Final (2024)

1. (a) Consider a solution with a solute species at a very low concentration. assume that solute molecules are uncorrelated from each other; the total number of solute molecules is $N = \text{const}$.

The solute molecules undergo conformational transitions between 2 isomers: $A \leftrightarrow B$, s.t. the numbers of A & B isomers, N_A & N_B, are stochastic variables; note also that

$$N_A + N_B = N.$$

Show that $\langle (N_A - \langle N_A \rangle)^2 \rangle = x_A x_B N$,

where
$$\begin{cases} x_A = \dfrac{\langle N_A \rangle}{N}, \\ x_B = \dfrac{\langle N_B \rangle}{N} = 1 - x_A \end{cases}$$

(b) Assume that

$$\Delta E = \underbrace{E_A}_{\text{energy of state A}} - \underbrace{E_B}_{\text{energy of state B}}$$

and that the degeneracies of states A & B are g_A & g_B, respectively.

Write $\dfrac{\langle N_A \rangle}{\langle N_B \rangle}$ using the Boltzmann distribution at temp. T

[Rederive $\dfrac{\langle N_A \rangle}{\langle N_B \rangle}$ using the chemical equilibrium condition, $\mu_A = \mu_B$.]

extra credit, +10 pt

Hint: use $\log N! \simeq N \log N - N$

2. (a) Consider a system with the total energy

vibrational energy

$$E = E_0 + E_A + E_B + E_C$$

const zero-point energy; electronic energy; rotational energy

Show that the total heat capacity

el. vibr. rot.

$C_V = C_V^A + C_V^B + C_V^C$ and that it is indep. of E_0.

(b) Derive C_V^A under the assumption that there are 3 electronic states with energies and degeneracies

$\varepsilon_0, g_0;\ \varepsilon_1, g_1;\ \varepsilon_2, g_2.$

(i.e., derive C_V^A as an explicit function of the energies and the degeneracies)

(3) Consider an Ising model with two relevant scaling fields:

$$\begin{cases} g_1 = t = \dfrac{T-T_c}{T_c}, & T_c = \text{critical } T, \\ h = \dfrac{H}{k_B T} & H = \text{magnetic field} \end{cases}$$

Use the scaling form of the reduced free energy per spin, $\bar{f}(t,h)$ to find β, the critical exponent for zero-field magnetization:

$$M \sim (-t)^{\beta}$$

and δ, the critical exponent in the critical isotherm:

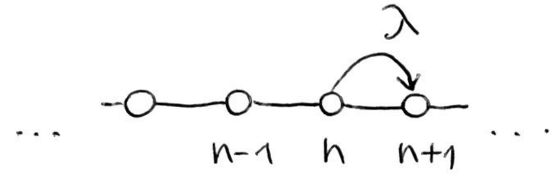
$$H \sim |M|^{\delta} \operatorname{sgn}(M) \qquad T = T_c$$

in terms of d, the number of dimensions, and y_1 & y_2, the scaling exponents for t & h, respectively.

4. Consider a continuous-time stochastic process where a particle jumps from site n to a neighboring site $n+1$ with a rate λ. assume that the lattice is infinite and the backward jumps are not allowed:

<u>Initial condition:</u>

$n=0$ @ $t=0$



Write down and solve the master equation for this stochastic process. What is the name of the probability distribution that satisfies the master equation?

<u>Hint</u>: you may want to use the generating function

$$p(s,t) = \sum_{n=0}^{\infty} s^n \underbrace{p(n,t)}_{\text{prob. to be at site } n \text{ @} t}$$