canonical ensemble $z = \sum_s e^{-\epsilon_s/\tau}$ **I** $P(s) = \frac{1}{Z}e^{-\epsilon_s/\tau}$ **I** $U = \langle \epsilon \rangle = \sum_s \epsilon_s P(s) = \frac{1}{z}\sum_s \epsilon_s e^{-\epsilon_s/\tau} = \tau^2 \frac{\partial \ln z}{\partial \tau}$ **I** characteristic function: $\sigma = \ln(\Gamma)$ **I** **w5 d1 The law of increase of energy** Thermal contact entropy before $\sigma_I = \ln(g_1(U_1,0)g_2(U_2,0))$, $\sigma_F = \ln\left(\sum_{U_1} g_1(U_1)g_2(U-U_1)\right) = \ln((g_1,g_2)max)$ **I** when you remove a constraint you expect the entropy to increase **I** Law of increase in entropy is a statistical statement, Law of Thermodynamics, **I** 0th If system a is in equilibrium with system b and b is in equilibrium with system c, then a is in equilibrium with system c **I** 1st Energy conservation, heat is a form of energy **I** 2nd Law of increase of entropy, when you remove a constraint you expect the entropy increase **I** 3rd The entropy approaches a constant as $\tau \to 0$ and $\sigma(\tau = 0) = \ln g(\tau = 0)$ **I** the multiplicity of the ground state of the system **Thermal contact** Q. which direction is the energy flow? upon thermal contact. **I** $\tau_1 > \tau_2$ **I** $\sigma = \ln g$ **I** $\tau = \frac{\partial U}{\partial \sigma}$ **I** $\partial \sigma = \partial \sigma_1 + \partial \sigma_2 = \frac{\partial \sigma_1}{\partial U_1}\partial U_1 + \frac{\partial \sigma_2}{\partial U_2}\partial U_2 = \frac{\partial \sigma_1}{\partial U_1}\partial - U + \frac{\partial \sigma_2}{\partial U}\partial U = (\frac{1}{\tau_2} - \frac{1}{\tau_1})\partial U \geq 0$ if $\tau_1 > \tau_2$ then $\partial U > 0$ if $\tau_1 < \tau_2$ then $\partial U < 0$ **I** $\partial U = \frac{\partial U}{\partial \sigma}\partial \sigma + \frac{\partial U}{\partial V}\partial V$ **I** $\partial U = \tau \partial \sigma - P \partial V$ (first law of thermo dynamics) **pressure** Quantum state $V \to V - V_0$ **I** $\delta U = -\frac{\partial \epsilon_s}{\partial V}\cdot \delta V$ **I** $\delta U = P_s \delta V$ **I** $P_s = -(\frac{\partial \epsilon_s}{\partial V})$(pressure from a single quantum mechanical state) **I** Pressure $P = \langle P_s \rangle = -(\frac{\partial U}{\partial V})$ (P_s pressure for a particular quantum state) **I** $= \sum_s P(s)P_s$ ($P(s)$ probability of quantum state) **I** $= \sum_s p(s) - (\frac{\partial \epsilon_s}{\partial V})$ **I** $= -(\frac{\partial(\sum_s p(s)\epsilon_s)}{dV}) = -(\frac{\partial U}{\partial V})$ **I** Review $\partial U = \tau \partial \sigma - P \partial v$ **I** **w5 d2 chapter 3** Boltsman Distribution and Helmholts free energy, a system in equilibrium with the environment, temperature is fixed **I** Q. pdf for Microstates **I** S: system, ϵ, $s = (s_s, s_r)$ **I** R: reservoir $U_0 - \epsilon$, $P(s_s, s_R) = $ constant **I** $R >> s$, $R + s$: closed system U_0, $P(s_s) = \sum_{s_r} P(s_s, s_R)$ **I** $\frac{P(1)}{P(2)} = \frac{g_R(u_0-\epsilon_1)}{g_R(u_0-\epsilon_2)}$ **I** 1,2 are Microstates of the System s **I** $\frac{P(1)}{P(2)} = \frac{e^{\sigma_R(U_0-\epsilon_1)}}{e^{\sigma_R(U_0-\epsilon_2)}} = e^{\sigma_R(U_0-\epsilon_1) - \sigma_R(U_0-\epsilon_2)}$ **I** $\epsilon_1 << U_0$, $\epsilon_2 << U_0$ **I** $\epsilon_R(U_0-\epsilon) \simeq \sigma_R(U_0) - \epsilon(\frac{\partial \sigma_R}{\partial U})$ **I** $\frac{P(1)}{P(2)} = e^{-(\epsilon_1-\epsilon_2)/\tau}$ **I** Taylor expansion $P(s) \propto e^{-\epsilon_s/\tau}$ **probability of microstates in thermal equilibrium with its environment** $P(s) = \frac{1}{Z}e^{-\epsilon_s/\tau}$ **I** $U = \langle \epsilon \rangle = \sum_s \epsilon_s P(s) = \frac{1}{z}\sum_s \epsilon_s e^{-\epsilon_s/\tau} = \tau^2 \frac{\partial \ln z}{\partial \tau}$ **I** at $\tau = 0$, the system settles in the ground state. $\sum_s p(s) = 1 \to z = \sum_s e^{\epsilon_s/\tau}$ **I** Z: partition function **I** $e^{-\epsilon_s/\tau}$: Boltsman factor **I** $e^{-\epsilon_s/\tau}$ **I** $z = \sum_s e^{-(\epsilon_s + \Delta)/\tau} = e^{-\Delta/\tau}\sum_s e^{-\epsilon_s/\tau}$ **I** $P(s) \to \frac{e^{-(\epsilon_s + \Delta)/\tau}}{z'} = \frac{e^{-\epsilon_s/\tau}}{z}$ **I** $Z(\tau)$: high temp limit $T \to \infty$, $P(s) \to$ uniform $= \frac{1}{z}$, Z: number of microstates in the system, low temp limit $\tau \to 0$ **I** $P(s) \to 0$ if $\epsilon_s \neq 0$ and $= \frac{1}{z}$ if $\epsilon_s = 0$

ex: one particle, only two states state 1 energy 0, and state 2 energy ϵ **I** $z = 1 + e^{-\epsilon/\tau}$ **I** $U = \frac{1}{1 + e^{-\epsilon/\tau}}(\epsilon e^{\epsilon/\tau})$ **I** 1. microstates and energetics 1.5 decide the ensemble 2. z get the partition function 3. U,... $\to z$(from partition function) **I** $z = e^{-0/\tau} + e^{-\epsilon/\tau} = 1 + e^{-\epsilon\tau}$ **I** $U = \langle \epsilon \rangle = \frac{\epsilon e^{-\epsilon/\tau}}{1 + e^{-\epsilon\tau}} = \frac{\tau \partial \ln z}{d\tau}$ **I** review $P(s) = \frac{e^{-\epsilon_s/\tau}}{z}$ and $z = \sum_s e^{-\epsilon_s/\tau}$

w6 d1 how do we relate free energy F to microscopic quantities $F = -\tau \ln z(B, V, N)$ **I** demonstrate $-\tau \ln(z) = U - \tau \sigma$ **I** connection with ThermoDynamics: free energy [Helmholtz free energy] $F \equiv U - \tau \sigma$ **I** $\partial U = \tau \partial \sigma - P \partial V$ **I** $\partial F \equiv \partial U - \partial(\tau \sigma) = \tau \partial \sigma - P \partial v - (\tau \sigma + \sigma \partial \tau) = -\sigma \partial \tau - P \partial V$ **Proof** **I** if we identify $\sigma = -\frac{\partial F}{\partial \tau}$ **I** main framework for canonical ensemble from T.D. $\partial F = -\sigma \partial \tau - P \partial v$ **I** $\sigma = -\frac{\partial F}{\partial \tau}$ **I** $P = -\frac{\partial F}{\partial V}$ **I** $F = U - \tau \sigma$ **I** **another expression of σ** for an isolated system $\sigma = \log g$ for a system with a given temperature τ $\sigma = -(\frac{\partial F}{\partial \tau}) = -\sum_s p(s)\ln p(s)$ for isolated system $p(s) = \frac{1}{g}$ **I** $\sigma = -\ln \frac{1}{g}$ **I** $P(s) = \ln g$ review $F = -\tau \ln z(\tau)$ **I** $\sigma = -\frac{\partial F}{\partial \tau} \to \sigma = -\sum_s p(s)\ln p(s)$ **I** $P = -(\frac{\partial F}{\partial V})$ **w6 d2 dU and ideal gas law** $\partial U = \partial(\sum_s p(s)\epsilon_s) = \sum_s \epsilon_s \partial p(s) + \sum_s p(s)\partial \epsilon_s$ **I** 1st term, change in distribution on Microstates, 2. energy spectrum changes, no change in distribution **I** a) lets say change V $\sum_s p(s)\partial \epsilon_s = \sum_s p(s)\frac{\partial \epsilon_s}{\partial v}\partial v = -p\partial v$ **I** proof for a quantum system $P_s = -\frac{\partial \epsilon_s}{\partial v}$ **I** for thermal system, carry out ensemble average $P = -\sum_s p(s)\frac{\partial \epsilon_s}{\partial v} = -\sum_s \frac{e^{-\epsilon_s/\tau}}{z}\frac{\partial \epsilon_s}{\partial v} = \frac{\tau}{z}\frac{\partial}{\partial v}\sum_s e^{-\epsilon_s/\tau} = \frac{\tau}{z}\frac{\partial z}{\partial v} = \tau(\frac{\partial \ln z}{\partial v}) = P$ **I** **using canonical ensemble Proof** $\sum_s \epsilon_s \partial p(s) = \tau \partial \sigma$ **ideal gas** System of particles where they do not interact with each other, point particles **one atom in a box** $V = L^3$ **I** $\epsilon = \frac{\hbar^2}{2m}(\frac{\pi}{L})^2(n_x^2 + n_y^2 + n_z^2)$ **I** calculate partition function $Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\frac{\hbar^2}{2M}(\frac{\pi}{L})^2(n_x^2+n_y^2+n_z^2)} = \sum_{n_x} e^{-\frac{\hbar^2}{2M}n_x^2}... $ **I** $N \to \infty$ and $v \to \infty$ where $\frac{N}{V} = $ constant **I** can approximate $\sum_{n_x}$ with $\int$ **I** $\sum_{n_x} e^{\alpha^2 n^2}$ where $\alpha^2 \equiv \frac{\hbar^2 \pi^2}{2mL^2 \tau}$ **I** $= \int_0^\infty \partial n e^{-\alpha^2 n^2} = \frac{1}{2}\frac{1}{\alpha}\int_0^\infty \partial x e^{-x^2}$ **I** $\chi \equiv \alpha n$ **I** $\frac{1}{2}\frac{1}{\alpha}\pi^{1/2}$ **I** $Z_1 = \frac{\pi^{3/2}}{8\alpha^3} = \frac{V}{(2\pi\hbar^2/M\tau)^{3/2}}$ **I** rewrite as a ratio of two densities $n = \frac{1}{v}$ **I** $n_a = (\frac{M\tau}{2\pi\hbar^2})^{3/2} = \frac{1}{\lambda^3}$ quantum concentration **I** $\lambda = (\frac{2\pi\hbar^2}{M\tau})^{1/2}$ where λ is the thermal wavelength **I** $F = -\tau \ln z = -\tau \ln \frac{n_q}{n}$ **I** $U = \tau^2 \frac{\partial \ln z}{\partial \tau} = \frac{3}{2}\tau$ **I** $U = \frac{3}{2}N\tau$ internal energy of a system with N particles **I** **N atoms in a box** if particles do not interact $Z_2 = \sum_{n_{s1}n_{s1}n_{s1}}\sum_{n_{s2}n_{s2}n_{s2}} e^{-(\epsilon_1+\epsilon_2)/\tau} = z_1 \cdot z_1$ **N identical particles in a box.** $Z_n = \frac{1}{N!}Z_1^N = \frac{1}{N!}(n_q v)^N$ **I** $U = \frac{3}{2} = n\tau$ **I** equation of state $pV = n\tau$

w8 d1 Free energy as a force towards equilibrium Helmholtz free energy F, F is a minimum for a system in thermal contact with a reservoir R, if the volume of the system is kept constant. Consider the total energy of the system plus the reservoir temperature. $\partial \sigma_{total} = \partial \sigma + \partial \sigma_R$ **I** $\partial \sigma_R = \frac{1}{\tau}\partial U_R + \frac{P}{\tau}\partial V_R$ P = pressure and given no volume change **I** $\partial \sigma_{total} = \partial \sigma + \frac{1}{\tau}\partial U_R$ **I** $\partial U + \partial U_R = 0$ (Total energy conserved) **I** $\partial \sigma_{total} = \partial \sigma + \frac{1}{\tau}\partial U$ **I** $\partial U + \partial U_R = 0$(total energy) **I** $\partial \sigma_{total} = \partial \sigma - \frac{1}{\tau}\partial U$ **I** $\partial \sigma_{total} = -\frac{1}{\tau}\partial F$ **I** $F = U - \tau \sigma$ **I** $\partial F = \partial U - \tau \partial \sigma - \sigma \partial \tau$ **I** under the condition of fixed τ and V **I** $\partial F \leq 0 \to F$is a minimum in equilibrium **I** **example using a minimization principle** binary model system $N_{\uparrow\uparrow}$, $N = N_\uparrow + N_\downarrow$ **I** $N_{\downarrow\downarrow}$, $2s = N_\uparrow - N_\downarrow$ **I** $U(s) = -2smB$ **I** U usually (internal energy) thermal average of the systems energy **I** $Z = \sum_s e^{-\epsilon_s/\tau}$ **I** $U = \frac{\sum_s \epsilon_s e^{-\epsilon_s/\tau}}{z}$ **I** when given τ, B can you find $\langle s \rangle$ **I** two approaches, use canonical ensemble approach, energetics table, partition function, or minimize F with respect to s **I** $F = U - \tau \sigma$ **I** $\sigma(s) \approx \ln\binom{N}{N_\uparrow} = -(\frac{N}{2} + s)\ln(\frac{s}{N} + \frac{1}{2}) - (\frac{N}{2} - s)\ln(\frac{1}{2} - \frac{s}{N})$ **I** $U(s) \approx -2smB$ **I** Free energy $F(s) = U(s) - \tau \sigma(s) = -2smB + -(\frac{N}{2} + s)\tau \ln(\frac{1}{2} + \frac{s}{N}) + (\frac{N}{2} - s)\tau \ln(\frac{1}{2} - \frac{s}{N})$ **I** At equilibrium $F(s) \to$min. $\frac{\partial F}{\partial s} = 0$ **I** **remember** $\langle s \rangle$ = the average of the spin axis **I** $\therefore -smB + \tau \ln(\frac{n+2\langle s \rangle}{N-2\langle s \rangle}) = 0$ **I** and $\langle s \rangle = \frac{N}{2}\arctan\frac{mB}{2}$ **w8 d2 chapter 4 Planck distribution/black body radiation** emission spectrum of the sun, the em spectrum in thermal equilibrium within a cavity Strategy, canonical ensemble, identify microstates, in a cavity the eigenstates of EM waves are modes, lets first look at a single mode $\epsilon_s = s\hbar\omega$, $s = 0, 1, 2, ...$ **I** $Z = \sum_{s=0}^\infty e^{-s\hbar\omega/\tau} = \frac{1}{1-e^{-\hbar\omega/\tau}}$ **I** $(1-x)(1+x+x^2 + ...) = 1$ and $\therefore (1 + x + x^2 + ...) = \frac{1}{(1-x)}$ **I** Average number of photons $\langle s \rangle = \frac{1}{z}\sum_s se^{-s\hbar\omega/\tau} = \frac{1}{e^{\hbar\omega/\tau}-1}$ plank distribution for any number of photons in a single mode of frequency $omega$ **I** Average energy: $\langle \epsilon \rangle = \hbar\omega \langle s \rangle = \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}$ if $\tau >> \hbar\omega$ then τ if $\tau << \hbar\omega$ then $e^{\hbar\omega/\tau}$ **I** Now: in a cavity, we have multiple modes Q/ what are the modes, A/ From EM: For a perfectly conducting cavity of L^3 **I** $E_x = E_{x0}\sin \omega t \cos \frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}$ **I** $E_y = E_{y0}...$ **I** $E_z = E_{z0}...$ **I** first sin is time dependence, the rest is spatial dependence **I** $\nabla \cdot \vec{E} = 0$ **I** $E_{x0}n_x + E_{y0}n_y + E_{z0}n_z = \vec{E}_0 \cdot \vec{n} = 0$ field vector and n vector are perpendicular **I** For a given $\vec{N}$ we can choose two independent $\vec{e}_0$, $\to$ for each $\vec{n}$ two distinct modes **I** Q/ how is ω related to (n_x, n_y, n_z) sub. eigenmodes into wave equation **I** $C^2(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2})E_x = \frac{\partial^2 E_x}{\partial \tau^2}$ **I** $\omega_{n_x n_y n_z}$ Now consider all modes, the modes are independent $U = 2\sum_{n_x n_y n_z}\langle \epsilon_{n_x n_y n_z} \rangle$ **I** $\sum_{n_x n_y n_z} \approx \frac{1}{8}\int_0^\infty dn_x dn_y dn_z$ Integrand depends only on $n = \sqrt{(n_x^2 + n_y^2 + n_z^2)}$ **I** $\frac{1}{8}\sum_0 4\pi n^2 \partial n$ **I** $U = \frac{\pi^2 V \tau^4}{15\hbar^3 c^3}\int_0^\infty dn \frac{n^3}{e^{\hbar\omega/\tau}-1}$ **change of variable** $x = \frac{\pi\hbar cn}{L\tau}$ **I** $U = \frac{\pi^2 \hbar c}{L}(\frac{\tau L}{\pi\hbar c})^4\int_0^\infty dx \frac{x^3}{e^x-1}$ **I** $U = \frac{\pi^2 \hbar c}{L}(\frac{\tau L}{\pi\hbar c})^4\frac{\pi^4}{15}$ **I** $U = V \cdot \frac{\pi^2}{15\hbar^3 c^3}\tau^4 \propto \tau^4 \to$ stephan-Boltzmann law of radiation **I** $U = v\int \partial \omega U_\omega$ **I** $U_\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}$ (plank radiation law) $\tau = 2.73K$ **I** Q/ σ A/ at constant volume $\partial \sigma = \frac{\partial U}{\tau}$ where $\partial U = \tau \partial \sigma - P \partial v$ **I** $\sigma(\tau) = \int_{-\infty}^\tau \frac{\partial v}{\tau} = \frac{4\pi^2 V}{45}(\frac{\tau}{\hbar})^3 \propto \tau^3$ **w11 d1 Phonons in solids** quantum harmonic oscillator, partition function $Z = \frac{1}{1-e^{-\hbar\omega/\tau}}$ **I** photon gas numbers of em modes is infinite, phonon gas of number of elastic modes is finite **I** photon two possible polarizations, phonon longitudinal 1 and transverse 2 **I** $U = \frac{3n}{2}\int_0^{n_D} dn n^2 \frac{\hbar\omega_n}{e^{\hbar\omega/\tau}-1}$ **I** $\omega_n = \frac{n\pi V}{L}$ **I** V =speed of sound in the system **I** Make the integral dimensionless $X \equiv \frac{\pi\hbar Vn}{L\tau}$ therefor $U = (\frac{3\pi^2\hbar n}{L\tau})(\frac{\tau L}{\pi\hbar V})^4\int_0^{x_d} dx \frac{x^3}{e^x-1}$ **I** $X_D = \frac{\pi\hbar vn_D}{L\tau} = \frac{\theta}{\tau}$ Debye temp $\theta = \hbar v(6\pi^2\frac{N}{V})^{1/3}$ **I** of particular interest: low $\tau << \theta$ where $x_D \to \infty$ **I** $U \approx \frac{3\pi^4 N\tau^4}{5\theta^3} \propto \tau^4$ **I** $C_v = (\frac{\partial U}{\partial \tau})_v \propto \tau^3$ **I** chemical potential and gibbs distribution, when two systems are in diffuse contact and can exchange particles, which way would the particles flow. **I** chemical potential μ flow form high μ to low μ, diffusive contact - particles exchange, thermal contact - temperature exchange **I** consider $s_1 + s_2$, $N_1 + N_1$, $V_1 + V_2$, τ **I** Helmholtz free energy F for $s_1 + s_2 \to$ minimum **I** $F = F_1 + F_2 = U_1 + U_2 - \tau(\sigma_1 + \sigma_2)$ **I** Now consider a small variation **I** $\partial N_1 = -\partial N_2$ **I** At equilibrium: $\partial F = (\frac{\partial F_1}{\partial N_1})\partial N_1 + (\frac{\partial F_2}{\partial N_2})\partial N_2 = 0$ **I** equilibrium condition$\Rightarrow (\frac{\partial F_1}{\partial N_1})_{\tau,V_1} = (\frac{\partial F_2}{\partial N_2})_{\tau,V_2}$ **I** Define: $\mu(T, V, N) = (\frac{\partial F}{\partial N})_{\tau,V}$ **I** p: pressure $\partial \sigma = \frac{\partial u}{\tau} + \frac{P\partial v}{\tau}$ **I** $\partial u = \tau \partial \sigma - p \partial v + \mu \partial N$ Another expression for chemical potential **I** $\mu = -\tau(\frac{\partial \sigma}{\partial N})_{U,V}$ **I** $\partial \sigma = (\frac{\partial \sigma}{\partial U})\partial U + (\frac{\partial \sigma}{\partial V})\partial V + (\frac{\partial \sigma}{\partial N})\partial N = \frac{1}{\tau}(\frac{\partial U}{\partial N})_{T,V} + (\frac{\partial \sigma}{\partial N})_{U,V}$ **I** $\mu = (\frac{\partial}{\partial N})_{T,V}(U - \tau \sigma)$ **I** $\mu = (\frac{\partial U}{\partial N})_{T,V} - \tau(\frac{\partial \sigma}{\partial N})_{T,V} = -\tau(\frac{\partial \sigma}{\partial N})_{U,V}$ **I** next topic $U_0 = U + U_R$ and $N_0 = N + N_R$, $S + R$ is an isolated system **w11 d2 when system constant temperature and volume** $U_0 = U_R + U$ **I** $N_0 = N_R + N$ **I** $\propto g(R, S) = g_R \cdot g_s = g_R \cdot 1$ **I** $P(s_N) \propto g_r(N_0 - N, U_0 - \epsilon_{sn})$ **I** $\frac{P(S_1,N_1)}{P(S_2,N_2)} = \frac{g_R(N_0 - N_1, U_0 - \epsilon_{s1})}{g_R(N_0 - N_2, U_0 - \epsilon_{s2})}$ **I** $\sigma_R = \ln g_R$ **I** $\frac{P(S_1)}{P(S_2)} = \frac{\exp[\sigma_R(\sigma_R(N_0-N_1, U_0-\epsilon_{s1})]}{\exp[\sigma_R(\sigma_R(N_0-N_2, U_0-\epsilon_{s2})]} = \exp[\Delta \sigma_R]$ **I** $\Delta \sigma_R \equiv \sigma_R(\mu_0 - \mu_1, \mu_0 - \epsilon_{s1}) - \sigma_R(\mu_0 - \mu_2, \mu_0 - \epsilon_{s2})$ **I** $\Delta \sigma_R = -(N_1 - N_2)(\frac{\partial \sigma_R}{\partial N_0})U_0 - (\epsilon_{s1} - \epsilon_{s2})(\frac{\partial \sigma_R}{\partial U_0})_{N0} = \frac{\Delta N}{\tau}\mu - \frac{\Delta \epsilon}{\tau}$ **I** $\frac{P(S_1,N_1)}{P(S_2,N_2)} = \frac{\exp[(N_1\mu - \epsilon_{s1})/\tau]}{\exp[(N_2\mu - \epsilon_{s2})/\tau]}$ **I** $P(s_N) = \frac{1}{Z_g}\exp[(N\mu - \epsilon_s)/\tau]$ **I** $Z_g = \sum_{N=0}^\infty \sum_{S(n)} \exp[(N\mu - \epsilon_s)/\tau]$ **I** $\langle N \rangle = \frac{1}{Z_g}\sum_N \sum_{S(N)} NP(S_n) = \frac{\tau \partial \ln Z_g}{\partial \mu}$ **I** Approach number 1 $\mu = (\frac{\partial F}{\partial N})_{T,V}$ **I** $F = -\tau \ln z$ **I** $\mu = (\frac{\partial F}{\partial V})_{T,V}$ **I** $F = -\tau \ln z$ **I** $Z_n = \frac{1}{N!}Z_1^N$ **I** $Z_1 = n_Q \cdot v$ **I** $F = -\tau[N \ln z_1 - \ln N!]$ **I** $\frac{\partial F}{\partial N} = [-\tau \ln z_1 + \partial N \ln\binom{n}{\sqrt{2\pi n}}$ **I** $(\frac{\partial F}{\partial N})_{T,V} = -\tau \ln \frac{n}{n_Q}$ and $density = \ln \frac{V}{N}$ **I** Approach 2 $\langle N \rangle = \frac{\tau \partial \ln Z_g}{\partial \mu} = z_1 e^{\mu/\tau}$ **I** $\mu = \tau \ln \frac{\langle N \rangle}{Z_1} = \tau \ln \frac{n}{n_Q} - density$ **w12 d1 Chemical Potential** $\mu_{tot}(h) = Mgh + c \ln\binom{n(n)}{n_Q}$ **I** $\mu_{tot}(0) = \mu_{tot}(h)$ **I** $\mu_{tot}(h) = \mu_{tot}(h = 0)$ **I** $Mgh + \tau \ln(\frac{n(h)}{n_Q}) = \tau \ln(\frac{n(0)}{n_Q})$ **I** $n(h) = \frac{n(0)}{e^{Mgh/\tau}} = n(0)e^{-Mgh/\tau}$ **I** $PV = nRT$ **I** $n_\uparrow = n(0)\frac{e^{2mB/\tau}}{e^{2mB/\tau}+1}$ **I** $n_\downarrow = \frac{n(0)}{e^{2mB/\tau}+1}$ **w12 d2 chapter 6: ideal gas** $\mu_{tot} = \mu_{ext} + \mu_{int}$ ideal gas in gravity **I** $\mu_{int} = \tau \ln(\frac{n(h)}{n_Q})$ **I** $\mu_{ext} = Mgh$ Identical particles: Fermions: $\frac{1}{2}$ integer spin, 0 or 1 on an orbital **I** Bosons: integer spin, occupation number on an orbital can arbitrarily 0,1,2... **I** Grand partition function $Z_g = \sum_N \sum_{S_n} e^{(\mu n - \epsilon_{sn})/\tau}$ **I** $\langle N \rangle = \frac{1}{Z_g}\sum_N \sum_{S_n} NP(S_n)$ **I** Bose Einstein Distribution $f_{BE} = \frac{1}{e^{(\epsilon-\mu)/\tau}-1}$ **I** Fermi-Dirac Distribution $f_{FD} = \frac{1}{e^{(\epsilon-\mu)/\tau}+1}$ **w13 d1** For classical system $\langle N \rangle = \lambda \sum_{orb} e^{-\epsilon/\tau}$ **I** $\lambda = e^{\mu/\tau}$ In classical limit $f \approx e^{(\mu-\epsilon)/\tau}$ **I** $\mu = \tau \ln\binom{n}{n_Q}$ **I** $F(N, V, \tau) = \int_0^N dN \cdot \mu(n, V, \tau)$ **I** $P = -(\frac{\partial F}{\partial V})_{T,N} = \frac{n\tau}{V}$ **I** Microstates: orbital + internal $\epsilon = \epsilon_n + \epsilon_{int}$ **I** One orbital $Z_{int} = \sum_{int} e^{-\epsilon_{int}/\tau}$ **I** Reversible isothermal expansion $p_f v_f = p_i v_i = N\tau$ **I** $\Delta \sigma = \sigma_f - \sigma_i$ **I** $\Delta \sigma = N \ln \frac{V_f}{V_i}$ **I** $\Delta U = 0$ **I** $U = \frac{3N\tau}{2}$ **I** $U_f = U_i$ **I** $Q = -W = N\tau \ln \frac{V_f}{V_i}$ **w13 d2 reversible expansion at constant entropy** $\sigma(\tau, V) = N(\ln \tau^{3/2} + \ln v + constant)$ **I** $\tau_f^{3/2}v_f = \tau_i^{3/2}v_i$ **I** $\tau_f = \tau_i(\frac{v_i}{v_f})^{2/3}$ **I** $PV = N\tau$ **I** $\Delta U = \frac{3}{2}N\Delta \tau$ **I** energy going out of the system is via the work **I** Sudden expansion into a vacuum $W = 0$ and $Q = 0$ and $\Delta \tau = 0$ and $U_f = U_i$ and $U = \frac{3}{2}N\tau$ and $\sigma = N[\ln V + \ln \tau^{3/2} + constant]$ - Reversible process is an approximation $\Delta \sigma = N \ln \frac{V_f}{V_i}$

Chapter 7 Fermi and Bose Gas For classical ideal gas $\mu = \tau \ln \frac{n}{n_Q}$ **I** $f_{Boltsman} = \frac{n}{n_Q}e^{\epsilon/\tau} << 1$ **I** $\frac{n}{n_Q} << 1$ classical regime ≥ 1 quantum **I** In cases where n is fixed and τ adjustable $\tau_0 \equiv (\frac{2\pi\hbar^2}{M})n^{2/3}$ **I** Fermi gas $\langle N \rangle = \sum_{orbital} f_{orbital}(\mu, \tau)$ **I** $\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{3/2}$ **I** what is total energy at ground state $U = 2\sum_{n<n_f} \epsilon_n = 2 \cdot \frac{1}{8} \cdot 4\pi \int^{n_F} dn n^2 \epsilon_n = \frac{3}{5}N\epsilon_F$ **I** Fermi gas How to determine ϵ_F **I** $\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 \frac{N}{V})^{3/2}$ Keep N constant V_i and $\epsilon_F \uparrow$ **I** $\frac{V}{N} = \frac{3}{5}\epsilon_F \uparrow$ **I** symmetry -¿ effective repulsion **w14 day 1** Fermi gas $\langle X \rangle = \int \partial\epsilon D(\epsilon)f(\epsilon, \tau, \mu)x(\epsilon)$ **I** How to calculate $D(\epsilon)$ density of states **I** $N(\epsilon) = (\frac{V}{3\pi^2})(\frac{2m}{\hbar^2})^{3/2}\epsilon^{3/2}$ total number of states under ϵ **I** $D(\epsilon) = \frac{\partial N}{\partial \epsilon} = \frac{3N}{2\epsilon} = \frac{V}{(2\pi^2)}(\frac{2m}{\hbar^2})^{3/2}\epsilon^{1/2}$ **I** In high τ classical $c_v \approx \frac{3}{2}K_B N$ **I** $c_v \approx N \frac{\tau}{\epsilon_F} \propto \tau$ quantum **I** what is low τ **I** $\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$ for Cu : $n = 8.7 \times 10^{28}m^{-3}$ **I** for room temperature $\frac{\epsilon_F}{\tau} \approx 260 >> 1$ **w14 day 2 Bose Gas and Bose Einstein** $N = \int \partial\epsilon f(\epsilon, \tau, \mu)D(\epsilon)$ ground state ($\tau = 0$) **I** all particle occupy the ground orbital $\to \epsilon = 0$ **I** $f(\epsilon = 0, \tau) = \frac{1}{e^{-\mu/\tau}-1} \geq 0$ **I** $\mu \leq 0$ **I** At τ small $f(0, \tau) \approx \frac{1}{(1-\frac{\mu}{\tau})-1} = \frac{-\tau}{\mu}$ **I** $\frac{-\tau}{\mu} \approx N$ close to zero **I** $\frac{U}{L} \approx \frac{3}{2}\tau + 0\frac{1}{L}$ take thermodynamic limit at the ver last state **I** occupancy $N_0 + N_e = N$ **I** $N_0(\tau, \mu) = \frac{1}{e^{-\mu\tau}-1} = \frac{-1}{\frac{\mu}{\tau}-1}$ **I** $N_e(\tau, \mu) \approx \frac{V}{4\pi^2}(\frac{2M}{\hbar^2})^{3/2}\tau^{3/2}\int_0^\infty dx \frac{x^{1/2}}{e^x-1}$ **I** $\frac{N_0}{N} = 1 - \frac{N_e}{N}$ BE condensation $\tau_E = \frac{2\pi\hbar^2}{M}(\frac{N}{2.612V})^{2/3}$ **I** $\frac{N_0}{N} = 1 - (\frac{T}{\tau})^{3/2}$ **I** The critical temperature does not scale linearly with N anymore **I** **chapter 8 hear transfer and work are path dependent** **I** $\partial U = \partial Q + \partial \omega$ **I** $dQ \equiv \tau \partial \sigma$ **I** $\partial \omega = -\rho \partial V$ **I** heat transfer and work are path dependent, work 100 percent to heat, however not hear to work, there is directionality **I** pay price from going from disorder to order **w15 day 1 thermal engine** First Law $\partial U = Q + W$ **I** Second law: difference between heat and work **I** $(\Delta \sigma_{total}) = (\Delta \sigma)_{RL} + (\Delta \sigma)_s = \frac{-Q_L}{\tau_h} + \frac{-Q_l}{\tau_l} + 0$ **I** Efficiency $\eta = \frac{\omega}{Q_h} = \frac{Q_h - Q_l}{Q_h} = 1 - \frac{Q_l}{Q_h}$ **I** For a reversible cycle $\eta = 1 - \frac{\tau_l}{\tau_h}$ upper limit for efficiency of thermal energy **I** $\eta_c = $ carnot efficiency $= 1 - \frac{\tau_l}{\tau_h}$ **I** $\eta \leq \eta_c$ **I** Refrigerator/air conditioner $(\Delta \sigma)_{totalentropy} = \frac{Q_h}{\tau_h} - \frac{Q_l}{\tau_l} \geq 0$ **I** $\Rightarrow \gamma \leq \gamma_c$ **I** $\gamma_c = \frac{\tau_l}{\tau_h - \tau_l}$ achievable only for a reversible process **I** isothermal expansion, isothermal expansion, realization of carnot engine classification ideal gas -¿ reversible cycle **I** **w15 day 2** isothermal $Q_{12} = \tau_h(\sigma_h - \sigma_l)$ and $Q_{34} = \tau_l(\sigma_h - \sigma_l)$ isentropic $Q_{23} = 0$ and $Q_{41} = 0$ **I** $W = |Q_{12}| - |Q_{34}| = (\tau_h - \tau_l)\cdot \Delta \sigma = $ area **I** isothermal $PV = N\tau$ **I** isentropic$PV^\gamma = constant$ where $\gamma > 1$ **I** $1 \to 2$ Isothermal expansion $\Delta = 0$ and $PV = constant$ and $P = Cont \cdot \frac{1}{V}$ and $|Q_{12}| = |W_{12}| = \int p\partial V = N\tau_N \ln\binom{v_2}{v_1}$ **I** objective $\eta = \frac{W}{Q_h}$ **I** $Q_h = n\tau_h \ln \frac{v_2}{v1}$ **I** $W = |Q_h| - |Q_l| = N\tau \ln\binom{v_2}{v_1} - N\tau \ln\binom{v_3}{v_4}$ **I** $\eta = \frac{\omega}{Q_h} = \frac{\tau_n - \tau_l}{\tau_h} = 1 - \frac{\tau_l}{Q_h}$ carnot cycle has carnot efficeicny **I** Irreversible cycle $\Delta \tau = (\tau_R - \tau_D) \approx 0$ **I** reversible cycle $\Delta \sigma_s = \int \frac{\partial \sigma}{\tau}$ in reversible there is no net entropy increase **I** $\Delta \sigma_R = \int \frac{-\partial \sigma}{\tau}$ **I** $\Delta \sigma_{total} = 0$ **w16 day 1 chemical work** $\partial U = \partial Q + \partial \omega - p \partial v$ Chemical work: work performed by the transfer of particles **I** $U(\sigma, V, N) \propto \partial U = \tau \partial \sigma - p \partial v + \mu \partial N$ chemical work **I** $\partial \omega = -p \partial v + \mu \partial N$ Assuming no mechanical work for $\partial w_l = \partial w_{c1} + \partial w_{c2} = M_2\partial N_1 + M_2\partial N_2$ - total number of particles **I** ideal gas $\mu = \tau \ln\binom{n_1}{n_Q}$ **I** $\mu_2 + \mu_1 = \tau \ln \frac{n_2}{n_1}$ **I** $W_c = \tau \ln \frac{n_2}{n_1}\Delta N$ **I** Why G $\partial G = \partial U - \partial(\tau \sigma) + \partial(pv)$ **I** What happens for spontaneous charges $\Delta \sigma_{total} = \Delta \sigma_s - \frac{Q_s}{\tau}$ **I** $\Delta Q_s \leq W_s^1$ does not incur reversibility **I** Simple case if $\omega_s^1 = 0$ the process is reversible, $\Delta G_s = 0$ **I** G_s reaches minimum when equilibrium **I** $W_s \neq 0$ and $\partial w_s^1 = \mu \partial N$ **I** $G_F - G_i \leq \omega_s^1$ the maximum amount of work the system can deliver the decrease in Gibbs free energy. **I** Now lets $\partial \omega^1 = \mu \partial N$ **I** Extensive and Intensive Quantity $G_{total} = G_{1+2} = G_1 + G_2 = 2G_1$ **I** $U_{total} = U_1 + U_2 = 2U_1$ **I** intensive quantities, no dependence on number of particles, τ temperature, P pressure, n density, μ chemical potential, σ entropy, F free energy, V volume, N number of particles **I** extensive quantities, dependence on number of particles **I** Example of simple ideal gas $\mu = \tau \ln\binom{n}{n_Q} = \tau \ln\binom{p}{n_Q \tau}$ **I** $F(T, V, \mu) = N\tau[\ln\binom{n}{n_Q} - 1]$ **I** Gibbs free energy $G = F + pV = N\tau \ln\binom{n}{n_Q} = N\mu$