

Studentnumber: \_\_\_\_\_

**English** Page 1 of 1

NORGES TEKNISK-  
NATURVITENSKAPELIGE UNIVERSITET  
INSTITUTT FOR FYSIKK

Contact during the exam:  
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**EXAM: TFY4245 FASTSTOFF-FYSIKK VK**

Friday 2. june 2006  
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	A	D	A	C	D	C	D	B	C	B	D	D

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

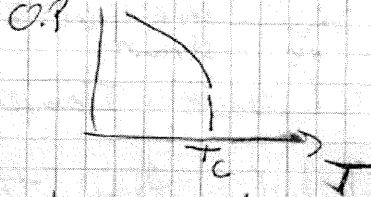
**Solution Problem 1. Phase transitions:**

a) Discuss the terms "first order" and "second order" phase transitions.

**Solution:**

1st order transition:

Discontinuity of o.p below transition point



$\Rightarrow$  Discontinuous entropy at  $T_c$

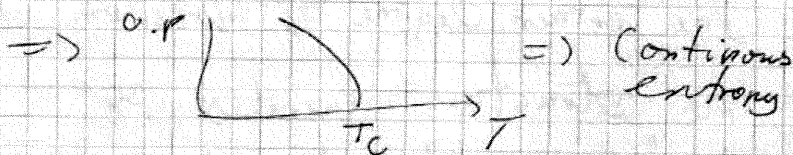
$$\Rightarrow S = - \left( \frac{\partial F}{\partial T} \right)_p = - \left( \frac{\partial G}{\partial T} \right)_p$$

$\leftarrow$  Helmholtz                       $\leftarrow$  Gibbs free energy

$\Rightarrow$  Discontinuity of 1st derivative of free energy for 1st order transition

2nd order transition

Continuous o.p at transition point



$\Rightarrow$  Continuous entropy

$$\text{If specific heat } C_p = T \left( \frac{\partial S}{\partial T} \right)_p = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_p$$

is discontinuous,  $\Rightarrow$  discontinuity of 2nd derivative of free energy  $\Rightarrow$  2nd order transition

3rd order transition  $\Rightarrow$  Discontinuity of 3rd order derivative and so on

- b) What is meaning of an order parameter in the context of phase transitions? Give examples of order parameters for real systems.

**Solution:**

## Chapter 3 Molecular fields and Critical Phase Transitions

Spontaneous polarization  
or  
magnetization  
or  
strain  
below Curie-Temperature  $T_c$

⇒ Self stabilization through  
Second order phase transition  
upon cooling through  $T_c$ .

2<sup>nd</sup> order phase transitions less  
common than 1<sup>st</sup> order.

In general for such phase transitions

One certain degree of freedom in  
the structure generates a  
molecular field which can  
self stabilize, i.e. "order" itself.

Order parameter describes how  
large the order is, ex.  $\vec{P}$  or  $\vec{M}$ .

Another example of such a phase transition:

Nematic liquid crystal

Isotropic  $\rightarrow$  Nematic transition

Orientational dependent interaction forces favour parallel arrangement of the rodlike molecules which may self stabilise.

$S_2$  is the order parameter

$\leftarrow$  Characterises degree of orientation

Fourth example:

Binary fluid polymer mixtures

$\rightarrow$  continuous transition to two-phase structure may occur

Here order parameter is the difference in composition between the two phases

Landau theory is a thermodynamic theory describing phase transitions, and this theory considers the Helmholtz free energy  $f(\eta, T)$ , where  $\eta$  is the order parameter, and  $T$  is the temperature: Landau theory assumes that near the phase transition temperature  $T_C$ , it is possible to expand the free energy in powers of  $\eta$ , thus

$$f(\eta, T) = f_0 + c_2\eta^2 + c_3\eta^3 + c_4\eta^4 + c_5\eta^5 + c_6\eta^6 + \dots + c_n\eta^n + \dots$$

Assume that  $c_2(T) = b(T - T_C)$ , where  $b$  is a positive constant, and also assume that  $c_3, c_4, c_5, c_6, \dots, c_n, \dots$  are constants independent of  $T$ .

Consider the following cases:

- c)  $c_3 = 0$ ,  $c_4$  is positive, and  $c_n = 0$  for  $n > 4$ . Does this case describe a first order, or a second order phase transition? Without any detailed calculations, first sketch and discuss  $\eta(T)$ , and sketch and discuss  $f(\eta, T)$  for various  $T$ . Then derive the temperature dependence of the order parameter for this case. Do you know of any real systems that belong to this case? What difference does it make if  $c_4$  is negative?

**Solution:**

In the following rename  $\eta$  to  $P$ :

(The solution is scanned from Strobl: Condensed Matter Physics)

Real systems:

Some ferroelectric transitions belong to this case. Some ferroelastics, etc.

**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

$$f(P, T) \text{ .}$$

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

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

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

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

Since the following must of course be valid

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

only even-order terms appear in the expansion:

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

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:

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

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

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

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

$$f = f_0 + b(T - T_c)P^2 + c_4P^4 \text{ .} \quad (3.15)$$

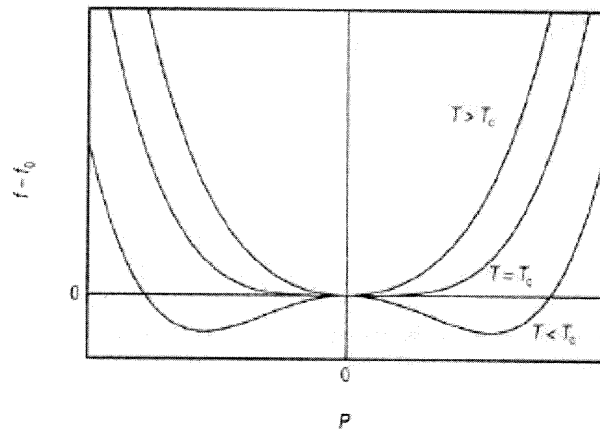
Figure 3.5 shows this dependence for a fixed, positive coefficient  $c_4$  for three different temperatures, namely one above  $T_c$ , one at the Curie temperature and one below  $T_c$ . The consequences are immediately recognisable: Above the Curie temperature, the equilibrium is, as observed, at  $P = 0$ , 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:

$$\frac{\partial f}{\partial P} = 0 = 2b(T - T_c)P + 4c_4P^3 \text{ .} \quad (3.16)$$

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

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



**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 below  $T_c$ . The case of a second-order transition.

i.e.,

$$|P_s| \propto (T_c - T)^{1/2} \text{ .} \quad (3.18)$$

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

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

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.

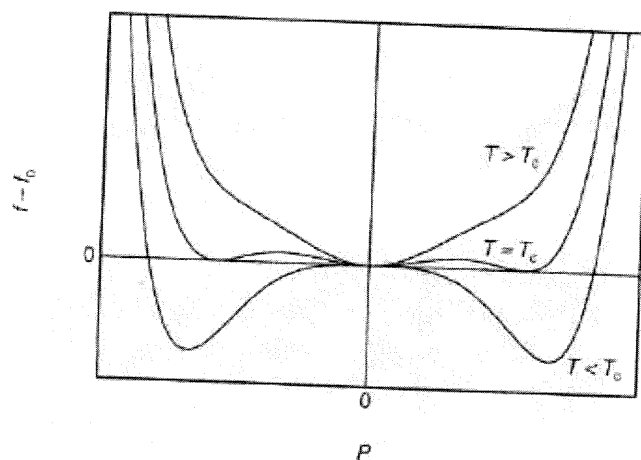


Fig. 3.6. The Landau expansion of the Helmholtz free energy density at the transition into the ferroelectric phase ( $T_c$ ) as well as for temperatures above and below  $T_c$ . The case of a 'weakly first order' transition.



- d)  $c_3$  is negative,  $c_4$  is positive, and  $c_n = 0$  for  $n > 4$ . Does this case describe a first order, or a second order phase transition? Without any detailed calculations, first sketch and discuss  $\eta(T)$ , and sketch and discuss  $f(\eta, T)$  for various  $T$ . Then derive the temperature dependence of the order parameter for this case. Do you know of any real systems that belong to this case?

**Solution:**

In the following rename  $\eta$  to  $S_2$ , and  $T_c$  to  $T^*$ .

(The solution is scanned from Strobl: Condensed Matter Physics)

Real systems:

Isotropic to nematic transitions.

**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

$$f - f_0 = b(T - T^*)S_2^2 - c_3S_2^3 + c_4S_2^4 \quad (3.40)$$

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.

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  $S_2$ :

$$\frac{df}{dS_2} = 0 = 2b(T - T^*)S_2 - 3c_3S_2^2 + 4c_4S_2^3 \quad (3.41)$$

The co-existence condition is given by

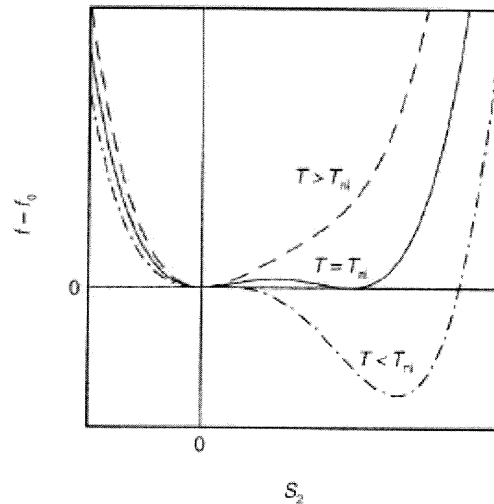
$$f(S_2 = 0) - f_0 = f(S_2 = S_2(T_{ni})) - f_0 = 0 \quad (3.42)$$

which means that

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

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

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



**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 ( $T > T_{ni}$ ) or only the nematic phase ( $T < T_{ni}$ ) exists.

The situation at the temperature  $T^*$  is given by

$$T_{ni} - T^* = \frac{c_3^2}{4bc_4} \quad (3.45)$$

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

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

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.

- e) Assume that there exists an external field,  $X$ , which couples linearly to the order parameter,  $\eta$ , i.e. an extra term  $-\eta X$  must be added in the free energy expression (i.e. use Gibbs free energy rather than Helmholtz free energy given above). Derive an expression the susceptibility for case c).

**Solution:**

In the following rename  $\eta$  to  $P$ , and  $X$  to  $E$ .

(The solution is scanned from Strobl: Condensed Matter Physics)

$$\hat{g} = f - EP = f_0 + b(T - T_c)P^2 + c_4P^4 - EP \quad (3.19)$$

The minimum condition

$$\frac{\partial \hat{g}}{\partial P} = 0 = -E + 2b(T - T_c)P + 4c_4P^3 \quad (3.20)$$

leads to

$$\frac{1}{\epsilon_0 \chi} = \frac{dE}{dP}(E=0) = 2b(T - T_c) + 12c_4P_{eq}^2 \quad (3.21)$$

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

$$\epsilon_0 \chi = \frac{1}{2b(T - T_c)} \quad (3.22)$$

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  $T < T_c$ . Using the value for  $P_{eq}$  given by Eq. (3.17) gives

$$\frac{1}{\epsilon_0 \chi} = 2b(T - T_c) + 12 \frac{b(T_c - T)}{2} \quad (3.23)$$

and thus

$$\epsilon_0 \chi = \frac{1}{4b(T_c - T)} \quad (3.24)$$

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.

f) Discuss the validity of the Landau theory for phase transitions.

**Solution:**

**Critical Fluctuations.** A further consideration of Figs. 3.7 and 3.8 shows that while the prediction of Landau's theory reproduces the curves very well overall, upon a closer examination, systematic differences are observed. Differences of this type are always found for second-order phase transitions. Sometimes, they exist, as in the example, over a wider temperature range, while, in other cases, they are focused on a very small region near  $T_c$ . Landau's **molecular field theory** actually loses its validity here. The origin for this is, in principle, easy to understand, and follows as a consequence of a fundamental property of critical transitions. The trigger for the phase transition is the fact that the restoring forces in the material, which make the polarisation or magnetisation generated by an external field disappear again after switching off the external field, become ever smaller upon approaching the Curie temperature. In this temperature range, a magnetisation or polarisation can temporarily emerge without an external field, simply via thermal fluctuations. Local regions form, in which there is a preferred orientation of the electric dipoles or the spins. They are not stable, but vanish again. Their lifetime depends on the weak but still present restoring forces; the weaker they are, the larger and longer-lasting the temporarily ordered regions become. In Landau's theory, the stabilising action is attributed solely to the average value of the molecular field, the latter being expressed via the polarisation  $P$  or the magnetisation  $M$ . If the fluctuations are very strong, the average field is no longer the decisive parameter, and Landau's theory which is based on this loses its validity.

Actually, it is also possible to describe theoretically the region very close to the Curie temperature, which is marked by strong fluctuations. The basis for this is a symmetry property which **critical fluctuations** possess near to  $T_c$ , namely their self-similarity. In this range, magnetised or polarised regions of all sizes appear, without there being a definite characteristic length. As a consequence images of the varying magnetic or polarization structure are invariant upon changing the spatial resolution, i.e., they always have a similar appearance. It is exactly this property which is used in a **renormalisation group theory** due to Wilson in order to make precise statements about the changes in the order parameter and susceptibility in the vicinity of  $T_c$ . It is found that power laws are always obtained for the magnetisation,

$$M \propto (T_c - T)^\nu, \quad (3.36)$$

and also for the susceptibilities below the Curie temperature,

$$\kappa \propto (T_c - T)^{-\gamma} \quad (3.37)$$

and above  $T_c$ ,

$$\kappa \propto (T - T_c)^{-\gamma'} \quad (3.38)$$

Renormalisation group theory provides algorithms by which the **critical coefficients**  $\nu$ ,  $\gamma$  and  $\gamma'$  can be calculated. The results of these calculations are in general in very good agreement with the observations.

In spite of this, Landau's theory maintains its validity within the proper limits: Its applicability begins when the fluctuation effects no longer play a large role and the molecular field takes over control in terms of the average field.

**Solution Problem 2. Fields, response functions and relaxation processes:**

Consider a material for which one of the molecules may be in one of two states separated by an energy barrier,  $E$ . At finite temperatures, the molecule in question changes back and forth between the two situations (states) with a "jump" frequency between states given by a so-called Arrhenius expression  $f = 1/\tau = \tau_0^{-1} \exp(-E/k_B T)$ , where  $\tau_0$  is a local time characteristic for oscillations within one of the states, and  $k_B$  is Boltzmann's constant. Assume further that by application of an external field,  $\sigma$ , a local preference for one of the states is introduced, thus resulting in a redistribution of the population of the two states, and that this may be described by a simple Debye type relaxation process.

- a) Use common sense to write down a simple linear differential equation describing the simple relaxation process.

A creep experiment means application of constant external field  $\sigma^0$  at and for all times after some time  $t_0$ , and  $\sigma^0 = 0$  for  $t < t_0$ .

We define the response field as  $\Delta\gamma = \Delta J(\omega) \sigma$ , where  $\Delta J(\omega)$  is the frequency ( $\omega$ ) - dependent response function.

Show that the response field,  $\Delta\gamma$ , for the case when a "creep experiment" is performed on a sample of the material, may be written as

$$\Delta\gamma(t > t_0) = \Delta J(0) \sigma^0 (1 - \exp(-t/\tau))$$

Sketch and discuss the result as a function of time for various temperatures.

**Solution:**

In the following we drop the subscripts  $zx$ . The solution is scanned from Strobl.

$$\Delta\gamma(t \rightarrow \infty) = \Delta J \sigma_{zx}^0,$$

it is possible to describe the adjustment process in the following way:

$$\frac{d\Delta\gamma}{dt} = -\frac{1}{\tau} (\Delta\gamma(t) - \Delta J \sigma_{zx}^0) \quad (2.75)$$

This relaxation equation implies that a system, which is forced from equilibrium (here, this is achieved by applying a stress), returns to equilibrium at

a rate which increases proportionally with the perturbation. The solution of the differential equation is

$$\Delta\gamma(t) = \Delta J \sigma_{zx}^0 \left( 1 - \exp\left(-\frac{t}{\tau}\right) \right) \quad (2.76)$$

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

omdøring av variabel

$$\Delta J = \alpha$$

$$\sigma = \sigma$$

$$\sigma^0 = \sigma_0$$

↑ ↙ oppgave tekst

↳ smuss  
↳ klug

- b) Perform a dynamic experiment as a function of external applied frequency (assuming constant force amplitude) on the same material. Derive the expression for the frequency dependent complex compliance response function. Sketch and discuss the result as a function of frequency and temperature. The real and imaginary parts of the compliance are often referred to as the storage part and the loss part respectively. Discuss the physics behind this distinction.

**Solution:**

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

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

gives

$$\frac{d\Delta\gamma}{dt} = -\frac{1}{\tau} [\Delta\gamma(t) - \Delta J \sigma_{zx}^0 \exp(-i\omega t)] \tag{2.78}$$

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

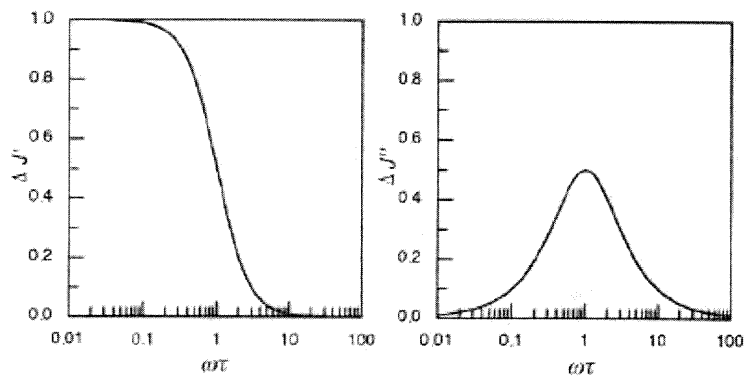
$$\Delta\gamma(t) = \sigma_{zx}^0 [\Delta J'(\omega) + i\Delta J''(\omega)] \exp(-i\omega t) \tag{2.79}$$

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

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

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

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.

observation that the imaginary part, for a logarithmic frequency scale, corresponds to a symmetric 'Lorentzian' curve is apparent if it is re-expressed as

$$\Delta J''(\omega) = \frac{\Delta J}{10^{-\log(\omega\tau)} + 10^{\log(\omega\tau)}} \quad (2.82)$$

An important conclusion can be drawn from this result, namely that the maximum loss occurs when

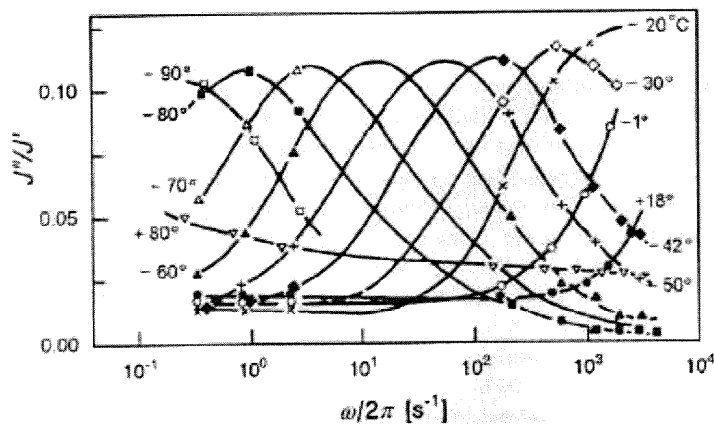
$$\omega\tau = 1 \quad (2.83)$$

i.e., exactly when the frequency of the external force which causes the excitation corresponds to the relaxation rate  $\tau^{-1}$ . Around the same condition,  $\Delta J'(\omega)$  decreases in a step-like fashion from one to zero. In our example of the cyclohexyl side groups, the relaxation rate is identical to the jump rate with which the side groups change between the two possible conformations. It is to be emphasised that the applied force does not alter this jump rate. At thermodynamic equilibrium, jumps between the two conformations take place at the same rate, and this determines the time required for the system to react to external changes. Thus, dynamic-mechanical experiments allow the investigation of the dynamics of conformational redistributions, i.e., the determination of the time associated with a particular process. The method is, therefore, sometimes referred to as **relaxation spectroscopy**.

The temperature-dependent change in the rate of the transition between the chair and boat conformations can be determined from the shift in the location of the loss maxima in Fig. 2.15. An analysis shows that the temperature dependence of this process is consistent with the Arrhenius law

$$\tau^{-1} \propto \exp -\frac{\Delta\tilde{u}_b}{RT} \quad (2.84)$$

A value of 47 kJ mol<sup>-1</sup> is obtained for the activation energy. This is the energy barrier which must be overcome during the transition from one conformation to the other.



**Fig. 2.15.** The frequency dependence of the imaginary part of the dynamic shear compliance ( $J' \approx \text{const}$ ), as measured on poly(cyclohexylmethacrylate) at different temperatures in the glassy state (from Heijboer [14]).

In the following, replace  $\Delta J$  with  $D_t$  and  $\gamma$  with  $e_{zz}$ , we drop the  $zz$  subscripts for simplicity. The solution is scanned from Strobl.

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

$$\frac{dw}{dt} = \Re(\sigma_{zz}(t)) \frac{d\Re(e_{zz}(t))}{dt} \quad (2.53)$$

(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

$$e_{zz}(t) = D_t(\omega)\sigma_{zz}^0 \exp(-i\omega t) = (D_t' + iD_t'')\sigma_{zz}^0 [\cos(\omega t) - i \sin(\omega t)] \quad (2.54)$$

The real part is then given by

$$\Re(e_{zz}(t)) = D_t'\sigma_{zz}^0 \cos(\omega t) + D_t''\sigma_{zz}^0 \sin(\omega t) \quad (2.55)$$

Therefore, the following expression is obtained for the power

$$\frac{dw}{dt} = \sigma_{zz}^0 \cos(\omega t) [-\omega\sigma_{zz}^0 D_t' \sin(\omega t) + \omega\sigma_{zz}^0 D_t'' \cos(\omega t)] \quad (2.56)$$



or, upon applying a well-known trigonometric relation

$$\frac{dw}{dt} = -\frac{(\sigma_{zz}^0)^2}{2} \omega D_t' \sin(2\omega t) + (\sigma_{zz}^0)^2 \omega D_t'' \cos^2(\omega t) \quad . \quad (2.57)$$

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

$$\overline{\frac{dw}{dt}} = \frac{1}{2} (\sigma_{zz}^0)^2 \omega D_t'' \quad . \quad (2.58)$$

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

$$d\mathcal{U} = \mathcal{V}dw + dQ \quad . \quad (2.59)$$

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:

$$\mathcal{V} \overline{\frac{dw}{dt}} = -\overline{\frac{dQ}{dt}} \quad . \quad (2.60)$$

### Solution Problem 3. Microscopic dynamics:

- a) Discuss the physics contained in the Einstein relation for the “self-diffusion coefficient”

$$D_s = k_B T \nu$$

, where  $k_B$  is Boltzmann's constant,  $T$  is the temperature, and  $\nu$  is the mobility. In the discussion, consider that it can be shown that  $6D_s = \langle |\mathbf{r}(t)|^2 \rangle / t$  which is the mean squared displacement achieved by a diffusing particle per unit time,  $t$ .

Consider a suspension of non-interacting colloidal particles, and assume the following:

- a particle density gradient  $\nabla \rho$  resulting in Fick's law for the diffusive particle current  $\mathbf{j}_D = -D_s \nabla \rho$ .
- an external force (for example gravity)  $\mathbf{f} = \nabla u_{\text{pot}}$ , where  $u_{\text{pot}}$  is the potential energy difference set by the external force that drives a particle current  $\mathbf{j}_f = \rho \nu \mathbf{f}$ .
- at equilibrium, the particle density  $\rho = \rho_{\text{eq}} = \exp(-u_{\text{pot}}/k_B T)$  according to Boltzmann statistics

Using these assumptions, show how the Einstein relation can be derived.

Discuss the difference between the “self-diffusion coefficient”,  $D_s$ , and the “diffusion coefficient”,  $D$ .

**Solution:**

Scanned from Strobl:

#### 5.2.2 Mobility and the Einstein Relation

It might seem at first that nothing further can be said about the value of a self-diffusion coefficient. In fact, this is not the case. Einstein derived, on the basis of a thought experiment for the case of non-interacting colloidal particles in solution, an expression which can be immediately used. The thought experiment concerns the situation of a colloidal solution in a potential field, which can be simply the gravitational field, or, in the case of charged particles, also an electric field. It is generally observed that a colloid in solution

moves, under the influence of an external force, at a constant velocity, which is proportional to the force:

$$\mathbf{v} \propto \mathbf{f} \quad (5.161)$$

The proportionality factor

$$\nu = \frac{v}{f} \quad (5.162)$$

is referred to as the **mobility**, while its inverse

$$\zeta = \frac{1}{\nu} = \frac{f}{v} \quad (5.163)$$

has the meaning of a coefficient of friction.

In spite of the motion caused by the field, there is a stationary state,  $\rho_{\text{eq}}(\mathbf{r})$ , for the density distribution of the colloids. It is given by Boltzmann statistics as

$$\rho_{\text{eq}} \propto \exp\left(-\frac{u_{\text{pot}}}{k_{\text{B}}T}\right) \quad (5.164)$$

Einstein explained the existence of this stationarity in terms of the existence of a dynamic equilibrium between two compensating particle currents. There is a particle current density

$$\mathbf{j}_f = \rho \mathbf{v} = \rho \nu \mathbf{f} \quad (5.165)$$

which is caused to flow by the forces of the potential field. With the force

$$\mathbf{f} = -\nabla u_{\text{pot}} \quad (5.166)$$

it follows that

$$\mathbf{j}_f = -\rho \nu \nabla u_{\text{pot}} \quad (5.167)$$

The second particle current in the opposite direction is driven by the gradients in the particle density – Fick's law applies in this case. For non-interacting colloids, it is not necessary to distinguish between  $D$  and  $D_s$ , i.e.,

$$D = D_s \quad ,$$

and the diffusive particle current is then given as

$$\mathbf{j}_D = -D_s \nabla \rho \quad (5.168)$$

At equilibrium, i.e., for  $\rho = \rho_{\text{eq}}$ , the two currents compensate each other:

$$\mathbf{j}_D + \mathbf{j}_f = 0 \quad (5.169)$$

It, thus, follows that

$$D_s \nabla \rho_{\text{eq}} + \rho_{\text{eq}} \nu \nabla u_{\text{pot}} = 0 \quad (5.170)$$

Upon introducing the equilibrium distribution, Eq. (5.164), a generally applicable relation between the self-diffusion coefficient and the mobility is obtained. It is referred to as the **Einstein relation** and is given as

$$D_s = k_B T \nu \quad (5.171)$$

On the right-hand side, the mobility, a reaction parameter, describes the effect exerted by an external force of arbitrary nature on the motion of a colloid in solution. The result of the action is a motion with constant velocity. The left-hand side of the relation contains a parameter which has a purely statistical character – it describes the mean squared displacement of a colloid which would result in the absence of any external force, being solely driven by collisions with the solvent molecules. The Einstein relation states that these very different parameters are linked by the factor  $k_B T$ .

With the help of the Einstein relation it is possible to make a further step. **Stokes' law**, which is derived using the laws of hydrodynamics, specifies the size of the force which arises when a spherical particle undergoes a motion with a constant velocity  $\mathbf{v}$  through a liquid with viscosity  $\eta$ . The force depends on the radius of the particle according to

$$\mathbf{f} = 6\pi R\eta\mathbf{v} \quad (5.172)$$

Since the viscous force equals the external driving force, Stokes' law provides an explicit expression for the mobility of a colloid. Inserting it into the Einstein relation yields

$$D_s = \frac{k_B T}{6\pi R\eta} \quad (5.173)$$

This is an equation, which can be directly used in order to determine the self-diffusion coefficient of a colloid of radius  $R$  in a solution with viscosity  $\eta$  at a temperature  $T$ .

The question then arises as to whether this equation also gives sensible values when applied to the case of diffusion of individual molecules in a molecular liquid, using, together with the macroscopic viscosity, an estimate for  $R$ , namely the molecular radius, which is a variable in the nm range. In fact, a comparison with experimental results reveals that the so-obtained results are generally correct to at least within an order of magnitude.

The self-diffusion coefficient  $D_s$  and the diffusion coefficient  $D$  in Fick's law are necessarily the same for the case of free, non-interacting colloids. The situation changes when interacting particles are involved. In Fick's law, the gradient of the particle density is then to be replaced by the gradient of the chemical potential, and  $D$  becomes a **cooperative diffusion coefficient**, which differs from the self-diffusion coefficient. The definition of the latter remains unchanged;  $D_s$  always describes, according to Eq. (5.147), the mean squared displacement per unit time.

- b) The probability of finding a diffusing particle at distance  $\mathbf{r}(t)$  at time  $t$ , assuming  $\mathbf{r}(t=0) = 0$ , is given by the time-dependent auto-correlation function  $g_1(\mathbf{r}(t),t) = (1/(4\pi D_s t))^{3/2} \exp(-|\mathbf{r}(t)|^2/(4D_s t))$  which follows from a Greens function solution of the diffusion equation for  $g_1(\mathbf{r}(t),t)$ .

For such non-interacting particles the time dependent structure function  $S(\mathbf{q},t)$  equals the Fourier transform of  $g_1(\mathbf{r}(t),t)$ , where the scattering vector  $\mathbf{q}$  is the difference between the outgoing and incoming wave-vectors respectively.

Discuss (in terms of words and equations) a light-scattering experiment which may be used to measure  $D_s$  for non-interacting colloidal particles in solution.

**Solution:**

Scanned from Strobl:

**5.5.2 Dynamic Light Scattering in Liquids**

**Colloidal Diffusion.** Figure 5.22 shows the result of a dynamic light scattering experiment performed on a dilute solution of polystyrene in toluene. The presented data were obtained after a subtraction of the scattering due to pure toluene from that observed for the solution, such that they represent only the dynamic scattering effects due to the polymer molecules. It was stated

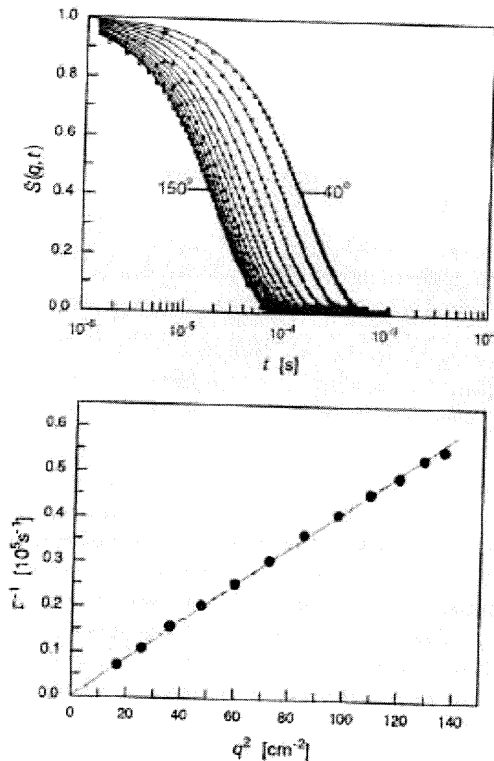


Fig. 5.22. Dynamic light scattering of a dilute solution of polystyrene in toluene. Time-dependent scattering function for different scattering vectors (above). The dependence of the decay constant on the scattering vector (below).

above that the dynamic light scattering experiment yields the intermediate scattering law  $S(\mathbf{q}, t)$ . The upper part of the figure shows the time-dependence of  $S(\mathbf{q}, t)$  as measured for different scattering angles. Each of the curves can be described by a simple exponential function, with it being apparent that the characteristic time  $\tau$  becomes ever smaller as the scattering angle increases. In the lower part of the figure, it is seen that a square law  $\tau^{-1} \propto q^2$  is obeyed.

The cause and significance of this result are readily understood. A polymer molecule in dilute solution exhibits a diffusive motion which is independent from that of the other polymer molecules. The time-dependent auto-correlation function  $g_1(\mathbf{r}, t)$  which was introduced in Sect. 5.2 can be used to describe this motion. According to Eq. (5.249),  $g_1(\mathbf{r}, t)$  is a part of the van Hove function, indeed, in the absence of pair-correlation functions, it is the only contribution.  $S(\mathbf{q}, t)$  can be calculated using Eq. (5.250), making use of the calculated expression (Eq. (5.157)) for the auto-correlation function

$$g_1(\mathbf{r}, t) = \frac{1}{(4\pi D_s t)^{3/2}} \exp\left(-\frac{|\mathbf{r}|^2}{4D_s t}\right) .$$

Upon realising that the pair correlation term  $g_2$  is given by

$$g_2 = \rho \tag{5.261}$$

in the case of a dilute solution in the absence of interactions between the polymers, it follows that

$$S(\mathbf{q}, t) = \int_{\mathcal{V}} \exp(-i\mathbf{q}\mathbf{r}) g_1(\mathbf{r}, t) d^3\mathbf{r} = \exp(-D_s q^2 t) . \tag{5.262}$$

This corresponds exactly to the observed experimental behaviour,  $\tau^{-1} \propto q^2$ . Moreover, the theoretical analysis has revealed that the self-diffusion coefficient  $D_s$  can be determined from the slope of the line in the figure.