

Studentnumber: _____

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INSTITUTT FOR FYSIKK

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

Monday 18. May 2009
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
English-Norwegian and/or Norwegian-English Dictionary

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
Answer	D	C	B	D	A	B	D	D	D	B

Question	11	12	13	14	15	16	17	18	19	20
Answer	B	D	A	B	A	B	A	D	D	D

Solutions referred to in boxes inserted in the text below

Problem 1. Dielectrics and Ferroelectrics**1a)**

Assume that we are studying a dielectric sample applying an external electric field E to it, such that the responding polarization $P = \epsilon_0 \chi E$, where $\chi = \epsilon - 1$ is the dielectric susceptibility, ϵ is the dielectric constant and ϵ_0 is the vacuum permittivity.

- Discuss the distinction between orientational (or) P_{or} and distortional (d) P_d polarizations respectively, in dielectrics.

Strobl pages 94-95

In a dielectric, one needs to distinguish between the externally applied field, E , and the local field, E_{loc} , in the sample. It is the local field at the site of a molecule that acts to polarize or reorient that molecule. The relation between the polarization P and the local field for monomolecular dielectrics is

$$P = P_{or} + P_d = \rho \beta E_{loc} \quad (1.1)$$

where ρ is the particle density, and $\beta = \beta_{or} + \beta_d$ is the polarisability.

- Discuss without entering into details, how it can be shown that for isotropic liquids and symmetric crystals

$$E_{loc} = E + P/(3\epsilon_0) \quad (1.2)$$

where E is the externally applied electric field, and $P/(3\epsilon_0) = E_L$ is the so-called Lorentz-field, which represents the average (mean-field) contribution to E_{loc} acting on one molecule from all the other molecules in the sample.

Strobl pages 98-100

- Show that for this case:

$$(\epsilon - 1)/(\epsilon + 2) = \rho \beta / (3\epsilon_0) \quad (1.3)$$

which is the Clausius-Mosotti equation for dielectrics.

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1b)

P_{or} is related to the orientation of molecular dipoles in the dielectric. The potential energy, u , of a molecule with dipole moment p_0 in an electric field E_{loc} is:

$$u = -p_0 E_{loc} \cos \theta \quad (1.4)$$

where θ is the angle between the dipole - direction and the E_{loc} - direction.

Defining the orientational distribution function for dipolar molecules in the dielectric as $w(\varphi, \theta)$, and thus obtaining the fraction of molecular dipoles in the angular interval $d\varphi d\theta$ as $w(\varphi, \theta) \sin(\theta) d\varphi d\theta$ (for $0 < \theta < \pi$ and $0 < \varphi < 2\pi$), we get by using standard Boltzmann statistics i.e. $w(\theta, \varphi) \propto \exp(-u/k_B T)$, where k_B is the Boltzmann constant and T is the temperature, that:

$$P_{or} = \rho p_0 \langle \cos \theta \rangle = \rho p_0 \left(\int d\varphi \int d\theta w(\varphi, \theta) \sin(\theta) \cos \theta \right) / \left(\int d\varphi \int d\theta w(\varphi, \theta) \sin(\theta) \right) \\ = \rho p_0 \int d\theta [2\pi \sin(\theta) \cos(\theta) \exp(x \cos(\theta))] / Z \quad (1.5)$$

where the variable $x = p_0 E_{loc} / (k_B T)$, the integral over θ run from 0 to π , the one over φ from 0 to 2π , and the normalization Z is the partition function:

$$Z = \int d\varphi \int d\theta w(\varphi, \theta) \sin(\theta) = \int d\theta [2\pi \sin(\theta) \exp(x \cos(\theta))] \\ = 2\pi [\exp(x) - \exp(-x)] / x \quad (1.6)$$

• Show that for temperatures $T \gg p_0 E_{loc} / k_B$, the orientational part of the polarisability in a dielectric can be written as:

$$\beta_{or} \approx (p_0)^2 / (3k_B T) \quad (1.7)$$

Strobl pages 101-102

• How can this result be used in a practical experiment to measure the distortional polarisability β_d ?

Strobl page 102

1c)

• Using Equation (1.3), show that

$$\epsilon_0 \chi = \rho \beta / (1 - \rho \beta / (3\epsilon_0)) \quad (1.8)$$

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• Discuss what happens, and what it means in terms of physics, if β increases with decreasing T in such a way that the Lorentz-field contribution $\rho \beta / (3\epsilon_0) = 1$ at some temperature $T = T_C$.

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The simplest T -dependence one can think of for this case, is linear in T , i.e. $\rho \beta / (3\epsilon_0) = 1 - c(T - T_C)$, where c is a constant.

• How does χ depend on temperature for this case, for temperatures $T > T_C$?

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1d)

Landau developed a phenomenological thermodynamic theory applicable to ferroelectrics (as well as other systems displaying phase transitions) describing the

observations that the susceptibility diverges on approaching T_C both from above and below in T .

Landau theory assumes that near the phase transition temperature T_C , it is possible to expand the Helmholtz free energy in powers of the order parameter η (in the case of ferroelectrics $\eta = P$), thus

$$f(\eta, T) = f_0 + c_2\eta^2 + c_3\eta^3 + c_4\eta^4 + c_5\eta^5 + c_6\eta^6 + \dots + c_n\eta^n + \dots \quad (1.9)$$

We 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 .

- Argue that for ferroelectrics (second order phase transitions by observation): $c_3 = 0$, c_4 is positive, and one need not consider any c_n for $n > 4$, i.e. $c_n = 0$ for $n > 4$.

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- Sketch and discuss $f(\eta, T)$ for various T .

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- Derive the temperature dependence of the order parameter for this case.

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Assume that there exists an external field, X (in the case of ferroelectrics $X = E$), which couples linearly to the order parameter, η , i.e. an extra term $-\eta X$ must be added in the free energy expression (i.e. we use Gibbs free energy rather than Helmholtz free energy).

- Use Landau theory to derive an expression for the temperature dependence of the susceptibility both above and below T_C , thus also verifying the result obtained in 1c).

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Problem 2. Diffusion

2a)

Diffusive motion of individual particles can formally be described by the time-dependent auto-correlation function $g_1(\mathbf{r}, t)$, defined such that the quantity $g_1(\mathbf{r}, t)d^3\mathbf{r}$ gives the probability that a particle moves during a time t from its starting point into a volume element $d^3\mathbf{r}$ which is $\mathbf{r}$ away from the starting point. $g_1(\mathbf{r}, t)$ is a probability distribution, and as such is normalized, i.e.

$$\int g_1(\mathbf{r}, t)d^3\mathbf{r} = 1 \quad (2.1)$$

We follow Einstein, and choose to break up $g_1(\mathbf{r}, t' + t)$ into two steps, and we write

$$g_1(\mathbf{r}, t' + t) = \int g_1(\mathbf{r} - \mathbf{r}', t') g_1(\mathbf{r}', t)d^3\mathbf{r}' \quad (2.2)$$

where the first step, during time t' , achieves a displacement $\mathbf{r}-\mathbf{r}'$ of the particle, while the second step, in the remaining time t , brings the particle to $\mathbf{r}$.

- What is the basic assumption underlying that we write the total probability as a product of two individual probabilities representing the two steps?

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- Show that Equation (2.2) can be rewritten (assuming $t \ll t'$ and $|\mathbf{r}'| \ll |\mathbf{r}|$) as a diffusion equation:

$$\partial g_1(\mathbf{r}, t') / \partial t = D_S \nabla^2 g_1(\mathbf{r}, t') \quad (2.3)$$

where the self-diffusion coefficient

$$D_S = (\int g_1(\mathbf{r}', t) |\mathbf{r}'|^2 d^3 \mathbf{r}') / (6t) = \langle |\mathbf{r}'|^2 \rangle / (6t) \quad (2.4)$$

represents the mean-squared displacement per unit time (divided by a factor 6).

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2b)

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

- A particle density gradient $\nabla \rho$ resulting in a diffusive particle current described by Fick's law

$$\mathbf{j}_D = -D_S \nabla \rho \quad (2.5)$$

- An external force (for example gravity) $\mathbf{f} = -\nabla u_{\text{pot}}$, where u_{pot} is the potential energy difference set by the external force, driving particle current

$$\mathbf{j}_f = \rho v \mathbf{f} = (\rho / \zeta) \mathbf{f} \quad (2.6)$$

where v is the mobility, and ζ is the friction coefficient.

- At equilibrium, the particle density $\rho = \rho_{\text{eq}} = \exp(-u_{\text{pot}}/k_B T)$ according to Boltzmann statistics, where k_B is Boltzmann's constant, and T is the temperature.

Using these three assumptions:

- Show how one derives the Einstein relation:

$$D_S = k_B T v = k_B T / \zeta \quad (2.7)$$

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Considering the result obtained in Equation (2.4):

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

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Finally:

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

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2c)

Equation (2.1), including the boundary condition $\mathbf{r}(t=0) = 0$, i.e. $g_1(\mathbf{r}, t=0) = \delta(\mathbf{r})$, has the Greens-function solution

$$g_1(\mathbf{r}(t), t) = (1/(4\pi D_s t))^{3/2} \exp(-|\mathbf{r}(t)|^2/(4D_s t)) \quad (2.8)$$

For non-interacting particles the time dependent structure function $S(\mathbf{q}, t)$ equals the Fourier transform of $g_1(\mathbf{r}(t), t)$.

- Discuss (briefly in terms of words and equations) the theoretical basis for a light-scattering experiment which may be used to measure D_s for non-interacting colloidal particles in solution. The scattering vector $\mathbf{q}$ is the difference between the outgoing and incoming wave-vectors respectively.

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Problem 3. Polymers**3a)**

We define the end-to-end vector of a coiled polymer chain to be $\mathbf{R}$.

Assume that the chain can be broken up into N_S individual uncorrelated segments $\mathbf{a}_j$ ($j = 1, 2, 3, \dots, N_S$), i.e.

$$\mathbf{R} = \sum_j \mathbf{a}_j \quad (3.1)$$

For uncorrelated unrestricted $\mathbf{a}_j$ vectors, the chain geometry is equivalent to stepwise independent Brownian motion of a diffusing particle, and we can directly adopt the results obtained in Equations (2.4) and (2.8) for the Gaussian probability distribution $w(\mathbf{R})$ for the chain end-to-end distance $\mathbf{R}$, and its mean-squared end-to-end distance

$$R_0^2 = \langle |\mathbf{R}|^2 \rangle = \int w(\mathbf{R}) R^2 4\pi R^2 dR \quad (3.2)$$

- Show that $R_0^2 \propto N \propto M$, where N is the degree of polymerization, and M is the chain molecular weight.

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- Show that a coiled Gaussian chain is an object with fractal dimension $D_f = 2$.

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3b)

The "tube model" for polymer dynamics introduced by Sam Edwards, takes entanglement effects among different chains into account in order to describe the chain dynamics in a polymer sample. This is a mean-field type model that focuses on individual chains, that includes interactions with other chains by representing them collectively as a "tube" inside which an individual chain is restricted to move, like a reptile (the de Gennes "reptation model") in linear diffusive motion (Equation (2.7)).

- Show that the disentanglement time, τ_d , for entangled polymer chains scales as

$$\tau_d \propto M^3 \quad (3.3)$$

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3c)

Internal relaxation times such as τ_d , may be measured by means of dielectric relaxation experiments. This can be described by a general set of linear equations valid also for dielectric measurements.

Consider a physical system that is forced out of equilibrium by applying a time (t) dependent external force, $\sigma(t)$, to it. For linear response, the response field perturbation of the system is:

$$\gamma(t) = \alpha \sigma(t) \quad (3.4)$$

where α is a linear response function which is characteristic of the specific system under consideration.

- What do γ , α and σ represent for the dielectric case?

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Assuming that after “turning off σ ”, the system returns to equilibrium, $\gamma(t = \infty)$, at a rate, $d\gamma(t)/dt$, which increases proportionally with the magnitude of the perturbation, $\gamma(t)$, we may write:

$$d\gamma(t)/dt = (\gamma(t = \infty) - \gamma(t))/\tau_d \quad (3.5)$$

where the system characteristic time, τ_d , is the constant of proportionality between the rate and the perturbation. Equation (3.5) represents a simple relaxation process (Debye relaxation).

Assume, that we apply a time dependent periodic force to the system, such that:

$$\sigma(t) = \sigma_0 \exp(-i\omega t) \quad (3.6)$$

where ω is the applied frequency, and σ_0 is the force amplitude. ($i = \sqrt{-1}$)
The resulting linear response can be written:

$$\gamma(t) = \alpha(\omega) \sigma(t) = \gamma_0 \exp(-i\omega t + i\delta(\omega)) \quad (3.7)$$

where $\delta(\omega)$ is the phase difference between the force and the response, and γ_0 is the response amplitude.

- Use the above Equations in order to derive an expression for the complex frequency dependent linear response function

$$\alpha(\omega) = \gamma(t)/\sigma(t) = \alpha'(\omega) + i\alpha''(\omega) \quad (3.8)$$

for the case of a simple relaxation process like the one in Equation (3.5).

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- Sketch both $\alpha'(\omega) = \text{Re}(\alpha(\omega))$ and $\alpha''(\omega) = \text{Im}(\alpha(\omega))$ for this case.

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- 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.

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