

Problem set 3, due on October 27, **before** the beginning of the lecture

### 1 Order parameter of a nematic liquid crystal (group exercise, 15 points)

As discussed in class, the order parameter  $\eta$  is a physical quantity reflecting the degree of order of a given system; it is  $\eta = 0$  for full disorder and  $\eta = 1$  when the system is fully ordered. One possible way to define an order parameter for a nematic liquid crystal is the following:

$$\eta = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle \quad (1)$$

where

$$\langle f(\theta) \rangle = \int_{\theta=0}^{\pi} f(\theta) p(\theta) \sin(\theta) d\theta \quad (2)$$

is the expectation value of  $f(\theta)$ , i.e. the average value of  $f(\theta)$  over all molecules,  $p(\theta)$  is the probability density of finding a molecule at an angle  $\theta$  from the director orientation (Fig. 1) and the factor  $\sin(\theta)$  is because we are working in spherical coordinates.

a) Using the above formulas, show that for an isotropic distribution, i.e.  $p(\theta) = 1$ ,  $\eta = 0$ , as expected.

b) Show that for the case of perfect orientation of all molecules along the director,  $\eta = 1$ . (Hint: One could in principle use the formula (2), however one would need to deal with the delta-function,  $\delta(\theta)$ ; there is much simpler way: what is the expectation value in (1) if  $\theta$  is fixed for all molecules?) What is  $\eta$  in the case of all molecules distributed in a plane perpendicular to the director?

c) In an ordered magnet the value of its order parameter (macroscopic magnetization) changes by a factor of -1 when rotated through  $180^\circ$ . Why does the liquid crystal not exhibit a macroscopic polarization, although individual molecules can have a permanent dipole moment? It follows that the Gibbs free energy function  $G(\eta, T)$  cannot be symmetric with respect to  $\eta$  and we include an odd power in the series expansion:

$$G(\eta, T) = a(T - T^*)\eta^2 - C\eta^3 + B\eta^4 \quad (3)$$

where  $a$ ,  $C$  and  $B$  are positive parameters and  $T^*$  is a characteristic temperature of the system, which we will show to be related to the nematic transition temperature  $T_{\text{nem}}$  but not identical

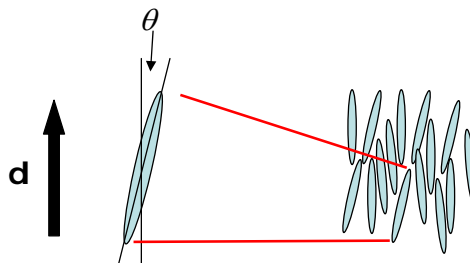


Figure 1: The deviation of the orientation of each individual molecule from the director orientation is  $\theta$ .  $\theta$  will fluctuate with time but we assume that a “snapshot” at a given time will yield a representative distribution of different  $\theta$  angles.

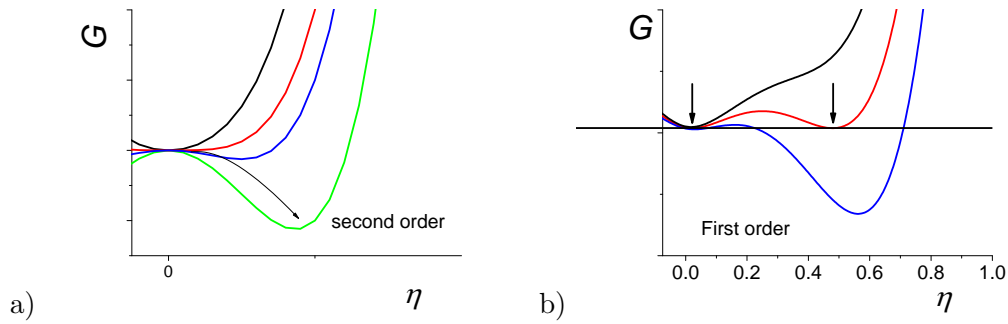


Figure 2: Comparison of the behavior of second order, (a), and first order, (b), phase transitions. The dependence of the Gibbs free energy  $G$  on the order parameter  $\eta$  is shown. In the case of a second order phase transition, the total minimum is *either* at  $\eta = 0$  *or* at finite  $\eta$ , and the order parameter sets in gradually below the transition temperature. In the case of a first order phase transition, at the transition temperature, there is the same minimum at  $\eta_0 = 0$  and at a finite  $\eta_1$  (i.e.  $G(\eta_0) = G(\eta_1)$ ) while the minimum is at  $\eta = 0$  above the transition temperature and at finite  $\eta$  below. Consequently, the order parameter will jump from  $\eta = 0$  to  $\eta_1$  at the transition temperature.

with it. To get an idea of the behavior at temperatures far above and far below the transition temperature, plot  $G$  for  $a(T - T^*) = B = C = 1$  and  $-a(T - T^*) = B = C = 1$ , respectively (you can use a computer program if you want).

Here we want to show that the description of a nematic liquid crystal by eq. (3) results in a first order transition. The relevant properties of a first-order phase transition become apparent from Fig. 2: In particular, at the transition temperature  $T_{\text{nem}}$  there are two minima, at  $\eta = \eta_0 = 0$  and  $\eta_1 \neq 0$ , with  $G(\eta_0) = G(\eta_1)$ .

This leads to two equations which must simultaneously hold at  $T_{\text{nem}}$ :  $dG/d\eta = 0$  and  $G = 0$ . Write down these equations. Show that  $\eta = 0$  is a common solution. Show that there is a second solution,  $\eta = C/2B$ . Which is the corresponding temperature, i.e. at which  $T = T_{\text{nem}}$  does  $\eta = C/2B$  solve both  $dG/d\eta = 0$  and  $G = 0$ ? Hint: You have two equations  $dG/d\eta = 0$  and  $G = 0$ , and two variables...

Finally, calculate how  $\eta$  depends on  $T$  for  $T < T_{\text{nem}}$ .

## 2 Thermodynamic finger exercise (10 points)

a) In class we defined the specific heat at constant volume,  $c_V$ , through the internal energy  $U$ , and at constant pressure,  $c_p$ , through the enthalpy  $H$ . Express  $c_V$  through the free energy  $F$  and  $c_p$  through the Gibb's free energy  $G$ .

b) Derive a general expression for the entropy  $S$  at fixed  $p$  from the differential form of the Gibb's free energy  $dG$  given in class. We modeled the special case of a second-order phase transition by the following Gibb's free energy

$$G = G_0 + a(T - T_c)\eta^2 + B\eta^4 \quad (4)$$

and derived an expression for  $\eta$  which minimizes  $G$ . What is then the minimal  $G$  above and below  $T_c$ , respectively? From the expressions for this minimal  $G$ , derive  $S$  above and below  $T_c$ . Derive expressions for  $c_p$  below and above  $T_c$ . Sketch how  $G$ ,  $S$  and  $c_p$  behave across  $T_c$  (smooth? Is there a jump or a kink?)

### 3 Bravais lattices in two dimensions (11 points)

Here we want to review different lattices in two dimensions. In Fig. 3a), you see a square lattice; obviously, such a lattice is a Bravais lattice and a possible set of primitive vectors is shown in the figure. With respect to the given cartesian coordinate system defined by the two perpendicular, equally long vectors  $\mathbf{z}_1$  and  $\mathbf{z}_2$ , these vectors are  $\mathbf{a}_1 = 2\mathbf{z}_1$  and  $\mathbf{a}_2 = 2\mathbf{z}_2$ .

For each of the five lattices shown in Fig. 3a)–e), indicate whether it is a Bravais lattice, and if yes, draw the following:

(i) a set of primitive unit vectors (also provide a formula how they are defined with respect to the given cartesian coordinate system, following the example above);

(ii) a possible choice of a primitive unit cell which is *not* the Wigner-Seitz cell;

(iii) the Wigner-Seitz cell;

(iv) For each lattice (out of the five shown) which is *not* a Bravais lattice by itself, show how it can be represented by a Bravais lattice with a basis of two instead of one individual atoms, indicating a set of primitive unit vectors defining the points of the underlying Bravais lattice. Calculate these primitive unit vectors with respect to the given coordinate system; also calculate the position of the atoms in the basis with respect to the given coordinate system. (Hint: the origin of the given coordinate system is already at one of the possible Bravais lattice points...)

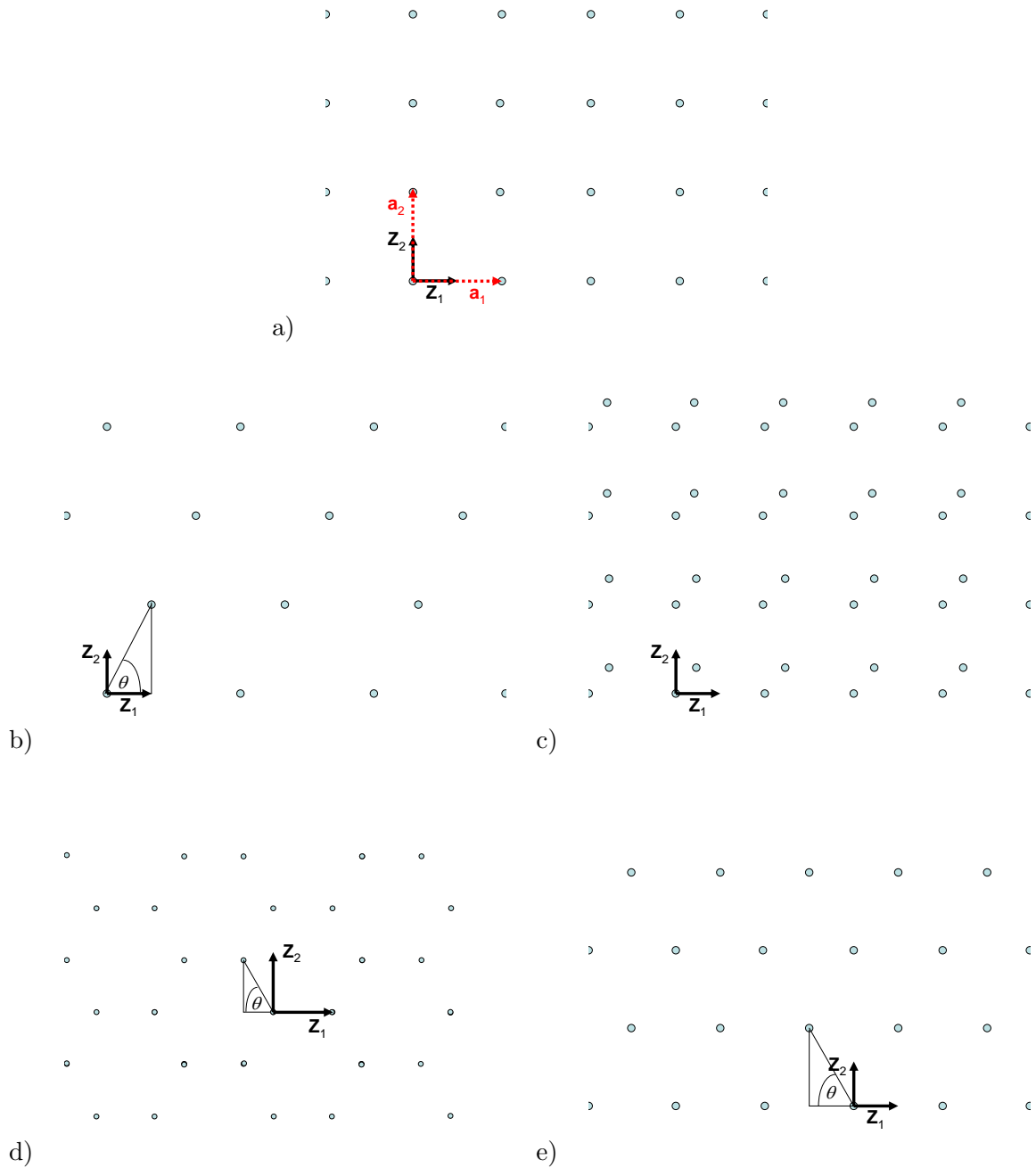


Figure 3: Different two-dimensional lattices. Panel a) shows a square Bravais lattice; a set of possible primitive vectors is defined by  $\mathbf{a}_1 = 2\mathbf{z}_1$  and  $\mathbf{a}_2 = 2\mathbf{z}_2$ . In b),  $\tan \theta = 2$ , and in d) and e),  $\theta = 60^\circ$ .