Name: Quiz #3 Solutions 4/28/03

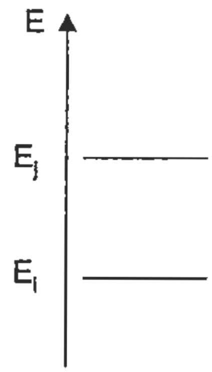
BE.011/2.993J
Spring 2003
QUIZ III
April 28, 2003

You have 1 hour for this exam.

CLOSED BOOK
1 page notes allowed

1 (15 points)	
2 (35 points)	
3 (50 points)	
total (100 points)	

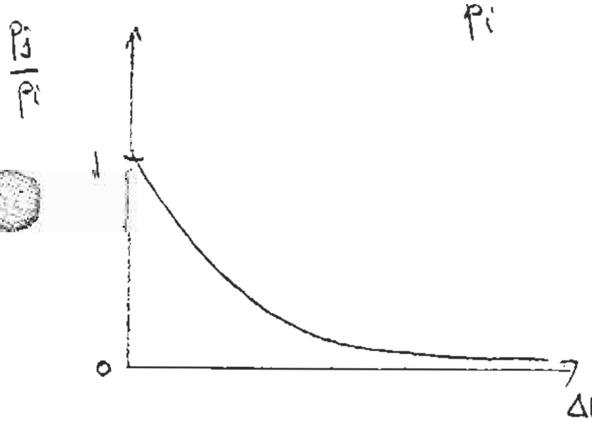
1.)(15 points) Schottky two level system



Sketch the relative populations (p_j/p_i) as a function of the energy separation $\Delta E = (E_j - E_i)$. At which temperature does the equilibrium population of $p_j > p_i$?

$$p_j = \frac{e^{-E_j/kT}}{q} \qquad \frac{p_j}{p_i} = \frac{e^{-E_j/kT}/q}{e^{-E_i/kT}/q} = \frac{e^{-E_j/kT}}{e^{-E_i/kT}} = e^{-(E_j-E_i)/kT}$$

since $E_j - E_i = \Delta E$, $\frac{p_j}{p_i} = e^{-\Delta E/kT}$



@ $\Delta E = 0$, $e^{-0} \sim 1$

@ $\Delta E = \infty$, $e^{-\infty} \sim 0$

* At no temperature does $p_j > p_i$!

$$\lim_{T\to\infty} e^{-\Delta E/kT} = e^{-0} = 1$$

$\frac{p_j}{p_i} = 1$, or populations are equal @ $T = \infty$

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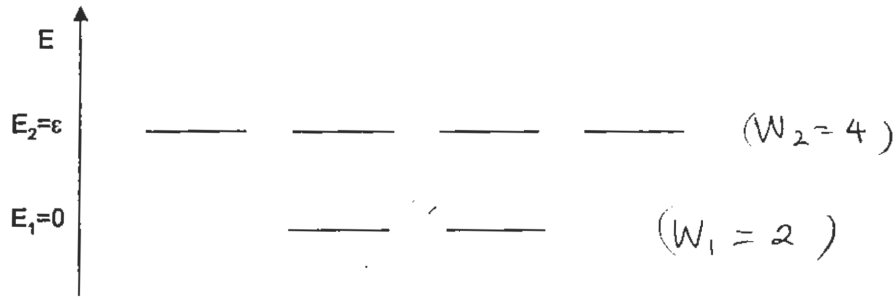
2). (35 points) A system has the following energy levels:



a) (5 points) Write down an expression for the partition function in terms of the energies.

$$q = \sum_{j=1}^{2} W(j)\, e^{-\varepsilon_j/kT}$$

$$= 2e^{-0} + 4e^{-\varepsilon/kT} = \boxed{2 + 4e^{-\varepsilon/kT}}$$

b) (5 points) Calculate the value of the partition function at T=300K assuming $\varepsilon = 9\times10^{-21}$ J. Use $k = 1.38\times10^{-23}$ J/K.

@ 300K.

$$q = 2 + 4\exp\left(\frac{-9\times10^{-21}\,J}{(1.38\times10^{-23}\,J/K)(300K)}\right) = \underline{2.46}$$

c) (10 points)You observe a population of 70% in the lower, 30% in the higher state at a temperature of 300K. Is this is the population of these states expected at equilibrium? If not, what is? Assume the same value for ε as in part b.

@ equilibrium,

$$p_i = \frac{W(i)\, e^{-E_i/kT}}{q}$$

q ← value @ 300K (from b)

$$P_1 = \frac{2}{2.46} = \boxed{0.81}$$ → ∴ 70/30 is not @ equilibrium

$$P_2 = \frac{4\exp\left(\frac{-9\times10^{-21}\,J}{1.38\times10^{-23}\,J/K \cdot 300K}\right)}{2.46} = \boxed{0.12}$$

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d) (5 points) As T→∞, what is q?

$$q = 2 + 4e^{-\varepsilon/kT}$$ @ any temperature

@ $T \to \infty$, $q = 2 + 4 \cdot e^{-\varepsilon/\infty}$ $\quad e^{-1/\infty} \approx e^{-0} \approx \underline{\underline{1}}$

so $q = 2 + 4(1) = \boxed{6 = q}$ Note: this makes sense; as T increases, all 6 states become accessible.

e) (5 points) As T→∞, what would the populations of the states be?

Like in part c, $p_i = \frac{W(i)e^{-\varepsilon_i/kT}}{q}$, but now $q = 6$

so $p_1 = \frac{2}{6} = \boxed{\frac{1}{3} = p_1}$

$$p_2 = \frac{4e^{-\varepsilon/\infty}}{6} = \frac{4(e^{-0})}{6} = \frac{4(1)}{6} = \boxed{\frac{2}{3} = p_2}$$

f) (5 points) Calculate the numerical value of the entropy of the system at equilibrium for T = 300K.

There's a couple ways to do this. The first way is to use the probabilities, p_j:

$S = -k \sum_{i=1}^{2} p_i \ln p_i$, where $p_i = \frac{W(i)e^{-\varepsilon_i/kT}}{q}$. We calculated these values in part c) already so $S = -k[p_1 \ln p_1 + p_2 \ln p_2] = -k[0.81 \ln(0.81) + 0.19 \ln(0.19)]$

$$\boxed{S = 6.7 \times 10^{-24}\ J/K}$$

The other way is to use $S = kN \ln q + \frac{U}{T}$ Now, N=1 (we don't have a collection of these molecules— in fact, we don't know anything about where the energy levels are from, just what they are!)

For this we'll need $U = N\langle\varepsilon\rangle = N \sum_{i=1}^{2} \varepsilon_i p_i$, use N=1 $\Rightarrow U = 1[0.81(0) + 0.19(\varepsilon)] = 1.71 \times 10^{-21} J$

so $\boxed{S = 1.81 \times 10^{-23} J/K}$ Why are these different values?

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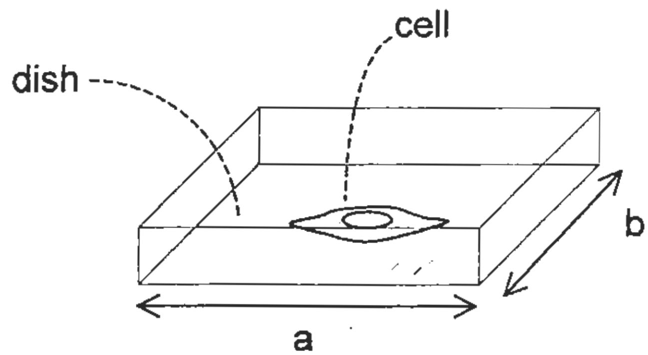

3.) (50 points) N Cells of type 1 are confined to petri dish of dimensions a × b where a = b = .
The cells can move in the x or y direction but cannot move in z direction and also cannot rotate.
Ignore vibrations and electronic excitations of the cell. $\Rightarrow q_{trans}$ only

a) (10 points) Approximating the cell as a particle-in-a-box, write down the expected energy levels for the cell and the ranges of the quantum numbers n_x and n_y.

$$\varepsilon_{n_x,n_y} = \left(\frac{h^2 n_x^2}{8ma^2} + \frac{h^2 n_y^2}{8mb^2}\right) = \frac{h^2}{8ma^2}(n_x^2+n_y^2)$$

$$\left.\begin{aligned} n_x &= 1, 2, \ldots \infty \\ n_y &= 1, 2, \ldots \infty \end{aligned}\right\}$$

$n_{x,y}$ are integer values and can go to ∞! They are not restricted by dimensions of box

b) (10 points) Write down an expression for the partition function based on the energy levels from a).

$$q_{trans} = \sum_{n_x,n_y}^{\infty} e^{-(\varepsilon_{n_x,n_y}/kT)} = \sum_{n_x,n_y}^{\infty} \exp\left(\frac{h^2}{8ma^2kT}(n_x^2+n_y^2)\right)$$

In simplified form:

$$q_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{2/2} a \cdot b = \left(\frac{2\pi mkT}{h^2}\right) \cdot \text{area}$$

(Note: we had $q_{trans,1D} = \left(\frac{\quad}{h^2}\right)^{1/2} \cdot (\text{length})$

$q_{trans\ 3D} = \left(\frac{\quad}{h^2}\right)^{3/2} \cdot (\text{Volume})$ in class)

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c) (5 points) using the simplified expression in b), calculate q_{trans} at T = 37°C (// 310K) assuming the cell has a mass of 5×10^{-13} kg and that a = b = 3cm. Use k = 1.38×10^{-23} J/K, h = 6.626×10^{-34} J·s.

$$q_{trans} = \frac{2\pi\,(5\times10^{-13}\,kg)\,(1.38\times10^{-23}\,J/K)\,(310K)}{(6.626\times10^{-34}\,J\cdot s)^2}\cdot 9\times10^{-4}\,m^2 = \boxed{2.76\times10^{31}\ \text{states}}$$

so we can treat it like a continuum.

d) (10 points) What is the internal energy, U, due to translation? Use $\frac{\partial \ln Q}{\partial T} = \frac{1}{Q}\frac{\partial Q}{\partial T}$. Does this make sense in terms of the equipartition theorem?

$$U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right) = kT^2\frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right)$$

$Q = \frac{q^N}{N!}$ because indistinguishable

$q = C\cdot T$, $C = \left(\frac{2\pi m k\cdot a^2}{h^2}\right)$

$$\frac{\partial Q}{\partial T} = \frac{N\cdot(C\cdot T)^{N-1}\cdot C}{N!} \ ; \quad U = kT^2\,\frac{\cancel{N!}}{(CT)^N}\cdot\frac{N(CT)^{N-1}}{\cancel{N!}}\cdot C = \frac{kT^2\cdot N\cdot \cancel{C}}{\cancel{C}T} = \boxed{NkT = U}$$

This makes sense because equipartition says: 2 degrees of freedom (x and y) so $U = \frac{2}{2}NkT = NkT$ ✓ (That's the easy way to get to the answer)

e) (5 points) What temperature would you have to go to for q_{trans}<10? This is the quantum limit.

$$q_{trans} = 10 = \frac{2\pi\,(5\times10^{-13}\,kg)(1.38\times10^{-23}\,J)\,(9\times10^{-4}\,m^2)}{(6.626\times10^{-34}\,J.s)^2}\cdot T$$

$$\boxed{T = 1.12\times10^{-28}\,K}$$

that's pretty cold!

NOTE: ONE MORE QUESTION!!! ⇨ ⇨⇨

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f) (10 points) A second cell type is added which is distinguishable from type 1, but within 1 and 2 they are **not** distinguishable. Write down an expression for the translational contribution to the energy of the entire system in terms of the partition functions of the individual cell types (q_{trans1} and q_{trans2}).

Now we have N_1 cells of type 1, N_2 of type 2

since they are indistinguishable from each other (but not within themselves)

$$Q_{system} = \left(\frac{q_1^{N_1}}{N_1!}\right)\cdot\left(\frac{q_2^{N_2}}{N_2!}\right)$$

To get the energy, U, we can use equipartition. There are still 2 degrees of freedom (x and y translation) but now we have $N_1 + N_2$ cells

so $U = \frac{2}{2}(N_1+N_2)kT = \boxed{(N_1+N_2)kT = U}$

OR, we can use $U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)$ where $Q = \left(\frac{q_1^{N_1}}{N_1!}\right)\left(\frac{q_2^{N_2}}{N_2!}\right)$ $q_1 = c_1 T$, $q_2 = c_2 T$

$U = kT^2 \frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right)$ + use chain rule:

$$\frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right) = \frac{N_1!}{(c_1T)^{N_1}}\frac{N_2!}{(c_2T)^{N_2}}\left[\frac{N_1(c_1T)^{N_1-1}}{N_1!}c_1 \cdot \frac{(c_2T)^{N_2}}{N_2!} + \frac{N_2(c_2T)^{N_2-1}\cdot c_2}{N_2!}\cdot\frac{(c_1T)^{N_1}}{N_1!}\right]$$

$$= \frac{N_1c_1}{(c_1T)} + \frac{N_2c_2}{(c_2T)} = \left(\frac{N_1}{T} + \frac{N_2}{T}\right)$$

so $U = kT^2 \frac{1}{T}(N_1+N_2) = \boxed{(N_1+N_2)kT}$ same answer as equipartition!

See how much work it saved us?