

Fundamentals I

Energy Transfer and Work:

$$W = F dx = -P dV$$

Moles and Mole Fractions:

$$N_i = \frac{M_i}{m_i} \quad x_i = \frac{N_i}{\sum_j N_j}$$

Internal and Fiducial Energy:

$$U = E - E^f \quad E^f = \sum_i N_i \varepsilon_i^f$$

Simple Systems and Parameters:

"A system completely defined by its Internal Energy (U), Volume (V) and Mole Numbers (N_i)"

Extensive (U, S, V, N) and Intensive (T, P, μ) Parameters:

$$\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 + \dots \quad \mathcal{I} \neq \mathcal{I}_1 + \mathcal{I}_2 + \dots$$

$$\mathcal{E}(\lambda S, \lambda V, \lambda N) = \lambda \mathcal{E}(S, V, N) \quad \mathcal{I}(\lambda S, \lambda V, \lambda N) = \mathcal{I}(S, V, N)$$

Equilibrium States:

POSTULATE I - For simple systems, there exist particular states which macroscopically are characterised completely and uniquely by specifying only U , V and the N_i . Such systems are called equilibrium states.

Walls and Constraints:

$$\text{Rigid: } \dot{V} = 0 \quad \text{Diathermal: } \Delta Q \neq 0 \quad \text{Adiabatic: } \Delta Q = 0$$


$$\text{Semi-permeable Membrane: } \dot{N} \neq 0$$

State Variables (U, V, T, P):

1ST LAW OF THERMODYNAMICS - Energy is conserved. Heat added (Q) and work done (W) are forms of energy.

$$\Delta U = Q + W \quad dU = \delta Q + \delta W$$

Differentials and State Functions:

Perfect: $df = M(x, y) dx + N(x, y) dy : \left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$

 State Function

Imperfect: $\delta g = P(x, y) dx + L(x, y) dy : \left(\frac{\partial P}{\partial y} \right)_x \neq \left(\frac{\partial L}{\partial x} \right)_y$

Quasistatic Process:

"A quasistatic process is a slow process such that the system is always relaxed in equilibrium."

$$\delta W = -P dV \quad \delta Q = C dT = T dS$$

Ideal Gas

Equation of State and Internal Energy:

$$PV = NRT \quad U = cNRT$$

$$\text{Monatomic: } c = \frac{3}{2} \quad \text{Diatomic: } c = \frac{5}{2}$$

Heat Capacitance:

$$C_V = cNR \quad C_P = (c+1)NR \quad C_P - C_V = NR$$

$$c_V = \frac{C_V}{N} \quad c_P = \frac{C_P}{N}$$

Quasistatic, Isothermal ($dT = 0$) Expansion:

Consider an isothermal, quasistatic expansion of an ideal gas from volume V_A to V_B ...

$$dU = cNR dT = 0 \implies \delta Q + \delta W = 0$$

Using $PV = NRT$, we can solve for the heat...

$$Q = \int \delta Q = - \int \delta W = \int_{V_A}^{V_B} P dV = NRT \int_{V_A}^{V_B} \frac{dV}{V}$$

$$Q = NRT \ln \left(\frac{V_B}{V_A} \right)$$

Quasistatic, Adiabatic ($\delta Q = 0$) Expansion:

Consider an adiabatic, quasistatic expansion of an ideal gas from state A to state B...

$$\delta Q = 0 \implies dU = cNR dT \equiv \delta W = -P dV$$

Using $PV = NRT$, we can solve for the temperature...

$$\int_{T_A}^{T_B} \frac{dT}{T} = -\frac{1}{c} \int_{V_A}^{V_B} \frac{dV}{V} = \ln(T_B/T_A) = -\frac{1}{c} \ln(V_B/V_A)$$

$$T_A V_A^{1/c} = T_B V_B^{1/c} = \text{const.}$$

$$PV^\gamma = \text{const.} \quad \gamma = 1 + \frac{1}{c}$$

Fundamentals II

The Basic Problem of Thermodynamics:

POSTULATE 2 - All the constrained equilibrium states of any system have a well-defined property (state variable) that is a fundamental relation of the extensive variables U , V and N_i , called the entropy (S). The 'special' equilibrium state with no constraints is the state with the maximum entropy ($dS = 0$).

POSTULATE 3 - The fundamental relation is valid if...

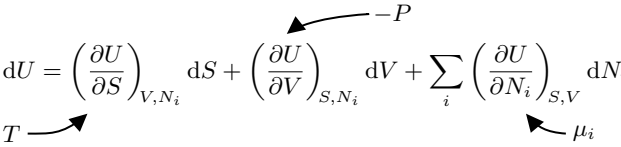
- S is extensive: $S(\lambda U, \lambda V, \lambda N_i) = \lambda S(U, V, N_i)$
- S is continuous and differentiable w.r.t. U , V and N
- S increases monotonically with U : $\frac{\partial S}{\partial U} = \frac{1}{T} > 0$

POSTULATE 4 - The entropy of any system vanishes in the state for which...

$$\frac{\partial U}{\partial S} = 0 \equiv T$$

Intensive Thermodynamic Parameters:

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, N_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N_i} dV + \sum_i \left(\frac{\partial U}{\partial N_i} \right)_{S, V} dN_i$$



$$dU = T dS - P dV + \sum_i \mu_i dN_i$$

$$\text{Equilibrium: } T_1 = T_2 \quad P_1 = P_2 \quad \mu_1 = \mu_2$$

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The Euler Relation:

$$U = TS - PV + \sum_i \mu_i N_i$$

The Gibbs–Duhem Relation:

$$S dT - V dP + \sum_i N_i d\mu_i = 0$$

Fundamental Relation of an Ideal Gas:

$$S = S_0 + cNR \ln\left(\frac{U}{U_0}\right) + NR \ln\left(\frac{V}{V_0}\right)$$

In general, apply the above and solve the intensive thermodynamic relations. Examples include for mixing ideal gases, Van der Waals gas, Electromagnetic Radiation...

Thermodynamic Engines

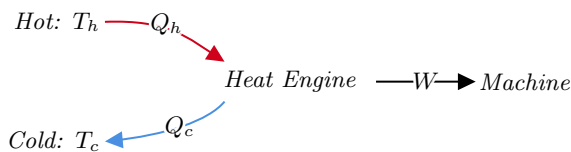
Reversible and Irreversible Processes:

$$\text{Reversible: } A \rightleftharpoons B \implies S_A = S_B$$

$$\text{Irreversible: } A \rightarrow B \implies S_A < S_B$$

MAXIMUM WORK THEOREM - *The work delivered is a maximum in a reversible process ($\Delta S = 0$).*

Reversible Heat Engines:



$$dS = \frac{dQ_h}{T_h} + \frac{dQ_c}{T_c} = 0 \quad W_{\max} = |Q_h| - Q_c$$

$$\implies -\frac{dW}{dQ_h} = \eta_{\max} = \left[1 - \frac{T_c}{T_h}\right]$$

Refrigerators and Heat Pumps:

Refrigerators transfer heat out of a cold system...

$$\eta_r = \left(\frac{-dQ_c}{-dW}\right)_{\max} = \frac{T_c}{T_h - T_c}$$

Heat pumps transfer heat into a warm system...

$$\eta_p = \left(\frac{dQ_h}{-dW}\right)_{\max} = \frac{T_h}{T_h - T_c}$$

Carnot Cycle:

The Carnot cycle is an example of a heat engine which uses reversible, isothermal expansion of a gas.

Traditional Presentation of Thermodynamics:

2ND LAW OF THERMODYNAMICS -

Clausius: *No process is possible whose only result is the transfer of heat from a colder body to a hotter body.*

Kelvin: *No process is possible whose only result is the complete conversion of heat into work.*

Thermodynamic Potentials

The Equilibrium Principles:

MAX ENTROPY - *The equilibrium state is the state with the maximum S under fixed U , V and N_i conditions.*

MIN ENERGY - *The equilibrium state is the state with the minimum U under fixed S , V and N_i conditions.*

Thermodynamic Potential Energies:

$$\text{Internal: } \underline{U}(S, V, N) = U$$

$$\text{Helmholtz Free: } \underline{F}(\underline{T}, V, N) = U - TS$$

$$\text{Enthalpy: } \underline{H}(S, \underline{P}, N) = U + PV$$

$$\text{Gibbs Free: } \underline{G}(\underline{T}, \underline{P}, N) = U - TS + PV$$

$$\text{Grand: } \underline{\Omega}(\underline{T}, V, \underline{\mu}) = U - TS - \mu N$$

$$\text{Fixed Natural Variables} \iff \text{Potential Minimised}$$

Differential Relations:

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

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

$$dH = \dots$$

"Swap natural variable and negate"

Thermodynamic Derivatives

The Maxwell Relations:

$$dU = T dS - P dV + \mu dN \implies \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

The Independent Second Derivatives:

$$\text{Molar Heat Capacity at Constant Pressure: } c_P = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{P,N}$$

$$\text{Coefficient of Thermal Expansion: } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N}$$

$$\text{Coefficient of Isothermal Compressibility: } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,N}$$

$$\text{Molar Heat Capacity at Constant Volume: } c_V = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{V,N}$$

Partial Differential Transforms:

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \left[\left(\frac{\partial Y}{\partial X}\right)_Z\right]^{-1}$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \frac{\left(\frac{\partial X}{\partial W}\right)_Z}{\left(\frac{\partial Y}{\partial W}\right)_Z} \quad \left(\frac{\partial X}{\partial Y}\right)_Z = -\frac{\left(\frac{\partial Z}{\partial Y}\right)_X}{\left(\frac{\partial Z}{\partial X}\right)_Y}$$

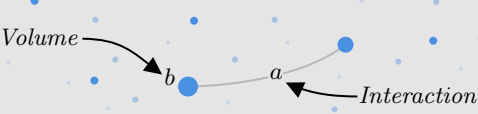
Reduction Method:

1. Eliminate the potentials U, H, F, G
2. Eliminate μ using the Gibbs-Duhem relation
3. Eliminate S
4. Eliminate V

Cooling of Gases

Van der Waals Gas: "VdW"

The Van der Waals gas is an extension of the ideal gas to include the size of molecules and their interactions...



$\left[P + \frac{aN^2}{V^2}\right][V - Nb] = NRT$

Joule Expansion:
Joule expansion is when a volume of gas expands into a vacuum chamber (dW = 0) with no heat transfer (dQ = 0)...

$dU = 0$

Joule Coefficient:

$$\mu_j = N \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{c_V} \left[P - \frac{\alpha T}{\kappa_T}\right]$$

Ideal: $\mu_j = 0$ VdW: $\mu_j = -\frac{a}{c_V V^2}$

Isothermal Expansion:
Isothermal expansion is the temperature remains constant...

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \implies \Delta U = \int_{V_1}^{V_2} \left\{ T \left(\frac{\partial P}{\partial T}\right)_V - P \right\} dV$$

Ideal: $\Delta U = 0$ VdW: $\Delta U = aN^2 \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

Joule-Kelvin Expansion:
Joule-Kelvin expansion describes the temperature change of a real gas as it expands...

$$H = U_1 + P_1 V_1 = U_2 + P_2 V_2$$

Joule-Kelvin Coefficient:

$$\mu_{jk} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{N c_P} [\alpha T - 1]$$

Ideal: $\mu_{jk} = 0$ VdW: μ_{jk} changes sign

Phase Changes

Latent Heat:

$$L = T_c(S_g - S_l) \approx 7NRT_b$$

Discontinuity in S \implies At $T = T_b$ $C \rightarrow \infty$

Phase Diagrams:

$$\mu_1(T, P) = \mu_2(T, P)$$

Tripple Point: $\mu_s(T, P) = \mu_l(T, P) = \mu_g(T, P)$

Clausius–Clapeyron Equation:

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{S_2 - S_1}{V_2 - V_1}$$

Ehrenfest’s Classification of Phase Transitions:
The nth transition is discontinuous in the nth derivative of G...

Transition	Variables	Example
1st	S, V	Matter State
2nd	c, α	Semiconduction
3rd	...	Ferromagnetism

"Today we understand only the 1st transitions is discontinuous and the rest are continuous"

Third Law of Thermodynamics

Vanishing of Entropy:

NERNST POSTULATE - The entropy of any system vanishes at the zero of temperature...

$$S_0 = k_b \ln(\Omega_0) = k_b \ln(1) = 0$$

Vanishing of Heat Capacity:

$$c_V(0) = \lim_{T \rightarrow 0} T \left(\frac{\partial S}{\partial T}\right)_{V,N} = 0$$

Vanishing of Thermal Expansion:

$$\alpha(0) = \lim_{T \rightarrow 0} \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N} \equiv \lim_{T \rightarrow 0} -\frac{1}{V} \left(\frac{\partial S}{\partial P}\right)_{T,N} = 0$$

Unattainability of Absolute Zero:
"We cannot reach absolute zero in finite cooling steps"

Introductory Principles

Microstates:

"A Macrostate is a complete description of a system"

$$\sum_i n_i = N \qquad \sum_i n_i \varepsilon_i = E$$
$$\Omega = \frac{N!}{n_1! \cdot n_2! \cdot \dots}$$

Classical Microstates:

$$(\Delta x \Delta p_x)(\Delta y \Delta p_y)(\Delta z \Delta p_z) = h^3$$

Number of States = $\frac{\text{Volume in Phase Space}}{h^3}$

Statistical Principles:

AVERAGING PRINCIPLE - In equilibrium, all accessible microstates are equally likely due to ergodicity.

FUNDAMENTAL PRINCIPLE OF STATISTICAL MECHANICS - The macrostate with the most accessible microstates is most probable and constitutes the equilibrium.

Planck’s Analysis:

Plank predicted that there must be a link between the entropy and the number of microstates...

$$S = k_B \ln(\Omega)$$

The Boltzmann Distribution

Stirling’s Approximation:

$$\ln(N!) \approx N \ln(N) - N$$

The Partition Function:

$$Z = \sum_{\text{states}, i} e^{-\varepsilon_i / k_B T} = \sum_{\text{levels}, j} \omega_j e^{-\varepsilon_j / k_B T}$$

Non-Interacting Particles: $Z_N = (Z_1)^N$

The Boltzmann Distribution Law:

$$n_i = \omega_i \frac{N}{Z} \exp \left[-\frac{\varepsilon_i}{k_B T} \right]$$

Helmholtz Free Energy:

$$F = -k_B T \ln(Z_N) = -N k_B T \ln(Z_1)$$

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

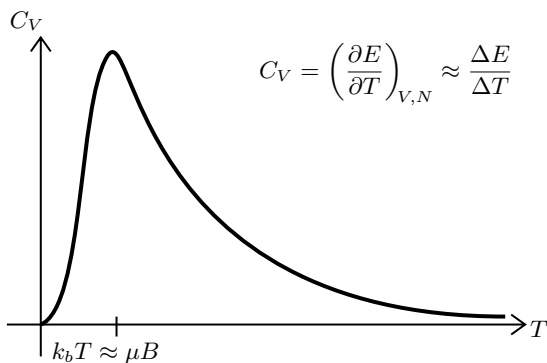
Energy:

$$E = - \frac{\partial \ln(Z_N)}{\partial \beta} = -N \frac{\partial \ln(Z_1)}{\partial \beta} \quad \beta = \frac{1}{k_B T}$$

The Paramagnetic Solid

Schottky Anomaly:

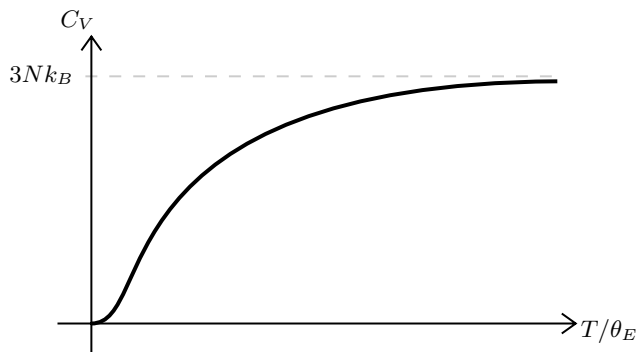
The Schottky Anomaly is the observed peak in the heat capacity of paramagnetic solids at low temperatures...



The Harmonic Oscillator

Einstein's Model of C_V for Solids:

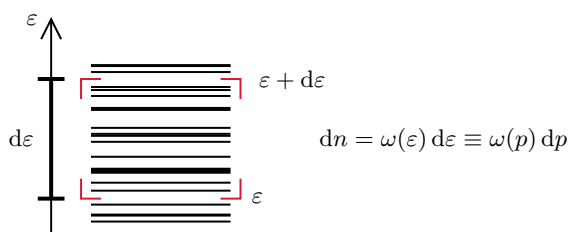
Einstein's models the interactions between atoms in a solid as harmonic oscillators...



The Density of States

Density of State:

The Density of States (DOS) is the number of allowed energy states dn across a unit energy range $d\varepsilon$...



$$Z = \sum_{\text{states}, i} f(\varepsilon_i) = \int_{\text{energy}} \omega(\varepsilon) f(\varepsilon) d\varepsilon$$

DOS Spins: "Multiply by N^s of spin states"

The Dilute Gas

Factorisation of Z :

Distinguishable, localised particles: $Z_N = Z_1^N$

Indistinguishable, non-localised particles: $Z_N = Z_1^N / N!$

Dilute Gases:

"A dilute gas has either low density or high temperature such that no state is occupied more than once (acts ideal)"

Quantum Concentration:

$$\frac{N}{V} = n \ll n_Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

The Monatomic Ideal Gas:

$$\varepsilon = \varepsilon_{\text{trans}}$$

Consider the partition of a monatomic ideal gas...

$$Z_{\text{trans}}^{(1)} = \int_0^\infty \omega(\varepsilon) e^{-\varepsilon/\beta} d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2m}{h^2} \right)^{3/2} \int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/\beta} d\varepsilon$$

By solving this, the full partition function can be found...

$$Z_{\text{trans}}^{(N)} = \frac{1}{N!} \left(Z_{\text{trans}}^{(1)} \right)^N = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}$$

We can then find the energy...

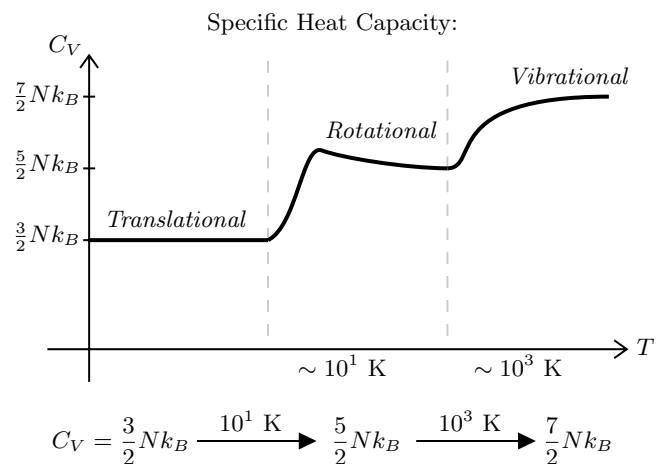
$$E = - \frac{\partial}{\partial \beta} \left[\ln \left(Z_{\text{trans}}^{(N)} \right) \right]$$

$$E_{\text{trans}}(N) = \frac{3}{2} N k_B T$$

The Diatomic Molecule:

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$$

"Each different energy domain unlocks $k_B T/2$ per each of its degrees of freedom"

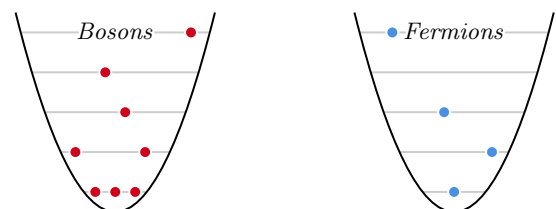


The Distribution Functions

Indistinguishability and Quantum Mechanics:

$$\psi(2, 1) = \pm \psi(1, 2)$$

Positive symmetric solutions are Bosons with integer spin and no state occupancy restrictions. Negative asymmetric solutions are Fermions with half-integer spin and one occupancy per state due to the pauli exclusion principle...



Fermi-Dirac:



$$f_{\text{FD}}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1}$$

Bose-Einstein:



$$f_{\text{BE}}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} - 1}$$

Maxwell-Boltzmann:

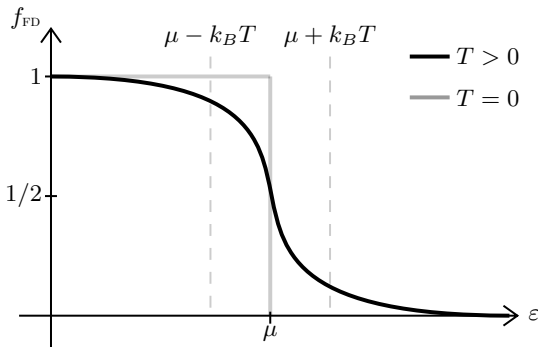
$$f_{\text{MB}}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} \quad \mu_{\text{MB}} = -k_B T \ln(Z)$$

Distribution Calculations:

$$N = \int_0^\infty \omega(\varepsilon) f(\varepsilon) d\varepsilon \quad E = \int_0^\infty \varepsilon \omega(\varepsilon) f(\varepsilon) d\varepsilon$$

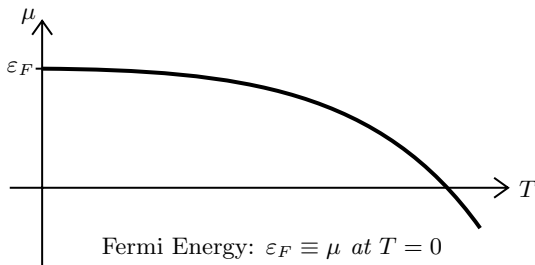
The Fermi-Dirac Gas

Fermi-Dirac Distribution:



The Chemical Potential:

The Chemical Potential (μ) is the energy where half the states are occupied, such that $f_{\text{FD}}(\mu) = 1/2$...



Degenerate Gas:

$$k_B T \ll \varepsilon_F \quad f_{\text{FD}}(\varepsilon) = \begin{cases} 1, & \varepsilon \leq \varepsilon_F, \\ 0, & \varepsilon > \varepsilon_F. \end{cases}$$

Specific Heat Capacity:

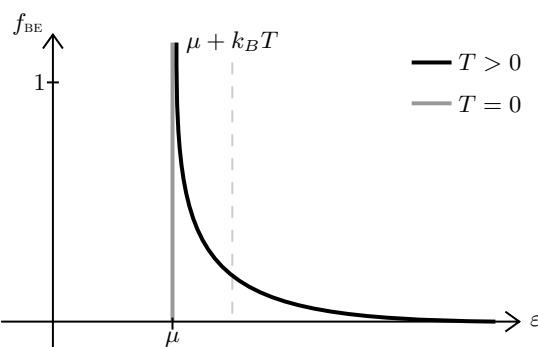
$$C_V \propto T$$

Pressure:

$$PV = \frac{2}{3} E$$

The Bose-Einstein Gas

Bose-Einstein Distribution:



Phoney-Bosons:

"Phoney-Bosons are bosons that have no rest mass (photons, phonons) and so can easily be created/destroyed (unfixed N)"

$$\mu = 0 \implies f_{\text{BE}}^{\text{phon}}(\varepsilon) = \frac{1}{e^{\varepsilon/k_B T} - 1}$$

Black Body Radiation Laws:

Wien's Displacement:

Stefan-Boltzmann:

$$\lambda_{\text{max}} T = \frac{hc}{2.82 k_B} = \text{const.}$$

$$\text{Flux} \equiv \sigma T^4$$

Phonons and Lattice Vibrations:

Einstein - Atoms are harmonic oscillators, vibrating in three dimensions ($3N$) at the same frequency ω_E ... $C_V \propto T$

Debye - Atoms vibrate in a correlated way (like a sound wave) at a frequency $\omega_D = c_s q$... $C_V \propto T^3$

$$\text{Debye Cutoff in 3D : } 3N = \int_0^{\nu_F} \omega(\nu) d\nu$$

Massive-Bosons:

"Massive-Bosons are bosons that have rest mass (W, Z, ^4He) and so cannot easily be created/destroyed (fixed N)"

$$\mu \neq 0$$

Bose-Einstein Condensation:

"As temperature cools below a critical point T_c , Bosons can accumulate in the ground state forming a BEC"

