Studentnumber:__Løsningsforslag___

**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

Monday 19. May 2008
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 |
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| Answer | **D** | **B** | **B** | **C** | **D** | **D** | **B** | **B** | **A** | **B** | **B** | **C** |

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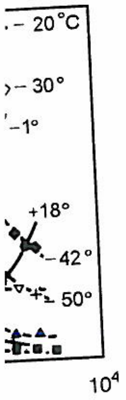
| Answer | **D** | **D** | **A** | **B** | **D** | **A** | **A** | **A** |



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Problem 1 a)

~~a rate which increases proportionally with the perturbation. The solut the differential equation is~~

~~$\Delta\gamma(t) = \Delta J \; \sigma^0_{zx} \left(1 - \exp - \frac{t}{\tau}\right)$~~ (2.76)

~~and it describes an adjustment process with a time constant $\tau$.~~

Consider now the dynamic-mechanical experiment. The relaxation equation can also be applied in this case. Replacing the time-independent stress $\sigma^0_{zx}$ by

$$\sigma_{zx}(t) = \sigma^0_{zx} \exp(-\mathrm{i}\omega t) \tag{2.77}$$

gives

$$\frac{\mathrm{d}\Delta\gamma}{\mathrm{d}t} = -\frac{1}{\tau}[\Delta\gamma(t) - \Delta J \sigma^0_{zx} \exp(-\mathrm{i}\omega t)] \quad . \tag{2.78}$$

A solution with a periodically changing extension $\Delta\gamma(t)$ is required, and we therefore write

$$\Delta\gamma(t) = \sigma^0_{zx}[\Delta J'(\omega) + \mathrm{i}\Delta J''(\omega)] \exp(-\mathrm{i}\omega t) \quad . \tag{2.79}$$

This leads to the following expression for the complex compliance $\Delta J(\omega)$:

$$\Delta J'(\omega) + \mathrm{i}\Delta J''(\omega) = \frac{\Delta J(0)}{1 - \mathrm{i}\omega\tau} \tag{2.80}$$

$$= \frac{\Delta J}{1 + \omega^2\tau^2} + \mathrm{i}\frac{\Delta J \; \omega\tau}{1 + \omega^2\tau^2} \quad . \tag{2.81}$$

Figure 2.16 shows the frequency dependence of $\Delta J'(\omega)$ and $\Delta J''(\omega)$. The

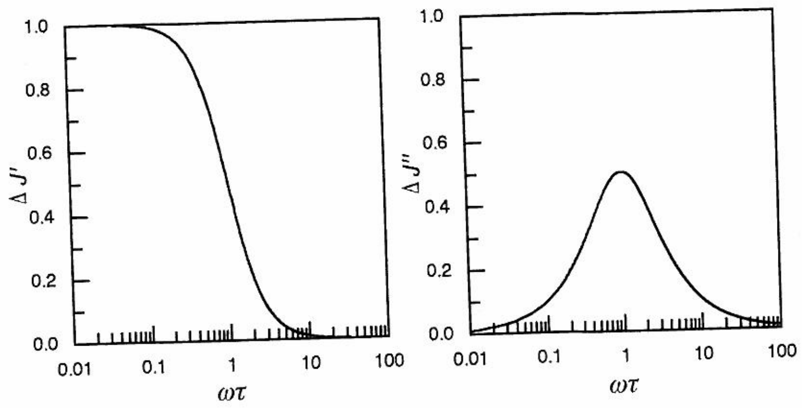

**Fig. 2.16.** The real and imaginary parts of the dynamic shear compliance for a simple relaxation process.

Problem 1(b)

which cover many orders of magnitude. Such experiments yield the frequency dependence of the real and imaginary parts of the complex compliance, $D'_{\mathrm{t}}(\omega)$ and $D''_{\mathrm{t}}(\omega)$, respectively. The phase shift, $\delta$, is given by

$$\tan\delta(\omega) = \frac{D''_{\mathrm{t}}(\omega)}{D'_{\mathrm{t}}(\omega)} \quad . \tag{2.50}$$

As an alternative to the dynamic tensile compliance, the **dynamic Young's modulus** can also be used to describe the experimental results. It is defined by

$$E_{\mathrm{t}}(\omega) = \frac{\sigma^0_{zz}}{e^0_{zz}} = E'_{\mathrm{t}}(\omega) - \mathrm{i}E''_{\mathrm{t}}(\omega) \tag{2.51}$$

and corresponds to the inverse of the compliance:

$$E_{\mathrm{t}}(\omega) = \frac{1}{D_{\mathrm{t}}(\omega)} \quad . \tag{2.52}$$

By convention, a negative sign is chosen for the imaginary part.

In the previous examples, we have only discussed reactions to tensile stresses. There are, of course, corresponding expressions for a shear, i.e., a time-dependent shear compliance $J(t)$, a time-dependent shear modulus $G(t)$ and the two corresponding frequency-dependent and in general complex functions $J(\omega)$ and $G(\omega)$.

Dynamic-mechanical experiments have the advantage, as compared to time-dependent experiments, that they provide a particular physical insight. During the deformation, work is done on the sample by the external force. On the one hand, this increases the potential energy, on the other hand, it leads to the generation of heat. The real and imaginary parts of the dynamic compliance correspond exactly to this separation. That this is so can be easily demonstrated. It is only necessary to analyse the power provided by the external force. Taken per unit volume the power is given by

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \Re(\sigma_{zz}(t))\frac{\mathrm{d}\Re(e_{zz}(t))}{\mathrm{d}t} \tag{2.53}$$

(for the calculation of a product a transition from the complex notation to the actual physical quantity given by the real part is necessary). The time-dependent extension is given by

$$e_{zz}(t) = D_{\mathrm{t}}(\omega)\sigma^0_{zz}\exp(-\mathrm{i}\omega t) = (D'_{\mathrm{t}} + \mathrm{i}D''_{\mathrm{t}})\sigma^0_{zz}[\cos(\omega t) - \mathrm{i}\sin(\omega t)] \quad . \tag{2.54}$$

The real part is then given by

$$\Re(e_{zz}(t)) = D'_{\mathrm{t}}\sigma^0_{zz}\cos(\omega t) + D''_{\mathrm{t}}\sigma^0_{zz}\sin(\omega t) \quad . \tag{2.55}$$

Therefore, the following expression is obtained for the power

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \sigma^0_{zz}\cos(\omega t)[-\omega\sigma^0_{zz}D'_{\mathrm{t}}\sin(\omega t) + \omega\sigma^0_{zz}D''_{\mathrm{t}}\cos(\omega t)] \tag{2.56}$$

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or, upon applying a well-known trigonometric relation

$$\frac{\mathrm{d}w}{\mathrm{d}t} = -\frac{(\sigma^0_{zz})^2}{2}\omega D'_\mathrm{t}\sin(2\omega t) + (\sigma^0_{zz})^2\omega D''_\mathrm{t}\cos^2(\omega t) \quad . \tag{2.57}$$

It is apparent that there are two contributions to the power. The first term oscillates between positive and negative values with double the frequency of the stress. This expresses an exchange: Work, which is stored up in the sample during a quarter period, goes back out in the next quarter period. This part clearly describes the storing and release of elastic potential energy. Its magnitude is given only by the real part of the dynamic compliance. The second part, which is proportional to the imaginary part, behaves completely differently. It describes a take up of power which is always positive, with a time-averaged magnitude

$$\overline{\frac{\mathrm{d}w}{\mathrm{d}t}} = \frac{1}{2}(\sigma^0_{zz})^2\omega D''_\mathrm{t} \quad . \tag{2.58}$$

What does this mean? Generally, the internal energy of the sample $\mathcal{U}$ changes as work is done and heat is exchanged according to

$$\mathrm{d}\mathcal{U} = \mathcal{V}\mathrm{d}w + \mathrm{d}\mathcal{Q} \quad . \tag{2.59}$$

If the experiment is, as usual, performed under isothermal conditions, there is no change in the internal energy of the sample. The supplied work must therefore be completely released as heat:

$$\mathcal{V}\overline{\frac{\mathrm{d}w}{\mathrm{d}t}} = -\overline{\frac{\mathrm{d}\mathcal{Q}}{\mathrm{d}t}} \quad . \tag{2.60}$$

~~**The Relationships Between the Response Functions.** With the time-dependent compliance $D_\mathrm{t}(t)$, the time-dependent Young's modulus $E_\mathrm{t}(t)$, the frequency-dependent dynamic compliance $D_\mathrm{t}(\omega)$, the dynamic Young's modulus $E_\mathrm{t}(\omega)$, and the corresponding functions for shearing, a range of material functions has been introduced which describe the mechanical reaction of samples in the linear viscoelastic region. It is naturally to be expected that relationships exist between these different **response functions**, and they will now be derived. In order to make the expressions independent of the type of load, we denote the force as $\xi$ and the deformation as $X$.~~

~~The above discussion has dealt with static and periodically changing conditions. These are definitely the most important cases, but nevertheless the question arises as to whether it is possible to treat the general case of a completely arbitrary time dependence. In fact, this is possible, the condition being solely the knowledge of a further response function of particular importance: It must be known how a sample reacts upon applying a force as a short pulse~~

$$\xi(t) = \xi_\mathrm{t}\delta(t) \quad . \tag{2.61}$$

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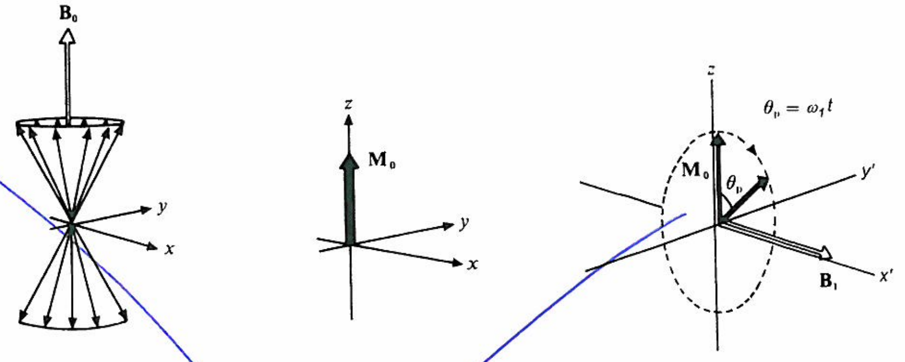
Problem 1c)



~~**Fig. 2.26.** System of spins in a static magnetic field $\mathbf{B}_0$. Precession with the Larmor frequency (*left*) and resulting longitudinal magnetisation (*centre*). Rotation of the spin system by a transverse magnetic field $\mathbf{B}_1$ oscillating with the Larmor frequency. Precession in the rotating coordinate system $x', y'$ (*right*).~~

~~$xy$ plane. If the frequency of the irradiated field is chosen to agree with the precession frequency of the spins, the irradiated field is able to cause the spins to rotate. This can be understood by considering a coordinate system which rotates at the Larmor frequency – this is denoted by $x'$ and $y'$ in the drawing on the right-hand side. In this rotating frame, the field with an amplitude $B_1$ is again responsible for a precessional motion, this time about the direction of the varying field. The change in the angle due to this precessional motion in the rotating coordinate frame is denoted by $\theta_{\mathrm{P}}$ and grows proportionally with time. The pulse duration can be chosen to ensure that $\theta_{\mathrm{P}}$ equals exactly 90° such that a purely transverse initial state is generated, whose free induction decay can subsequently be detected.~~

## 2.4 General Properties of Susceptibilities

The subject of this chapter has been the effects which external fields can cause in matter. It has been seen that linear dependences are observed over a wide range of conditions: Deformations are proportional to the applied tensile or shear stress, polarisations are proportional to the electric field which is acting, while magnetisations are proportional to the magnetic field which exists. We are always dealing with linear responses which can be quantitatively described by means of response functions such as the compliance and susceptibility. For these response functions, there exists a series of generally applicable laws, some of which have already been introduced at the end of Sect. 2.1.3. Equations were derived which link different response functions together. The relationship between the creep compliance $\alpha_{\mathrm{c}}(t)$ and the time-dependent modulus $a(t)$ is given by the integro-differential equation

$$1 = \int_0^t \frac{\mathrm{d}\alpha_\mathrm{c}}{\mathrm{d}t}(t - t')\mathrm{a}(t')\mathrm{d}t'$$

(Eqs. (2.66) and (2.68)), while the relation between the pulse response function $\alpha_\mathrm{p}(t)$ and the dynamic compliance or **mechanical susceptibility** $\alpha(\omega)$ is expressed by (Eq. (2.73)):

$$\alpha(\omega) = \alpha'(\omega) - \mathrm{i}\alpha''(\omega) = \int_0^\infty \alpha_\mathrm{p}(t'')\exp(\mathrm{i}\omega t'')\mathrm{d}t'' \quad .$$

An important result was that the real and imaginary parts of $\alpha(\omega)$ have a well-defined physical meaning. The real part expresses for a periodic load the part of the external power which is reversibly introduced and removed again, while the imaginary part describes the loss, i.e., the part of the power which is dissipated and lost as heat. The proof of this was given for the dynamic-mechanical experiment; the statement, though, is, as already mentioned, valid for all discussed susceptibilities. In the mechanical case, the work per unit volume is given by

$$\mathrm{d}w = \sigma_{zz}\mathrm{d}e_{zz} \quad . \tag{2.205}$$

In the dielectric case, the following is valid

$$\mathrm{d}w = E\mathrm{d}P \tag{2.206}$$

while we have the following for the application of a magnetic field:

$$\mathrm{d}w = \mu_0 H\mathrm{d}M \quad . \tag{2.207}$$

For variables which are related to each other by means of a susceptibility, one is dealing with a pair of energy-conjugated variables (see Eq. (A.4) in Appendix A). Therefore, it is always true that the imaginary part describes the energy dissipation, i.e., the transfer of work or field energy into disordered thermal motion.

A further one will now be added to these previously stated general laws. It may sound amazing at first but the real and imaginary parts of a susceptibility are actually not independent, but rather they are coupled with each other. This may be surprising since both, as described above, have completely different meanings. The relationship is expressed by means of the **Kramers–Kronig relations**.

**The Kramers–Kronig Relations.** In order to describe the relations, fundamental laws from the mathematical theory of complex functions, in particular the theorem of residues, are used. Consider as a starting point Eq. (2.73): It gives the frequency dependence of the susceptibility on the basis of pulse z value in place of a real frequency. The singularity for a simple relaxation process gives

$$X(t) \propto \exp(-\mathrm{i}\mathrm{z}t) = \exp -\frac{t}{\tau} \quad , \tag{2.214}$$

while the following results for a damped harmonic oscillator

$$X(t) \propto \exp\left[\pm\mathrm{i}\left(\frac{1}{\tau'^2} - \frac{\tau^2}{4\tau'^4}\right)^{1/2} t - \frac{\tau}{2\tau'^2}t\right] \quad . \tag{2.215}$$

These are, however, exactly the time dependences of the eigenmodes of the systems which become visible during the subsequent decay process after switching off an external force. The singularities in $\alpha(\mathrm{z})$ occur at the positions of the system eigenmodes. It is also understandable, for it is exactly the eigenmodes which can exist without excitation by an external force. An infinitely large susceptibility expresses this. Why can no singularity appear in the lower half of the complex plane? The answer is that the associated modes would be described by processes with an exponentially increasing amplitude, and these cannot exist for stable linear systems.

In order to derive the Kramers–Kronig relation, consider now not $\alpha(\mathrm{z})$ but rather the function

$$\frac{\alpha(\mathrm{z})}{\mathrm{z} - \omega_0} \quad . \tag{2.216}$$

It is also analytic in the whole upper half of the plane including the $\omega'$ axis with one exception: There is a singularity at the location $\mathrm{z} = \omega_0$ on the $\omega'$ axis. Consider the calculation of a special integral over a closed path, namely that shown in Fig. 2.27. According to a basic theorem valid for complex functions the integral must vanish since no singularity is included. The integral can be expressed as a sum of four pieces, namely two straight lines and two semicircles:

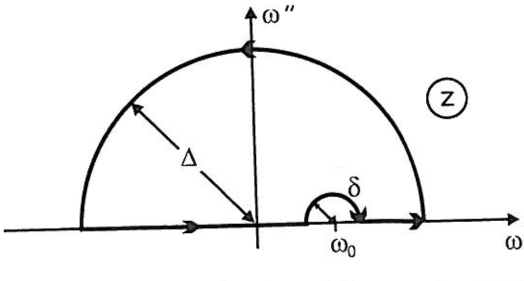


**Fig. 2.27.** The integration route in the plane of the complex frequency z= $\omega' + \mathrm{i}\omega''$, as selected in the derivation of the Kramers–Kronig relations.

$$0 = \int\limits_{-\infty}^{\omega_0 - \delta} \frac{\alpha(\mathrm{z})}{\mathrm{z} - \omega_0} \mathrm{dz} + \int\limits_{\pi}^{2\pi} \alpha(\omega_0 + \delta \exp \mathrm{i}\vartheta) \mathrm{i} \mathrm{d}\vartheta \tag{2.217}$$

$$+ \int\limits_{\omega_0 + \delta}^{+\infty} \frac{\alpha(\mathrm{z})}{\mathrm{z} - \omega_0} \mathrm{dz} + \lim_{\Delta \to \infty} \int\limits_{0}^{\pi} \alpha(\omega_0 + \Delta \exp \mathrm{i}\vartheta) \mathrm{i} \mathrm{d}\vartheta \ . \tag{2.218}$$

The large semicircle with radius $\Delta$ should run into infinity. The first term runs from infinity to a distance $\delta$ from the singularity at $\omega_0$, the second term corresponds to going round the singularity via the small semi-circle with radius $\delta$, the third term goes from there to infinity, while the fourth term gives the contribution of the large semi-circle with the radius $\Delta \to \infty$. The following was used for the small circle:

$$\mathrm{z} = \omega_0 + \delta \exp \mathrm{i}\vartheta \ , \tag{2.219}$$

where $\vartheta$ is a variable angle. It, thus, follows that

$$\mathrm{dz} = \mathrm{i}\delta \exp \mathrm{i}\vartheta \mathrm{d}\vartheta \tag{2.220}$$

and therefore

$$\frac{\mathrm{dz}}{\mathrm{z} - \omega_0} = \mathrm{i}\mathrm{d}\delta \ . \tag{2.221}$$

This expression is equally valid for the large semi-circle and was used in the second and fourth terms. The theorem of residues can now be applied to determine the value of the integral which goes round the singularity $\omega_0$:

$$\lim_{\delta \to 0} \int\limits_{\pi}^{2\pi} \alpha(\omega_0 + \delta \exp \mathrm{i}\vartheta) \mathrm{i} \mathrm{d}\vartheta = -\mathrm{i}\pi\alpha(\omega_0) \ . \tag{2.222}$$

The fourth term makes no contribution since the susceptibility disappears at infinity in the lower half of the space. The following is thus obtained

$$0 = -\mathrm{i}\pi\alpha(\omega_0) + \lim_{\delta \to 0} \left[ \int\limits_{-\infty}^{\omega_0 - \delta} \frac{\alpha(\mathrm{z})\mathrm{dz}}{\mathrm{z} - \omega_0} + \int\limits_{\omega_0 + \delta}^{\infty} \frac{\alpha(\mathrm{z})\mathrm{dz}}{\mathrm{z} - \omega_0} \right] \ . \tag{2.223}$$

The expression in square brackets, which formulates a coupled simultaneous approach from both sides to the singularity, is referred to as the 'principal value'; it can be written in the following short-hand form:

$$\mathrm{P} \int\limits_{-\infty}^{\infty} \frac{\alpha(\omega)}{\omega - \omega_0} \mathrm{d}\omega = \lim_{\delta \to 0} \left[ \int\limits_{-\infty}^{\omega_0 - \delta} \frac{\alpha(\omega)}{\omega - \omega_0} \mathrm{d}\omega + \int\limits_{\omega_0 + \delta}^{\infty} \frac{\alpha(\omega)}{\omega - \omega_0} \mathrm{d}\omega \right] \ . \tag{2.224}$$

In this way, the result has already been obtained. The breaking up of the susceptibility into real and imaginary parts and the comparison to the real and imaginary parts in Eq. (2.223) leads to the two equations

$$\alpha'(\omega_0) = \frac{1}{\pi} \mathrm{P} \int_{-\infty}^{\infty} \frac{\alpha''(\omega)}{\omega - \omega_0} \mathrm{d}\omega \quad , \tag{2.225}$$

$$\alpha''(\omega_0) = -\frac{1}{\pi} \mathrm{P} \int_{-\infty}^{\infty} \frac{\alpha'(\omega)}{\omega - \omega_0} \mathrm{d}\omega \quad . \tag{2.226}$$

These equations link the real and imaginary parts of the susceptibility in a one-to-one way and are referred to as the Kramers–Kronig relations.

~~A consideration of the susceptibilities which are measured in dynamic-mechanical experiments on viscoelastic materials such as polymers reveals that the Kramers–Kronig relations in the above form require the addition of a small supplementary term. The contribution of the plastic component, which is always found for polymers, hasn't yet been included. The eigenmode of a plastic body is at z = 0. This can be recognised from the fact that the above-stated singularity associated with a simple relaxation process approaches z = 0 for $\tau \to \infty$, i.e., upon the transition into a plastic body. Alternately, it can be seen by solving the equation of motion for a plastic body~~

$$\frac{\mathrm{d}X}{\mathrm{d}t} \propto \xi \quad . \tag{2.227}$$

~~Inserting~~

$$\xi(t) = \xi_0 \exp(-\mathrm{i}\omega t) \tag{2.228}$$

~~and~~

$$X(t) = X_0 \exp(-\mathrm{i}\omega t) \tag{2.229}$$

~~leads to the following expression for the susceptibility:~~ $\alpha(\omega)$

$$\frac{X_0}{\xi_0} = \alpha(\omega) \propto \frac{\mathrm{i}}{\omega} \quad , \tag{2.230}$$

~~and the corresponding expression for~~ $\alpha(\mathrm{z})$

$$\alpha(\mathrm{z}) \propto \frac{\mathrm{i}}{\mathrm{z}} \quad . \tag{2.231}$$

~~Such a singularity at the origin was not taken into account in the above calculation of the integral. A later consideration of such processes is possible. As is implied in Eq. (2.230), plastic bodies only make a contribution to the imaginary part of the susceptibility,~~

$$\alpha''(\omega) = \frac{A_{\mathrm{v}}}{\omega} \quad , \tag{2.232}$$

Problem 2a)

~~is liquid-like; they can, thus, be considered as two-dimensional liquids. The name is also of Greek origin, coming from $\sigma\mu\eta\gamma\mu\alpha$, which means soap – Friedel found that soap, when mixed with water, also forms such a layer-like structure. Smectic phases are more viscous than nematic phases because of their different nature. In contrast to the case of nematogens, no significant technical use has been found so far for substances in the smectic phase.~~

### 1.3.2 Orientational Order and Optical Anisotropy

As is illustrated in the earlier sketch of the nematic liquid-crystal, there is not a strict parallel arrangement of all molecules, but rather a collective preferred orientation. The distribution of orientations covers the whole range of possible angles. The width of the distribution determines the optical anisotropy, and it is, therefore, important to define a parameter which describes in a suitable way the **degree of orientation** of a nematic phase.

In order to describe the distribution of the orientation of the molecular axes, we introduce, in the framework of the spherical coordinates with $\vartheta = 0$ corresponding to the direction of the director, a function $w(\vartheta, \varphi)$, where

$$w(\vartheta, \varphi) \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi$$

gives the fraction of molecules whose long axis lies within the range of angles $\mathrm{d}\vartheta\mathrm{d}\varphi$. In the case here of uniaxial symmetry, $w$ does not depend on $\varphi$, and we write, upon introduction of a second distribution function $w'$ which is only dependent on $\vartheta$

$$w(\vartheta, \varphi) = \frac{w'(\vartheta)}{2\pi} \quad . \tag{1.41}$$

The following normalisation equation applies

$$1 = \int\limits_{\vartheta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} w(\vartheta) \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi = \int\limits_{\vartheta=0}^{\pi} w'(\vartheta) \sin\vartheta \mathrm{d}\vartheta \quad . \tag{1.42}$$

It is a fundamental property of a nematic phase that

$$w'(\vartheta) = w'(\pi - \vartheta) \quad . \tag{1.43}$$

Even in the case that a molecule possesses an electric dipole moment, the nematic phase is always non-polar. This also means that the director $\boldsymbol{n}$ is not uniquely fixed – it can always be chosen as well in the opposite direction.

Orientation distribution functions $w'(\vartheta)$ can be expanded as a series of Legendre polynomials $P_l(\cos\vartheta)$:

$$w'(\vartheta) = \sum_{l=0}^{\infty} \frac{1}{2}(2l+1) S_l P_l(\cos\vartheta) \quad . \tag{1.44}$$

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These polynomials are orthogonal to each other – this is expressed mathematically by

$$\int_{\vartheta=0}^{\pi} P_l P_k \sin\vartheta \mathrm{d}\vartheta = \frac{2}{2l+1}\delta_{lk} \quad . \tag{1.45}$$

The series coefficients $S_l$ can be calculated according to:

$$S_l = \int_{\vartheta=0}^{\pi} P_l(\cos\vartheta) w'(\vartheta) \sin\vartheta \mathrm{d}\vartheta = \langle P_l \rangle \quad . \tag{1.46}$$

Regardless of the form of $w'$, it is always true that

$$S_0 = 1 \quad . \tag{1.47}$$

In the given case of a non-polar system, the first-order series coefficient is zero:

$$\langle \cos\vartheta \rangle = 0 \quad . \tag{1.48}$$

The first non-zero contribution after the constant $S_0$ term is thus the second-order term, whose coefficient is given by

$$S_2 = \left\langle \frac{3\cos^2\vartheta - 1}{2} \right\rangle \quad . \tag{1.49}$$

$S_2$ characterises the degree of orientation and is suited to take the role of the **nematic order parameter**. There are two limiting cases for $S_2$:

- for an isotropic distribution, $S_2 = 0$
- for a perfect orientation, $S_2 = 1$.

~~There is a further reason for the choice of $S_2$ as the order parameter: The difference in the refractive indexes, $\Delta n = n_{\parallel} - n_{\perp}$, which is responsible for birefringence is proportional to $S_2$. We present here the proof of this and introduce first two coordinate systems. The first, with the coordinates $x, y$ and $z$, has its $z$ axis aligned parallel to the director, while the second, with the coordinates $x', y'$ and $z'$, is fixed at the molecule. The $z'$ axis corresponds to the long axis of the molecule, such that the matrix representation of the polarisability tensor $\boldsymbol{\beta}'$ in the second system is diagonal~~

$$\boldsymbol{\beta}' = \begin{pmatrix} \beta_{\perp} & 0 & 0 \\ 0 & \beta_{\perp} & 0 \\ 0 & 0 & \beta_{\perp} + \Delta\beta \end{pmatrix} \quad . \tag{1.50}$$

~~We assume here that the molecule has uniaxial symmetry. $\boldsymbol{\beta}'$ can be transformed into the director-fixed axes system:~~

$$\boldsymbol{\beta} = \boldsymbol{\Omega}^{-1} \cdot \boldsymbol{\beta}' \cdot \boldsymbol{\Omega} \quad . \tag{1.51}$$

(Problem 26)

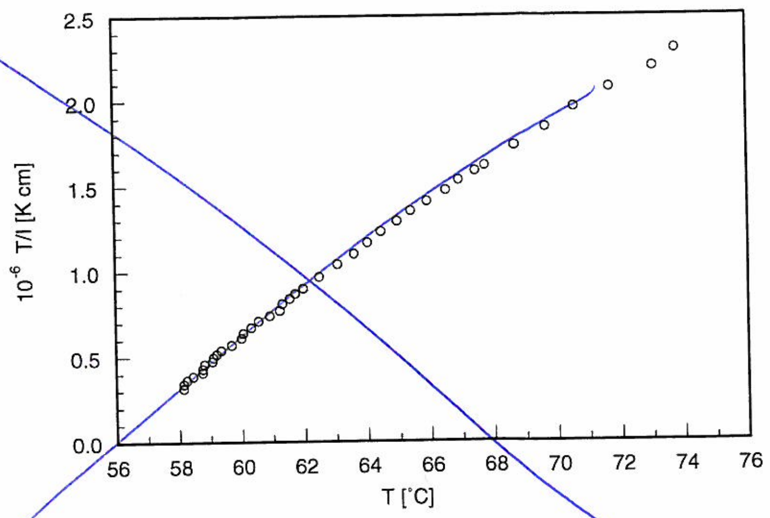


**Fig. 3.13.** PCH7: The increase in intensity of depolarised scattered light upon approaching the temperature $T_{\mathrm{ni}}$ of the transition into the nematic phase.

### 3.3.1 The Landau–de Gennes Expansion

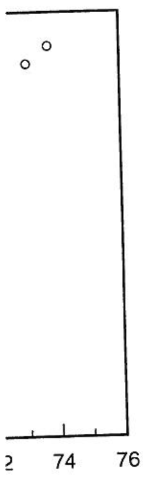
What would be the form of a Landau expansion which describes the isotropic-nematic phase transition in a qualitatively correct fashion? The answer to this question was given by de Gennes. In order to describe the Helmholtz free energy density as a function of the nematic order parameter and the temperature

$$f(S_2, T)$$

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:

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

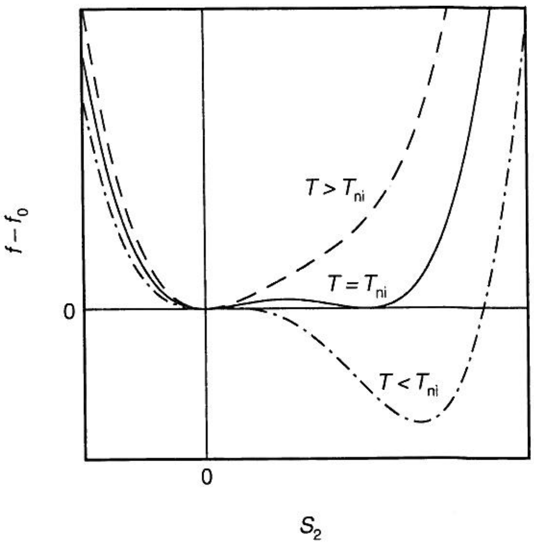

**Fig. 3.14.** The Landau–de Gennes expansion for the Helmholtz free energy density of a nematic liquid crystal at the clearing point $T_{\mathrm{ni}}$ as well as for temperatures where only the isotropic ($T > T_{\mathrm{ni}}$) or only the nematic phase ($T < T_{\mathrm{ni}}$) exists.

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.

Problem 2c)

### 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 $\vartheta$ and 180°-$\vartheta$ 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

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

or

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

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$$x = \frac{3u_0 S_2}{2k_\mathrm{B}T} \ , \tag{3.50}$$

and determine the partition function $\mathcal{Z}'$ using

$$\frac{1}{\mathcal{Z}'} \int\limits_{\vartheta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} \exp(x\cos^2\vartheta) \cdot \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi = 1 \ . \tag{3.51}$$

$\mathcal{Z}'(x)$ can be expressed as a function of $x$:

$$\mathcal{Z}'(x) = 2\pi \int\limits_{\vartheta=0}^{\pi} \exp(x\cos^2\vartheta)\mathrm{d}(-\cos\vartheta) = 4\pi \int\limits_{0}^{1} \exp(xy^2)\mathrm{d}y \ . \tag{3.52}$$

If the orientation distribution function is known, the order parameter follows generally as:

$$S_2 = \int\limits_{\vartheta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} w(\vartheta,\varphi) \frac{3\cos^2\vartheta - 1}{2} \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi \ . \tag{3.53}$$

The equation expresses here a self-consistency condition: $S_2$ is not only the result on the left-hand side, but it is also contained in the distribution function $w$ on the right. The equation can be solved – i.e., self-consistency is achieved – and gives the value of the order parameter. Equation (3.53) is re-expressed as

$$S_2 = -\frac{1}{2} \int\limits_{\vartheta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} w(\vartheta,\varphi)\mathrm{d}\varphi \sin\vartheta \mathrm{d}\vartheta \tag{3.54}$$

$$+\frac{3}{2} \cdot \frac{1}{\mathcal{Z}'} \int\limits_{\vartheta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} \exp(x\cos^2\vartheta)\cos^2\vartheta \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi$$

$$= -\frac{1}{2} + \frac{3}{2}\frac{4\pi}{\mathcal{Z}'} \int\limits_{0}^{1} \exp(xy^2)y^2\mathrm{d}y \ . \tag{3.55}$$

This leads to

$$S_2 = -\frac{1}{2} + \frac{3}{2}\frac{1}{\mathcal{Z}'}\frac{\mathrm{d}\mathcal{Z}'}{\mathrm{d}x} \ . \tag{3.56}$$

Denoting the right-hand side of Eq. (3.56) as $\Phi(x)$ and expressing $S_2$ as a function of $x$ yields

$$\frac{2k_\mathrm{B}T}{3u_0} x = \Phi(x) \ . \tag{3.57}$$

We find here functions of the variable $x$ on both sides of the equation. Figure 3.15 shows the dependence of both functions and points to the solution: It is necessary to make the left-hand side of the equation intersect with $\Phi(x)$. For high temperatures, i.e., the gradient of the line is large, the only intersection point is at the origin of the co-ordinate system. This changes at the temperature $T_{\mathrm{ni}}$, where there is a second solution: It is associated with a definite value of the order parameter, namely $S_2 = 0.44$. This actually agrees well with experimental observations. The Maier–Saupe theory also gives the temperature dependence of the order parameter in the nematic phase. The figure contains a straight line which corresponds to this case – it can be shown that the highest intersection point corresponds to the equilibrium value.

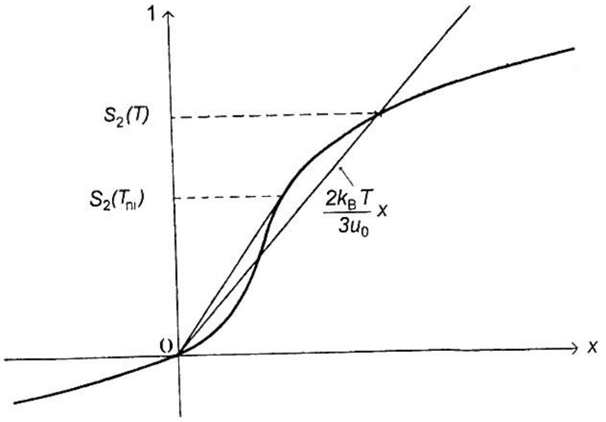

**Fig. 3.15.** The graphical solution of the self-consistent Eq. (3.57) for $S_2$.

## ~~3.4 Phase Separation in Binary Polymer Melts~~

~~The discussion of the properties of polymer materials has up to now only dealt with single component systems. In fact, a large part of, in particular, application-oriented research is devoted to mixtures or blends of different polymers. The basis for this is the observation that mixtures often have better mechanical properties than the pure substances. It is possible in this way to reduce the brittleness of materials and hence increase their fracture resistance. In order to optimise the properties of polymer blends, a good basic understanding of the mixing behaviour is important. It would be desirable to know~~

- ~~whether two particular polymers are miscible or not, and whether this can be predicted,~~

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Problem 3a)

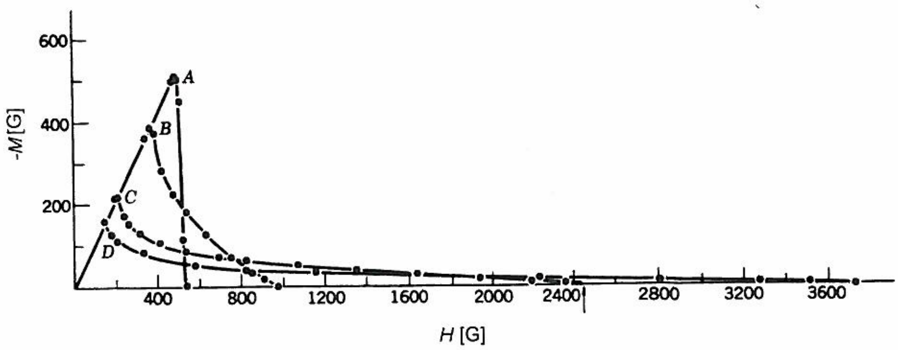

**Fig. 4.34.** Magnetisation curves for lead (A) and different lead-indium (2.8–20.4%) alloys (B, C, D). The alloys are type II superconductors (from Livingston in [23]).

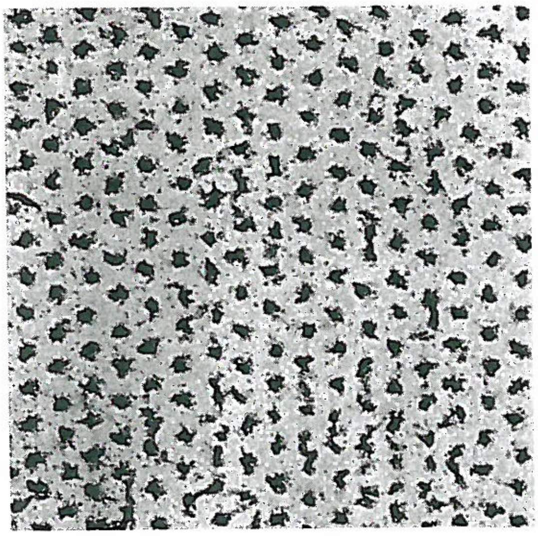

**Fig. 4.35.** Type II superconductors with regularly arranged normal conducting tubes, which were made visible on the surface of a sample with a cylinder form with the help of ferromagnetic particles (from Träuble and Essmann [23]).

~~Ginzburg and Landau, together with Abrikosov, provided an explanation for the appearance of such two-phase structures. Again starting with the wavefunction $\Psi$, an equation for the density of the Gibbs free energy was formulated which took into account the possibility of a spatial variation in the concentration of superconducting charge carriers as well as the presence of an external magnetic field $H$. Equation (4.265) is extended in the following way:~~

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Problem 3b)

$$\frac{\varepsilon_0}{2}E_0^2 = \rho_{\mathrm{ph}}\hbar\omega \tag{4.239}$$

The charge carriers in a superconductor, the Cooper pairs, behave like bosons, which means that they, like photons, are able to occupy, in large numbers, an individual quantum-mechanical state. Ginzburg and Landau had suggested already in 1950, before the postulation of the possible existence of Cooper pairs, that the stationary states, which are occupied by charge carriers in a superconductor, can be described by a complex wavefunction $\Psi(\boldsymbol{r})$. The wavefunction determines by means of

$$|\Psi|^2 = \rho_{\mathrm{s}} \quad , \tag{4.240}$$

i.e., by its modulus, the local density $\rho_{\mathrm{s}}$. $\Psi$ also contains, like the electromagnetic oscillation, a further important attribute, namely a phase factor:

$$\Psi(\boldsymbol{r}) = |\Psi(\boldsymbol{r})| \exp[\mathrm{i}\theta(\boldsymbol{r})] \quad . \tag{4.241}$$

Eigenstates in superconductors can be associated with a current of particles. Schrödinger wave mechanics provides an expression for the current which is in a general form also valid in the presence of a magnetic field, and it is used in the **Ginzburg–Landau wave mechanics** of superconductors:

$$\boldsymbol{j}_{\mathrm{s}} = \frac{1}{2}\left(\Psi^* \frac{-\mathrm{i}\hbar\nabla - (-2e)\boldsymbol{A}}{2m_{\mathrm{e}}}\Psi + \Psi\left[\frac{-\mathrm{i}\hbar\nabla - (-2e)\boldsymbol{A}}{2m_{\mathrm{e}}}\Psi\right]^*\right) \quad . \tag{4.242}$$

Here $\boldsymbol{j}_{\mathrm{s}}$ is the particle current density of the Cooper pairs (charge $-2e$, mass $2m_{\mathrm{e}}$) and $\boldsymbol{A}$ denotes the vector potential. A frequently encountered case is that of a superconductor, inside of which there are macroscopic regions with a constant density of charge carriers. In this case, only the phase $\theta$ of the wavefunction changes, and the electric current density associated with the Cooper pairs

$$\boldsymbol{j}_{\eta\mathrm{s}} = -2e\boldsymbol{j}_{\mathrm{s}} \tag{4.243}$$

is given as

$$\boldsymbol{j}_{\eta\mathrm{s}} = -2e\left(\frac{\hbar}{2m_{\mathrm{e}}}\nabla\theta(\boldsymbol{r}) - \frac{(-2e)}{2m_{\mathrm{e}}}\boldsymbol{A}\right)|\Psi|^2 \quad . \tag{4.244}$$

In particular, it follows, for a planar wave

$$\Psi(\boldsymbol{r}) = |\Psi| \exp(\mathrm{i}\boldsymbol{k}\boldsymbol{r}) \tag{4.245}$$

that the current density is

$$\boldsymbol{j}_{\eta\mathrm{s}} = -2e|\Psi|^2\left(\frac{\hbar\boldsymbol{k}}{2m_{\mathrm{e}}} + \frac{2e}{2m_{\mathrm{e}}}\boldsymbol{A}\right) \quad . \tag{4.246}$$

In this way, a description has been obtained of the situation which exists in a circular closed superconductor where a persistent current flows. The flow of

**London Penetration Depth, Flux Quantisation, and Electron Tunnelling.** Using the wave-mechanical Eq. (4.244) as a starting point, it is possible to explain the Meissner effect and also a further characteristic phenomenon, the **flux quantisation**. The calculation of the curl on both sides of the equation yields

$$\nabla \times \boldsymbol{j}_{\eta\mathrm{s}} = -\rho_\mathrm{s} \frac{(-2e)^2}{2m_\mathrm{e}} \boldsymbol{B} \quad . \tag{4.253}$$

This is referred to as the **London equation** and it describes a basic property of all superconducting materials. The London equation applies to all superconductors in the same way that Ohm's law $\boldsymbol{j}_\eta = \sigma \boldsymbol{E}$ applies to all conductors. Combining the London equation with one of the Maxwell equations,

$$\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j}_{\eta\mathrm{s}} \quad , \tag{4.254}$$

according to

$$\nabla \times (\nabla \times \boldsymbol{B}) = \nabla(\nabla \cdot \boldsymbol{B}) - \Delta \boldsymbol{B} = -\Delta \boldsymbol{B} = \mu_0 \nabla \times \boldsymbol{j}_{\eta\mathrm{s}} \quad , \tag{4.255}$$

results in

$$\Delta \boldsymbol{B} = \mu_0 \frac{\rho_\mathrm{s}(-2e)^2}{2m_\mathrm{e}} \boldsymbol{B} \quad . \tag{4.256}$$

Using this differential equation, it is possible to describe the decay of a magnetic field in a superconductor, for the case where the field impinges the superconductor at its surface. As represented in Fig. 4.31, the fall-off is described by the solution of Eq. (4.256):

$$\boldsymbol{B} \propto \exp -\frac{x}{\lambda_\mathrm{L}} \quad , \tag{4.257}$$

where $\lambda_\mathrm{L}$ is the **London penetration depth** given by

$$\lambda_\mathrm{L}^2 = \frac{2m_\mathrm{e}}{\mu_0 \rho_\mathrm{s} (-2e)^2} \quad . \tag{4.258}$$

There is a current of superconducting charge carriers in the $y$ direction associated with the decaying magnetic field, which is polarised in the $z$ direction. It correspondingly only flows in a surface zone of thickness $\lambda_\mathrm{L}$.

~~Figure 4.32 shows what happens if an initially present external magnetic field, which passes through a closed superconducting loop, is switched off. In the general case, it is observed that surface currents of superconducting charge carriers remain in existence, with this being apparent because of a magnetic field which remains. It is observed that the remaining flux, which flows through the surface enclosed by the loop, is quantised, and increases in discrete steps of~~

$$\Phi_0 = \frac{\pi \hbar}{e} \quad . \tag{4.259}$$

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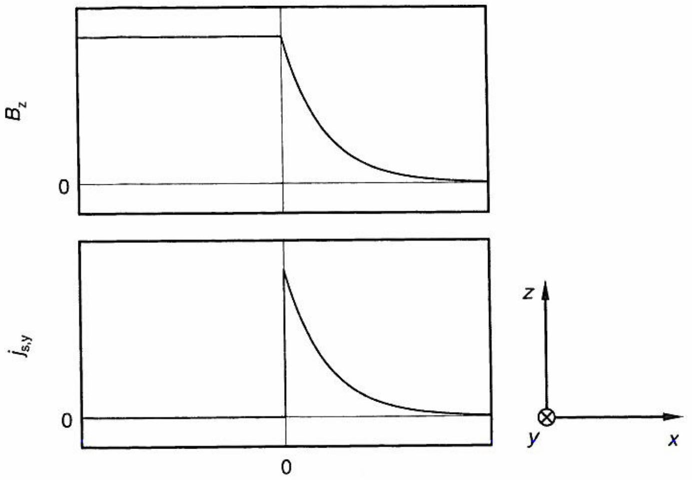

**Fig. 4.31.** The surface of a superconductor ($x > 0$) upon applying an external magnetic field: the exponential decay of the magnetic field strength $B_z$ and the current $j_{s,y}$ of the Cooper pairs.

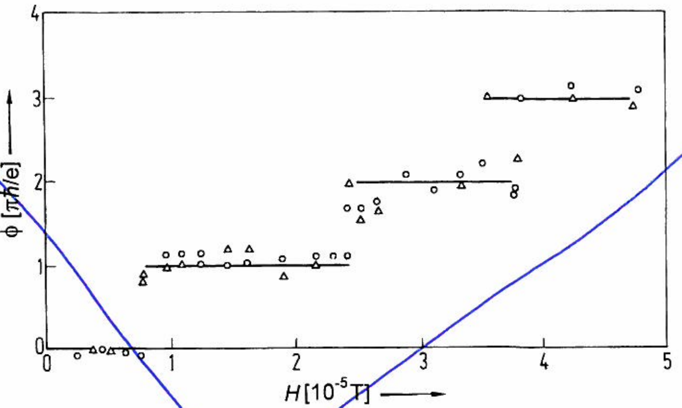

**Fig. 4.32.** The quantisation of the magnetic flux $\Phi$ which remains in a ring of superconducting tin after switching off an external field. The jump-like changes in the flux upon changing the strength of the field $H$ applied before the transition into the superconducting phase (from Deaver and Fairbank [37]).

Equation (4.244) can also be used to describe this phenomenon of flux quantisation. Consider a closed path inside the loop-like conductor where no current flows. Since

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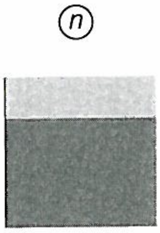

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Problem 3c)

~~must, in the first instance, penetrate the insulating layer, something which is possible by means of the tunnel effect for microscopic layers. The electrons can only do this, though, if there exists on the side of the superconductor an unoccupied level with the same energy which is, in principle, accessible for individual electrons. In the initial state, this is evidently not the case, and this remains so until a voltage is applied which is sufficiently strong that the situation on the right-hand side of the figure is attained. This means that current only flows if the energy gap is overcome with the help of an applied voltage which exceeds the minimum value~~

$$e\Delta V_{\min} = \frac{\Delta\epsilon_s}{2} \quad . \tag{4.264}$$

### 4.4.3 The Critical Magnetic Field. Type II Superconductors

Ginzburg and Landau also showed how a thermodynamic theory for describing the transition from the normal to the superconducting state can be developed within the framework of the description of superconductors by the wavefunction $\Psi$. The approach is the same as that which was used to treat other second-order phase transitions, such as the transition into the ferromagnetic or ferroelectric state: A suitable expansion of the Gibbs free energy density in terms of powers of the order parameter, which controls the phase transition, is chosen. This order parameter is now the wavefunction $\Psi$. $\Psi$ exhibits the desired behaviour in that, upon cooling, it sets in at zero at the critical point $T_c$ and then continually rises. In fact, the phase transition is correctly described by the following expression:

$$g(\Psi) = g(0) + b(T - T_c)|\Psi|^2 + c_4|\Psi|^4 \quad , \quad \text{where } b > 0 \text{ and } c_4 > 0 \ . \tag{4.265}$$

The expression is identical with those in Eqs. (3.15) and (3.31) for ferroelectrics and ferromagnets, and the conclusions derived there can be directly carried over. The order parameter, now $\Psi$, earlier $P$ and $M$, is thermodynamically an inner variable. Equilibrium corresponds to the minimum in the Gibbs free energy. Plots of the Gibbs free energy density above and below $T_c$ are shown in Fig. 3.5. In the superconducting state, the equilibrium value is given by analogy to Eq. (3.17) as

$$|\Psi|^2_{\text{eq}} = \frac{b(T_c - T)}{2c_4} \quad , \tag{4.266}$$

while, in the normal conducting state, it must be equal to zero. The result shows that the concentration of superconducting charge carriers, i.e., the Cooper pairs, increases linearly upon cooling below $T_c$:

$$\rho_s = |\Psi|^2_{\text{eq}} \propto T_c - T \quad . \tag{4.267}$$

Problem 3 d)

$$g(\Psi(\boldsymbol{r})) = g(0)+b(T-T_\mathrm{c})|\Psi|^2+c_4|\Psi|^4+\frac{1}{4m_\mathrm{e}}\left|(-\mathrm{i}\hbar\nabla-(-2e)\boldsymbol{A})\,\Psi\right|^2-\int\limits_0^H B\mathrm{d}H' \tag{4.274}$$

Seen from the point of view of quantum mechanics, the fourth term has the meaning of a kinetic energy of the superconducting particles (charge $-2e$, mass $2m_\mathrm{e}$). Empirically, it is also the simplest term which can take into account a spatial variation of $\Psi$. The fifth term describes the lowering of the density of the Gibbs free energy upon the penetration of a magnetic field into the sample (Eq. (A.10)), something which happens for the two-phase states of type II superconductors in the normal conducting parts and a transition region with a thickness corresponding to the London penetration depth.

On the basis of the Ginzburg–Landau equation (4.274), two-phase structures can be handled and an explanation can also be provided as to under which circumstances they appear. It is not possible to explain this exactly here, and the discussion is limited to a few short explanations. In principle, in order to determine the equilibrium state, it is necessary to find the wavefunction $\Psi(\boldsymbol{r})$ which is associated, for the given boundary conditions, with the minimum in the total Gibbs free energy of the sample

$$\mathcal{G} = \int\limits_{\mathcal{V}} g(\Psi(\boldsymbol{r}))\mathrm{d}^3\boldsymbol{r} \quad . \tag{4.275}$$

Standard variation methods can be used to solve this problem. Figure 4.36 shows a schematic representation of one of the solutions found in this way. It represents an individual normal conducting tube in a superconducting matrix. The upper and lower pictures depict the concentration distribution of the superconducting charge carriers $\rho_\mathrm{s}(\boldsymbol{r}) = |\Psi|^2(\boldsymbol{r})$ and the spatial variation of the magnetic field $B$, respectively. For both parameters, there is not an abrupt change between the two phases. As was established above, an external magnetic field also penetrates into the superconducting part to a depth corresponding to the London penetration depth $\lambda_\mathrm{L}$. The Ginzburg–Landau theory now yields a second characteristic length, which is referred to as the **coherence length** $\xi_\mathrm{G}$; this characterises the width of the region within which the concentration of the superconducting charge carriers changes from a value of zero in the normal conductor to the end value $|\Psi|^2_\mathrm{eq}$ in the superconductor. The parameter $\xi_\mathrm{G}$ can be derived from the Ginzburg–Landau equation (4.274) by making a plausible argument. If all field contributions are neglected, $g$ can be re-expressed as

$$g(\Psi(\boldsymbol{r}))-g(0) \propto -\frac{|\Psi|^2(\boldsymbol{r})}{|\Psi|^2_\mathrm{eq}}+\frac{|\psi|^4(\boldsymbol{r})}{2|\Psi|^4_\mathrm{eq}}+\xi_\mathrm{G}^2\frac{|\nabla\Psi|^2(\boldsymbol{r})}{|\Psi|^2_\mathrm{eq}} \quad , \tag{4.276}$$

where, according to Eq. (4.266), the end value of the superconducting charge carrier concentration is given by

$$|\Psi|^2_{\mathrm{eq}} = \frac{b(T_\mathrm{c} - T)}{2c_4}$$

and

$$\xi_\mathrm{G}^2 = \frac{\hbar^2}{4m_\mathrm{e} b(T_\mathrm{c} - T)} \quad . \tag{4.277}$$

$\xi_\mathrm{G}$ is the only parameter in the expression, and it has the dimensions of length. In Fig. 4.36, the only length is the width of the transition region, and it must, therefore, be determined by $\xi_\mathrm{G}$. Equation (4.277) states that $\xi_\mathrm{G}$ diverges upon approaching $T_\mathrm{c}$ and follows the power law

$$\xi_\mathrm{G} \propto (T_\mathrm{c} - T)^{-1/2} \quad . \tag{4.278}$$

In the figure, $\lambda_\mathrm{L}$ is chosen to be larger than $\xi_\mathrm{G}$. In fact, this is a fundamental prerequisite for the appearance of a two-phase structure, i.e., a type II superconductivity. The reason for this is qualitatively easy to recognise. A normal conducting tube only spontaneously forms in a superconducting matrix if a lowering of the Gibbs free energy of the system results in the presence of a magnetic field $H$. Here, two terms, which act against each other, come into consideration: Firstly, the increase in the Gibbs free energy because of the higher value in the normal conducting phase corresponding to Eq. (4.272), and, secondly, the lowering in the Gibbs free energy due to the penetration of the magnetic field, as described by Eq. (A.10). Even if the core region of the normal conducting tube should be vanishingly small, it has, because the

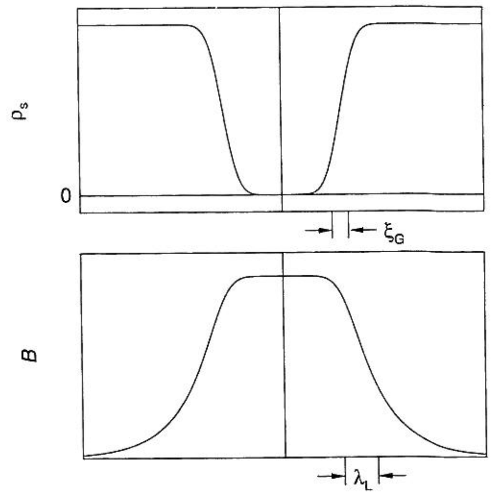

**Fig. 4.36.** The distribution of the magnetic field $B$ and the density of Cooper pairs $\rho_\mathrm{s}$ in the region of a normal conducting tube. The London penetration depth $\lambda_\mathrm{L}$ and the coherence length $\xi_\mathrm{G}$.