Studentnumber:___SOLUTION________

English Page 1 of 1

NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET
INSTITUTT FOR FYSIKK

Contact during the exam:
Department of Physics
Professor Jon Otto Fossum, mob, 91139194

EXAM: TFY4245 FASTSTOFF-FYSIKK VK

Thursday 31. May 2007
Tid: kl 09.00-13.00

Allowed exam material: Alternative C
Standard pocket calculator
Rottman: Mathematical Formula (all language editions)
Barnett og Cronin: Mathematical Formula

The exam consists of:

1. The first page (the present page) which must be delivered with answers to the multiple choice questions.
2. 3 "normal" Problems 1, 2 and 3 (Appendix A)
3. One set of multiple choice questions, Problem 4 (Appendix B)

The three "normal" problems count altogether 50%, and the multiple choice questions count altogether 50%. Only ONE of the alternatives A-D must be marked for each of the 20 multiple choice questions. Correct answer gives one point, wrong answer gives zero points.

Answers to the multiple choice questions in Appendix B:

Question	1	2	3	4	5	6	7	8	9	10	11	12
Answer	**C**	**A**	**D**	**C**	**B**	**D**	**C**	**B**	**D**	**B**	**C**	**B**

Question	13	14	15	16	17	18	19	20
Answer	**B**	**A**	**A**	**C**	**B**	**C**	**A**	**B**

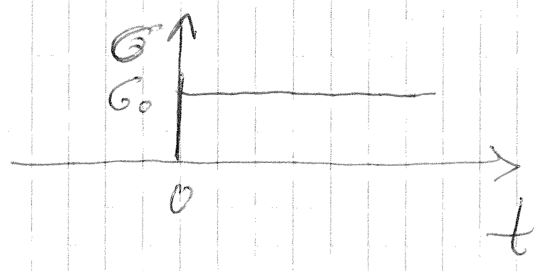
There is an error in question 19, so every one gets right answer to this question

Problem 1

a)

$$\frac{d\gamma}{dt} = \left(\gamma_{(\infty)} - \gamma\right) 1/\tau$$

1. Step:



$$\frac{d\gamma}{dt} = \left(\alpha\sigma_0 - \gamma\right) 1/\tau = z/\tau$$

$$= \frac{d}{dt}\left(-(\alpha\sigma_0 - \gamma)\right) = -\frac{dz}{dt}$$

$$z(t) = \alpha\sigma_0 - \gamma(t) \;\Big|\; \frac{d(\overbrace{\alpha\sigma_0}^{\text{constant}})}{dt} = 0$$

$$\Rightarrow z(t) = z(0)\, e^{-t/\tau}$$

$$\Rightarrow \alpha\sigma_0 - \gamma(t) = \alpha\sigma_0\, e^{-t/\tau}$$

$$\Rightarrow \boxed{\gamma(t) = \alpha\sigma_0\left(1 - e^{-t/\tau}\right)}$$

2. Pulse:

$$\frac{d\gamma}{dt} = -\frac{\gamma}{\tau} \Rightarrow \gamma(t) = \gamma(0)\, e^{-t/\tau}$$

$$\Rightarrow \boxed{\gamma(t) = \alpha\sigma_0\, e^{-t/\tau}}$$

Problem 1 continued

3. Dynamic

$$\frac{d\gamma}{dt} = -i\omega\gamma_0 e^{-i\omega t + i\delta(\omega)}$$

$$= \Big[\underbrace{\alpha(\omega=0)\,\sigma_0\, e^{-i\omega t}}_{\gamma(t=\infty)\ \Leftrightarrow\ t=\infty\ \Leftrightarrow\ \omega=0} - \gamma_0 e^{-i\omega t + i\delta(\omega)}\Big]\frac{1}{\tau}$$

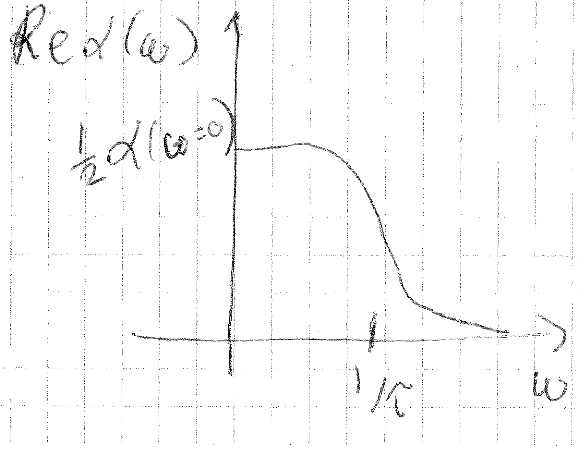
For $\omega = 0 \Rightarrow \underbrace{\delta(0) = 0}_{\text{No phase shift at zero frequency}}$

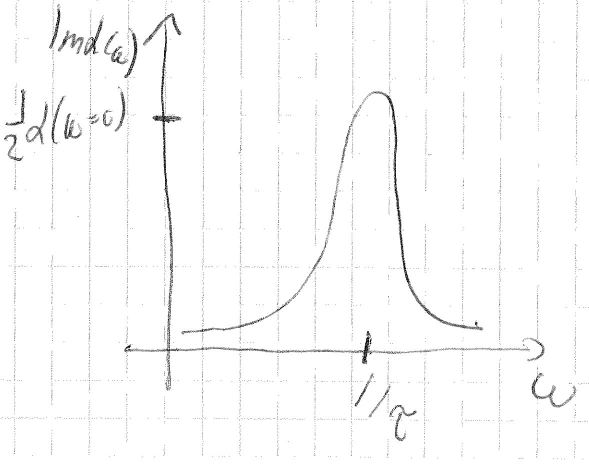
$$\Rightarrow (1-i\omega\tau)\, e^{i\delta(\omega)}\frac{\gamma_0}{\sigma_0} = \alpha(\omega=0)$$

From definition of $\delta(\omega)$ and $\alpha(\omega)$:

$$e^{i\delta(\omega)}\frac{\gamma_0}{\sigma_0} = \alpha(\omega)$$

$$\Rightarrow \alpha(\omega) = \frac{\alpha(\omega=0)}{1-i\omega\tau} = \frac{\alpha(\omega=0)}{1+(\omega\tau)^2} + \frac{i\omega\tau\,\alpha(\omega=0)}{1+(\omega\tau)^2}$$





Problem 7 continued.

b) Pages 94-95 in Strobl.

Pages 97-100 in Strobl.

Pages 128-131 in Strobl

c) Pages 101-102 in Strobl.

2.2.2 Orientational and Distortional Polarisation

The polarisation of liquid or solid matter in an electric field arises from several contributions, which differ very markedly in their frequency dependence. This is illustrated by the schematic plot of the frequency dependence of the real part of the dielectric susceptibility in Fig. 2.17. A first contribution, which can be very strong, is found for liquids made up of polar molecules. In the absence of an external field, the permanent dipole moments carried by all the molecules are distributed over all directions. In a field, there is a preferred orientation and this results in an **orientational polarisation** $P_{\mathrm{or}} \propto \varepsilon_0 \chi_{\mathrm{or}}$. It is clear that at too high frequencies the molecules will no longer be able to follow the field, because of their moment of inertia. Empirically, this is found to occur when the frequency significantly exceeds $10^{12}\,\mathrm{s}^{-1}$. After this, as is indicated in the figure, no further orientational polarisation is observed.

A second mechanism which contributes to the polarisation can be observed in ionic crystals, molecular crystals and molecular liquids. In molecules, there are always charge centres. An electric field can push these centres of positive and negative charge in opposite directions and, in this way, induce dipole moments. Particularly strong polarisation effects are to be expected in the infra-red region, since these frequencies correspond to the eigenfrequencies of

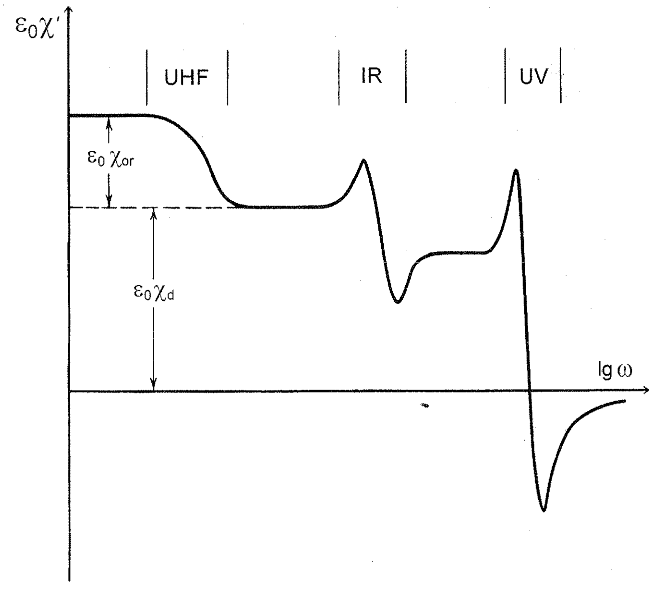


Fig. 2.17. A schematic representation of the frequency dependence of the real part of the dielectric susceptibility: The contributions due to dipolar orientation (χ_{or}, up to the UHF region) as well as a deformation of the nuclear skeleton and displacements of the electrons (χ_{d}, in the IR and UV region).

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There remains a final polarisation mechanism which is always present in the case of atomic systems, namely the displacement of the electron shells relative to the nuclei. The eigenfrequencies of the displaceable outermost electrons lie in the visible light and ultra-violet region. Polarisation effects are thus particularly large in this frequency range. In the visible range, the refractive index n is usually used as the material-specific parameter in place of ε or χ. n is related to ε and χ by means of the Maxwell relation

$$n^2 = \varepsilon = 1 + \chi \quad . \tag{2.93}$$

Like ε and χ, n is in the general case a complex variable.

The frequency dependence of the orientational polarisation and that of the **distortional polarisation** $P_{\mathrm{d}} \propto \varepsilon_0\chi_{\mathrm{d}}$ – this encompasses the other two contributions – differ in a characteristic manner. While only a simple decay is observed for the orientational polarisation, resonance effects are observed for the contributions to the distortional polarisation. ~~Using classical equations, it is possible to describe in a straightforward manne~~r the frequency dependence of both processes. The orientational polarisation P_{or} is correctly described using the following relaxation equation:

$$\frac{\mathrm{d}P_{\mathrm{or}}}{\mathrm{d}t} = -\frac{1}{\tau}(P_{\mathrm{or}} - \varepsilon_0\chi_{\mathrm{or}}E_0) \quad . \tag{2.94}$$

The starting point is identical with that which was introduced for the treatment of anelastic deformations in Eq. (2.75). The time constant τ now has the meaning of the reorientation time of the polar molecule. The solution of the relaxation equation has been given above and can be directly used again: Upon switching on a static field E_0, an orientational polarisation appears according to

$$P_{\mathrm{or}} = \varepsilon_0\chi_{\mathrm{or}}E_0\left(1 - \exp -\frac{t}{\tau}\right) \quad . \tag{2.95}$$

For a field oscillating at a frequency ω, the (complex) amplitude P_0 is given by

$$P_0 = \frac{\varepsilon_0\chi_{\mathrm{or}}}{1 - \mathrm{i}\omega\tau}E_0 \quad . \tag{2.96}$$

This leads for the real and imaginary part of the orientational dielectric susceptibility to

$$\begin{aligned}\frac{P_0}{E_0} &= \varepsilon_0\chi'_{\mathrm{or}}(\omega) + \mathrm{i}\varepsilon_0\chi''_{\mathrm{or}}(\omega)\\ &= \frac{\varepsilon_0\chi_{\mathrm{or}}}{1+\omega^2\tau^2} + \mathrm{i}\frac{\varepsilon_0\chi_{\mathrm{or}}\omega\tau}{1+\omega^2\tau^2} \quad .\end{aligned} \tag{2.97}$$

Plots of these functions have been shown previously in Fig. 2.16. Evidently the situation here again corresponds to a simple relaxation process. In fact,

$$\tau'^2 \frac{\mathrm{d}^2 P_\mathrm{d}}{\mathrm{d}t^2} = -\tau \frac{\mathrm{d}P_\mathrm{d}}{\mathrm{d}t} - P_\mathrm{d} + \varepsilon_0 \chi_\mathrm{d} E \ . \tag{2.98}$$

It differs from the relaxation equation through the term on the left-hand side which takes the inertia effects into account. Equation (2.98) is the equation of motion for a driven damped harmonic oscillator. For a varying electric field

$$E(t) = E_0 \exp(-\mathrm{i}\omega t) \tag{2.99}$$

there exists a stationary solution for P_d,

$$P_\mathrm{d}(t) = P_0 \exp(-\mathrm{i}\omega t) \ . \tag{2.100}$$

Inserting it into Eq. (2.98) leads to

$$\left(-\omega^2 \tau'^2 - \mathrm{i}\omega\tau + 1\right) P_0 = \varepsilon_0 \chi_\mathrm{d} E_0 \tag{2.101}$$

and, thus, to the following expression for the frequency-dependent distortional part of the dielectric susceptibility:

$$\frac{P_0}{E_0} = \varepsilon_0 \chi'_\mathrm{d}(\omega) + \mathrm{i}\varepsilon_0 \chi''_\mathrm{d}(\omega) \tag{2.102}$$

$$= \frac{\varepsilon_0 \chi_\mathrm{d} \left(1 - \omega^2 \tau'^2\right)}{\left(1 - \omega^2 \tau'^2\right)^2 + \omega^2 \tau^2} + \mathrm{i} \frac{\varepsilon_0 \chi_\mathrm{d} \omega \tau}{\left(1 - \omega^2 \tau'^2\right)^2 + \omega^2 \tau^2} \ . \tag{2.103}$$

In formulating this equation, the resonance curve associated with a single oscillation process of the molecular skeleton or of the electrons relative to the nucleus is considered; the total curve for all distortional polarisation processes corresponds to the sum of a large number of such contributions. The real part, for each individual contribution, has the form shown in Fig. 2.17, while the imaginary part is a bell-shaped curve with its maximum near the eigenfrequency and a width being given by τ'.

In Sect. 2.1, it was shown for the dynamic compliance that the imaginary part describes the loss process, i.e., the part of the work which is dissipated. The same is true for the polarisation induced by an electric field, and this regardless of whether the orientational or the distortional part is being concerned. The imaginary part of the dielectric susceptibility specifies always to what extent the energy of the electromagnetic field is dissipated when interacting with the material. Thus, $\chi''(\omega)$ represents the absorption spectrum of a sample.

The Local Field – The Clausius–Mosotti Equation. For liquids made up of polar molecules, i.e., molecules with a permanent dipole moment, we find all the different contributions to the polarisation. We consider now the question: What value for the dielectric constant ε would be measured in a capacitor under static conditions? Both the orientational and distortional part are proportional to the electric field strength E_{loc} at the location of the molecule – that which acts there to polarise the molecule – and we express this as

$$P_{\mathrm{or}} = \rho\beta_{\mathrm{or}}E_{\mathrm{loc}} \quad , \tag{2.104}$$

$$P_{\mathrm{d}} = \rho\beta_{\mathrm{d}}E_{\mathrm{loc}} \quad . \tag{2.105}$$

In addition to the particle density ρ, the equations contain the coefficients β_{or} and β_{d}. They are termed **polarisabilities**, and describe in an empirical way the reaction of an individual molecule to the electric field. The total polarisation is given by

$$P = \rho\beta E_{\mathrm{loc}} \quad , \tag{2.106}$$

where the polarisability β contains now the contributions from all mechanisms.

At first, it could be thought that the electric field in the capacitor, which is given by the voltage and the plate separation, acts directly on the molecule and is identical to E_{loc}. This is not, however, the case. Figure 2.19 shows the way one must proceed in order to determine the local electric field. Think about the selection of a particular 'on-molecule', placed in the centre of a sphere of mesoscopic size with a radius a. This opens up the possibility of explicitly considering the fields arising from the neighbouring molecules, which can be separated from the continuous charge distribution in the dielectric and on the capacitor plates. The figure illustrates that the local field can then be split up into four contributions:

$$E_{\mathrm{loc}} = E_0(\sigma_{\mathrm{P}}) + E_1(\sigma_{\mathrm{M}} = P) + E_{2z}(\sigma_{\mathrm{L}}) + E_{3z} \quad . \tag{2.107}$$

All fields are oriented in the same direction, which is here chosen to be z. E_0 is the homogeneous field which is generated by the charges on the capacitor plates, with the surface density being σ_{P}. A second homogeneous field, E_1, is due to the surface charges of the dielectric (charge density σ_{M}) directly at the plates. The two fields together, E_0 and E_1, which act against each other,

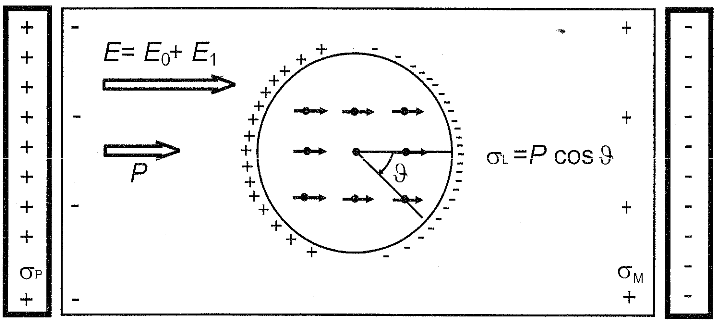

Fig. 2.19. The sources of the local electric field at the location of a molecule inside a block of material in a capacitor.

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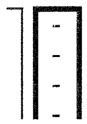

determine the average field strength E within the capacitor. As will become apparent from the following discussion, it is the contribution E_{2z} from the charges at the surface of the sphere which is decisive for the local field. This surface charge density, σ_{L}, is proportional to the polarisation and depends on the angle ϑ according to

$$\sigma_{\mathrm{L}} = P \cos\vartheta \quad . \tag{2.108}$$

The fourth and final contribution to consider comes from the fields arising from the molecular dipoles inside the sphere; these add up to give E_{3z}.

E_{2z} is referred to as the **Lorentz field** and can be calculated in the following way. An amount of charge $\mathrm{d}Q$ on the surface of the sphere gives rise to a contribution to the Lorentz field of magnitude

$$\mathrm{d}E_2 = \frac{1}{4\pi\varepsilon_0}\frac{\mathrm{d}Q}{a^2} \quad . \tag{2.109}$$

Only the component in the z direction has an effect, and its magnitude is given by

$$\mathrm{d}E_{2z} = \cos\vartheta \frac{1}{4\pi\varepsilon_0}\frac{\mathrm{d}Q}{a^2} \quad . \tag{2.110}$$

Using the spherical coordinates ϑ and φ, the integration over the charge distribution on the surface of the sphere can be directly carried out, and gives

$$\begin{aligned} E_2 &= \frac{1}{4\pi\varepsilon_0}\int\limits_{\varphi}\int\limits_{\vartheta}\cos\vartheta\frac{\mathrm{d}Q}{a^2} = \frac{1}{4\pi\varepsilon_0}\int\limits_{\varphi}\int\limits_{\vartheta}\frac{\cos\vartheta}{a^2}P\cos\vartheta\; a^2\sin\vartheta\mathrm{d}\vartheta\mathrm{d}\varphi \\ &= \frac{2\pi P}{4\pi\varepsilon_0}\int\limits_{\vartheta}\cos^2\vartheta\sin\vartheta\mathrm{d}\vartheta = \frac{1}{3\varepsilon_0}P \quad . \end{aligned} \tag{2.111}$$

This result shows that the Lorentz field E_2 is, first, oriented in the same direction as the external field E and, second, proportional to the polarisation.

It can easily be shown that the field E_{3z} due to the molecular dipoles within the sphere disappears in the case of isotropic liquids and also symmetric crystals, and this applies to the figure. If the molecule is located at the position $\boldsymbol{r}_j$ inside the region cut out by the sphere and carries a dipole moment $\boldsymbol{p}$, the strength of the field $\boldsymbol{E}_3$ at the centre of the sphere is given by

$$E_{3z} \propto \left\langle \sum_j \frac{3z_j^2 - r_j^2}{r_j^5} \right\rangle \quad . \tag{2.114}$$

Upon expanding the numerator, it follows that

$$E_{3z} \propto \left\langle \sum_j \frac{3z_j^2 - x_j^2 - y_j^2 - z_j^2}{r_j^5} \right\rangle = 0 \quad , \tag{2.115}$$

since the following is true from symmetry arguments:

$$\left\langle \sum_j \frac{x_j^2}{r_j^5} \right\rangle = \left\langle \sum_j \frac{y_j^2}{r_j^5} \right\rangle = \left\langle \sum_j \frac{z_j^2}{r_j^5} \right\rangle \quad . \tag{2.116}$$

Putting all the different contributions together yields the sought-after result: The local field which acts upon an individual molecule is a sum of the capacitor field E and the Lorentz field:

$$E_{\text{loc}} = E + \frac{1}{3\varepsilon_0} P \quad . \tag{2.117}$$

The polarisation can now be calculated by substituting Eq. (2.117) into Eq. (2.106):

$$P = \rho\beta E_{\text{loc}} = \rho\beta \left(E + \frac{1}{3\varepsilon_0} P \right) \quad . \tag{2.118}$$

P appears on both sides of this equation, which indicates that a feedback mechanism is acting. The following expression is obtained for the dielectric constant

$$\frac{P}{E} = \frac{\rho\beta}{1 - \rho\beta/3\varepsilon_0} = \varepsilon_0(\varepsilon - 1) \quad . \tag{2.119}$$

Solving for the polarisability gives

$$\frac{1}{3\varepsilon_0} \rho\beta = \frac{\varepsilon - 1}{\varepsilon + 2} \quad . \tag{2.120}$$

The above discussion has been restricted to monomolecular liquids; in the general case, different types of molecules with densities ρ_j and polarisabilities β_j can exist, and Eq. (2.120) then becomes

$$\frac{1}{3\varepsilon_0} \sum_j \rho_j \beta_j = \frac{\varepsilon - 1}{\varepsilon + 2} \quad . \tag{2.121}$$

This is referred to as the **Clausius–Mosotti equation.**

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~~The fourth example is of a completely different nature and deals with the phase behaviour of binary fluid polymer mixtures. If the composition of the mixture is suitably chosen, a transition from the mixed homogeneous state into a two-phase structure occurs in a continuous fashion. The difference in the composition of the two phases which form on crossing a critical temperature is initially infinitely small and then gradually grows. It is this difference which assumes, in this case, the role of the order parameter. Order is generated through the separation of the homogenous mixture into two different phases.~~

~~By means of these examples, we will recognise the common features in second-order phase transitions, or as is also said **critical phase transitions**; the changes in properties near the transition temperature occur in a characteristic manner. Second-order phase transitions are theoretically very well understood. A large proportion of observations can be described using a simple thermodynamic theory which was developed by Landau. It will be described and correspondingly applied.~~

3.1 The Ferroelectric State

Equation (2.119), which was obtained in the derivation of the Clausius–Mosotti equation, shows immediately that a polarisation of matter can stabilise itself and gives the criterion for this. The dielectric susceptibility diverges for

$$1 = \frac{\rho\beta}{3\varepsilon_0} \ . \tag{3.1}$$

A divergence means that the external field which must be applied in order to generate a definite polarisation becomes ever smaller and finally disappears. The basis of this phenomenon is the Lorentz field which is in the same direction as the external field and always amplifies it. For the condition described by Eq. (3.1), it is exactly strong enough for a self-stabilisation. This follows immediately from the equation

$$P = \rho\beta E_{2z} = \rho\beta \frac{P}{3\varepsilon_0} \ . \tag{3.2}$$

The condition for the transition into the ferroelectric state is thus solely a sufficiently high polarisability or atom density in the solid.

3.1.1 Transition Scenarios

Figure 3.1 shows as an example the structural changes which arise for $BaTiO_3$ – a crystal with the perovskite structure – upon the transition into

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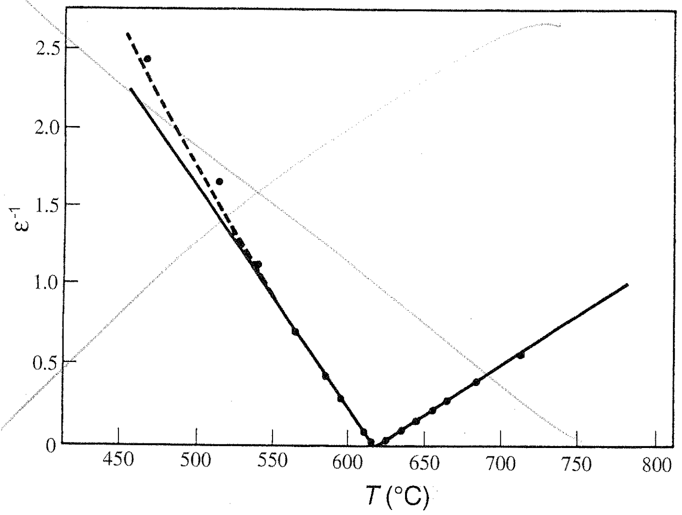

Fig. 3.4. $LiTaO_3$ in the region around the Curie temperature: Temperature dependence of the (inverse) dielectric constant (from Lines [20]).

$$\frac{1}{3\varepsilon_0}\sum_j \rho_j\beta_j = 1 - c(T - T_c) \quad . \tag{3.4}$$

This starting equation suggests itself. Above T_c, the expression on the left-hand side becomes less than the critical value of one and this is expressed here in the simplest possible way, by using a linear term. Using now the Clausius–Mosotti equation, we obtain

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3\varepsilon_0}\sum_j \rho_j\beta_j = 1 - c(T - T_c) \quad . \tag{3.5}$$

It, thus, follows that

$$-\frac{3}{\varepsilon + 2} = -c(T - T_c) \tag{3.6}$$

and, therefore,

$$\varepsilon + 2 \propto \frac{1}{T - T_c} \quad . \tag{3.7}$$

For ε, $\chi \gg 1$ this becomes

$$\varepsilon \approx \chi \propto \frac{1}{T - T_c} \quad . \tag{3.8}$$

This is exactly the behaviour shown in Fig. 3.4 by the dielectric constant for $T > T_c$.

For the first example of $BaTiO_3$, a finite spontaneous polarisation immediately establishes itself at the Curie temperature, which must of course be

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Orientational Polarisability. The orientation of the dipoles in a polar liquid in a static electric field is incomplete because of thermal rotational motion. The higher the temperature, the lower the observed degree of orientation. The form of this dependence can be directly calculated. First, it is known that the potential energy u of a molecule with a permanent dipole p_0 in an external field of strength E_loc depends on the included angle ϑ according to

$$u = -p_0 E_\mathrm{loc} \cos\vartheta \quad . \tag{2.122}$$

The orientational distribution function follows from Boltzmann statistics, as

$$w \sin\vartheta \mathrm{d}\varphi \mathrm{d}\vartheta \propto \exp -\frac{u}{k_\mathrm{B}T} \sin\vartheta \mathrm{d}\varphi \mathrm{d}\vartheta = \exp \frac{p_0 E_\mathrm{loc} \cos\vartheta}{k_\mathrm{B}T} \sin\vartheta \mathrm{d}\varphi \mathrm{d}\vartheta \tag{2.123}$$

($w \sin\vartheta \mathrm{d}\varphi \mathrm{d}\vartheta$ is the fraction of dipoles in the angular interval $\mathrm{d}\varphi \mathrm{d}\vartheta$). From this, we obtain the orientational part of the polarisation P_or as

$$P_\mathrm{or} = \rho p_0 \langle \cos\vartheta \rangle = \rho p_0 \frac{1}{\mathcal{Z}} \int\limits_0^\pi \cos\vartheta \exp \frac{p_0 E_\mathrm{loc} \cos\vartheta}{k_\mathrm{B}T} 2\pi \sin\vartheta \mathrm{d}\vartheta \tag{2.124}$$

(as always, ρ denotes the particle density). The partition function $\mathcal{Z}$ is introduced for normalisation purposes; it is a function of the variable

$$x = \frac{p_0 E_\mathrm{loc}}{k_\mathrm{B}T} \quad , \tag{2.125}$$

and can be calculated:

$$\begin{aligned} \mathcal{Z}(x) &= \int\limits_0^\pi \exp(x \cos\vartheta) 2\pi \sin\vartheta \mathrm{d}\vartheta \\ &= \frac{2\pi}{x} [\exp x - \exp(-x)] \quad . \end{aligned} \tag{2.126}$$

It can be recognised that P_or is given by

$$P_\mathrm{or} = \rho p_0 \frac{1}{\mathcal{Z}} \frac{\mathrm{d}\mathcal{Z}}{\mathrm{d}x} \quad . \tag{2.127}$$

To obtain the orientational part of the polarisability, β_or, expand $\mathcal{Z}$ as a power series and keep only the lowest order terms

$$\mathcal{Z} = 4\pi + \frac{2\pi x^2}{3} + \dots \quad . \tag{2.128}$$

This leads to

$$P_\mathrm{or} \approx \rho p_0 \frac{x}{3} = \rho \frac{p_0^2}{3 k_\mathrm{B} T} E_\mathrm{loc} \tag{2.129}$$

and, thus, to the following expression for β_{or}

$$\beta_{\mathrm{or}} = \frac{p_0^2}{3k_{\mathrm{B}}T} \quad . \tag{2.130}$$

The total polarisability of a polar liquid is a sum of the distortional part β_{d} and β_{or}:

$$\beta = \beta_{\mathrm{d}} + \frac{p_0^2}{3k_{\mathrm{B}}T} \quad . \tag{2.131}$$

This result shows that temperature dependent measurements using the Clausius–Mosotti equation (2.121) provide a means of determining β_{d} and p_0.

~~2.2.3 The Piezo Effect~~

~~The subject of the first section of this chapter was the deformation which results from the application of a mechanical field. The second section then discussed the polarisation which arises due to an electric field. There are some crystals, where cross correlations are observed in the sense that, first, mechanical stresses cause not only deformations but also generate polarisation, and, second, electric fields do not simply polarise the sample but also cause deformations at the same time. This is referred to as the **Piezo effect**. The Piezo effect is of technological importance and has been broadly applied. The most important material in this respect is quartz. Small single crystals of quartz serve as ultra-sound sources, stabilisers in oscillating circuits – in this application, they are found in almost all watches, and transmitting and receiving devices – or as positioning elements in situations where a precision in the nm or Å range is required. The construction of an atomic force microscope, in which quartz crystals are used to shift the cantilever and to make it oscillate, would be unthinkable without the piezoelectric properties of quartz. In addition to quartz, poly(vinylidenefluoride) is becoming increasingly more important. If a foil made from this polymer is stretched at high temperatures, where the chains are sufficiently mobile, in an electric field, and then cooled rapidly to room temperature, the electric dipoles carried by the CF_2 groups retain a permanent preferred direction. The so-achieved permanently polarised foil shows a piezoelectric effect which surpasses that of quartz. In order to use it, thin-layer electrodes are placed on both sides of the foil. Upon applying a voltage, changes in the thickness and also the length and width are achieved. As an example, this allows the construction of spherical loud speakers.~~

~~In order to describe how piezoelectric materials function, it is necessary to extend Eqs. (2.87) and (2.4). Equation (2.87) is replaced by~~

$$P = \varepsilon_0 \chi E + d_1 \sigma_{zz} \tag{2.132}$$

Problem 2

a) The order parameter is a quantity that contains all the information about the symmetry breaking taking place at the phase transition.

$O.P. = 0$ for $T > T_c$

$O.P \neq 0$ for $T < T_c$

O.P needs to be chosen as to contain all the symmetries broken as $T < T_c$.

System	Order Parameter	External field conjugate to order parameter
Ferroelectric	Polarization P	Electric field E
Ferromagnetic	Magnetization M	Magnetic field H
Ferroelastic	Strain γ	Stress σ
Nematic	$S_2 = \langle \frac{3\cos^2\theta - 1}{2} \rangle$	System dependent
Dipolar nematic	$S_1 = \langle \cos\theta \rangle$	System dependent (ex. E or H)
Superconductor	Wavefunction $\lvert\psi\rvert$	—
⋮		

Problem 2 continued

b)

Case 1: Page 133-134 in Strobl ⇒ 2nd order

$$g = g_0 - \eta x + b(T-T_c)\eta^2 + C_4\eta^4$$

Case 2: Page 135 in Strobl ⇒ 1st order

$C_6 > 0$

$$g = g_0 - \eta x + b(T-T_c)\eta^2 - C_4^*\eta^4 + C_6\eta^6$$

$C_4^* = -C_4 > 0$

Case 3: Page 144-146 in Strobl ⇒ 1st order

$C_4 > 0$

$$g = g_0 - \eta x + b(T-T_c)\eta^2 - C_3^*\eta^3 + C_4\eta^4$$

$C_3^* = -C_3 > 0$

c) Page 133-134 in Strobl.

Relation to Clausius-Mosotti relation:
Page 128-131 in Strobl.
i.e. same as in
question 1 b)

associated with a jump to some distinct displacement of the two parts of the lattice. The other two examples show that this is not always the case. For $SrTiO_3$ and $LiTaO_3$, the polarisation sets in continuously at the Curie temperature, beginning with $P_s = 0$.

3.1.2 The Landau Theory of Critical and Nearly-Critical Phase Transitions

Figure 3.4 shows that a divergence of the dielectric susceptibility upon approaching the Curie temperature is also observed for the low temperature side, i.e., in the ferroelectric phase. Landau presented a way by which this behaviour and also other properties of ferroelectrics can be understood using a simple thermodynamic theory. The polarisation is the variable which controls the phase transition; P disappears above T_c, while below T_c, P begins to increase. The value of P represents, for every temperature, an equilibrium value in the sense of thermodynamics and the equilibrium condition can be directly formulated. The requirement is a knowledge of the Helmholtz free energy as a function of the polarisation and the temperature, i.e., of the expression

$$f(P,T) \quad .$$

The equilibrium value of the polarisation at a particular temperature then follows from the minimum condition

$$\left.\frac{\partial f}{\partial P}\right|_{\mathrm{eq}} = 0 \quad . \tag{3.9}$$

Landau suggested that the Helmholtz free energy density in the region of the Curie temperature be expressed as a series expansion:

$$f = f_0 + \sum_j c_j(T) P^j \quad . \tag{3.10}$$

Since the following must of course be valid

$$f(P) = f(-P) \quad , \tag{3.11}$$

only even-order terms appear in the expansion:

$$f = f_0 + c_2 P^2 + c_4 P^4 + c_6 P^6 + \ldots \quad . \tag{3.12}$$

In the discussion of the transverse-optical mode, the force constant a was introduced to describe the restoring forces, which become active upon a relative shift of the two parts of the lattice. This force constant determines the value of the second-order term in the series expansion for the Helmholtz free energy density:

$$\frac{\partial^2 f}{\partial P^2}(P = 0) = 2c_2 \propto \mathrm{a} \quad . \tag{3.13}$$

Since a becomes zero at the Curie temperature and then increases linearly above it the following can be written:

$$c_2 = b(T - T_c) \quad , \quad \text{with} \quad b > 0 \quad . \tag{3.14}$$

Limiting the expansion to the next term then leads to the following expression for the Helmholtz free energy density

$$f = f_0 + b(T - T_c)P^2 + c_4 P^4 \quad . \tag{3.15}$$

Figure 3.5 shows this dependence for a fixed, positive coefficient c_4 for three different temperatures, namely one above T_c, one at the Curie temperature and one below T_c. The consequences are immediately recognisable: Above the Curie temperature, the equilibrium is, as observed, at $P = 0$, while below T_c, a non-vanishing value for P establishes itself – this is likewise in agreement with what is observed. The latter corresponds to the permanent polarisation P_s.

Evaluating the expression yields the temperature dependence of the polarisation below T_c. The minimum condition for the Helmholtz free energy leads to:

$$\frac{\partial f}{\partial P} = 0 = 2b(T - T_c)P + 4c_4 P^3 \quad . \tag{3.16}$$

It follows that the equilibrium value of the permanent polarisation is given by

$$P_{\text{eq}}^2 = P_{\text{s}}^2 = \frac{b(T_c - T)}{2c_4} \quad , \tag{3.17}$$

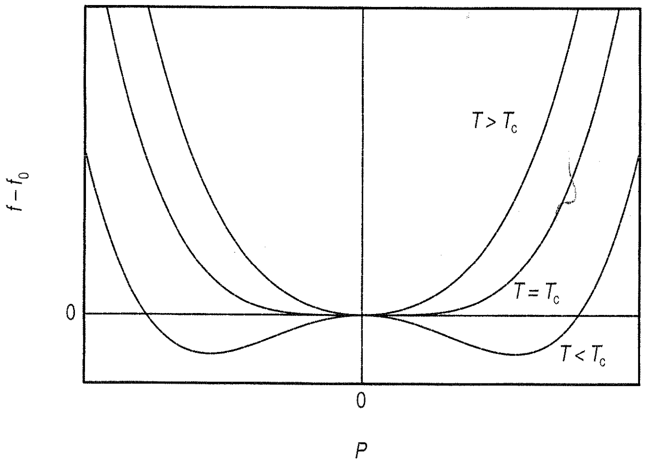

Fig. 3.5. The Landau expansion for the Helmholtz free energy density at the transition into the ferroelectric phase ($T = T_c$) as well as for temperatures above and

i.e.,

$$|P_{\mathrm{s}}| \propto (T_{\mathrm{c}} - T)^{1/2} \quad . \tag{3.18}$$

Hence, the polarisation which arises obeys a square root law.

For the calculation of the dielectric susceptibility, equilibrium states are sought which arise in the presence of a given electric field. These are also determined by a minimum condition, but this time with respect to the Gibbs free energy. We choose the reduced form $\hat{g}$, which is given by Eq. (A.11) in Appendix A:

$$\hat{g} = f - EP = f_0 + b(T - T_{\mathrm{c}})P^2 + c_4 P^4 - EP \quad . \tag{3.19}$$

The minimum condition

$$\frac{\partial \hat{g}}{\partial P} = 0 = -E + 2b(T - T_{\mathrm{c}})P + 4c_4 P^3 \tag{3.20}$$

leads to

$$\frac{1}{\varepsilon_0 \chi} = \frac{\mathrm{d}E}{\mathrm{d}P}(E = 0) = 2b(T - T_{\mathrm{c}}) + 12 c_4 P_{\mathrm{eq}}^2 \quad , \tag{3.21}$$

where P_{eq} denotes the equilibrium polarisation in the absence of an electric field. Two cases can now be distinguished. For $T > T_{\mathrm{c}}$, there is $P_{\mathrm{eq}} = 0$, which leads to

$$\varepsilon_0 \chi = \frac{1}{2b(T - T_{\mathrm{c}})} \quad . \tag{3.22}$$

This result was already obtained, via a different route, in Eq. (3.8). The Landau expansion yields now, though, an additional expression for the dielectric susceptibility in the ferroelectric phase, i.e., for $T < T_{\mathrm{c}}$. Using the value for P_{eq} given by Eq. (3.17) gives

$$\frac{1}{\varepsilon_0 \chi} = 2b(T - T_{\mathrm{c}}) + 12 \frac{b(T_{\mathrm{c}} - T)}{2} \tag{3.23}$$

and thus

$$\varepsilon_0 \chi = \frac{1}{4b(T_{\mathrm{c}} - T)} \quad . \tag{3.24}$$

It can be seen that the expressions for the dielectric susceptibilities above and below the Curie temperature differ by a factor of 2. This agrees with the experiment as is apparent from a look at Fig. 3.4.

The square root law for the emergence of a polarisation upon going below the Curie temperature, as predicted by Landau's treatment, describes second-order phase transitions. The law is obviously not applicable to the transition of $\mathrm{BaTiO_3}$ into the ferroelectric phase, where a finite polarisation is immediately established. However, a change of the parameters in the power series expansion for the Helmholtz free energy also allows this transition to be described in a qualitatively correct fashion. This is achieved when the following form is chosen:

$$f - f_0 = b(T - T^*)P^2 + c_4P^4 + c_6P^6 \quad . \tag{3.25}$$

T^* is a temperature which lies somewhat below the temperature T_c of the phase transition. If, in addition,

$$c_4 < 0 \qquad \text{and} \qquad c_6 > 0$$

are selected, plots of the Helmholtz free energy as a function of P have the forms shown in Fig. 3.6. The consequences here are also immediately recognisable. For $T > T_c$, the equilibrium value of the polarisation is zero, while for $T < T_c$, the polarisation has a finite value, which is determined by the minimum. The phase transition occurs at the Curie temperature T_c. As is evident, a non-vanishing polarisation arises immediately at the phase transition. The non-polar and ferroelectric phase co-exist at this point; both have the same Helmholtz free energy.

It can be easily realised that the susceptibility is generally linked to the curvature of $f(P)$ at the minimum, i.e., that

$$\varepsilon_0\chi \propto \left(\frac{\partial^2 f}{\partial P^2}(P_{\mathrm{eq}})\right)^{-1} \tag{3.26}$$

is valid. A consideration of the form of the curves in Fig. 3.6 reveals that there is now no longer a divergence. For $BaTiO_3$, the transition into the ferroelectric phase is associated with a jump-like change and thus corresponds to a first-order phase transition. The course of the transition deviates, however, from the normal case. The distinctive feature is that the phase transition is

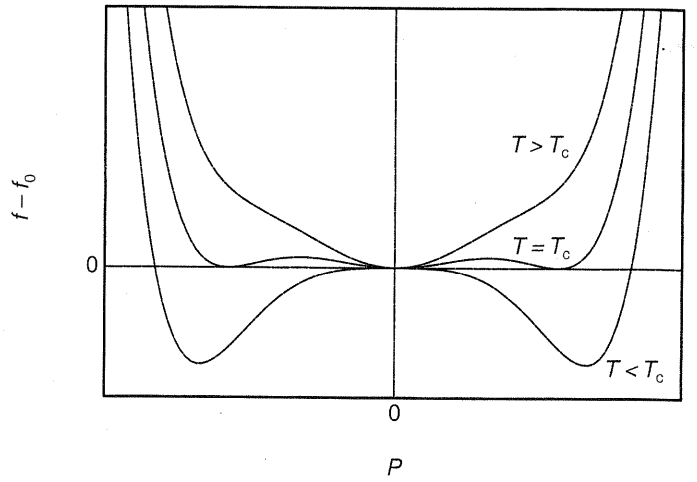

Fig. 3.6. The Landau expansion of the Helmholtz free energy density at the transition into the ferroelectric phase (T_c) as well as for temperatures above and below T_c.

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dependent interaction forces favour a parallel arrangement of the rod-like molecules in a nematogen material and, thus, create a molecular field which can maintain itself. The spontaneous self-organisation begins at the transition from the isotropic liquid into the nematic phase. The order parameter here is the variable S_2 which characterises the degree of orientation.

The fourth example is of a completely different nature and deals with the phase behaviour of binary fluid polymer mixtures. If the composition of the mixture is suitably chosen, a transition from the mixed homogeneous state into a two-phase structure occurs in a continuous fashion. The difference in the composition of the two phases which form on crossing a critical temperature is initially infinitely small and then gradually grows. It is this difference which assumes, in this case, the role of the order parameter. Order is generated through the separation of the homogenous mixture into two different phases.

By means of these examples, we will recognise the common features in second-order phase transitions, or as is also said **critical phase transitions**; the changes in properties near the transition temperature occur in a characteristic manner. Second-order phase transitions are theoretically very well understood. A large proportion of observations can be described using a simple thermodynamic theory which was developed by Landau. It will be described and correspondingly applied.

3.1 The Ferroelectric State

Equation (2.119), which was obtained in the derivation of the Clausius–Mosotti equation, shows immediately that a polarisation of matter can stabilise itself and gives the criterion for this. The dielectric susceptibility diverges for

$$1 = \frac{\rho\beta}{3\varepsilon_0} \quad . \tag{3.1}$$

A divergence means that the external field which must be applied in order to generate a definite polarisation becomes ever smaller and finally disappears. The basis of this phenomenon is the Lorentz field which is in the same direction as the external field and always amplifies it. For the condition described by Eq. (3.1), it is exactly strong enough for a self-stabilisation. This follows immediately from the equation

$$P = \rho\beta E_{2z} = \rho\beta\frac{P}{3\varepsilon_0} \quad . \tag{3.2}$$

The condition for the transition into the ferroelectric state is thus solely a sufficiently high polarisability or atom density in the solid.

3.1.1 Transition Scenarios

Figure 3.1 shows as an example the structural changes which arise for $BaTiO_3$ – a crystal with the perovskite structure – upon the transition into

Problem 2 continued

c) continued.

$T > T_c \Rightarrow \eta_{eq} = 0$

$\Rightarrow g = g_0$

$T < T_c \Rightarrow \eta_{eq}^2 = \frac{b}{2c_4}(T_c - T)$

$\Rightarrow g = g_0 - \frac{b^2}{2c_4}(T_c - T)^2 + \frac{b^2}{4c_4}(T_c - T)^2$

$= g_0 - \frac{b^2}{4c_4}(T_c - T)^2$

$\Rightarrow$

$T > T_c \quad C_V = -T \frac{d^2 g_0}{dT^2} = \text{const}$

$T < T_c \quad C_V = -T \frac{d^2 g}{dT^2}$

$= C_V\big|_{T>T_c} + T \frac{1}{2} \frac{b^2}{c_4}$

d) Page 144-146 in Strobl

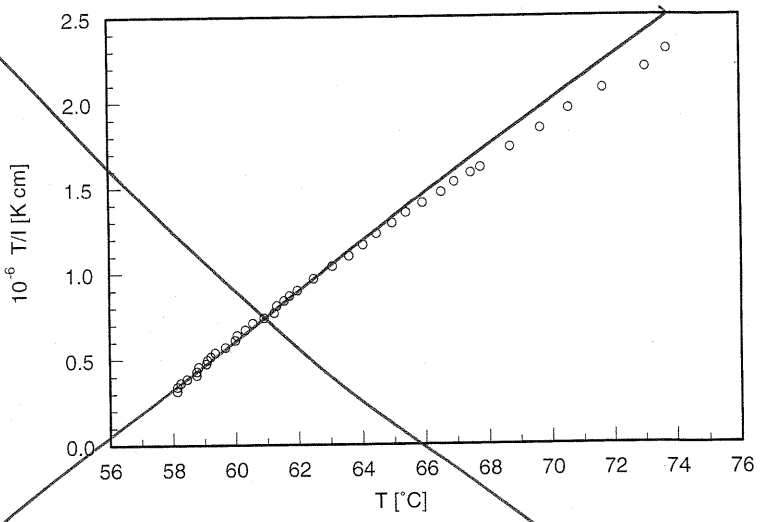


Fig. 3.13. PCH7: The increase in intensity of depolarised scattered light upon approaching the temperature T_{ni} of the transition into the nematic phase.

3.3.1 The Landau–de Gennes Expansion

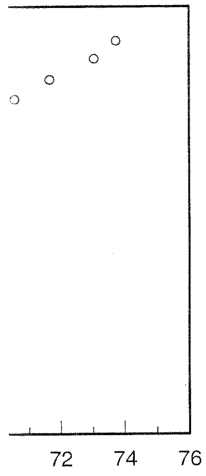
What would be the form of a Landau expansion which describes the isotropic-nematic phase transition in a qualitatively correct fashion? The answer to this question was given by de Gennes. In order to describe the Helmholtz free energy density as a function of the nematic order parameter and the temperature

$$f(S_2, T)$$

the following power series expansion is to be used

$$f - f_0 = b(T - T^*)S_2^2 - c_3 S_2^3 + c_4 S_2^4 \quad . \tag{3.40}$$

A difference as compared to the power series expansions for ferroelectrics and ferromagnetics is the inclusion of a third-order term, which appears because the symmetry has changed. While previously a sign reversal of the order parameter left the Helmholtz free energy unchanged, there is a change for a nematic liquid crystal. This becomes immediately clear upon considering an example. $S_2 = -1/2$ corresponds to an orientation distribution, where all molecules have their long axes perpendicular to the director, with their orientations being uniformly distributed in this plane. By comparison, the structure is completely different for an order parameter $S_2 = +1/2$: Here, there is a wide distribution with a maximum in the director direction. Under these conditions, it is clear that a third-order term must be included in the Landau expansion for the Helmholtz free energy.



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The consequences are shown in Fig. 3.14, which shows the dependence of the Helmholtz free energy on S_2 for three temperatures. The middle curve corresponds to the transition temperature, where the isotropic liquid and a nematic phase with a well-defined order parameter co-exist. At higher and lower temperatures, there is of course only the isotropic state and only the nematic state, respectively.

The Landau expansion in Eq. (3.40) can be evaluated to determine the position of the transition point. The following applies for the equilibrium value of S_2:

$$\frac{\mathrm{d}f}{\mathrm{d}S_2} = 0 = 2b(T - T^*)S_2 - 3c_3S_2^2 + 4c_4S_2^3 \quad . \tag{3.41}$$

The co-existence condition is given by

$$f(S_2 = 0) - f_0 = f(S_2 = S_2(T_{\mathrm{ni}})) - f_0 = 0 \quad , \tag{3.42}$$

which means that

$$0 = b(T - T^*)S_2(T_{\mathrm{ni}})^2 - c_3S_2(T_{\mathrm{ni}})^3 + c_4S_2(T_{\mathrm{ni}})^4 \quad . \tag{3.43}$$

Combining Eqs. (3.43) and (3.41) leads immediately to an expression for the order parameter at the phase transition:

$$S_2(T_{\mathrm{ni}}) = \frac{c_3}{2c_4} \quad . \tag{3.44}$$

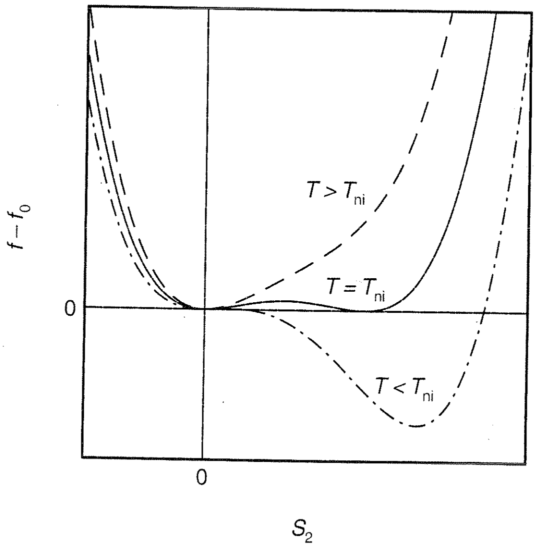

Fig. 3.14. The Landau–de Gennes expansion for the Helmholtz free energy density of a nematic liquid crystal at the clearing point T_{ni} as well as for temperatures where only the isotropic ($T > T_{\mathrm{ni}}$) or only the nematic phase ($T < T_{\mathrm{ni}}$) exists.

The situation at the temperature T^* is given by

$$T_{\mathrm{ni}} - T^* = \frac{c_3^2}{4bc_4} \quad . \tag{3.45}$$

Finally, it follows that the temperature dependence of the order parameter in the nematic phase is described by

$$S_2 = \frac{3c_3}{8c_4} + \left(\left(\frac{3c_3}{4c_4} \right)^2 - \frac{2b}{4c_4}(T - T^*) \right)^{1/2} \quad . \tag{3.46}$$

As a thermodynamic theory, the Landau approach works with phenomenological coefficients. If experimental data exist, these can be determined by a fitting procedure. Further experimental results, for example, the dependence of S_2 on T, can then be predicted.

3.3.2 The Maier–Saupe Theory

A specific theory allows the order parameter at the transition temperature to be calculated. It was developed by Maier and Saupe in 1958 and is briefly described here. The theory deals directly with the self-stabilisation in the nematic phase. The starting point is the following expression for the molecular field which acts to orientate the rod-like molecules:

$$u(\vartheta) = -u_0 S_2 \frac{3\cos^2\vartheta - 1}{2} \quad . \tag{3.47}$$

$u(\vartheta)$ is the 'nematic potential' appearing in this phase, which each molecule experiences upon a rotation. The angle $\vartheta = 0$ corresponds to the director direction. The chosen form of the potential ensures that the positions ϑ and 180°-ϑ are equivalent, as is required. The decisive step is the inclusion of the order parameter S_2 in the description of the strength of the molecular field. The chosen form means that it becomes ever more difficult for a molecule to deviate from the director direction, the higher the order parameter in the nematic phase is. In addition, the expression contains a variable which is material dependent, namely the coefficient u_0.

The orientation distribution function $w(\vartheta, \varphi)$ of the molecules can be calculated, for a given potential $u(\vartheta)$, using Boltzmann statistics. It is given as

$$w(\vartheta, \varphi) = \frac{1}{\mathcal{Z}} \exp\left(\frac{u_0 S_2}{k_{\mathrm{B}}T} \cdot \frac{3\cos^2\vartheta - 1}{2} \right) \tag{3.48}$$

or

$$w(\vartheta, \varphi) = \frac{1}{\mathcal{Z}'} \exp\left(\frac{3u_0 S_2}{2k_{\mathrm{B}}T} \cos^2\vartheta \right) \quad . \tag{3.49}$$

We introduce a new variable,

Problem 3

a) The basic assumption underlying Eq. (2) is that diffusive motion occur in uncorrelated steps.

Page 291 in Strobl.

Page 292 in Strobl.

b)

Page 37 - 40 in Strobl

c) Page 309 - 311 in Strobl:

Short version here:

The time it takes for a polymer chain to "leave a tube" and "enter a new one" is the disentanglement time $= \tau_d$.

Mean square displacement for linear diffusion of a chain:

$$\langle r^2 \rangle \approx 6 D_s \Delta t \Rightarrow \tau_D \sim \frac{R_0^2}{6 D_S}$$

where $R_0 \sim$ length of the chain.

Problem 3 continued

c) continued

The Einstein equation for the self diffusion constant

$$D_S = \frac{k_B T}{\zeta} \sim \frac{k_B T}{\zeta_0 R_0}$$

where ζ_0 is the friction coefficient per unit length of the chain

$$\Rightarrow \tau_d \sim \frac{R_0^2}{6 D_s} \sim \frac{\zeta_0}{6 k T} R_0^3 \underline{\propto M^3}$$

sine $R_0 \propto M$ for a chain.

5.2 Liquids: Diffusive Motion

Propagating wave-like excitations are also found in liquids in the form of sound waves. In contrast to the case of crystals, it is not to be expected that these waves will continue to exist into the meso- and microscopic region. On these length-scales, liquids lose their macroscopic homogeneous structure. For decreasing wavelengths, this leads, first of all, to an increasing scattering, with an associated reduction in the lifetime of the sound waves, and finally to their complete disappearance. As was mentioned in the introduction to this chapter, only local vibrations of individual molecules in the environment of their neighbours appear in liquids on the microscopic scale, and these are only short-lived because of the constant changes. A qualitatively new type of dynamics is encountered here, namely the diffusion of molecules. This makes the long-range transport of material possible, something which is not the case for crystals. How this can be described will be discussed in the following.

5.2.1 Diffusion Coefficients

The trajectories followed by individual molecules in a liquid or by colloids in solution are subject to statistical laws. As is always the case for processes which do not occur in a deterministic fashion, but rather where there is a large number of different possibilities by which the process may advance, it is necessary to introduce a suitable distribution function in order to describe the time-dependent development. This is, for the case of diffusive motion of individual particles, the **time-dependent auto-correlation function** $g_1(\boldsymbol{r},t)$. It is defined such that

$$g_1(\boldsymbol{r},t)\mathrm{d}^3\boldsymbol{r}$$

describes the probability that a particle moves within a time t from its starting point into a volume element $\mathrm{d}^3\boldsymbol{r}$ which is $\boldsymbol{r}$ away. g_1 is a probability distribution and, therefore, must be normalised:

$$\int g_1(\boldsymbol{r},t)\mathrm{d}^3\boldsymbol{r} = 1 \quad . \tag{5.140}$$

Einstein presented a differential equation by which $g_1(\boldsymbol{r},t))$ can be calculated. The starting point is equation

$$g_1(\boldsymbol{r},t+\Delta t) = \int g_1(\boldsymbol{r}-\boldsymbol{r}',t)g_1(\boldsymbol{r}',\Delta t)\mathrm{d}^3\boldsymbol{r}' \quad . \tag{5.141}$$

The displacement over a distance $\boldsymbol{r}$ within a time $t+\Delta t$ is broken up into two steps which follow one another. The first step, which is completed during a time t, achieves a displacement of $\boldsymbol{r}-\boldsymbol{r}'$, while a second step, in the remaining time Δt, brings the molecule to the point $\boldsymbol{r}$. The special feature of this integral notation is that the probability that these

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two steps follow each other is given by the product of the associated individual probabilities, with an integration over all possible step combinations being then performed. This product notation expresses exactly the basic property of all diffusive motions, namely that they occur in steps, between which there is no correlation at all. The total probability can only be written as the product of the individual probabilities if this is the case.

The integral equation, Eq. (5.141), can be transformed into a differential equation. Carrying out a series expansion with respect to time on the left-hand side and with respect to the position on the right-hand side leads to the following equation

$$g_1(\boldsymbol{r},t)+\Delta t\frac{\partial g_1}{\partial t}\approx\int\Big[g_1(\boldsymbol{r},t)-\sum_i r'_i\frac{\partial g_1}{\partial r_i}(\boldsymbol{r},t)+\frac{1}{2}\sum_{ij}r'_ir'_j\frac{\partial^2 g_1}{\partial r_i\partial r_j}(\boldsymbol{r},t)\Big]g_1(\boldsymbol{r}',\Delta t)\mathrm{d}^3\boldsymbol{r}' . \qquad (5.142)$$

Upon performing the integration on the right-hand side, it is found that several terms disappear, since from symmetry reasons

$$\int g_1(\boldsymbol{r}',\Delta t)r'_i\mathrm{d}^3\boldsymbol{r}'=0 \qquad (5.143)$$

and also

$$\int g_1(\boldsymbol{r}',\Delta t)r'_ir'_{j\neq i}\mathrm{d}^3\boldsymbol{r}'=0 \ . \qquad (5.144)$$

$g_1(\boldsymbol{r},t)$ appears on both sides and can thus be removed. The only term which remains on the right-hand side is

$$\int g_1(\boldsymbol{r}',\Delta t)r'^2_i\mathrm{d}^3\boldsymbol{r}'=\frac{1}{3}\int g_1(\boldsymbol{r}',\Delta t)|\boldsymbol{r}'|^2\mathrm{d}^3\boldsymbol{r}' \qquad (5.145)$$

such that we obtain

$$\Delta t\frac{\partial g_1}{\partial t}=\nabla^2 g_1(\boldsymbol{r},t)\cdot\frac{1}{6}\int g_1(\boldsymbol{r}',\Delta t)|\boldsymbol{r}'|^2\mathrm{d}^3\boldsymbol{r}' \ . \qquad (5.146)$$

This equation only contains a single parameter, namely the quantity

$$D_\mathrm{s}=\frac{1}{6\Delta t}\int g_1(\boldsymbol{r}',\Delta t)|\boldsymbol{r}'|^2\mathrm{d}^3\boldsymbol{r}'=\frac{\langle|\boldsymbol{r}'|^2\rangle}{6\Delta t} \ , \qquad (5.147)$$

which is termed the 'self-diffusion coefficient'. Using D_s, we arrive at a differential equation for the auto-correlation function $g_1(\boldsymbol{r},t)$:

$$\frac{\partial g_1}{\partial t}(\boldsymbol{r},t)=D_\mathrm{s}\nabla^2 g_1(\boldsymbol{r},t) \ . \qquad (5.148)$$

Boltzmann distribution. For an energy difference $\Delta\tilde{u}_{\mathrm{tg}} \simeq 2 - 3\ \mathrm{kJmol}^{-1}$, the population probability for the two local gauche minima at room temperature is given by

$$w_{\mathrm{g}} = \frac{2\exp(-\Delta\tilde{u}_{\mathrm{tg}}/\tilde{R}T)}{1 + 2\exp(-\Delta\tilde{u}_{\mathrm{tg}}/\tilde{R}T)} \simeq 0.5 \tag{1.71}$$

($\tilde{R}$ is the universal gas constant). This equation assumes that each C-C bond can arrange itself independent of the others. Although this is not really true, Eq. (1.71) does provide a reasonable estimate for w_{g}.

In the liquid state, i.e., in a polyethylene melt or the melt of some other polymer, all the different rotational isomeric states can be occupied. Virtually all the chains exist in forms which can be referred to as coil-like. As they are densely packed they must interpenetrate each other. A polymer melt thus represents a dense packing of entangled coiled chains.

1.4.2 Polymer Melts

In a polymer melt, the chains take up all possible conformations in a statistical distribution. The exact description of this distribution seems at first a very difficult problem. It could be thought that it is necessary, for each polymer, to consider its particular chemical structure, which then determines the distribution over the rotational isomeric states for the bonds comprising the polymer backbone. All details such as the position of the local minima as well as bond lengths and bond angles which are important for structural properties would then have to be considered. This would mean that each polymer would amount to a new problem to be solved. The situation is actually much simpler. For many polymer properties, the behaviour in the Å range is not important; it is the structure and dynamics over length-scales greater than 10 nm which are decisive. As is easily appreciated, differences between different polymer chains disappear over such mesoscopic length scales. Figure 1.26 shows how a typical polymer coil would then appear: All details of the chemical structure have disappeared and only a worm-like object is observed.

The question arises as to the extent to which a polymer molecule extends itself in a melt, i.e., we ask what is the diameter of the sphere which is just big enough to encompass a coiled polymer molecule? The latter corresponds, for a large number of polymer conformations, to the case where both chain ends, i.e., the two most distant structural building blocks along the chain, lay within the sphere. The average distance between the chain ends can be estimated by calculating the square root of the mean squared chain-end distance $\langle R^2 \rangle$. The distance vector between the chain ends, $\boldsymbol{R}$, is shown in Fig. 1.26. In order to calculate $\langle R^2 \rangle$, we break the chain up into N_s segments, which have, as shown, end-to-end distance vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \ldots, \boldsymbol{a}_{N_{\mathrm{s}}}$. The vectors $\boldsymbol{a}_j$ of different segments are completely uncorrelated in their orientation provided that the chain segments are sufficiently long. It is this property which allows $\langle R^2 \rangle$ as well as the distribution function of the vector $\boldsymbol{R}$ to be determined.

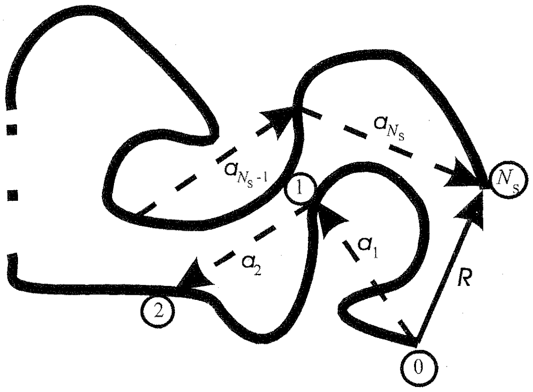


Fig. 1.26. A polymer molecule at low resolution and an associated model chain made up of freely jointed segments.

The problem is equivalent to that of the motion of a Brownian colloidal particle in a liquid. The motion of a Brownian particle away from its starting point takes place by means of a large number of uncorrelated single steps, hence, in the same way as the end-to-end distance vector of a polymer chain is set-up. Representing $\boldsymbol{R}$ as the sum of uncorrelated steps $\boldsymbol{a}_j$,

$$\boldsymbol{R} = \sum_{j=1}^{N_s} \boldsymbol{a}_j \quad , \tag{1.72}$$

the probability distribution for the motion of a Brownian particle away from its starting point can be directly used for the polymer chain. As will be explained in Sect. 5.2 (Eqs. (5.157) and (5.158)), the Brownian motion is described by a Gaussian distribution function. The probability

$$w(\boldsymbol{R})\mathrm{d}^3\boldsymbol{R} \quad ,$$

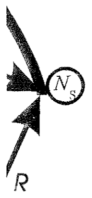
that the second end of a polymer chain finds itself in a volume element $\mathrm{d}^3\boldsymbol{R}$ at a distance $\boldsymbol{R}$ from the first end is, thus, also given by a Gaussian distribution, of the form

$$w(\boldsymbol{R}) = \left(\frac{3}{2\pi\left\langle R^2\right\rangle}\right)^{3/2} \exp -\frac{3R^2}{2\left\langle R^2\right\rangle} \qquad (R = |\boldsymbol{R}|) \quad . \tag{1.73}$$

The pre-factor comes from the normalisation condition

$$\int w(\boldsymbol{R})\mathrm{d}^3\boldsymbol{R} = 1 \quad . \tag{1.74}$$

The only free parameter in the expression for the distribution is $\left\langle R^2\right\rangle$, which is defined as



associated model chain

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(1.72)

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volume element $\mathrm{d}^3\boldsymbol{R}$ at
a Gaussian distribution,

$R = |\boldsymbol{R}|)$. (1.73)

n

(1.74)

tribution is $\langle R^2 \rangle$, which

$$\langle R^2 \rangle = \int\limits_{R=0}^{\infty} w(\boldsymbol{R}) R^2 4\pi R^2 \mathrm{d}R \quad . \tag{1.75}$$

Considering the breaking up of the chain into segments as described by Eq. (1.72), it follows that

$$\langle R^2 \rangle = \left\langle \left| \sum_{j=1}^{N_\mathrm{s}} \boldsymbol{a}_j \right|^2 \right\rangle = \left\langle \sum_{j,j'=1}^{N_\mathrm{s}} \boldsymbol{a}_j \cdot \boldsymbol{a}_{j'} \right\rangle \quad . \tag{1.76}$$

The absence of any correlation in the orientation of the different segments means that

$$\langle \boldsymbol{a}_j \cdot \boldsymbol{a}_{j'} \rangle = \langle | \boldsymbol{a}_j |^2 \rangle \, \delta_{jj'} \quad , \tag{1.77}$$

giving the result

$$\langle R^2 \rangle = N_\mathrm{s} \langle | \boldsymbol{a}_j |^2 \rangle \quad . \tag{1.78}$$

It was stated above that the square root of $\langle R^2 \rangle$ can serve as a measure of the extension of a polymer molecule in the melt, and we choose for this quantity the symbol R_0:

$$R_0 = \langle R^2 \rangle^{1/2} \quad . \tag{1.79}$$

The number of segments N_s is proportional to the degree of polymerisation N. We therefore obtain for the size of a polymer chain in a melt the characteristic power law

$$R_0 \propto N^{1/2} \quad .$$

Upon introducing the constant of proportionality a_0, we write

$$R_0 = a_0 N^{1/2} \quad . \tag{1.80}$$

a_0 corresponds to an effective length per structural unit and depends on all the microscopic properties of the chain, such as the bond lengths, bond angles, and the stiffness of the chain – the last property is determined by the occupation probabilities of the rotational isomeric states of the main-chain bonds.

Our attention above was on the distribution function for the chain end distance. It is clear that the distance distribution for any two points in the chain is also Gaussian-like provided that the points are far enough apart and are thus separated by many individual segments $\boldsymbol{a}_j$; this is true for all length-scales for which the chemical structure is no longer of importance. This has an important consequence, namely, that no change in the general appearance is seen when observing the interior parts of a chain at different resolutions. The structures always look the same, i.e., they always have the appearance of a Gaussian coil and hence, are similar to each other. Polymer chains in a melt are **self-similar objects**.

For self-similar objects, the question about their **fractal dimension** comes up. The answer is found in the power law of Eq. (1.80). If applied to a volume which encloses only a part of the polymer chain – say, a sphere of diameter r – we obtain for the number of structural units n which are found on average

$$n \propto r^2 \quad . \tag{1.81}$$

The power to which the distance is raised corresponds, by definition, to the fractal dimension. Thus, for polymer chains in a melt, the fractal dimension takes the value two. Polymer chains are objects which exist in three dimensions; however, since they only partially fill the available space, a lower dimension is found.

The self-similarity property of the objects applies only over a limited range: The upper limit is set by the size of the whole molecule, i.e., R_0, while the lower limit is reached for microscopic regions where the chemical structure becomes visible.

1.4.3 Solid Polymers

~~Upon cooling to sufficiently low temperatures, it is found, also for polymer systems, that the melt solidifies. There are two completely different processes which can cause a solidification. Polymers which are sufficiently regular in their chemical and steric structures can crystallise, although this process follows rules which differ fundamentally from those for the case of the crystallization of atomic and molecular systems. Alternatively, if the chain structure is irregular, it is impossible that a crystalline structure forms; a solidification process occurs, nevertheless, but this time by a transition to a rigid glassy state. In the following, both processes are considered.~~

~~**The Semi-Crystalline State.** A little thought allows us to envisage how a three-dimensional crystal with a periodic structure can be constructed from polymer chains. The polymer chains are fully stretched out and transferred into the state with the lowest conformational energy which is always periodic in structure. A three-dimensional structure, i.e., a polymer crystal, forms if such chains are packed together parallelly in a regular side-by-side fashion. Such a crystal is characterised by a marked internal anisotropy with strong covalent bonds in one direction and weak van der Waals forces in the other two directions. In principle, it would be possible to form single crystals out of polymers if all the chains had the same molecular weight and, thus, the same length. The end groups could then be arranged together in the upper and lower surfaces of a crystal formed from all the extended chains. In fact, this doesn't happen, and not only because, as stated above, polymer systems always exhibit a molecular weight distribution. The actual factor which prevents the transition into such an ideal crystalline state is present in the melt. Here the coiled molecules interpenetrate each other and, thus, form a large number of entanglements which cannot easily be resolved. The complete disentangling with a separation of all molecules from each other as would be~~