Introduction. Atomic Origin of Structure of Solids

Adiabatic approximation.

The most important property of condensed matter is that it is formed by atoms, consisting of heavy nuclei and light electrons. The ratio of their masses, M/m, is 2000 for the lightest nucleus, proton, and could be two orders of magnitude larger. This strong inequality determines typical energies in condensed matter. Nuclei are situated at distances of the order of the Bohr's radius $a_B = \hbar^2/me^2$ from each other and coupled by means of chemical bonds, the cohesion energy being of the order of the atomic energy $E_a = me^4/\hbar^2$. If we forget for a minute about the zero-point motion of nuclei, the cohesion energy of condensed matter can be well described in terms of the potential energy $U(x)$ as a function of displacements of nuclei from their position of equilibrium. If the displacement x is of the order of a_B, then the change in potential is of the order of E_a. Assuming quadratic expansion of the potential near its minimum, we can estimate the frequency ω of nucleus vibrations:

$$M\omega^2 a_B^2 \sim E_a, \qquad \omega \sim \sqrt{\frac{m}{M}}\frac{E_a}{\hbar}. \tag{1}$$

The second part of Eq (1) justifies the adiabatic approximation, which implies that in a zeroth order the electron

problem is solved for fixed coordinates of nuclei and in the first approximation the frequencies of vibrations are found, and the energy of zero-point oscillations is small, compared with electron energies.
The amplitude of zero-point oscillations $\bar{x}$ is

$$\bar{x} \sim \sqrt{\frac{\hbar}{M\omega}} \sim a_B \left(\frac{m}{M}\right)^{1/4}. \tag{2}$$

This means that, with an accuracy of order $(m/M)^{1/4}$, the nucleus oscillations are harmonic and anharmonicity is small. Since the frequency of oscillations is small, $\hbar\omega \ll E_a$, quantum effects are significant only at low temperatures $T \ll \hbar\omega$, while in a broad range of temperatures $\hbar\omega \leq T \ll E_a$, the oscillations could be treated as classical.

Crystals and crystalline structures. Defects.

It remains unclear why the minimum of the energy corresponds to the density $\rho(\mathbf{r})$ being a periodic function with three non-coplanar periods $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Nevertheless, it is an empirical fact. There are very few materials, which disobey this empirical rule. The first example is given by the isotopes of He: they remain liquids at atmospheric pressure even at temperature $T = 0$[1]. It has been discovered recently that several materials form the quasi-crystalline phase, which means that their density is not periodic but

[1] The first order transition from these liquids into the crystalline phase occurs at a relatively low pressure of the order of 30 bar.

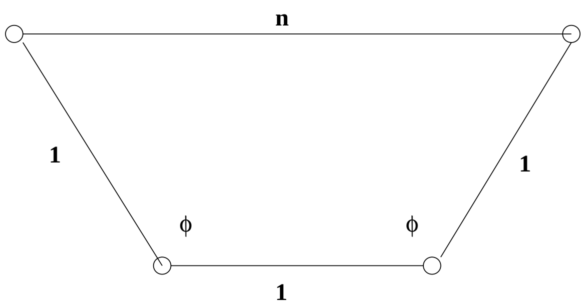

Figure 1: On rotations compatible with translations

is a sum of components with incommensurable periods $\mathbf{K}_i$:

$$\rho(\mathbf{r}) = \sum_i \rho_i \; e^{i\mathbf{K}_i\mathbf{r}} \tag{3}$$

The crystalline structure can be symmetric with respect to rotations through the angle ϕ around some axis. These rotations are compatible with translations only if (see Fig 1) the condition

$$1 - 2\cos\phi = n,$$

where n is an integer, is fulfilled. So, ϕ is equal either to π, or $2\pi/3$, or $\pi/2$, or $\pi/3$. In other words, the crystalline structure can only be symmetric with respect to rotations around binary, 3-fold, 4-fold and 6-fold axes. Quasi-crystalline structures are not restricted by this rule. Moreover, experimental study discovered icosahedral quasi-crystalline structures with 5-fold axes.

A liquid phase has usually no structure and, therefore, is characterized only by its density $\rho(\mathbf{r})$. Its free energy F

is a functional of density and its gradients:

$$F = F_0 + \frac{K_0}{2} \int d\mathbf{r} \left[\nabla \rho(\mathbf{r})\right]^2 . \tag{4}$$

A liquid can undergo a phase transition directly into a crystal. Another possibility is that this transformation goes through intermediate meso-phases. A common name for these meso-phases is “liquid crystals”, because some of them have no positional order (they are liquids), but have orientational order, which leads to anisotropy. The closest to solid is a phase, called smectic. It is characterized by one-dimensional density modulation: $\rho(x, y, z) = \rho(z)$, where $\rho(z)$ is a periodic function. A slight distortion of this structure is caused by displacement $u(x, y, z)$ of this layered structure along the z-axis. The free energy is a functional of the gradients of u:

$$F = F_0 + \int d\mathbf{r} \left\{ \frac{K_{zz}}{2} \left(\frac{\partial u}{\partial z}\right)^2 + \frac{K_{xx}}{2} \left[\left(\frac{\partial^2 u}{\partial x^2}\right) + \left(\frac{\partial^2 u}{\partial x^2}\right) \right]^2 \right\}^2 . \tag{5}$$

Using the Fourier transform of u and free energy (5), we can find the correlation function of thermal displacements u at two different points in space:

$$\begin{aligned} \langle [u(0,0) - u(z,x,y)]^2 \rangle &= T \int \frac{dk_z dk_x dk_y}{(2\pi)^3} \frac{1 - \cos\left(k_z z + k_x x + k_y y\right)}{K_{zz} k_z^2 + K_{xx} \left(k_x^2 + k_y^2\right)^2} \\ &= \frac{T}{8\pi \sqrt{K_{zz} K_{xx}}} \ln \left\{ a^{-1} \left| z + \sqrt{\frac{K_{zz}}{K_{xx}}} (x^2 + y^2) \right| \right\}, \end{aligned} \tag{6}$$

[2]Linear variation of displacement u with in-plane coordinates x and y corresponds to the rotation of the layered structure as a whole and, therefore, does not lead to any contribution to energy F.

where a is the distance between the layers. At long enough distances z, x and y, the mean square of the fluctuations $\langle [u(x,y,z) - u(0,0,0)]^2 \rangle$ exceeds any number. This means that the correlation in the position of any layered structure is destroyed by thermal fluctuations. In practice, for a realistic sample size, these correlations can still be strong. A more interesting question is whether the rigidities K_{zz} and K_{xx} remain finite if thermal fluctuations are taken into account. The answer to this question is positive. Therefore, smectics (like all meso-phases) are characterized by strong thermal fluctuations, which, nevertheless, do not destroy their inner rigidity.

Both liquids and solids have the short range order, while the long range order exists in solids only. This means that solids keep the shape of their samples, while liquids take the shape of the vessel. This is true in the large time limit, while at finite frequency ω the shear modulus $\mu(\omega)$ remains finite:

$$\mu(\omega) = \mu_0 + i\omega\eta,$$

where η is the liquid viscosity. Very viscous liquids (paraffin, tar) keep their shape for days and weeks. An interesting point is that some viscous liquids can undergo transition to a new (glassy) state, in which the viscosity is formally infinite and the shape of the sample remains unchanged, though it strongly depends on the prehistory of sample preparation. We leave the exciting subject of glassy phase, glass transition, etc, noticing that this is one of the numerous mysteries of condensed matter.

If a solid is seen as a single oscillator, like H_2-molecule, the mean square of its vibration amplitude $\langle u^2 \rangle$ is of the order of $a^2 T/E_{\rm at}$, and the crystalline order is destroyed, if(when) the temperature T is of the order of atomic energy, i.e. more, than 10 000 K. In practice, such temperature corresponds to evaporation of solids, while the melting occurs at temperature, which is 10 - 30 times lower. The lowering of the melting temperature T_m occurs due to a large number of different meta-stable deformations of the crystalline lattice. This degeneracy helps the melting in two ways: first of all, the potential, which has extra minima, has lower values at the maxima; secondly, the extra entropy makes the free energy of the liquid state comparable to that of the solid at lower temperature. As a result, the melting temperature T_m is estimated from, the so called, Lindemann criterium:

$$T_m \sim \alpha_L E_{\rm at}, \qquad \alpha_L \approx \frac{1}{25}. \tag{7}$$

Therefore, the liquid phase corresponds to a temperature T, much smaller than the mean potential energy of deformation of the atoms[3].

[3]This is not a specific property of atomic systems. Interacting electrons form a nearly ideal gas at high density, when $e^2/\hbar v_F \ll 1$ (v_F is their Fermi velocity) and a Wigner solid at $e^2/\hbar v_F > 37$ for 2D ($e^2/\hbar v_F > 180$ for 3D). The intermediate range of electron densities corresponds to strongly correlated classical liquid, in which Coulomb correlations are much stronger than zero-point fluctuations.
Another example is provided by liquids containing molecules with large dipole momenta. Water, for instance, has a quite large dielectric constant $\epsilon = 81$, which clearly shows that the dipole-dipole interaction between its molecules is much larger, than temperature.

Spin dependent effects. Magnetism.

Typically, an electron moves in an atom (molecule, solid, etc) with atomic velocity

$$v \sim \frac{p}{m} \sim \frac{\hbar Z}{m a_B} \sim \frac{Ze^2}{\hbar} = \frac{Zc}{137},$$

where c is the speed of light and Z is the atomic number. Therefore, in not very heavy elements or in outer atomic shells, electrons move with non-relativistic velocities and relativistic effects can be neglected. This decouples the orbital motion of electrons from orientations of their spins. In other words, in the non-relativistic approximation the electron energy can depend on the total spin, but is independent of the spin orientation with respect to the crystalline lattice. The dependence of electron energy on spin comes from the quantum identity of electrons (the Pauli exclusion principle). Similar to the Hund phenomenon in many-electron atoms and the Heitler-London phenomenon in homeopolar molecules, electron-electron correlation energy can depend on total spin. This energy is of the order of the atomic energy E_{at} or, more explicitly, it is the difference of two energies of order E_{at}. The mentioned spin dependent energy difference, called the exchange energy, is typically less than the atomic energy and has, at most, the value of order 1000 K. In those materials, where electron wave functions overlap less, the exchange energy is even smaller than that. This is why magnetism occurs below the temperature $T_c \sim 1000K$ in iron and below 1 - 10 K in magneto-dielectrics.

Magnetic anisotropy, i.e. the interaction, which depends on the orientation of electron spins with respect to the crystalline axes, is caused by relativistic interactions and, therefore, is usually weaker than the exchange energy, while both energies can be of the same order if magnetism occurs at very low temperature.