Ph12c Book Notes

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Multiplicity Or degeneracy. Number of quantum states with very nearly the same energy.

Stirling approximation $N! \approx (2\pi N)^{1/2} N^N \exp\left(-N + \frac{1}{12N} + \ldots\right)$.

Binary System Multiplicity function Define the spin excess $2s = N_\uparrow - N_\downarrow$. Then the multiplicity $g(N,s) = \frac{N!}{N_\uparrow! \cdot N_\downarrow!} \approx g(N,0)e^{-2s^2/N}$. $g(N,0) = \frac{N!}{(\frac{1}{2}N)!(\frac{1}{2}N)!} \approx \sqrt{\frac{2}{\pi N}} 2^N$.

Entropy $\sigma(N,U) = \log g(N,U)$ where N is the number of entities and U is the energy.

Temperature and Thermal equilibrium Define $\frac{1}{T} = k_B \left(\frac{\partial \sigma}{\partial U}\right)_N$ and the fundamental temperature as $\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N, \tau = k_B T$, which has units of energy.Then the condition for thermal equilibrium between two systems is:

$$\tau_1 = \tau_2 \iff T_1 = T_2 \iff \left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}$$

Classical Entropy $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$ so $S = k_B \sigma$.

Zeroth Law If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other.

First Law PoCoE

Second Law If a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will monotonically increase in successive instants of time.

Third law The entropy of a system approaches a constant value as the temperature approaches zero.

Boltzmann factor Taylor expand the entropy about U_0 in the limit of an infinitely large reservoir: $\sigma(U_0 - \epsilon) = \sigma_{\mathcal{R}}(U_0) - \epsilon\left(\frac{\partial \sigma_{\mathcal{R}}}{\partial U}\right)_{V,N} = \sigma_{\mathcal{R}}(U_0) - \frac{\epsilon}{\tau}$. Hence the ratio of probabilities is $\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{e^{-\epsilon_1/\tau}}{e^{-\epsilon_2/\tau}}$ and a term of the form $e^{-\epsilon/\tau}$ is called a Boltzmann factor.

Partition function Define partition function as the sum of the Boltzmann factor (using the energy eigenvalues) over all the states s of the system $Z(\tau) = \sum_s e^{-\epsilon_s/\tau}$. Then the probability of being in a certain state is given by $P(\epsilon_s) = \frac{e^{-\epsilon_s/\tau}}{Z}$ and the ensemble average energy is $U = \frac{\sum_s \epsilon_s e^{-\epsilon_s/\tau}}{Z} = \tau^2 \left(\frac{\partial \log Z}{\partial \tau}\right)$.

Heat capacity $C_v = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V = \left(\frac{\partial U}{\partial \tau}\right)_V, C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_P = \left(\frac{\partial U}{\partial \tau}\right)_P$. $C_V = \frac{3}{2}N$ for an ideal monoatomic gas of N atoms with spin zero.

Reversible process A process is reversible if the system is always infinitesimally close to equilibrium at every stage. The entropy is well defined at every stage. Any process in which the entropy change vanishes is an isentropic reversible process.

Pressure $p = \langle p \rangle = -\left(\frac{\partial U}{\partial V}\right)_\sigma = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U$.

Thermodynamic Identity $\tau d\sigma = dU + pdV$. Define pdV as the work done **by** the system.

Helmholtz Free Energy $F = U - \tau\sigma$. F is an extremum (actually minimum) in equilibrium at constant τ and V. Note that $dF = -\sigma d\tau - pdV$. Differential relations (directly from differential form of F):

$$\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma, \quad \left(\frac{\partial F}{\partial V}\right)_\tau = -p$$

$$\implies p = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

First term is the energy pressure, second is the entropy pressure.

Maxwell Relation

$$\left(\frac{\partial \sigma}{\partial V}\right)_\tau = \left(\frac{\partial p}{\partial \tau}\right)_V$$

using the equality of mixed partials $\frac{\partial^2 F}{\partial V \partial \tau} = \frac{\partial^2 F}{\partial \tau \partial V}$.

Helmholtz Free Energy from Partition Function $F = -\tau \log Z \implies P(\epsilon_s) = \exp[(F - \epsilon_s)/\tau]$.

Quantum Concentration $n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$, the concentration associated with an atom in a cube of side length equal to the thermal average de Broglie wavelength.

Single atom in a box $Z_1 = \frac{n_Q}{n}$, n is the concentration $\frac{1}{V}$.

N atoms in a box Distinct particles: $Z_N = \prod_{i=1}^{N} Z_1(i)$. Identical particles: $Z_N = \frac{1}{N!}Z_1^N$.

Ideal gas law $pV = N\tau \iff pV = Nk_BT$

Sackur-Tetrode equation $\sigma = N[\log(n_Q/n) + \frac{5}{2}]$ for monoatomic ideal gas.

Planck Distribution Function

$$\langle s \rangle = \frac{1}{e^{\hbar\omega/\tau} - 1}$$

for the thermal average number of photons in a single mode of frequency ω.

Stefan-Boltzmann Law of Radiation Radiant energy density is proportional to the 4th power of temperature: $\frac{U}{V} = \frac{\pi^2}{15\hbar^2c^3}\tau^4$. In terms of frequency: $u_\omega = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}$.

Radiant Energy Flux $J_U = \frac{\pi^2\tau^4}{60\hbar^3c^2} = \sigma_B T^4, \sigma_B = \frac{\pi^2k_B^4}{60\hbar^3c^2}$.

Nyquist Theorem for electrical noise due to thermal fluctuations across a resistor while no current is flowing

$$\langle V^2 \rangle = 4R\tau\Delta f$$

where Δf is the frequency (not angular frequency) bandwidth within which voltage fluctuation are measured.

Total number of photon modes Consider a solid with N atoms and 3 degrees of freedom (and hence 3 possible polarizations). The maximum n such that $\frac{3}{8}\int 4\pi n^2 dn = 3N$ is $n_D = \left(\frac{6N}{\pi}\right)^{1/3}$.

Debye T-cubed law for heat capacities $C_v = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{12\pi^4 N}{5}\left(\frac{\tau}{k_B\theta}\right)^3$ with τ^3 dependence. θ is the Debye temperature: $\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$, where v is the speed of sound.

Chemical Potential governs the flow of particles between systems. Particles will flow from the system at the higher chemical potential to the system at the lower chemical potential. In diffusive equilibrium, the systems will minimise the total Helmholtz free energy subject to a constant number of particles. We define:

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

Chemical Potential of Ideal Gas $\mu = \tau \log \frac{n}{n_Q}$. n_Q is the quantum concentration $n_Q \equiv \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$ and $n = \frac{N}{V}$ is the concentration.

Effect of external potentials Just add it to the chemical potential. $\mu = \mu_{int} + \mu_{ext}$, where μ_{ext} can be Mgh, V, etc.

Chemical Potential and Entropy

$$\mu = -\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$