Units and Values

Avogradro's number: $N_A = 6.023 \times 10^{23}$

Boltzmann's cosntant: $k = 1.381 \times 10^{-23}$ J/K

Boltzmann's cosntant: $k = 8.617 \times 10^{-5}$ eV/K

$R = 8.31 J/K$mol, $nR = Nk$.

Calorie: 1cal = 4.2J (amount of heat needed to raise the temperature of a gram of water by 1°C.)

Absolute zero: $0K = -273.15°C$.

Plank's constant: 6.626×10^{-34} J/s, 4.136×10^{-15} eV/s

One atmosphere pressure: 1atm = 101.325kPa.

One atomic mass unit: $1.6605402 \times 10^{-27}$ kg

Definitions

Isotherm: constant temperature

Isobar: constant pressure

Isothermal compression: so slow that temperature does not rise

Adiabatic: so fast heat does not escape ($Q = 0$)

Quasi static: Process with constant entropy ($\Delta S = 0$), slow process so that system can always equilibrate to the changing conditions.

Isentropic: Adiabatic ($Q = 0$) and quasistatic ($\Delta S = Q/T = 0$)

isochoric: Constant volume $\Delta V = 0$. **fundamental assumption of statistical mechanics:** In an isolated system in thermal equilibrium, all accessible microstates are equally probable **thermodynamic limit:** Let number of particles go to infinity

$P = T \left(\frac{\partial S}{\partial V}\right)_{U,N}$, $T^{-1} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$, $\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$

The laws of thermodynamics

1. Defines temperature

2. Defines energy (U), and energy transformation (W, Q).

3. Defines entropy S

4. Fixes the value of entropy at $T = 0K$.

Important formulas

$$\Omega_{total}(N, n) = \Omega_A(N, n)\Omega_B(N, n)$$
$$\Delta S = 0 \quad \rightarrow \quad \text{reversible}$$
$$\Delta S \geq 0 \quad \rightarrow \quad \text{irrreversible}$$

Important facts

- Macrostates with maximum multiplicity are the most likely and they correspond to the average values

- ΔS is path independent, choose the simplest path between the states to compute

Mol

For a given substance, find it's atmoic mass, in units of u (hydrogen 1u, oxygen 16u, lead 207u). Then the mole is the mass of the substance in gram (for example 1g), and divide with the atomic mass (for example 16u). The substance is then 1/16mole.

Ideal Gas

Low density gas $PV = NkT$, ignore particle interactions. $\langle v^2 \rangle = 3kT/m$. Compression $W = NkT \ln V_i/V_f$. For indistinhuishable particles (we get $1/N!$)

$$\Omega(U, V, N) = f(N)V^N U^{3N/2} \approx \frac{V^N}{N!(3N/2)!}(2\pi mU/h^2)^{3N/2}$$

$$S = Nk \left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right] \text{ (Sackur-Tetrode)}$$

$$\Delta S = Nk \ln V_f/V_i \quad (U, N \text{ fixed})$$

Equipartition theorem

For each quadratic degree of freedom (kinetic v^2, spring k^2, rotational ω^2, etc.) contributes to $1/2kT$ to the average energy at equillibrium at temperature T. For N particles with f degrees of freedom $U = NfkT/2$. Safest to apply in changes of energy. Coutning f: one for each dimension, 2 from rotation (as one axis is symmetric), vibrateing counts twice (frozen out at room temperature) in a solid 3 vibrational directions $f+ = 6$. Equipartition theorem only works for kinetic energy in liquids. Use $f = 3$ for a monatmoic gas and $f = 5$ for a diatomic gas, 6 for polyatomic.

Derived by Boltzmannfactors and converting to integral

$$Z = \frac{1}{\Delta q} \sum_q e^{-\beta c q^2} \Delta q$$

and calculating energy from partition function

Heat and Work

Heat = any spontaneous flow of energy frrom one object to another due to a difference in temperature; konduction, konvection, radiation.

Work = any other transfer of energy inn and out of system. Both refer to energy in transit.

$$\Delta U = Q + W$$

Assuming quasistatic compression $W = -P\delta V$. Use pressure from POV of gas, negative work means gas is doing work, positive work means the outside is doing work on the gas.

$$W = -\int_{V_i}^{V_f} P(V)dV \qquad \text{quasistatic}$$

For a quasistatic process $Q = TdS$.

Heat Capacity

Heat capacity: amount of heat needed to raise temperature per degree temperature increase $C = Q/\Delta T$.

Specific heat capacity: Heat capacity per unit mass $c = C/m$.

$$C = (\Delta U - W)/\Delta T, C_V = \left(\frac{\partial U}{\partial T}\right)_V, C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

At the phase transition you can put heat into system without increasing temperature, $C = \infty$. Latent heat $L = Q/m$ is the heat needed to accomplish phase transition per mass, assume constant pressure 1atm, and no other work.

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$
$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$
$$C_V \rightarrow \text{constant} \quad \text{as} \quad T \rightarrow \infty$$
$$dS = \frac{dU}{T} = \frac{Q}{T} = \frac{C_V dT}{T} \rightarrow \Delta S = \int_0^{T_f} \frac{C_V}{T}dT$$

Adiabatic compression

So fast no heat flows out, still quasistatic, $\Delta U = W$.

$$V^\gamma P = \text{constant}, \gamma = (f + 2)/f$$

Derived from $\Delta U = W$, from equipartition $dU = fNk/2dT = -PdV$, plugging in ideal gas law: $f/2dT/T = -dV/V$.

Two state system

Multiplicity of the macrostate with N particles where $N_\uparrow$ point up

$$\Omega(N, n) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!} = \frac{N!}{N_\uparrow! N_\downarrow!}$$

Einstein solid

$N/3$ atoms as harmonic oscillators which can oscillate in 3 dimensions with $q = (U_n - N\hbar\omega/2)/\hbar\omega$ units of energy

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \approx \frac{(q + N)!}{q!N!}N_\downarrow!$$

If a composite system: $q = q_A + q_B$ and $N = N_a + N_b$ and $\Omega = \Omega_A \Omega_B$.

$$\text{low } T \qquad \Omega \approx \left(\frac{Ne}{q}\right)^q, \qquad q << N$$
$$\text{high } T \qquad \Omega \approx \left(\frac{qe}{N}\right)^N, \qquad N << q$$
$$S = kN\left[\ln\left(\frac{q}{N} + 1\right)\right], \quad q = U/\hbar\omega$$

thermodynamic potentials

- Internal Energy: U Total internal thermal energy of the system. The change in the stored energy equal the sum of «energies in transit» $\Delta U = Q + W$ (first law of thermodynamics). The infinitesimal change in internal energy: $dU = \delta Q + \delta W$. For infinitesimal reversible process: $dU = TdS - PdV$. Can also be $dU = TdS - PdV + \mu dN$

- Enthalpy: $H = U + PV$, $\Delta F \leq W$ (at constant T). Energy needed to create the system out of nothing, and make room for it.
$dH = TdS + VdP + \mu dN$

- Helmholtz free energy: $F = U - TS$, (constant pressure). Total energy needed to create the system, minus the heat you get from enviorment. Thermodynamic identity: $dF = -SdT - PdV + \mu dN$. Minimized in thermal bath, with only energy exchange. $\Delta F \leq W$.
$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$, $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$.

- Gibbs free energy: $G = U - TS + PV = \mu N$, $\Delta G \leq W_{other}$. Create system in constant temperature and pressure. Minimized when change in volume with constant pressure. $dG = -SdT + VdP + \mu dN$.
$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$, $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$, $-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$

- Chemical potential, the energy increase by adding a particle in to the system with constant temperature and pressure. Diffusive equilibrium → equal chemical potentials.
$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$, $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$, $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$
Particles tend to flow from the system with higher μ to the system with lower μ.

For monatomic ideal gas $\mu = -kT \ln\left(\frac{VZ_{int}}{NV_Q}\right)$ must be equal

At constant U and T, S increases.

At constant V and T, F decreases.

At constant T and P, G decreases.

Reversible process

At every step of the path the system is at equilibrium.

For infinitesimal reversible process: $dU = TdS - PdV$.

Clausius equality: $dS = \delta Q_{rev}/T$, constant volume, no work.

Irreversible heat transfer is smaller than the reversible heat exchange at a given T

$$\frac{\delta Q_{irrev}}{T} < \frac{\delta Q_{rev}}{T}$$

Clausius inequality: $dS \geq \delta Q/T$. For an isolated system entropy tends to increase as the system spontaneously finds its equilibrium state $dS \geq 0$.

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right) \rightarrow dU = C_V dT$$

Isolated system at equilibrium

Multiplicity of a macrostate $\Omega(U, V, N)$ counts all equally likely accessible microstates, if the particles are indistinguishable the total number of microstates is reduced by $N!$. Boltzmann's formula $S = k \ln \Omega = -k \sum_s P(s) \ln P(s)$, for equilibrium state at fixed U, entropy is maximized at equilibrium, $dS = 0$.

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

For a composite system

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \qquad \text{(thermal equilibrium)}$$
$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \qquad \text{(mechanical equilibrium)}$$
$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \qquad \text{(diffusive equillibrium)}$$

Extensive and Intensive Quantities

An extensive quantity doubles when you double a system. All the four thermodynamic potentials U, H, F and G are extensive quantities. The quantities which are unchanged when you double the system are intensive.

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

- **Intensive:** T, P, μ, density

$$\text{extensive} \times \text{intensive} = \text{extensive}$$
$$\frac{\text{extensive}}{\text{extensive}} = \text{intensive}$$
$$\text{extensive} \times \text{extensive} = \text{neither, you did something wrong}$$
$$\text{extensive} + \text{extensive} = \text{extensive}$$
$$\text{extensive} + \text{intensive} = \text{not allowed}$$

Van der Waals Equation

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

Nb makes it impossible to compress to zero volume. The a term accounts for short range attractive forces. Low density gas $PV = NkT$, ignore particle interactions. $\langle v^2 \rangle = 3kT/m$. Compression $W = NkT \ln V_i/V_f$.

Maxwell Construction and phase transition

Phase transiton is a discontinous change in the substance properties when the surroundings changes infinitesimaly. Makes it possible to find the pressure at the phase transition from the PV-diagram, create straight line which makes even areas in the PV-line. Gives us the point of phase transition between liquid and gas. Gas at high volume, liquid at low volume. The intersected regions are unstable. The phase transition happens at constant PRESSURE! We find the pressure on the P-V diagram by the equal areas construction of a given isotherm. Phase transition from liquid to vapor at a constant Gibbs free energy $G(P, T, N)$, since the entropy effects the temperature dependence of the Gibbs, and the pressure effects the volume dependence of the gibbs, this connects the gibbs free energies $dG_{liquid} = dG_{gas}$.

Clausius Clapeyron relation

$$-S_l dT + V_l dP = -S_g dT + V_g dP$$

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$

Entropy jumps going from a liquid to a gas. Volume expansion going from a liquid to a gas. The Clausius Clapeyron relation tells us how much the phase transition pressure changes with changing temperature. Derivation: $dG = SdT + VdP + \mu dN$, Along the phase boundary where we at any point have chemical equilibrium between substances, the changes dG for solid and gas must be the same for changes dT and dP. $S_g dT + V_g dP = S_s dT + V_s dP$.

Sterlings approximation

$$N! \approx N^N e^{-N}\sqrt{2\pi N}$$
$$N! \approx N^N e^{-N}$$
$$\ln(N!) \approx N \ln N - N$$
$$\ln\binom{N}{n} \approx N \ln N - n \ln n - (N - n)\ln(N - n)$$

Maxwell relations

Functions are usually well behaved, so order of differential does not matter, can then use

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

By using thermodynamic identities for dU one can derive the maxwell relations, here they are

$$\frac{\partial^2 U}{\partial S \partial V} \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
$$\frac{\partial^2 H}{\partial S \partial P} \rightarrow \left(\frac{\partial T}{\partial P}\right)_S = +\left(\frac{\partial V}{\partial S}\right)_P$$
$$-\frac{\partial^2 F}{\partial T \partial V} \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$$
$$\frac{\partial^2 G}{\partial T \partial P} \rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Maxwell distribution

Derived from multiplying the probability of having velocity v, and the number of vectors corresponding to velocity v. Probability is $e^{-mv^2/2kT}$. Number of vectors corresponding to v is $4\pi v^2$. Find $D(v)$ by normalizing, $\int_0^\infty \mathrm{d}v\, D^{3D}(v) = 1$. get

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

Boltzmann statistics

Thermal Bath

Can only exchange energy, system + bath is isolated. Probability for the system to be in a specific microstate at fixed T: $P_i = \frac{1}{Z} e^{-E_i/kT}$, with the partition function: $Z = \sum_i e^{-E_i/kT}$, counts all accessible microstates weighted by the Boltzmann factor. The partition function determines the thermodynamic potential which is minimized at given T, V and N. Due to energy exchange with the thermal bath the equilibrium macrostate is an average

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z \qquad \text{equilibrium, reservoir}$$

$$\langle E^2 \rangle = -\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \qquad \text{equilibrium, reservoir}$$

Boltzmann distribution for the average number of particles (occupation number) in a given energy state

$$\langle N_s \rangle = N P(s) = e^{-\beta(E_s - \mu)}$$

We also have the following proerties

$$\langle A^n \rangle = \frac{1}{Z}\sum_i A^n e^{-E_i/kT}$$

$$U = N\langle E \rangle$$
$$F = -kT \ln Z$$
$$Z = e^{-F/kT}$$
$$S = \frac{U - F}{T}$$

The average occupation number of the given energy state ϵ at fixed T and μ in classical limit, using Boltzmann:

$$\langle n_B \rangle = \frac{1}{e^{(\epsilon - \mu)/kT}}$$

Dont have to use quantum statistics if $e^{(\epsilon-\mu)/kT} >> 1$, very little chance of two particles occupying same state.

$$N = \sum_{j=0}^\infty \frac{1}{e^{(\epsilon-\mu)/kT}} = e^{\mu/kT}\sum_{j=0}^\infty e^{-\epsilon/kT} = e^{\mu/kT} Z_1$$

Many particle partition function

$Z_{tot} = Z_1 Z_2 ... Z_N$ distinguishable, identical and independent

$Z_{tot} = \dfrac{Z^N}{N!}$ indistinguishable, identical and independent

If fixed number of particles a and b, which do not interact, in a solid, the partition function

$$Z_{total} = \binom{N}{N_a}(Z_1^a)^{N_a}(Z_1^b)^{N_b}$$

Two systems who are independent and distinguishable

$$Z_{tot} = Z_A Z_B$$

Thermal Bath and particle reservoir

System can exchange energy and particles with a reservoir. Equilibrium at a fixed T and μ. Probability of the system in a specific microstate at fixed T and μ

$$P(s) = \frac{1}{Z_g} e^{-\beta(E_s - \mu N_s)}, \qquad Z_g = \sum_s e^{-\beta(E_s - \mu N_s)}$$

Probability of the occupation number N of for given state is

$$P(s) = \frac{e^{-\beta N(E_s - \mu)}}{\sum_N e^{-\beta N(E_s - \mu)}}$$

From this one derives the quantum statistics:

Quantum Statistics

$$\text{Gibbs factor} = e^{-(E_s - \mu_s N_s)/kT}$$

$$\text{Grand partition function } Z = \sum_s e^{-(E_s - \mu_s N_s)/kT}$$

$$(\text{P of occup num at } \epsilon,\, T,\, \mu\,)\, P(N) = \frac{e^{-\beta N(\epsilon - \mu)}}{\sum_{N=0}^\infty e^{-\beta N(\epsilon-\mu)}}$$

$$v_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi m kT}}\right)^3$$

$$\text{quantum condition } Z_t = Z^N/N!: \quad \frac{V}{N} >> v_Q$$

$$Z = 1 + e^{-(\epsilon - \mu)/kT}$$

$$P(N) = \frac{e^{-\beta N(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}}$$

$$\langle n_{FD} \rangle = \sum_N P(N) N = \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}} = \frac{1}{1 + e^{(\epsilon-\mu)/kT}}$$

$\langle n_{FD} \rangle$ is the average occupation number of the given energy state ϵ at fixed T and μ.

BOSONS:

$$Z = 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT} + ... = \left(1 - e^{-\beta(\epsilon-\mu)}\right)^{-1}$$

$$P(N) = e^{-\beta N(\epsilon-\mu)}\left(1 - e^{-\beta(\epsilon-\mu)}\right)$$

$$\langle n_{be} \rangle = \sum_N P(N) N = Z^{-1}\sum_N N e^{-N\beta(\epsilon-\mu)} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1}$$

$\langle n_{BE} \rangle$ is the average occupation number of the given energy state ϵ at fixed T and μ. The distribution becomes the boltzmann distribution in the limit $\beta(\epsilon - \mu) \to \infty$ and $\beta \to 0$. In the limit $T \to 0$ all states with energy less than μ will be filled, called degenerate gas, has zeror entropy.
For quantum statistics to be nessecary $V/N << v_Q$, same as $kT << \epsilon_F$.

Density of state

Average energy:

$$U = \sum_{n_x, n_y, n_z} \langle N(\epsilon) \rangle \epsilon(n) = \int_0^\infty \mathrm{d}\epsilon\, g(\epsilon) \cdot \epsilon \cdot \langle n \rangle$$

$$U = \int_0^{\epsilon_F} \epsilon\, g(\epsilon) \mathrm{d}\epsilon \qquad (T = 0)$$

Average number of particles

$$N(T, V, \mu) = \int_0^\infty \mathrm{d}\epsilon\, g(\epsilon)\langle n \rangle$$

$$N = \int_0^{\epsilon_F} g(\epsilon)\mathrm{d}\epsilon \qquad (T = 0)$$

$$N = \sum_{j=0}^\infty \langle n(\epsilon_j) \rangle$$

Density of state $g(\epsilon)$ to count all the quantum states at a given energy ϵ. The number of states with energy between ϵ and $\epsilon + \mathrm{d}\epsilon$ = Number of states with state number between n and $n + \mathrm{d}n$ (positive quadrant). Different for different dimensions

$$\boxed{g(n)\mathrm{d}n =} \quad (3D)\,\frac{1}{8}4\pi n^2 \mathrm{d}n, \quad (2D)\,\frac{1}{4}2\pi n\mathrm{d}n, \quad (1D)\mathrm{d}n$$

the energy is determined by quantum mechanics

- particle in a box: $\epsilon(n) = h^2 n^2/(8mL^2)$
- harmonic oscillator: $\epsilon(n) = n\hbar\omega$
- relativistic particles: $\epsilon(n) = hf = hcn/(2L)$

$$g(\epsilon)\mathrm{d}\epsilon = D(n)\mathrm{d}n \to g(\epsilon) = \frac{D(n)}{\frac{\mathrm{d}\epsilon}{\mathrm{d}n}}$$

$$\epsilon_F(N) = \epsilon(n_{max})$$
$$\epsilon_F = \mu \qquad (T = 0)$$

$$N_{3D} = 4\pi n_{max}^3/(8 \cdot 3), \quad N_{2D} = 2\pi n_{max}^2/4, \quad N_{1D} = 2n_{max}$$

$$U(T, V, \epsilon_F) = \int_0^{\epsilon_F} \mathrm{d}\epsilon\, g(\epsilon)\,\epsilon$$

$$N(T, V, \epsilon_F) = \int_0^{\epsilon_F} \mathrm{d}\epsilon\, g(\epsilon)$$

For FERMIONS multiply by 2, spin up and spin down.
For PHOTONS multiply by 2, for the two transverse polarization of EM waves, $\mu = 0$.
For PHONONS multiply by 3, for all three polarizations of the sound waves.
For a fermi gas at $T = 0$ all states with $\epsilon < \epsilon_F$ are occupied, while all states with $\epsilon > \epsilon_F$ are unoccupied.
If $g(\epsilon)$ is greater above ϵ_F than below $\epsilon_F \to \mu$ will decrease as T increases, as the total area has to be the same (since we can not create particles by increasing the temperature). If $g(\epsilon)$ increases with ϵ while $\langle n_{FD}(\epsilon) \rangle$ is symmetric about μ, leading to an increasing number $N(T)$ if μ is held fixed.

Integrals

$$\int_0^\infty \frac{x^3}{e^{bx} - 1} = \frac{\pi^4}{15b^4}$$

$$\int_0^\infty \frac{x^3}{e^{bx} + 1} = \frac{7\pi^4}{120b^4}$$

$$\int_0^\infty x^n e^{-x/a}\mathrm{d}x = n! a^{n+1}$$

Taylor expansions

$$\ln(1 + x) \approx x - x^2/2$$

$$\sinh x = \sum_{n=0} \frac{x^{2n+1}}{(2n+1)!} \approx x + x^3/3!$$

$$\cosh x = \sum_{n=0} \frac{x^{2n}}{2n!} \approx 1 + x^2/2!$$

$$\tanh x \approx x - x^3/3 + 2x^5/15$$

$$\sqrt{1 + x} = 1 + \frac{x}{2} - \frac{x^2}{8}$$

Definitions

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

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

$$\cosh(\operatorname{arctanh} x) = \frac{1}{\sqrt{1 - x}}$$

$$\cosh(\operatorname{arcsinh} x) = \sqrt{1 + x^2}$$

$$\frac{\partial}{\partial x}(\cosh x) = \sinh x \qquad \frac{\partial}{\partial x}(\sinh x) = \cosh x$$

Tricks

$$\sum^N \frac{N!}{n!(N-n)!} a^n b^{N-n} = (a + b)^N$$

$$\sum_n^N n\frac{N!}{n!(N-n)!} a^n b^{N-n} = a\frac{\partial}{\partial a}\sum_n^N \frac{N!}{n!(N-n)!}a^n b^{N-n}$$

$$R p^R = p\frac{\partial}{\partial p} R^p$$

$$\frac{1}{1 - x} = 1 + x + x^2 + x^3 + ...$$

$$\text{Surface area sphere in d dimensions} = \frac{2\pi^{d/2}}{\left(\frac{d}{2} - 1\right)!} r^{d-1}$$

$$\sum_{n=0}^\infty n e^{-an} = \frac{e^a}{(e^a - 1)^2}$$

$$\sum_{n=0}^\infty n x^n = \frac{x}{(1 - x)^2}$$

Examples

Degrees of freedom, H2O

3 translational d.o.f. Since such a molecule has no symmetry axis, like a diatomic molecule has, there are 3 rotational d.o.f. Three possible modes/motions of vibration: two atomic bonds (connecting the two H-atoms to the O-atom) which can stretch/contract, and there can be a flexing motion where the angle at which the two H-atoms are bound to the O-atom increases/decreases (the H-atoms move towards and away from each other). For each of these three vibrational modes there are 2 d.o.f. Total 12.

Quantum Ideal Gas

$$\epsilon_n = \frac{\vec{p} \cdot \vec{p}}{2m} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$Z_1(T, V) = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{\frac{-h^2\left(n_x^2 + n_y^2 + n_z^2\right)}{8mL^2 kT}} = \left(\sum_n e^{\frac{-h^2 n^2}{8mL^2 kT}}\right)$$

$$Z_1(T, V) \approx_{highT} \frac{1}{2}\int_{-\infty}^\infty \mathrm{d}n\, e^{\frac{-h^2 n^2}{8mL^2 kT}} = \frac{V}{\Lambda^3(T)}, \Lambda = \sqrt{\frac{h}{2\pi m}}$$

$$Z_N(T, V) = \frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N$$

$$F_N = -kT \ln Z_N(T, V) = -NkT\left(\ln\left(\frac{V}{N\Lambda^3(T)}\right) - 1\right)$$

$$\mu(T, V) = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\left(\frac{V}{N\Lambda^3(T)}\right)$$

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

$$U = -\frac{\partial}{\partial \beta}\left(\ln Z_N(T, V)\right) = 3NkT/2$$

$$S = \frac{U - F}{T} = Nk\left[\ln\left(\frac{V}{N\Lambda^3(T)}\right) + \frac{5}{2}\right]$$

Reversible processes

Use Clausius inequality, and find Q, integrate to find change in entropy. Only true for reverislbe processes.
Isothermal process: $T_1 = T_2$, $\Delta U = 0$, $W = -NkT\ln V_2/V_1$, $\Delta S = Q/T = -W/T$.
Isobaric process: $P_1 = P_2$, $\Delta U = C_P \mathrm{d}T = T\mathrm{d}S - P\mathrm{d}V$, $W = -P(V_2 - V_1)$, $\Delta S = \int \delta Q/T = C_P\int \mathrm{d}T/T = C_P \ln T_2/T_1$.
Adiabatic process: $Q = 0$, $\Delta U = C_V \mathrm{d}T = -P\mathrm{d}V$, put in for ideal gas and integrate $T_2/T_1 = (V_1/V_2)^{C_P/C_V - 1}$, $W = -\int P\mathrm{d}V = C_V(T_2 - T_1)$, $\Delta S = 0$.
Isochoric process: $V_1 = V_2$, $\Delta U = C_V \mathrm{d}T = -T\mathrm{d}S$, $W = 0$, $\Delta S = \int Q/T = C_V\int \mathrm{d}T/T = C_V \ln T_2/T_1$.

Planck distribution

For photons are bosons with $\mu = 0$, means that the number of photons is not conserved, will always fluctuate around an equilibrium value minimizing F for given T and V. For a photon gas in a container, photons are all the time absorbed and re-emitted from the walls, $\epsilon = hcn/(2L)$.

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\epsilon^3}{(hc)^3(e^{\epsilon/kT} - 1)} = \frac{8\pi^5(kT)^4}{15(hc)^3}$$

$$C_V(T) = \frac{32\pi^5 k(kT)^3}{15(hc)^3}$$

$$S(T) = \frac{32\pi^5 Vk}{45}\left(\frac{kT}{hc}\right)^3$$

Derivation of thermodynamic identity

First change the energy with constant volume, than change volume with constant energy. $\Delta S = (\Delta S)_1 + (\Delta S)_2$. Multiply first term with $\mathrm{d}U$, second term with $\mathrm{d}V$: $\Delta S = (\Delta S/\mathrm{d}U)_V \mathrm{d}U + (\Delta S/\mathrm{d}V)_U \mathrm{d}V$, using identities we get $\Delta S = 1/T\mathrm{d}U - P\mathrm{d}V$.