Exchanged Quantity	Type of equilibrium
energy	thermal
volume	mechanical
particles	diffusive

Fundamental Stuff

Stirling

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \quad \ln N! \approx N \ln N - N + \frac{1}{2} \ln(2\pi N) \tag{1}$$

Three laws

- $\Delta U = Q - W$

- $\Delta S \geq 0$

- Entropy of a perfect crystal of any pure substance approaches zero as the temperature approaches absolute zero

Glossary

- Isobaric - Constant Pressure

- Isochoric/isovolumetric - Constant volume

- Isothermal - Constant temperature

- Adiabatic - No heat transfer

- Isentropic - Constant entropy

- Isenthalpic - Constant enthalpy

- Quasistatic - System is always in internal equilibrium

1 Energy in Thermal Physics

1.1 Thermal Equilibrium

1.2 Ideal Gas

To derive velocity:

$$\overline{P} = \frac{\overline{F}_{x,on\ piston}}{A} = -\frac{m\left(\overline{\frac{\Delta v_x}{\Delta t}}\right)}{A} \tag{2}$$

Use $\Delta t = 2L/v_x$ and $\Delta v_x = -2v_x$ to get $\overline{P} = m\overline{v_x^2}/V$. Then, using that $PV = NkT$, $1/2m\overline{v_x^2} = 1/2kT$, so that $\overline{E}_k = 3/2kT$. Introduce $v_{\rm rms} = \sqrt{\overline{v^2}}$.

1.3 Equipartition of Energy

At temperature T the average energy of any quadratic degree of freedom is $1/2kT$. $U_{\rm thermal} = Nf/2kT$.

1.4 Heat and Work

$$\Delta U = Q + W \tag{3}$$

Heat is spontaneous flow of energy from one object to another caused by a difference in temperature bewteen the objects. Work is every energy flow that is *not* heat.

1.5 Compression Work

$dW = -PdV$ if compression quasistatically (pressure always well-defined). Then:

$$W = -\int_{V_i}^{V_f} P(V)\ dV \tag{4}$$

Isothermal Compression - Slow that the temperature of the gase does not rise at all. For ideal gas, this implies $\Delta U = 0$.
Adiabatic compression - So fast that no heat escapes from the gas

$$W = NkT \ln \frac{V_i}{V_f} \quad \text{(isothermal)} \tag{5}$$

For adiabatic: use $dU = f/2NkdT$ and $dW = -pdV$. Get differential equation, giving:

$$VT^{f/2} = \text{constant} = V^{(f+2)/f}P = V^\gamma P \quad \text{(adiabatic)} \tag{6}$$

1.6 Heat Capacities

Heat capacity: $C = Q/\Delta T$. Specific heat capacity: $c = C/m$. Ambiguous definition, so define:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_T \tag{7}$$

Usually $C_P > C_V$, as things tend to expand when heated. For ideal gas $C_V = Nfk/2$, $C_P = C_V + Nk = C_V + nR$.

Latent heat: Q/m (ambiguous, other work could be done).

1.7 Rates of processes

Heat condution:

$$\frac{Q}{\Delta t} = -k_t A \frac{dT}{dx} \quad \text{(Fourier's law)} \tag{8}$$

Where k_t is the thermal conductivity, Δt is the time that passes while we look. This is energy transport
Conductivity of an ideal gas:
Mean free path, l: volume of cylinder traced out by molecule equals the average volume per molecule. Collision occurs if molecule is within $2r$ of another molecule (pretend molecule has radius $2r$ all others are points:

$$\pi(2r)^2 l \approx \frac{V}{N} \implies l \approx \frac{1}{4\pi r^2}\frac{V}{N} \tag{9}$$

Note that $V/N = kT/P$ for an ideal gas. Average time between collisions: $l/\overline{v}$. Now assume two boxes, length l and thermal energy U_1 and U_2. Half the molecules will cross from one box to the other (those with positive x-velocity), giving the net heat flow:

$$Q = \frac{1}{2}(U_1 - U_2) = -\frac{1}{2}C_V(T_2 - T_1) = -\frac{1}{2}C_V l \frac{dT}{dx} \tag{10}$$

So that $k_t = (1/2)(C_V/V)l\overline{v}$. For an ideal gas (use $C_V = Nkf/2$), $C_V/V = fP/(2T)$. If f constant then, as $l \propto V/N$, k_t goes as $\sqrt{T}$ (from $\overline{v}$).
Viscosity
Viscosity: different layers of a fluid give up momentum. This is momentum transfer. Assume two parallell surfaces with area A, separated by Δz with laminar flow between them, with velocity u, then:

$$F_x \propto \frac{A(u_{\text{x,top}} - u_{\text{x,bottom}})}{\Delta z} \implies \frac{|F_x|}{A} = \eta \frac{du_x}{dz} \tag{11}$$

For ideal gas: viscosity if independent of pressure and increases with temperature. Horizontal momentum trasfers depends on momentum density, mean free path and average thermal speed. First two factors cancel (cf. last paragraph), so depends on $\sqrt{T}$. In real fluids: lower temperature means molecules can latch onto each other - viscosity increases as temperature decreases.
Diffusion
Particle transport. Depends on concentration of particles, $n = N/V$. Get:

$$J_x = -D\frac{dn}{dx} \quad \text{(Fick's Law)} \tag{12}$$

Where J is the flux of particles (number per unit area per unit time). D generally increases with temperature.

2 The second law

2.1 Two-state systems

$$\Omega(N, n) = \frac{N!}{n! \cdot (N-n)!} = \binom{N}{n} \quad \Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{13}$$

2.2 Einstein Crystals

$$\Omega(N, q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \approx \left(\frac{eq}{N}\right)^N \leftarrow \text{when q >> N} \approx \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q(q+N)/N}} \leftarrow \text{when q, N large} \tag{14}$$

$$S = k\ln(eq/N)^N = Nk[\ln(q/N) + 1] = Nk\ln U - Nk\ln(\epsilon N) + Nk \tag{15}$$

Assuming that $U = \epsilon q$. Differentiate S to find $U = NkT$. Gives $C_V = Nk$. Also get:

$$\mu = -kT \ln\left(\frac{N+q}{N}\right) \tag{16}$$

2.3 Interacting Systems

Fundamental assumption of statistical mechanics (ergodic hypothesis): "*In an isolated system in thermal equilibrium, all accessible microstates are equally probable*".

2.4 Large Systems

Sharpness of multiplicity function: For a (large) Einstein crystal:

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N}(q_A q_B)^N \quad \Omega_{max} = \left(\frac{e}{N}\right)^{2N}\left(\frac{q}{2}\right)^{2N} \tag{17}$$

Look at *near* peak ($q_A = q/2 + x$, $q_B = q/2 - x$) to get (after series expansion of logarithm):

$$\Omega \approx \Omega_{max} \exp\left(-N\left(\frac{2x}{q}\right)^2\right) \tag{18}$$

Gaussian with mean 0 and $\sigma = q/2\sqrt{N}$. Thermodynamic limit: *measurable fluctuations away from the most likely macrostate never occur.*

2.5 Ideal Gas

Multiplicity has to be proportional to V and V_p (volume in momentum space). Single particle: molecule's kinetic energy must be U so $U = m/2(v_x^2 + v_y^2 + v_z^2)$, $p_x^2 + p_y^2 + p_z^2 = 2mU$ (sphere with radius $L_p = \sqrt{2mU}$. Number of distinct position states is $L/\Delta x$ (with L length of the box) and distinc momentum states $L_p/\Delta p$. Total number of states $LL_p/(\Delta x \Delta p) = LL_p/h$. In 3D: $\Omega_1 = VV_p/h^3$ for a single particle. More particles: Total energy is constrained so $p_{1x}^2 + p_{2x}^2 + ... = 2mU$. So for two particles: $\Omega_2 = V^2/h^6\cdot$ (area of momentum hypersphere). Indistinguishable:

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \times \text{area of momentum hypersphere} = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!}(\sqrt{2mU})^{3N-1} \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2mU}\right)^{3N} = f(N)V^N U^{3N/2} \tag{19}$$

So that entropy:

$$S = Nk\ln V + \frac{3}{2}Nk\ln U + k\ln f(N) \tag{20}$$

Interacing ideal gases: multiply functions. Width of peak: $U_{tot}/\sqrt{3N/2}$. Exchange volume: $V_{tot}/\sqrt{N}$.

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{2Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right] \quad (\text{Sackur} - \text{Trode}) \quad \Delta S = Nk\ln\frac{V_f}{V_i} \quad (\text{U, N fixed}) \tag{21}$$

Differentiating S and using $U = 3NkT/2$ gives:

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \tag{22}$$

Alternatively: use $G = N\mu$ to get $\partial\mu/\partial P = 1/N\partial G/\partial P = V/N = kT/P$. Integrate to get:

$$\mu(T,P) = \mu^o(T) + kT\ln(P/P_0) \tag{23}$$

Ideal gas: take P to be the partial pressure.

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \tag{24}$$

Differentiating the entropy gives $U = 3NKT/2$, so that $C_V = 3Nk/2$.

2.6 Entropy

$S = k\ln\Omega$. $S_{tot} = k\ln\Omega_{tot} = k\ln(\Omega_A\Omega_B) = S_A + S_B$.

Entropy of mixing

Distinguishable particles, initially separated into $V/2$ then allowed to expand:

$$\Delta S = 2Nk\ln 2 \quad (\text{distinguishable}) \tag{25}$$

If a fraction of molecules, x is of species B::

$$\Delta S_{\text{mixing}} = -Nk\left[x\ln x + (1-x)\ln(1-x)\right] \tag{26}$$

For an ideal mixture (denser system, two types of molecules are of the same size and interact with each other the same way):

$$\Delta S_{\text{mixing}} = k\ln\binom{N}{N_A} \tag{27}$$

3 Interactions and Implications

3.1 Temperature

For entropy to be maximal, need to have $\partial S_{tot}/\partial q_A = 0$ and $\partial S_{tot}/\partial q_B = 0$ (equivalently $\partial S_{tot}/\partial U_A = 0$ and $\partial S_{tot}/\partial U_B = 0$). As $S_{tot} = S_A + S_B$ and $dU_A = -dU_B$, this is equivalent to $\partial S_A/\partial U_A = \partial S_B/\partial U_B$ (at equilibrium). Most systems become hotter as they gain energy, so the tendency to receive entropy will decrease. May have systems that become colder with increasing energy, hug more entropy. Generally:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{28}$$

3.2 Entropy and Heat

$C_V = (\partial U/\partial T)_{N,V}$. From the theoretical definition of temperature:

$$dS = \frac{dU}{T} = \frac{Q}{T} = \frac{C_V \, dT}{T} \quad \text{Constant volume, no work (or changing volume but quasistatic)} \tag{29}$$

Note that this equation is valid if the volume changes quasistatically (pressure is always uniform throughout the system), no other variables (i.e. N) are changing and no other form of work is being done.

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT \tag{30}$$

If you know $C_V(0)$ can compute absolute entropy, if $S(0)$ is known. Note that $S(0)$ is theoretically 0 (*third law of thermodynamics*) but in practice can have minuscule disturbances, i.e. change orientation without changing energy by much - residual entropy. Third law:

$$C_V \to 0 \quad \text{as} \quad T \to 0 \tag{31}$$

So expression for C_V is only correct if this is true (else the integral above diverges).

3.3 Paramagnetism

Energy flips from $-\mu B$ (for $N_\downarrow$) to μB (for $N_\uparrow$). Total energy, magnetization and multiplicity:

$$U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow) \quad M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B} \quad \Omega(N_\uparrow = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{32}$$

Find the approximate entropy as $S/k \approx N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow)$. Use this to find:

$$\frac{1}{T} = \frac{k}{2\mu B} \ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right) \quad U = N\mu B\left(\frac{1 - \exp(2\mu B/kT)}{1 + \exp(2\mu B/kT)}\right) = -N\mu B \tanh\left(\frac{\mu B}{kT}\right) \quad M = N\mu \tanh\left(\frac{\mu B}{kT}\right) \tag{33}$$

Heat capacity at constant B-field:

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk \frac{(\mu B/kT)^2}{\cosh^2(\mu/kT)} \tag{34}$$

For small $x = \mu/kT$, $\tanh x \approx x$ so $M \approx N\mu^2 B/kT$ (Curie's law).

3.4 Mechanical Equilibrium and Pressure

$\partial S_A/\partial V_A = \partial S_B/\partial V_B$ at equilibrium. Define:

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{35}$$

Get the thermodynamic identity by considering the total differential of $S(U, V)$, to get:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \tag{36}$$

Plug this into the first law of thermodynamics to get the familiar formula for entropy, but also with changing volume. Note: *adiabatic+quasistatic = isentropic*. Allows us to define ΔS_P as:

$$(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T} dT \tag{37}$$

Note further that $dS > Q/T$ when $W > -PdV$.

3.5 Diffusive equilibrium and Chemical Potential

$\partial S_A/N_A = \partial S_B/N_B$ at equilibrium. Define:

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{38}$$

Particles tend to flow from the system with higher μ into the system with lower μ. Gives a new thermodynamic identity, with μdN - Chemical work. Normally, to hold entropy fixed whilst adding particles, we need to remove energy - so μ is often negative. If multiple species: chemical potential must be equal for each species *separately*.

4 Engines and Refrigerators

4.1 Heat Engines

Heat absorbed from a hot reservoir, T_h, waste heat dumped into a cold reservoir T_c. Heat abstakenorbed from the hot reservoir is Q_h, heat expelled to the cold reservoir is Q_c. Efficiency: benefit/cost ratio: $e = W/Q_h$. For cyclic engines: must have that the heat absorbed precisely equals the heat expelled, so $Q_h = Q_c + W$. Get:

$$e = 1 - \frac{Q_c}{Q_h} \tag{39}$$

Invoke second law: entropy cannot decrease: must expel at least as much entropy as it absorbs to be cyclical. This gives:

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \implies e \leq 1 - \frac{T_c}{T_h} \tag{40}$$

Less effective: must get rid of more entropy, so the heat dumped into the cold reservoir has to increase. Note that if the temperature of the heat engine when taking in heat from the hot reservoir is less than T_h, then efficiency will be lower.

Carnot

For Carnot cycle: begin at tempererature only infinitesimally smaller than T_h, absorb Q_h (slowly) - expand gas isothermally. Same when the gas is dumping the waste heat - compress isothermally. To change temperature: do an adiabatic compression/expansion (no
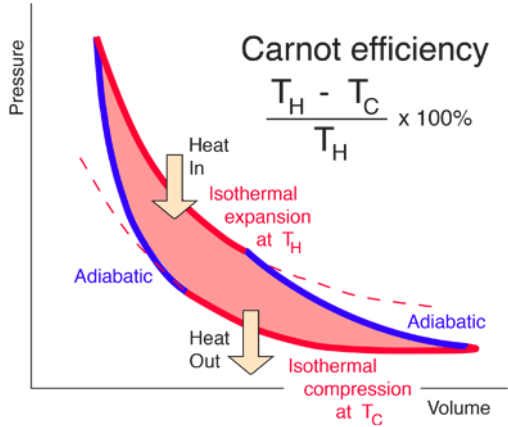
heat flow, so $\Delta S = 0$).

4.2 Refrigerators

Heat engine in reverse - simply reverse the arrows (put in work to suck out heat from the cold reservoir Q_c and dump it into the hot reservoir Q_h. Coefficient of performance, COP is benefit/cost = Q_c/W. By the first law, $Q_h = Q_c + W$ (we put *in* work) so that the Coefficient of Performance becomes:

$$COP = \frac{Q_c}{Q_h - Q_c} \tag{41}$$

By the second law, the inequalities are now reversed from previously (entropy flows in the opposite direction) so that:

$$\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c} \tag{42}$$

Which gives:

$$\text{COP} \leq \frac{T_c}{T_h - T_c} \tag{43}$$

5 Free Energy and Chemical Thermodynamics

$$H = U + PV \quad F = U - TS \quad G = U - TS + PV = H - TS \tag{44}$$

$$\Delta U = Q + W_{\text{other}} \quad \text{P constant} \quad \Delta F \leq W, \text{ T = constant} \quad \Delta G \leq W_{other} \text{ T, P = constant} \tag{45}$$

If no new entropy is created, $Q = T\Delta S$. Generally, $Q - T\Delta S \leq 0$. Note that we for chemical reactions may assume minimal entropy change.

$$dH = TdS + VdP + \sum_i \mu_i dN_i$$

$$dF = -SdT - PdV + \sum_i \mu_i dN_i \tag{46}$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

- At constant energy, N and volume, S tends to increase

- At constant temperature, N and volume, F tends to decrease

- At constant temperature, N and pressure, G tends to decrease

Proof: $dS_{tot} = dS + dS_R$, but $dS = 1/T dU + P/T dV - \mu/T dN$. Assume V and N fixered, then $dS_R = dU_R/T_R$ so $dS_{tot} = dS + 1/T_R dU_R = -1/T(dU - TdS) = -1/T dF$. Similar for dG but let V, not P be constant.

- Extensive: V,N,S,U,H,F,G, mass

- Intensive: T,P, μ, density

- Extensive $\times$ intensive=extensive

- Extensive/Extensive = Intensive

- Extensive$\times$ Extensive = Neither (wrong)

- Extensive+Extensive or Intensive+Intensive ok, but not Extensive+Intensive

- Exponentiating extensive quantity gives a multiplicative quantity

As $\mu = (\partial G/\partial N)_{T,P}$ is an extensive quantity divided by an extensive quantity, holding only intensive quantities fixed. Hence $G = N\mu$. Generally $G = \sum_i N_i \mu_i$, but with potentially different i.

5.1 Phase transformations

Most substances: more pressure raises melting temperature. Opposite for water. Liquid-gas phase boundary always has a positive slope (x-axis:T, y-axis: P), liquid and gas in equilibrium: increasing temperature requires higher pressure. Higher pressure implies denser gas - difference vanishes.

$$G_l = G_g \implies dG_l = dG_g \quad \text{at phase boundary} \tag{47}$$

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta V} \ (\text{Clausis} - \text{Claperyon}) \tag{48}$$

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \quad (\text{Van der Waals Model}) \tag{49}$$

Van Der Waal: Limit equation to minimum Nb and add potential energy from neighbors. The force is proportional to N/V, so the total energy is $-N^2/V$, then use $P = -(\partial U/\partial V)_S$ to get $P = -aN^2/V^2$. Insert into ideal gas equation. Equal area construction:

$$0 = \int_{\text{loop}} dG = \int_{\text{loop}} \left(\frac{\partial G}{\partial P}\right)_T dP = \int_{\text{loop}} V dP \tag{50}$$

So look at PV-diagram and find where the area is 0 to get phase changes. Note that the isotherms become straight lines (volume increases whilst pressure stays constant), defining an intermediate region. For high temperature isotherms, the phase transition disappears - critical point.

5.2 Chemical Equilibrium

Equilibrium condition: Gibb's free energy minimized (if at room temperature and atmospheric pressure), i.e. $dG = \sum_i \mu_i dN_i = 0$. Generally: replace species by chemical potential, keep stochiometric ratio. Example:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \implies \mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3} \tag{51}$$

5.2.1 Gaseous:

Nitrogen fixation, $N_2 + 3H_2 \leftrightarrow 2NH_3$. Assume ideal gas, use $\mu_{N_2} = \mu^o_{N_2} + kT \ln(P_{N_2}/P_0)$, where μ_0 is the chemical potential when its partial pressure is P_0. Gather all μ_0 on one side, and multiply through by N_A to get ΔG^o. Get:

$$\frac{P^2_{NH_3}(P^o)^2}{P_{N_2} P^3_{NH_3}} = K = e^{-\Delta G^o/RT} \tag{52}$$

Where each pressure is raised to the power of its stochiometric coefficient and there are enough powers of P^o to make the expression unitless.

5.3 Disassociation:

$H_2O \leftrightarrow H^+ + OH^-$. Use $\mu^o_{H_2O} = \mu^o_{H^+} + kT \ln m_{H^+} + \mu^o_{OH^-} + kT \ln m_{OH^-}$ assuming the disassociation is small and m is the molality (mole solute per kilogram solvent). Get:

$$m_{H^+} m_{OH^-} = e^{-\Delta G^o/RT} \tag{53}$$

Where the standard states are 1 molal.

5.4 Oxygen dissolving:

$O_2(g) \leftrightarrow O_2(aq)$. Use $\mu^o_{gas} + kT \ln(P/P^o) = \mu^o_{solute} + kT \ln m$ to get:

$$\frac{m}{P/P^o} = e^{-\Delta G_0/RT} \tag{54}$$

5.5 Ionization of hydrogen

$H \leftrightarrow p+e$. Treat all as ideal gases, use equation 24. Put in ionization energy I explicitly, so that $\mu_H = \mu - I$ where μ is from equation 24 and I is 13.6 eV. Use ideal gas law to express with pressure, use that mass of proton and hydrogen are approximately equal, and get:

$$\frac{P_p}{P_H} = \frac{kT}{P_e} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-I/kT} \quad \text{(Saha equation)} \tag{55}$$

Note that $P_e/kT = N_e/V$.

6 Boltzmann Statistics

$$P(s) = \frac{1}{Z} e^{-E(s)/kT} \tag{56}$$

Arrive at by considering ratios of probabilities which must be directly proportional to the number of microstates accessible to the reservoir. Usse $S = k \ln \Omega$ (where Ω is the number of microstates accesible to the reservoir), then use the thermodynamic identity. Throw away PdV and μdN. Get that ratio of probabilities is proportional to ratio of exponentials. Note that this is the probability of finding a particle in a state with this energy. If there are multiple states with this energy, then you must multiply by the multiplicity. Note **VALID FOR SINGLE PARTICLE**.

$$Z = \sum_s e^{-E(s)/kT} = \sum_s e^{-\beta E(s)} \qquad \beta = \frac{1}{kT} \tag{57}$$

$$\overline{E} = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z = kT^2 \frac{\partial \ln Z}{\partial T} \tag{58}$$

Additive so $U = N\overline{E}$.

6.1 Paramagnetism

$$Z = 2\cosh(\beta\mu B) \quad P_\uparrow = \frac{e^{+\beta\mu B}}{Z} \quad P_\downarrow = \frac{e^{-\beta\mu B}}{Z} \quad \overline{E} = -\mu B \tanh(\beta\mu B) \quad U = -N\mu B \tanh(\beta\mu B) \tag{59}$$

$$\overline{\mu}_z = \sum_s \mu_Z(s) P(s) = (+\mu)P_\uparrow + (-\mu)P_\downarrow = \mu \tanh(\beta\mu B) \quad M = N\overline{\mu}_z = N\mu \tanh(\beta\mu B) \tag{60}$$

6.2 Rotation of a diatomic molecule

$E(j) = j(j+1)\epsilon$ for a diatomic molecule. Number of degenerate states are $2j + 1$. $Z = kT/\epsilon$ when $kT >> \epsilon$ (use an integral), $\overline{E}_{rot} = kT$ when $kT >> \epsilon$. For identical atoms in the limit $kT >> \epsilon$, insert a factor of $1/2$ ($Z = kT/2\epsilon$).

6.3 Equipartition theorem

Assume $E(q) = cq^2$, where q is any degree of freedom, and sum over all q. Multiply and divide by Δq, approximate by integral, get Gaussian, get:

$$Z = \frac{1}{\Delta q} \sqrt{\frac{\pi}{\beta c}} \quad \overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{2} kT \tag{61}$$

Applies only when the spacing between energy levels is much less than kT.

6.4 The Maxwell Speed Distribution

From equipartition: $v_{rms} = \sqrt{3kT/m}$. To find distribution function: realize that it must be proportional to the probability of having velocity $\vec{v}$ and to the number of vectors $\vec{v}$ corresponding to speed v. The probability of having velocity $\vec{v}$ is proportional to $e^{-mv^2/2kT}$ (neglect other factors affecting states, i.e. position - valid for ideal gas). Number of vectors $\vec{v}$ corresponding to speed v is proportional to $4\pi v^2$. Constants are determined from normalization (integrate from 0 to ∞) to get (note: *scalar* v):

$$D(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} \tag{62}$$

$v_{max} = \sqrt{2kT/m}$, $\overline{v} = \sqrt{8kT/\pi m}$.

6.5 Partition functions and free energy

$F = -kT \ln Z$. Also, for a large system of indistinguishable noninteracting particles, $\mu = -kT \ln(Z_1/N)$.

6.6 Partition functions for Composite Systems

$$Z_{\text{total}} = \sum_s e^{-\beta(E_1(s) + E_2(s))} \tag{63}$$

If distinguishable and noninteracting sum runs over all possible pair of states, $Z_{\text{total}} = Z_1 Z_2$ (if noninteracting, distiguishable). If the system is not too dense and the particles are indistinguishable, then $Z_{\text{tot}} = Z^N/N!$ (noninteracting, indistinguishable).
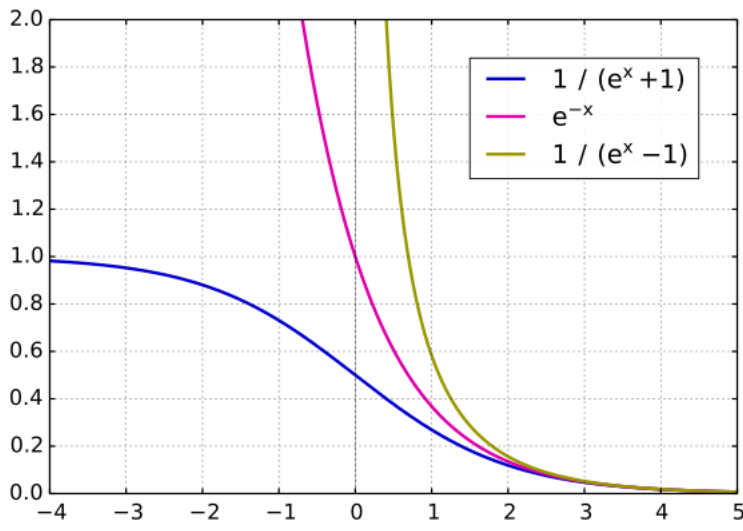
6.7 Ideal Gas Revisited

$Z_1 = Z_{tr} Z_{int}$. Note that, for a 1D-box: $p = h/\lambda$, $p_n = hn/2L$, $E_n = h^2 n^2/(8mL^2)$. Thus:

$$Z_{tr,1d} = \sum_n e^{-h^2 n^2/8mL^2 kT} \approx \sqrt{\frac{2\pi mkT}{h^2}} L = \frac{L}{l_Q} \tag{64}$$

For 3D: $Z_{tr} = V/v_Q$, where $v_Q = (h/\sqrt{2\pi mkT})^3 = l_Q^3$. Thus the total partition function is:

$$Z = \frac{1}{N!}\left(\frac{V Z_{int}}{v_Q}\right)^N \implies \ln Z = N[\ln V + \ln Z_{int} - \ln N - \ln v_Q + 1] \tag{65}$$

This gives the following relations:

$$U = U_{int} + \frac{3}{2}NkT \quad C_V = \frac{\partial U_{int}}{\partial T} + \frac{3}{2}Nk \quad F = -NkT[\ln V - \ln N - \ln v_Q + 1] + F_{int} \tag{66}$$

$$P = \frac{NkT}{V} \quad S = Nk\left[\ln\left(\frac{V}{Nv_Q}\right) + \frac{5}{2}\right] - \frac{\partial F_{int}}{\partial T} \quad \mu = -kT\ln\left(\frac{V}{N}\frac{Z_{int}}{v_Q}\right) \tag{67}$$

For ideal gas: can often let $Z_{int} = 1$ if there are no internal interactions.

7 Quantum Statistics

$$\Phi = U - TS - \mu N = -kT\log Z_G \tag{68}$$

To derive grand partition function, use same approach as for partition function, but do not throw away μdN. Get Gibbs factor: $e^{-(E(s)-\mu N(s))/kT}$ and grand partition function:

$$\mathcal{Z} = \sum_s \exp\left(-[E(s) - \mu N(s)]/kT\right) \quad \Phi = -kT\ln Z \tag{69}$$

If mutliple species: $\sum \mu_i N_i$. Get from this $\overline{N} = (kT/\mathcal{Z})\partial Z/\partial\mu$ at fixed temperature and volume. For fermions/bosons, $Z = Z_1^N/N!$ applies only when $Z_1 >> N$, which is equivalent (for an ideal gas) to $V/N >> v_Q$. If not, then consider a single particle state and use Gibbs. For fermions then, $n = 0$ or $n = 1$:

$$\mathcal{Z} = 1 + \exp\left(-(\epsilon - \mu)/kT\right) \quad \overline{n} = \sum_n nP(n) = \frac{\exp(-(\epsilon - \mu)/kT)}{1 + \exp(-(\epsilon - \mu)/kT)} = \frac{1}{\exp(\epsilon - \mu)/kT) + 1} \quad (\text{Fermi} - \text{Dirac}) \tag{70}$$

Goes to 0 when $\epsilon >> \mu$, goes to 1 when $\epsilon << \mu$. For bosons, n can be any number so:

$$\mathcal{Z} = 1 + \exp(-(\epsilon - \mu)/kT) + \exp(-2(\epsilon - \mu/kT) + ... = \frac{1}{1 - \exp(-(\epsilon - \mu)/kT}$$

$$\overline{n} = \sum_n \frac{n}{\mathcal{Z}}\exp(-n\underbrace{(\epsilon - \mu)/kT}_{=x}) = -\frac{1}{\mathcal{Z}}\sum_n \frac{\partial}{\partial x}e^{-nx} = -\frac{1}{\mathcal{Z}}\frac{\partial Z}{\partial x} = \frac{1}{\exp(\epsilon - \mu)/kT - 1} \quad (\text{Bose} - \text{Einstein}) \tag{71}$$

Goes to 0 when $\epsilon >> \mu$, goes to ∞ as $\epsilon \to \mu^+$. For bosons: need to assume $\mu < \epsilon$. Three distributions agree if $(\epsilon - \mu)/kT >> 1$. Can then use $\mu = -kT\ln(Z_1/N)$. Classical limit: average occupancy must be small, so denominator must be very large, hence $(\epsilon - \mu)/kT >> 1$.

7.1 Degenerate Fermi Gas

Need to look at v_Q. For metals, $V/N << v_Q$, too low temperature to use Boltzmann, can pretend $T = 0$. Then Fermi-Dirac is a step function, lowest occupied energy is ϵ_F so $\epsilon_F = \mu(T = 0)$. Ignoring interactions (assuming free particles), $\epsilon = (h^2/8mL^2)(n_x^2 + n_y^2 + n_z^2)$. Note that ϵ_F is energy of a state sitting at the edge of the sphere (positive octant), so $\epsilon_F = h^2 n_{max}^2/(8mL^2)$. But the volume in n-space is $2 \times 1/8 \times 4/3\pi n_{\max}^3 = \pi n_{max}^3/3$. So:

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \quad \text{(intensive)} \tag{72}$$

$$U = 2\int_0^{n_{max}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin\theta \, \epsilon(n) = \frac{3}{5}N\epsilon_F = \int_0^{\epsilon_F} \underbrace{\left[\frac{\pi}{2}\left(\frac{8mL^2}{h^2}\right)^{3/2}\sqrt{\epsilon}\right]}_{=g(\epsilon)} d\epsilon \quad (T = 0) \tag{73}$$

Note that $V/N << v_Q$ is the same as $kT << \epsilon_F$. Fermi temperature: $T_F = \epsilon_F/k$. Use $P = -(\partial U/\partial V)_{S,N}$ to get $P = 2U/(3V)$. If small, nonzero temperature: The number of particles that escape the sphere is NkT (must be proportional to T, and N a extensive).

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F} \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\pi^2 Nk^2 T}{2\epsilon_F} \tag{74}$$

General temperature:

$$N = \int_0^\infty g(\epsilon)\overline{n}_{FD}(\epsilon)d\epsilon \quad U = \int_0^\infty \epsilon g(\epsilon)\overline{n}_{FD}(\epsilon)d\epsilon \tag{75}$$

Generally, chemical potential decreases as T increases (Fermi-Dirac is symmetric about $\epsilon = \mu$). More precisely:

$$\frac{\mu}{\epsilon_F} = 1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + ... \tag{76}$$

7.2 Blackbody Radiation

Ultraviolet catastrophe: Each mode in the field has energy kT, infinite number of modes, infinite energy. Solution: $E_n = nhf, n \in \mathbb{N}^+$. For a single oscillator then:

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + ... = \frac{1}{1 - e^{-\beta hf}} \quad \overline{E} = \frac{hf}{e^{hf/kT} - 1} \tag{77}$$

Average number of "units of energy" (photons) in a single oscillator is $\overline{n} = 1/(\exp(hf/kT) - 1)$ (Planck Distribution). But photons are bosons, must follow Bose-Einstein $\rightarrow \mu = 0$ for photons (follows also because N arbitrary for photons so $(\partial F/\partial N)_{T,V} = 0 = \mu$ or from $e \leftrightarrow e + \gamma \implies \mu_e = \mu_e + \mu_\gamma$). Energy for photons is $\epsilon = pc = hcn/2L$. Each wave shape can hold two photons. Gives the total energy per unit volume as:

$$\frac{U}{V} = \int_0^\infty \underbrace{\frac{8\pi\epsilon^3/(hc)^3}{\exp(\epsilon/kT) - 1}}_{\text{Spectrum of photon}} d\epsilon = \frac{8\pi^5(kT)^4}{15(hc)^3} \tag{78}$$

Spectrum peaks at $\epsilon = 2.82kT$ (Wien's law). Heat capacity/entropy:

$$C_V = 4aT^3 \quad S(T) = \int_0^T \frac{C_V(T')}{T'}dT' = 4aT^3 \quad N = 8\pi V\left(\frac{kT}{hc}\right)^3 \int_0^\infty \frac{x^2}{e^x - 1}dx \tag{79}$$

Where $a = 8\pi^5 k^4 V/15(hc)^3$.

7.3 Photons Escaping through a Hole

Spectrum outside of box with hole is same as inside, as all photons travel at the same speed. Energy comes from spherical shell, distance R from hole, with angle θ to the normal of the hole. Look at chunk of spherical shell: volume $R^2 \sin\theta c \, dtd\theta d\phi$. Energy is this times U/V. Probability of escape is $A\cos\theta/4\pi R^2$ with A aperture size. Total energy escaping:

$$\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \frac{A\cos\theta}{4\pi}\frac{U}{V}cdt\sin\theta = \frac{A}{4}\frac{U}{V}cdt \tag{80}$$

Which gives power per unit area as:

$$P = \frac{2\pi^5}{15}\frac{(kT)^4}{h^3 c^2} = \sigma T^4 \, (\text{Stefan} - \text{Boltzmann law}) \tag{81}$$

If reflecting: remember to include emissitivity, e.

7.4 The Sun and the Earth

Absorbed power: solar constant $\times \pi R^2 = 4\pi R^2 \sigma T^4$: emitted power.

8 Summary of thermodynamic potentials

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
INTERNAL ENERGY U	S, V, N	$T = \left(\dfrac{\partial U}{\partial S}\right)_{V,N}$ $P = -\left(\dfrac{\partial U}{\partial V}\right)_{S,N}$ $\mu = \left(\dfrac{\partial U}{\partial N}\right)_{S,V}$	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$
ENTROPY S	U, V, N	$\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial U}\right)_{V,N}$ $\dfrac{P}{T} = \left(\dfrac{\partial S}{\partial V}\right)_{U,N}$ $-\dfrac{\mu}{T} = \left(\dfrac{\partial S}{\partial N}\right)_{U,N}$	
FREE ENERGY $F = U - TS$	T, V, N	$S = -\left(\dfrac{\partial F}{\partial T}\right)_{V,N}$ $P = -\left(\dfrac{\partial F}{\partial V}\right)_{T,N}$ $\mu = \left(\dfrac{\partial F}{\partial N}\right)_{T,V}$	$\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$ $U = -T^2\dfrac{\partial}{\partial T}\left(\dfrac{F}{T}\right)$
ENTHALPY $H = U + PV$	S, P, N	$T = \left(\dfrac{\partial H}{\partial S}\right)_{P,N}$ $V = \left(\dfrac{\partial H}{\partial P}\right)_{S,N}$ $\mu = \left(\dfrac{\partial H}{\partial N}\right)_{S,P}$	$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$
GIBBS ENTHALPY $G = H - TS = N\mu$	T, P, N	$S = -\left(\dfrac{\partial G}{\partial T}\right)_{P,N}$ $V = \left(\dfrac{\partial G}{\partial P}\right)_{T,N}$ $\mu = \left(\dfrac{\partial G}{\partial N}\right)_{T,P}$	$\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$ $H = -T^2\dfrac{\partial}{\partial T}\left(\dfrac{G}{T}\right)$

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
GRAND CANONICAL POTENTIAL $\Omega = F - \mu N = -PV$	T, V, μ	$S = -\left(\dfrac{\partial \Omega}{\partial T}\right)_{V,\mu}$ $P = -\left(\dfrac{\partial \Omega}{\partial V}\right)_{T,\mu}$ $N = -\left(\dfrac{\partial \Omega}{\partial \mu}\right)_{T,V}$	
CHEMICAL POTENTIAL $\mu = \dfrac{G}{N}$	T P	$s = \dfrac{S}{N} = -\left(\dfrac{\partial \mu}{\partial T}\right)_{P}$ $v = \dfrac{V}{N} = \left(\dfrac{\partial \mu}{\partial P}\right)_{T}$	