

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
Adiabat: Process with constant entropy

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

$$\Omega_{total}(N, n) = \Omega_A(N, n)\Omega_B(N, n)$$
$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$
$$C_V \rightarrow \text{constant} \quad \text{as} \quad T \rightarrow \infty$$
$$\Delta S = 0 \quad \rightarrow \quad \text{reversible}$$
$$\Delta S \geq 0 \quad \rightarrow \quad \text{irreversible}$$

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), vibrating 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

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

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, po-
sitive work means the outside is doing work on the gas.

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

Heat Capacity

Heat capacity: amount of energy 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 1atm, 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 di-
mensions with $q = (U_n - N\hbar\omega/2)/\hbar\omega$ units of energy

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

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

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

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 thermodynamic). 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 enviornment. Thermodyna-
mic 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: $G = U - TS + PV$, $\Delta G \leq W_{other}$. Create system in constant temperature and pressure. Minimized when change in volume with constant pressure. $dG = -SdT + VdP + \mu dN$.
 $\mu = \frac{\partial G}{\partial N}, V = \frac{\partial G}{\partial P}, -S = \frac{\partial G}{\partial T}$
- Chemical potential $\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$. The energy in-
crease by adding a particle in to the system with con-
stant temperature and pressure.

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: $dS = \delta Q_{rev}/T$.
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 en-
tropy 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 like-
ly 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

$$\begin{aligned} \frac{\partial S_A}{\partial U_A} &= \frac{\partial S_B}{\partial U_B} & (\text{at equilibrium}) \\ \frac{\partial S_A}{\partial V_A} &= \frac{\partial S_B}{\partial V_B} & (\text{at equilibrium}) \\ \frac{\partial S_A}{\partial N_A} &= \frac{\partial S_B}{\partial N_B} & (\text{at equilibrium}) \end{aligned}$$

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.
The phase transition happens at constant PRESSURE! We find
the pressure on the P-V diagram by the equal areas construc-
tion of a given isotherm. Phase transition from liquid to va-
por at a constant Gibbs free energy $G(P, T, N)$, $dG_{liquid} =$
 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.

Sterlings approximation

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

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

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

Maxwell distribution

Derived from multiplying the probability of having velocity v ,
and the number of vectors corresponding to velocity v . Prob-
ability 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. Probabil-
ity 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 en-
ergy 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 (oc-
cupation number) in a given energy state

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

We also have the following proerties

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

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

$$F = -kT \ln Z$$

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

$$S = \frac{U - F}{T}$$

Many particle partition function

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

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

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

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

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

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

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

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

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

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

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

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

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

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: $\epsilon(n) = \hbar f = \hbar c n / (2L)$

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

Quantum Ideal Gas

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

$$Z_1(T, V) = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{\frac{-\hbar^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2 kT}} = \left(\sum_n e^{\frac{-\hbar^2 n^2}{8mL^2 kT}} \right)^3$$

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

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

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

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

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

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

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

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

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

$$\sinh x = \sum_{n_0} \frac{x^{2n+1}}{(2n+1)!}$$

$$\cosh x = \sum_{n_0} \frac{x^{2n}}{2n!}$$

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

Tricks

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

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

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

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

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.