

Chem 220A Midterm Exam #2 SynopsisDefinitions and Formulas:

First law of thermodynamics:

$$dE = dW + dQ, \quad dW = \mathbf{f}_{\text{ext}} \cdot d\mathbf{X}$$

Second law of thermodynamics: For spontaneous processes,

$$dS \geq \frac{dQ}{T}$$

Common thermodynamic functions:

$$E = TS + \mathbf{f} \cdot \mathbf{X}, \quad A = E - TS, \quad G = E - TS + pV$$

Differential changes in thermodynamic functions:

$$dE = TdS - pdV + \sum_j \mu_j dN_j, \quad dA = -SdT - pdV + \sum_j \mu_j dN_j$$

Stirling's approximation: For large  $N$ ,  $\ln N! \approx N \ln N - N$ .

Dilute limit: For  $M \gg N$ ,  $\frac{M!}{(M-N)!N!} \approx M^N/N!$

Partition functions:

$$Q = \sum_{\nu} \exp[-\beta E(\nu)], \quad \Xi = \sum_{\nu} \exp[-\beta E(\nu) + \beta \mu N(\nu)]$$

Thermodynamic connections:

$$\frac{P(B)}{P(C)} = \frac{e^{-\beta A(B)}}{e^{-\beta A(C)}} = \frac{Q(B)}{Q(C)} = e^{-\beta w_{\text{rev}}}$$

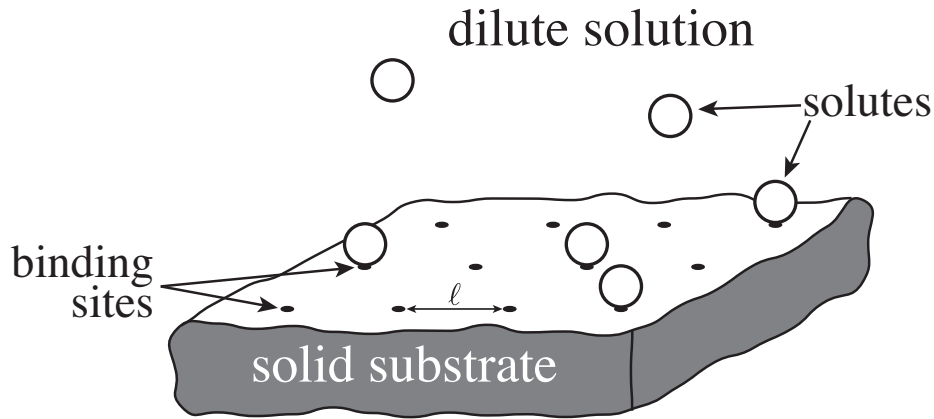
Critical temperature of the Ising model on a cubic lattice:

$$k_B T_c = 0, \quad d = 1$$

$$k_B T_c \approx 2.3J, \quad d = 2$$

$$k_B T_c \approx 4.5J, \quad d = 3$$

Questions on this exam concern the adsorption of solutes from a dilute solution onto a macroscopic solid substrate. (These solutes might be small molecules, nanocrystals, or proteins; the substrate might be a glass bead, metal, or surface of a living cell. Pick your favorite.) We will imagine throughout that the set of binding sites is discrete, as sketched below, with one site per unit  $\ell^2$  of area. Each binding site can accommodate at most one solute.



Denoting the total number of binding sites as  $M_s \gg 1$ , we can write the total surface area of the substrate as  $M_s \ell^2$ .

In all questions we will take the bulk solution to be dilute, so that interactions between dissolved solutes can be neglected in that environment. Adsorbed solutes may or may not be sparse on the substrate, and interactions between adsorbed solutes may or may not be present, as will be specified in each question.