LECTURE 1.

Phases and Phase Transitions. Symmetries and Symmetry Breaking.

1. In this course, we deal with Statistical Mechanics of condensed substances. Free energy $\tilde{G}(T, p, N, v)$ of any system of N constituting particles at temperature T under pressure p has a minimum as a function of any other parameter, say a volume $v = V/N$ per particle. Therefore,

$$\left(\frac{\partial \tilde{G}}{\partial v}\right)_{p,T} = 0 \tag{1}$$

When solution of Eq (1) $v = v(T, p)$ is substituted in the function $\tilde{G}(T, p, N, v)$, we obtain the free energy at equilibrium

$$\tilde{G}(T, p, N, v(T, p)) = N\ g(T, p), \tag{2}$$

where $g(T, p)$ denotes the density of free energy. Condition (1) means only that the solution $v = v(T, p)$ corresponds to the stationary point. Conditions of minimum are complimentary and have the following form

$$\frac{\partial^2 g}{\partial p^2} < 0, \quad \frac{\partial^2 g}{\partial T^2} < 0, \quad \frac{\partial^2 g}{\partial p^2} \cdot \frac{\partial^2 g}{\partial T^2} - \left(\frac{\partial^2 g}{\partial p \partial T} \right)^2 < 0. \quad (3)$$

A system at a stable equilibrium is called *the phase.* An interesting thing occurs when Eq (1) has not one but several - say two - solutions for volumes $v_1(p,T)$ and $v_2(p,T)$ with the free energies $g_1(p,T)$ and $g_2(p,T)$ respectively. We have now two phases. Each of them is stable with respect to small variation of internal parameters. Still, the free energy of one of the phases is larger, then that of the other. Therefore, the phase with the larger free energy is unstable if it could be transformed into the phase with lower free energy by a strong variation of internal parameters.

2. Thus, the free energy $\tilde{G}(T,p,N,v)$ as the function of volume v has two minima at $v_1(p,T)$ and at $v_2(p,T) > v_1(p,T)$. There is, at least, one maximum at $v_m(p,T)$ ($v_2(p,T) > v_m(p,T) > v_1(p,T)$, see Fig 1). Let assume that Eq (1) has a polynomial character

$$(v - v_1)(v - v_m)(v - v_2) = 0$$

In this case, the Gibbs free energy has following form

$$\tilde{G} = \frac{v^4}{4} - \frac{v_1 + v_2 + v_m}{3} v^3 + \\ + \frac{v_1 v_2 + v_1 v_m + v_2 v_m}{2} v^2 + v_1 v_2 v_m v \quad (4)$$

When the temperature T and the pressure p vary, the

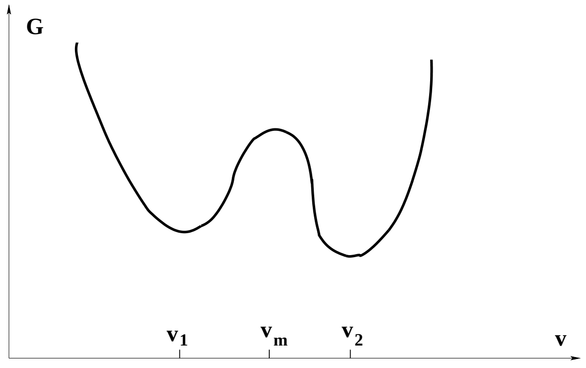

Figure 1: Gibbs Free energy G as a function of the volume v.

difference of the values of free energy $\tilde{G}$ at the volumes v_1 and v_2 may change its sign, being equal at $T_*(p)$. This corresponds to equilibrium of two phases 1 and 2 - *phase*

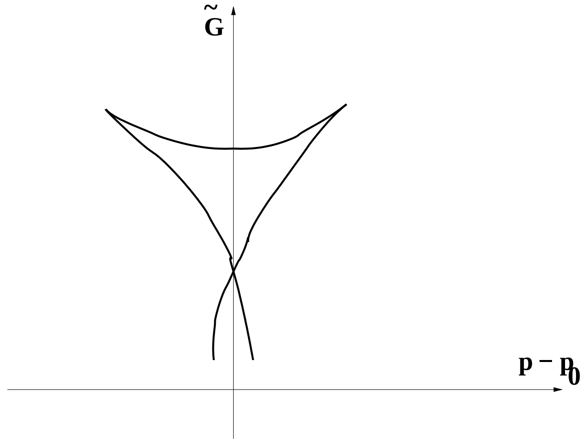

Figure 2: Gibbs Free energy $\tilde{G}$ as a function of the pressure difference $p - p_0$.

transition. At the phase transition

$$v_m = \frac{v_1 + v_2}{2}$$

If $v_2(p,T) > v_m(p,T) > v_1(p,T)$, the values v_1 and v_2 of the volume correspond to minima of the Gibbs free energy $\tilde{G}$. If $v_1(p, T_s^{(1)}(p)) = v_m((p, T_s^{(1)}(p))$, then $\tilde{G}$ has no minimum at $v = v_1$. Analogously, if $v_2(p, T_s^{(2)}(p)) = v_m((p, T_s^{(2)}(p))$, then $\tilde{G}$ has no minimum at $v = v_2$. Two lines $T_s^{(1)}(p)$ and $T_s^{(2)}(p)$ correspond to the boundaries of stabilities of the phases 1 and 2 respectively. The graph of Gibbs free energy at given value of the pressure p is shown in Fig 2.

3. With variation of the pressure, all solutions v_1, v_2 and v_m vary. They could get equal at $p = p_c$ and $T = T_c = T_*(p_c)$, which corresponds to the *critical point.* At critical point $T_s^{(1)}(p_c) = T_s^{(2)}(p_c) = T_c$. The phase diagram in the (p,T) plane is shown in Fig 3. Since at the line of phase equilibrium

$$g_1(p,T) = g_2(p,T),$$

variation of both the pressure p and the temperature T along this line gives

$$\left(\frac{\partial g_1}{\partial T}\right)_p d\,T + \left(\frac{\partial g_1}{\partial p}\right)_T d\,p = \left(\frac{\partial g_2}{\partial T}\right)_p d\,T + \left(\frac{\partial g_2}{\partial p}\right)_T d\,p \quad (5)$$

Since

$$\left(\frac{\partial g_{1,2}}{\partial T}\right)_p = -S_{1,2}, \qquad \left(\frac{\partial g_{1,2}}{\partial p}\right)_T = v_{1,2},$$

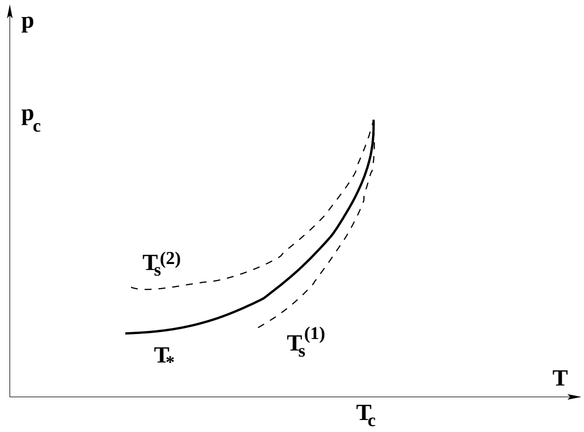

Figure 3: The phase diagram in T, p plane. Solid line $T_*(p)$ corresponds to the first order phase transition, when the phases 1 and 2 are at equilibrium, the dashed lines $T_s^{(1)}(p)$ and $T_s^{(2)}(p)$ corresponds to borders of stability for phases 1 and 2 respectively. All three lines meet at the critical point.

Eq (5) leads to the following equation (*Clapeyron-Clausius* equation) for line of equilibrium

$$\left(\frac{\partial p}{\partial T}\right)_{eqv} = \frac{q}{T\ (v_2 - v_1)}, \tag{6}$$

where $S_{1,2}$ denote the entropies per particle in the phases 1 and 2, q is the latent heat and $v_2 - v_1$ is the volume difference.

4. Introducing reduced variables

$$\tau = T - T_c, \qquad \pi = p - p_c, \qquad \phi = v - v_c\ ,$$

one could re-write the Gibbs free energy - up to arbitrary coefficients - in the *van der Waals form*:

$$\tilde{G} = -\pi \; \phi + a \; \tau \; \phi + \frac{\tau}{2} \; \phi^2 + \frac{\phi^4}{4}, \tag{7}$$

At $\tau \geq 0$, the condition of equilibrium $\partial\tilde{G}/\partial\phi = 0$ has only one solution $\phi(\tau, \pi)$. The conditions of stability are automatically fulfilled under these conditions. At $\tau < 0$, the condition of equilibrium has three solutions. Minima of the free energy $\tilde{G}$ correspond to

$$\phi_{\pm} = \pm\sqrt{|\tau|} \tag{8}$$

and the line of phase transition - to

$$\pi_* = a \; \tau, \qquad \tau < 0+ \tag{9}$$

Eqs (7-9) allow to calculate the entropy discontinuity at the transition ΔS and the latent heat q:

$$q \propto \sqrt{|\tau|} \tag{10}$$

Close to critical point, the specific heat C_p is

$$C_p \propto \frac{1}{\tau + \phi^2} \tag{11}$$

In particular, at the transition point

$$C_p \propto \frac{1}{\sqrt{|\tau|}} \tag{12}$$

Boundaries of stabilities are given by equations

$$\pi_s^{(1,2)} = -a \; |\tau| \pm \frac{2\sqrt{3}}{9} \; |\tau|^{3/2}, \qquad \tau < 0 \tag{13}$$

5. So far, both phases 1 and 2 were characterised by the same internal variable v and, therefore, had the same symmetry. This is why it is possible at $\tau > 0$ to have a continuous transition between different states of matter. A good example of such a situation is presented by a liquid/gas system. If the temperature and pressure are large enough, a continues transition from a dense gas into a liquid is possible[1].

The mentioned situation is not generic. If a liquid is formed by anisotropic molecules, a transition is possible between the phase of isotropic liquid, when orientation of the molecules is random, into a *nematic liquid crystal*, when an axes of anisotropy are oriented along a unit vector $\mathbf{n}$ ($\mathbf{n}^2 = 1$). Such a transition brings an example of a symmetry breaking. Obviously, the transition line at the phase diagram cannot have an ending point, because, otherwise it is possible to pass around such a point and acquire different symmetry by the means of a continuous process.

As it had been mentioned, the phase of nematic liquid crystal is characterised by the axis of director $\mathbf{n}$.[2] As an example, the anisotropy of dielectric tensor $\epsilon_{\alpha\beta}$ is

$$\epsilon_{\alpha\beta} = \epsilon_0 \, \delta_{\alpha\beta} + \epsilon_a \, \left(n_\alpha \, n_\beta - \frac{\delta_{\alpha\beta} s}{3} \right) \tag{14}$$

All possible states of the system with broken symmetry is characterised by the *space of degeneracy*. Space of degeneracy $\mathcal{R}_N$ of a nematic liquid crystal is the *real projective*

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[1] There are many other examples. For instance, a phase separation in solutions.

[2] An important caveat is that that states characterised by directors, meaning that $\mathbf{n}$ and $-\mathbf{n}$ correspond to an identical state.

plane $RP_1 = S^2/Z_2$. The last notation means that different states of nematic liquid crystals are characterised by a point at the surface of 2D sphere, identifying the opposite points. The structure of the space of degeneracy allows to classify the defects of the liquid crystals. We return to this in Appendix 1.

6. The symmetry of a phase is determined its properties. For instance, a ferromagnet is characterised by a certain spontaneous magnetisation $\mathbf{M}$. The operation of time inversion $\hat{T}: \ t \to -t$ leads to transformation $\mathbf{M} \to -\mathbf{M}$. Therefore, the phase of a ferromagnet is characterised by the breaking of the time inversion symmetry $\hat{T}$. This leads to a number of other properties of a ferromagnet. For instance, the dielectric permeability $\epsilon_{\alpha\beta}(\omega)$ at a finite frequency ω of a ferromagnet has the following form

$$\epsilon_{\alpha\beta} = \epsilon_0 \ \delta_{\alpha\beta} + i \ g \ e_{\alpha\beta\gamma} M_\gamma, \tag{15}$$

i.e. demonstrate the *Faraday effect*, rotation of polarisation plane. The form (15) obeys the condition

$$\epsilon_{\alpha\beta}(\mathbf{M}) = \epsilon^*_{\alpha\beta}(-\mathbf{M}) \tag{16}$$

imposed by the time inversion symmetry.

The other examples of special properties imposed by the symmetry breaking could be found in problems to this lecture.

7. In the presence of external forces, the internal parameter, which characterises the phase with a broken symmetry might depend on space coordinates $\mathbf{r}$. As an example, a nematic liquid crystal in inhomogeneous electric field $\mathbf{E}(\mathbf{r})$ is characterised by director $\mathbf{n}(\mathbf{r})$ dependent on coordinates $\mathbf{r}$[3]. This leads us to the conclusion that the free energy of heterogenous nematic liquid crystal G is presented as a functional of the director $\mathbf{n}(\mathbf{r})$ as a function of coordinates[4]

$$G = G_0 + \frac{1}{2}\int d\mathbf{r}\ K_1\,(\mathrm{div}\ \mathbf{n})^2 + \\ \frac{1}{2}\int d\mathbf{r}\left\{K_2\,(\mathbf{n}\cdot \mathrm{curl}\ \mathbf{n})^2 + K_3\,(\mathbf{n}\times \mathrm{curl}\ \mathbf{n})^2\right\} + \\ \frac{\epsilon_a}{12\pi}\int d\mathbf{r}\ (\mathbf{n}\ \mathbf{E})^2 \tag{17}$$

Here G_0 presents the free energy in case, when the director $\mathbf{n}$ is space homogeneous and electric field $\mathbf{E}$ vanishes. Independence of the free free energy on direction of $\mathbf{n}$ - independence at all the ponts of the space of degeneracy $\mathcal{R}_N$ - expresses the fact of the symmetry breaking. The low symmetry phase of a nematic liquid crystal presents an example of spontaneous breaking of *continuous* symmetry, which is characterised by director $\mathbf{n}$. In all cases of the breaking of continuous symmetry, the free energy of a heterogeneous depends on gradients of internal parameter (director $\mathbf{n}$ in the case of nematic liquid crystal). This fact - well known

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[3] This dependence occurs because, due to anisotropy of dielectric properties (12), the free energy density acquires an etra term

$$\delta g = \epsilon_a\ \frac{(\mathbf{n}\ \mathbf{E})^2}{12\pi}$$

[4] In the theory of liquid crystals, this functional is called *the Oseen-Frank functional*

yet in 19th century - is often called in the literature *Goldstone theorem.* Three coefficients K_1, K_2 and K_3 in Eq (17) are called the Frank moduli. They parametrise the rigidity of a homogeneous state of nematic liquid crystal with respect to deformations of different kind.

8. Let us return to arguments of the Sections 2 and 3. We have seen that, in case when the both phases correspond to the same symmetry, the phase diagram takes the shape presented in Fig 3 (with a critical point). In case, when two phases correspond different - higher and lower - symmetries, the critical point cannot appear. The phase diagram, in this case, has, for instance the shape, presented in Fig 4a. The solid line at this figure corresponds to equality of free energies - first order phase transition - and two dashed lines mark the boundaries of stability for two phases. An alternative to this case is brought by Fig

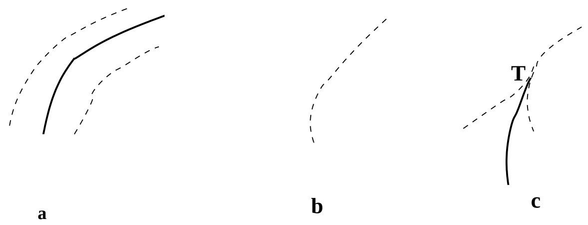

Figure 4: Phase diagrams for cases of First order phase transition (a), Second order phase transition (b) and the transition with a three-critical point T, i.e. being of the first and the second order at the different part of the diagram. The solid line corresponds to the first order transition, the dashed lines corresponds to the boundaries of stability and the second order transitions.

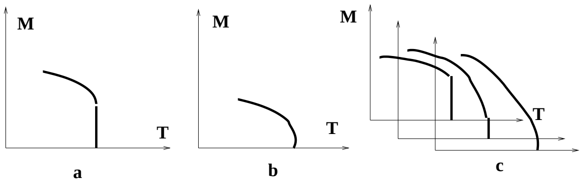

Figure 5: Dependence of Magnetisation $|\mathbf{M}|$ on temperature T for case of First order phase transition (a), Second order phase transition (b) and the phase diagram with a three-critical point (c). For the case c, dependence of $|\mathbf{M}(T)|$ is given for three different point at the line of transion.

4b, when the boundaries of stability for symmetric and nonsymmetric phases coincide. This corresponds to the Second order phase transition. The Fig 4c presents the phase diagram for a transition, which is the First order at the part of the phase diagram and the Second order - at the other.

For an example of above mentioned phase transition from a paramagnetic to a Ferromagnetic phase, dependence of spontaneous magnetisation $|\mathbf{M}|$ and a parameter across the transition line (say, the temperature T) for phase diagrams 4a, 4b and 4c are shown in Fig 5.

LECTURE 1.
Phases and Phase Transitions. Symmetries and Symmetry Breaking
PROBLEMS

P1.1. Saturating Vapour at Low Temperature

Find dependence of the pressure of the Saturating Vapour (i.e. the vapour at a thermal equilibrium with the liquid) on temperature T at low temperature, when the equation of state for the vapor is

$$p\ v = RT, \tag{1}$$

where R is universal gaseous constant. The volume v_L of the liquid could be neglected in comparison with the volume of vapour v_V.

P1.2. Tripple Point

The tripple point T at the $(p - T)$ phase diagram (see Fig) iis the point at which the phase boundaries SL, SG and LG meet of the gaseous G, solid S and liquid L phases.

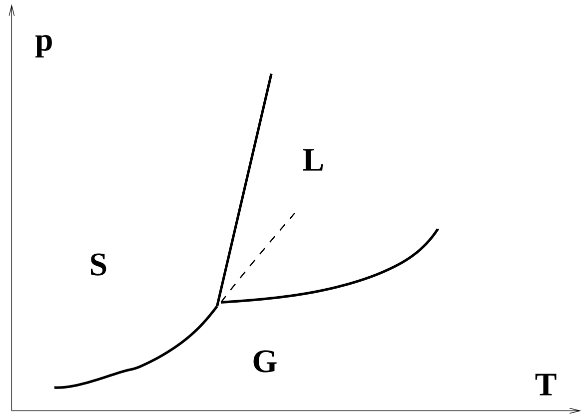

Figure 1: Phase Diagram with Gaseous G, Liquid L and Solid S phases. The dashed line corresponds to continuation of the SG phase boundary beyond the tripple point.

Show that continuation of SG phase boundary lies withing the corner formed by the phase boundaries SL and LG.

P1.3. Spaces of Degeneracy Analyse the following examples of the symmetry breaking and find relevant spaces of degeneracy.

- **P1.3.A. Crystal**
- **P1.3.B. Low-temperature phase of a Bose gas or Bose liquid, characterised by the macroscopic wave function of the condensate**
- **P1.3.C. Cholesteric Liquid Chrystal**
  A cholesteric liquid is characterised by a director $\mathbf{n}$,

which changes periodically - with a fixed period - in space.

P1.4. Properties of phases with a low symmetry

- **Piezo-electricity**

  Show that a crystal of the symmetry class $\mathbf{T_d}$ demonstrates piezo-electricity, i.e. a deformation

  $$u_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha}\right)$$

  leads to polarisation $\mathbf{E}$:

  $$P_\alpha = d_\alpha^{\beta\gamma}\ u_{\beta\gamma}$$

  Hint. Piezo-electricity corresponds to an extra-term in free energy

  $$\mathcal{F}_P = d_\alpha^{\beta\gamma}\ P_\alpha\ u_{\beta\gamma}$$

  Find permitted components of the tensor $\hat{d}$.

P1.5. Effective Free Energy Consider inhomogeneous states of different phases with the symmetry breaking and find out free energy functionals for these phases.

- **P1.5.A. Isotropic solid**

  Hint In an isotropic solid, the density could depend on coordinates $\rho(\mathbf{r})$. A heterogeneous state has the density $\rho(\mathbf{r}) = \rho_0(\mathbf{r} + \mathbf{u}(\mathbf{r}))$. Due to translational invariance, the free energy $\mathcal{F}$ depends not on a displacement $\mathbf{u}(\mathbf{r})$, but rather on its derivatives $\partial u_\alpha/\partial \mathbf{r}_\beta$

- **P1.5.B. A crystal with cubic symmetry**

- **P1.5.C. Smectic**
  Hint Smectic is a substance, in which the density $\rho(\mathbf{r})$ depends, say periodically, on one of three coordinates: $\rho(\mathbf{r}) = \rho(z)$. Under this condition, the heterogeneous state has the density $\rho\left(z + u(\mathbf{r})\right)$. Due to translational invariance, the free energy $\mathcal{F}$ depends not on $u(\mathbf{r})$, but rather on its derivatives. If $\partial u/\partial \mathbf{r}_{\parallel} = \text{const}$, this corresponds to the axes x, y and z being tilted to the layers of the smectic under certain angle. Therefore, the free energy $\mathcal{F}$ depends not on $\partial u/\partial \mathbf{r}_{\parallel}$, but rather on $\partial^2 u/\partial \mathbf{r}_{\parallel}^2$.