

Units and Values

Avogadro’s number: $N_A = 6.023 \times 10^{23}$
Boltzmann’s cosntant: $k = 1.381 \times 10^{-23} J/K$,
 $R = 8.31 J/Kmol$, $nR = Nk$.
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.

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

$$\Omega_{total}(N, n) = \Omega_A(N, n)\Omega_B(N, n)$$
$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$
$$\ln(N!) \approx N \ln N - N$$

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

(isolated system)

$$\text{Clausius} \quad \Delta S \geq \frac{dQ}{T} \rightarrow TdS = dU + p dV \quad \text{reversible}$$
$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$
$$C_V \rightarrow \text{constant} \quad \text{as} \quad T \rightarrow \infty$$
$$\Delta S = 0 \quad \rightarrow \quad \text{reversible}$$
$$\Delta S \geq 0 \quad \rightarrow \quad \text{irreversible}$$
$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \quad (\text{at equilibrium})$$
$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad (\text{at equilibrium})$$
$$dU = TdS - PdV$$
$$dU = TdS - PdV + \mu dN$$
$$\frac{\partial F}{\partial N} = \mu$$
$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

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 indistinguishable 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 , rotational ω^2 , etc.) contributes to $1/2kT$ to the average energy at equilibrium 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), vibrate 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 monatomic 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

$$\Delta U = Q + W$$

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.

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

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

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

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

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

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: $F = U - TS$, (constant pressure). Total energy needed to create the system, minus the heat you get from enviornment. Thermodynamic identity: $dF = -SdT - PdV + \mu dN$. Minimized in thermal bath, with only energy exchange. $\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V}, S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}, P = - \left(\frac{\partial F}{\partial V} \right)_{T, N}$.
- Gibbs free energy: $G = U - TS + PV$, $\Delta G \leq W_{other}$. Create system in constant temperature and pressure. Minimized when change in volume with constant pressure. $\mu = \frac{\partial G}{\partial N}, V = \frac{\partial G}{\partial P}, -S = \frac{\partial G}{\partial T}$
- Chemical potential $\mu = \left(\frac{\partial G}{\partial N} \right)_{T, P}$. The energy increase by adding a particle in to the system with constant temperature and pressure.

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 system are intensive.

- **Extensive**: V, N, S, U, H, F, G , mass
- **Intensive**: T, P, μ , density

extensive \times intensive = extensive
extensive = 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 volume. The intersected regions are unstable

Tricks

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

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

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

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

Thermodynamic identities

$$dU = TdS - PdV - \mu dN$$

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, $\int_0^\infty dv D^{3D}(v) = 1$. 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 macro-state is an average

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

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

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

$$\langle N_s \rangle = NP(s) = e^{-\beta(E_s - \mu)} \quad (5)$$

We also have the following proerties

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

$$U = N \langle E \rangle$$

$$F = -kT \ln Z$$

$$Z = e^{-F/kT}$$

$$Z_{tot} = Z_1 Z_2 \dots Z_N \text{ distinguishable, identical and independent}$$

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

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

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

Can be showed that the probability of the occupation number N of the 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

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

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

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

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

FERMIONS:

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

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

BOSONS:

$$Z = 1 + e^{-(\epsilon - \mu)/kT} + e^{-2(\epsilon - \mu)/kT} + \dots$$

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

The distribution becomes the boltzmann distribution in the high T limit ($\beta 0$)

Density of state

Average energy:

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

Average number of particles

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

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

$$\boxed{g(\epsilon) \mathrm{d}\epsilon = } \quad (3D) \frac{1}{8} 4 \pi n^2 \mathrm{d}n, \quad (2D) \frac{1}{4} 2 \pi n \mathrm{d}n, \quad (1D) \mathrm{d}n \quad (6)$$

the energy is determined by quantum mechanics

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

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

For **FERMIONS** multiply by 2, spin up and spin down.
For **PHOTONS** multiply by 2, for the two transverse polarization of EM waves.
For **PHONONS** multiply by 3, for all three polarizations of the sound waves.

Integrals

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

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

Taylor expansions

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

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, $\mathrm{d}S = 0$.

$$T \mathrm{d}S = \frac{1}{T} \mathrm{d}U + \frac{P}{T} \mathrm{d}V - \frac{\mu}{T} \mathrm{d}N \tag{7}$$

Quantum Ideal Gas

$$\epsilon_n = \frac{\vec{p} \cdot \vec{p}}{2m} = \frac{\hbar^2}{8mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$
$$Z_1(T, V) = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{\frac{-\hbar^2 \left(n_x^2 + n_y^2 + n_z^2 \right)}{8mL^2 kT}} = \left(\sum_n e^{\frac{-\hbar^2 n^2}{8mL^2 kT}} \right)^3$$
$$Z_1(T, V) \approx_{highT} \frac{1}{2} \int_{-\infty}^\infty \mathrm{d} n e^{\frac{-\hbar^2 n^2}{8mL^2 kT}} = \frac{V}{\Lambda^3(T)}, \Lambda = \sqrt{\frac{\hbar}{2\pi m kT}}$$
$$Z_N(T, V) = \frac{1}{N!} \left(\frac{V}{\Lambda^3(T)} \right)^N$$
$$F_N = -kT \ln Z_N(T, V) = -NkT \left(\ln \left(\frac{V}{N\Lambda^3(T)} \right) - 1 \right)$$
$$\mu(T, V) = \left(\frac{\partial F}{\partial N} \right)_{T, V} = -kT \ln \left(\frac{V}{N\Lambda^3(T)} \right)$$
$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N} = \frac{kT}{V}$$
$$U = - \frac{\partial}{\partial \beta} \left(\ln Z_N(T, V) \right) = 3NkT/2$$
$$S = \frac{U - F}{T} = Nk \left[\ln \left(\frac{V}{N\Lambda^3(T)} \right) + \frac{5}{2} \right]$$