Phys 971 Stat Mech: Midterm 2

11/12/2013

1

(30 points) N binding sites are arranged in a lattice on the surface of a large reservoir of particles. The when a particle binds to a lattice site (each site can only accommodate one particle) there is an interaction energy ϵ. When the system reaches equilibrium it is found that, on average, one-half of the binding sites are occupied with particles. If the binding energy is made more favorable by $1k_BT$, what fraction of the lattice sites will be occupied after equilibrium is restored?

sites are independent, so grand partition function is

$$Q = \Big(\underbrace{1}_{\text{empty}} + \underbrace{e^{-\beta(\varepsilon-\mu)}}_{\text{occupied}}\Big)^N = \left(1+ze^{-\beta\varepsilon}\right)^N$$

μ = chemical potential of reservoir

$$N_{occ} = z\frac{\partial \ln Q}{\partial z} = \frac{N\,ze^{-\beta\varepsilon}}{1+ze^{-\beta(\varepsilon)}} = \frac{N}{z^{-1}e^{\beta\varepsilon}+1}$$

fraction occupied

$$\frac{N_{occ}}{N} = \frac{1}{z^{-1}e^{\beta\varepsilon}+1} = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$

if $\frac{N_{occ}}{N} = \frac{1}{2}$ then $\mu = \varepsilon$

Now $\varepsilon \rightarrow \underbrace{\varepsilon - kT}_{\varepsilon'}$

$$\frac{N_{occ}}{N} = \frac{1}{e^{\beta(\varepsilon'-\mu)}+1} = \frac{1}{e^{\beta(\varepsilon'-\varepsilon)}+1} = \frac{1}{e^{\beta(-kT)}+1} = \boxed{\frac{1}{e^{-1}+1}}$$

2

(40 points) A gas of N_ℓ large particles and N_s small particles occupies a container of fixed volume V. The free energy of the gas is $F = N_\ell k_b T(\ln(c_\ell \lambda_\ell^3) - 1) + N_s k_b T(\ln(c_s \lambda_s^3) - 1)$. Here the particle concentrations are $c_i = N_i/V$ $(i = \ell, s)$, $\lambda_i = h/(2\pi m_i k_B T)^{1/2}$ is the momentum partition function, and $N_i \sim 10^{23}$. On the surface of the container there are two binding sites spaced closely together. The spacing between the binding sites is small enough that one large particle occupies both sites. The binding energy is $-\varepsilon$ per particle.

a) Calculate the grand partition function of the system.

b) Now assume that the ratio N_ℓ/N_s is adjusted so that when a single particle is bound to the sites it is equally likely to be small or large (no restriction is placed on the unoccupied or double occupied states). What should this ratio be?

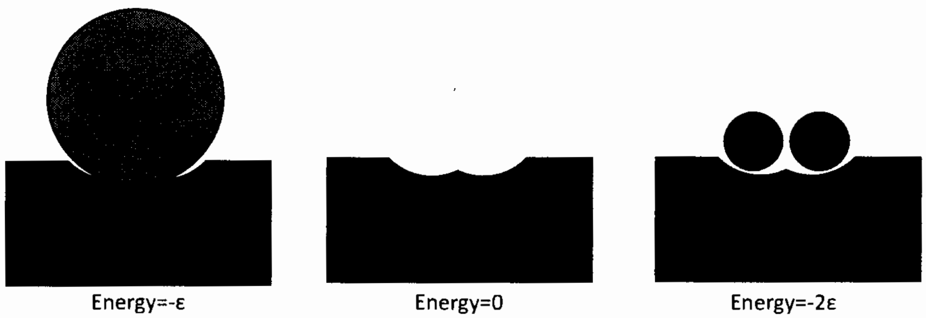

Figure 1: A partial list of the states available to the system.

a) $Q =$ 

$$= 1 + 2e^{-\beta\varepsilon + \beta\mu_s} + e^{-2\beta(\varepsilon+\mu_s)} + e^{-\beta(\varepsilon-\mu_\ell)}$$

b) $P(\text{single small}) = \dfrac{2e^{-\beta\varepsilon+\beta\mu_s}}{Q}$

$P(\text{large}) = \dfrac{e^{-\beta(\varepsilon-\mu_\ell)}}{Q}$

set equal

$$2e^{-\beta\varepsilon+\beta\mu_s} = e^{-\beta(\varepsilon-\mu_\ell)} \qquad \text{so} \longrightarrow 2e^{\beta\mu_s} = e^{\beta\mu_\ell}$$

Now find μ's

$$\mu_s = \frac{\partial F}{\partial N_s} = kT\left(\ln\frac{N_s\lambda_s^3}{V} - 1\right) + \cancel{N_s} kT\frac{1}{\cancel{N_s}} = kT\ln\left(\frac{N_s}{V}\lambda_s^3\right)$$

so $\mu_\ell = kT\ln\dfrac{N_\ell\lambda_\ell^3}{V}$

equal probability condition:

$$2e^{\beta\mu_s} = e^{\beta\mu_e}$$

$$2e^{\ln N_e\lambda_e^3/V} = e^{\ln \frac{N_s}{V}\lambda_s^3}$$

$$\frac{2N_e\lambda_e^3}{V} = \frac{N_s}{V}\lambda_s^3$$

$$\boxed{\frac{N_e}{N_s} = \frac{\lambda_s^3}{2\lambda_e^3}} = \frac{1}{2}\frac{h^3}{(2\pi m_s kT)^{3/2}}\frac{(2\pi m_e kT)^{3/2}}{h^3}$$

$$= \frac{m_e^{3/2}}{2m_s^{3/2}}$$

3

(30 points) Consider the diatomic reaction

$$A + A \rightleftharpoons A_2$$

in a container of volume V. Assume that the A atoms are spin 0 bosons and that the temperature is low enough that the electrons remain in the ground state and the vibration modes are not excited. Derive an expression for the equilibrium constant

$$K(T) = \frac{N_{A_2}}{N_A^2}$$

in terms of the ground state electronic energies ϵ_1, ϵ_2. You can assume that the vibration zero point energy is included in ϵ_2. (Note: rotation states are indexed with a quantum number l, have energy $l(l+1)\hbar^2/2I$ (I is the moment of inertia), and have a degeneracy $2l+1$.)

$$K(T) = \frac{N_{A_2}}{N_A^2} = \frac{q_{A_2}}{q_A^2}$$

where q_i is single particle partition function

$$q_i = q_{pos}\, q_{mom}\, q_{elec}\, q_{vib}\, q_{rot}\, q_{nuc}$$

$$q_{pos} = V \qquad q_{mom} = \lambda_i^3 \qquad q_{elec} = e^{-\beta \varepsilon_i} + \cancel{\text{excited terms}}$$ drop

$q_{vib} = 1$ (not excited) $\quad q_{nuc} = 1$ (spin 0)

$q_{rot} = 1$ (for monoatomic)

$$q_{rot} = \sum_{l=even} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}$$

$$K(T) = \frac{V \lambda_{A_2}^3\, e^{-\beta \varepsilon_2} \sum_{l=even} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}}{V^2 \lambda_A^6\, e^{-2\beta\varepsilon_1}}$$

$$\boxed{= \frac{\lambda_{A_2}^3}{V \lambda_A^6}\, e^{-\beta(\varepsilon_2 - 2\varepsilon_1)} \sum_{l=even} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}}$$

some refinements?

$$\lambda_i = \frac{h}{\sqrt{2\pi m_i kT}}$$

$$\frac{\lambda_{A_2}^3}{\lambda_A^6} = \frac{(2\pi m_A kT)^3 h^3}{h^{\cancel{6}} (2\pi 2 m_A kT)^{3/2}}$$

$$= \frac{(kT\pi m_A)^{3/2}}{h^3}$$

$$\sum_{l=\text{even}} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}$$

$$\simeq \frac{1}{2}\int (2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}\, dl$$

$$x = l(l+1)$$
$$dx = 2l+1\, dl$$

$$= \frac{1}{2}\int_0^\infty e^{-\beta x \hbar^2/2I}\, dx$$

$$= \frac{2I}{2\beta\hbar^2} = \frac{I}{\beta\hbar^2}$$

$$\boxed{K(T) = \frac{(\pi kT m_A)^{3/2}}{V}\, e^{-\beta(\varepsilon_2 - 2\varepsilon_1)}\, \frac{I}{\beta\hbar^2}}$$