

## 0. PHYSICAL CONSTANTS

$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$ ,  $N_A = 6.022 \times 10^{23}$ ,  $R = 8.315 \text{ J/mol} \cdot \text{K}$ ,  $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} = 4.136 \times 10^{-15} \text{ eV} \cdot \text{s}$

## 1. ENERGY IN THERMAL PHYSICS

**1.1. Thermal equilibrium.** *Temperature* is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously *lose* energy is at the *higher* energy. Room temperature  $300\text{K}$

**1.2. The ideal gas.**  $PV = nRT = Nk_B T$ .  $n$  is no of moles,  $N = nN_A$  is number of molecules.  $k_B = R/N_A$ . Latter equation is valid when avg. space b/w molecules is larger than size of molecules.  $\bar{E}_{K,trans} = \frac{3}{2}kT$ .

**1.3. Equipartition of energy.** Theorem: at temperature  $T$ , the average energy of any quadratic degree of freedom is  $\frac{1}{2}kT$ .  $U_{thermal} = Nf\frac{1}{2}kT$ . Monoatomic gas:  $f = 3$ . Diatomic gas:  $f = 5, 6$  (3 trans., 2-3, rot.) or  $f = 8$  (3 trans., 3 rot., 2 vibr. K, P). Solid:  $f = 6$  (6 vibr. 3K, 3P). Some vibrational energies may be "frozen out" at room temperature.

**1.4. Heat and work.** First law of thermodynamics  $\Delta U = Q + W$ . The change in energy is equal to the heat added and the work done. Heat transfer happens by *conduction*, *convection* and *radiation*.

**1.5. Compression work.** Consider a piston. The force is  $F = PA$ . Assumes that the pressure is uniform. Compression must be slow enough so the gas has time to continually equilibrate to the changing conditions  $\rightarrow$  *quasistatic*. A compressed gas, i.e. negative  $\Delta V$  gives  $W = F\Delta x = P\Delta x = -P\Delta V$ .

**1.5.1. Compression of ideal gas.** Two idealised ways: *Isothermal* compression is so slow that the temperature of the gas does not rise (quasistatic). *Adiabatic* compression is so fast that no heat escapes during the compression.  $VT^{f/2} = \text{constant}$ ,  $V^\gamma P = \text{constant}$ .  $\gamma = \frac{f+2}{f}$  is the adiabatic exponent.

**1.6. Heat capacities.** Amount of heat needed to raise an object's temperature, per degree temperature increase:  $C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$ .  $W = 0$  and  $V = \text{constant}$  is called heat capacity at *constant volume*, else there would be compression work,  $-P\Delta V$ .  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ . If an object expand when heated and do work on surroundings, there is negative  $W$ . At constant  $P$ ,  $Q$  is unambiguous  $\rightarrow$  heat capacity at *constant pressure*:  $C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\frac{\partial V}{\partial T}_P$ .

**1.6.1. Latent heat.** During a phase transformation  $C = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty$ . While  $L = \frac{Q}{m}$  is the heat required to accomplish the transformation, the *latent heat*.

**1.6.2. Enthalpy.** To create a rabbit out of nothing, the sorcerer must summon up not only the energy  $U$  of the rabbit, but also some additional energy, equal to  $PV$ , to push the atmosphere out of the way to make room. The *enthalpy*:  $H = U + PV$ . At constant  $P$ ,  $\Delta H = Q + W_{other}$ .

## 2. THE SECOND LAW

Entropy, and multiplicity, tends to increase.

**2.1. Two-state systems.** Multiplicity is given by the binomial coefficient.  $\Omega(N, n) = \frac{N!}{n!(N-n)!} = \binom{N}{n}$ . How many ways to pick  $n$  objects out of  $N$ . Permutations:  ${}_n P_k = n(n-1)(n-2)\dots(n-k) = \frac{n!}{(n-k)!}$ . Unordered permutations:  ${}_n C_k = {}_n P_k / k! = \binom{n}{k}$ .

**2.2. Einstein model of a solid.** One energy unit is  $h\nu = \hbar\omega$ . Multiplicity of Einstein solid with  $N$  oscillators ( $N/3$  atoms) and  $q$  energy units:  $\Omega(N, q) = \binom{q+N-1}{q}$ .

**2.3. Interacting systems.** Two solids are *weakly coupled* when flow of energy between them is much slower than flow of energy between atoms within each solid. Macrostate is the combined system, specified by temporarily constrained values  $U_A, U_B$ . Over time they will change, with the sum  $U_{tot} = U_A + U_B$  remaining fixed. All parameters in such a system is  $N_A, N_B, q_{tot} = q_A + q_B, \Omega_{tot} = \Omega_A \Omega_B$ . Fundamental assumption of statistical mechanics: In an isolated system, all accessible microstates are equally probable.

**2.4. Large systems.** If  $|x| \ll 1$ , a Taylor expansion gives  $\ln(x+1) \approx x$ . If  $N \gg 1$  one can apply *Stirling's approximation*:  $N! \approx N^N e^{-1} \sqrt{2\pi N}$ . If  $N$  is a large number, and  $N!$  is very large, the square root factor can be omitted. This is usually good enough:  $\ln N! = N \ln N - N$ . In a large Einstein solid  $q \gg N$  is the high temperature limit:  $\Omega \approx \frac{(q+N)!}{q!N!}$ ,  $\ln \Omega \approx (q+N) \ln(q+N) - q \ln q - N \ln N$ , where  $\ln(q+N) \approx \ln q + \frac{N}{q}$ . S.T.:  $\ln \Omega \approx N \ln \frac{q}{N} + N + \frac{N^2}{q}$ .

**2.5. The ideal gas.**  $\Omega(U, V, N) = f(N) V^N U^{3N/2}$ , where  $f(N)$  is a complicated function of  $N$ .

$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times (\text{area of momentum hypersphere})$ . "area" =  $\frac{2\pi^{d/2}}{(\frac{d}{2}-1)} r^{d-1}$ , where in general  $d = 3N$  and  $r = \sqrt{2mU}$ .

**2.6. Entropy.**  $S = k \ln \Omega$ . Now you see why the logarithm of the multiplicity is nice to have. Entropy of an ideal gas:  $S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$  (The Sackur-Tetrode equation). Depends on  $V, E, N$ . Increasing any of them increases  $S$ .

**2.6.1. Mixing.** One gas into another chamber:  $\Delta S_A = Nk \ln \frac{V_f}{V_i} = Nk \ln 2$ . Two gases mixing, by removing a partition:  $\Delta S_{tot} = \Delta S_A + \Delta S_B = 2Nk \ln 2$ . Must be distinguishable gases. Gibbs Paradox.

**2.6.2. Irreversible.** Processes that create new entropy are said to be irreversible. A sudden expansion is irreversible. A reversible volume change must in fact be quasistatic such that  $W = -P\Delta V$ .

### 3. INTERACTIONS AND IMPLICATIONS

**3.1. Temperature.** Two Einstein solids:  $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$  at equilibrium with  $N_A, N_B$  fixed. Temperature is defined as  $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$ . If the slope is large the temperature must be small and vice versa.

**3.2. Entropy and heat.** Algorithm to predict the heat capacity of a system: 1. Express the multiplicity  $\Omega$  as a function of  $N, V$  and  $N$ . 2. Take the logarithm to find the entropy:  $S = k \ln \Omega$ . 3. Differentiate with respect to  $U$  and take the reciprocal to find the temperature,  $T$  as a function of  $U$  and other var's. 4. Solve for  $U$  as a function of  $T$  (and others). 5. Differentiate  $U(T)$  to obtain a prediction of heat capacity (others held fixed).  $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$ . At very low temperatures all degrees of freedom must "freeze out", meaning  $C_V \rightarrow 0$  as  $T \rightarrow 0$ . This is the *third law*.

**3.3. Paramagnetism.** A system consists of  $N$  spin- $\frac{1}{2}$  particles, often referred to as dipoles, immersed in a constant magnetic field  $\mathbf{B}$ . Total energy is  $U = \mu B(N_\downarrow + N_\uparrow) = \mu B(N - 2N_\uparrow)$ . Magnetisation is  $M = \mu(N_\downarrow - N_\uparrow) = -\frac{U}{B}$ . Multiplicity is  $\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$ .

**3.4. Mechanical equilibrium and pressure.** Pressure is  $P = \left(\frac{\partial S}{\partial V}\right)_{U,N}$ . Another proof of ideal gas law:  $\Omega = f(N)V^N U^{3N/2}$ ,  $S = Nk \ln V + \frac{3}{2}Nk \ln U + k \ln f(N)$ ,  $P = T \frac{\partial}{\partial V}(Nk \ln V) = \frac{NkT}{V} \rightarrow PV = NkT$ .

**3.4.1. Thermodynamic identity.** Two steps:  $\Delta U$  and  $\Delta V$ . Sum of entropy change:  $\Delta S = (\Delta S)_1 + (\Delta S)_2$ . S.T.  $dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$ , then for a small change  $dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$ . Inserting definitions of temperature and pressure yields  $dS = \frac{1}{T}dU + \frac{P}{T}dV$  which can be rearranged to  $dU = TdS - PdV$ .

**3.4.2. Entropy and heat again.**  $dU = Tds - PdV = Q + W$  if any volume change is quasistatic. If  $Q = 0$  the process is also adiabatic  $\rightarrow$  isentropic. We have  $(\Delta S)_V = \int_{T_i}^{T_f} \frac{C_V}{T} dT$  and  $(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T} dT$

**3.5. Diffusive equilibrium and chemical potential.** The chemical potential is  $\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\Delta U}{\Delta N}\right)_S = -\epsilon$ , where  $\epsilon$  is the size of a unit of energy. The generalised thermodynamic identity becomes  $dU = TdS - PdV + \sum \mu_i dN_i$

### 4. ENGINES AND REFRIGERATORS

**4.1. Heat engine.** A device that absorbs heat and converts part of that energy into work. The work produced is the difference between the heat absorbed and the waste expelled:  $W = Q_h - Q_c$ , where  $Q_h$  is heat absorbed from the hot reservoir and  $Q_c$  is heat expelled to cold reservoir. Efficiency:  $e \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$ . First law: energy is conserved. Second law: entropy is a fluid that can be created but never destroyed, ergo  $\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h}$  and  $\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$ . One concludes  $e \leq 1 - \frac{T_c}{T_h}$ .

**4.1.1. The Carnot cycle (max efficiency).** Four steps:

1. Isothermal expansion at  $T_h$  while absorbing heat. 2. adiabatic expansion to  $T_c$ . 3. Isothermal compression at  $T_c$  while expelling heat. 4. Adiabatic compression back to  $T_h$ . The system must be but in contact with the hot reservoir during step 1 and with the cold reservoir during step 3.

**4.2. Refrigerators.** A heat engine in reverse. Efficiency now called coefficient of performance  $\text{COP} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{\frac{Q_h}{Q_c} - 1}$ . Some inequalities:  $\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c}$  which gives  $\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$ . One can conclude  $\text{COP} \leq \frac{1}{\frac{T_h}{T_c} - 1} = \frac{T_c}{T_h - T_c}$ .

### 5. FREE ENERGY AND CHEMICAL THERMODYNAMICS

Processes that are not cyclic. Interaction with environment s.t.  $T$  and  $P$  are constant, not  $E$  and  $V$ .

**5.1. Free Energy as Available work.** Environment with constant  $P$ , related to *enthalpy* is **Helmholtz free energy**:  $F \equiv U - TS = U - T\Delta S$ . Energy needed to create system, minus energy for from environment at temp  $T$ .

Environment with constant  $P$  and  $T$ , work needed to create/destroy is Gibbs free energy  $G = U - TS + PV = H - TS$ . The magician needs not the entire enthalpy, some comes for free as heat.

The four functions  $U, H, F$  and  $G$  are called **thermodynamic potentials**. Identities:  $H$ :  $dH = dU + PdV + VdP = TdS + VdP + \mu dN$ ,  $F$ :  $dF = dU - TdS - SdT = -SdT - PdV + \mu dN$ ,  $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ ,  $P = \left(\frac{\partial F}{\partial V}\right)_{T,N}$ ,  $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,P}$ .  $G$ :  $dG = -SdT + VdP + \mu dN$ ,  $S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$ ,  $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ ,  $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$ .

Example of **Maxwell relation**:  $\left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_{V,N}\right)_{S,N} = \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_{S,N}\right)_{V,N} \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ .

**5.2. Free Energy as a Force toward Equilibrium.** An increase in total entropy. Constant  $N, U, V$ :  $S$  increase. Constant  $N, T, V$ :  $F$  decrease. Constant  $N, T, P$ :  $G$  decrease. Extensive properties:  $V, N, S, U, H, F, G, m$ . Intensive properties:  $T, P, \mu, \rho$ .

**5.3. Phase Transformations of Pure Substances.** The **Clausius-Clapyron relation**:  $G_l = G_g$  at phase boundary, to remain  $G_l = dG_g$ . Thermodynamic identity for  $G$ :  $-S_l dT + V_l dP = -S_g dT + V_g dP$  gives  $\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}$ . Write  $S_g - S_l = \frac{L}{T}$ , where  $L$  is latent heat, to get  $\frac{dP}{dT} = \frac{L}{T\Delta V}$ . Applies to the slope of any phase boundary line on a  $PT$  diagram.

The **van der Waals equation** is  $\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$ . Mod of ideal gas with molecular interaction.

### 6. BOLTZMANN STATISTICS

**6.1. The Boltzmann factor.** System in contact with reservoir and assume equal probability for all microstates. Boltzmann factor =  $e^{-E(s)/kT}$ . Partition function:  $Z = \sum_s e^{-E(s)/kT}$ . Boltzmann/canonical distribution:  $\mathcal{P}(s) = \frac{1}{Z} e^{-E(s)/kT}$ .

**6.2. Average Values.**  $\bar{X} = \sum_s X(s)P(s)$ .  $\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$ . Example: Rotation of diatomic molecules (2 rot d.o.f.). Assuming low density. Allowed energies  $E(j) = j(j+1)\epsilon$ ,  $j = 0, 1, \dots$  with degeneracy  $\Omega(j)2j+1$ . Then  $X_{rot} = \sum_{j=0}^{\infty} (2j+1)e^{-E(j)/kT}$ . One can approximate with an integral if  $kt \gg \epsilon$ :  $Z_{rot} \approx \int_0^{\infty} (2j+1)e^{-E(j)/kT} dj = \frac{kT}{\epsilon} \rightarrow \bar{E} = kT$  in agreement with the equipartition theorem (identical atoms, divide by 2).  $C_V = \frac{\partial \bar{E}}{\partial T} = k$ . At low  $T$ ,  $C_V \rightarrow 0$  according to third law. Agrees with exact  $Z$ .

**6.3. The Equipartition Theorem.** Applies to systems with energy in the form of quadratic degrees of freedom:  $E(q) = cq^2$  where  $c$  is a constant and  $q$  is a coordinate or momentum variable ( $x, p_x, L_x$ ). Each  $q$  corresponds to a separate, independent state. Pretend they're discretely spaced, separated by intervals  $\Delta q$ .  $Z = \sum_q e^{-\beta cq^2} \approx \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq$ . Approximate to integral if  $\Delta q$  is small. Bell curve. Calculate  $\bar{E} = \frac{1}{2}kT$  from this to confirm equipartition theorem. Only true in high  $T$  limit, or when spacing b/w energy levels is much less than  $kT$ .

**6.4. The Maxwell Speed Distribution.** From equipartition theorem,  $v_{rms} = \sqrt{\frac{3kT}{m}}$ . This is an average, we want a distributions for speed of molecules.  $v$  can vary continuously  $\rightarrow$  infinitely small probabilities. Use intervals, area under graph:  $\mathcal{P}(v_1 \dots v_2) = \int_{v_1}^{v_2} \mathcal{D}(v) dv$ , where  $\mathcal{P}(v) \propto e^{-mv^2/2kT}$  and  $\mathcal{D}(v) \propto \mathcal{P}(v) \times \Omega(v)$ , where  $\Omega(v)$  is no of vectors  $\vec{v}$  corresponding to  $v$  ( $\propto 4\pi v^2$ ). Must be set of vectors on surface of sphere with Area =  $4\pi v^2$ . Then  $\mathcal{D}(s) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$ . Find  $C$  by normalising, with substitute  $x = \sqrt{m/2kT} v$ ,  $1 = 4\pi C \left(\frac{2kT}{m}\right)^{3/2} \int_0^{\infty} x^2 e^{-x^2} dx \rightarrow C = (m/2\pi kT)^{3/2}$ . Final result:  $\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}$ , note that  $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$ .

**6.5. Partition Functions and Free Energy.** System at fixed  $U$  in contact with reservoir at  $T$ .  $Z(T)$  analogous to  $\Omega(T)$ .  $F = U - TS = -kT \ln Z$ , tends to decrease.  $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ ,  $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ ,  $\mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$ .

**6.6. Partition Functions for Composite Systems. Two particles:**  $Z_{tot} = \sum_s e^{-\beta[E_1(s)+E_2(s)]} = \sum_s e^{-\beta E_1(s)} e^{-\beta E_2(s)}$ . Distinguishable  $Z_{tot} = \sum_{s_1} \sum_{s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)} = Z_1 Z_2$ . Indistinguishable  $Z_{tot} = \frac{1}{2} Z_1 Z_2$ .  **$N$  particles:** Distinguishable  $Z_{tot} = Z_1 Z_2 Z_3 \dots Z_N$ . Indistinguishable  $Z_{tot} \frac{1}{Z} Z_1^N$ . Assumes low density, i.e.

**6.7. Ideal gas revisited.** Boltzmann factors  $e^{-E(s)/kT} = e^{-E_{tr}(s)/kT} e^{-E_{int}(s)/kT}$ , additionally  $Z_1 = Z_{tr} Z_{int}$ . Translational first: Standing wave patterns are limited to  $\lambda_n = \frac{2L}{n}$ , using de Broglie ( $p = h/\lambda$ ),  $p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$ . Energy-momentum relation ( $E = p^2/2m$ ),  $E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2}$ .  $Z_{1D} = \sum_n e^{-E_n/kT} = \sum_n e^{-h^2 n^2/8mL^2 kT}$ . Integral approx  $Z_{1D} = \int_0^{\infty} e^{-h^2 n^2/8mL^2 kT} dn = \frac{\sqrt{\pi}}{2} \sqrt{\frac{8mL^2 kT}{h^2}} = \sqrt{\frac{2\pi mkT}{h^2}} L \equiv \frac{L}{\ell_Q}$ . In 3D:  $E_{tr} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$  and  $Z_{tr} = \frac{L_x}{\ell_Q} \frac{L_y}{\ell_Q} \frac{L_z}{\ell_Q} = \frac{V}{v_Q}$ . Partition function for one particle:  $Z_1 = \frac{V}{v_Q} Z_{int}$  and for  $N$ :  $Z = \frac{1}{N!} \left(\frac{V Z_{int}}{v_Q}\right)^N$ .

## 7. QUANTUM STATISTICS

**7.1. The Gibbs Factor.** Gibbs factor  $= e^{-[E(s)-\mu N(s)]/kT}$ .  $\mathcal{P}(s) = \frac{1}{Z} e^{-[E(s)-\mu N(s)]/kT}$ . The grand partition function  $\mathcal{Z} = \sum_s e^{-[E(s)-\mu N(s)]/kT}$ .

**7.2. Bosons and Fermions.** Particles with integer spin are bosons, while particles with half-integer spin are fermions. Two identical fermions cannot occupy the same space (**Pauli exclusion principle**). If  $Z_1 \gg N$  chance of two particles in same state is negligible. For ideal gas  $Z_1 = \frac{V Z_{int}}{v_Q}$ . The quantum volume is  $v_Q = \ell_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$ , a cube of the average de Broglie wavelength. Then:  $\frac{V}{N} \gg v_Q$ . Distance b/w particles must be greater than de Broglie w.l. **Fermi-Dirac:**  $n$  can only be 0 or 1, so  $\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT}$ . Occupancy:  $\bar{n} = \sum_n n \mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) = \frac{e^{-(\epsilon-\mu)/kT}}{1 + e^{-(\epsilon-\mu)/kT}}$ . Simplification yields distribution  $\bar{n}_{FD} = \frac{1}{e^{(\epsilon-\mu)/kT} + 1}$ . **Bose-Einstein:**  $n$  can be any non-negative integer, so the grand partition function is  $\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT} + \dots = 1 + e^{-(\epsilon-\mu)/kT} + (e^{-(\epsilon-\mu)/kT})^2 + \dots = \frac{1}{1 - e^{-(\epsilon-\mu)/kT}}$ .  $\mu$  must be less than  $\epsilon$ , the series must converge. Occupancy:  $\bar{n} = \sum_n n \mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) + 2 \cdot \mathcal{P}(2) + \dots$ , abbreviate  $x \equiv (\epsilon - \mu)/kT$ . Then  $\bar{n} = \sum_n \frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}} \sum_n \frac{\partial}{\partial x} e^{-nx} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x}$ . Distribution:  $\bar{n}_{BE} = -(1 - e^{-x}) \frac{\partial}{\partial x} (1 - e^{-x}) = (1 - e^{-x})(1 - e^{-x})^{-2} (e^{-x}) = \frac{1}{e^{(\epsilon-\mu)/kT} - 1}$

**7.3. Degenerate Fermi Gases.** At  $t = 0$  Fermi-Dirac becomes step function. All states  $\epsilon_s < \mu$  are occupied and v.v.  $\mu$  is the **Fermi energy**:  $\epsilon_F \equiv \mu(T = 0)$ . A free electron in a box have allowed wavelengths  $\lambda_n = \frac{2L}{n}$ ,  $p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$ , in 3D  $p_x = \frac{hn_x}{2L}$  etc. which yields allowed energies  $\epsilon = \frac{|p|^2}{2m} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$ .  $\epsilon_F$  is the energy of a state that sits just on the surface of an eight-sphere in " $n$ -space", so  $\epsilon_F = \frac{h^2 n_{max}^2}{8mL^2}$ . Because fermions have two spin orientations, the number of occupied states is twice the volume of an eight-sphere  $N = 2 \times (\text{volume of eighth-sphere}) = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_{max}^3 = \frac{\pi n_{max}^3}{3}$ . Combining gives the Fermi energy  $\epsilon_F = \frac{h^2}{8m} \left(\frac{3N}{\pi V}\right)^{2/3}$ .

The number of states in  $n$ -space with magnitude  $n$  between  $n$  and  $n + dn$  is  $D(n)dn = 2 \cdot \frac{1}{8} \cdot 4\pi n^2 dn = \pi n^2 dn$ . No of states:  $N = \sum_{n_x, n_y, n_z} 2\bar{n}(\epsilon(n_x, n_y, n_z), \mu, T) = \int_0^{\infty} \bar{n}(\epsilon(n), \mu, T) D(n) dn$ . Avg energy:  $\bar{E} = \sum_{n_x, n_y, n_z} 2\epsilon(n_x, n_y, n_z) \bar{n}(\epsilon(n_x, n_y, n_z), \mu, T) = \int_0^{\infty} \epsilon(n) \bar{n}(\epsilon(n), \mu, T) D(n) dn$ . Substitute:  $d\epsilon(n) = \frac{d\epsilon}{dn} dn$ . Which gives  $N = \int_0^{\infty} \bar{n}(\epsilon(n), \mu, T) D(n(\epsilon)) \frac{1}{d\epsilon/dn} d\epsilon$  and  $\bar{E} = \int_0^{\infty} \epsilon(n) \bar{n}(\epsilon(n), \mu, T) D(n(\epsilon)) \frac{1}{d\epsilon/dn} d\epsilon$ . See that  $D(n)dn = D(\epsilon)d\epsilon$ . Apply relation  $\epsilon(n) = \frac{h^2}{2m} \left(\frac{\pi}{L}\right)^2 n^2 = an^2 \rightarrow n = \sqrt{\frac{\epsilon}{a}}$  and  $\frac{d\epsilon}{dn} = 2an$ . Then:  $D(\epsilon) = D(n) \frac{1}{d\epsilon/dn} = \pi n^2 \frac{1}{2an} = \frac{\pi}{2a} n = \frac{\pi}{2a} \sqrt{\frac{\epsilon}{a}} = \frac{\pi}{2a^{3/2}} \epsilon^{1/2} = \frac{\pi(8m)^{3/2}}{2h^3} V \sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon}$ .

**7.4. Blackbody Radiation.** QHO allowed energies:  $E_n = 0, hf, 2hf, \dots$ . Partition function:  $Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + \dots = \frac{1}{1 - e^{-\beta hf}}$ . Average energy:  $\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{hf}{e^{\beta hf/kT} - 1}$ . Average number of units of energy is  $\bar{n}_{Pl} = \frac{1}{e^{\beta hf/kT} - 1}$ .

**7.5. Bose-Einstein Condensation.** Energy of atoms in box:

$\epsilon_0 = \frac{3h^2}{8mL^2}$ . Atoms in this state (B-E):

$N_0 = \frac{1}{e^{(\epsilon_0 - \mu)/kT} - 1}$ . Taylor series gives  $\frac{kT}{\epsilon_0 - \mu}$ . Total number of atoms approximated by integral  $N = \int_0^\infty g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon$ .

Density of states:  $g(\epsilon) = \frac{2}{\sqrt{\pi}} \left( \frac{2\pi m}{h^2} \right)^{3/2} V \sqrt{\epsilon}$ . Guess  $\mu =$

0, switch  $x = \epsilon/kT$ .  $N = \frac{2}{\sqrt{\pi}} \left( \frac{2\pi m}{h^2} \right)^{3/2} V \int_0^\infty \frac{\sqrt{x} dx}{e^{x/kT} - 1} = \frac{2}{\sqrt{\pi}} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V \int_0^\infty \frac{\sqrt{x} dx}{e^x - 1}$ . The integral is 2.315. Wrong

result.  $N_{excited} = 2.612 \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V = \left( \frac{T}{T_c} \right)^{3/2} N$  when

$T < T_c$ . Rest is in ground state,  $N_0 = N - N_{excited} = \left[ 1 - \left( \frac{T}{T_c} \right)^{3/2} \right] N$ . Abrupt accumulation of atoms in ground

state at temperatures below  $T_c$  is called **Bose-Einstein condensation**.