NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET
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 $P = \varepsilon_0 \chi E$, where $\chi = \varepsilon - 1$ 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

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

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

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

$$E_{loc} = E + P/(3\varepsilon_0) \qquad (1.2)$$

where E is the externally applied electric field, and $P/(3\varepsilon_0) = E_L$ 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:

$$(\varepsilon-1)/(\varepsilon+2) = \rho\beta/(3\varepsilon_0) \qquad (1.3)$$

which is the Clausius-Mosotti equation for dielectrics.
Strobl page 100

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:

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

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:

$$P_{or} = \rho p_0 <\cos\theta> = \rho p_0 (\int d\varphi \int d\theta w(\varphi,\theta)\sin(\theta)\cos\theta)/(\int d\varphi \int d\theta w(\varphi,\theta)\sin(\theta))$$
$$= \rho p_0 \int d\theta [2\pi\sin(\theta)\cos(\theta)\exp(x\cos(\theta))]/Z \qquad \textbf{(1.5)}$$

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:

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

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

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

Strobl pages 101-102

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

Strobl page 102

1c)
• Using Equation **(1.3)**, show that

$$\varepsilon_0 \chi = \rho\beta/(1-\rho\beta/(3\varepsilon_0)) \qquad \textbf{(1.8)}$$

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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 $\rho\beta/(3\varepsilon_0) = 1$ 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. $\rho\beta/(3\varepsilon 0) = 1 - c(T-T_C)$, 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 η = P), thus

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

We assume that $c_2(T) = b(T - T_C)$, where b is a positive constant, and also assume that $c_3, c_4, c_5, c_6, ..., c_n, ...$ 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.

Strobl page 132-133

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

Strobl page 132-133

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

Strobl page 132-133

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.

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

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

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

where the first step, during time t', achieves a displacement **r-r'** of the particle, while the second step, in the remaining time t, brings the particle to **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<<t' and |**r'**|<<|**r**|) as a diffusion equation:

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

where the self-diffusion coefficient

$$D_S = (\int g_1(\mathbf{r'},t)|\mathbf{r'}|^2 d^3\mathbf{r'})/(6t) = <|\mathbf{r'}|^2>/(6t) \tag{2.4}$$

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

Strobl page 291

2b)
Consider a suspension of non-interacting colloidal particles, and assume the following:

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

$$\mathbf{j}_D = -D_S\nabla\rho \tag{2.5}$$

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

$$\mathbf{j}_f = \rho\nu\mathbf{f} = (\rho/\varsigma)\mathbf{f} \tag{2.6}$$

where ν is the mobility, and ς is the friction coefficient.

iii) At equilibrium, the particle density $\rho = \rho_{eq} = \exp(-u_{pot}/k_BT)$ 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:

$$D_S = k_BT\nu = k_BT/\varsigma \tag{2.7}$$

Strobl page 294-295

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

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

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.

Strobl page 319-320

Problem 3. Polymers

3a)
We define the end-to-end vector of a coiled polymer chain to be **R**.
Assume that the chain can be broken up into N_S individual uncorrelated segments $\mathbf{a}_j$ (j = 1,2,3,.....,N_S), i.e.

$$\mathbf{R} = \Sigma_j\, \mathbf{a}_j \qquad\qquad (3.1)$$

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(**R**) for the chain end-to-end distance **R**, and its mean-squared end-to-end distance

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

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

Strobl page 38-39

• 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

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

Stroble page 310-312

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:

$$\gamma(t) = \alpha\, \sigma(t) \qquad\qquad (3.4)$$

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?

Sroble page 93

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:

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

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:

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

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

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

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

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

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

Strobl page 90-91

• 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.

Strobl page 82-83