

Definitions and Useful Formulas:

Partition functions:

$$Q(\beta, V, N) = \sum_{\nu} \exp[-\beta E(\nu)], \quad \Xi(\beta, V, \beta\mu) = \sum_{\nu} \exp[-\beta E(\nu) + \beta\mu N(\nu)], \quad \beta = 1/(k_{\text{B}}T)$$

Common thermodynamic functions:

$$E = TS - pV + \mu N, \quad A = E - TS$$

Helmholtz free energy:

$$\beta A(\beta, V, N) = -\ln Q, \quad dA = -SdT - pdV + \mu dN$$

, Reversible work at fixed temperature: $(\bar{d}w_{\text{rev}})_T = (dA)_T$

Thermodynamic connections:

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

Stirling's approximation:

$$\ln N! \approx N \ln N - N, \quad \text{for large } N$$

Boltzmann's definition of entropy:

$$S = k_{\text{B}} \ln W(E, V, N)$$

Second law of thermodynamics:

For spontaneous processes, $(\Delta S)_{E,V,N} \geq 0$ or $(\Delta A)_{T,V,N} \leq 0$.At equilibrium, S is maximized at fixed E , V , and N ; or A is minimized at fixed T , V , and N .

Critical temperature of the Ising model on a cubic lattice:

$$k_{\text{B}}T_c = 0, \quad d = 1$$

$$k_{\text{B}}T_c \approx 2.3J, \quad d = 2$$

$$k_{\text{B}}T_c \approx 4.5J, \quad d = 3$$

Hyperbolic functions:

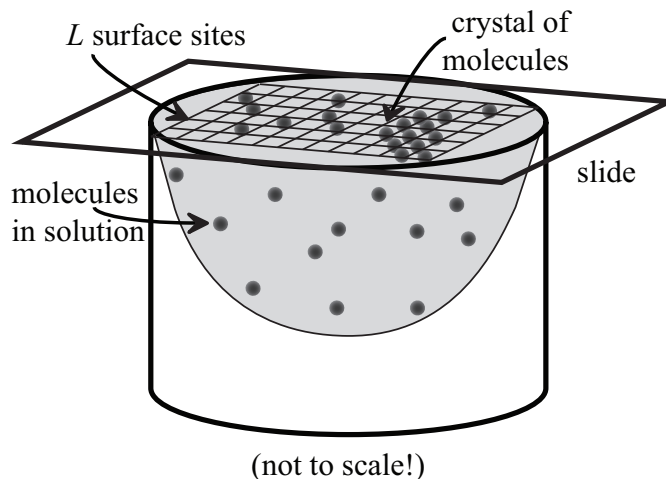
$$\cosh x = \frac{1}{2}(e^x + e^{-x}), \quad \sinh x = \frac{1}{2}(e^x - e^{-x}), \quad \tanh x = \frac{\sinh x}{\cosh x}$$

$$\frac{d}{dx} \cosh x = \sinh x, \quad \frac{d}{dx} \sinh x = \cosh x, \quad \frac{d}{dx} \tanh x = 1 - \tanh^2 x$$

You will note that this exam is somewhat sequential in nature. Fear not! You will not be penalized for substituting an incorrect answer from a previous part into a latter part.

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Questions on this exam focus on the process of crystallization of molecules on a surface, as illustrated in the diagram below as a hanging drop approach. Such crystallization processes are ubiquitous in many areas of chemistry and biochemistry, yet it is often unclear how to best balance the thermodynamic driving forces to achieve crystallization. Our goal is to shed light on these physical underpinnings of the crystallization process with a model system.



We will focus exclusively on the two-dimensional (2D) subsystem of structureless solute molecules at the surface of the slide, which we shall represent using a lattice of L sites that can be occupied by at most a single molecule.

For the purposes of this exam, consider the droplet of solution to merely be a macroscopic reservoir of molecules that can exchange with the surface subsystem and that holds the subsystem at a well-defined temperature, T . The corresponding chemical potential for molecules comprising this subsystem is $\mu(T)$.

You may neglect gravity and solvent effects throughout this exam.

A molecule can bind to a surface lattice site with an affinity represented by the favorable energy $-\sigma$, where $\sigma > 0$.

Although a molecule in the surface subsystem can translate along the surface, we will not explicitly consider its translational motion (kinetic energy) or entropy.

We will also introduce a pairwise intermolecular affinity such that molecules occupying neighboring lattice sites contribute to the subsystem energy an amount $-\epsilon$, where $\epsilon > 0$, unless otherwise stated.

NEW! \Rightarrow In sum, we will model the energy of the 2D surface subsystem of molecules with the following energy function:

$$E_{\text{surf}} = -\sigma \sum_{i=1}^L n_i - \epsilon \sum'_{i,j} n_i n_j,$$

where the occupation number n_i for an individual lattice site is given by either 0 or 1, and $\sum'_{i,j}$ indicates a summation over all distinct pairs of nearest neighbor sites.

We will work our way toward understanding and optimizing the crystallization process as a function of the interaction energies in the above prescription.

1. In this first question we will begin by considering properties of the subsystem of molecules at the slide surface in the simplified case of $\epsilon = 0$ where there are no intermolecular interactions.

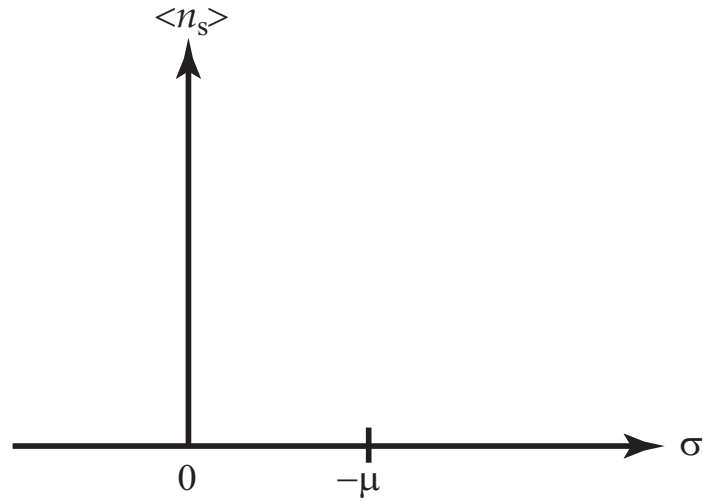
8 pts (i) Calculate the grand canonical partition function $\Xi_s(\mu, L, T; \epsilon=0)$ for the molecular subsystem at the surface of the slide. Express your answer in terms of the temperature T , the fixed total number of lattice sites L , the chemical potential μ , the molecular affinity for the surface σ , and fundamental constants.

8 pts (ii) By differentiating Ξ_s appropriately, compute the average number of molecules attached to the slide surface $\langle N_s \rangle$ at equilibrium.

Use your answer to write an expression for the average occupation of surface sites, $\langle n_s \rangle = \langle N_s \rangle / L$.

8 pts (iii) Plot the average occupation number of surface sites $\langle n_s \rangle$ as a function of σ , the molecular affinity for the surface, on the axes provided below.

Take $\mu < 0$, mark the value of your function at $-\mu$, and be sure to indicate the limiting values of $\langle n_s \rangle$ for high and low affinity, σ .



2. In this next question we will examine the combined influence of surface–molecule interactions (σ) and intermolecular interactions in the surface subsystem by including $\epsilon > 0$ in the subsystem energy E_{surf} .
- 6 pts (i) Write an expression for the surface subsystem grand canonical partition function, $\Xi_s(\mu, L, T; \epsilon > 0)$. You need not obtain a closed form expression for Ξ_s , i.e., it is acceptable for your answer to include summations. Briefly explain the difficulty in obtaining a closed form solution.

Our model for the surface subsystem is not quite the same as that of a lattice gas, but it is isomorphic to the lattice gas and to the Ising magnet. For the Ising magnet,

$$E_{\text{Ising}} = -h \sum_{i=1}^L s_i - J \sum'_{i,j} s_i s_j,$$

where the spin state s_i for an individual lattice site i is given by either -1 or 1, h corresponds to the interaction of a spin with an external magnetic field, and J corresponds to the interaction of neighboring spins. Here, L corresponds to the total number of spin sites in the lattice.

- 6 pts (ii) Write an expression for the canonical partition function Q_{Ising} for the Ising magnet.

8 pts (iii) From your answers to parts (i) and (ii), determine two equations that specify the isomorphism between our surface subsystem and the Ising magnet by comparing their statistical weightings through the identity $s_i = 2n_i - 1$.

Your answer should relate the parameters in the two models and may also include the number of nearest neighbors of a given lattice site, Z . (You need not keep track of constant terms in these statistical weightings.)

You may also find it helpful to use the following identity:

$$\sum'_{i,j} n_i = \frac{Z}{2} \sum_i n_i.$$

3. To make further progress toward learning how our model parameters affect the thermodynamics of surface crystallization, we will resort in this question to a mean field approximation. Here, the effect of nearest neighbor coupling that we have introduced through $\epsilon > 0$ will be accounted for (as best we can) through an average effective molecule-surface affinity σ_{MF} . To do so we note that the energy of a single fluctuating site “1” on the slide surface is

$$E(n_1) \cong -\sigma n_1 - \epsilon Z n_1 \bar{n} = -\sigma_{\text{MF}} n_1$$

where

$$\sigma_{\text{MF}} = \sigma + \epsilon Z \bar{n}$$

and where the mean occupation number $\bar{n} = \langle n_j \rangle$ for $j \neq 1$.

- 6 pts (i) Compute the single site grand canonical partition function, z_1 , for site “1” in this mean field approximation in terms of σ_{MF} and any other variables that you need.

- 4 pts (ii) Rewrite your answer to part (i) by multiplying creatively by 1 so that the partition function bears the form:

$$z_1 \propto \{\text{some exponential function}\} \times \{\text{some hyperbolic function}\}.$$

6 pts (iii) Appropriately differentiate your new expression for z_1 in order to obtain an expression for $\langle n_1 \rangle$, the average occupation number of site “1”.

(Even though the functional forms may differ, you might want to check that your expression for $\langle n_1 \rangle$ as a function of σ_{MF} has the same limiting behavior as the average occupation number versus σ that you obtained and plotted in question #1.)

4 pts (iv) By requiring the self-consistency, $\langle n_1 \rangle = \bar{n}$, and using the above definition for σ_{MF} , write a “mean field equation” relating \bar{n} , β , μ , σ , ϵ , and Z .

In the next few questions you will use your equation for \bar{n} in order to identify the critical temperature T_c^{MF} above which molecules on the surface are disordered and below which we expect to observe an ordered crystal phase coexisting with a sparse phase.

Recall that when we identified the critical temperature in the mean field approximation for the Ising model, we did so at zero external magnetic field, $h = 0$. This was because the condition $h = 0$ ensures that there is equal probability to find domains with net positive (\uparrow) and net negative (\downarrow) magnetization of equal magnitude. In our isomorphism with the lattice gas, this condition of $h = 0$ furthermore determined the chemical potential at which liquid and vapor coexist.

In question #2 part (iii) you developed expressions that define the relationship between our surface subsystem and the corresponding Ising magnet system.

- 4 pts (v) Set $h = 0$ in your answer to question #2 part (iii) to establish the chemical potential μ_{coex} that enables coexistence of the crystalline and sparse phases. By eliminating parameters that belong explicitly to the Ising model write μ_{coex} exclusively in terms of the surface subsystem parameters and the number of nearest neighbors, Z .

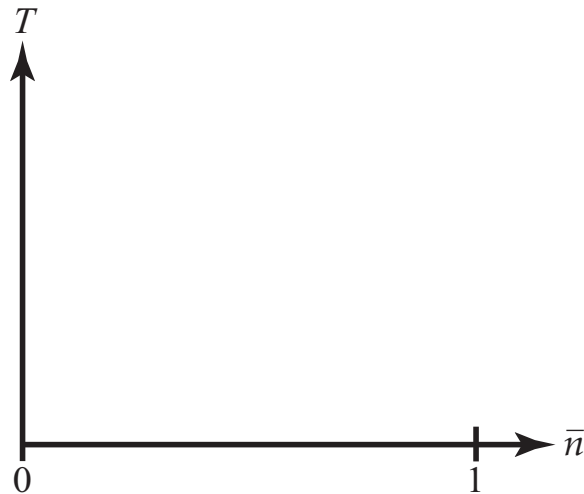
- 4 pts (vi) Combine your expression for μ_{coex} and your equation from part (iv) to write a mean field equation at coexistence.

8 pts (vii) Use your mean field equation at coexistence to determine an expression for the critical temperature T_c^{MF} of the *two-dimensional* surface subsystem in terms of parameters in your equation and fundamental constants.

[Hints: (a) Although you are not required to provide a graphical solution to your mean field equation, you might find it helpful to plot the two sides of your equation. (b) It might also help to recall that $\tanh x \approx x$ for small x . (c) Last, it may be helpful, though certainly not necessary, to first rewrite your equation so that the only term on the righthand side is a term that includes a transcendental function.]

If your equation doesn't seem quite right, describe the analogous procedure to find the critical temperature for the Ising model at $h = 0$.

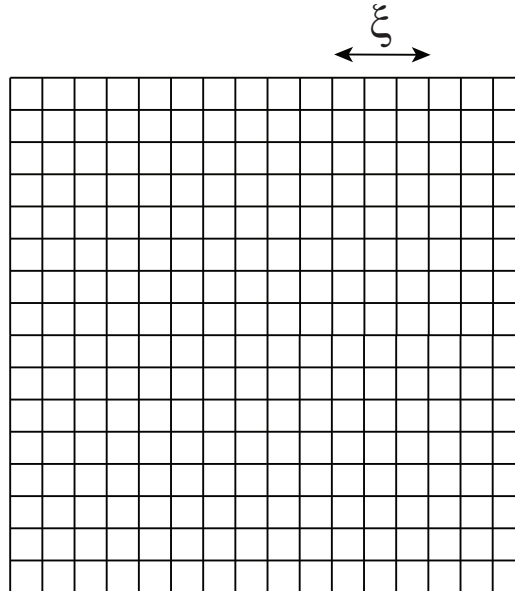
- 6 pts (viii) On the phase diagram below sketch the boundary of the coexistence region for the surface subsystem. Label (with values or expressions) the coordinates of the critical point on your diagram. (You need not derive an equation for the behavior of the coexistence curve near T_c^{MF} . A sketch of the general shape and correct sign of curvature should suffice.)



- 6 pts (ix) Explain physically how the strength of intermolecular attraction, ϵ , affects the onset temperature for the crystallization transition. How do you expect our mean field approximation to affect this onset temperature?

8 pts (x) On the lattice below, illustrate an instantaneous realization of the system for $\bar{n} \simeq 0.5$ and $0 < T < T_c^{\text{MF}}$ that has a correlation length ξ of extent indicated next to the lattice.

If the nature of these phases is not completely obvious to you for the surface subsystem, sketch a realization of the Ising magnet under analogous conditions, and you should be able to draw some analogies based on that!



Extra Credit (xi) Below the transition temperature for crystallization do you expect $\bar{n}(\sigma, \epsilon)$, the average occupation number for the surface subsystem with surface affinity σ and intermolecular affinity ϵ , to be greater than, less than, or equal to the average occupation number that you would obtain at the same value of σ , but when $\epsilon = 0$? (The latter is what you calculated in question #1, where you neglected intermolecular interactions.) Briefly explain your logic.