

Exchanged quantity	Type of equilibrium
Energy	Thermal
Volume	Mechanical
Particles	Diffusive

Theoretical definition of temperature

Temperature is the thing that's the same for two objects, after they've been in contact long enough.

The Laws of Thermodynamics

The first law

$$\Delta U = Q + W,$$

Heat: any spontaneous flow of energy due to difference in temperature between objects. Work: any other transfer of energy into or out of a system. The first law is just a statement about energy conservation. Heat transfer is divided into: Conduction, convection, radiation.

The second law:

Any large system in equilibrium will be found in the macrostate with the greatest entropy (aside from fluctuations that are normally too small to measure.) Entropy tends to increase.

The third law:

At zero temperature, a system should settle into its unique lowest energy-state, so $\Omega = 1$ and $S = 0$. This also means that $C_V \rightarrow 0$ as $T \rightarrow 0$.

The Ideal Gas

The ideal gas law (the equation of state for an ideal gas):

$$PV = NkT = nRT$$

Where

$$N = n \times N_A, \quad nR = Nk$$

The temperature of an ideal gas says something about the average kinetic energy of the gas molecules

$$\overline{K}_{\text{trans}} = \frac{3}{2}kT, \quad v_{\text{rms}} \equiv \sqrt{v^2} = \sqrt{\frac{3kT}{m}}$$

Heat capacities

$$C_P = C_V + Nk = C_V + nR$$

Macroscopic model of ideal gas

A cylinder contains a single gas-molecule, colliding elastically with the walls. The pressure from the "gas" on the area A equals average force over time

$$\bar{P} = \frac{\bar{F}}{A} = \frac{mv_x^2}{AL} = \frac{mv_x^2}{V}.$$

Now assume N non-interacting particles, when N is large, the instantaneous pressure equals the average

$$PV = Nm\overline{v_x^2} \Rightarrow m\overline{v_x^2} = kT.$$

Using the same argument for y and z gives

$$\overline{K}_{\text{molecules}} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{3}{2}kT.$$

and we define

$$v_{\text{rms}} \equiv \sqrt{v^2} = \sqrt{\frac{3kT}{m}}$$

Compression Work

$$W = \vec{F} \cdot d\vec{r}$$

$$W = -P dV \quad (\text{quasistatic})$$

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

Compression of Ideal Gas

Generally for a quasistatic process:

$$PV^\alpha = K; \quad \alpha = \frac{C - C_P}{C - C_V}; \quad \Delta S = C \ln \frac{T_f}{T_i}$$

$$W = \frac{K}{\alpha - 1} \left(\frac{1}{V_f^{\alpha-1}} - \frac{1}{V_i^{\alpha-1}} \right), \quad Q = C\Delta T$$

Isothermal

$$PV = NkT = \text{const.} \Rightarrow \alpha = 1. \quad C \rightarrow \infty$$

$$Q = -W = NkT \ln \frac{V_f}{V_i}, \quad \Delta S = \frac{Q}{T} = Nk \ln \frac{V_f}{V_i}$$

Adiabatic

$$VT^{f/2} = \text{const.}, \quad PV^\gamma = \text{const.}, \quad \alpha = \gamma = \frac{f+2}{f}$$

$$Q = 0 \Rightarrow C = 0 \Rightarrow \Delta S = 0$$

Isochoric

$$W = 0; \quad Q = C_V \Delta T; \quad \Delta S = C_V \ln \frac{T_f}{T_i}$$

Isobaric

$$C = C_P \Rightarrow \alpha = 0; \quad W = -P\Delta V$$

$$\Delta S = C_P \ln \frac{T_f}{T_i}; \quad Q = C_P \Delta T$$

Equipartition of Energy

Equipartition theorem: At temperature T , the average energy of any quadratic degree of freedom is $\frac{1}{2}kT$. If a system contains N molecules, each with f degrees of freedom, and there are no other (non-quadratic) temperature-dependant forms of energy, then its total thermal energy is

$$U_{\text{thermal}} = N \cdot f \cdot \frac{1}{2}kT.$$

Where f denotes the degrees of freedom.

- Spatial translation—3 degrees of freedom, x , y , and z .
- Rotation—2 degrees of freedom for diatomic gas, 3 degrees for a polyatomic gas.
- Vibration—2 degrees per vibration mode, one for kinetic, and one for potential. For diatomic gases, there are 2 degrees of freedom, but they are usually frozen out at room temperature. For solids we have 6 rotational degrees of freedom (one vib. mode in each dir. x , y , and z).

Heat Capacity

The heat capacity of an object is the the amount of heat needed to raise it's temperature, per degree temperature increase:

$$C \equiv \frac{Q}{\Delta T}.$$

Specific heat capacity is heat capacity per unit mass:

$$c \equiv \frac{C}{m}.$$

This definition is ambiguous!

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}.$$

We define heat capacity when $W = 0$, meaning $\Delta V = 0$

$$C_V = \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (\text{energy capacity})$$

and when $P = \text{const.}$, meaning $W = -P\Delta V$

$$C_P = \left(\frac{\Delta U + P\Delta V}{\Delta T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P.$$

If we only have quadratic degree of freedom, we can use the equipartition principle

$$C_V = \frac{d}{dT} N f \frac{1}{2} kT = \frac{f}{2} N k = \frac{f}{2} nR.$$

For ideal gas we have

$$C_P = C_V + Nk = C_v + nR.$$

Latent heat

$$C = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty \quad (\text{during a phase transformation})$$

$$L \equiv \frac{Q}{m}$$

The latent heat for boiling water is 2260 J/g, or 540 cal/g.

Two-state systems

Multiplicity of n heads when N coins are flipped:

$$\Omega(N, n) = \frac{N!}{n! \cdot (N - n)!} = \binom{N}{n}$$

Two-State Paramagnet

System consists of N dipoles that can point up or down

$$\Omega(N_{\uparrow}) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}! N_{\downarrow}!}$$

The Einstein Model of a Solid

System consists of N oscillators with q units of energy shared between them. Stars and bars then gives

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

For a large Einstein solid we can approximate the multiplicity

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

Using coarse Stirling

$$\ln \Omega = (q + N) \ln(q + N) - N \ln N - q \ln q$$

High-temperature approximation $q \gg N$:

$$\Omega(N, q) \approx \left(\frac{eq}{N} \right)^N$$

Low-temperature approximation $N \ll q$:

$$\Omega(N, q) \approx \left(\frac{eN}{q} \right)^q$$

Sharpness of the Multiplicity Function

Two Einstein solids with N oscillators share a total of q units of energy. Using high-temperature approx ($q \gg N$):

$$\Omega = \Omega_A \Omega_B = \left(\frac{eq_A}{N} \right)^N \left(\frac{eq_B}{N} \right)^N = \left(\frac{e}{N} \right)^{2N} (q_a q_b)^N$$

Which has a peak of height

$$\Omega_{\max} = \left(\frac{e}{N} \right)^{2N} \left(\frac{q}{2} \right)^{2N}$$

We now look at multiplicity close to maximum, so

$$q_A = \frac{q}{2} + x, \quad q_B = \frac{q}{2} - x,$$

where x is any number much smaller than q .

$$\Omega = \left(\frac{e}{2N} \right)^{2N} \left[\left(\frac{q}{2} \right)^2 - x^2 \right]^N$$

$$\ln \left[\left(\frac{q}{2} \right)^2 - x^2 \right]^N \approx N \left[\ln \left(\frac{q}{2} \right)^2 - \left(\frac{2x}{q} \right)^2 \right]$$

Exponentiating back

$$\Omega = \left(\frac{e}{N} \right)^{2N} \left(\frac{q}{2} \right)^{2N} e^{-N(2x/q)^2} = \Omega_{\max} \cdot e^{-N(2x/q)^2}$$

which is a Gaussian function.

Multiplicity of a monatomic ideal gas

$$\Omega_N \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2mU})^{3N}$$

$$\Omega(U, V, N) = f(N) V^N U^{3N/2}$$

General theorem: For any system with only quadratic degrees of freedom, having so many units of energy that energy quantization is unnoticeable (high-temp limit), the multiplicity is proportional to $U^{Nf/2}$, where Nf is the total number of degrees of freedom.

Fundamental assumption of statistical mechanics

In an isolated thermal equilibrium, all accessible microstates are equally probable.

This is a result of detailed balance, any process that takes the system from X to Y is reversible, so the system can just as easily go from Y to X . (Microscopic T -symmetry).

Very Large Numbers

Large numbers are much larger than small numbers, and are frequently made by exponentiating small numbers. The most important property of large numbers is that you can add a small number to large number without changing it

$$10^{23} + 23 = 10^{23}$$

Very large numbers are even larger than large numbers and can be made by exponentiating large numbers. Very large numbers have the property that you can multiply them by large numbers without changing them

$$10^{10^{23}} \cdot 10^{23} = 10^{10^{23}+23} = 10^{10^{23}}$$

Stirling's Approximation

Fine	$N! \approx N^N e^{-N} \sqrt{2\pi N}$
Coarse	$N! \approx N^N e^{-N}$
Coarse	$\ln N! \approx N \ln N - N$

Approximations

For two numbers $a \gg b$ we can approximate (Taylor)

$$\ln(a+b) = \ln a + \ln\left(1 + \frac{b}{a}\right) \approx \ln a + \frac{b}{a}$$

For a small number $|\epsilon| \ll 1$ we can approximate (Taylor):

$$(1+\epsilon)^q \approx 1 + q\epsilon$$

For $x \ll 1$ we have

$$\frac{1}{1-e^{-x}} \approx \frac{1}{x}$$

Entropy

$$S \equiv k \ln \Omega$$

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

Sackur-Tetrode Equation

For a monatomic ideal gas

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$

for distinguishable particles, replace $5/2$ with $3/2$ and V/N with N .

Entropy of Mixing

For an ideal gas, a volume change gives a change in entropy

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

if we consider a box with a partition containing gas of A and gas of B . Removing the partition gives change in entropy

$$\Delta S = \Delta S_A + \Delta S_B = Nk \ln 2 + Nk \ln 2 = 2Nk \ln 2$$

If we look at N total particles, let x be the fraction of the particles that are of species B , this gives

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

Reversible

Any process where $\Delta S_{\text{Total}} = 0$, is reversible. Vice versa we have that any process that universally creates new entropy must be irreversible.

Temperature

At thermal equilibrium

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \Rightarrow \frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N,V}$$
$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

Pressure

At mechanical equilibrium

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \Rightarrow P = T \left(\frac{\partial S}{\partial U} \right)_{U,N}$$

Chemical potential

At diffusive equilibrium

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$
$$\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{U,V}, \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}$$

The chemical potential is the quantity that is the same for two systems when they are in diffusive equilibrium. If two systems are not in diffusive equilibrium, the system with the highest chemical potential will spontaneously lose particles to a system with a lower chemical potential.

Measuring entropy

$$ds = \frac{dU}{T} = \frac{Q}{T}, \quad dS = \frac{C_V}{T} dT$$

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

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT'$$

Thermodynamic Potentials

Enthalpy

$$H \equiv U + PV$$

Helmholtz free energy

$$F \equiv U - TS$$

Gibbs free energy

$$G \equiv U - TS + PV$$

PV : work needed to make room for system in a constant-pressure environment.

TS : heat that needs to be dumped to get rid of a system's entropy in a constant-temperature environment.

$$\Delta H = \Delta U + P\Delta V = Q + W_{\text{other}} \quad (\text{constant } P)$$

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S \leq W \quad (\text{constant } T)$$

$$\Delta G = Q + W + P\Delta V - T\Delta S \leq W_{\text{other}} \quad (\text{constant } P, T)$$

The Thermodynamic Identities

$$dU = T dS - P dV + \mu dN$$

$$dH = T dS + V dP + \mu dN$$

$$dF = -S dT - P dV + \mu dN$$

$$dG = -S dT + V dP + \mu dN$$

$$T = \left(\frac{\partial H}{\partial S} \right)_{P,N} \quad V = \left(\frac{\partial H}{\partial P} \right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{S,P}$$

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

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

Maxwell Relation

Mixed partial derivatives are independent of order

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

Using the thermodynamic identity to evaluate the derivatives in the fraction we find

$$\left(\frac{\partial T}{\partial V} \right)_S = -\left(\frac{\partial P}{\partial S} \right)_V$$

Force towards equilibrium

It is the entropy of the system and reservoir combined that always increases, so we have

Constant	Force towards equilibrium
U, V	S tends to increase
T, V	F tends to decrease
T, P	G tends to decrease

Extensive/Intensive

Extensive : $V, N, U, H, F, G, \text{mass}$

Intensive : $T, P, \mu, \text{density}$

extensive \times intensive = extensive
 extensive / extensive = intensive
 extensive + extensive = extensive
 intensive + intensive = intensive
 intensive + extensive (Not allowed)

Gibbs Free Energy and Chemical Potential

From Gibbs free energy:

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$$

When a particle is added to the system, the Gibbs free energy increases by μ , and μ can't change as particles are added, as T and P are held fixed

$$G = N\mu.$$

The same argument doesn't hold for Helmholtz.

$$\frac{\partial \mu}{\partial P} = \frac{1}{N} \frac{\partial G}{\partial P} = \frac{V}{N} = \frac{kT}{P}$$

$$\mu(T, P) = \mu^\circ(T) + kT \ln(P/P^\circ)$$

Phase transformations for pure substances

$$G(T, P) = N\mu(T, P)$$

In general, $G(T, P)$ will decrease with increasing T and increase with increasing P

$$\left(\frac{\partial G}{\partial T} \right)_{P,N} = -S, \quad \left(\frac{\partial G}{\partial P} \right)_{P,N} = V$$

At given T and P , substances will spontaneously be transformed into its most stable phase (phase with lowest $G(T, P)$.) Phase transformation: Discontinuous change in the properties of a substance at a small change in conditions, typically P and/or T .

Vapour pressure $P_v(T)$:

Pressure $P(T)$ where gas and liquid can coexist in equilibrium, phase boundary.

Trippel point:

Point in a TP -diagram where all three phases can coexist in equilibrium.

Critical point:

Point in TP -diagram where difference between gas and liquid ceases to exist, refer to it as a fluid.

1. order phase transition:

Discontinuous first derivative of G .

2. order phase transition:

Discontinuous second derivative of G .

Clausius-Clayperon

At a phase boundary, two (or more) phases can coexist in equilibrium, meaning the Gibbs free energy of the phases have to be the same

$$G_l = G_g \quad \text{at phase boundary}$$

If we want to change T and P but stay on boundary, identity gives us

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

Giving the slope of the phase boundary line

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

Often we approximate $\Delta V = V_g - V_l \approx V_g$.

The van der Waals Equation

A model for liquid-gas systems

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = NkT = nRT$$

Adjustment of ideal gas law, taking into account some interaction.

Heat Engines

The efficiency of an engine is defined as the benefit/cost ratio—benefit: work produced by the engine, cost: heat absorbed.

$$e \equiv \frac{\text{benefit}}{\text{cost}} = \frac{W_{\text{net}}}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

To analyze heat engines we use three assumptions: the engine returns to its original state after a complete cycle, energy conservation and the fact that the entropy of the reservoirs and the engine combined can only increase, never decrease.

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \Rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$$

$$e \leq 1 - \frac{T_c}{T_h}$$

The Carnot cycle realizes the maximum possible efficiency. For Carnot $\Delta S_{\text{tot}} = 0$, meaning it must be totally reversible. All heat transfer is isothermal, and all temperature-change happens adiabatically.

For a refrigerator, we talk about the coefficient of performance

$$\text{COP} = \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W}$$

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

Boltzmann' Statistics

The partition function

$$Z = \sum_s e^{-\beta E_s}; \quad \mathcal{P}(s) = \frac{1}{Z} e^{-E(s)/kT}$$

$$\bar{X} = \sum_s X(s) \mathcal{P}(s) = \frac{1}{Z} \sum_s X(s) e^{-\beta E(s)}$$

$$U = N\bar{E}, \quad \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$

$$F = -kT \ln Z; \quad Z = e^{-F/kT}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$$

The Gibbs Factor

Consider a system that can exchange particles and energy with a reservoir. The ratio of probabilities of different microstates can be written

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{[S_R(s_2) - S_R(s_1)]/k}$$

For the reservoir, the change in entropy is small, so we can invoke the thermodynamic identity

$$dS_R = \frac{1}{T}(dU_R + P dV_R - \mu dN_R)$$

we can replace all the changes in the reservoir with minus the change for the system

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T}[E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)]$$

Meaning

$$\text{Gibbs factor} = e^{-[E(s) - \mu N(s)]/kT}$$

and

$$P(s) = \frac{1}{Z} e^{-[E(s) - \mu N(s)]/kT}$$

where Z is the grand partition function

$$Z = \sum_s e^{-[E(s) - \mu N(s)]/kT}$$

If there are two types of particles, the Gibbs factor becomes

$$\text{Gibbs factor} = e^{-[E(s) - \mu_A N_A(s) - \mu_B N_B(s)]/kT}$$

Quantum Statistics

The quantum volume is

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

roughly the cube of the average de Broglie wavelength. We then make the distinction

$$\begin{aligned} V/N &\gg v_Q && \text{(Normal gas)} \\ V/N &\approx v_Q && \text{(Quantum gas)} \end{aligned}$$

For a quantum gas we think of the system as consisting of one single-particle state, rather than a particle itself.

Think of a single-particle state whose energy is $n\epsilon$ when it is occupied by n particles, we then have

$$\mathcal{Z} = \begin{cases} 1 + e^{-(\epsilon - \mu)/kT} & \text{(fermions),} \\ \frac{1}{1 - e^{-(\epsilon - \mu)/kT}} & \text{(bosons)} \end{cases}$$

We are now interested in the occupancy of the state, or how many particles inhabit the state on average as a function of ϵ , μ , and T , this is given by

$$\bar{n} = \sum_n n \cdot \mathcal{P}(n) = -\frac{1}{Z} \frac{\partial Z}{\partial x}$$

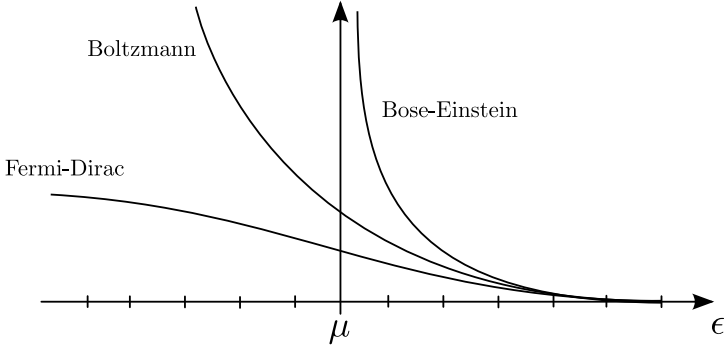
From this we find that the occupancy of the states are

$$\bar{n}_{\text{FD}} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

$$\bar{n}_{\text{BE}} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$$

Both distributions go to zero when $\epsilon \gg \mu$. As $\epsilon \rightarrow \mu$ Bose-Einstein goes to ∞ . Fermi-Dirac goes to 1 when $\epsilon \ll \mu$, thus a state with energy much greater than μ tend to be unoccupied, while a state with energy much lower than μ

tends to be occupied. A state at $\epsilon = \mu$ has a 50% of being occupied.



Degenerate Fermi Gas

Consider a gas of fermions at low temperature ($V/N \ll v_Q$).

Zero Temperature: At $T = 0$ the Fermi-Dirac distribution becomes a step-function. All single-states with energy less than μ is occupied, none of the states with energy greater than μ are occupied. We call μ the Fermi-energy $\epsilon_F \equiv \mu(T = 0)$.

$$\epsilon_F = \frac{h^2 n_{\max}^2}{8mL^2} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}$$

The total energy of a the gas is

$$U = \frac{3}{5} N \epsilon_F$$

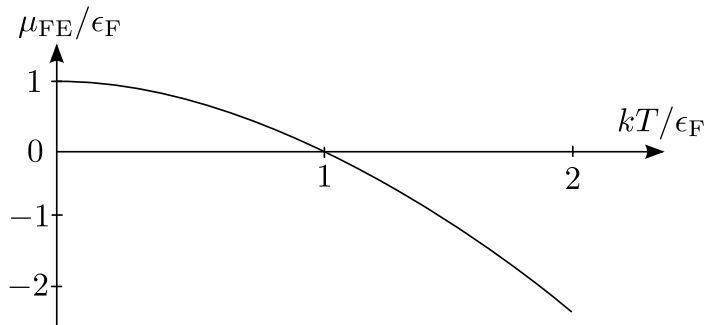
$$\frac{V}{N} \ll v_Q \quad \text{is the same as} \quad kT \ll \epsilon_F$$

$$N = \sum_{\text{all } s} \bar{n}_{\text{FD}}$$

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

$$U = \int_0^{\infty} \epsilon g(\epsilon) \bar{n}_{\text{FD}} d\epsilon \quad N = \int_0^{\infty} g(\epsilon) \bar{n}_{\text{FD}} d\epsilon \quad (T > 0)$$

where $g(\epsilon)$ is the density of states, $g(\epsilon) = (d/d\epsilon)f(\epsilon)$, where $f(\epsilon)$ denotes the number of states with energy less than ϵ .



Bose-Einstein Condensation

Looking at gas of Bosons with a conserved particle number N .

When $T \rightarrow 0$ all particles will go to ground state, so

$$N_0 = \frac{1}{e^{(\epsilon_0 - \mu)/kT} - 1} = N$$

meaning $(\epsilon_0 - \mu)/kT$ must be very small:

$$N_0 \approx \frac{kT}{\epsilon_0 - \mu} \quad (N_0 \gg 1)$$

How large must T be for N_0 to be large? μ is given by

$$N = \sum_{\text{all } s} \bar{n}_{\text{BE}} = \sum_{\text{all } s} \frac{1}{e^{(\epsilon_s - \mu)/kT} - 1}$$

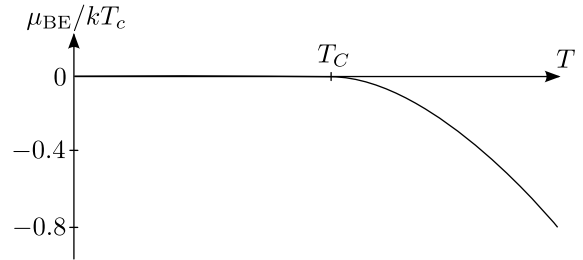
when $kT \gg \epsilon_0$, the energy spectra can be considered continuous and we can approximate the sum as an integral

$$N = \int_0^{\infty} g(\epsilon) \frac{1}{e^{(\epsilon_s - \mu)/kT} - 1} d\epsilon$$

For small T and large N we can set $\mu = 0$, note that the ground state is not included in the integrand, as $\epsilon_0 - \mu_{\text{BE}} \approx 0$ giving

$$N_{\text{excited}} \approx \int_0^{\infty} g(\epsilon) \frac{1}{e^{\epsilon/kT} - 1} d\epsilon$$

For $T < T_C$ replacing the sum is bad approx, for $T > T_C$ we see μ must be significantly less than 0.



$$N_{\text{excited}} = 2.612 V \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \quad (T < T_C),$$

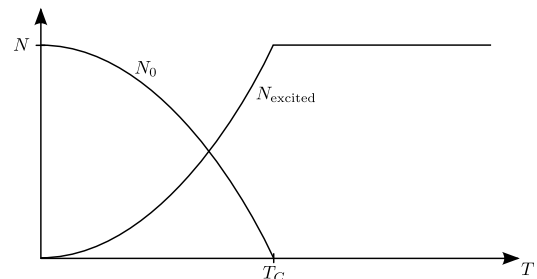
$$N_{\text{excited}} = \left(\frac{T}{T_C} \right)^{3/2} N \quad (T < T_C), \quad N_0 = N - N_{\text{excited}}$$

$$N_0 = N - N_{\text{excited}}$$

At $T = T_C$ we get $N_{\text{excited}} = N$, can be used to find T_C

$$kT_C = 0.527 \left(\frac{h^2}{2\pi m} \right) \left(\frac{N}{V} \right)^{2/3},$$

the higher the density (N/V), the longer the condensate survives.



The abrupt accumulation of atoms in the ground state at temperatures below T_C is known as Bose-Einstein Condensation.

At high enough T , properties will become as in a classic ideal gas $\mu_{BE} \rightarrow \mu_{Boltzmann}$.

Density of states for a Boson gas in box is

$$g(\epsilon) = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \sqrt{\epsilon}.$$

The energy becomes

$$U = \int_0^\infty \epsilon \cdot g(\epsilon) \cdot \bar{n}_{BE}(\epsilon) d\epsilon$$

As $T < T_C$ we have $\mu = 0$, giving

$$U = \frac{3}{2} V \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \cdot kT \cdot 1.342.$$

We see that U is dependant on T and V , but not N . Only excited particles contribute to U , and the number of excited particles is independant of N . This gives

$$P = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} kT \cdot 1.342 = \frac{2U}{3V}.$$

Meaning pressure of a Bose-Einstein condensate is only dependant of U , not V or N . Only excited particles contribute to pressure, adding particles or reducing V will only give more states in the ground state, and the pressure is unchanged. Note that $P \rightarrow 0$ as $T \rightarrow 0$, the system shows no resistance to being compressed, unlike Fermi-gases.

Planck Radiation

Allowed energies are

$$E_n = n \cdot hf, \quad n = 0, 1, 2, \dots$$

Partition function

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + \dots = \frac{1}{1 - e^{-\beta hf}}$$

Giving average energy

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{hf}{e^{hf/kT} - 1}$$

If we think of energy as coming in units of hf (photons), then the average number of units of energy is

$$\bar{n}_{Pl} = \frac{1}{e^{hf/kT} - 1} \quad (\text{Planck distribution.})$$

Modes of radiation with short-wavelengths ($hf \gg kT$) are exponentially suppressed; they are “frozen out”.

Photons

Photons are bosons, so the Planck distribution and the Bose-Einstein distribution should match. This gives $\mu = 0$ for photons. This is because photons can appear and disappear, meaning the photon number is not conserved. If $\mu > 0$ photons will be created, and if $\mu < 0$ photons will disappear quickly.

$$e \leftrightarrow e + \gamma \quad \mu_e = \mu_e + \mu_\gamma$$

Photons are ultrarelativistic

$$\epsilon = pc = \frac{hcn}{2L}, \quad p = \frac{hn}{2L}, \quad \lambda = \frac{2L}{n}$$

Total energy per unit volume is

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

here the integrand is the energy density per unit photon energy, or the spectrum of the photons

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon}{e^{\epsilon/kT} - 1}$$

Wien's law: The spectrum peaks at

$$\epsilon = 2.82kT.$$

The total energy of a photon gas is

$$\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15(hc)^3} = aT^4, \quad a \equiv \frac{8\pi^5 k^4}{15(hc)^3},$$

giving

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 4aVT^3.$$

Integrating gives

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = 4aV \int_0^T T'^2 dT' = \frac{4}{3} aVT^3$$

$$P = \frac{1}{3} aT^4$$

Stefan-Boltzmann

$$\text{power per unit area} = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3 c^2} = \sigma T^4$$

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$$

$$\text{Entropy flux:} \quad \frac{4}{3} \sigma T^3$$

Total number of photons in a volume V at temp. T is

$$N = V \int_0^\infty n(\epsilon) \, d\epsilon \approx 2.404 \frac{8\pi V 8(kT)^3}{(hc)^3}$$

where N will be prop. to the entropy, meaning the entropy per photon will be small and constant $S/N \approx 3.6k$.

Random results

Barometric Equation

$$\frac{dP}{dz} = -\frac{mg}{kT}P$$

Konstanter

$$k_{\text{b}} = 1.381 \cdot 10^{-23} \text{ J/K}$$

$$= 8.617 \cdot 10^{-5} \text{ eV/K}$$

$$N_{\text{A}} = 6.022 \cdot 10^{23}$$

$$R = N_{\text{A}}k_{\text{b}} = 8.315 \text{ J/mol} \cdot \text{K}$$

$$h = 6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}$$

$$= 4.136 \cdot 10^{-15} \text{ eV} \cdot \text{s}$$

$$c = 2.998 \cdot 10^8 \text{ m/s}$$

$$G = 6.673 \cdot 10^{-11} \text{ N} \cdot \text{m}^2/\text{kg}^2$$

$$e = 1.602 \cdot 10^{-19} \text{ C}$$

$$m_e = 9.109 \cdot 10^{-31} \text{ kg}$$

$$m_p = 1.673 \cdot 10^{-27} \text{ kg}$$

$$1 \text{ atm} = 1.103 \text{ bar} = 1.1013 \cdot 10^5 \text{ N/m}^2$$

$$(T \text{ in } ^\circ\text{C}) = (T \text{ in K}) - 273.15$$

$$(T \text{ in } ^\circ\text{F}) = \frac{9}{5}(T \text{ in K}) + 32$$

$$1^\circ\text{R} = \frac{5}{9}K$$

$$1 \text{ cal} = 4.186 \text{ J}$$

$$1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$$

$$1 \text{ u} = 1.661 \cdot 10^{-27} \text{ kg}$$

$$\hbar c = 1240 \text{ eV nm (MeV fm)}$$

$$\hbar c = 197.3 \text{ eV nm (MeV fm)}$$

$$m_e = 0.511 \text{ MeV}/c^2$$

$$m_p = 938.3 \text{ MeV}/c^2$$

$$m_n = 938.6 \text{ MeV}/c^2$$

$$m_{\text{hydrogen}} = 938.8 \text{ MeV}/c^2$$

$$u = 931.48 \text{ MeV}/c^2$$

$$k_e e^2 = e^2/4\pi\epsilon_0 = 1.44 \text{ eV nm}$$

$$h = 4.136 \cdot 10^{-15} \text{ eVs}$$

$$\hbar = 6.582 \cdot 10^{-16} \text{ eVs}$$

$$\text{eV} = 1.602 \times 10^{-19} \text{ J}$$

$$e = 1.602176 \cdot 10^{-19} \text{ C}$$

$$a \equiv \frac{\hbar^2}{m_e k_e e^2} = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 0.0529 \text{ nm}$$

$$E_0 = -13.6 \text{ eV}$$

Integraler Rottman side 155

$$\int_{-\infty}^{\infty} e^{-\lambda x^2} dx = 2 \int_0^{\infty} e^{-\lambda x^2} dx = \sqrt{\frac{\pi}{\lambda}} \quad (\lambda > 0)$$

$$\int_{-\infty}^{\infty} \exp [-(ax^2 + 2bx + c)] dx = \sqrt{\frac{\pi}{a}} \exp \left[\frac{b^2 - ac}{a} \right] \quad (a > 0)$$

$$\int_{-\infty}^{\infty} x \exp [-(ax^2 + 2bx + c)] dx = -\frac{b}{a} \sqrt{\frac{\pi}{a}} \exp \left[\frac{b^2 - ac}{a} \right]$$

$$\int_{-\infty}^{\infty} x^2 \exp [-(ax^2 + 2bx + c)] dx = \frac{a + 2b^2}{2a^2} \sqrt{\frac{\pi}{a}} \exp \left[\frac{b^2 - ac}{a} \right]$$

$$\int x \sin(ax) dx = \frac{1}{a^2} \sin(ax) - \frac{x}{a} \cos(ax)$$

$$\int x \cos(ax) dx = \frac{1}{a^2} \cos(ax) + \frac{x}{a} \sin(ax)$$

$$\int x \sin^2(x) dx = \frac{1}{4}x^2 - \frac{1}{8} \cos(2x) - \frac{1}{4}x \sin(2x)$$

$$\int x \cos^2(x) dx = \frac{1}{4}x^2 + \frac{1}{8} \cos(2x) + \frac{1}{4}x \sin(2x)$$

$$\int \sin^2(x) dx = \frac{x - \sin x \cos x}{2}$$

$$\int \cos^2(x) dx = \frac{x + \sin x \cos x}{2}$$

$$\int \sin^3(x) dx = \frac{1}{12} (\cos(3x) - 9 \cos(x))$$

$$\int \cos^3(x) dx = \frac{1}{12} (\sin(3x) + 9 \sin(x))$$

$$\int_0^{\infty} u^n e^{-u} du = n!$$

KAP. 3 INTERACTIONS AND IMPLICATIONS.

Kjemisk likevekt og min.punkt for G

Reaksjonsligning: $\nu_1 X_1 + \nu_2 X_2 + \dots \leftrightarrow \nu_3 X_3 + \nu_4 X_4 + \dots$. Der ν_i kalles støkiometriske koeffisienter. I en kjemisk reaksjon vil $G = U - TS + PV = \sum_i N_i \mu_i$ alltid ha et minimum for mengde av stoffene som tilsvarer 'delvis gjennomført' reaksjon, fra itegningsstoffer til produkter.

Dette skyldes bidraget fra blandingsentropien $\Delta S_{bland}(x)$, der x er 'gjennomført grad' av reaksjonen ($x = 0$: rene utgangsstoffer. $x = 1$: rene produkter). G vil falle med dervert mot $-\infty$ i punktet $x = 0$, og stige med dervert $+\infty$ i punktet $x = 1$. Minimum må derfor være i $0 < x < 1$.

Likevektsbetingelser og massevirkningsloven

Ved likevekt, der G har minimum, for konst. T, P : $dG = \sum_i \mu_i dN_i = 0$. der dN_i er støkiometriske koeffisienter med fortegn: $-$ for utangsstoffer, $+$ for produkter.

Kjemisk potensiale for ideelle gasser kan ved gitt partialtrykk P_i og temperatur T uttrykkes som: $\mu_i(T, P) = \mu_i(T, P_0) + kT \ln \frac{P_i}{P_0}$, der referansetrykket P_0 normalt er 1 atm. P_i er partialtrykket for gass i , og totalt trykk er $P = \sum_i P_i$.

Setter inn de kjemiske potensialene for endring i Gibbs: $dG(T, P_0) = -kT \sum_i \ln(P_i/P_0) dN_i$. Dette er endringer i Gibbs for 1 sett molekyler ved temp T og partial trykk P_i generelt gjelder at $dG(T, P_0) \neq 0$. Eksponensiering gir: $\Pi_i \left(\frac{P_i}{P_0} \right) = e^{-\Delta G(T, P_0)/RT}$. Ved inndeling i utg.stoffer og produkter: $\Pi_{i, \text{produkt}} (P_i/P_0)^{|dN_i|} / \Pi_{i, \text{utg.stoff}} (P_i/P_0)^{|dN_i|} = e^{-\Delta G(T, P_0)/RT} = K(T)$. Som er masse virkningsloven, $K(T)$ er konst ved gitt temp. Og $P_i = P_0$ for alle gassene. **Eks:** Amoniak $N_2 + 3H_2 \leftrightarrow 2NH_3$. Massevirkningsloven blir: $\frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = e^{-\Delta G(T, P_0)/RT} = K(T)$

Le Chateliers prinsipp: Når et system i likevekt forstyrres, vil det respondere på en måte som opphever forstyrrelsen.

Rotasjon av toatomige molekyler:

Rotasjonsenergier er kvantiserte. $E(j) = j(j+1)\epsilon$, $j = 0, 1, 2, \dots$. Degenerasjonsgrad er $g(j) = 2j+1$. For diatomige molekyler med to forskjellige atomer er alle rot.kv.tall tillatt og $Z_{\text{rot}} = \sum_{j=0}^{\infty} g(j) e^{-\beta E(j)}$. For $kT \gg \epsilon \rightarrow$ integral: $Z_{\text{rot}} \approx \int_0^{\infty} (2j+1) e^{-\beta j(j+1)\epsilon} dj = 1/\beta\epsilon$. For $kT \gg \epsilon$ er midlere rotasjons energi og varmekap.-bidrag per molekyl: $\langle E_{\text{rot}} \rangle = -\frac{\partial}{\partial \beta} \ln Z_{\text{rot}} \approx kT$, $C_{\text{rot}}/N = \frac{\partial \langle E_{\text{rot}} \rangle}{\partial T} \approx k$. I samsvar med ekvipartisjonsteoremet for $f = 2$.

For lave T: Nok a ta med de to første leddene i Z , $j = 0, 1$. Gir $\Delta E = 2\epsilon$, og $C_{\text{rot}}(T) \approx 3k (\Delta E/kT)^2 e^{-\beta \Delta E}$.

Identiske partikler i diatomisk molekyl

Rotasjon: Samme situasjon etter rotasjon en halv rotasjon, partisjonsfunksjon for $kT \gg \epsilon$: $Z \approx 1/2\beta\epsilon$. Ellers hvis begge atomene er:

Bosoner: Symmetrisk tot BF, $\Psi_{1,2} = \Psi_{2,1}$.

- Symmetrisk - spinndel og romdel: summér over **partallige** j .

- Antisymmetrisk - spinndel og romdel: summér over **oddetallige** j .

Fermioner: Antisymmetrisk tot. BF:

$$\Psi_{1,2} = -\Psi_{2,1} :$$

- Symmetrisk spinndel og antisymmetrisk romdel: Summér over **oddetallige** j .
- Antisymmetrisk spinndel og symmetrisk romdel: Summér over **partallige** j .

Ekvipartisjonsteoremet

gjelder kun for systemer der energien avhenger av kvadratiske frihetsparametre. La $E(q) = cq^2$. $Z = \frac{1}{\Delta q} \sum_q e^{-\beta cq^2} \Delta q$. Dersom $E(q + \Delta q) - E(q) \gg kT$ får vi: $Z \approx \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq = \frac{1}{\Delta q} \sqrt{\frac{\pi}{\beta c}}$. Midlere energi blir da $\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{2} kT$. Generelt: $\langle E \rangle = \frac{f}{2} kT$.

Maxwells fartsfordeling

Fartsfordelingsfunksjon $D(v)$, for partikler i en ideell gass. Sannsynligheten for et molekyl med fart i intervallet $(v, v+dv)$ er $P(v+dv) = D(v)dv$. Der $D(v)dv \propto e^{-\beta mv^2/2} 4\pi v^2 dv$. Det siste er \propto **degenerasjonsfaktoren** = antall hastighetsvektorer med lengde v . Fra normalisering er finner vi $D(v)dv = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-\beta mv^2/2}$. Noen farter: $v_{\text{max}} = \sqrt{2kT/m}$, $\langle v \rangle = \sqrt{8kT/\pi m}$, $v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{3kT/m}$.

Partisjonsfunksjoner og fri energi:

For et systemi termisk likevekt med et reservoar med konst. temp T : $Z = \sum_s e^{-U(s)/kT} = \sum_U \Omega(U) e^{-U/kT}$. For et stort system trenger vi bare inkludere ett, eller noen få ledd av partisjonsfunksjonen og finner $\ln Z = \ln \Omega(U) - U/kT$. Med $S = k \ln \Omega(U)$ finner vi

$$F = -kT \ln Z.$$

for **Helmholtz fri energi**.

Alternativ def. av entropi

$S = -k \sum_s P(s) \ln P(s)$. $-P(s)$ er sannsynligheten for at systemet er i tilstand s . Gyldig for isolerte systemer, og systemer i likevekt med omgivelsene.

Partisjonsfunksjoner for sammensatte systemer

Viktig å skille mellom enpartikkel-tilstander s_1 , som definerer enpartikkel-partisjonsfunksjonen $Z_1 = \sum_{s_1} e^{-\beta E(s_1)}$. Og systemtilstander $s_N = \{s_i\} = \{s_1, s_2, \dots\}$ der enpartikkel tilstanden til samtlige N partikler må være spesifisert:

$Z_N = \sum_{s_N} e^{-\beta U(s_N)} = \sum_{s_1} \dots \sum_{s_N} e^{-\beta \sum_{i=1}^N E_i(s_i)}$. En systemtilstand har totalenergi $U(s_N) = \sum_{i=1}^N E_i(s_i)$. For et system med N **forskjellige** partikler gjelder: $Z_{\text{tot}} = \Pi_{i=1}^N (\sum_{s_i} e^{-\beta E(s_i)}) = \Pi_{i=1}^N Z_i$. Der Z_i er partisjonsfunksjonen til partikkel i . Permutasjoner av N forskjellige enpartikkeltilstander gir $N!$ forskjellige systemtilstander.

For N **identiske partikler og fortynnede systemer** ($Z_1 \gg N$) gjelder med god tilnærming:

$Z_{\text{tot}} \approx \frac{1}{N!} Z_1 \cdot \dots \cdot Z_N = \frac{1}{N!} Z_1^N$. Siden alle Z_i er like for identiske partikler. $1/N!$ korrigerer for at de $N!$ forskjellige permutasjonene gir samme systemtilstand nå partiklene er identiske.

Til nå neglisjert tilstander der flere partikler er i samme enpartikkeltilstand og korreksjonsfaktoren $1/N!$ ikke gjelder.

Z, og frihetsgrader

Har to frihetsgrader a og b . Partisjonsfunksjonen blir da $Z_1 = \sum_{s_a} e^{-\beta E_a(s_a)} \sum_{s_b} e^{-\beta E_b(s_b)} = Z_a Z_b$.

Z for ideell gass

I ideell gass (per def fortynnet) med N identiske molekyler er $Z_{\text{tot}} = \frac{1}{N!} Z_1^N$, $Z_1 = Z_{\text{trans}} Z_{\text{indre}}$, $Z_{\text{indre}} = Z_{\text{rot}} Z_{\text{vib}} Z_e$. Z_e er lektronisk eksitasjon.

Z for translasjon

Kvantiserte energinivåer for partikkel i 3D-boks med volum V :

$E(n_x, n_y, n_z) = p^2/2m = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mV(2/3)}$, $n_i = 1, 2, \dots$ Partisjonsfunksjon blir da: $Z_{3D} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\beta E(n_x, n_y, n_z)} \rightarrow \int d^3\vec{n} e^{-\beta E(n_x, n_y, n_z)}$, et integral over n_x, n_y, n_z . Gjør om til sfæriske koordinater, med $n^2 = n_x^2 + n_y^2 + n_z^2$ og svaret blir: $Z_{3D} = \frac{V}{v_Q}$, der v_Q er

knvantevolumet $v_Q = \left(\frac{h^2}{2\pi m kT}\right)^{3/2}$.

Partisjonsfunksjonen for 1 partikkel blir da: $Z_1 = \frac{V}{v_Q} Z_{\text{indre}}$. For N identiske partikler i fortynnet system: $Z_N = \frac{1}{N!} Z_1^N$.

Z og indre frihetsgrader

$Z_{\text{indre}} = Z_{\text{rot}} Z_{\text{vib}} Z_e$. **Rotasjon:** For diatomisk molekyll med **ulike atomer:** $Z_{\text{indre,ulike}} = \sum_{j=1}^{\infty} (2j+1) e^{-\beta j(j+1)\epsilon_r} \approx \frac{kT}{\epsilon_r}$ For **like atomer:** $Z_{\text{rot,ulike}} = \sum_{j,\text{partall}} (2j+1) e^{-\beta j(j+1)\epsilon_r}$ eller $Z_{\text{rot,ulike}} = \sum_{j,\text{oddtall}} (2j+1) e^{-\beta j(j+1)\epsilon_r} \approx \frac{kT}{2\epsilon_r}$. Der vi antar $kT \gg \epsilon_r$.

Vibrasjon: $E_{\text{vib}} = n\epsilon_v$. Psrtisjonsfunksjon: $Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta n\epsilon_v} = \frac{1}{1-e^{-\beta\epsilon_v}}$. For romtemperatur er gjerne $kT < \epsilon_v$. **Elektronisk:** Partisjonsfunksjonen for elektronisk eksitasjon er bidraget fra eksitererte nivåer neglisjerbart ved normale temperaturer. $Z_e \approx g_0$. Der g_0 er degenerasjonsgraden for den elektroniske grunntilstanden.

Termodynamiske egenskaper for ideell gass

For ideell gass er U og C_V gitt som summen av bidrag fra translasjon og fra indre frihetsgrader: $U = -\frac{\partial}{\partial \beta} \ln Z_{\text{tot}} = U_{\text{trans}} + U_{\text{rot}} + u_{\text{vib}} + e$, $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$. For diatomige (like eller ulike) molekyler ved romtemp. og høyere har vi for de ulike energibidragene: $U_{\text{trans}} = \frac{3}{2} NkT$, $U_{\text{rot}} = NkT$, $U_{\text{vib}} = \frac{N\epsilon_v}{e^{\epsilon_v/kT} - 1}$, $U_e \approx 0$. **Varmekap.:** $C_{V,\text{trans}} = \frac{3}{2} Nk$, $C_{V,\text{rot}} = Nk$ For vibrasjonsbidragene får vi $C_{V,\text{vib}} \approx Nk \left(\frac{\epsilon_v}{kT}\right)^2 e^{-\epsilon_v/kT}$, når $kT \ll \epsilon_v$ og $C_{V,\text{vib}} \approx Nk$, når $kT \gg \epsilon_v$.

De andre termodynamiske egenskapene finner vi fra $F = -kT \ln Z$:

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

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

$$Nk \left[\ln \left(\frac{V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} Z_{\text{indre}} \right) + \frac{5}{2} \right]$$

$$+ NkT \left(\frac{\partial}{\partial T} \ln Z_{\text{indre}} \right)_{V,N}.$$

For monoatomisk gass får vi Sackur-Tetrode. For diatomisk gass med like atomer er $S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \frac{kT}{2\epsilon_r} \right) + \frac{7}{2} \right]$.

Kjemisk potensiale blir:

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

$$= -kT \ln \left(\frac{V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} Z_{\text{indre}} \right).$$

Di- og polyatoniske ideelle gasser har høyere S og større negativ μ en monoatomiske, grunnet Z_{indre} - bidraget som gir effektivt et mer fortynnet system.

Statistikk for ikke-forynnede systemer

For fortynnede systemer ($V/N \gg v_Q$) har vi at $Z_{\text{tot}} = \frac{1}{N!} Z_1^N$. korreksjonsfaktoren $1/N!$ er kun gyldig når alle systemtilstandene har partiklene i forskjellige enpartikkeltilstander. For flere partikler i samme enpartikkeltilstand avhenger av om det er fermioner eller bosoner.

Flere **identiske fermioner** kan ikke være i samme enpartikkel-quantetilstand - Paulis eksklusjonsprinsipp. Vilkarlig mange **bosoner** kan være i samme enpartikkel-quantetilstand.

Eksempel på kombinatorikk for fermioner og bosoner

Vi har et system for g degenererte enpartikkeltilstander og N ikke-distingverbare partikler ($q \gg N$).

For **Bosoner** er antall systemtilstander gitt ved: $\Omega_{\text{boson}} = \frac{(g+N-1)!}{N!(g-1)!} \approx \frac{(g+N)!}{N!g!}$, (g, N store).

For **fermioner** er antall systemtilstander gitt ved: $\Omega_{\text{fermion}} = \frac{g!}{N!(g-N)!}$, ($N \leq g$).

Til sammenligning gir **Boltzmann-tilnærmelsen** antall systemtilstander som: $\Omega_{\text{Boltzmann}} = \frac{1}{N!} g^N$.

Kan vises at generelt for et gitt sett av enpartikkeltilstander: $\Omega_{\text{fermion}} < \Omega_{\text{Boltzmann}} < \Omega_{\text{boson}}$.

Fordelingsfunksjoner for bosoner og fermioner

Ser på system som en enkelt enpartikkel-quantetilstand. Enpartikkeltilstanden har energi ϵ og kan være besatt av n partikler, som gir tot. energi $n\epsilon$ for hele systemet. Sannsynligheten for at det er n partikler i systemet:

- **Fermioner:** $n = 0, 1$ er de eneset tillatt. Gibbs-sum: $\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT}$. Midlere partikkeltall for fermioner kalles **Fermi-Dirac** - fordelingen: $\bar{n}_{FD}(\epsilon) = \sum_{n=0}^1 n P(n) = \frac{1}{e^{(\epsilon-\mu)/kT} + 1}$. Egenskap: Step-funksjon.

$\bar{n}_{\text{FD}} \rightarrow 1$ for $\epsilon \ll \mu$. $\bar{n}_{\text{FD}} \rightarrow 0$ for $\epsilon \gg \mu$, og $\bar{n}_{\text{FD}} = 1/2$ for $\epsilon = \mu$. Bredden opp fordelings falende flanke er av størrelses orden kT .

- **Bosoner:** Alle $n \geq 0$ tillatt. Får partisjonsfunksjon $\mathcal{Z} = \sum_{n=0}^{\infty} e^{-n(\epsilon-\mu)/kT} = \frac{1}{1-e^{-(\epsilon-\mu)/kT}}$. Betingelsen $\epsilon > \mu$ må være oppfylt for alle ϵ . Midlere partikkeltall, kalt **Bose-Einstein-fordelingen** blir: $\bar{n}_{\text{BE}}(\epsilon) = \sum_{n=0}^{\infty} nP(n) = \frac{1}{e^{(\epsilon-\mu)/kT}-1}$. Egenskaper: går mot 0 når $\epsilon \gg \mu$. Og mot ∞ når $\epsilon \rightarrow \mu$ ovenfra.

- **Boltzmann-partikler:** Midlere partikkeltall er, hvor $\mu = -kT \ln(Z_1/N) \Rightarrow \frac{N}{Z_1} = e^{\mu/kT} : \bar{n}_{\text{Boltzm.}}(\epsilon) = NP(\epsilon) = \frac{N}{Z_1} e^{-\epsilon/kT} = \frac{1}{e^{(\epsilon-\mu)/kT}}$. Egenskaper: Går mot 0 når $\epsilon \gg \mu$. Lik 1 for $\epsilon = \mu$.

For de tre gjelder: $\bar{n}_{\text{FD}}(\epsilon) < \bar{n}_{\text{Boltzm.}}(\epsilon) < \bar{n}_{\text{BE}}(\epsilon)$.

Totalt partikkeltall N og kj.pot. μ

Totalt partikkeltall må være lik summen av alle okkupasjonstall for alle enpartikkeltilstander. For bevart tot. partikkeltall N , er det kjemiske potensialet μ entydig bestemt ved følgende:

- **Fermioner:**

$$N = \sum_{j=0}^{\infty} \bar{n}_{\text{FD}}(\epsilon_j) = \sum_j \frac{1}{e^{(\epsilon_j-\mu)/kT} + 1}.$$

Ved lav T er $\bar{n}_{\text{FD}}(\epsilon) \approx 1$ for $\epsilon < \mu$, 0 for $\epsilon > \mu$. Dette betyr at $\mu \approx \epsilon_N$ - høyeste okkuperte enpartikkel-energinivå. $\mu = \mu_{\text{FD}}$ for lave T er typisk et stort og positivt tall.

- **Bosoner:**

$$N = \sum_{j=0}^{\infty} \bar{n}_{\text{BE}}(\epsilon_j) = \sum_j \frac{1}{e^{(\epsilon_j-\mu)/kT} - 1}.$$

For lav T ender alle bosoner opp i laveste enpartikkel-nivå, ϵ_0 : $N = \frac{1}{e^{(\epsilon_0-\mu)/kT}-1} \Rightarrow \mu \approx \epsilon_0 - \frac{kT}{N}$. $\mu = \mu_{\text{BE}}$ ligger da nesten infinitesimalt under grundtilstandsen-ergien ϵ_0 og synker lineært med stigende T .

- **Boltzmann-partikler:**

$$N = \sum_{j=0}^{\infty} \bar{n}_{\text{Boltzm.}}(\epsilon_j) = \sum_j \frac{1}{e^{(\epsilon_j-\mu)/kT}} = e^{\mu/kT} Z_1.$$

For lav T bidrar bare laveste enpartikkelnivå, $Z_1 \approx e^{-\epsilon_0/kT}$:

$$e^{\mu/kT} = \frac{N}{Z_1} \approx \frac{N}{e^{-\epsilon_0/kT}} \Rightarrow \mu \approx \epsilon_0 + kT \ln N.$$

$\mu = \mu_{\text{Boltzm.}}$ stiger da lineært med T inntil Z_1 begynner å få bidrag fra eksiterte tilstander.

Det kjemiske potensialet er temperaturavhengig, $\mu = \mu(T)$, og antar alltid en verdi som bevare totalt partikkeltall N . For høye T er μ for alle systemene stor og negativ, og faller med økende T . Forstatt har vi

$$\mu_{\text{FD}} > \mu_{\text{Boltzm.}} > \mu_{\text{BE}}$$

overalt, men verdiene konvergerer i grensen høy T .

\mathcal{Z} og det store potensialet Φ

For et system i termisk - og diffusjons likevekt med et reser-voar ved konst temperatur T og kjemisk pot μ er \mathcal{Z} gitt ved:

$$\mathcal{Z} = \sum_s e^{-[U(s)-\mu N(s)]/kT} = \sum_U \sum_N \Omega(U, N) e^{-U/kT} e^{\mu N/kT}.$$

For et stort system trenger vi bare inkludere ett, eller noen få ledd i \mathcal{Z} , med $U = \langle U \rangle$ og $N = \langle N \rangle$, siden systemet kan antas å være sin mest sannsynlige makrotilst.:

$$\mathcal{Z} \approx \Omega(U, N) e^{-U/kT} e^{\mu N/kT} \Rightarrow \ln \mathcal{Z} \approx \ln \Omega(U, N) - \frac{U}{kT} + \frac{\mu N}{kT}.$$

Innsetting av $S = k \ln \Omega$ gir følgende nyttig relasjon mellom \mathcal{Z} og **Det Store Potensialet**, Φ :

$$\Phi = -kT \ln \mathcal{Z} = U - TS - \mu N = F - \mu N.$$

Med termodynamisk identitet:

$$d\Phi = -SdT - PdV - Nd\mu.$$

Og vi kan finne P, N og S ved å derivere mhp diverse, og holde andre konst.

Degenerert Fermi-gass ved $T = 0$

For $T = 0$ er \bar{n}_{FD} en eksakt step-funk. med $\bar{n}_{\text{FD}} = 1$ for $(\epsilon - \mu) < 0$ og $\bar{n}_{\text{FD}} = 0$ for $(\epsilon - \mu) > 0$.

Det kjemiske potensialet $\mu(T = 0)$ er lik **fermi-energien**, ϵ_f , som tilsvarer det høyeste okkuperte enpartikkelnivået ved denne temperaturen.

For et system med N fermioner ved $T = 0$, fylles alltid enpartikkel-tilstandene fra laveste ϵ og oppover, i henhold til Paulis eksklusjonsprinsipp.

Grensebetingelsene for romlige bølgefunksjoner gir følgende diskrete energier i en 3-dim pot. brønn med volum V (ikke-relativistiske fermioner):

$$\epsilon = \frac{h^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2) = \frac{h^2 n^2}{8mV^{2/3}}, \quad n_i = 1, 2, \dots$$

Antall unike enpartikkel-quantetilstander kan bestemmes ved å telle alle mulige romlige quantetall (n_x, n_y, n_z) , og ta hensyn til at hvert fermion kan ha egenspinns-orienteringene \uparrow og \downarrow , som gir hver romlige orbital en degenerasjonsgrad 2. Da er **antall fermioner** i positive oktant av n -rommet

$$N = 2 \frac{1}{8} \frac{4}{3} \pi n_{\text{max}}^3 = \frac{\pi}{3} n_{\text{max}}^3 \Rightarrow n_{\text{max}} = \left(\frac{3N}{\pi} \right)^{1/3}.$$

- Det dobbelte av volumet av en oktant.

Totalt partikkeltall kan også finnes ved å bruke **tilstandstettheten** eller degenerasjonsgraden $g(n)dn = 2 \cdot \frac{1}{8} 4\pi n^2 dn = \pi n^2 dn$.

$$N = \int_0^{n_{\text{max}}} g(n) dn.$$

Alle enpartikkeltilstander er okkupert opp til Fermi-energien ϵ_F , som er gitt ved:

$$\epsilon_F = \frac{h^2 n_{\text{max}}^2}{8mV^{2/3}} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}.$$

Total energien for fermi-gassen er

$$U = \int_0^{n_{max}} \epsilon(n) g(n) dn$$

$$= \int_0^{n_{max}} \frac{h^2 n^2}{8mV^{2/3}} \cdot 2 \cdot \frac{4\pi}{8} n^2 dn = \frac{3}{5} N \epsilon_F.$$

Fermi-temperatur er definert som $T_F = \epsilon_F/k$.

Egenskaper ved deg.fermigass, $T = 0$

Energi er gitt over. Trykk er gitt ved

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S,N} = \frac{2}{5} \left(\frac{3}{\pi} \right)^{2/3} \frac{h^2}{8m} \left(\frac{N}{V} \right)^{5/3}.$$

Degenerasjons trykket som øker dramatisk med tettheten $\propto (N/V)^{5/3}$ er ikke relatert til termisk bevegelse, men skyldes at faserommet er fullt okkupert opp til Fermienergien ϵ_F . Vi kan også bestemme inkompressibilitet (**bulk modulus**) B . Ved $T = 0$ er Fermigassen i en unik grunntilstandskonfigurasjon, med $S = 0$, og **isoterm-** og **adiabatisk** inkompressibilitet B_T og B_S blir like:

$$B_T = -V \left(\frac{\partial P}{\partial V} \right)_{T,N} = B_S = -V \left(\frac{\partial P}{\partial V} \right)_{S,N}$$

$$= \frac{2}{3} \left(\frac{3}{\pi} \right)^{2/3} \frac{h^2}{8m} \left(\frac{N}{V} \right)^{5/3}.$$

Fermigass ved liten, endelig T

Grov tilnærming. partikkeltallet N' opp til et vilkårlig energinivå ϵ er gitt ved:

$$N' = \frac{\pi}{3} \left(\frac{8m\epsilon}{h^2} \right).$$

Tilstandstettheten $g(\epsilon)$, dvs. antall enpartikkeltilstander innenfor et enhets intervall i energi $\Delta\epsilon = 1$, er gitt ved:

$$dN' = g(\epsilon) d\epsilon = \frac{\partial N'}{\partial \epsilon} d\epsilon$$

$$\Rightarrow g(\epsilon) = \frac{\partial N'}{\partial \epsilon} = \frac{\pi}{2} V \left(\frac{8m}{h^2} \right)^{3/2} \epsilon^{1/2}.$$

Total energi ved temperatur T kan ved en grov tilnærming angis som midlere eksitasjonsenergi pr. partikkel, $\Delta\epsilon \approx kT$, ganger antallet eksiterbare partikler nær fermienergien, $g(\epsilon_F)\delta\epsilon$:

$$U(T) \approx U(T=0) + (\Delta\epsilon)^2 g(\epsilon_F)$$

$$\approx \frac{3}{5} N \epsilon_F + \frac{3}{2} (kT)^2 \frac{N}{\epsilon_F}.$$

Og varmekap. blir:

$$C_V \approx 3Nk \frac{kT}{\epsilon_F}.$$

En mer nøyaktig beregning som tar hensyn til Fermi-Diracfordelingen ved liten, endelig temperatur er **Sommerfeldt utviklingen**. Som gir kvalitativt samme resultater for tot. energi og varmekap:

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} \approx \frac{\pi^2}{2} Nk \frac{kT}{\epsilon_F}.$$

Tetthet i ikke-rel. fermigass

For $T = 0$ der fordelingsfunksjonen er en eksakt step-funksjon kan vi beregne partikkeltall N og energi U som:

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon, \quad U = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon.$$

Der $g(\epsilon)$ er tilstandstettheten. $g(\epsilon)$ kan bestemmes ved å betrakte partikkeltallets avhengighet av energinivået ϵ , som pot.brønnen er fylt opp til. Evt kan vi se på $g(n)dn = \pi n^2$ i 3D n -rommet. Der $\epsilon(n) = h^2 n^2 / 8mV^{2/3}$. Slik at:

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

$$= \frac{\pi}{2} V \left(\frac{8m}{h^2} \right)^{3/2} \epsilon^{1/2} = g_0 \sqrt{\epsilon}.$$

Egenskaper for fermigass, ved endelig T

Uttrykk for tilstands tetthet $g(\epsilon) = g_0 \sqrt{\epsilon}$ er gyldig for ikke-vekselvirkende spinn-1/2 fermioner.

$$N = \int_0^{\epsilon_F} g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon, \quad U = \int_0^{\epsilon_F} \epsilon g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon.$$

$T > 0$ er $\epsilon_F \neq \mu$ lenger. $\mu(T)$ kan bestemmes fra kravet om at tot. partikkeltall skal være bevart for enhver temp. Der N er gitt av uttrykket over, og skal være konst. Med andre ord må integral over ubesatte tilstander under ϵ_F være lik integralet over besatte tilstander over ϵ_F :

$$\int_0^{\epsilon_F} g(\epsilon) P(0) d\epsilon = \int_{\epsilon_F}^{\infty} g(\epsilon) \bar{n}_{FD}(\epsilon) d\epsilon.$$

Dette er det samme som:

$$\int_0^{\epsilon_F} g(\epsilon) \frac{e^{(\epsilon-\mu)/kT}}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon = \int_{\epsilon_F}^{\infty} g(\epsilon) \frac{1}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon.$$

Finner at $\mu(T)$ må synke med økende T for at N bevart. Om vi antar at $T \ll T_F$ finner vi ved Sommerfeldt-utviklingen:

$$\frac{\mu}{\epsilon_F} \approx 1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2.$$

Som også gir de nevnte tilnærmingene til varmekap. og tot. energi.

Relativistisk, degenerert fermigass, $T = 0$

$\epsilon = \sqrt{(pc)^2 + (mc^2)^2}$. For $pc \gg mc^2$ har vi $\epsilon \approx pc$. Samt. $\lambda = 2L/n$, gir de-Broglie

$$\epsilon = \frac{hcn}{2V^{1/3}}, \quad n = \sqrt{n_x^2 + n_y^2 + n_z^2}.$$

Antallet enpartikkeltilstander er volumet av en oktant i n -rommet, med radius $n_{max} = \vec{n}_{max}$, ganger 2 for spinorientering.

$$N = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_{max}^3 \Rightarrow n_{max} = \left(\frac{3N}{\pi} \right)^{1/3}.$$

fermi-energien: $\epsilon_F = \frac{hc}{2V^{1/3}} n_{max}$. **Tilstandstettheten:** $N(\epsilon) = \frac{8\pi V}{3(hc)^3} \epsilon_F^3 = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \Rightarrow g(\epsilon) = \frac{8\pi V}{(hc)^3} \epsilon^2$. Total energi U av rel. Fermigass:

$$U = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon = \frac{3}{4} N \epsilon_F.$$

Nivåstruktur for elektroner i krystaller

Tiltrekkende krefter mellom elektroner og positive ioner i en krystall vil modifisere nivåstrukturen. Vi får **valensbånd** ($\epsilon \leq \epsilon_v$) og **ledningsbånd** ($\epsilon \geq \epsilon_c$), adskilt av energigap $\Delta\epsilon_{gap} = \epsilon_c - \epsilon_v$. Tilstandstettheten kan skrives som:

$$g_c(\epsilon) = g_0 \sqrt{\epsilon - \epsilon_c}, \quad g_v(\epsilon) = g_0 \sqrt{\epsilon_v - \epsilon},$$

$$g_0 = \frac{\pi}{2} V \left(\frac{8m}{h^2} \right)^{3/2}.$$

Tre klasser:

- **leder:** ϵ_F ligger innenfor valensbåndet eller ledningsbåndet. Ubesatte og besatte tilst. ved samme ϵ gir stor mobilitet for e^- .
- **Isolatorer:** ϵ_F ligger mellom valensbåndet og ledningsbånd. $\Delta\epsilon_{gap}$ er stor (flere eV's.) Termisk eksitasjon er neglisjerb. valensbånd fullt, ledn.bånd tomt.
- **Halvleder:** ϵ_F er mellom valensbånd og ledn.bånd. $\Delta\epsilon_{gap}$ liten ($\sim 1\text{eV}$). gir signifikant eksitasjon av elektroner fra valensb. til ledn.b.