Unifying concepts: Problems

Although you should try all of these questions, some of them are deliberately quite challenging. If you don't get very far with some, don't worry. We'll be going over them in problems classes, so you can just regard them as worked examples.

1. Existence of a phase transition in $d = 2$.

In lectures it was argued that no long ranged order occurs at finite-temperatures in a one dimensional system because of the presence of domain walls. Were macroscopic domain walls to exist in two dimensions at finite temperature, they would similarly destroy long ranged order and prevent a phase transition. By calculating the free energy of a 2D domain wall for an Ising lattice, show that domain walls do not in fact exist for sufficiently low T.

(Hint: Model the domain wall as a non-reversing N-step random walk on the lattice and find an expression for its energy and -from the number of random walk configurations- its entropy.)

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2. Correlation Length

For a 1D Ising model, show that the correlation between the spins at sites i and j, is

$$\langle s_i s_j \rangle = \sum_m p_m (-1)^m$$

where m is the number of domain walls between i and j and p_m is the probability of finding m domain walls between them.

Hence show that when $R_{ij} = |i - j|a$ is large (with a the lattice spacing) and the temperature is small, that

$$\langle s_i s_j \rangle = \exp(-R_{ij}/\xi)$$

with $\xi = a/2p$ and p the probability of finding a domain wall on a bond.

Hint: In the second part note that p_m is given by a binomial distribution because there is a probability p of each bond containing a domain wall and $(1-p)$ that it doesn't. What special type of distribution does p_m tend to when p is small (as occurs at low T)?

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3. A model fluid

The van der Waals (vdW) equation of state is essentially a mean field theory for fluids. It relates the pressure and the volume of a fluid to the temperature:

$$\left(P + \frac{a}{V^2}\right)(V - b) = N_A k_B T$$

where a and b are constants and N_A is Avogadro's number.

The critical point of a fluid corresponds to the point at which the isothermal compressibility diverges, that is

$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

Additionally, one finds that isotherms of P versus V exhibit a point of inflection at the critical point, that is

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

- Use these two requirements to show that the critical point of the vdW fluid is located at

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad N_A K_B T_c = \frac{8a}{27b}$$

- Hence show that when written in terms of reduced variables

$$p = \frac{P}{P_c}, \qquad v = \frac{V}{V_c} \qquad t = \frac{T}{T_c}$$

  the equation takes the form

$$\left(p + \frac{3}{v^2}\right)(v - \frac{1}{3}) = \frac{8t}{3}$$

- Write a Python script to plot a selection of isotherms close to the critical temperature (you will need to choose suitable units for your axes). Plot also the gradient and second derivative of P vs V on the critical isotherm and confirm numerically that it exhibits a point of inflection at the critical pressure and temperature.
- Obtain the value of the critical exponent γ of the vdW model and confirm that it takes a mean-field value.

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4. Mean field theory of the Ising model heat capacity

Using results derived in lectures, obtain an expression for the mean energy $\langle E\rangle$ of the Ising model in zero field, within the simplest mean field approximation $\langle s_i s_j\rangle = \langle s_i\rangle\langle s_j\rangle = m^2$. Hence show that for $H = 0$ the heat capacity $\partial\langle E\rangle/\partial T$ has the behaviour

$$C_H = 0 \quad T > T_c \tag{1}$$
$$C_H = 3Nk_B/2 \quad T \leq T_c \tag{2}$$

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5. Magnetisation and fluctuations

A system of spins on a lattice, has, in the absence of an applied field, a Hamiltonian H. In the presence of a field h the Hamiltonian becomes

$$\tilde{H} = H - hM$$

where M is the total magnetisation and h is the magnetic field. By considering the partition function $Z(T, h)$ and its relationship to the free energy F show that in general

$$\langle M\rangle = -\left(\frac{\partial F}{\partial h}\right)_T$$

Show also that the variance of the magnetisation fluctuations is

$$\langle M^2\rangle - \langle M\rangle^2 = -k_B T\left(\frac{\partial^2 F}{\partial h^2}\right)_T$$

(*Hint: This is an important standard derivation found in many text books on Statistical Mechanics. You will need to differentiate F (twice) and use the product and chain rules.*)

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6. Spin-1 Ising model

A set of spins on a lattice of coordination number q can take values $(-1, 0, 1)$, as opposed to just $(-1, 1)$ as in the spin-1/2 Ising model. The Hamiltonian is

$$H = -J \sum_{<ij>} s_i s_j + h \sum_i s_i$$

Find the partition function and hence show that in the mean field approximation, the magnetisation per site obeys

$$m = \frac{2\sinh[\beta(Jqm + h)]}{2\cosh[\beta(Jqm + h)] + 1}$$

and find the critical temperature T_c at which the net magnetisation vanishes.

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7. Transfer Matrix.

Verify the calculation of the free energy of the 1D periodic chain Ising model in a field outlined in lectures using the Transfer Matrix method.

Use your results to show that the spontaneous magnetisation is:

$$m = \frac{\sinh \beta H}{\sqrt{\sinh^2 \beta H + \exp -4\beta J}}$$

Comment on the value of m in zero field.

(*Hint: Follow the prescription given in lectures. Depending on your approach you may need to use the trigonometrical identities* $\cosh^2 x - \sinh^2 x = 1$, $\cosh(2x) = 2\cosh^2 x - 1$.)

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8. Landau theory

Check and complete the Landau theory calculations, given in lectures, for the critical exponents $\gamma = 1$ and $\alpha = 0$ of the Ising model. For the latter, you should first prove the result

$$C_H = -T\frac{\partial^2 F}{\partial T^2}$$

starting from the classical theormodynamics expression for changes in the free energy of a magnet $dF = -SdT - MdH$.

(*Hint: If you get stuck with the proof see standard thermodynamics text books. To get the susceptibility exponent in Landau theory add a term $-Hm$ to the Hamiltonian.*)

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9. Scaling equation of state

Consider a Landau expression for the free energy of a magnetic system having magnetisation m:

$$F = F_0 + \tilde{a}_2 t m^2 + a_4 m^4 - Hm \; ,$$

where $t = T - T_c$ and H is an applied magnetic field; $\tilde{a}_2$ and a_4 are positive constants and F_0 is a constant background term.

Show that the equation of state for the model is

$$H = 2\tilde{a}_2 t m + 4a_4 m^3 \; .$$

Use the near-critical power law behaviour of m to show that the equation of state may be written in the scaling form

$$\frac{H}{m^\delta} = g\left(\frac{t}{m^{1/\beta}}\right) \; ,$$

and find the (mean field) values of the critical exponents δ and β.

Deduce that $g(x) = x + 1$ up to a choice of scale for $\tilde{a}_2$ and a_4.

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10. Scaling laws

Using the generalised homogeneous form for the free energy given in lectures, take appropriate derivatives to find the relationships to the critical exponents:

$$\beta = \frac{1-b}{a}; \quad \gamma = \frac{2b-1}{a}; \quad \delta = \frac{b}{1-b}; \quad \alpha = 2 - \frac{1}{a}.$$

Hence derive the scaling laws among the critical exponents:

$$\alpha + \beta(\delta + 1) = 2 \tag{3}$$
$$\alpha + 2\beta + \gamma = 2 \tag{4}$$
$$\tag{5}$$

(*Hint: For the heat capacity exponent α use the result from problem 8:* $C_H = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{h=0}$)

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11. Classical nucleation theory

A supercooled liquid metal is undergoing solidification. According to classical nucleation theory, the Gibbs free energy change ΔG for forming a spherical solid nucleus of radius r in the liquid is given by:

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

where $\Delta G_v < 0$ is the free energy change per unit volume due to the phase change, and $\gamma > 0$ is the interfacial energy between the solid and liquid phases.

(a) Derive the expression for the critical radius r^* at which the nucleus becomes stable and begins to grow.

(b) Show that the critical energy barrier for nucleation ΔG^* is given by:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

(c) Explain qualitatively how the degree of undercooling ΔT affects the rate of nucleation. You may use the fact that $\Delta G_v \propto \Delta T$ to support your answer.

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12. Colloidal diffusion

A large colloidal particle of mass M moves in a fluid under the influence of a random force $F(t)$ and a coefficient of Stokes friction drag γ, both per unit mass. If the solution of the corresponding Langevin equation for the velocity of the colloidal particle is given by

$$u = u_0 e^{-\gamma t} + \frac{e^{-\gamma t}}{M} \int_0^t dt'\, e^{\gamma t'} F(t'),$$

where u_0 is the velocity at $t = 0$, show that for long times the velocity of the particle satisfies the relation

$$\langle u^2 \rangle = \frac{kT}{M} + \left(u_0^2 - \frac{kT}{M} \right) e^{-2\gamma t},$$

where k is the Boltzmann constant and T is the absolute temperature.

State clearly any assumptions that you make.

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13. Einstein's expression for the diffusion coefficient

In 1905, Einstein showed that the friction coefficient γ (per unit mass) of a colloidal particle must be related to the diffusion coefficient D of the particle by

$$D = \frac{kT}{\gamma}.$$

If a marked particle covers a distance X in a given time t (assuming a one-dimensional random walk), the diffusion coefficient is defined to be

$$D = \lim_{t \to \infty} \frac{1}{2t} \langle [X(t) - X(0)]^2 \rangle,$$

where the average $\langle \cdot \rangle$ is taken over an ensemble in thermal equilibrium.

Use the fact that $X(t) - X(0) = \int_0^t u(t')\, \mathrm{d}t'$ to show that the Einstein relation may be written as

$$\gamma = \frac{1}{\mu} = \frac{D}{kT} = \frac{1}{kT} \int_0^\infty \langle u(t_0) u(t_0 + t) \rangle \, dt,$$

where μ is known as the mobility of the particle and t_0 is any arbitrarily chosen time.

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14. Life in one dimension

A particle lives on the sites of a one-dimensional lattice. At any instant it has probability α per unit time that it will hop to the site on its right and probability α per unit time of hopping to the site on its left.

Write down the master equation for the set of probabilities $p_n(t)$ of finding the particle at the n^{th} site, where $-\infty < n < \infty$.

Solve the master equation for the p_n, subject to the initial condition that the particle was at the site $n = 0$ at time $t = 0$. Hence obtain the mean position $\langle n \rangle$ and root mean square deviation from the mean, both as functions of time.

Hint: The second part of the question is most easily done by introducing the generating function

$$F(z,t) = \sum_{n=-\infty}^{\infty} p_n(t) z^n.$$

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15. Master equation

A system of N atoms, each having two energy levels $E = \pm\epsilon$, is brought into contact with a heat bath at temperature T. The atoms do not interact with each other, but each atom interacts with the heat bath to have a probability $\lambda_{-\to+}(T)$ per unit time of transition from lower to higher level, and a probability $\lambda_{+\to-}(T)$ per unit time of the reverse transition.

If at any time t there are $n_+(t)$ atoms at the higher level and $n_-(t)$ at the lower level, then $n(t) = n_-(t) - n_+(t)$ is a convenient measure of the non-equilibrium state.

Obtain the master equation for $n(t)$ and hence the relaxation time τ which characterizes the exponential approach of the system to equilibrium.

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16. Detailed balance

(a) Starting from the principle of detailed balance for an isolated system, show that for two groups of states within it, A and B, the overall rate of transitions from group A to group B is balanced, in equilibrium, by those from B to A:

$$\lambda_{A\to B}p_A^{\mathrm{eq}} = \lambda_{B\to A}p_B^{\mathrm{eq}}$$

(b) Deduce that the principle applies to microstates in the canonical ensemble, and hence that the jump rates between states of a subsystem (of fixed number of particles) connected to a heat bath must obey

$$\frac{\lambda_{i\to j}}{\lambda_{j\to i}} = e^{-(E_j - E_i)/kT}.$$

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17. Jump processes

An isolated system can occupy three possible states of the same energy. The kinetics are such that it can jump from state 1 to 2 and 2 to 3 but not directly from 1 to 3. Per unit time, there is a probability λ_0 that the system makes a jump, from the state it is in, into (each of) the other state(s) it can reach.

(a) Show that the occupancy probabilities $p = (p_1, p_2, p_3)$ of the three states obey the master equation

$$\dot{p} = M \cdot p$$

where the rate matrix is

$$M = \lambda_0 \begin{bmatrix} -1 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -1 \end{bmatrix}$$

(b) Confirm that an equilibrium state is $p = (1, 1, 1)/3$.

(c) Prove this equilibrium state is unique.

Hint: For part (c), consider the eigenvalues of M.