

Units and Values

Avogadro’s number: $N_A = 6.023 \times 10^{23}$
Boltzmann’s cosntant: $k = 1.381 \times 10^{-23} J/K$,
 $R = 8.31J/Kmol$, $nR = Nk$.
Calorie: 1cal = 4.2J (amount of heat needed to raise the tem-
perature of a gram of water by 1°C.)
Absolute zero: 0K = −273.15°C.

Definitions

Isotherm: constant temperature
Isobar: constant pressure
Isothermal compression: so slow that temperature does not rise
Adiabatic compression: so fast heat does not escape
fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible micro-
states are equally probable
thermodynamic limit: Let number of particles go to infinity

Important formulas

$$\Omega_{total}(N,n)=\Omega_A(N,n)\Omega_B(N,n)$$
$$N!\approx N^N e^{-N}\sqrt{2\pi N}$$
$$\ln(N!)\approx N\ln N-N$$
$$P=T\left(\frac{\partial S}{\partial V}\right)_{U,N}\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{N,V} \quad \text{(isolated system)}$$
$$\text{Clausius} \quad \Delta S \geq \frac{dQ}{T} \rightarrow TdS = dU + pdV \quad \text{reversible}$$
$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$
$$C_V \rightarrow \text{constant} \quad \text{as} \quad T \rightarrow \infty$$
$$\Delta S = 0 \rightarrow \text{reversible}$$
$$\Delta S \geq 0 \rightarrow \text{irreversible}$$
$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \quad \text{(at equilibrium)}$$
$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad \text{(at equilibrium)}$$
$$dU = TdS - PdV$$
$$dU = TdS - PdV + \mu dN$$
$$\frac{\partial F}{\partial N} = \mu$$
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

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

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 indis-
tinhuishable particles (we get 1/N!)

$$\Omega(U,V,N) = f(N)V^N U^{3N/2} \approx \frac{V^N}{N!(3N/2)!} (2\pi mU/h^2)^{3N/2}$$
$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$
$$\Delta S = Nk \ln V_f/V_i \quad (U, N \text{ fixed})$$

Equipartition theorem

For each quadratic degree of freedom (kinetic v^2 , spring k^2 , ro-
tational ω^2 , etc.) contributes to $1/2kT$ to the average energy at equilibrium at temperature T . For N particles with f de-
grees 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.
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

$$\Delta U = Q + W \tag{1}$$

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

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

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 $c = C/m$.

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

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 latm, and no other work.

Adiabatic compression

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

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

Two state system

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

$$\Omega(N,n) = \frac{N!}{N_\uparrow!(N-N_\uparrow)!} = \frac{N!}{N_\uparrow!N_\downarrow!} \tag{2}$$

Einstein solid

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

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \approx \frac{(q+N)!}{q!N!} N_\downarrow! \tag{3}$$

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

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

thermodynamic potentials

- Internal Energy: U Total thermal energy of the system
- 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
- Helmholtz free energy: $F = U - TS$, $\Delta G \leq W_{other}$ (constant pressure). Total energy needed to create the system, minus the heat you get from enviornment. Minimized in thermal bath, with only energy exchange.
 $\mu = \frac{\partial F}{\partial N}, -S = \frac{\partial F}{\partial T}$
- Gibbs free energy: $G = U - TS + PV$, Create system in constant temperature and pressure. Minimized when change in volume with constant pressure. $\mu = \frac{\partial G}{\partial N}$,
 $V = \frac{\partial G}{\partial P}, -S = \frac{\partial G}{\partial T}$

At constant U and T , S increases.
At constant V and T , F decreases.
At constant T and P , G decreases.

Extensive and Intensive Quantities

An extensive quantity doubles when you double a system. The quantities which are unchanged when you double the sys-
tem are intensive.

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

- **Intensive**: T, P, μ , density

extensive \times intensive = extensive
 $\frac{\text{extensive}}{\text{extensive}} = \text{intensive}$
extensive \times extensive = neither, you did something wrong
extensive + extensive = extensive
extensive + intensive = 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

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 vo-
lume. The intersected regions are unstable

Tricks

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

Thermodynamic identities

$$dU = TdS - PdV - \mu dN \tag{4}$$

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

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

Boltzmann statistics

$$P_i = \frac{1}{Z} e^{-E_i/kT}$$
$$Z = \sum_i e^{-E_i/kT}$$
$$\langle A^n \rangle = \frac{1}{Z} \sum_i A^n e^{-E_i/kT}$$
$$\langle E \rangle = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial}{\partial \beta} \ln Z \quad \text{equilibrium, reservoir}$$
$$\langle E^2 \rangle = - \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad \text{equilibrium, reservoir}$$
$$U = N \langle E \rangle$$
$$F = -kT \ln Z$$
$$Z = e^{-F/kt}$$
$$Z_{total} = Z_1 Z_2 Z_3 \dots Z_N \quad \text{non-interacting distinguishable}$$
$$Z_{total} = \frac{Z^N}{N!} \quad \text{non-interacting indistinguishable}$$

Maxwell distribution

Derived from multiplying the probability of having velocity v , and the number of vectors corresponding to velocity v . Probabi-
lity is $e^{-mv^2/2kT}$. Number of vectors corresponding to v is $4\pi v^2$. Find $D(v)$ by normalizing. Find

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

Quantum Statistics

$$\text{Gibbs factor} = e^{-(E(i) - \mu_A(i) N_A(i))/kT}$$
$$\text{Gibbs factor, two particles} = e^{-(E(i) - \mu_A(i) N_A(i))/kT}$$
$$\text{Grand partition function } Z = \sum_i e^{-(E_i - \mu_i N_i)/kT}$$
$$v_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi m kT}} \right)^3$$
$$\text{condition } Z_t = Z^N/N!: \quad \frac{V}{N} \gg v_Q$$

FERMIONS:

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

BOSONS:

$$Z = 1 + e^{-(\epsilon - \mu)/kT} + e^{-2(\epsilon - \mu)/kT} + \dots$$
$$\langle n_{BE} \rangle = \frac{1}{1 - e^{(\epsilon + \mu)/kT}}$$

Density of state

$$g(\epsilon) d\epsilon = D(n) dn \rightarrow g(\epsilon) = \frac{D(n)}{\frac{d\epsilon}{dn}}$$

Taylor expansions

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