

Phys 210A — Spring 2024
Problem Set #4: Phase Transition and Critical Phenomena
Due date: Friday June 7

1. **Liquid-Gas Transition** — Van der Waals' theory of interacting gas can be written in terms of the following equation of state:

$$\left(P + \frac{a}{v^2}\right) \cdot (v - v_0) = k_B T,$$

where $v \equiv V/N$ is the specific volume per particle, for a system of N fixed particles. a and v_0 are two interaction parameters.

- (a) Find the critical point (P_c, v_c, T_c) of this system in terms of the interaction parameters v_0 and a . Compute the dimensionless combination $(P_c v_c)/(k_B T_c)$. Show that in terms of the scaled variables $\tilde{P} \equiv P/P_c$, $\tilde{v} = v/v_c$, $\tilde{T} = T/T_c$, the van der Waals equation of state becomes

$$\left(\tilde{P} + \frac{3}{\tilde{v}^2}\right) (3\tilde{v} - 1) = 8\tilde{T}.$$

- (b) Obtain the variational free energy $\Psi(\tilde{v}; \tilde{P}, \tilde{T})$, and sketch its dependence on \tilde{v} for $(\tilde{P}, \tilde{T}) = (0.5, 0.5)$ and $(\tilde{P}, \tilde{T}) = (1, 1)$.
- (c) Expand Ψ in the vicinity of the critical point, i.e., for $t = (T - T_c)/T_c \ll 1$, $p = (P - P_c)/P_c \ll 1$ and $\nu = (v - v_c)/v_c \ll 1$, to $O(\nu^4)$. Find the phase coexistence line $p_{LG}(t)$ to leading order in t .
- (d) Show that along the coexistence line, the difference in specific volume of the two phases is $\Delta\nu(t) \approx 4(-t)^\beta$ to leading order in $t < 0$, and find the value of the exponent β . From the Clausius-Claperton equation, find the latent heat of evaporation.
- (e) For $t = 0$, find the equation of state to leading order in ν , thereby verifying the scaling law $\nu \sim p^{1/\delta}$. Find the value of the exponent δ .
- (f) For $|t| \ll 1$, find the isothermal compressibility $\kappa_T = -\left(\frac{\partial v}{\partial p}\right)_T$ along the “critical isochore” $\nu = 0$. Show that $\kappa_T \approx A_+ t^{-\gamma}$ for $t > 0$ and $\kappa_T \approx A_- |t|^{-\gamma}$ for $t < 0$. Find the value of the exponent γ and the coefficients A_\pm .
2. **Antiferromagnetism** — Consider an Ising *antiferromagnet* in a uniform magnetic field H , described by the Hamiltonian

$$\mathcal{H} = J \sum_{\langle i,j \rangle} s_i s_j - H \sum_i s_i,$$

with $J > 0$, and the spins $s_i \in \{\pm 1\}$ arranged on a 2D square lattice.

- (a) At $T = 0$ and $H = 0$, what is the (pair of) ground state spin configurations? Find the threshold field H_c above which this pair of antiferromagnetic states are no longer the lowest in energy. What is the ground state for $H > H_c$?

- (b) Generalize the Weiss mean-field theory to obtain *two* self-consistent equations relating the average magnetization of *neighboring* spins at finite temperature T .
[Hint: You will need to introduce *two* mean-field order parameters.]
- (c) For $H = 0$, find the critical point $T_c(0)$ and find the exponent β describing the onset of antiferromagnetic order for T slightly below $T_c(0)$. It will be helpful to obtain the qualitative behaviors at low and high temperatures by sketching graphical solutions to the equations obtained in part (b).
- (d) Obtain an equation describing the phase boundary (T_c, H_c) separating the different phases. Find explicitly $T_c(H)$ for small H . What is the exponent β for $H \neq 0$?
- (e) Sketch the phase diagram in the (T, H) plane, indicating clearly the nature of the different phases, and the order(s) of the phase transition(s).
- (f) Computer the magnetic susceptibility $\chi = \frac{\partial M}{\partial H}|_{H=0}$ where M is the mean magnetization, for $T > T_c(0)$ and $T < T_c(0)$. Compare it to the mean-field behavior of χ for the ferromagnet discussed in class.

3. **Isotropic ferromagnet** — An isotropic ferromagnet may be described by the classical Heisenberg model,

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{\sigma}(i) \cdot \vec{\sigma}(j) - \mu \vec{H} \cdot \sum_i \vec{\sigma}(i),$$

where $\vec{\sigma}(i)$ is a 3d unit vector giving the direction of a classical spin vector located on lattice site i , $J > 0$ is the strength of the ferromagnetic interaction energy, $\mu \vec{H} \cdot \vec{\sigma}(i)$ gives the magnetic energy of the spin of magnetic moment μ at site i in an uniform external magnetic field \vec{H} , and $\langle i, j \rangle$ denotes sum over q nearest-neighbor sites.

- (a) Apply Weiss' mean-field approximation and write down the mean-field Hamiltonian in term of a sum of non-interacting single-site Hamiltonian $\tilde{\mathcal{H}}$. Show that a self-consistent equation for the average magnetization per site $\vec{m} \equiv \langle \vec{\sigma} \rangle$ can be obtained as the following,

$$m_\alpha = \frac{\partial}{\partial x_\alpha} \log \tilde{Z}(x)$$

where m_α is the component of \vec{m} in direction α , x_α is the component of $\vec{x} \equiv \mathcal{J}\vec{m} + \vec{h}$ in direction α (with $\mathcal{J} = qJ\beta$, and $\vec{h} = \beta\mu\vec{H}$), and $\tilde{Z} = \int d\vec{\sigma} e^{-\beta\tilde{\mathcal{H}}}$ is the single-site partition function which depends on a single dimensionless combination of parameters, $x \equiv |\vec{x}|$.

- (b) Compute $\log \tilde{Z}(x)$ and its derivative by referring to Lecture #7. To explore behaviors close to the critical point, it will be sufficient to expand $\log \tilde{Z}(x)$ to $O(x^4)$. Show that for a vector \vec{v} with magnitude $|\vec{v}| \equiv v$, $\frac{\partial}{\partial v_\alpha} v = v_\alpha/v$, and use this result to derive the self-consistent equation for m_α to $O(m^2 m_\alpha)$ and $O(h_\alpha)$.
- (c) Find the critical temperature T_c in the absence of the external field (i.e., for $\vec{h} = 0$) as the lowest temperature for which the solution of the self-consistent equation is $m = 0$. Explain why the numerical value of T_c is smaller or larger than the result $T_c = qJ/k_B$ derived in class for the Ising model.

- (d) For $T < T_c$, system enters the ferromagnetic phase where $m > 0$ even with $h = 0$. Obtain the dependence of the spontaneous magnetization, m , on the reduced temperature $t = (T - T_c)/T_c$ in the vicinity of the critical temperature for $h = 0$. How does m depend on the magnitude of the applied field h along $T = T_c$?

For a vector order parameter \vec{m} , the magnetic susceptibility is a tensor:

$$\chi_{\alpha\beta} \equiv \lim_{h \rightarrow 0} \frac{\partial m_\alpha}{\partial h_\beta},$$

and can be generally written in the form

$$\chi_{\alpha\beta} = \lim_{h \rightarrow 0} \left[\chi_L \frac{h_\alpha h_\beta}{h^2} + \chi_T \left(\delta_{\alpha\beta} - \frac{h_\alpha h_\beta}{h^2} \right) \right],$$

where χ_L and χ_T are the longitudinal and transverse susceptibility, respectively. In a Cartesian coordinate system, if a small field \vec{h} is applied in the z-direction, then $\chi_{zz} = \chi_L$ and $\chi_{xx} = \chi_{yy} = \chi_T$, while all off-diagonal components are 0.

In the following, you will calculate χ_L and χ_T by starting with the self-consistent equation for $m_\alpha(h_\alpha)$ derived in part (b).

- (e) Let $\vec{h} = h_0 \hat{z} + \delta h_z \hat{z}$. Correspondingly, we expect $\vec{m} = \vec{m}_0(h_0) \hat{z} + \delta m_z \hat{z}$. Insert these forms of \vec{h} and \vec{m} into the equation of state, and find $\chi_L = \lim_{h_0 \rightarrow 0} \frac{\delta m_z}{\delta h_z}$ in the vicinity of the critical temperature by using the result $m(t, h = 0)$ obtained in part (d). State the results both above and below the critical temperature.

- (f) Now let $\vec{h} = h_0 \hat{z} + \delta h_x \hat{x}$ and $\vec{m} = \vec{m}_0(h_0) \hat{z} + \delta m_x \hat{x}$. Again insert these forms of \vec{h} and \vec{m} into the equation of state, and find $\chi_T = \lim_{h_0 \rightarrow 0} \frac{\delta m_x}{\delta h_x}$ in the vicinity of the critical temperature by using the result $m(t, h = 0)$ obtained in part (d). Why does χ_T behave so differently from χ_L below T_c ?

[Hint: Consider the difference in changing the magnitude and direction of \vec{m} in the ferromagnetic phase.]

4. **Potts model** — Consider the following system defined on a square lattice of N sites. On each lattice site i , there is a discrete spin-like variable $s(i)$ which may take on one of q discrete values, e.g., $s(i) \in \{1, 2, \dots, q\}$. The energetics of the system is given by the Hamiltonian

$$\mathcal{H} = -J \sum_{\langle i, j \rangle} [q \delta_{s(i), s(j)} - 1]$$

such that if the nearest neighbor spins (indicated by $\langle i, j \rangle$) belong to the same state, there is an energy gain of $-(q - 1)J$, while if the nearest neighbor states are different, there is an energy cost of $+J$. This model is known as the q -state Potts model; it is a generalization of the Ising model for $q > 2$. Here you are asked to provide a mean-field solution to the Potts model for $q = 3$, which is a model of, e.g., the adsorption of Krypton gas on graphite (where each Krypton atom can occupy one of three equivalent sites on the hexagonal lattice of graphite).

- (a) Let the fraction of sites belonging to state s be x_s , with $x_1 + x_2 + x_3 = 1$. Find the mixing entropy $S(x_1, x_2, x_3)$ by computing first the number of configurations Ω that the N sites have N_1 sites in state 1, N_2 sites in state 2, and N_3 sites in state 3. [Hint: You may assume N_1, N_2, N_3 are all much larger than 1 and use the Stirling approximation, $\ln(x!) \approx x \ln(x) - x$ valid for large x .]
- (b) Write down an expression for the average energy $E(x_1, x_2, x_3)$ assuming that each site may belong to state s with probability x_s independently of the states of the other sites.
- (c) Anticipating spontaneous symmetry breaking at low temperatures, one can describe the fraction x_s 's in terms of a single order parameter m (with $0 \leq m \leq 1$) such that when $m = 0$, the $x_s = \frac{1}{3}$ for all 3 states s (corresponding to the complete lack of ordering), and when $m = 1$, one of the state (e.g., $s = 1$) is selected by all sites such that $x_1 = 1$, and $x_2 = x_3 = 0$. Find the linear functions $x_s(m) = a_s m + b_s$ satisfying the above requirements.
- (d) Using $x_s(m)$ found in part (c) for the entropy S and average energy E obtained earlier to show that the *mean-field* free energy $\psi(m) \equiv E - TS$ is of the form

$$\frac{\psi(m)}{Nk_B T} \approx c_0 + \frac{T - T_0}{T} m^2 - \frac{1}{3} m^3 + \frac{1}{2} m^4$$

for small m , with c_0 being an unimportant constant, and T_0 being a characteristic temperature scale set by J/k_B . In what sense is what we have done the “mean-field approximation”?

- (e) Sketch $\psi(m)/(Nk_B T)$ for $T = T_0$ and $T \gg T_0$, and find the value of m (referred to as m^*) which minimizes $\psi(m)$ for the two cases. Show that there is a phase transition at some temperature $T_c > T_0$ and sketch $\psi(m)$ at T_c . Based on the qualitative behavior of $m^*(T)$ above and below T_c , predict the order of this phase transition.