## Mean field approaches to Phase transitions

**1.** *Surfactant condensation:* $N$ surfactant molecules are added to the surface of water over an area $A$. They are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p_i}^{\,2}}{2m} + \frac{1}{2}\sum_{i,j} \mathcal{V}(\vec{q_i} - \vec{q_j}),$$

where $\vec{q_i}$ and $\vec{p_i}$ are two dimensional vectors of position and momentum for particle $i$.

(a) Write down the expression for the partition function $Z(N,T,A)$ in terms of integrals over $\vec{q_i}$ and $\vec{p_i}$, and perform the integrals over the momenta.

The inter–particle potential $\mathcal{V}(\vec{r})$ is infinite for separations $|\vec{r}\,| < a$, and attractive for $|\vec{r}\,| > a$ such that $\int_a^\infty 2\pi r dr \mathcal{V}(r) = -u_0$.

(b) Estimate the total non–excluded area available in the positional phase space of the system of $N$ particles.

(c) Estimate the total *potential* energy of the system, within a *uniform density approximation* $n = N/A$. Using this potential energy for all configurations allowed in the previous part, write down an approximation for $Z$.

(d) The addition of surfactants modifies the surface tension of water, from an initial value of $\sigma_0$, by $\sigma_s = -\left.\partial \ln Z/\partial A\right|_{T,N}$ (similar to a two-dimensional pressure. Calculate the surface tension $\sigma(n,T)$ in the presence of surfactants.

(e) Show that below a certain temperature, $T_c$, the above expression for $\sigma$ violates stability requirements. What do you think happens at low temperatures?

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**2.** *Critical behavior of a gas:* The pressure $P$ of a gas is related to its density $n = N/V$, and temperature $T$ by the truncated expansion

$$P = k_B T n - \frac{b}{2}n^2 + \frac{c}{6}n^3 \quad ,$$

where $b$ and $c$ are assumed to be positive, temperature independent constants.

(a) Locate the critical temperature $T_c$ below which this equation must be invalid, and the corresponding density $n_c$ and pressure $P_c$ of the critical point. Hence find the ratio $k_B T_c n_c / P_c$.

(b) Calculate the isothermal compressibility $\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$, and sketch its behavior as a function of $T$ for $n = n_c$.

(c) On the critical isotherm give an expression for $(P - P_c)$ as a function of $(n - n_c)$.

(d) The instability in the isotherms for $T < T_c$ is avoided by phase separation into a liquid of density $n_+$ and gas of density $n_-$. For temperatures close to $T_c$, these densities behave as $n_\pm \approx n_c\,(1 \pm \delta)$. Using a Maxwell construction, or otherwise, find an implicit equation for $\delta(T)$, and indicate its behavior for $(T_c - T) \to 0$. (Hint: Along an isotherm, variations of chemical potential obey $d\mu = dP/n$.)

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**3. (Optional)** *Dieterici's equation of state* has the form

$$P(v-b) = k_B T \exp\left(-\frac{a}{k_B T v}\right), \qquad \text{where} \;\; v = V/N.$$

(a) Find the ratio $Pv/k_BT$ at its critical point.

(b) Calculate the isothermal compressibility $\kappa_T$ for $v = v_c$ as a function of $T - T_c$.

(c) On the critical isotherm expand the pressure to the lowest non-zero order in $(v - v_c)$.

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**4.** *Magnetic thin films:* A crystalline film (simple cubic) is obtained by depositing a finite number of layers $n$. Each atom has a three component (Heisenberg) spin, and they interact through the Hamiltonian

$$-\beta\mathcal{H} = \sum_{\alpha=1}^{n}\sum_{<i,j>} J_H \vec{s}_i^{\,\alpha}\cdot\vec{s}_j^{\,\alpha} + \sum_{\alpha=1}^{n-1}\sum_{i} J_V \vec{s}_i^{\,\alpha}\cdot\vec{s}_i^{\,\alpha+1}.$$

(The unit vector $\vec{s}_i^{\,\alpha}$ indicates the spin at site $i$ in the $\alpha$th layer. The subscript $< i, j >$ indicates that the spin at $i$ interacts with its 4 nearest-neighbors, indexed by $j$ on the square lattice on the same layer.) A mean–field approximation is obtained from the variational density $\rho_0 \propto \exp\left(-\beta\mathcal{H}_0\right)$, with the trial Hamiltonian

$$-\beta\mathcal{H}_0 = \sum_{\alpha=1}^{n}\sum_{i} \vec{h}^{\,\alpha}\cdot\vec{s}_i^{\,\alpha}.$$

(Note that the most general single–site Hamiltonian may include the higher order terms $L^{\alpha}_{c_1,\cdots,c_p} s^{\alpha}_{c_1} \cdots s^{\alpha}_{c_1}$, where $s_c$ indicates component $c$ of the vector $\vec{s}$.)

(a) Calculate the partition function $Z_0\left(\left\{\vec{h}^{\alpha}\right\}\right)$, and $\beta F_0 = -\ln Z_0$.

(b) Obtain the magnetizations $m_\alpha = \left|\langle \vec{s}_i^{\,\alpha}\rangle_0\right|$, and $\langle \beta\mathcal{H}_0\rangle_0$, in terms of the *Langevin function* $\mathcal{L}(h) = \coth(h) - 1/h$.

(c) Calculate $\langle \beta\mathcal{H}\rangle_0$, with the (reasonable) assumption that all the variational fields $\left(\left\{\vec{h}^{\alpha}\right\}\right)$ are parallel.

(d) The exact free energy, $\beta F = -\ln Z$, satisfies the Gibbs inequality (see below), $\beta F \leq \beta F_0 + \langle \beta\mathcal{H} - \beta\mathcal{H}_0\rangle_0$. Give the self-consistent equations for the magnetizations $\{m_\alpha\}$ that optimize $\beta\mathcal{H}_0$. How would you solve these equations numerically?

(e) Assuming all couplings scale inversely with temperature, e.g. $J = \hat{J}/k_B T$, find the critical temperature, and the behavior of the magnetization *in the bulk* by considering the limit $n \to \infty$. (Note that $\lim_{m\to 0} \mathcal{L}^{-1}(m) = 3m + 9m^3/5 + \mathcal{O}(m^5)$.)

(f) By linearizing the self-consistent equations, show that the critical temperature of film depends on the number of layers $n$, as $kT_c(n \gg 1) \approx kT_c(\infty) - \hat{J}_V \pi^2/(3n^2)$.

(g) Derive a continuum form of the self-consistent equations, and keep terms to cubic order in $m$. Show that the resulting non-linear differential equation has a solution of the form $m(x) = m_{\text{bulk}} \tanh(kx)$. What circumstances are described by this solution?

(h) How can the above solution be modified to describe a *semi–infinite* system? Obtain the critical behaviors of the healing length $\lambda \sim 1/k$.

(i) Show that the magnetization of the surface layer vanishes as $|T - T_c|$.

† The result in (f) illustrates a quite general trend that the transition temperature of a finite system of size $L$, approaches its asymptotic (infinite–size) limit from below, as $T_c(L) = T_C(\infty) - A/L^{1/\nu}$, where $\nu$ is the exponent controlling the divergence of the correlation length. However, some liquid crystal films appeared to violate this behavior. In fact, in these films the couplings are stronger on the surface layers, which thus order before the bulk. For a discussion of the dependence of $T_c$ on the number of layers in this case, see H. Li, M. Paczuski, M. Kardar, and K. Huang, Phys. Rev. B **44**, 8274 (1991).

• **Proof of the Gibbs inequality:** To approximate the partition function $Z = \text{tr}\left(e^{-\beta\mathcal{H}}\right)$ of a difficult problem, we start we a simpler Hamiltonian $\mathcal{H}_0$ whose properties are easier to calculate. The Hamiltonian $\mathcal{H}(\lambda) = \mathcal{H}_0 + (\mathcal{H} - \mathcal{H}_0)$ interpolates between the two as $\lambda$ changes from zero to one. The corresponding partition function

$$Z(\lambda) = \mathrm{tr}\{\exp\left[-\beta\mathcal{H}_0 - \lambda\beta\left(\mathcal{H} - \mathcal{H}_0\right)\right]\},$$

must satisfy the convexity condition $d^2 \ln Z(\lambda)/d\lambda^2 = \beta^2 \left\langle (\mathcal{H} - \mathcal{H}_0)^2 \right\rangle_{0c} \geq 0$, and hence

$$\ln Z(\lambda) \geq \ln Z(0) + \lambda \left. \frac{d \ln Z}{d\lambda} \right|_{\lambda=0} .$$

But it is easy to show that $d \ln Z/d\lambda|_{\lambda=0} = \beta \left\langle \mathcal{H}_0 - \mathcal{H} \right\rangle_0$, where the subscript indicates expectation values with respect to $\mathcal{H}_0$. Defining free energies via $\beta F = -\ln Z$, we thus arrive at the inequality

$$\beta F \leq \beta F_0 + \left\langle \beta\mathcal{H} - \beta\mathcal{H}_0 \right\rangle_0 .$$

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**5.** *Superfluid He$^4$–He$^3$ mixtures:* The superfluid He$^4$ order parameter is a complex number $\psi(\mathbf{x})$ . In the presence of a concentration $c(\mathbf{x})$ of He$^3$ impurities, the system has the following Landau–Ginzburg energy

$$\beta\mathcal{H}[\psi, c] = \int d^d\mathbf{x} \left[ \frac{K}{2} \left|\nabla\psi\right|^2 + \frac{t}{2} \left|\psi\right|^2 + u \left|\psi\right|^4 + v \left|\psi\right|^6 + \frac{c(\mathbf{x})^2}{2\sigma^2} - \gamma c(\mathbf{x}) |\psi|^2 \right],$$

with positive $K$, $u$ and $v$.

(a) Integrate out the He$^3$ concentrations to find the effective Hamiltonian, $\beta\mathcal{H}_{\mathrm{eff}}[\psi]$, for the superfluid order parameter, given by

$$Z = \int \mathcal{D}\psi \exp\left(-\beta\mathcal{H}_{\mathrm{eff}}[\psi]\right) \equiv \int \mathcal{D}\psi\mathcal{D}c \exp\left(-\beta\mathcal{H}[\psi, c]\right) .$$

(b) Obtain the phase diagram for $\beta\mathcal{H}_{\mathrm{eff}}[\psi]$ using a saddle point approximation. Find the limiting value of $\sigma^*$ above which the phase transition becomes discontinuous.

(c) The discontinuous transition is accompanied by a jump in the magnitude of $\psi$. How does this jump vanish as $\sigma \to \sigma^*$?

(d) Show that the discontinuous transition is accompanied by a jump in He$^3$ concentration.

(e) Sketch the phase boundary in the $(t, \sigma)$ coordinates, and indicate how its two segments join at $\sigma^*$.

(f) Going back to the original joint probability for the fields $c(\mathbf{x})$ and $\Psi(\mathbf{x})$, show that $\langle c(\mathbf{x}) - \gamma\sigma^2 |\Psi(\mathbf{x})|^2\rangle = 0$.

(g) Show that $\langle c(\mathbf{x})c(\mathbf{y})\rangle = \gamma^2\sigma^4\langle|\Psi(\mathbf{x})|^2|\Psi(\mathbf{y})|^2\rangle$, for $\mathbf{x} \neq \mathbf{y}$.

(h) Qualitatively discuss how $\langle c(\mathbf{x})c(0)\rangle$ decays with $x = |\mathbf{x}|$ in the disordered phase.

(i) Qualitatively discuss how $\langle c(\mathbf{x})c(0)\rangle$ decays to its asymptotic value in the ordered phase.

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**6.** *Potts model in mean field:* Each site of a square lattice can be occupied by one of $q$ possible states (Potts spins) $S_i = 1, 2, \cdots, q$. Interactions between neighboring sites are constrained by a permutation symmetry, and described by the energy

$$\mathcal{H} = -J \sum_{<i,j>} \delta_{S_i,S_j} ,$$

i.e. neighboring sites reduce energy by $-J$ only if they are in the same state. A mean-field estimate of free energy of the system can be obtained by assuming that $N_\alpha = Np_\alpha$ total spins of type $\alpha = 1, 2, \cdots, q$, randomly distributed among the $N$ lattice sites.

(a) Estimate the energy of the system in terms of the probabilities $\{p_\alpha\}$.

(b) Estimate the mixing entropy of the system in the same approximation.

(c) Obtain the free energy estimate $F(\{p_\alpha\})$. Anticipating a Taylor expansion, compute $\partial^n F/\partial {p_\alpha}^n$ for $n \leq 4$. (Note the absence of mixed partial derivatives.)

(d) Given $\sum_{\alpha=1}^{q} p_\alpha = 1$, the disordered state we have $p_\alpha = 1/q$. A spontaneously broken symmetry enriching say $\alpha = 1$ states, would then lead to (for $x \geq 0$) $p_1 = 1/q + x$, with $p_2 = \cdots = p_q = 1/q - x/(q-1)$. Expand the free energy up to fourth order in $x$.

(e) By examining the signs of the low order terms in the expansion of $F(x)$, discuss (qualitatively, computation not needed) the nature of the phase transition for different values of $q$.

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**7.** **(Optional)** *Crumpled surfaces:* The configurations of a crumpled sheet of paper can be described by a vector field $\vec{r}(\mathbf{x})$, denoting the position in three dimensional space,

$\vec{r} = (r_1, r_2, r_3)$, of the point at location $\mathbf{x} = (x_1, x_2)$ on the flat sheet. The energy of each configuration is assumed to be invariant under translations and rotations of the sheet of paper.

(a) Show that the two lowest order (in derivatives) terms in the quadratic part of a Landau–Ginzburg Hamiltonian for this system are:

$$\beta\mathcal{H}_0[\vec{r}] = \sum_{\alpha=1,2} \int d^2\mathbf{x} \left[ \frac{t}{2} \partial_\alpha \vec{r} \cdot \partial_\alpha \vec{r} + \frac{K}{2} \partial_\alpha^2 \vec{r} \cdot \partial_\beta^2 \vec{r} \right].$$

(b) Write down the lowest order terms (there are two) that appear at the quartic level.

(c) Discuss what happens when $t$ changes sign, assuming that quartic terms provide the required stability (and $K > 0$).

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