho(k)\frac{dk}{d\varepsilon}$$

2D: $\rho(k) = \frac{Ak}{2\pi^2}$

3D: $\rho(k) = \frac{Vk^2}{2\pi^2}$

$$k_B T = \frac{\hbar^2\pi^2}{2ML^2}\left(\ell^2 + m^2 + n^2\right)$$

Single Particle Partition Function:

$$\zeta = \sum_{\substack{all\ k\\ states}} e^{-\frac{\varepsilon(k)}{k_B T}}$$

Grand Single-state partition function:

$$\zeta_G = 1 + e^{\beta(\mu - \varepsilon)} = \sum_{N_s = 0}^{\infty} e^{N_s \beta(\mu - \varepsilon)}$$

N particle partition function:

$$Z = \sum_{\substack{all\\ microstates}} e^{-\frac{E}{k_B T}} = \frac{\zeta^N}{N!}$$

Grand Canonical Partition Function

$$Z_G = \sum_{N_s, S} e^{\beta(\mu N_s - E_s)} = \prod_{\substack{all\ single\\ particle\ states}} \zeta_G$$

$$E = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon$$

$$N = \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon$$

Energy:

Particles: $\varepsilon = \frac{k^2\hbar^2}{2M}$

Photons: $E = pc = \hbar c k$

Bosons:

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu}{k_B T}} - 1}$$

Fermions:

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu}{k_B T}} + 1}$$

Number of particles (fixed):

$$N = \sum_{\substack{all\\ states}} \frac{1}{e^{\beta(\varepsilon - \mu)} \pm 1}$$

Fermi wavenumber (etc):

$$k_f = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

$$\varepsilon_f = \frac{1}{2} M {v_f}^2$$

$$p_f = \hbar k_f$$

$$\lambda_f = \frac{2\pi}{k_f}$$

$$T_f = \frac{\varepsilon_f}{k_B}$$

$$E = \left(n + \frac{1}{2}\right)\hbar\omega$$

Mean number of excited quanta:

$$\bar{n} = \frac{1}{e^{\beta\hbar v} - 1}$$

Debye frequency

$$\omega_D = \left(\frac{6N}{V}\pi^2\right)^{1/3} \bar{v}$$

$$\lambda_D = \frac{2\pi}{k_D} = \frac{2\pi}{\omega_D}\bar{v}$$

Laws of Thermodynamics

Zeroth Law:

If two systems are separately in equilibrium with a third system, then they must be in thermal equilibrium with each other.

First Law

$$\Delta E = Q + W$$

$$dE = đQ + đW$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

Q is heat added to the system.

W is work done on the system.

Asides:

Joule's Law: $dQ = cdT$

Work Done: $dW_{rev} = -PdV$

Stretched string: $dW = \Gamma dl$ $\Gamma =$ tension in string

Stretched surface: $dW = \gamma dA$ where $\gamma =$ surface tension

$$dE = TdS - PdV + \mu dN$$

Second Law:

"It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work." (Kelvin-Planck)

"It is impossible to construct a refrigerator which, operating in a cycle, will produce no other effect than the transfer of heat from a cooler body to a hotter one." (Clausius)

$$\oint \frac{đQ}{T} \geq 0$$

Third Law

Absolute Zero, $T = 0$, is unobtainable.

Para-Magnets

Energy: $dE = TdS - VMdB$

Work Done

$$dW_{rev} = -\mu_o V \underline{M} \cdot \underline{dB} = -V \underline{M} \cdot \underline{dH}$$

V is Volume

M is Magnetic Moment per unit volume

Radiation

Planck Distribution: $\overline{E} = \frac{hc}{\lambda}\left[e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right]^{-1}$

Planck Distribution Function:

$$I(\lambda)d\lambda = \frac{2\pi hc^2}{\lambda^5\left[e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right]} d\lambda$$

Stefan's Law:

$$I = \sigma T^4$$

$$\frac{dQ}{dt} = Ae\sigma T^4$$

Wein's Law: $\lambda_m T = 2.9x10^{-3} k \cdot m$

Statistics

Macrostates

This is the bulk motion of the system, i.e. an overall view. Calculated by averaging over all microstates, e.g.

$\langle x \rangle = \sum_i p_i X_i = \frac{1}{\Omega}\sum_i X_i$, for an isolated system.

Equilibrium is when the macrostate has the maximum possible number microstates.

Microstates

This is a description of the system at a microscopic level, where the position and momentum (or quantum state) of each particle is specified. Total number $\Omega = {}^nC_r$.

Average: $\langle Q \rangle = \frac{\int_{-\infty}^{\infty} Qf(Q)dQ}{\int_{-\infty}^{\infty} f(Q)dQ}$

Binomial:

$$P\left(r/n; p\right) = {}^nC_r p^r (1-p)^{(n-r)}$$

$$= \frac{n!}{r!(n-r)!} p^r (1-p)^{(n-r)}$$

Boltzmann Distribution: $P(E)dE = Ae^{-\frac{E}{kT}} dE$

Gaussian Distribution:

Generally: $p(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\left(\frac{(x-\bar{x})^2}{2\sigma^2}\right)}$

For gases:

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}}$$

$$= \frac{4}{\sqrt{\pi}}\left(\frac{M}{2RT}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

Gibbs Distribution

$$P_i = \frac{e^{-(\varepsilon_i - \mu N_i)\beta}}{\mathbb{Z}}$$

This is the same as the Boltzmann distribution, except it includes the number of particles.

Grand Potential:

$$\Phi_G = F - \mu N = -kT \ln \mathbb{Z} = -PV$$

Mean:

$$\bar{x} = \frac{1}{N}\sum x_i = \int_{-\infty}^{\infty} xP(x)\,dx$$

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2 P(x)\,dx$$

Normalisation: $\int_{-\infty}^{\infty} P(x)\,dx = 1$

Partition Function

$g(\varepsilon)$ is the degeneracy of that energy

$Z_{N,dist}$ is the total partition function for distinguishable particles, while $Z_{N,indist}$ is for indistinguishable particles.

$$Z = \sum_{\varepsilon} g(\varepsilon) e^{-\varepsilon\beta}$$

$$Z_1 = Vn_Q$$

$$Z_{N,dist} = (Z_1)^N$$

$$Z_{N,indist} = \frac{(Z_1)^N}{N!}$$

Grand Partition Function:

$$\mathbb{Z} = \sum_i e^{-(\varepsilon_i - \mu N)\beta}$$

Poisson Distribution: $p(r;\lambda) = \dfrac{\lambda^r e^{-\lambda}}{r!}$

Scale Height: $\dfrac{\rho(z+z_o)}{\rho(z)} = e^{-1}$

Standard Deviation: $\sigma^2 = \overline{x^2} - \bar{x}^2$

Sterling's Approximation: $\ln N! = N \ln N - N$

Temperatures

Centigrade System:

$$T_{centigrade} = \lim_{p \to 0} \frac{PV}{(PV)_{triple\ point}} \times 273.16k$$