8.334 Statistical Mechanics II: Statistical Physics of Fields
Spring 2008

Phase transitions

1. *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 $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}\big|_T$, 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 $d\mu = dP/n$.)

(e) Now consider a gas obeying Dieterici's equation of state:

$$P(v - b) = k_B T \exp\left(-\frac{a}{k_B T v}\right),$$

where $v = V/N$. Find the ratio $Pv/k_B T$ at its critical point.

(f) Calculate the isothermal compressibility κ_T for $v = v_c$ as a function of $T - T_c$ for the Dieterici gas.

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

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2. *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 αth 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 $L_{c_1,\cdots,c_p}^{\alpha} s_{c_1}^{\alpha} \cdots s_{c_1}^{\alpha}$, 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) 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 $kT_c(n \gg 1) \approx kT_c(\infty) - J_V \pi^2/(3n^2)$.

(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 ν 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 $Z = \mathrm{tr}\left(e^{-\beta \mathcal{H}}\right)$ 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 λ 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 $d\ln Z/d\lambda|_{\lambda=0} = \beta \langle \mathcal{H}_0 - \mathcal{H}\rangle_0$, 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

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

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3. *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 σ^* above which the phase transition becomes discontinuous.

(c) The discontinuous transition is accompanied by a jump in the magnitude of ψ. 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, σ) coordinates, and indicate how its two segments join at σ^*.

(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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4. *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:

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

(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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