PHYS 333 - Thermal Physics

1   Multiplicity

1.1   Microstates

The number of way to arrange n items in a set of N items without considering the ordering is

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

1.2   Einstein Model of a Solid

For a system of N oscillators and q energy units

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

For a large system of Einstein Solid, in the case q $>>$ N

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

1.3   Multiplicity of a Monoatomic Gas

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

1.4   Entropy

1.4.1   General Form

$$S = k \cdot ln(\Omega)$$

1.4.2   Entropy of an Ideal Gas

$$S = Nk\left(\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right)$$

$$\Delta S = S_f - S_i = Nk \cdot ln\left(\frac{V_f}{V_i}\right)$$

with the **Internal Energy of a system of Ideal Monoatomic gas** particles defined as

$$U = \frac{3}{2}NkT$$

1.5   Entropy and Temperature

At equilibrium $(T_A = T_B = T_{eq})$, we have

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} = \frac{1}{T_{eq}}$$

1.5.1 Heat Capacity

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

For an ideal gas we have

$$C_V = \frac{3}{2}Nk$$

2 Boltzmann Statistics

2.1 Boltzmann Factor and the Partition Function

$$P(s) = \frac{1}{Z}e^{-\frac{E(s)}{kT}}$$

$$Z = \sum_s e^{-\frac{E(s)}{kT}}$$

2.2 Average Values

$$\langle E \rangle = \frac{1}{Z}\sum_s E(s)e^{-\beta E(s)} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

2.3 Equipartition Theorem

Each quadratic degree of freedom contributing to the total energy has a time average energy per particle of

$$\langle E \rangle = \frac{1}{2}kT$$

2.4 The Maxwell Speed Distribution

From the Equipartition Theorem, we can define

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

We can define The Maxwellian Distribution such that one can intregrate in the see the proportion of molecules occupying a certain range of velocities

$$D(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kt}}$$

The average velocity is

$$v_{avg} = \sqrt{\frac{8kT}{\pi m}}$$

The maximum velocity is

$$v_{max} = \sqrt{\frac{2kT}{m}}$$

3 Helmholtz Free Energy

We recall the *First Law of Thermodynamics*

$$dU = TdS - PdV + \mu dN$$

The free energy is defined as

$$F = U - TS = -kT \cdot ln(Z)$$

With the following relations

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

3.1 Partition Function for Composite Systems

In the case of **non-interacting distinguishable particles**, we have

$$Z_{Total} = Z_1 \cdot Z_2 \ldots Z_N$$

For **non-interacting indistinguishable particles**

$$Z_{Total} = \frac{1}{N!} \cdot Z_1^N$$

3.1.1 Partition Function for an Ideal monoatomic Gas

An ideal gas is non-interacting and we assume identical particles

$$Z = \frac{1}{N!}\left(\frac{V \cdot Z_{int}}{V_q}\right)^N$$

$$V_q = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$$

Note: An ideal gas with no internal degrees of freedom has $Z_{int} = 1$.

4 Quantum Statistics

4.1 The Gibbs Factor

The Boltzmann distribution allowed energy exchange but not particles. The Gibbs factor takes into account particles and energy exchange with some reservoir

$$GibbsFactor = e^{-\frac{1}{kT}(E(s)-\mu N(s))}$$

$$\mathcal{Z} = \sum_s e^{-\frac{1}{kT}(E(s)-\mu N(s))}$$

$$P(s) = \frac{1}{\mathcal{Z}} \cdot e^{-\frac{1}{kT}(E(s)-\mu N(s))}$$

4.2 Bosons and Fermions

When $Z_1 >> N$ or equivalently $\frac{V}{N} >> V_q$ the chances of particles wanting to occupy the same states is negligible and Boltzmann statistics hold. When that condition does not hold then we must take it into account. We define the occupancy as

$$\textbf{Fermions Occupancy: } \langle N \rangle (T) = \frac{1}{e^{\beta(E-\mu)} + 1}$$

$$\textbf{Bosons Occupancy: } \langle N \rangle (T) = \frac{1}{e^{\beta(E-\mu)} - 1}$$

$$\textbf{Boltzmann Occupancy: } \langle N \rangle (T) = \frac{1}{e^{\beta(E-\mu)}}$$

4.3 Degenerate Fermi Gases

The Fermi energy is the highest energy level occupied by particles in some system

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

The total energy of the gas is

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

The pressure of the Fermi gas is

$$P = - \left(\frac{\partial U}{\partial V} \right)_{N,T} = \frac{2}{3} \cdot \frac{U}{V}$$

In order to treat the system as a degenerate electron gas we require $T << T_F$ where

$$T_F = \frac{\epsilon_F}{k}$$

The bulk modulus is the change in pressure when a material is compressed

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T$$

4.4 Blackbody Radiation

We can use the bosons occupancy with $\mu = 0$ to describe the occupancy of some mode of oscillation. The modes are discrete.

$$\textbf{Planck Distribution: } n_{Pl} = \frac{1}{e^{\beta h v} - 1}$$

The average energy per oscillation mode is

$$\langle E \rangle = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = \frac{hv}{e^{hv/kT} - 1}$$

We can determine the peak wavelength of some emission spectrum as

$$\lambda_{peak} = \frac{0.29}{T} (cm)$$

4.4.1 Flux and Luminosity

$$Flux = \frac{Energy}{Area \cdot Time} = \sigma \cdot T^4$$

$$Luminosity = Flux \cdot Area = \sigma \cdot T^4 \cdot A$$

4.5 Debye Solid

The Debye temperature is

$$T_D = \frac{hc_s}{2k} \cdot \left(\frac{6N}{\pi V}\right)^{1/3}$$

The total energy is

$$U = \frac{3\pi^4 NkT^4}{5T_D^3}$$

We obtain two heat capacities depending on the limit considered

$$\textbf{For } T \ll T_D: \quad C_V = \frac{12\pi^4 Nk}{5T_D^3} \cdot T^3 \qquad \qquad \textbf{For } T \gg T_D: \quad C_V = 3Nk$$

4.6 Bose-Einstein Condensation

Under some critical temperature T_c a gas will spontaneously condensate into the ground state of the system. Below T_c the chemical potential μ will approach zero and become negative for $T > T_c$ to populate the excited states. We can define

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

The number of electrons in the excited/ground state is

$$N_{excited} = N \cdot \left(\frac{T}{T_c}\right)^{3/2} \qquad \qquad N_0 = N \cdot \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]$$

5 Ferromagnetism

An ideal paramagnet, the dipoles only respond to some external magnetic field. In practise without the presence of a magnetic field we have

- **Ferromagnet:** dipoles align with neighbours

- **Antiferromagnet:** dipoles anti-align with neighbours

5.1 Ising Model

We have N magnetic dipoles with $s_i = \pm 1$ depending if the dipole is up or down. Each pair of interacting dipole has energy $|\epsilon|$. That is we define the toal energy as

$$U = -\epsilon \sum_{i,j} s_i \cdot s_j$$

And the partition function as the sum over all possible dipoles alignments (2^N)

$$Z = \sum_{s_i} e^{-\beta U}$$

We can use the method of *Next-Nearest-Neighbour* and approximate for the 1-D case

$$Z \approx (2cosh(\beta\epsilon))^N \qquad \qquad \langle U \rangle = -N\epsilon \cdot tanh(\beta\epsilon)$$

5.1.1 Mean Field Approximation

Instead, we can look at the neighbours(up, down, left, right) of some dipole i and state that it will point where the mean $\bar{s}$ points. For 1-D, n = 2

$$E_{s_i} = -\epsilon s_i(n\bar{s}) \qquad\qquad Z_i = 2 \cdot cosh(\beta\epsilon n\bar{s}) \qquad\qquad \bar{s}_i = tanh(\beta\epsilon n\bar{s})$$

The approximation here is to set $\bar{s}_i = \bar{s}$. In other words, we assume that when visiting every neighbour, they will all have the same mean spin surrounding and then so will the total system. We will have a transcendental equation and intersection points are solutions.
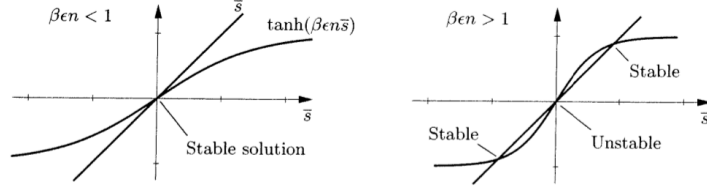
There exist a critical temperature above which the system is unmagnetized as a whole and below there are spontaneous magnetic regions yielding net magnetization for the solid of value oscillating between the two solutions for the system.

$$kT_c = n\epsilon$$

6 Appendix

6.1 Sterling's Approximation

$$N! \approx N^N \cdot e^{-N} \cdot \sqrt{2\pi N} \tag{1}$$

$$ln(N!) \approx N \cdot ln(N) - N \tag{2}$$