

Problem 1. Phase transitions and Landau theory:

Landau theory is a phenomenological thermodynamic theory describing phase transitions. This theory considers a free energy $g(\eta, T)$ of the system, where T is the temperature, and η is an order parameter.

Landau theory assumes that near T_C , when η is small, it is possible to expand the free energy in powers of η , thus:

$$g(\eta, T) = g_0 - X\eta + c_2\eta^2 + c_3\eta^3 + c_4\eta^4 + c_5\eta^5 + c_6\eta^6 + \dots + c_n\eta^n + \dots \quad (1.1)$$

Here, X is an external field, which couples bilinearly to the order parameter, η , and c_n ($n = 2, 3, 4, \dots$) are constants.

We generally assume based on physical arguments, that $c_2(T) = b(T - T_C)$, where b is a positive constant, and that $c_3, c_4, c_5, c_6, \dots, c_n, \dots$ are constants independent of T . g_0 is the part of the free energy that is not related to the phase transition system under consideration.

Below (1b-d)), we will consider the three *Cases* in the following table:

<i>Case 1:</i> $c_3 = 0$, c_4 is positive, and $c_n = 0$ for $n > 4$
<i>Case 2:</i> $c_3 = c_5 = 0$, c_4 is negative, c_6 is positive, and $c_n = 0$ for $n > 6$
<i>Case 3:</i> c_3 is negative, c_4 is positive, and $c_n = 0$ for $n > 4$.

1a)

Discuss in general what is meant by “first order” and “second order” phase transitions. What do “first order” and “second order” refer to?

What is the general meaning of, and the general definition of, an order parameter in the context of phase transitions?

Give examples of specific order parameters (η) and their corresponding external fields (X) for some real physical systems: For example for ferroelectrics, ferromagnets, ferroelastics, nematics, dipolar nematics, superconductors, etc.

1b)

Show that for *Case 1*, the equilibrium value of the order parameter

$$\eta_{\text{eq}}(T > T_C, X=0) = 0 \quad \text{and} \quad \eta_{\text{eq}}(T < T_C, X=0) = [(b/2c_4)(T_C - T)]^{1/2} \quad (1.2)$$

Sketch and also discuss how $\eta_{\text{eq}}(T, X=0)$ relates to the set of curves defined by different T for $g(\eta, T, X=0)$ versus η for *Case 1*.

Is the *Case 1* transition of first or of second order kind?

Compare *Case 1* to the *Case 2* in the Table, and sketch and also discuss the set of curves defined by different T for $g(\eta, T, X=0)$ versus η , for *Case 2*.

Is the *Case 2* transition of first or of second order kind?

1c)

For *Case 1*, derive an expression for the temperature dependence of the equilibrium value of the order parameter $\eta_{eq}(X = 0)$, and show that for this *Case 1*, the order parameter susceptibility

$$\chi(T > T_C, X=0) = -2\chi(T < T_C, X=0) \quad (1.3)$$

where $\chi = d\eta/dX$ is the linear response function for application of external field X resulting in response η .

For *Case 1*, also show that for the specific heat $C_v = -T(dS/dT) = -T(d^2g/dT^2)$, we can write:

$$C_v(T > T_C, X=0) = \text{constant} \quad \text{and} \quad C_v(T < T_C, X=0) = C_v(T > T_C, X=0) + Tb^2/(2c_4) \quad (1.4)$$

1d)

For *Case 3*, (also called the Landau - de Gennes expansion), derive an expression for the temperature (T) dependence of the equilibrium value of the order parameter

$$\eta_{eq}(T, X = 0) = ? \quad (1.5)$$

Sketch and also discuss how $\eta_{eq}(T, X=0)$ relates to the set of curves defined by different T for $g(\eta, T, X=0)$ versus η for *Case 3*.

Is the *Case 3* transition of first or of second order kind?

Discuss a physical system that *Case 3* applies to.

1e)

For the isotropic to nematic transition of rod like molecules (nematogens), the order parameter $\eta = S_2$, where S_2 is a measure of the magnitude of orientational ordering of the nematogens.

The Maier-Saupe theory for nematics introduces a molecular field which acts to orient the rod-like molecules. This molecular field has the form

$$u(\theta) = -u_0 S_2 ((3\cos^2\theta - 1)/2) \quad (1.6)$$

Discuss the physical meaning of this molecular field.

Boltzmann statistics gives the orientation distribution function $w(\theta, \phi)$ for this case, i.e.

$$w(\theta, \phi) = \exp(u(\theta)/k_B T) / Z \quad (1.7)$$

where k_B is Boltzmann's constant, T is the temperature, and the normalization factor Z is the partition function.

Show how it can be calculated from this model that $S_2(T_{ni}) = 0.44$

Discuss how the Maier-Saupe theory relates to the Landau-de Gennes theory introduced in **1d**).

Problem 2. Ferroelectrics:

Assume that we are studying a dielectric sample, and that we are applying an external electric field E to it, such that the responding polarization $P = \epsilon_0 \chi E$, where $\chi = \epsilon - 1$ is the dielectric susceptibility, ϵ is the dielectric constant and ϵ_0 is the vacuum permittivity.

In a dielectric, one needs to distinguish between the externally applied field, E , and the local field, E_{loc} , in the sample. It is the local field at the site of a molecule that acts to polarize or reorient that molecule. The relation between the polarization P and the local field for monomolecular dielectrics is

$$P = P_{or} + P_d = \rho \beta E_{loc} \quad (2.1)$$

where ρ is the particle density, and $\beta = \beta_{or} + \beta_d$ is the polarisability.

2a)

Discuss the distinction between orientational (or) P_{or} and distortional (d) P_d polarizations respectively, in dielectrics.

Discuss without entering into details, how it can be shown for isotropic liquids and symmetric crystals, that

$$E_{loc} = E + P/(3\epsilon_0) \quad (2.2)$$

where E is the externally applied electric field, and the term $P/(3\epsilon_0) = E_L$ is the so-called Lorentz-field, which represents the average (mean-field) contribution to E_{loc} acting on one molecule from all the other molecules in the sample.

Show that for this case:

$$(\epsilon - 1)/(\epsilon + 2) = \rho \beta / (3\epsilon_0) \quad (2.3)$$

which is the Clausius-Mosotti equation for dielectrics.

2b)

Using Equation (2.3), show that

$$\epsilon_0 \chi = \rho\beta / (1 - \rho\beta / (3\epsilon_0)) \quad (2.4)$$

Discuss what happens, and what it means in terms of physics, if β increases with decreasing T in such a way that the Lorentz-field contribution $\rho\beta / (3\epsilon_0) = 1$ at some temperature $T = T_C$.

The simplest T -dependence one can think of for this case, is linear in T , i.e. $\rho\beta / (3\epsilon_0) = 1 - c(T - T_C)$, where c is a constant.

How does χ depend on temperature for this case, for temperatures $T > T_C$?

Discuss the result in relation to the Landau theory discussed in Problem 1 above.

Problem 3. Superconductivity:

Using Ginzburg-Landau wave mechanics, the superconducting current density (for Cooper pairs) may be written

$$\mathbf{j} = -2e|\psi|^2 (\hbar \nabla \theta(\mathbf{r}) / 2\pi + 2e\mathbf{A}) / 2m_e \quad (3.1)$$

where $\psi(\mathbf{r}) = |\psi(\mathbf{r})| \exp(i\theta(\mathbf{r}))$ is the wavefunction with phase $\theta(\mathbf{r})$, $2e$ is the Cooper pair charge, $2m_e$ is the Cooper pair mass, and \mathbf{A} is the vector potential, related to the magnetic field through $\nabla \times \mathbf{A} = \mathbf{B}$.

The Ginzburg-Landau thermodynamic theory for superconductivity assumes Equation (1.1) for superconductivity with $|\psi|$ as the orderparameter, and that *Case 1* in Problem 1 applies.

3a)

Using these assumptions, write down the equilibrium (eq) value $(\rho_S)_{eq} = |\psi|_{eq}^2$ for $T < T_C$.

3b)

Show and argue how we can combine Equation (3.1) with the Maxwell equation

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} \quad (3.2)$$

in order to derive the London equation

$$\nabla^2 \mathbf{B} = \mathbf{B} \lambda_L^{-2} \quad (3.3)$$

where λ_L is the so-called London penetration depth, defined as $\lambda_L^{-2} = \mu_0 \rho_S (-2e)^2 / (2m_e)$ and the Cooper pair density $\rho_S = |\psi|^2$.

Discuss and sketch the physical meaning of λ_L .

3c)

Sketch and discuss magnetization curves (i.e. magnetization \mathbf{M} vs magnetic field \mathbf{H}) for type I and type II superconductors respectively.

In particular, discuss what it means in terms of physics that type II superconductors may involve spatial variations of ρ_S throughout the sample, i.e. that Equation (1.1) may not be applicable, since it represents a spatially homogenous order parameter.

In the Ginzburg-Landau-Abrikosov theory for type II superconductors, Equation (1.1) is replaced by the following expression for the free energy:

$$g(|\psi|, T) = g_0 + b(T - T_C)|\psi|^2 + c_4|\psi|^4 + [(h/8\pi)^2/m_e]|\nabla\psi|^2 + (\text{magn. field dep. terms}) \quad (3.4)$$

Use dimensional analysis to show that there must be a length describing spatial variations of $\rho_S = |\psi|^2$ in the sample, and that this length, ξ_G , which is called the coherence length, has the form

$$\xi_G \propto (T_C - T)^{-1/2} \text{ for } T < T_C \quad (3.5)$$

Discuss the physical meaning of ξ_G in relation to λ_L derived in 3b) above, in the context of type II superconductors.

Problem 4. Multiple choice questions

1. Structure characterization:

The dynamic structure factor $S(\mathbf{q}, t)$ is a direct measure of:

- a) The positions of the atoms contained within the unit cell at time t ?
- b) The time-dependent Fourier transform of the order parameter correlations over distances larger than the wavelength λ ?
- c) The Fourier transform of correlations between two particles at the same \mathbf{q} ?
- d) None of the above?

2. Scattering of radiation:

Which among the following types of radiation has the shortest penetration depth into materials:

- a) X-rays?
- b) Electrons?
- c) Neutrons?
- d) They all have roughly the same penetration depth?

3. Diffusion:

For an independent Brownian particle, we define the mean-squared displacement $\langle |\mathbf{r}'|^2 \rangle = \int g_1(\mathbf{r}', t) |\mathbf{r}'|^2 d^3 \mathbf{r}'$, where $g_1(d^3 \mathbf{r}') d^3 \mathbf{r}'$ is the probability of finding the particle in volume $d^3 \mathbf{r}'$, at position \mathbf{r}' at time t . D_S is the self-diffusion coefficient, which is a constant independent of time. For such an independent Brownian particle:

- a) $\langle |\mathbf{r}'|^2 \rangle \propto D_S/t$?
- b) $\langle |\mathbf{r}'|^2 \rangle \propto D_S t$?
- c) $\langle |\mathbf{r}'|^2 \rangle \propto D_S/t^2$?
- d) None of the above?

4. Diffusion:

The Einstein relation for the self-diffusion coefficient D_S is: $D_S = k_B T / \zeta$, where k_B is the Boltzmann constant, T is the temperature, and

- a) ζ is the friction coefficient?
- b) ζ is the mobility?
- c) ζ is the viscosity?
- d) None of the above?

5. Polymer dynamics:

The "tube model" for polymer dynamics introduced by Sam Edwards, takes entanglement effects among different chains into account in order to describe the chain dynamics in a polymer sample. This is a mean-field type model that focuses on individual chains, that includes interactions with other chains by representing them collectively as a "tube" inside which an individual chain is restricted to move, like a reptile in linear diffusive motion (the de Gennes "reptation model"). In this model, the disentanglement time, τ_d , for entangled polymer chains scales as (M is the molecular mass of the chain):

- a) $\tau_d \propto M$?
- b) $\tau_d \propto M^2$?
- c) $\tau_d \propto M^3$?
- d) None of the above?

6. DLS:

In a Dynamic Light Scattering (DLS) experiment, the dynamic structure factor $S(\mathbf{q}, t)$ is measured, where \mathbf{q} is the scattering vector. Typical scattering curves from samples made from a dilute suspensions of Brownian diffusing colloidal spheres follow a simple relaxational behavior of the kind $S(\mathbf{q}, t) = \exp(-t/\tau(|\mathbf{q}|))$, where the relaxation time $\tau(|\mathbf{q}|)^{-1} = C |\mathbf{q}|^2$. The proportionality constant C is:

- a) $C = D_s$, the self diffusion constant?
- b) $C = 1/D_s$, the inverse of the self diffusion constant?
- c) $C = 1/\eta$, the inverse of the viscosity of the suspending liquid?
- d) None of the above?

7. Polymer chain structure:

A self-avoiding random walk in 3 dimensions will create an open object with a fractal dimension D of:

- a) $D > 3$?
- b) $D < 2$?
- c) $D < 1$?
- d) None of the above?

8. The rubber polymer elastic force is referred to as an entropic force. By this we mean that:

- a) When a polymer chain is stretched isothermally, the entropy does not change?
- b) When a polymer chain is stretched isothermally, only the internal energy changes?
- c) When a polymer chain is stretched isothermally, the entropy changes and the internal energy does not change?
- d) None of the above?

9. Piezoelectricity in a material means that:

- a) There is a linear relationship between elastic and magnetic fields in a material?
- b) There is a linear relationship between elastic and electric fields in a material?
- c) There is a linear relationship between electric and magnetic fields in a material?
- d) None of the above?

10. Diamagnetism:

- a) Diamagnetism is the term used for magnetism in materials with induced electric dipoles?
- b) The atomic diamagnetic susceptibility depends on the number of electrons in the atom?
- c) Diamagnetism is present in only a few materials?
- d) None of the above?

11. Paramagnetism:

- a) Paramagnetism is present in all materials, except in diamagnetic materials?
- b) The paramagnetic susceptibility for a sample with localized magnetic moments is inversely proportional to the temperature squared?
- c) The paramagnetic susceptibility is in general negative?
- d) None of the above?

12. Ferromagnetism is basically a result of:

- a) Classical interaction between magnetic dipoles?
- b) Quantum mechanical exchange forces between spins of neighboring atoms?
- c) Quantum mechanical exchange of phonons resulting in paired electrons?
- d) None of the above?

13. Weiss domains:

In zero applied magnetic field, the size and shape distributions of Weiss domains in a ferromagnet are in general given as a result of:

- a) A competition between the diamagnetic energy and the paramagnetic energy?
- b) A competition between the stray field energy and the earth magnetic field energy?
- c) A competition between the stray field energy and the domain wall energy?
- d) None of the above?

14. Simple relaxation processes:

Assume that we apply a constant force σ to a system which responds linearly according to $\gamma = \alpha\sigma$, where α is the response function characteristic of the system. Assume that after “turning off σ ”, our system returns to equilibrium, $\gamma(t = \infty)$, at a rate, $d\gamma(t)/dt$, which increases proportionally with the magnitude of the perturbation, $\gamma(t)$, i.e. $d\gamma(t)/dt = [\gamma(t = \infty) - \gamma(t)]/\tau$, where the system characteristic time, τ , is the constant of proportionality between the rate and the perturbation.

If we instead excite our system with a frequency (ω) dependent force with amplitude σ_0 , such that $\sigma = \sigma_0 \exp(i\omega t)$, then:

- The real part of the response function will display a resonance peak at $\omega = 2\pi/\tau$
- The imaginary part of the response function will display a resonance peak at $\omega = 2\pi/\tau$
- The imaginary part of the response function will display a resonance step at $\omega = 2\pi/\tau$
- None of the above?

15. The Kramers-Kronig (K-K) formulas give relations between the real (α') and imaginary (α'') parts of generalized linear response functions, i.e. between the storage and the loss moduli respectively:

$$\alpha'(\omega_0) = (1/\pi)P\int[\alpha''(\omega)/(\omega-\omega_0)]d\omega$$

$$\alpha''(\omega_0) = -(1/\pi)P\int[\alpha'(\omega)/(\omega-\omega_0)]d\omega$$

where the integral limits are from $-\infty$ to $+\infty$, and the principal value, P is defined as

$$P\int[\alpha(\omega)/(\omega-\omega_0)]d\omega = \lim_{\delta \rightarrow 0} \{ \int_1[\alpha(\omega)/(\omega-\omega_0)]d\omega + \int_2[\alpha(\omega)/(\omega-\omega_0)]d\omega \}$$

and the limits of integral 1 (\int_1) are between $-\infty$ and $\omega_0 - \delta$, and those of integral 2 (\int_2) are between $\omega_0 - \delta$ and ∞ .

The physics behind the K-K relations is:

- That the system obeys simple Debye relaxation behaviour?
- There is no physics behind the K-K relations, they are purely mathematical?
- Causality, i.e. no response before the force has been applied?
- None of the above?

16. Power distribution:

During a cyclic force experiment, $\sigma = \sigma_0 \exp(i\omega t)$, the power per unit volume provided by the external force may be written: $dw/dt = \text{Re}\sigma(t)d[\text{Re}\gamma(t)]/dt$, where Re means Real part. This equation may be rewritten into:

$$dw/dt = -(1/2) \sigma_0^2 \omega \alpha'(\omega) \sin(2\omega t) + \sigma_0^2 \omega \alpha''(\omega) \cos^2(\omega t)$$

This result means that the imaginary part, α'' , of a frequency dependent linear susceptibility describes:

- The heat loss from the sample before any force is applied?
- The loss of potential energy from the sample when the force is applied and released?
- The power taken up by the sample from the applied force, and in general distributed as heat loss?
- None of the above?

17. Rayleigh-Brillouin scattering:

The frequency-shift positions, $\pm\omega_B$, of the Brillouin doublet peaks measured in Rayleigh-Brillouin experiments depends on the chosen scattering vector, \mathbf{q} , so that

- a) $\omega_B \propto q$?
- c) $\omega_B \propto q^{-1}$?
- b) $\omega_B \propto q^2$?
- d) None of the above ?

18. Nuclear Magnetic Resonance:

The static magnetic field in NMR is:

- a) Usually on the order of a few 100 tesla?
- b) Used to align nuclear magnetic moments and generate a macroscopic magnetization in the sample?
- c) Used to produce a radiofrequency signal that excites energy transitions?
- d) None of the above?

19. Magnetic fields:

The earth magnetic field is of order magnitude:

- a) 1 Tesla?
- b) 1 Gauss = 10^{-4} Tesla?
- c) 10^{-3} Tesla?
- d) None of the above?

20. Phase transitions:

For second order phase transition, near the critical temperature T_C , critical fluctuations may become important for the observed behavior.

Which of the following statements is true?

- a) Critical fluctuations are included in the classical Landau theory?
- b) Critical fluctuations are caused by infinitely small restoring forces giving emergent dynamic and spontaneous self-similar regions of finite order parameter near T_C ?
- c) Critical fluctuations are considered to be objects with a size proportional to the lattice spacing of the material?
- d) None of the above?