Tutorial 4, Statistical Mechanics: Concepts and applications
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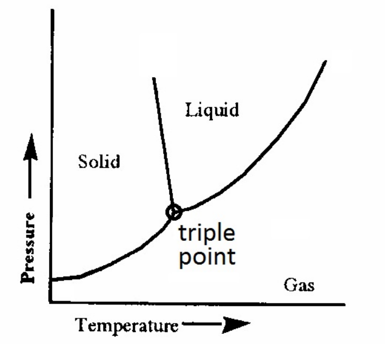
Tutorial exercises

I. EXERCISE (EASY): CLAPEYRON'S EQUATION

The Landau tricritical point of a certain substance in which solid, liquid and gas phases coexist has temperature T^* and pressure P^*.



The Clausius–Clapeyron equation relates the slope of the coexistence curve for phases α and β and the latent heat $\lambda_{\alpha\beta} = T(s_\alpha - s_\beta)$ where s is entropy per unit mass:

$$\frac{dP_{\alpha\beta}}{dT} = \frac{\lambda_{\alpha\beta}}{T(v_\alpha - v_\beta)} \tag{1}$$

where v is specific volume. When T is close to T^* the latent heat can be considered almost constant and the specific volume of the solid state v_S and of the liquid phase v_L are also constant. Moreover we have $v_S \ll v_G(T)$ with $v_G(T)$ the specific volume of the gas phase.

1. Find an approximate expression for the function $P_{SL}(T)$ for the coexistence liquid-solid on the plane (P, T), close to the critical point

: *Clapeyron's equation for the curve of coexistence of liquid and solid is*

$$\frac{dP_{SL}}{dT} = \frac{\lambda_{SL}}{(v_L - v_S)T} \tag{2}$$

As $\lambda_{SL} \sim$ const. we can integrate over T and we find

$$P_{SL}(T) = P^* + \frac{\lambda_{SL}}{v_L - v_S} \log(T/T^*) \tag{3}$$

2. Find an approximate expression for the function $P_{SG}(T)$ for the coexistence gas–solid on the plane (P, T), close to the critical point

: *Clapeyron's equation for the curve of coexistence of gas and solid is*

$$\frac{dP_{SG}}{dT} = \frac{\lambda_{SG}}{(v_S - v_G)T} \tag{4}$$

As $v_S \ll v_G$ *we can set*

$$\frac{dP_{SG}}{dT} \sim -\frac{\lambda_{SG}}{v_G T} = -\frac{n\lambda_{SG}}{V_G T} \tag{5}$$

where V_G *is the volume of the gas and* n *is the number of moles of the system. We can now use*

$$\frac{V_G}{n} \sim RT/P_{SG}(T). \tag{6}$$

Then the equation becomes

$$\frac{dP_{SG}}{dT} \sim \left(\frac{\lambda_{SG}}{R}\right)\frac{P_{SG}(T)}{T^2} \tag{7}$$

which we can integrate and obtain

$$P_{SG}(T) = P^* e^{-\alpha/T^*} e^{\alpha/T} \quad \alpha = \left(\frac{\lambda_{SG}}{R}\right) \tag{8}$$

II. EXERCISE (HARD): FIRST-ORDER PHASE TRANSITIONS IN LIQUID CRYSTALS

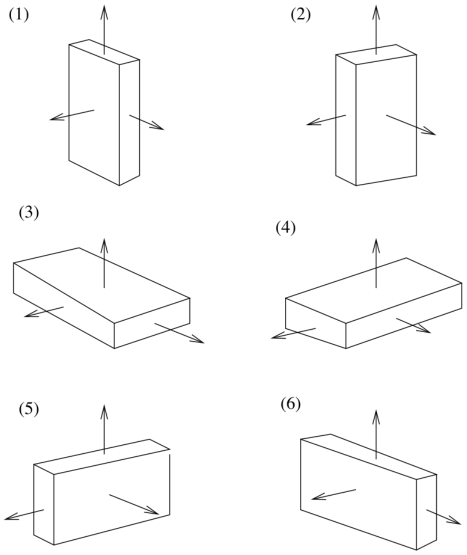
Source: R. A. Sauerwein and M. J. De Oliveira, J. of Chem. Phys. **144***, 194904 (2016).*

1. **Lattice model for biaxial and uniaxial liquid crystals**

Reminder: Liquid crystals are states of matter that can be thought of as something in between conventional liquids and solid crystals. They can exhibit various phases, one of the most common being the nematic phase. In nematics, the molecules tend to have the same alignment but their positions are not correlated. Thus, their center of mass positions are randomly distributed as in a liquid, but still maintain a long-range directional order.

The molecules are generally three-dimensional objects, often elongated in one direction. If there is a preferred direction for one of the axis (most commonly, the major one), the nematic is said to be *uniaxial*. If there is a secondary preferred direction that is perpendicular to the other one, such a nematic is called *biaxial*. At sufficiently high temperature, thermal fluctuations are able to destroy the ordering of the nematic phase, and the system reaches a conventional isotropic liquid phase.

The model: Although we emphasize that there is no positional order (i.e., underlying lattice structure) in liquid crystals, we start with a simple lattice model in order to describe the phase transitions in nematics. In particular, we consider a regular lattice where, at each site, there is a parallelepiped-shaped molecule. We assume that the molecules can take only the 6 orientations shown in Fig. 1.



$$W_1 = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, \qquad W_2 = \begin{pmatrix} b & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix},$$

$$W_3 = \begin{pmatrix} b & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & a \end{pmatrix}, \qquad W_4 = \begin{pmatrix} c & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & a \end{pmatrix},$$

$$W_5 = \begin{pmatrix} c & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \qquad W_6 = \begin{pmatrix} a & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & b \end{pmatrix},$$

FIG. 1. Left: The six possible orientations of a molecule. Right: The matrix representation of the orientations.

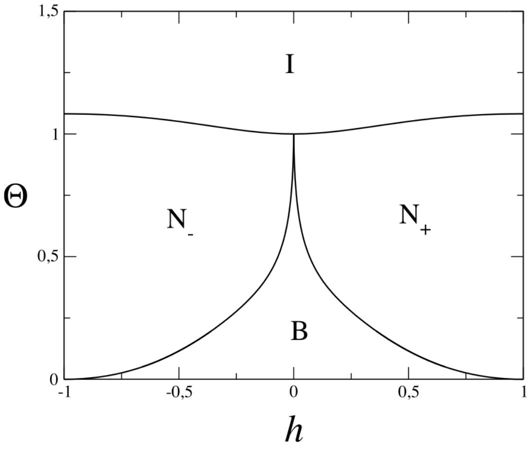


FIG. 2. Sketch of the phase diagram in the variables h (*cf.* (17)) and $\Theta = \frac{12kT}{J\gamma r^2(h^2+3)}$, where γ is the coordination number. The phases are isotropic (I) uniaxial nematic ($N_\pm$), and biaxial nematic (B).

A rod-like nematic phase occurs when the major axes are mostly parallel to each other whereas the other two axes point in arbitrary directions. A disc-like nematic phase occurs when the minor axes are mostly parallel to each other whereas the other two axes point in arbitrary direction. A biaxial phase takes place when both the major axes are mostly parallel to each other, and the minor axes are mostly parallel to each other. In this case, same can be said about the third axis as well.

The system is described by the Hamiltonian

$$H = -\epsilon \sum_{(i,j)} \mathrm{Tr}[\Omega^i \Omega^j]\,, \tag{9}$$

where the sum is over nearest neighbor pairs, $\Omega_i \in \{W_1, \dots, W_6\}$ are the diagonal matrices shown in fig. 1 (for the moment, you can interpret a, b, and c as the lengths in the various directions).

(a) Show that, without loss of generality, the matrices W_i can be chosen to be traceless, *i.e.* $a+b+c=0$.

: *Define*

$$\alpha = \mathrm{Tr}\left[\Omega^i\right]$$

so that $(\Omega^i - \alpha/3)$ *is traceless.*

$$H = -\epsilon \sum_{(i,j)} \mathrm{Tr}\left[(\Omega^i - \alpha/3)(\Omega^j - \alpha/3)\right] + \mathrm{const}$$

(b) Within the mean-field approximation, neglect the fluctuations, *i.e.* use the following approximation: $(x - \langle x\rangle)(y - \langle y\rangle) \to 0$. Define $Q_\mu = \langle \Omega^i_{\mu\mu}\rangle$ and write down an effective mean-field Hamiltonian linear in Ω^i. The coordination number of the lattice is γ.

:

$$(x - \langle x\rangle)(y - \langle y\rangle) \approx 0$$

$$xy \approx \langle x\rangle y + x\langle y\rangle - \langle x\rangle\langle y\rangle$$

$$\Omega^i\Omega^j \approx Q(\Omega^i + \Omega^j) - Q^2$$

$$H = -\epsilon\gamma\left[\sum_i \mathrm{Tr}(Q\Omega^i) - \frac{N}{2}\mathrm{Tr}(Q^2)\right]$$

(c) Within mean field, calculate the free energy and write down the system of equations satisfied by the diagonal elements of Q. The total number of molecules is N, and you can leave the equations in matrix form.

:

$$Z = \sum_{\{\Omega\}} e^{-\beta H} = e^{-\frac{N}{2}\beta \mathrm{Tr}(Q^2)} \left(\sum_{s=1}^{6} e^{\beta \mathrm{Tr}(QW_s)}\right)^N$$

Free energy per molecule $f = -\beta^{-1}\log Z$*:,* $\beta = \epsilon\gamma/T$

$$f = -\frac{1}{T}\left(-\frac{\beta}{2}\mathrm{Tr}(Q^2) + \ln\left[\sum_{s=1}^{6} e^{\beta \mathrm{Tr}(QW_s)}\right]\right) = \frac{\epsilon\gamma}{2}(Q_1^2 + Q_2^2 + Q_3^2) - T\ln\left[\sum_{s=1}^{6} e^{\beta \mathrm{Tr}(QW_s)}\right]$$

Q is the expectation value of Ω, which you can find using the partition function

$$Q = \frac{\sum_{s=1}^{6} W_s e^{\beta \mathrm{Tr}(QW_s)}}{\sum_{s=1}^{6} e^{\beta \mathrm{Tr}(QW_s)}}$$

therefore, using

$$\zeta_1 = e^{\beta(aQ_1+bQ_2+cQ_3)} \qquad \zeta_2 = e^{\beta(bQ_1+aQ_2+cQ_3)} \tag{10}$$

$$\zeta_3 = e^{\beta(bQ_1+cQ_2+aQ_3)} \qquad \zeta_4 = e^{\beta(cQ_1+bQ_2+aQ_3)} \tag{11}$$

$$\zeta_5 = e^{\beta(cQ_1+aQ_2+bQ_3)} \qquad \zeta_6 = e^{\beta(aQ_1+cQ_2+bQ_3)} \tag{12}$$

$$\zeta = \sum_{i=1}^{6} \zeta_i \tag{13}$$

we have

$$Q_1 = \frac{1}{\zeta}(a\zeta_1 + b\zeta_2 + b\zeta_3 + c\zeta_4 + c\zeta_5 + a\zeta_6) \tag{14}$$

$$Q_2 = \frac{1}{\zeta}(b\zeta_1 + a\zeta_2 + c\zeta_3 + b\zeta_4 + a\zeta_5 + c\zeta_6) \tag{15}$$

$$Q_3 = \frac{1}{\zeta}(a\zeta_1 + c\zeta_2 + a\zeta_3 + a\zeta_4 + b\zeta_5 + b\zeta_6) \tag{16}$$

(d) Use the following parametrization

$$Q = \begin{pmatrix} -\frac{q+\eta}{2} & 0 & 0 \\ 0 & -\frac{q-\eta}{2} & 0 \\ 0 & 0 & q \end{pmatrix} \qquad W_1 = \begin{pmatrix} -\frac{r}{6}(h-3) & 0 & 0 \\ 0 & -\frac{r}{6}(h+3) & 0 \\ 0 & 0 & \frac{r}{3}h \end{pmatrix}. \tag{17}$$

Identify the phases of matter parametrized by q, η.

: *$q = \eta = 0 \to$ isotropic*
$q \neq 0, \quad \eta = 0 \to$ uniaxial nematic ($q > 0$: rod-like, $q < 0$ disk-like)
$q \neq 0, \quad \eta \neq 0 \to$ biaxial nematic

(e) Write down the free energy in the uniaxial (rod-like and disk-like) nematic phases. Identify (i.e., write down the equation for) the line of the phase transition from the isotropic phase to the nematic phase. What can be an order parameter for the phase transition? Is it a first-order or a continuous transition (is there a jump in the order parameter)?

: *in the nemathic phase $\eta = 0$ so $Q_1^2 + Q_2^2 + Q_3^2 = 3/2q^2$*

$$f = \frac{3\epsilon\gamma}{4}q^2 - \frac{1}{T}\log 2(e^{3\beta aq/2} + e^{3\beta bq/2} + e^{3\beta cq/2}) \tag{18}$$

with

$$q = \frac{ae^{3\beta aq/2} + be^{3\beta bq/2} + ce^{3\beta cq/2}}{e^{3\beta aq/2} + e^{3\beta bq/2} + e^{3\beta cq/2}} \tag{19}$$

On the other hand in the isotropic regime the free energy is

$$f_0 = -\beta^{-1} \log 6 \tag{20}$$

The transition line is when

$$f_0 = \frac{3\epsilon\gamma}{4} q^2 - \beta^{-1} \log 2(e^{3\beta a q/2} + e^{3\beta b q/2} + e^{3\beta c q/2}) \tag{21}$$

At the transition line the order parameter q *jumps from* 0 *to the value in* (19).