

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN PHYSICS

Electromagnetic response of living matter

TOBIAS AMBJÖRNSSON

Department of Applied Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
GÖTEBORG UNIVERSITY
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TOBIAS AMBJÖRNSSON
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Chalmers University of Technology
Göteborg University
SE-412 96 Göteborg, Sweden
Telephone +46-(0)31-772 1000

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TOBIAS AMBJÖRNSSON
Department of Applied Physics
Chalmers University of Technology
Göteborg University

ABSTRACT

This thesis deals with theoretical physics problems related to the interactions between living matter and electromagnetic fields. The five research papers included provide an understanding of the physical mechanisms underlying such interactions. The introductory part of the thesis is an attempt to connect as well as provide a background for the papers. Below follows a summary of the results obtained in the research papers.

In paper I we use a time-dependent quantum mechanical perturbation scheme in order to derive a self-consistent equation for the induced dipole moments in a molecular aggregate (such as a cell membrane or the photosynthetic unit), including dipole interaction between molecules. Our model is shown to be superior to standard exciton theory which has been widely used in the study of photosynthesis.

In paper II we study the process of DNA translocation, driven by a static electric field, through a nano-pore in a membrane by solving the appropriate Smoluchowski equation. In particular we investigate the flux (the number of DNA passages per unit time through the pore) as a function of applied voltage. We find a threshold-like behaviour and exponential dependence on voltage in agreement with the recent experimental findings.

In paper III we investigate the drift velocity of polarizable ellipsoidal particles, driven through a viscous fluid by an electric or electromagnetic field intensity gradient. At off-resonant frequencies the drift velocity is proportional to the squared length of the principal axis along the direction of motion. Near a resonance frequency the drift velocity is sensitive to the particle shape.

Cells are in general of non-trivial shape. Furthermore the cell membrane is typically dielectrically anisotropic. These observations led to paper IV in which we investigate Gauss equation for an ellipsoidal particle with an anisotropic coating (the coating dielectric function being different parallel and perpendicular to the coating normal). We find that the solutions to this equation can be written in terms of solutions to Heun's equation. For the case of spheroidal particles the solutions can be written using hypergeometric functions.

Finally in paper V we use the result from paper I and IV and investigate the electromagnetic response of a dipole coupled ellipsoidal cell membrane. If the constituent membrane molecules have one prominent resonance frequency then the dipole coupled membrane has two new resonance frequencies. The geometric weights for the oscillator strengths of the resonances are sensitive to the membrane shape.

Keywords: electromagnetic response, living matter, polarizability, molecular aggregates, polymers, DNA, fluid mechanics, low Reynolds number, Heun's equation, cell membranes.

PREFACE

The work presented in this thesis was carried out in the Condensed Matter Theory and Materials and Surface Theory groups at the Department of Applied Physics, Chalmers University of Technology and Göteborg University between September 1998 and May 2003. The thesis is divided into two parts; the second part contains five research papers all related to the topic of interaction between electric and electromagnetic fields and living matter. The first part provides a background to (and tries to connect) the papers.

Many people have helped me during my five years of research: I feel very privileged for having had Peter Apell as my supervisor. I am deeply grateful for your continuous encouragement, enthusiasm and for always having an open mind. I enjoyed very much and learned a lot from the “Peter-way” of doing physics*, and especially the wisdom: never choose a problem which cannot be solved in an interesting way! Also thanks for introducing me to living matter physics and for encouraging me to go visit people all over the world from which I have benefited a lot.

I would like to thank Gautam Mukhopadhyay for, in practice, acting as my co-supervisor during the last one and a half years. I enjoyed and learned a great deal during this period. I am also grateful to Gautam and his wife Pragati for great hospitality during my month-long stay at IIT (Indian Institute of Technology) in Bombay at the beginning of this year (and for curing my stomach-problems!).

I enjoyed very much the collaboration we had with John Kasianowicz and Ed Di Marzio at NIST (National Bureau of Standard and Technology) outside Washington D.C. I am grateful to John for great hospitality during my stay in Washington D.C. the summer 2000. I thank Ed for proof-reading part of this thesis. In the same project I was also fortunate enough to work together with Zoran Konkoli - thanks for good collaboration and many interesting discussions.

I would also like to thank: Tomas Gillbro for sharing his knowledge about photosynthesis and experimental techniques used in this field. Olle Johansson at the Karolinska Institute for introducing me to his research on how electric and electromagnetic fields affect cells and tissue. Jerk Bjerneld, Mikael Käll and Tomas Carlsson for interesting discussions. Anders Hellman, Behrooz Razaznejad and Martin Hassel for being good friends. Especially I thank Anders for being a good office-mate and Martin for taking the time to read an early version of this thesis and giving useful comments. Pushan Ayyub at TIFR (Tata Institute of Fundamental Research) in Bombay for hospitality and interesting discussions. I would like to express my

*Do back-of-an-envelope-calculations and estimates, identify relevant dimensionless variables and proceed from there.

gratitude to all the people in the Materials and Surface Theory and Condensed Matter Theory groups and in particular: Bengt Lundqvist and Mats Jonson for having created pleasant working atmospheres. Tomas Nord for being a nice room mate. I am also very grateful to Alf Sjölander who proofread this thesis and provided valuable insights.

I thank my parents for their encouragement. Finally, Kajsa - thanks for your love - I feel very lucky to have you as part of my life!

Göteborg, April 2003
Tobias Ambjörnsson

LIST OF PUBLICATIONS

This thesis consists of an introductory text and the following papers:

- I T. Ambjörnsson and S.P. Apell,
Nature of polarized excitons,
J. Chem. Phys. **114**, 3365 (2001).
- II T. Ambjörnsson, S.P. Apell, Z. Konkoli, E.A. Di Marzio and J.J. Kasianowicz,
Charged polymer membrane translocation,
J. Chem. Phys. **117**, 4063 (2002).
- III T. Ambjörnsson and S.P. Apell,
Ellipsoidal particles driven by intensity gradients through viscous fluids,
Phys. Rev. E **67**, 031917 (2003).
- IV T. Ambjörnsson and G.M. Mukhopadhyay,
Solution of Gauss equation for an ellipsoidal particle with an anisotropic coating,
J. Phys. A (submitted).
- V T. Ambjörnsson, S.P. Apell and G.M. Mukhopadhyay,
Electromagnetic response of a dipole coupled ellipsoidal bilayer,
Phys. Rev. E (submitted).

BACKGROUND AND MY CONTRIBUTION TO THE PAPERS

Paper I: In this my first project that started in the beginning of 1999, we investigated the electromagnetic response of a molecular aggregate. My supervisor had noticed that there was a discrepancy between two commonly used theories (the standard exciton theory and the “classical” dipole coupling theory) for treating the interaction between electromagnetic fields and molecular aggregates. By using a time-dependent quantum mechanical perturbation approach we managed to “derive” the two models within the same framework and thereby resolve some of the discrepancies and illustrate the differences. The project was initiated by myself and my supervisor. I did the theoretical analysis, and wrote the paper except for the introduction.

Paper II: This project started by John Kasianowicz giving a lecture at Chalmers about some recent experiments of his where he had managed to drive single-stranded DNA molecules through a nanopore in a membrane by applying an external electrostatic potential. The experimental data on the flux of DNA through the pore showed some interesting features. A few months later, in the summer 2000, I visited John at NIST outside Washington D.C. and started investigating the problem. I then returned home and we completed the theoretical analysis roughly a year after the project was started. I initiated the project and the theoretical investigation was mainly done by myself and Zoran Konkoli, with creative input from the remaining three authors. I wrote the paper.

Paper III: This project started with me doing an estimate of the drift velocity of polarizable particles as a function of an electromagnetic field gradient for a different project at the end of year 2000. I showed the study to my supervisor, who realized that a more detailed study of ellipsoidal particles could yield interesting results. The project was initiated by my supervisor and me. I wrote the paper and did the calculations.

Paper IV: This project started with me talking to Tomas Carlsson (at the time in the Liquid Crystal Physics group at Chalmers), who convinced me that when studying the electric response of a cell the anisotropy in the dielectric function of the cell membrane could be important. During the spring 2002 I managed to solve Gauss equation for the case of a spheroid (an ellipsoid with two principal axes equal) with an anisotropic coating in a homogeneous external field. In the summer the same year Gautam Mukhopadhyay spent two months at Chalmers and we then managed to solve the full ellipsoidal problem. During the autumn I then worked out the solution to the Gauss equation for the case of large coating anisotropy. I initiated the project, did the major part of the calculations and wrote the paper.

Paper V: In this project we investigated the electromagnetic response of cells at frequencies where membrane molecular resonances (electronic and vibrational) are

important. This project was the natural continuation of paper I and IV. I initiated the project, did the analysis and wrote the paper.

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CHAPTER 1

Introduction

All systems (whether 'dead' or 'living') consist of charges and when a particular system is perturbed by an external electric, magnetic or electromagnetic field it responds by induced motion of these charges. Depending on the structure of the system and kind of perturbing external field the response differs; for example for a dielectric perturbed by an electric field the relevant induced quantity is the dipole moment per unit volume (the polarization), whereas for an electrolyte the induced charge density is often used to characterize the electric response. *Provided that* a sound theoretical framework exists which predicts how measurable quantities depend on the relevant physical parameters of the system one can use external fields to obtain information about the system. It is the aim of this thesis to try to provide such a theoretical framework relevant for living matter-electromagnetic field interactions. In the research papers different living matter systems are investigated and we derive expressions for relevant response entities.

In general it is difficult to identify a distinct difference between 'dead' and 'living' matter; the very same constituting atoms are used in all matter. But indeed, as we experience in everyday-life, there are differences. In this introduction we do not try to provide an exact definition of living matter. Instead we will take our starting point in the cell, which is the micrometer sized building block of all living beings [1, 2]. We will take a look at the various molecules in the cell and how they combine to form functional units, including membranes, polymers and electrolytes.

Let us first consider which atoms are most abundant in cells. It turns out that 24 of the 92 natural elements are essential to life [2]. Four of these, oxygen (O), carbon (C), hydrogen (H) and nitrogen (N), make up 96% of the human body. Calcium, phosphorous, potassium and sulphur and so-called trace elements (only required by the body in small quantities) account for the remaining 4%. Life's molecules are usually large on a molecular scale, containing thousands of atoms. A striking difference between our own technology and that of Nature is that whereas we use metals to a large extent, Nature only employ *single* metal atoms [3].

Many cell processes rely on the properties of the *cell membrane*, which separates the cell from its environment. The basic ingredient of a cell membrane is the phospholipid molecule [1, 2]. The most important property of this molecule is that it is amphiphilic; one of its ends (the phosphatic head) is polar and is therefore strongly attracted to water, while the other end (the hydrocarbon tail) is nonpolar and is hence repelled by water. This property of the phospholipid molecules makes it energetically favourable for them, when being put into water, to form a closed bilayer (of typical thickness 5-10 nm) with the phosphatic heads pointing outwards while the hydrocarbon tails are pointing inwards and are thereby kept from contact with the water. Due to the strong orientation of the lipid molecules in the membrane, a cell membrane is a highly *anisotropic* structure. Such systems are investigated in research paper IV, where the electric response of an ellipsoid with an anisotropic coating is studied. The chemical interaction between molecules in a membrane is usually so weak that the bilayer essentially behaves as a two-dimensional fluid. Structures, such as cell membranes, which have negligible chemical interaction between the constituting units are called *molecular aggregates*. Chapter 6, as well as research paper I and V, is therefore dedicated to the electromagnetic response of such aggregates (the photosynthetic unit is a different example of a molecular aggregate). There are furthermore usually proteins embedded in the cell membrane. The role of these proteins include enzymatic activities and being receptors for chemical messengers from other cells. There are also protein pores in the membrane. These protein pores allow passage of biomolecules that would otherwise not be able to penetrate the membrane. Research paper II in this thesis deals with the problem of passage of single stranded DNA molecules, driven by an electric field, through such pores.

Inside the cell there is a liquid called the *cytoplasm*. The cytoplasm consists, to a large extent, of water molecules (roughly 70 % of the cell consists of water) and ions. Chapter 7 in this thesis treats the electric and electromagnetic response of *electrolytes* (liquids consisting of water and ions), and chapter 2 treats particle motion in a liquid. Motion of particles as caused by electromagnetic intensity gradients through viscous liquids is also the topic of research paper III. In eukaryotic cells (cells with a nucleus) the cytoplasm consists also of so-called membranous organelles, examples of which include the cell nucleus, the endoplasmatic reticulum and the Golgi apparatus [1, 2]. The cell nucleus is the genetic control center of the cell. It is here that the DNA (the hereditary blueprint of the cell) is stored. The endoplasmatic reticulum and the Golgi apparatus are for instance involved in the synthesis of proteins using the genetic code. There are also nonmembraneous structures in the cell such as the cytoskeleton. The cytoskeleton is a supportive mesh of fine protein fibers and gives the cell structural support [4]. The cytoskeleton is also involved in cell movement and division as well as used as tracks for transport in the cell. DNA molecules as well as proteins are long “chain-like” molecules. Such molecules go under the name *polymers*. Polymers have many distinct properties compared to “point” particles, and chapter 3 in this thesis is dedicated to the physics of polymers.

The rest of this introductory text is aimed at giving an introduction to the topic

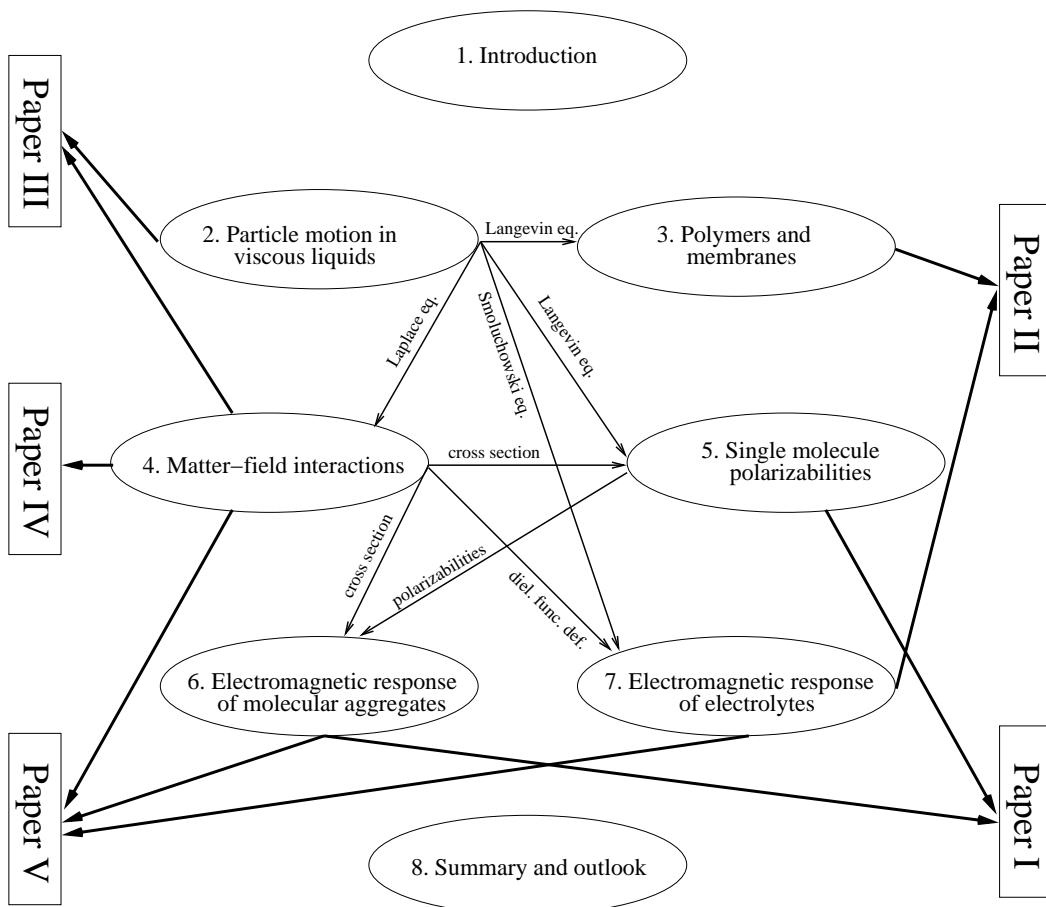


Figure 1.1: Interrelations between the different chapters of this thesis, as well as connections between the chapters and the five appended research papers.

living matter-electromagnetic field interactions as well as to provide a background to the research papers, and is organized as follows: Chapter 2 is devoted to the problem of particle motion in a liquid. The equations developed in this chapter will also prove useful for understanding the electromagnetic response of molecules and electrolytes, which is the reason that we take the rather unconventional route of starting a thesis about electromagnetic response by discussing particle motion through a liquid (indeed this shows the general feature of many physical phenomena). Chapter 3 describes the physics of polymers and the equilibrium physics of membranes. Chapter 4 proceeds by giving the general description, needed for subsequent chapters, of how electric and electromagnetic fields interact with matter. The next three chapters give specific examples of electric and electromagnetic response: Chapter 5 describes the electromagnetic response of single molecules. Chapter 6 deals with the interaction of molecular aggregates and external fields and chapter 7 treats the response of an electrolyte to an electric or electromagnetic field. Finally in chapter 8 a summary and outlook is given. The interrelations between the different chapters and connections to the five research papers are given in Fig. 1.1.

The research papers included in this thesis provide a deeper analysis compared to the introductory text; connections to the introductory text are found in Fig. 1.1. Paper I provides a theory for the electromagnetic response of a molecular aggregate using a quantum mechanical scheme. The relevant induced quantity is the dipole moments in the aggregate, for which we provide a general expression. Paper I is connected to chapters 5 and 6 (see Fig. 1.1). Paper II deals with the passage of DNA molecules (in an electrolyte) driven by an external static electric field through a nanopore in a cell membrane. In this paper the external perturbation is a static electric potential and the induced measureable quantity is the flux of DNA molecules through the nanopore (we find that the flux depends non-linearly on the applied potential). The relevant background for this study includes chapters 3 and 7. Paper III describes the behaviour of particles (such as cells) in a viscous liquid under the influence of an electric or electromagnetic field intensity gradient. The perturbing quantity in this study is the intensity gradient and the induced quantity is the particle drift velocity. Background material to this paper is provided in chapters 2 and 4. Paper IV gives the solution of Gauss equation for an ellipsoid with an anisotropic coating (relevant chapter 4) as perturbed by an external electric field (the relevant induced quantity is the induced dipole moment of the ellipsoid). Finally paper V describes the interaction between electromagnetic fields and ellipsoidally shaped cell membranes. In particular we provide an expression for the induced dipole moments in the membrane. The chapters that are relevant for that study are chapters 4, 6 and 7.

CHAPTER 2

Particle motion in viscous liquids

In this chapter we discuss the motion of a particle in a viscous liquid. We discuss the Langevin and the Smoluchowski equations for the particle motion. We also discuss the fluid dynamical equations for the (biologically relevant) case of motion of small particle at low velocities - so called low *Reynolds number* motion. In paper III we investigate the motion of a particle driven through a viscous fluid by an electric or electromagnetic field gradient. This chapter (together with chapter 4) provides a background to that paper. The present chapter also introduces concepts and equations that are important in the study of polymer dynamics in chapter 3 as well as for the understanding of the electromagnetic response of molecules (chapter 5) and the response of electrolytes as discussed in chapter 7.

2.1 The Langevin and Smoluchowski equations

In this section we investigate the equation of motion for a particle in a liquid.

Consider a particle in a liquid and let us assume that there is a time-dependent force $\vec{F}(t)$ on the particle. The molecules of the liquid collide in a stochastic fashion with the particle, which then exhibits a random type of motion that in the general case is described by Langevin's equation [5]:

$$m \frac{d\vec{v}}{dt} = \vec{F}(t) - \overleftrightarrow{\xi} \cdot \vec{v} + \vec{g}(t), \quad (2.1)$$

where $\vec{v}(t) = d\vec{x}(t)/dt$ is the velocity of the particle at time t . The term on the LHS is the inertial term. The second term on the RHS is a friction (dissipative) force as caused by the cooperative effect of the surrounding solvent molecules. $\overleftrightarrow{\xi}$ is in the general case a 3×3 tensor and is the friction tensor of the particle, which depends on the viscosity of the liquid as well as the size and shape of the particle (this tensor is thoroughly discussed in the next section where we investigate the fluid dynamics).

$\vec{g}(t)$ is a stochastic force (the ensemble average is zero, $\langle \vec{g}(t) \rangle = \vec{0}$) and represents the individual collisions between the molecules in the liquid and the particle. Since the friction and the stochastic force have the same origin (collisions between particle and solvent molecules) the amplitude of the stochastic force is related to the friction tensor, through the fluctuation-dissipation theorem [6]. For the case of a time-independent friction tensor the fluctuation-dissipation theorem takes the form (assuming a scalar friction tensor $\overset{\leftrightarrow}{\xi} = \xi$):

$$\langle \vec{g}(t) \cdot \vec{g}(t') \rangle = 2d\xi k_B T \delta(t - t') \quad (2.2)$$

where $\delta(z)$ is the delta-function and d is the number of dimensions in which the motion takes place. The Boltzmann constant is denoted by k_B and T is the temperature of the solvent. Eq. (2.2) gives an explicit expression for the friction constant ξ in terms of the correlations of the stochastic force. In the absence of any external and stochastic force the Langevin equation has the solution $\vec{v} = \vec{v}_0 \exp(-t/\tau)$, where the relaxation time is $\tau = m/\xi$ and \vec{v}_0 is the initial particle velocity. Because of the stochastic nature of the motion of the particle (as contained in Langevin's equation) the particle velocities must be described in terms of a *probability distribution* for different particle positions and velocities, $P(\vec{x}, \vec{v}, t)$. The probability distribution corresponding to Eq. (2.1) satisfies an equation, known as the Fokker-Planck equation [5]. At equilibrium (no time-dependence and no external force) the solution of the Fokker-Planck equation is the usual Maxwellian velocity distribution [5].

We now consider motion of small particles at low velocities. As we will see in the next section the friction force acting on a particle is $\sim \eta Lv$, where η is the viscosity of the liquid and L a typical linear size of the particle. We are primarily interested in applying our analysis to particles moving with small velocities through viscous liquids. For this kind of motion the ratio R_{part} between the inertial force and the viscous force is typically small. R_{part} can be written [7]

$$R_{\text{part}} = \frac{Lv\rho_{\text{part}}}{\eta}, \quad (2.3)$$

where ρ_{part} is the particle density. As an example of small R_{part} motion consider a bacterium in water. For water at room temperature, $\eta \approx 10^{-3}$ Ns/m². A bacterium is typically one micron ($L \sim 1 \mu\text{m}$) in size and has roughly the same density as water. If such an object moves by a speed, $v = 1 \text{ mm/s}$, we have $R_{\text{part}} \sim 10^{-3}$. We hence assume that $R_{\text{part}} \ll 1$ and Eq. (2.1) then becomes [6]

$$\overset{\leftrightarrow}{\xi} \cdot \frac{d\vec{x}}{dt} = \vec{F}(t) + \vec{g}(t). \quad (2.4)$$

This equation is valid for liquids with high viscosity, small particle velocities and sizes. The neglect of inertia [*i.e.* the term on the LHS in Eq. (2.1)] in practice means that we only study processes occurring on time scales larger than the relaxation time τ introduced above. The corresponding Fokker-Planck equation, the so called

Smoluchowski equation, for the probability distribution $P(\vec{x}, t)$ which corresponds to the Langevin equation, Eq. (2.4), is [8]:

$$\frac{\partial P(\vec{x}, t)}{\partial t} = \frac{1}{\xi} \vec{\nabla} \cdot [k_B T \vec{\nabla} P(\vec{x}, t) - \vec{F}(\vec{x}, t) P(\vec{x}, t)], \quad (2.5)$$

where we have assumed the friction tensor to be a scalar $\xi = \xi$ for simplicity. When the force is constant, the one-dimensional solution to this equation that satisfies the initial condition that the particle is at $x = 0$ at $t = 0$ [*i.e.*, $P(x, t = 0) = \delta(x)$] is

$$P(x, t) = \left(\frac{1}{4\pi D t} \right)^{1/2} \exp \left[- \frac{(x - v_{\text{drift}} t)^2}{4 D t} \right], \quad (2.6)$$

where we have introduced the diffusion constant, $D \equiv k_B T / \xi$ and the drift velocity of the particle

$$v_{\text{drift}} = F / \xi. \quad (2.7)$$

This expression for the drift velocity is used in paper III, where the force is taken as the force on a neutral polarizable particle in an electric or electromagnetic field gradient. From Eq. (2.6) we see that the mean distance, x_{drift} , a particle travels under the influence of the external force during a time t is $x_{\text{drift}} \equiv v_{\text{drift}} t$. In addition to this [due to the stochastic force, $\vec{g}(t)$] there is diffusive motion which tends to spread the positions of the particle around x_{drift} . Notice that if diffusion is absent ($D = 0$) the probability distribution is simply $P(x, t) = \delta(x - v_{\text{drift}} t)$. We also notice that for low Reynolds numbers the mass of the particle does not enter into the expression for the probability distribution. In the absence of any force there is no drift and only diffusion. Using the above probability distribution, it is straightforward to show that the mean square displacement is

$$\langle |\vec{x}(t) - \vec{x}(0)|^2 \rangle = 2dDt, \quad (2.8)$$

where we generalized the result to d dimensions [Eq. (2.8) can also be directly obtained from the Langevin equation Eq. (2.4) together with the fluctuation-dissipation theorem Eq. (2.2)]. The mean distance a particle travel by diffusion is thus proportional to the square root of time $\sim t^{1/2}$. This means that in small volumes (such as cells, which are $\sim 10 \mu\text{m}$) diffusion may suffice as a method of transportation. However for larger system diffusion is an inefficient way of transportation; for instance if the cell size would be increased by a factor ten, then the time required to diffuse from one end of the cell to the other is increased hundredfold.

2.2 Low Reynolds number fluid mechanics

In this section we study the fluid dynamical equations at low Reynolds number. In particular a general expression for the friction constant is obtained in terms of the viscosity of the liquid as well as the size and shape of the particle.

The total force \vec{F} (and hence the friction constant) acting on a particle moving (with a velocity \vec{v}_{part}) through a viscous liquid is obtained by integrating the μ -component ($\mu=x,y$ or z) of the force per unit area, f_μ , over the surface of the object [9, 10]

$$F_\mu = \oint f_\mu dS = \sum_\lambda \oint \sigma_{\mu\lambda} n_\lambda dS, \quad (2.9)$$

with n_ν being the normal to the surface and $\sigma_{\mu\lambda}$ is the stress tensor explicitly given by

$$\sigma_{\mu\lambda} = -p\delta_{\mu\lambda} + \eta\left(\frac{\partial v_\mu}{\partial x_\lambda} + \frac{\partial v_\lambda}{\partial x_\mu}\right), \quad (2.10)$$

assuming an incompressible fluid. $\vec{v}(\vec{x})$ is the induced velocity distribution in the liquid. The first term of the above equation is the direct momentum transfer of the liquid to the object [$p(\vec{x})$ is the pressure in the liquid] - the so called pressure drag [11]. The pressure exerts a force in the *normal* direction to the surface. The second term is the frictional drag caused by friction stress acting *tangentially* on the surface. η is the shear viscosity of the liquid. The relative importance of the pressure and frictional drag depends on the shape of the object. For example a plate moving edge-on in a liquid feels practically no pressure drag but only frictional drag. On the other hand if the plate moves with the flat side against the stream the pressure drag is much larger than the frictional drag [11].

The velocity distribution, $\vec{v}(\vec{x})$ and the pressure distribution $p(\vec{x})$ are in the general case determined by the Navier-Stokes equation [9, 11]. The fluid parameters entering this equation are the fluid density ρ and the viscosity η . We are primarily interested in applying our analysis to biological systems such as cells moving with small velocities through viscous fluids. We will therefore assume that the dimensionless number (L is a characteristic length of the particle)

$$R = \frac{Lv\rho}{\eta} \quad (2.11)$$

is small, *i.e.*, that $R \ll 1$. R is the so called *Reynolds number*, which plays an important role in hydrodynamics [9]. The above expression for the Reynolds number is identical to the ratio between the particle inertia and the viscous force as contained in Eq. (2.3) provided we replace the particle density ρ_{part} by the fluid density ρ . Assuming small Reynolds numbers thus corresponds to neglect of *fluid* inertia. At *small Reynolds number*, R and *steady flow*, the Navier-Stokes equation reduces to the linear equation [9, 12]

$$\eta \nabla^2 \vec{v} - \vec{\nabla} p = 0. \quad (2.12)$$

Notice that the above equation does not contain the density, ρ , of the liquid and the only parameter entering the fluid mechanical problem is the viscosity, η . This equation is supplemented by the mass conservation equation (the equation of continuity), which for incompressible liquids reduces to [9, 12]

$$\vec{\nabla} \cdot \vec{v} = 0. \quad (2.13)$$

There are always forces of molecular attraction between a viscous liquid and a solid - the liquid layers close to the body “adhere” to the body [10]. The boundary condition is then that the fluid velocity (both normal and tangential components) at the surface equals the particle velocity (no slip and no penetration), *i.e.* [9, 10]

$$\vec{v}|_{\text{surface}} = \vec{v}_{\text{part}}. \quad (2.14)$$

Eqs. (2.12), (2.13) and (2.14) together with the boundary condition $\vec{v}(|\vec{x}| \rightarrow \infty) = 0$ completely determines the velocity of the liquid and the pressures in the liquid.

Let us now obtain the friction constant for the particle motion. By taking the divergence ($\vec{\nabla} \cdot$) and the curl ($\vec{\nabla} \times$) on Eq. (2.12) and using Eq. (2.13) we obtain the alternative equations:

$$\begin{aligned} \nabla^2 p &= 0, \\ \nabla^2(\vec{\nabla} \times \vec{v}) &= 0. \end{aligned} \quad (2.15)$$

The pressure and the vorticity, $\vec{\nabla} \times \vec{v}$, are hence harmonic functions. We will in chapter 4 find that the electric and magnetostatic potentials satisfies an identical (Laplace) equation as does the pressure p above. Much of results obtained in the field of fluid dynamics can therefore be used for electric and magnetic problems as well (and vice versa), keeping in mind that the boundary conditions in general differ. Since the boundary condition, Eq. (2.14), is specified entirely in terms of the velocity field and the pressure can be eliminated from the fluid dynamical equations [see Eq. (2.15)] \vec{v} must at low Reynolds numbers everywhere be independent of η . The pressure, however, depends on the viscosity through Eq. (2.12). Since p is a harmonic function, see Eq. (2.15), it can be written as an expansion in spherical harmonics. The dominant term far from the particle has the form [9]

$$\frac{p|_{r \text{ large}} - p_\infty}{\eta} = \frac{3}{2} \sum_{\mu,\lambda} R_{\text{eff},\mu\lambda} \frac{x_\mu}{r^3} v_{\text{part},\lambda}, \quad (2.16)$$

where $R_{\text{eff},\mu\lambda}$ is the “effective radius” of the particle and is a 3×3 tensor with dimension of length and p_∞ is the uniform pressure in the fluid in the absence of the moving particle. The factor $3/2$ has been extracted for convenience. The asymptotic form for \vec{v} is then obtained through Eq. (2.12) and is (as may be verified by direct substitution)

$$v_\mu|_{r \text{ large}} = \frac{3}{4} \sum_{\lambda,\sigma} R_{\text{eff},\lambda\sigma} \left(\frac{\delta_{\lambda\mu}}{r} + \frac{x_\lambda x_\mu}{r^3} \right) v_{\text{part},\sigma}. \quad (2.17)$$

We notice that the induced velocity field around a moving particle at large distances is $\sim 1/r$. The velocity field thus decays slowly with distance r from the particle. This means that if a second particle is in the liquid at a distance, say, ten particle radii away, the liquid velocity at that second particle is one tenth of the velocity in the vicinity of the first particle, thereby inducing a long-range hydrodynamical force between the particles. This hydrodynamical coupling is for instance important in

polymer physics (see chapter 3), where hydrodynamical interaction between polymer segments strongly affect the total friction for the polymer motion. By using Gauss equation together with the fluid equations of motion the expression for the force, Eq. (2.9), can be turned into an integral at infinity [9]. Using the above expansions one thereafter finds that the force becomes $F_\mu = -\sum_\lambda \xi_{\mu\lambda} v_{\text{part},\lambda}$ where the friction constant is

$$\xi_{\mu\lambda} = 6\pi\eta R_{\text{eff},\mu\lambda}. \quad (2.18)$$

For a spherical particle the effective radius is a scalar equal to the radius of the particle, and the above equation becomes the well-known Stoke's law [9]. The general method for obtaining the friction constant for a particle moving steadily through a viscous liquid is hence (in the low Reynolds number approximation): (i) Solve Eqs. (2.12), (2.13) and (2.14) together with boundary condition $\vec{v}(|\vec{x}| = \infty) = 0$. (ii) Make an asymptotic expansion of the solution and identify $R_{\text{eff},\mu\lambda}$ through Eqs. (2.16) and (2.17). The friction constant is then given by Eq. (2.18).

Strictly speaking Eq. (2.18) is valid only for steady motion. However it can be shown [13] to be valid also for *unsteady* motion as long as the characteristic time for particle motion is longer than the relaxation time $\tau = \rho_f L^2/\eta$ (L is a characteristic length of the particle and ρ_f is the fluid density). In terms of the Reynolds number R [see Eq. (2.11)] we have $\tau = RL/v$. As long as the characteristic time scale of the problem is longer than τ we can safely assume that the friction constant is independent of time. By introducing the mass of the displaced fluid $m_f \sim \rho_f L^3$ we notice that the the relaxation time can be written $\tau \sim m_f/\xi$. This expression for the relaxation time is identical to the relaxation time introduced in connection to the Langevin equation, Eq. (2.1), but where the particle mass is replaced by the displaced fluid mass. Returning to our previous example of a μm -sized bacteria moving in water we straightforwardly obtain $\tau \sim 10^{-6}$ s [7]. For small objects the friction tensor thus quickly relaxes to the result as given by Eq. (2.18).

It is interesting to note that the viscous force is proportional to the effective *radius* (dimension of length) of the particle instead of (as might be intuitively assumed) the cross sectional *area* of the particle. This can be understood through dimensional arguments; the only parameters entering the analysis are η and the particle velocity v_{part} (since for low Reynolds numbers Navier-Stoke's equation is independent of the fluid density ρ). The only combination of these quantities giving dimension of force is $\eta L v_{\text{part}}$ (since $[\eta]=\text{kg/ms}$), where L is a typical length of the particle.

Let us now as an illustrative example find the solution of the low Reynolds number Navier-Stoke's equation for an ellipsoid (with principal radii a_x , a_y and a_z , see Fig. 2.1) moving through a viscous fluid and in particular obtain the friction tensor of the ellipsoid. We must then solve Eqs. (2.12) and (2.13) together with the boundary condition Eq. (2.14) for the flow around an ellipsoidal particle moving with velocity u along the x-axis, *i.e.*, $\vec{v}_{\text{part}} = (u, 0, 0)$. Following [14] we make the ansatz

$$v_x = A \frac{\partial^2 \Omega}{\partial x^2} + B(x \frac{\partial \chi}{\partial x} - \chi),$$

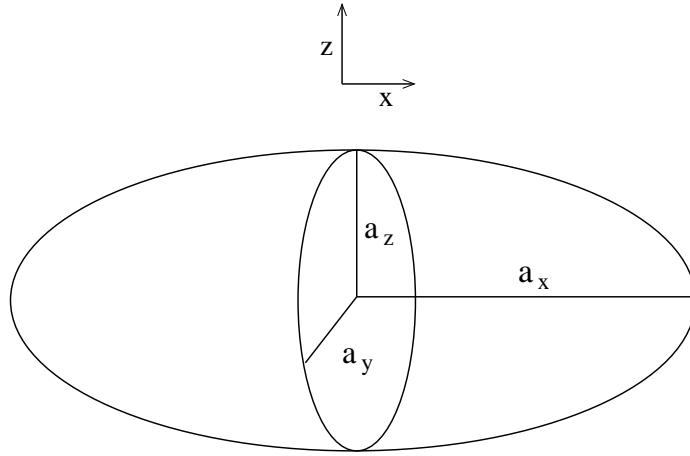


Figure 2.1: An ellipsoid. The principal radii are a_x , a_y and a_z .

$$\begin{aligned} v_y &= A \frac{\partial^2 \Omega}{\partial x \partial y} + Bx \frac{\partial \chi}{\partial y}, \\ v_z &= A \frac{\partial^2 \Omega}{\partial x \partial z} + Bx \frac{\partial \chi}{\partial z}, \end{aligned} \quad (2.19)$$

where Ω and χ are harmonic functions given by Eqs. (A.5) and (A.6) respectively. The ansatz, Eq. (2.19) yields $(v_x, v_y, v_z) = (0, 0, 0)$ at infinity as it should. By using Laplace equation, Eq. (A.7), it is straightforward to show that the ansatz, Eq. (2.19), satisfies the equation of continuity, Eq. (2.13). Let us now show that the low Reynolds number Navier-Stoke's equation, Eq. (2.12), can be satisfied with the ansatz above. We find

$$\nabla^2 \vec{v} = 2B \vec{\nabla} \left(\frac{\partial \chi}{\partial x} \right). \quad (2.20)$$

Comparing this with Eq. (2.12) we see that Navier-Stokes equation is satisfied for a pressure distribution in the liquid given by

$$p - p_\infty = 2B \eta \frac{\partial \chi}{\partial x}, \quad (2.21)$$

i.e., the pressure is related the spatial derivative of χ along x .

We now show that the constants A and B can be chosen such that the boundary condition Eq. (2.14) is satisfied. The surface of the ellipsoid corresponds to $\xi = 0$ [see Eq. (A.1)]. From Eqs. (2.19), (A.8) and (A.11) we then straightforwardly find that the boundary condition $v_z(\xi = 0) = v_y(\xi = 0) = 0$ gives the condition

$$\frac{2\pi A}{a_x^2} + B = 0 \quad (2.22)$$

for the constants A and B . Furthermore using the boundary condition for the x -component of the velocity field $v_x(\xi = 0) = u$ we obtain

$$4\pi A n_x - 2B Q = u, \quad (2.23)$$

where Q is given by Eq. (A.12) and n_x is the depolarization factor given by Eq. (A.13). Combining the results above we get

$$\begin{aligned} A &= -\frac{Ba_x^2}{2\pi}, \\ B &= -\frac{1}{2} \frac{u}{Q + n_x a_x^2}. \end{aligned} \quad (2.24)$$

The general solution to the Navier-Stokes equation is then given by Eqs. (2.19), (2.21) and (2.24). Notice that the fluid velocity is independent of η [see discussion following Eq. (2.15)].

The force exerted on the ellipsoid is obtained by finding the asymptotic expansion of the solution, Eq. (2.19). At large distances from the ellipsoid, Ω and χ take the form [14] $\Omega|_{r\text{large}} = -4\pi a_x a_y a_z / 3r$ and $\chi|_{r\text{large}} = 2a_x a_y a_z / r$. Inserting these asymptotic expansions in Eq. (2.19) we find

$$\begin{aligned} v_x|_{r\text{large}} &= -2Ba_x a_y a_z \left(\frac{1}{r} + \frac{x^2}{r^3} \right), \\ v_y|_{r\text{large}} &= -2Ba_x a_y a_z \frac{xy}{r^3}, \\ v_z|_{r\text{large}} &= -2Ba_x a_y a_z \frac{xz}{r^3}, \end{aligned} \quad (2.25)$$

where we have used the fact that the first terms of Eq. (2.19) are $\sim A/r^3$ and can therefore be neglected (the velocity far from the ellipsoid is hence completely determined by the function χ). Also note that the pressure, Eq. (2.21), far from the ellipsoid, decreases according to $p \sim B/r^2$. Comparing the above asymptotic expression for the velocity with Eq. (2.17), we identify the effective radius according to $\frac{3}{4}uR_{\text{eff},xx} = -2Ba_x a_y a_z$ or, using Eq. (2.24), the force is [see Eq. (2.18)] $F_\mu = -\sum_\mu \xi_{\mu\mu} u_\mu$, where the friction tensor is

$$\begin{aligned} \xi_{\mu\mu} &= 6\pi\eta R_{\text{eff},\mu\mu}, \\ R_{\text{eff},\mu\mu} &= \frac{1}{\pi} \frac{V}{Q + n_\mu a_\mu^2}, \end{aligned} \quad (2.26)$$

where $V = 4\pi a_x a_y a_z / 3$ is the volume of the ellipsoid. We have generalized the result to motion along any of the three principal axes ($\mu = x, y, z$). We notice that the friction tensor depends on both particle properties (through the effective radius) and solvent properties (through the viscosity). The result for the friction tensor, Eq. (2.26), is used in paper III.

We have in this chapter investigated the motion of particles through viscous liquids. In particular we have found that for small particles moving with small velocities (low Reynolds number motion) friction dominates inertia. The equations governing the particle motion are the Langevin equation, Eq. (2.4) or the Smoluchowski equation, Eq. (2.5). We have also obtained an explicit expression for the

friction tensor for an ellipsoidal particle [see Eq. (2.26)] in terms of the viscosity and the hydrodynamic effective radius of the particle, by solving the low Reynolds number hydrodynamic equations. These results provide a background to paper III in which the motion (as caused by an electromagnetic field gradient) of an ellipsoidal particle moving through a viscous liquid is investigated. The present chapter also gives background results relevant for chapters 3, 4, 5 and 7.

CHAPTER 3

Polymers and membranes

In this chapter we investigate the properties of soft matter [15, 16] - in particular polymers and fluid membranes. The physics of non-interacting polymers in a solvent is described. We find that the equilibrium properties of polymers are described by random walk physics. We also study polymer dynamics. Fluid membranes are the two dimensional “generalization” of polymers. We study the equilibrium physics of membranes and compare to the corresponding polymer results. In paper II the motion of charged polymers in an electrolyte driven through a nanopore in a membrane by an electric field is investigated. The concepts such as persistence length, radius of gyration and mobility matrix developed in this chapter are important for that paper (together with the discussion in chapter 7) .

3.1 Equilibrium physics of polymers

In this section we describe the equilibrium properties of polymers.

A polymer, as discussed here, is a linear chain of chemically bonded molecules. It is experimentally found that if the number of molecules in the chain is “sufficiently” large they have universal properties (*i.e.*, the properties are independent on chemical composition). Let us give a simple argument why this should be so. We consider a long polymer where the positions along the polymer are specified by $\vec{x}(p)$, where p is the parameter of the curve. The parameter p is chosen such that the vector $\vec{u}(p) = \partial\vec{x}/\partial p$ is a unit tangent vector to the chain, and a straight polymer thus corresponds to $\vec{u}(p)=\text{constant}$. We now assume that the polymer is characterized by a bending energy [17, 8]

$$U_{\text{bend}} = \frac{\kappa_p}{2} \int_0^L dp \left(\frac{\partial \vec{u}}{\partial p} \right)^2, \quad (3.1)$$

where L is the contour length of the polymer and κ_p is the bending modulus of the

polymer and is determined by local chemical interactions (κ_p has dimension of energy times length). When the polymer is in a solvent it is randomly “kicked” by collisions with the solvent molecules. The strengths of the collisions are determined by the thermal energy $k_B T$, where k_B is the Boltzmann constant and T is the temperature of the solvent. The effect of these collisions is that tangent vectors that are far away from each other along the polymer contour become uncorrelated. In fact one straightforwardly shows that for a polymer characterized by the bending energy as given by Eq. (3.1) [8]

$$\langle \vec{u}(p) \cdot \vec{u}(0) \rangle = \exp\left(-\frac{p}{a}\right), \quad (3.2)$$

i.e., correlations decay exponentially along the polymer. We have introduced a quantity known as the *persistence length* a of the polymer:

$$a = \frac{\kappa_p}{k_B T}. \quad (3.3)$$

The physical meaning of the persistence length is that it is the length over which the polymer appears rigid. We have above made the simplifying assumption that the chemical nature of the polymer can be described through a bending modulus. However the notion of persistence length as the length outside of which there are no correlations along the polymer does not depend on the exact model chosen and is universal [18]. We have, for long polymers, therefore reduced the chemical problem to that of determining the persistence length of the polymer. Notice that $L = Na$, where N is the number of persistence lengths. We then choose a and N as the relevant parameters describing a long polymer. As an example single stranded DNA molecules have a persistence length $a \sim 1$ nm, whereas double-stranded DNA molecules have $a \sim 50$ nm [17].

Now we proceed by investigating the statistical equilibrium properties of long linear polymers. We then have the following problem at our hands: A chain consisting of N segments of length a , where the direction of each segment is independent of the direction of the previous segment (this is as is discussed above caused by thermal collisions with the solvent molecules). The single polymer problem is then nothing but the random walk problem as illustrated in Fig. 3.1 We follow [19] and consider the polymer statistics as a random walk on a *lattice* for illustrative reasons. The number of nearest neighbours to a point on the lattice is denoted by s . We can now ask questions like: What is the expected end-to-end vector $\vec{R} = \vec{x}_N - \vec{x}_0$ of the polymer? Because the polymer performs a random walk (a step to the right is equally probable as a step to the left) we have

$$\langle \vec{R} \rangle = 0, \quad (3.4)$$

i.e., the expectation value of the polymer end-to-end vector equals zero. This quantity then does not provide us with any information about the size of the polymer. Instead we introduce the center-of-mass position $\vec{R}_C = (\sum_n \vec{x}_n)/N$ of the polymer. The deviations from the center-of-mass is then described by the *radius of gyration*

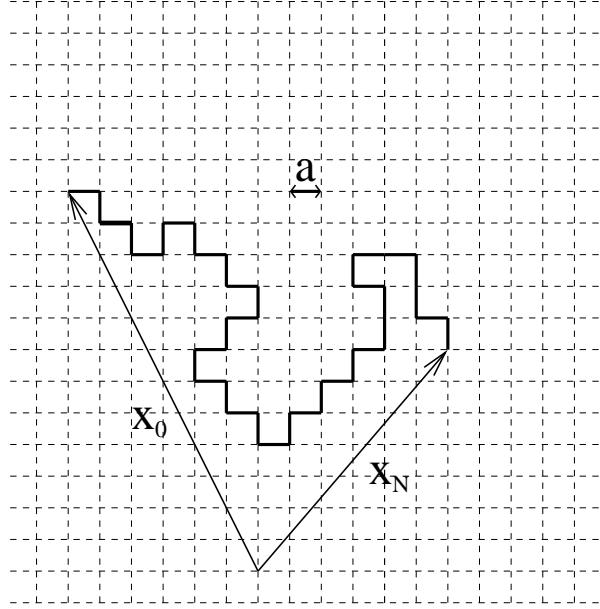


Figure 3.1: A polymer can be modeled as a random walk with step length a , where a is the persistence length of the polymer. The random walk starts at position \vec{x}_0 and ends at position \vec{x}_N . The number of nearest neighbours to a point on the lattice is denoted by s .

R_g of the polymer

$$R_g^2 \equiv \frac{1}{N} \sum_n \langle (\vec{x}_n - \vec{R}_C)^2 \rangle = \frac{Na^2}{6}, \quad (3.5)$$

where the last result follows straightforwardly [8]. The “size” of the polymer is thus $\sim N^{1/2}$, which is characteristic of any intersecting random walk. We have so far excluded the fact that a polymer cannot intersect itself. Including this so called excluded volume effect (non-intersecting random walk) one finds that $R_g \sim N^{3/5}$ [19], *i.e.*, the size of the polymer is increased as a result of the excluded volume effect. Which type of random walk statistics that is most appropriate for a given problem depends for instance on the nature of the solvent and is beyond the scope of this introductory text. The interested reader is referred to Refs. [8, 19, 18]. We will here mainly be concerned with intersecting random walks for simplicity.

We now introduce a mathematical entity known as the polymer Green function $G(\vec{x}, \vec{x}'; N)$. By definition we have that $s^N G(\vec{x}, \vec{x}'; N)$ gives the number of statistically weighted paths starting at \vec{x} and ending at \vec{x}' . The factor s^N , which gives the total number of paths of N steps, has been extracted for convenience. In the absence of any external potential and in the continuum limit the Green function becomes [8, 19, 18]

$$\begin{aligned} G^0(\vec{x}, \vec{x}', N) &= g_x^0(x, x'; N) g_y^0(y, y'; N) g_z^0(z, z'; N), \\ g_v^0(v, v'; N) &= \left(\frac{1}{4\pi R_g^2} \right)^{1/2} \exp \left[\frac{-(v - v')^2}{4R_g^2} \right], \end{aligned} \quad (3.6)$$

where $v = x, y, z$ and N is the number of polymer segments (the number of steps in

the random walk) as before. The Green function is thus a Gaussian the width of which is determined by the radius of gyration R_g . In the presence of an external potential $U(\vec{x})$ one must weight each polymer conformation by a Boltzmann factor [8, 19, 18]

$$\exp[-\beta \sum_n U(\vec{x}_n)], \quad (3.7)$$

when calculating the Green's function. The sum is over all segment positions and as before $\beta = 1/k_B T$ where k_B is the Boltzmann constant and T the temperature of the solvent. Taking $U(\vec{x})$ into account using the recipe above (*i.e.*, by explicitly weighting each conformation by a Boltzmann factor) is usually not very convenient for explicit calculations. Instead one can show that the polymer Green's function in the presence of an external potential satisfy the following differential equation [8, 19, 18]:

$$[\frac{\partial}{\partial N} - \frac{a^2}{6} \nabla^2 + \beta U(\vec{x})] G(\vec{x}, \vec{x}', N) = \delta(\vec{x} - \vec{x}') \delta(N), \quad (3.8)$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ and we have taken the continuum limit. This equation is appropriate for calculating the polymer Green's function.

We close this section by considering an example which serves to illustrate the importance of the *connectivity* of the polymer (*i.e.*, the fact that the molecules in the polymer are linearly attached to each other) as well as the usefulness of Eq. (3.8) for practical applications. Consider a polymer confined in a box of volume $V = L_x L_y L_z$. The confinement is imposed by letting the potential $U = \infty$ outside the box (and $U = 0$ inside). This is effectively the same as imposing the condition $G(\vec{x}, \vec{x}', N) = 0$ on the boundary of the box. The solution of Eq. (3.8) with this boundary condition is [8]

$$\begin{aligned} G(\vec{x}, \vec{x}', N) &= g_x(x, x'; N) g_y(y, y'; N) g_z(z, z'; N), \\ g_x(x, x'; N) &= \frac{2}{L_x} \sum_{p=1}^{\infty} \sin\left(\frac{p\pi x}{L_x}\right) \sin\left(\frac{p\pi x'}{L_x}\right) \exp(-p^2 \pi^2 R_g^2 / L_x^2) \end{aligned}$$

and similarly for g_y and g_z . Before proceeding we recall that for an ideal gas the pressure on the walls is $p_v = k_B T / V$ ($v = x, y, z$). Let us now calculate the pressure the polymer exerts. The pressure is $p_x = (k_B T / L_y L_z) \partial \ln Z / \partial L_x$ where we have introduced the partition function $Z = \int d^3x d^3x' G(\vec{x}, \vec{x}', N)$. Using the above expression for the Green function we find that the partition function becomes $Z = Z_x Z_y Z_z$ where

$$Z_v = \frac{8}{\pi^2} L_v \sum_{p=1,3,\dots}^{\infty} \frac{1}{p^2} \exp\left[-\pi^2 R_g^2 \frac{p^2}{L_v^2}\right]. \quad (3.9)$$

We now distinguish between two cases. First consider a polymer which is smaller than the box $R_g \ll L_v$. We then find $Z_v = (8L_v / \pi^2) \sum_{p=1,3,\dots}^{\infty} 1/p^2 = L_v$ and we therefore get the pressure

$$p_x = \frac{k_B T}{V} \quad (3.10)$$

and similarly for p_y and p_z . When the polymer is small compared to the size of the box it can be treated as a point particle and therefore satisfy the ideal gas law as expected. We proceed by considering the case when the radius of gyration of the polymer is larger than the size of the box $R_g \gg L_v$ (but where the persistence length is smaller than the box $a \ll L_v$). We then have $Z_v = (8/\pi^2)L_v \exp[-\pi^2 R_g^2/L_v^2]$ which gives the pressure

$$p_x \approx \frac{2\pi^2 R_g^2}{L_x^2} \frac{k_B T}{V} \quad (3.11)$$

in the x -direction (the expression for p_y and p_z are similar). We see that there is now a dependence on the parameter R_g/L_v in the expression for the pressure. We notice that this deviation from the ideal gas law is a direct consequence of the connectivity of the chain; since we assume $a \ll L_v$ unconnected chain segments would satisfy the ideal gas law. It is thus the mere ‘act’ of connecting the segments that gives rise to the deviations from ideal gas behaviour. The connectivity of a polymer proves to be important also for the results in paper II, in which the motion of a polymer through a nano-pore is investigated. We find that when the length of the pore is large compared to the polymer persistence length, the connectivity of the polymer enhances entropic confinement effects which in turn has a large impact on the polymer motion.

3.2 Polymer dynamics

In this section we discuss the dynamics of a single polymer in a solvent.

The equation of motion for a polymer satisfies a low Reynolds number equation of motion just as does a single particle in a solvent (see chapter 2). Two additional complications in the study of polymer dynamics are: (i) the connectivity of polymer segments (ii) hydrodynamics coupling between segments. The most general equation of motion for segment n at position $\vec{x}_n(t) = (x_n(t), y_n(t), z_n(t))$ at time t is [8, 18] [compare to Eq. (2.4)]

$$\sum_n \overset{\leftrightarrow}{H}_{mn}^{-1} \cdot \frac{\partial \vec{x}_n}{\partial t} = -\vec{\nabla}_m U + \vec{F}_{\text{ext}}(\vec{x}_m) + \vec{g}_m(t), \quad (3.12)$$

where $\vec{\nabla}_m = (\partial/\partial x_m, \partial/\partial y_m, \partial/\partial z_m)$ and we have in a standard fashion neglected inertial terms. The tensor $\overset{\leftrightarrow}{H}_{nm}$ is the so called mobility matrix and has dimension of inverse friction. $\vec{g}_m(t)$ is a stochastic force acting on segment m and the external force acting on the polymer is denoted $\vec{F}_{\text{ext}}(\vec{x})$. The first term on the RHS is the force as caused by the connectivity of the chain. A consistent choice of the potential U is

$$U = \frac{k}{2} \sum_n (\vec{x}_n - \vec{x}_{n-1})^2, \quad (3.13)$$

where $k = 3k_B T/a^2$. This choice of U makes sure that the Green’s function goes to its equilibrium value at long times [8, 19, 18]. We notice that U has the form of an interaction potential between harmonically coupled particles. The equation

above can be turned into a Smoluchowski equation for the probability distribution $P(\{\vec{x}_n\}_{n=1}^N, t)$ [8]. When hydrodynamic interactions between segments are excluded the mobility matrix takes the form ($\overset{\leftrightarrow}{I}$ is the 3×3 unit matrix)

$$\overset{\leftrightarrow}{H}_{nm} = \frac{\overset{\leftrightarrow}{I}}{\xi} \delta_{nm}, \quad (3.14)$$

i.e., mobility matrix is the inverse of the friction constant (ξ is the local friction constant for a segment), which in turn is caused by the local interaction of each segments with its local solvent environment. The above choice of the mobility matrix is the main assumption underlying the *Rouse model* of polymer dynamics. Eq. (3.12) can then be solved by a Fourier transform. The result and corresponding normal modes of the polymer can be found in most textbooks on polymer dynamics [8, 19, 18]. We here only give the result for the center-of-mass mean square displacement which is [compare to Eq. (2.8)]

$$\langle |\vec{R}_C(t) - \vec{R}_C(0)|^2 \rangle = 6Dt, \quad (3.15)$$

where

$$D = \frac{k_B T}{N\xi}. \quad (3.16)$$

The total friction is thus $\xi_{\text{tot}} = N\xi$, i.e., each segments contributes equally to the friction for the polymer. The diffusion of the center-of-mass of the polymer is the slowest dynamics process for a free polymer. The higher order normal modes in the Rouse model correspond to internal relaxation processes in the polymer.

Unfortunately the N^{-1} -dependence of the center-of-mass diffusion constant for a polymer as obtained in the Rouse model does not agree with experiments. This failure comes from the fact that we have neglected hydrodynamic interactions between segments; as we saw in the previous chapter the velocity field around a moving particle decays slowly with distance r between segments, $v \sim 1/r$. This long-range disturbance of the velocity is felt by other segments. Once the hydrodynamic coupling is included in the mobility matrix Eq. (3.12) is no longer analytically solvable. Using dynamical scaling laws and more elaborate approximation schemes [8, 18] (the so called *Zimm model* of polymer dynamics) one finds that $\xi_{\text{tot}} \sim N^{1/2}$, i.e., that the polymer behaves as a “ball” of radius $R = R_g \sim N^{1/2}$ (no excluded volume effects) where R_g is the polymer radius of gyration. This result originates from the fact that when a polymer is moving through a viscous liquid only the “outer” segments in the coil interact with the liquid. The “inner” segments are protected/screened from interaction with the solvent by the outer segments. Because of the long-range character of the liquid velocity field around a moving particle at low Reynolds numbers, the presence of walls affect the polymer friction. In particular when a polymer moves through a pore the presence of the surrounding walls affect the friction [19]. This observation is important for the results obtained in paper II.

3.3 Fluid membranes

As discussed in the introduction a cell membrane is a bilayer of phospholipid molecules, with cholesterol and proteins embedded or attached. In this section we mainly limit the discussion to the *equilibrium* physics of lipid membranes. We will also discuss *vesicles*, which are closed lipid membranes and thus provide the simplest possible model systems of cells.

The current theoretical understanding of the equilibrium properties of membranes is based on the concept of *bending elasticity* of a membrane [20, 21, 22, 23, 24]. When discussing the elastic theory of membranes there are three distinct possible deformation, see Fig. 3.2 (i) Stretching - in this kind of deformation the area of the membrane is locally changed (ii) A shearing motion is an in-plane deformation which preserves the area (iii) Bending is a deformation in the normal direction of the membrane. We now follow [20] and [25] when writing the elastic energy of a membrane: The membrane is in a 2-dimensional *fluid* state, which means that a shearing deformation cost a very small amount of energy and can be neglected in the free energy functional. Furthermore it is found that a membrane is essentially *unstretchable* (it is an incompressible two dimensional fluid). It is then possible to show that the most general expression for the elastic energy of a fluid membrane is:

$$U_{\text{bend}} = \frac{\kappa_m}{2} \int (2H - H_{\text{sp}})^2 dS + \bar{\kappa}_m \int K dS, \quad (3.17)$$

where the integrals go over the membrane surface. We have introduced H_{sp} called the spontaneous curvature which may be positive as well as negative and allows for a bilayer that have chemically different outside than inside environment (as caused for instance by proteins attached to the outer or inner bilayer). H is the mean curvature defined in Eq. (B.16) and K is the Gaussian curvature [Eq. (B.15)]. The above expression for the elastic energy is usually referred to as *the Helfrich Hamiltonian*. For *closed* membranes (vesicles) the last term can be rewritten using the Gauss-Bonnet theorem Eq. (B.19); the second term of the elastic bending energy is thus just a constant (for a given topology). For unclosed membranes the second term of Eq. (3.17) can be rewritten as an integral over the membrane boundary [26]. For most practical purposes the elastic energy of bending of a vesicle is therefore effectively determined by only *one* elastic constant, κ_m . Eq. (3.17) is the generalization of the bending energy for a polymer introduced in Eq. (3.1). Notice however that the elastic constant in the polymer case had dimension of energy times length, whereas the elastic constant in the present case has dimension of energy.

Given the internal energy of a membrane one may proceed as in the previous section to define a persistence length a as the length outside of which there are no correlations along the membrane (the membrane is randomly “kicked” by thermal collisions with the solvent molecules). Such an analysis for an unclosed membrane gives the result [25]

$$a = \Lambda^{-1} \exp\left(\frac{4\pi\kappa_m}{3k_B T}\right), \quad (3.18)$$

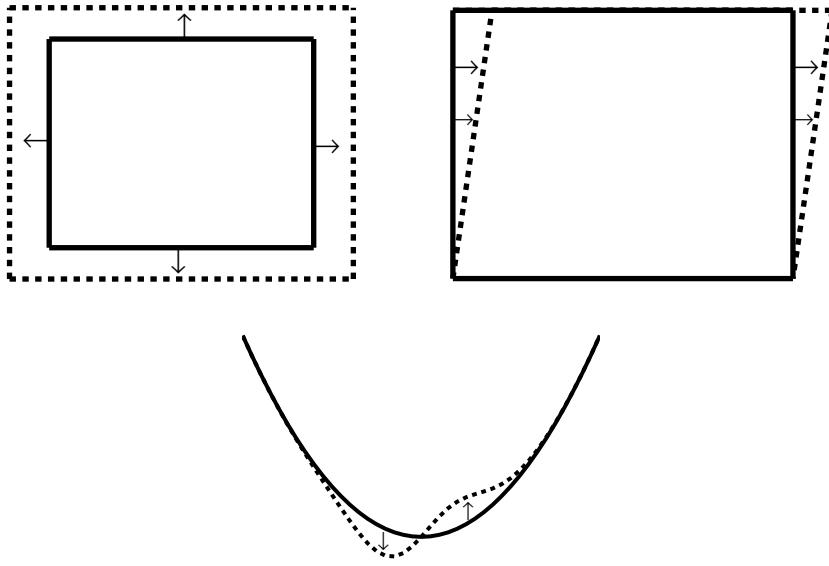


Figure 3.2: (top-left) A stretching deformation in the plane of a membrane (top-right) a shearing deformation in the plane of the membrane (bottom) a cut through a membrane undergoing a bending deformation.

where Λ is a cut off wavevector and Λ^{-1} is taken as the order of size of a lipid molecule (*i.e.*, a few Å). The above expression for the membrane persistence length should be compared to the corresponding polymer result, Eq. (3.3). The polymer persistence length is proportional to the elastic constant, whereas the membrane persistence length is exponential in the elastic constant. This difference hence occurs solely as an effect of going from a one to a two dimensional object. We can gain some insight into the difference by investigating the elastic bending constants. The only relevant energy scales in the problem are provided by the thermal energy $k_B T$ and the elastic constant. Since for a polymer the bending constant has dimension of energy times length we can directly obtain a relevant length scale as $\kappa_p/k_B T$. However for a membrane $\kappa_m/k_B T$ is dimensionless. One is therefore forced to introduce another relevant length scale, namely the cut-off distance Λ^{-1} . Since κ_m is usually a few tens of $k_B T$ [21] for realistic vesicles the persistence length [see Eq. (3.18)] is typically much larger than the vesicle (a typical vesicle size is $\sim 1 \mu\text{m}$) [21]. This observation is also important for the model developed in paper II, where we study the passage of charged polymers through a nano-pore in a membrane; in our model we assume that the membrane in which the nano-pore is reconstituted is flat (or rather the membrane is flat over distances larger than any other characteristic length in the problem, such as the size of the pore or the polymer radius of gyration). Since the persistence length of a membrane is typically much larger than the vesicle size the equilibrium shape of a vesicle is determined by the shape of lowest elastic energy (a universal random walk approach as applied to polymers cannot in general be applied to membranes). Furthermore vesicles (unlike the polymers considered in

the previous chapter) are closed structures, which requires us to take the constraints of fixed area and volume into account. A discussion of minimal shapes of vesicles with the appropriate constraints can for instance be found in [21].

We have in this chapter discussed the properties of polymers and fluid membranes. For both polymers and membranes we defined the persistence length as the length outside of which there are no correlations along the polymer or membrane. For many realistic polymers the persistence length is much smaller than its contour length, which allow us to describe polymer equilibrium properties by random walk statistics. For membranes, however, the persistence length is usually larger than the typical vesicle size, which makes the theoretical analysis different. We have furthermore emphasized the importance of the connectivity as well as hydrodynamic couplings in the study of soft matter. The results given in this chapter are particularly important as a background to paper II, in which electrostatically driven motion of charged polymers through a nanopore in a membrane is investigated.

CHAPTER 4

Matter-field interactions

In this chapter we discuss the response of a system to an external electric or electromagnetic field by defining the polarization and the dielectric function. These definitions are used in chapter 7 where we obtain the dielectric function of an electrolyte. We derive a general expression for the extinction cross section, which is used to obtain the cross section for molecules (chapter 5) and molecular aggregates in chapter 6. We also present the solution of Gauss equation for an ellipsoidal polarizable particle which is used explicitly in paper III and serves as a background to papers IV and V.

4.1 Mechanical work done by an electromagnetic field

In this section we give an expression for the extinction cross section.

Consider the physical situation where an external electromagnetic wave is incident on a system. The mechanical work, E_{mech} , done by this field on the system is then [27]

$$\frac{dE_{\text{mech}}}{dt} = \int \vec{J}^{\text{ind}}(\vec{x}, t) \cdot \vec{E}_0(\vec{x}, t) d^3x, \quad (4.1)$$

where $\vec{J}^{\text{ind}}(\vec{x}, t)$ is the induced current density in the system and $\vec{E}_0(\vec{x}, t)$ denotes the external electric field. Following [28] we proceed by dividing the charge into induced ρ^{ind} and external ρ^{ext} charge densities, *i.e.*,

$$\rho(\vec{x}, t) = \rho^{\text{ind}}(\vec{x}, t) + \rho^{\text{ext}}(\vec{x}, t). \quad (4.2)$$

The external charge density is simply charges that are situated outside the system under investigation (giving rise to the external electric field \vec{E}_0). The induced charge density arises by the polarization of the system by the electric fields. We can write

$$\rho^{\text{ind}}(\vec{x}, t) = -\vec{\nabla} \cdot \vec{P}(\vec{x}, t), \quad (4.3)$$

where $\vec{P}(\vec{x}, t)$ is the polarization of the medium. For the case of a number of molecules with non-overlapping electronic wavefunctions \vec{P} is simply the induced dipole moment per unit volume [28]. It is sometimes convenient to split the induced charge density into two contributions; “free” and “bound” charges. By free charges we mean for instance free electrons in a metal or ions in an electrolyte. By bound charges we mean charges such as bound electrons in a molecule, which are restricted to motion in a localized region. We shall *not* do this division here because it is sometimes confusing. Therefore \vec{P} as given above is such that when there are “free” charges they are included in our definition of the polarization. If we now restrict our attention to systems where the total charge is conserved (*i.e.*, no charge is added to the system from outside) and where magnetic polarization effects are small (this is usually the case [28]) then the relation between induced current density and induced charge density satisfies the equation of continuity: $\partial \rho^{\text{ind}}(\vec{x}, t)/\partial t = -\vec{\nabla} \cdot \vec{J}^{\text{ind}}(\vec{x}, t)$ or using Eq. (4.3) we find

$$\frac{\partial \vec{P}(\vec{x}, t)}{\partial t} = \vec{J}^{\text{ind}}(\vec{x}, t), \quad (4.4)$$

i.e., the rate of change of the polarization (as defined above) is simply the induced current. Using this relation in Eq. (4.1) we get the alternative expression

$$\frac{dE_{\text{mech}}}{dt} = \int \frac{\partial \vec{P}(\vec{x}, t)}{\partial t} \cdot \vec{E}_0(\vec{x}, t) d^3x, \quad (4.5)$$

for the mechanical work done by the external field on the system.

We now proceed by assuming a harmonic time-dependence $\vec{E}_0(t) = \text{Re}[\vec{E}_0(\vec{x})e^{-i\omega t}] = \frac{1}{2}[\vec{E}_0(\vec{x})e^{-i\omega t} + \vec{E}_0(\vec{x})^* e^{i\omega t}]$ and the same for $\vec{P}(\vec{x}, t)$. The time-averaged power of Eq. (4.5) then becomes

$$\langle \frac{dE_{\text{mech}}}{dt} \rangle = \frac{1}{2} \text{Re}(-i\omega \int \vec{P}(\vec{x}) \cdot \vec{E}_0(\vec{x})^* d^3x) = \frac{\omega}{2} \text{Im} \int \vec{P}(\vec{x}) \cdot \vec{E}_0(\vec{x})^* d^3x.$$

The mechanical energy can either be absorbed by the system or reradiated to the surroundings (scattering). It is customary to define the extinction (or total) cross section, σ , according to

$$\sigma \equiv \frac{(\text{Absorbed energy} + \text{scattered energy})/\text{unit time}}{\text{Energy flux of the incoming radiation}} = \sigma_{\text{abs}} + \sigma_{\text{scatt.}}$$

The energy flux of the incoming radiation is $c\epsilon_0|\vec{E}_0|^2/2$, where ϵ_0 is the permittivity of free space [27]. The extinction cross section for a harmonically time-varying field then takes the form

$$\sigma(\omega) = \frac{k}{|\vec{E}_0|^2 \epsilon_0} \text{Im} \int \vec{P}(\vec{x}) \cdot \vec{E}_0(\vec{x})^* d^3x. \quad (4.6)$$

Here, $k = |\vec{k}| = \omega/c = 2\pi/\lambda$, where \vec{k} is the propagation vector of the electric field. The correct quantum mechanical expression is obtained by replacing $\vec{P}(\vec{x})$ by the

corresponding quantum mechanical expectation value [29]. The calculation of the induced polarization (or induced charge density) requires (classical or quantum mechanical) microscopic theories for the dynamics of the system. We will encounter such theories in the remaining chapters in this study. If we assume that the wavelength is much larger than the molecules of the system then the electric field only probes the molecules as pointlike objects and we may write $\vec{P}(\vec{x}) = \sum_i \vec{p}_i \delta(\vec{x} - \vec{x}_i)$. Eq. (4.6) then becomes

$$\sigma(\omega) = \frac{k}{|\vec{E}_0|^2 \epsilon_0} \text{Im} \sum_i \vec{p}_i \cdot \vec{E}_{0,i}^*. \quad (4.7)$$

We point out that the extinction is a measureable quantity, and we will use the result above in chapter 5 to get the cross section for molecules and in chapter 6 to find the cross section for molecular aggregates.

The scattering cross section is proportional to k^4 [30], whereas, as seen above, the extinction cross section is proportional to k . Introducing L as a typical size of the aggregate the ‘‘strength’’ of the scattering relative to the extinction cross sections is determined by the dimensionless parameter, $(kL)^3 \sim (L/\lambda)^3$. Thus for small aggregates as compared to the wavelength of the external field the extinction cross section is much larger than the scattering cross section. A measurement of the absorption then gives the same result as a measurement of the extinction.

4.2 Gauss equation

In this section we state the Maxwell macroscopic equations. We focus especially on the non-retarded limit in which the Maxwell equations reduce to Gauss equation.

The total macroscopic electric \vec{E} and magnetic induction \vec{B} in vacuum are determined by the total charge density ρ and total currents \vec{J} in the system according to the equations (in SI units)

$$\begin{aligned} \vec{\nabla} \cdot \vec{E}(\vec{x}, t) &= \rho(\vec{x}, t)/\epsilon_0, \\ \vec{\nabla} \times \vec{E}(\vec{x}, t) &= -\frac{\partial \vec{B}(\vec{x}, t)}{\partial t}, \\ \vec{\nabla} \cdot \vec{B}(\vec{x}, t) &= 0, \\ \vec{\nabla} \times \vec{B}(\vec{x}, t) &= \frac{1}{c^2} \frac{\partial \vec{E}(\vec{x}, t)}{\partial t} + \mu_0 \vec{J}(\vec{x}, t), \end{aligned} \quad (4.8)$$

where ϵ_0 is the permittivity of free space as before, μ_0 is the permeability of free space and $c = 1/\sqrt{\mu_0 \epsilon_0}$ is the velocity of light in vacuum. The above set of equations are known as *Maxwell's macroscopic equations*. We point out that all fields appearing above are macroscopic quantities, *i.e.*, they are averaged over a microscopically large region of space [28]. A particularly interesting solution of the above equations are that of an electromagnetic wave; the electric and magnetic fields couple into a transverse wave moving with velocity c . The magnetic component of this field is of

the order c smaller than the electric component [27]. We now, as in the previous section, distinguish between induced and external charges. Maxwell's equations then become

$$\begin{aligned}\vec{\nabla} \cdot \vec{D}(\vec{x}, t) &= \rho^{\text{ext}}(\vec{x}, t), \\ \vec{\nabla} \times \vec{E}(\vec{x}, t) &= -\frac{\partial \vec{B}(\vec{x}, t)}{\partial t}, \\ \vec{\nabla} \cdot \vec{B}(\vec{x}, t) &= 0, \\ \vec{\nabla} \times \vec{H}(\vec{x}, t) &= \frac{\partial \vec{D}(\vec{x}, t)}{\partial t} + \vec{J}^{\text{ext}}(\vec{x}, t),\end{aligned}\quad (4.9)$$

where \vec{J}^{ext} is an external current density. The external current density is related to the external charge density ρ^{ext} through the equation of continuity: $\partial \rho^{\text{ext}}(\vec{x}, t)/\partial t = -\vec{\nabla} \cdot \vec{J}^{\text{ext}}(\vec{x}, t)$ [which is implicit in Eq. (4.8)]. We have introduced the displacement field

$$\vec{D}(\vec{x}, t) \equiv \epsilon_0 \vec{E}(\vec{x}, t) + \vec{P}(\vec{x}, t). \quad (4.10)$$

We notice from Maxwell's equations that the displacement field is directly related to the external charge density and is therefore an external field. We can thus write $\vec{D} = \epsilon_0 \vec{E}_0$, where \vec{E}_0 is an external electric field. We have above, like in the previous section, neglected induced magnetic polarization effects so that the magnetic induction \vec{B} is related to the magnetic field \vec{H} according to $\vec{B} = \mu_0 \vec{H}$.

It is customary to introduce a dielectric function $\overset{\leftrightarrow}{\epsilon}(\vec{x}, \vec{x}', t, t')$, which relates the external \vec{D} -field to the total electric field \vec{E} in the system according to

$$\vec{D}(\vec{x}, t) = \int d^3x' \int_{-\infty}^t dt' \overset{\leftrightarrow}{\epsilon}(\vec{x}, \vec{x}', t - t') \vec{E}(\vec{x}', t'). \quad (4.11)$$

We notice that the dielectric function includes the effect of polarization (induced charge density) by definition [see Eq. (4.10)], *i.e.*, we have swept all information about the microscopic dynamics into the dielectric function.

We now assume that we know the dielectric function of the system under investigation. Then the electric and magnetic fields are directly obtained through Maxwell's equations, Eq. (4.9). The general problem is difficult to solve. We will here therefore make the non-retarded field approximation. In this approximation the electric and magnetic fields decouple. In particular the magnetic correction to the electromagnetic field is zero and the two relevant equations in regions where there are no external charge density ($\rho^{\text{ext}} = 0$) are $\vec{\nabla} \cdot \vec{D} = 0$ and $\vec{\nabla} \times \vec{E} = 0$. The latter of these two equations allow us to introduce a scalar potential, Φ , according to

$$\vec{E}(\vec{x}, t) = -\vec{\nabla} \Phi(\vec{x}, t). \quad (4.12)$$

Inserting this equation into the equation for the \vec{D} -field and using Eq. (4.11) we get

$$\vec{\nabla} \cdot [\overset{\leftrightarrow}{\epsilon} \cdot \vec{\nabla} \Phi(\vec{x}, t)] = 0, \quad (4.13)$$

which is called *Gauss equation*. In regions where the dielectric function is a scalar and does not depend on position Gauss equation reduces to *Laplace* equation $\nabla^2\Phi = 0$.

We point out here that for regions where the current density vanishes the *magnetostatic* equations are of identical form as the non-retarded equations above [27]. We have so far assumed that there is no induced magnetization in the system; the magnetization is included into Maxwell's equation through the replacement $\vec{B} = \mu_0 \vec{H} \rightarrow \vec{B} = \overset{\leftrightarrow}{\mu} \cdot \vec{H}$, where $\overset{\leftrightarrow}{\mu}$ is the magnetic permeability [27]. From Eq. (4.9) we then find that, for regions with no current density, the two relevant magnetostatic equations are: $\vec{\nabla} \cdot \vec{B} = 0$ and $\vec{\nabla} \times \vec{H} = 0$. These equations are identical to the equations for the electric fields in the non-retarded limit given above, with the replacements $\vec{E} \rightarrow \vec{H}$ and $\vec{D} \rightarrow \vec{B}$. In particular we can introduce a *magnetic scalar potential* Φ_m according to $\vec{H} = -\vec{\nabla}\Phi_m$, which satisfies the equation $\vec{\nabla} \cdot (\overset{\leftrightarrow}{\mu} \cdot \vec{\nabla}\Phi_m) = 0$. This equation is identical to Gauss equation, Eq. (4.13), but where the dielectric function $\overset{\leftrightarrow}{\epsilon}$ is replaced by the magnetic permeability $\overset{\leftrightarrow}{\mu}$.

The Gauss equation (or Laplace equation) is a convenient tool for including *shape* effects on the electric response of macroscopic particles (see papers III, IV and V). As an illustration we solve Laplace equation for an ellipsoidal particle (see Fig. 2.1) in a homogeneous external electric field E_0 in the x -direction. The dielectric function of the particle is ϵ_{in} and the medium has dielectric function ϵ_m . We follow [31] and make the ansatz for the potential, Φ_{out} , outside the ellipsoid:

$$\Phi_{out} = \Phi_0 + \Phi_p, \quad (4.14)$$

where

$$\Phi_0 = -E_0 x. \quad (4.15)$$

For the induced potential Φ_p outside the particle we take

$$\Phi_p = Dx\gamma_x(\xi), \quad (4.16)$$

where $\gamma_x(\xi)$ is an elliptic integral of the second kind given by Eq. (A.8) and ξ is the “radial” ellipsoidal coordinate, see appendix A. D is an unknown constant which is determined through the boundary conditions (see below). From Eq. (A.9) we see that Φ_p satisfies Laplace’s equation. For the potential Φ_{in} , inside the the ellipsoid, we make the ansatz

$$\Phi_{in} = Ax, \quad (4.17)$$

i.e., we assume that the field inside the ellipsoid is linear in the x -coordinate. Let us show that it is possible to choose the constants A and D such that the boundary conditions that the potential as well as the normal components of the displacement field are continuous [27] are satisfied. Since the surface of the ellipsoid corresponds to $\xi = 0$ [see Eq. (A.1)] the two boundary conditions are:

$$\begin{aligned} \Phi_0(\xi = 0) + \Phi_p(\xi = 0) &= \Phi_{in}(\xi = 0), \\ \epsilon_m \frac{\partial \Phi_0(\xi = 0)}{\partial \xi} + \epsilon_m \frac{\partial \Phi_p(\xi = 0)}{\partial \xi} &= \epsilon_{in} \frac{\partial \Phi_{in}(\xi = 0)}{\partial \xi}, \end{aligned} \quad (4.18)$$

or explicitly using the ansatz above we find

$$\begin{aligned} A &= -\frac{E_0}{n_x \epsilon_i - 1 + 1/n_x}, \\ D &= \frac{E_0}{2n_x} \frac{\epsilon_i - 1}{\epsilon_i - 1 + 1/n_x}, \end{aligned} \quad (4.19)$$

where $\epsilon_i \equiv \epsilon_{in}/\epsilon_m$ is the relative dielectric function and the depolarization factor n_x is given by Eq. (A.13). The above equations for A and D together with Eqs. (4.16) and (4.17) completely determine the potential in all space. The shape of the particle enters through the depolarization factor n_x [31, 32]. The depolarization factor is an important entity which appear explicitly in papers III, IV and V. For a sphere $n_x = 1/3$ (see appendix A).

The electric field inside the ellipsoid is in the x -direction and of magnitude $E_{in} = -\partial\Phi_{in}/\partial x$ where explicitly, using the results above,

$$\frac{E_{in}}{E_0} = -\frac{A}{E_0} = \frac{1}{n_x} \frac{1}{\epsilon_i - 1 + 1/n_x}. \quad (4.20)$$

The electric field is hence screened inside the particle if the dielectric function of the ellipsoid is larger than that of the surrounding medium. In particular, for a particle having an electrolyte inside at low frequencies or being metallic we have $|\epsilon_i| \rightarrow \infty$ (see chapter 7) and hence the electric field inside the particle is zero (perfect screening).

We now make an asymptotic expansion of Φ_p for large distances from the ellipsoidal particle in order to identify the induced dipole moment. We have [see Eq. (A.8)]

$$\Phi_p \approx D \frac{V}{2\pi r^3} \frac{x}{r}, \quad (4.21)$$

where $V = 4\pi a_x a_y a_z / 3$ is the volume of the ellipsoid. The expression above for the potential is that of a dipole [27] with dipole moment $p_\mu = 4\pi\epsilon_0\epsilon_m\alpha_{\mu\mu}E_0$, where we have introduced the *polarizability* of the particle

$$\alpha_{\mu\mu} = \frac{V}{4\pi n_\mu} f(\omega, n_\mu), \quad (4.22)$$

with

$$f(\omega, n_\mu) = \frac{\epsilon_i(\omega) - 1}{\epsilon_i(\omega) - 1 + 1/n_\mu} \quad (4.23)$$

and we have generalized the result to allow the external field to be along any of the three principal axes ($\mu = x, y, z$). For a metal or an electrolyte at low frequencies $|\epsilon_i| \gg 1$ and the polarizability becomes $\alpha_{\mu\mu} \approx V/4\pi n_\mu$, *i.e.*, it is determined entirely by the volume and the inverse depolarization factor ($0 \leq n_\mu \leq 1$).

In this chapter we have discussed the work done by an external field by introducing the extinction cross section (a measurable quantity), Eqs. (4.6) and (4.7), which

is used in chapters 5 and 6. The definition of dielectric function Eqs. (4.10) and (4.11) will be used in chapter 7. We have furthermore discussed Gauss equation and in particular we studied the particle shape dependence of the solutions to this equation. We found that for an ellipsoidal particle the dependence on shape enters through the depolarization factors n_x , n_y and n_z . These entities appear explicitly in papers III, IV and V.

CHAPTER 5

Single molecule polarizabilities

In this chapter we discuss the electric response of a single molecule and in particular we study the polarizability $\overset{\leftrightarrow}{\alpha}(\omega)$ of the molecule. The polarizability is in general a 3×3 tensor, which relates the induced dipole moment to an external electric field \vec{E}_0 at that molecule according to $\vec{p} = 4\pi\epsilon_0 \overset{\leftrightarrow}{\alpha}(\omega) \cdot \vec{E}_0(\omega)$.^{*} When the molecules are situated in a medium of relative dielectric constant ϵ_m we make the replacement $\epsilon_0 \rightarrow \epsilon_0\epsilon_m$. Polarizabilities for a molecule with simple electronic levels and for electron-vibrationally coupled molecules are given. The results obtained in this chapter provide a background to chapter 6 as well as to paper I, in which the interaction between an external electromagnetic field and molecular aggregates is investigated; the polarizability of the constituent molecules there appear as important entities.

5.1 General formalism

In this section we give the formal expression for the polarizability in terms of the retarded dipole-dipole response function.

Let us consider a single molecule under the influence of an electric field $E^\mu(t) = E^\mu \exp[i(\vec{k} \cdot \vec{r} - \omega t)]$, where $\mu = x, y, z$ denotes vector components. In the linear regime the response to the electric field is contained in the polarizability of the molecule, which can be found as the Fourier transform [33]

$$\alpha^{\mu\nu}(\omega) = \frac{1}{4\pi\epsilon_0} \int_{-\infty}^{\infty} dt e^{i\omega t} \Pi^{\mu\nu}(t, 0), \quad (5.1)$$

^{*} notice that this definition of the polarizability differ from the one given in paper I; in paper I we define the polarizability $\overset{\leftrightarrow}{\alpha}_I$ according to $\vec{p} = \overset{\leftrightarrow}{\alpha}_I \cdot \vec{E}_0$. The relationship between the polarizability as given in that paper and the one given in this introductory part and paper III, IV and V is therefore: $\overset{\leftrightarrow}{\alpha}_I = 4\pi\epsilon_0 \overset{\leftrightarrow}{\alpha}$.

where \hbar is the Planck constant. $\Pi^{\mu\nu}(t, 0)$ is the retarded dipole-dipole response function given explicitly by

$$\Pi^{\mu\nu}(t, 0) = \frac{i}{\hbar} \Theta(t) \langle [|\hat{d}^\mu(t), \hat{d}^\nu(0)|] \rangle, \quad (5.2)$$

where $\Theta(t)$ is Heaviside's step function and $\hat{d}^\mu(t)$ is the μ -component of the dipole operator. At zero temperature, $T = 0$, $\langle |\dots| \rangle$ means the ground state expectation value in the absence of the external field and at $T \neq 0$ $\langle |\dots| \rangle$ means the thermal expectation value. The polarizability is thus a property of the system in the *absence* of the external field. The time-evolution of the dipole operator is

$$\hat{d}^\mu(t) = e^{iH_0 t/\hbar} \hat{d}^\mu e^{-iH_0 t/\hbar} \quad (5.3)$$

i.e., it is determined by the Hamiltonian H_0 of the molecule. Eq. (5.1) is a special case of a general result, the Kubo formula, that connects the response to a weak external perturbation of a system to some operator evaluated in equilibrium.

For a single molecule we may use Eq. (4.7) to obtain the extinction cross section

$$\sigma(\omega)|_{\text{single mol.}} = \frac{4\pi k}{3} \text{Im}[\alpha^{\mu\mu}(\omega)], \quad (5.4)$$

where we have taken the trace above in order to obtain the rotationally averaged spectra (repeated vector indices are summed over). The extinction (a measureable quantity) is thus determined by the imaginary part of the polarizability. The imaginary part is related to the real part of the polarizability through *Kramer-Kronig relation*, which is a relation valid for response functions, $\alpha^{\mu\nu}(\omega)$, satisfying the following requirements [34],

- The poles of $\alpha^{\mu\nu}(\omega)$ are all below the real axis.
- The integral of $\alpha^{\mu\nu}(\omega)/\omega$ vanishes when taken around an infinite semi-circle in the upper half of the complex ω -plane. It suffices that $\alpha^{\mu\nu}(\omega) \rightarrow 0$ as $|\omega| \rightarrow \infty$.
- The function $\text{Re}[\alpha^{\mu\nu}(\omega)]$ is even and $\text{Im}[\alpha^{\mu\nu}(\omega)]$ is odd.

For polarizabilities $\alpha^{\mu\nu}(\omega)$ satisfying these conditions the Kramer-Kronig relations are

$$\begin{aligned} \text{Re}[\alpha^{\mu\nu}(\omega)] &= \frac{2}{\pi} P \int_0^\infty \frac{\omega' \text{Im}[\alpha^{\mu\nu}(\omega')]}{(\omega')^2 - \omega^2} d\omega', \\ \text{Im}[\alpha^{\mu\nu}(\omega)] &= -\frac{2\omega}{\pi} P \int_0^\infty \frac{\text{Re}[\alpha^{\mu\nu}(\omega')]}{(\omega')^2 - \omega^2} d\omega'. \end{aligned} \quad (5.5)$$

The fact that the real part is related to the imaginary part of the polarizability is due to causality requirements [35].

5.2 Two-level molecules

For a system characterized by a set of discrete energy levels, Eq. (5.1) can be evaluated (see appendix C). The result for the polarizability is contained in Eqs. (C.4) and (C.5). Let us here for simplicity consider a system with two electronic levels, with energies E_0 and E_1 respectively. The polarizability then becomes

$$\alpha^{\mu\nu}(\omega) = \frac{\alpha_0^{\mu\nu} \omega_{10}^2}{\omega_{10}^2 - \omega^2 - i\omega L(\omega)}, \quad (5.6)$$

where

$$\alpha_0^{\mu\nu} = \frac{\langle \Phi_0 | \hat{d}^\mu | \Phi_1 \rangle \langle \Phi_1 | \hat{d}^\mu | \Phi_0 \rangle}{2\pi\hbar\omega_{10}\epsilon_0} \quad (5.7)$$

is the static polarizability of the molecules. $\hbar\omega_{10} \equiv E_1 - E_0$ is the energy difference between the electronic levels and $|\Phi_0\rangle$ ($|\Phi_1\rangle$) is the ground state (first excited state) eigenfunction. The parameter $L(\omega)$ corresponds to damping of the electronic motion.

The form for the polarizability as given by Eq. (5.6) can be derived by a “classical” approach; this approach also sheds some light on the damping parameter $L(\omega)$ and we therefore give the explicit derivation here. We assume that the motion of an electron is described by Langevin’s equation, Eq. (2.1), where m here is taken as the electron mass and the friction tensor is assumed to be a scalar ξ . The friction for the electronic motion can for instance occur because of radiation damping or interactions with the surroundings [36, 37]. The force on the electron from the nuclei is assumed to take the form of a Hooke’s restoring force, *i.e.*, we take the force appearing in Langevin’s equation as: $F = -m\omega_{10}^2 x$. Assuming harmonic time-dependence, $\exp(-i\omega t)$, of all quantities and averaging Eq. (2.1), we find that the expected electron position $\langle x \rangle$ satisfies the equation (limiting the discussion to one-dimensional motion for simplicity)

$$m\langle x \rangle (-\omega^2 + \omega_{10}^2 - i\omega L) = -eE_0 \quad (5.8)$$

where we have included the force $-eE_0$ from an external electric field ($-e$ is the electron charge). We have also defined a damping parameter $L \equiv \xi/m$. The expected dipole moment of the atom is $\langle p \rangle = -e\langle x \rangle$ and hence using Eq. (5.8) we write $\langle p \rangle = 4\pi\epsilon_0\alpha E_0$ where the polarizability is

$$\alpha(\omega) = \frac{\alpha_0 \omega_{10}^2}{\omega_{10}^2 - \omega^2 - i\omega L}, \quad (5.9)$$

with $\alpha_0 = e^2/(4\pi\epsilon_0 m \omega_{10}^2)$. The classical result Eq. (5.9) has the same form as Eq. (5.6). The difference between the quantum mechanical and the classical results enters through the static polarizability α_0 ; in the quantum mechanical expression α_0 depends on the transition dipole matrix element which can only be calculated with a knowledge of the molecular eigenfunctions. In the classical derivation above the

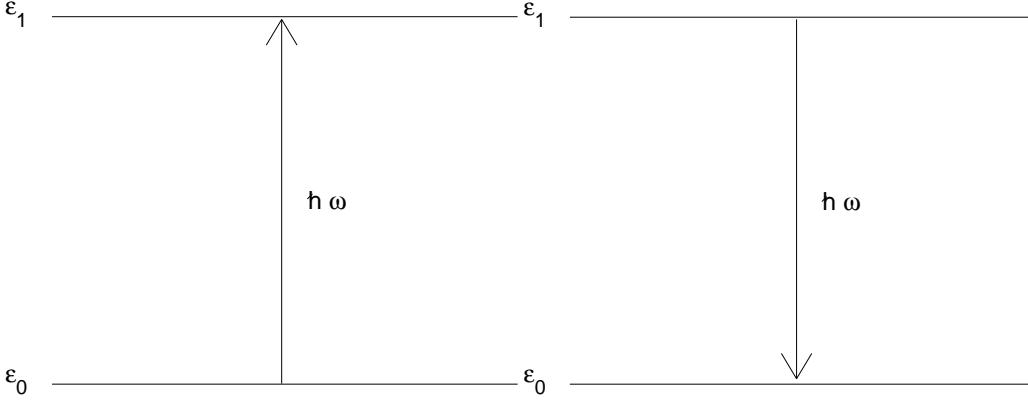


Figure 5.1: (left) Absorption: The molecule receives energy, $\hbar\omega$, from the electromagnetic field and ends up in an excited state. (right) Stimulated emission: The molecule gives up energy, $\hbar\omega$, to the electromagnetic field and ends up in a lower molecular level.

damping parameter L is the ratio of the friction constant and the electron mass. In terms of the relaxation time τ introduced in Sec. 2.1 we have $L = 1/\tau$, *i.e.*, the damping constant is related to the inverse relaxation time. In the general case the damping constant depends on frequency, for instance for radiative damping $L(\omega) = \omega^2\Upsilon$, where $\Upsilon = 2e^2/3mc^3$ is a radiative damping parameter [27, 38].

The real part of the polarizability [assuming $L(\omega)$ to be real] is,

$$Re[\alpha^{\mu\nu}(\omega)] = \frac{\alpha_0^{\mu\nu} \omega_{10}^2 (\omega_{10}^2 - \omega^2)}{(\omega_{10}^2 - \omega^2)^2 + \omega^2 L^2}, \quad (5.10)$$

while the imaginary part, which corresponds to extinction, is

$$Im[\alpha^{\mu\nu}(\omega)] = \frac{\alpha_0^{\mu\nu} \omega_{10}^2 \omega L}{(\omega_{10}^2 - \omega^2)^2 + \omega^2 L^2}. \quad (5.11)$$

Sharp resonances occur at frequencies $\omega = \pm\omega_{10}$, *i.e.*, when the energy of the incoming light matches that of the energy difference between energy levels (see Fig. 5.1). $\omega = \omega_{10}$ corresponds to the absorption of a photon, while at $\omega = -\omega_{10}$ the molecule gives up energy to the electromagnetic field (stimulated emission).

Note that in the limit of very high frequencies, $|\omega| \rightarrow \infty$, the polarizability goes to zero. This is due to the fact that at high frequencies the charges are unable to follow the rapidly changing field.

The polarizability is in general a 3×3 tensor. For spherically symmetrical molecules the induced dipole moment does not depend on the polarization of the incoming field and the polarizability is a scalar. For elongated molecules the induced dipole moment will in general be larger along the major axis - if the coordinate system is chosen such that this axis is along the x-axis then α^{xx} is larger than α^{yy} and α^{zz} . Off-diagonal elements of the polarizability corresponds to a situation where the induced dipole moment is in a different direction than the polarization vector of the external electromagnetic field.

5.3 Electron-vibrationally coupled molecules

For larger molecules (such as biomolecules, see introduction) intramolecular vibrations can be induced [39, 40], either directly by the external electromagnetic field or indirectly through the Coulomb coupling between electronically excited electrons and the nuclei. The latter mechanism and how it affects the polarizability is illustrated below.

The electrons and the nuclei are coupled through Coulomb interactions. When a molecule is electronically excited the nuclei will feel this and adjust themselves to the new electronic configuration. During the adjustment a vibration might be created [in the previous section we implicitly assumed the nuclei mass M to be infinite (the so-called Born-Oppenheimer approximation), *i.e.*, we excluded the possibility that vibrations are created (an infinitely heavy particle cannot move)]. For many systems it is only vibrations of a specific energy, $\hbar\omega_{\text{vib}}$, that couple significantly to the electronic motion (Einstein model). For this particular case the polarizability becomes [33, 40, 41]

$$\alpha^{\mu\nu}(\omega) = \alpha_0^{\mu\nu} e^{-g(2N+1)} \sum_{m=-\infty}^{\infty} I_m(2g[N(N+1)]^{1/2}) e^{\beta m \hbar \omega_{\text{vib}}/2} \times \frac{\omega_{10} \omega_m}{(\omega_m)^2 - \omega^2 - i\omega L}, \quad (5.12)$$

where $\alpha_0^{\mu\nu}$ is the static polarizability as previously defined and

$$\hbar\omega_m = \hbar\omega_{10} - \hbar\Delta_1 + \hbar\Delta_0 + \hbar\omega_{\text{vib}}m. \quad (5.13)$$

The dimensionless electron- vibrational coupling parameter, g , is sometimes referred to as the *Huang-Rhys factor* [40]. N is the occupation factor of the vibrational mode

$$N = \frac{1}{e^{\hbar\omega_{\text{vib}}/(k_B T)} - 1}. \quad (5.14)$$

I_m are the modified Bessel functions. $\hbar\Delta_0$ is an energy shift of the electronic ground state caused by fact that when the nuclei are allowed to relax the system can gain energy. Similarly $\hbar\Delta_1$ is the energy shift of the upper electronic level. The physics contained in the above expression for the polarizability is often described by a configurational coordinate diagram, Fig. 5.2. The horizontal axis of this diagram describes the normal “vibrational” coordinates, q , of the system. The vertical axis corresponds to electronic energies. The lower curve describes the ground state of the system. Due to the coupling between the electrons and the nuclei the minimum q -value is shifted from $q = 0$ to $q^{(0)}$ and the electronic energy is changed from E_0 to $E_0 - \hbar\Delta_0$. The upper curve describes the potential energy curve of vibrations and electrons of the excited electronic state. The minimum q -value for this parabola is $q^{(1)}$ and the minimum energy is $E_1 - \hbar\Delta_1$. During an optical transition the coupled electronic-vibrational system is lifted from the ground state to the excited state (two possibilities are given by lines A and B). If the energy of the absorbed photon is

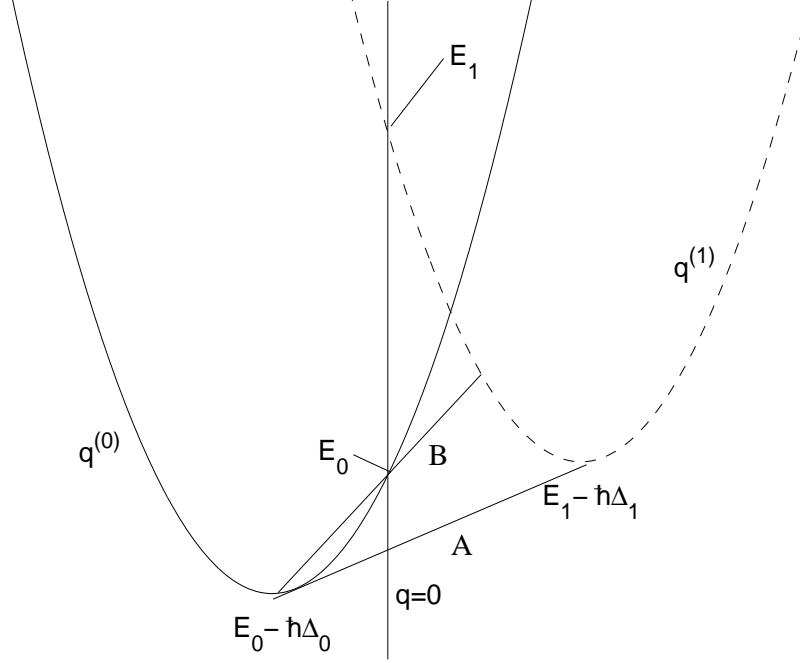


Figure 5.2: Typical configurational coordinate diagram.

larger than the energy difference between the minima (such as line B) the excited system tries to find the new equilibrium (the minimum of the upper parabola). During this process one or many vibrational quanta may be created. In the Einstein model a transition with non-zero probability occurs if the energy of the absorbed photon matches the energy between electronic levels plus the energy of one or many vibrational quanta [see Eq. (5.13)]. The probability that a transition where m vibrations are created is determined by the modified Bessel function, I_m . The direct transition between the potential minima (line A in Fig. 5.2) is called the *zero-phonon line* and involves no vibrations during the optical step. Let us introduce f as the vibrational energy divided by the thermal energy, $f = \hbar\omega_{\text{vib}}/k_B T$. In the limit $f \rightarrow \infty$ (low temperatures) the polarizability becomes [33]

$$\alpha^{\mu\nu}(\omega) = \alpha_0^{\mu\nu} e^{-g} \sum_{m=0}^{\infty} \frac{g^m}{m!} \frac{\omega_{10}\omega_m}{(\omega_m)^2 - \omega^2 - i\omega L}. \quad (5.15)$$

Notice that the peaks in the $\sigma(\omega)$ spectrum in the low temperature regime follow a Poisson distribution. The prefactors, $e^{-g} g^m / m!$, determining the strength of a transition are called *Franck-Condon factors*. In Fig. 5.3 the extinction cross section $\sigma(\omega)$ for $f = 1$ (intermediate temperatures) is plotted. For low temperatures all peaks are located above the uncoupled response frequency while in the intermediate temperature regime (as seen in Fig. 5.3) there are peaks below this value due to the fact that there are thermally excited vibrations in the system.

We have in this chapter introduced the molecular polarizability, which related

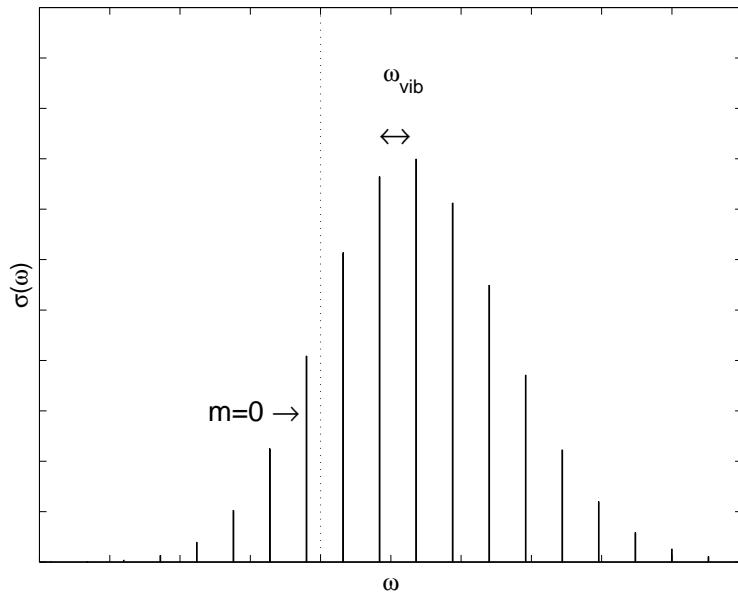


Figure 5.3: The extinction cross section $\sigma(\omega) \sim \omega Im\alpha(\omega)$ as a function of ω for electron-vibration coupling, $g=3$ and intermediate temperatures, $f = 1$. Due to the electron-vibrational coupling vibration are created during the optical transition. The vertical dotted line correspond to the position of ω_{10} .

the induced dipole moment to the electric field at a molecule. The results obtained in this chapter give a background to chapter 6 and paper I, where the interaction between electric fields and molecular aggregates is studied.

CHAPTER 6

Electromagnetic response of molecular aggregates

In this chapter we describe the interaction between a molecular aggregate (a system consisting of molecules that have negligible electronic overlap) and an external electromagnetic field, including local field effects. This chapter is directly related to papers I and V. In paper I general molecular aggregate response is treated using a quantum mechanical approach. Paper V deals with the response of an ellipsoidal cell membrane (a molecular aggregate, see introduction) at frequencies where membrane molecular resonances are important.

Let us consider the interaction between a set of polarizable molecules and an external electric field, $\vec{E}_0(\vec{r}, t) = \vec{E}_0 \exp[i(\vec{k} \cdot \vec{r} - \omega t)]$ where \vec{k} is the wavevector ($|\vec{k}| = k = 2\pi/\lambda$ where λ is the wavelength) and ω the frequency of the field. Each molecule “feels” a local electric field \vec{E}_{loc} which is the superposition of the external field and the induced dipolar field from all the other molecules in the system (see Fig. 6.1). In the linear regime the induced dipole moment $\vec{p}(\vec{r})$ of a molecule at a position \vec{r} is proportional to the local field $\vec{E}_{\text{loc}}(\vec{r})$, *i.e.*,

$$\vec{p}(\vec{r}) = 4\pi\epsilon_0 \overset{\leftrightarrow}{\alpha} \cdot \vec{E}_{\text{loc}}(\vec{r}), \quad (6.1)$$

where $\overset{\leftrightarrow}{\alpha}$ is the polarizability (a 3×3 tensor) of the molecule (see previous chapter) and ϵ_0 is the permittivity of vacuum as before. When the molecules are situated in a medium of relative dielectric constant ϵ_m we make the replacement $\epsilon_0 \rightarrow \epsilon_0\epsilon_m$. Explicitly the local electric field at molecule j at position \vec{r}_j is [42, 43, 44, 45, 46]

$$\vec{E}_{\text{loc},j} = \vec{E}_{0,j} + \sum_{i=1}^N \overset{\leftrightarrow}{\kappa}_{ji} \cdot \vec{p}_i, \quad (6.2)$$

where $\vec{E}_{0,j} = \vec{E}_0(\vec{r}_j)$, $\vec{p}_j = \vec{p}(\vec{r}_j)$ and the dipole coupling tensor is

$$\begin{aligned}\kappa_{ij}^{\mu\nu} &= \frac{k^3}{4\pi\epsilon_0}[A(kr_{ij})\delta_{\mu\nu} + B(kr_{ij})\frac{(r_i^\mu - r_j^\mu)(r_i^\nu - r_j^\nu)}{r_{ij}^2}] \\ A(x) &= (x^{-1} + ix^{-2} - x^{-3})e^{ix}, \\ B(x) &= (-x^{-1} - 3ix^{-2} + 3x^{-3})e^{ix},\end{aligned}\quad (6.3)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and μ, ν denotes vector components ($\mu, \nu = x, y, z$). Often the distance between electromagnetically interacting molecules is much smaller than the wavelength (the wavelength of optical fields ranges from about 400 nm to 650 nm). In this limit the dipole coupling tensor takes the form [27]:

$$\tilde{\kappa}_{ij}^{\mu\nu} = \frac{1}{4\pi\epsilon_0 r_{ij}^3} \left[\frac{3(r_i^\mu - r_j^\mu)(r_i^\nu - r_j^\nu)}{r_{ij}^2} - \delta_{\mu\nu} \right]. \quad (6.4)$$

We point out that the local electric field is in general different from the total macroscopic field \vec{E} (see chapter 4). The macroscopic field \vec{E} is an average over a microscopically large (but macroscopically small) region of space, whereas the local field is the true microscopic field at the molecule. Eq. (6.1) together with Eq. (6.2) constitute a self consistency equation for the induced dipole moments $\{\vec{p}_j\}_{j=1}^N$ in the system. We notice that the two entities appearing in the description of the interaction between electromagnetic fields and molecular aggregates are the polarizability of each molecule (see previous chapter) as well as the dipole coupling tensor [41, 47]. The approach given here is semiclassical; it combines classical expressions for the dipolar field with the molecular polarizabilities (which are quantum mechanical entities). In paper I we derive Eqs. (6.1) and (6.2) using a quantum mechanical scheme. The classical entity \vec{p}_j is then replaced by the corresponding quantum mechanical expectation value and the expression for the polarizability comes out naturally from the analysis and does not have to be taken from a separate calculation.

For the case when all molecules in the aggregate are identical Eq. (6.1) can be formally solved. We introduce a unitary matrix, U_{il} , that diagonalizes the dipole-dipole coupling ($\tilde{\kappa}_{jk}$), *i.e.*, U satisfies

$$\sum_{j,k} U_{pj}^{-1} \tilde{\kappa}_{jk} U_{kl} = \bar{\kappa}_l \delta_{pl}. \quad (6.5)$$

The columns of U are, by standard linear algebra, the eigenvectors of the matrix $\tilde{\kappa}_{jk}|_{j \neq k}$, $\tilde{\kappa}_{jj} = 0$. Applying this transformation to Eqs. (6.1) and (6.2) and assuming a scalar polarizability for all molecules (taken to be identical) we get $\bar{p}_l = \bar{E}_{0,l}/[(4\pi\epsilon_0\alpha)^{-1} - \bar{\kappa}_l]$ where $\bar{p}_l = \sum_j U_{lj}^{-1} p_j$ and $\bar{E}_{0,l} = \sum_j U_{lj}^{-1} E_{0,j}$. The extinction cross section, Eq. (4.7), can be written in terms of the U -matrix according to

$$\sigma(\omega) = \frac{k}{|E_0|^2 \epsilon_0} \text{Im} \sum_{l,i} U_{il} \bar{p}_l E_{0,i}^* = \frac{k}{\epsilon_0} \text{Im} \sum_l \frac{f_l}{(4\pi\epsilon_0\alpha)^{-1} - \bar{\kappa}_l}, \quad (6.6)$$

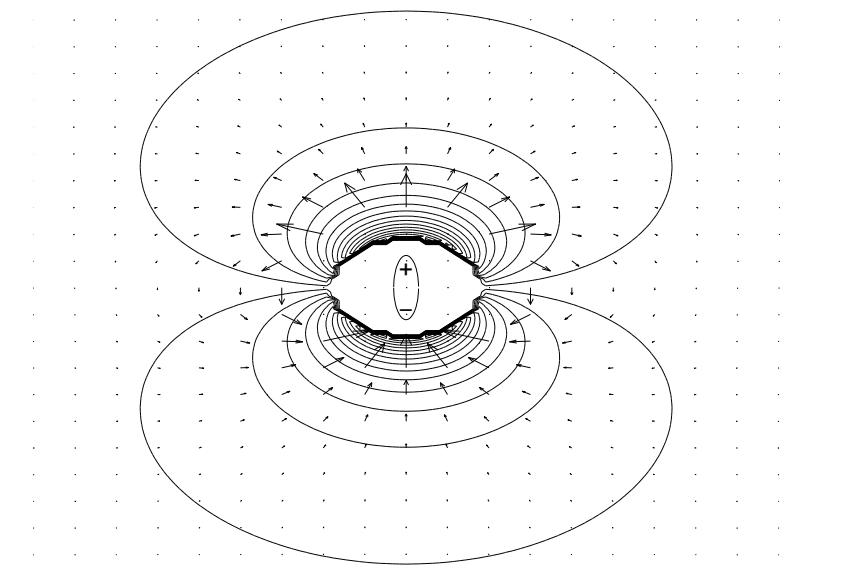


Figure 6.1: Equipotential lines and electric field distribution around a dipole. A molecule placed near this dipole “feels” a local field consisting of both the external as well as the dipole field.

where we have assumed that the wavelength is much larger than the aggregate so that we can assume $E_{0,i} = E_{0,j}$. We have also defined $f_l \equiv |\sum_i U_{il}|^2$, where f_l satisfies the sum rule: $\sum_l f_l = N$. If we now insert the expression for the polarizability, Eq. (5.6) for a two-level molecule, we obtain

$$\sigma(\omega) = 4\pi k \operatorname{Im} \sum_l f_l \frac{\alpha_0 \omega_{10}^2}{\omega_l^2 - \omega^2 - i\omega L} = \frac{\pi d^2}{\epsilon_0 \hbar c} \sum_l f_l \omega_{10} \delta(\omega \pm \omega_l), \quad (6.7)$$

where d is the transition dipole moment of each molecule and the normal mode energies are

$$\hbar\omega_l \equiv \hbar\omega_{10}(1 - \alpha_0 \bar{\kappa}_l)^{1/2}. \quad (6.8)$$

We have assumed the damping, L , to be “small” ($L \rightarrow 0^+$) above. The extinction cross section is a sum of delta functions located at frequencies ω_l given by Eq. (6.8). The strength of a peak l is determined by the oscillator strength, $d^2 f_l$.

For many problems there is no analytical solution available. One then has to solve the above equations numerically. Let us discuss two numerical codes which are available free of charge. Both of these codes can be downloaded from the webpage <http://atol.ucsd.edu/~pflatau/>. *MarCoDES* is a numerical FORTRAN package developed by V.A. Markel, New Mexico State University. It is designed to solve coupled dipole equation for arbitrary clusters of point dipoles. The numerical cost of the algorithm used scales as N^3 , where N is the number of monomers in the aggregate. *DDSCAT* is a FORTRAN package designed to solve the same equation as MarCoDES. It is created by B.T. Draine, Princeton University Observatory and P.J. Flatau, University of California. It uses Fast Fourier Transform (FFT) algorithms

to solve the dipole equation. This method scales as $N \ln N$, *i.e.*, it is much more efficient for large systems than MarCoDES. The drawback of the FFT technique is that it requires a square lattice on which the molecules are placed.

By using the formal expression Eq. (6.7) we see that ($\sum_l f_l = N$) the extinction cross section satisfies

$$\int \sigma(\omega) d\omega = N \int \sigma(\omega)|_{\text{single mol.}} d\omega. \quad (6.9)$$

i.e., the integral of the extinction, $\sigma(\omega)$, over all frequencies gives a constant independent on the state of aggregation - it satisfies a sum rule. The induced Coulomb coupling between the constituting molecules cannot change the total absorption, only change how the absorbed energy is divided onto different absorption bands - redistribution of spectral strength. N is the number of molecules as before. The integrated extinction for a single molecule is discussed in appendix D. If the vibrational coupling is neglected the above expression takes the simple form [using the sum rule for a molecule with n electrons, Eq. (D.6)]

$$\int \sigma(\omega) d\omega = \frac{\pi n Ne^2}{mc\epsilon_0}. \quad (6.10)$$

m and e are the mass and charge of the electron respectively. Note the integrated extinction is proportional to the total number of electrons in the system, nN . The above sum rules are useful for testing the validity of numerical results for the extinction cross section.

We have in this chapter given the relevant equations [see Eqs. (6.1) and (6.2)] for the electric response of a molecular aggregate. The important entities appearing in these equations are the polarizabilities for the constituting molecules as well as the dipole coupling tensor. The results obtained here provides a background to paper I (general molecular response using a quantum mechanical approach) and paper V (response of an ellipsoidal cell membrane).

CHAPTER 7

Electromagnetic response of electrolytes

In this chapter we derive an expression for the low frequency dielectric function of an electrolyte consisting of two types of ions by using the diffusion equation. We also discuss the dielectric function at higher frequencies. The result for the zero frequency dielectric function obtained in this chapter is related to paper II, in which electrostatically driven polymer motion through an electrolyte is investigated. The high frequency dielectric function enters the results obtained in paper V (electric response of ellipsoidal cells at high frequencies).

Consider a solution of two types of particles (type 1 and 2 respectively) with charge q_j ($j = 1, 2$) and friction constant ξ_j immersed in a solvent. For the case of low Reynolds number the probability $P_j(\vec{x}, t)$ of finding a particle of type j at position \vec{x} at time t is given by the Smoluchowski equation, Eq. (2.5), provided that the solution is "sufficiently" dilute. The force appearing in the Smoluchowski equation in general has several contributions; the force from the external field, the Coulomb force from the electric field from the other ions in the system, hydrodynamic forces etc. We recall (see chapter 4) that in order to determine the dielectric function we must obtain the induced *charge* density ρ^{ind} . The *density* $n_j(\vec{x}, t)$ of particles of type j is simply obtained by multiplying the probability of finding a particle of type j at position \vec{x} at time t , $P_j(\vec{x}, t)$, by the equilibrium density n_j^0 , *i.e.*,

$$n_j(\vec{x}, t) = n_j^0 P_j(\vec{x}, t), \quad (7.1)$$

where $n_j^0 = N_j/V$ and N_j is the total number of particles of type j and V is the volume of the system. The total density is $n = n_1 + n_2$. We require charge neutrality $q_1 n_1^0 + q_2 n_2^0 = 0$, *i.e.*, that the equilibrium charge density is zero. Combining Eq. (7.1) with the Smoluchowski equation, Eq. (2.5), we obtain the *diffusion* equation

for n_j :

$$\frac{\partial n_j(\vec{x}, t)}{\partial t} = \frac{1}{\xi_j} \vec{\nabla} [k_B T \vec{\nabla} n_j(\vec{x}, t) - q_j \vec{E}_{\text{loc}}(\vec{x}, t) n_j(\vec{x}, t)], \quad (7.2)$$

where we have used the fact that the electric force on a charged particle is $q_j \vec{E}_{\text{loc}}$, where \vec{E}_{loc} is the local field at the particle (including both the external as well as the Coulomb field from the other ions). We have above neglected hydrodynamic forces between the particles. We now proceed by writing

$$n_j(\vec{x}, t) = n_j^0 + \bar{n}_j(\vec{x}, t), \quad (7.3)$$

where the induced density $\bar{n}_j(\vec{x}, t)$ is caused by the presence of the external field. For the case that the external field is weak we expect $\bar{n}_j(\vec{x}, t) \ll n_j^0$. Then the diffusion equation Eq. (7.2) becomes, to first order in the electric field,

$$\frac{\partial \bar{n}_j(\vec{x}, t)}{\partial t} = \frac{1}{\xi_j} \vec{\nabla} [k_B T \vec{\nabla} \bar{n}_j(\vec{x}, t) - q_j \vec{E}(\vec{x}, t) n_j^0], \quad (7.4)$$

where we have used a *random phase approximation* [28] and replaced $\vec{E}_{\text{loc}}(\vec{x}, t) \approx \vec{E}(\vec{x}, t)$ i.e., we have replaced the local field by the total macroscopic field. The macroscopic field \vec{E} is an average over a microscopically large but macroscopically small region of space. For the situation that we have freely moving particles which we discuss here one may argue that the electric field is sufficiently “smoothed out” to allow such an approximation [28]. However for the case of a molecular aggregate where the position of the constituting molecules are fixed (as discussed in the previous section) the local and total electric field are in general not the same. Let us now proceed by introducing the Fourier transform $A(\vec{x}, t) = (1/2\pi)^4 \int d^3 q \int d\omega \exp[i(\vec{k} \cdot \vec{x} - \omega t)] A(\vec{k}, \omega)$ of all quantities. Eq. (7.4) can then be solved for $\bar{n}_j(\vec{k}, \omega)$ according to

$$\bar{n}_j(\vec{k}, \omega) = -i \frac{q_j n_j^0 D_j}{k_B T} \frac{1}{-i\omega + D_j k^2} \vec{k} \cdot \vec{E}, \quad (7.5)$$

where we have introduced the diffusion constant of ions of type j according to $D_j = k_B T / \xi_j$. Let us now proceed to identify a dielectric function for the electrolyte. By combining Eqs. (4.3) and (4.10) we find

$$\vec{k} \cdot \vec{D}(\vec{k}, \omega) = \epsilon_0 \vec{k} \cdot \vec{E}(\vec{k}, \omega) + i \rho^{\text{ind}}(\vec{k}, \omega), \quad (7.6)$$

where we have used the fact that ρ^{ind} is related to the polarization vector according to $\rho^{\text{ind}} = -i \vec{k} \cdot \vec{P}$ [see Eq. (4.3)]. Furthermore using the fact that $\rho^{\text{ind}} = q_1 \bar{n}_1 + q_2 \bar{n}_2$ and inserting the explicit expression, Eq. (7.5), for the induced density we obtain $\vec{k} \cdot \vec{D}(\vec{k}, \omega) = \epsilon(k, \omega) \vec{k} \cdot \vec{E}(\vec{k}, \omega)$, where the dielectric function is [see Eq. (4.11)]

$$\epsilon(k, \omega) = \epsilon_0 \epsilon_m [1 + \sum_j \frac{q_j^2 n_j^0 D_j}{\epsilon_0 \epsilon_m k_B T} \frac{1}{-i\omega + D_j k^2}], \quad (7.7)$$

which depends on frequency, temperature and wavevector. The particle parameters entering the dielectric function is the charge q_j as well as the density n_j . The diffusion constant D_j (or the friction constant ξ_j), which also enters into the dielectric function depend on both solvent (through the viscosity) and ion properties (the hydrodynamic “effective radius” of the ion). We have also in the final expression for the dielectric function, Eq. (7.7), introduced the dielectric response of the solvent molecules; we assume that the only role the solvent molecules have in the electric response is to screen the local field through the solvent relative dielectric constant ϵ_m (we thus make the replacement $\epsilon_0 \rightarrow \epsilon_0 \epsilon_m$). We recall that we have employed the Smoluchowski equation in order to obtain the above expression for the dielectric function of an electrolyte, *i.e.*, neglected inertia. We furthermore point out that we have neglected hydrodynamic couplings to obtain the above dielectric function as well as made a random phase approximation.

Let us proceed to investigate some limits. We first study the zero frequency limit $\omega \rightarrow 0$, but retain a finite wavevector. The dielectric function then becomes

$$\epsilon(k) = \epsilon_0 \epsilon_m \left(1 + \frac{k_D^2}{k^2}\right), \quad (7.8)$$

where we have introduced the Debye screening wavevector

$$k_D = \left(\sum_j \frac{q_j^2 n_j^0}{\epsilon_0 \epsilon_m k_B T}\right)^{1/2}. \quad (7.9)$$

We point out that Eq. (7.8) has the same form as the Thomas-Fermi static dielectric function for metals [48]. Let us consider the physical significance of the Debye wavevector by introducing a test point charge with charge Ze into our electrolyte. The external potential (*i.e.*, potential in the absence of any electrolyte) around the test charge is $\Phi_{\text{ext}}(r) = Ze/4\pi\epsilon_0 r$. In Fourier space we have $\Phi(k) = Ze/\epsilon_0 k^2$. The screened potential in the electrolyte is then $\Phi(k) = Ze/\epsilon(k)k^2 = Ze/\epsilon_0 \epsilon_m (k^2 + k_D^2)$ or in real space

$$\Phi(r) = \frac{Ze}{4\pi\epsilon_0 \epsilon_m r} e^{-r/l_D}, \quad (7.10)$$

where we have introduced the Debye screening length $l_D = 1/k_D$. We see that the potential vanishes for distances larger than the Debye screening length away from the test charge, *i.e.*, the test charge is screened over distance larger than l_D by the mobile ions. The relative dielectric constant of water is ~ 80 . At room temperature one then typically finds that the Debye screening length is $\sim 1 - 10$ nm for 0.001-0.1 M solutions [49]. The zero frequency dielectric function Eq. (7.8) can be obtained in a different way: By combining the first of Maxwell’s equations in Eq. (4.8) with Eq. (4.12) we get the Poisson equation $\nabla^2 \Phi = -\rho/\epsilon_0$. The total charge density ρ has one induced and one external component according to Eq. (4.2). The induced charge density is as before $\rho^{\text{ind}} = \sum_j q_j \bar{n}_j(\vec{x}, t)$. Since we assume no time dependence (zero frequency) the induced density is simply given by its equilibrium result, *i.e.*,

$$\bar{n}_j(\vec{x}, t) = n_j^0 (e^{-\beta q_j \Phi} - 1) \approx -n_j^0 \beta q_j \Phi, \quad (7.11)$$

where we have assumed that the thermal energy $k_B T$ is larger than the potential energy $q_j \Phi$ for a particle in the electrolyte in order to make a linear approximation. Inserting this result into the expression for the induced charge density and using the charge neutrality condition, the Poisson equation becomes $\epsilon_0 \epsilon_m (\nabla^2 \Phi - k_D^2 \Phi) = 0$, where we have made the replacement $\epsilon_0 \rightarrow \epsilon_0 \epsilon_m$ to account for the solvent and assumed that $\rho^{\text{ext}} = 0$. Taking the Fourier transform of this equation and comparing to the Fourier transform of Eq. (4.13) the dielectric function is identified as the same one as given by Eq. (7.8). In this derivation of the dielectric function we made a linear approximation in Eq. (7.11). If the potential energy is not small compared to the thermal energy such an approximation is not justified and one has to retain the exponential in Eq. (7.11). The corresponding non-linear equation for the potential is called the Poisson-Boltzmann equation [50, 13].

Let us investigate the limit of zero wavevector $\vec{k} \rightarrow 0$. Eq. (7.7) then becomes

$$\epsilon(\omega) = \epsilon_0 \epsilon_m + \frac{i\sigma^0}{\omega}, \quad (7.12)$$

where $\sigma^0 = \sum_j q_j^2 n_j^0 D_j / k_B T$ is the static conductivity of the electrolyte [51]. We see that at zero frequency we have $\epsilon \rightarrow \infty$. This behaviour has the effect that for instance the field inside a cell is “perfectly” screened (see the solution of Laplace equation for an ellipsoidal particle in section 4.2). One can similarly solve Laplace equation for a flat dielectric membrane surrounded by electrolytes on either side, with a static external field along the membrane normal using the dielectric function above. Since $\epsilon \rightarrow \infty$ there is no electric field in the electrolyte but the potential drop occurs only across the membrane (in a more detailed study one must take $\vec{k} \neq 0$). One then finds that the potential (at $\omega = 0$) extends a distance $\sim l_D$ out from the surface [50]). These results are important for paper II, where electrostatically driven charged polymer motion through a nanopore in a membrane is studied.

Strictly speaking the results obtained so far are only valid at “infinitely” diluted electrolytes. At larger concentrations one must be careful to include hydrodynamic couplings, as well as the local field. The result of such an investigation gives that the static conductivity σ_0 in Eq. (7.12) is replaced by the conductivity [49, 51, 52, 53]:

$$\sigma(\omega) = \sigma^0 (1 - \Lambda_E k_D - \Lambda_R k_D) \quad (7.13)$$

where Λ_E and Λ_R are positive constants (with dimension of length) which are independent of the concentration. The first correction term to the conductivity is the so called *electrophoretic* correction and has the following physical origin: The motion of an ion causes motion of its screening cloud, which in turn induces a motion of the solvent. This solvent motion is felt by the ion. The electrophoretic correction is thus of hydrodynamical origin [51]. For the case that the ions have identical friction constants, which can be written using Stoke’s law [see Eq. (2.18)] $\xi = 6\pi\eta R$ where R is the “radius” of ions we have $\Lambda_E \approx R$ [49]. The importance of the electrophoretic correction is thus determined by the ratio between the radius of the particle and the Debye screening length, R/l_D . The second correction is the so called *relaxation* correction: The motion of the ion changes the charge distribution of the screening cloud,

which in turn cause an additional field (local field correction) on the ion. For the case that the ions have identical friction constants and identical but opposite charges, we have $\Delta_R \sim q^2/(\epsilon_0 \epsilon_m k_B T) \sim k_D^2/n$, where $n = n_1 = n_2$ [49]. The significance of the relaxation correction is thus determined by the ratio between the inverse concentration and the Debye screening volume, $1/(nl_D^3)$. The relaxation correction has a low frequency dispersion as a result of screening cloud relaxation (the so called *Debye-Falkenhagen effect*) [52]. Explicitly the characteristic time scale of relaxation for the screening cloud is $\tau \sim l_D^2/D$ where D is the diffusion constant of the ions (assumed equal for all ionic species) [53]. Using $D \sim 10^{-5} \text{ cm}^2/\text{s}$ and $l_D \sim 10 \text{ nm}$ [49] we find $\tau \sim 10^{-7} \text{ s}$, which corresponds to frequencies $\omega \sim 10^7 \text{ Hz}$ [53]. It is interesting to note that both the corrections to conductivity are proportional to the Debye screening wavevector, *i.e.*, to the square root of the concentration. Furthermore both corrections are negative, which has the effect that the specific conductivity (conductivity divided by the molar concentration) is decreased as the concentration of ions is increased. One typically finds that $(\sigma^0 - \sigma)/\sigma^0$ vary between 0.05 and 0.50 for 0.001-0.10 M solutions [49].

Let us finally discuss the dielectric function at higher frequencies. We recall that the implicit approximation used for obtaining Eq. (7.7) is that we neglect particle inertia, which corresponds to the assumption that we do not study processes occurring on a time scale smaller than $\tau_p = m/\xi$, where m is the mass of the particle, which corresponds frequencies above $\omega_p = 1/\tau_p$. The mass of an ion (such as potassium or chloride ion) is $\sim 10^{-25} \text{ kg}$, whereas its diffusion constant is $D \sim 10^{-5} \text{ cm}^2/\text{s}$ [54] leading to $\omega_p = 10^{13} \text{ Hz}$ [52, 55]. As long as we stay below this frequency we are justified (as we have done so far) in neglecting inertia effects. One must also in general include relaxation effects of the solvent, *i.e.*, frequency dependent of the friction constant. As we saw in section 2.2 this frequency dispersion occurs at frequencies $\omega_f = 1/\tau_f$, where the relaxation time is $\tau_f = m_f/\xi$ and m_f is the displaced fluid mass. This relaxation time is hence of the same order of magnitude as the particle relaxation time τ_p . Another complication in the study of high-frequency response of an electrolyte is that the solvent usually consists of water molecules (which are dipolar) and therefore dipolar relaxation effects introduce a frequency dispersion in the dielectric function. Experimentally one finds that this dispersion occurs at frequencies $\omega \sim 10^{11} - 10^{12} \text{ Hz}$ [54]. At higher frequencies the dielectric function of water is described by a (real and frequency independent) relative dielectric constant $\epsilon_\infty \sim 5$ [54]. This result is important for the discussion of the high frequency response (at optical frequencies $\omega \sim 10^{15} \text{ Hz}$) of an ellipsoidal cell in paper V. The cell (vesicle) interior and the surroundings are there assumed to have real frequency independent dielectric functions and that therefore the only frequency dependence comes from the membrane molecular polarizabilities.

We have in this chapter investigated the electric and electromagnetic response of an electrolyte. For dilute electrolytes and low frequencies the result is given in Eq. (7.7). In particular we have introduced the Debye screening length (the length over which a test charge is screened out in an electrolyte) which is an important entity for

electrolytes. The results obtained here give a background to papers II and V.

CHAPTER 8

Summary and outlook

In this thesis the interaction between electric, magnetic and electromagnetic fields and living matter, taking as our starting point the cell, is investigated. The cell and its constituents prove to be an interesting physical system, requiring concepts and methods from diverse fields of physics [56]. We have here encountered physical problems such as fluid mechanics, polymer and membrane (soft matter) physics. Furthermore the electric and electromagnetic response of molecules, molecular aggregates (such as the cell membrane of the photosynthetic unit) and electrolytes has been discussed.

The five research papers included in this thesis are studies related to electromagnetic field interaction with living matter: Paper I provides a theory for the electromagnetic response of a molecular aggregate. In particular it describes how the induced dipole coupling between the molecules in the aggregate gives rise to collective resonances. The frequency distribution of these resonances depend on the geometric arrangement of the constituent molecules, and the results in paper I can therefore be used by experimentalist in order to obtain the shape of their investigated system. In artificial photosynthesis the aim is to mimic Nature's way of using specially designed aggregates for harvesting sunlight; the insights provided in paper I could help in the proper design of such artificial photosynthetic aggregates. Paper II deals with the passage of charged polymers, in an electrolyte, driven by a static applied voltage through a nanopore in a cell membrane. We find that the flux (number of polymers passing through the pore per unit time) has a threshold voltage. Above this threshold the flux depends exponentially on applied voltage. Polymer transport through nanopores occur in many biological processes including DNA transfer from a virus to a host cell. The understanding of such processes (and how to prevent them) are thus of importance in biology and medicine. Translocation of polymers (such as DNA or proteins) through nanopores could also find technological applications such as sequence determination of DNA or analyte detection. Paper III investigates the drift velocity of particles in a viscous liquid under the influence of an electromag-

netic field intensity gradient. At off-resonant frequencies the drift velocity is found to be proportional to the squared length of the principal axis along the direction of motion (size). Near a resonance frequency the drift velocity is sensitive to the shape of the particle. The techniques discussed in this paper could find applications such as the characterization or separation of solutions consisting of particles (for instance cells or antibodies) of different shapes or sizes. Paper IV gives the solution of Gauss equation for an ellipsoid with an anisotropic coating (the coating dielectric function being different parallel and perpendicular to the coating normal). In the general case the solutions of this equation can be written in terms of solutions to Heun's equation. For the case of spheroids the solutions are given using hypergeometric functions. Many particles belong to the class of ellipsoidal particles with anisotropic coatings. Particularly interesting examples include cells and fullerenes, for which the results of paper IV can be used for understanding the electric, magnetic and electromagnetic response properties. Paper V, which describes the interaction of electromagnetic fields and ellipsoidally shaped cell membranes, connects paper I and IV. If the constituent membrane molecules has one prominent resonance frequency then the dipole coupled membrane has two new resonance frequencies. The geometric weight for the oscillator strengths of the resonances are sensitive to shape, which allows for experimental determination of cell shapes (for instance using the separation techniques described in paper III). The electromagnetic response of cell-like structures is currently a hot topic. Knowledge coming from this field of science will have a large potential impact on future human friendly design of for instance mobile phones; a recent survey of problems related to interactions between radiofrequent fields (like the ones mobile phones produce) with biological systems can be found in [57].

Let us finally comment on the role of physics in biology. It is nowadays not uncommon to take the view that the genetic code contains all relevant information about a living being. One then forgets, however, that physical laws were present long before the first organisms, and that Nature and evolution therefore has to play by the laws of physics - a bird cannot turn off gravity, a bacteria can move only at low Reynolds numbers, proteins rely on physical forces for obtaining its three dimensional structure etc. Understanding the properties of living matter thus requires not only the genetic code, but also the physical forces which determines the rules which constrain the genetic code. At relevant cellular length scales ($\sim 10^{-10} - 10^{-5}$ m) the electromagnetic force is in general the most important one of the four forces of Nature. This thesis provides concepts and results relevant for the electromagnetic response of living matter and it is the hope that physicists who want to pursue research in this important and interesting field of physics find the thesis useful.

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APPENDIX A

Ellipsoidal coordinates and elliptic integrals

In this appendix we give the definition of ellipsoidal coordinates and other entities useful for problems of ellipsoidal symmetry.

The ellipsoidal coordinates, $(p=\xi, \eta, \zeta)$, are given by the roots to the cubic equation [32]

$$\frac{x^2}{a_x^2 + p} + \frac{y^2}{a_y^2 + p} + \frac{z^2}{a_z^2 + p} = 1. \quad (\text{A.1})$$

For $a_x \geq a_y \geq a_z$, the range of the ellipsoidal coordinates are: $\xi \geq -a_z^2$, $-a_z^2 \geq \eta \geq -a_y^2$ and $-a_y^2 \geq \zeta \geq -a_x^2$. Solving the above equation we obtain the Cartesian coordinates according to

$$\begin{aligned} x &= \pm \left[\frac{(\xi + a_x^2)(\eta + a_x^2)(\zeta + a_x^2)}{(a_y^2 - a_x^2)(a_z^2 - a_x^2)} \right]^{1/2}, \\ y &= \pm \left[\frac{(\xi + a_y^2)(\eta + a_y^2)(\zeta + a_y^2)}{(a_z^2 - a_y^2)(a_x^2 - a_y^2)} \right]^{1/2}, \\ z &= \pm \left[\frac{(\xi + a_z^2)(\eta + a_z^2)(\zeta + a_z^2)}{(a_x^2 - a_z^2)(a_y^2 - a_z^2)} \right]^{1/2}. \end{aligned} \quad (\text{A.2})$$

Laplace's equation in ellipsoidal coordinates is [32]:

$$\begin{aligned} \nabla^2 \Phi &= \frac{4}{(\xi - \eta)(\zeta - \xi)(\eta - \zeta)} \left[(\eta - \zeta)R(\xi) \frac{\partial}{\partial \xi} (R(\xi) \frac{\partial \Phi}{\partial \xi}) \right. \\ &\quad \left. + (\zeta - \xi)R(\eta) \frac{\partial}{\partial \eta} (R(\eta) \frac{\partial \Phi}{\partial \eta}) + (\xi - \eta)R(\zeta) \frac{\partial}{\partial \zeta} (R(\zeta) \frac{\partial \Phi}{\partial \zeta}) \right] = 0, \quad (\text{A.3}) \end{aligned}$$

where

$$R(p) = [(a_x^2 + p)(a_y^2 + p)(a_z^2 + p)]^{1/2}. \quad (\text{A.4})$$

Let us now define

$$\Omega(\xi) \equiv \pi a_x a_y a_z \int_{\xi}^{\infty} \frac{d\xi'}{R(\xi')} \left(\frac{x^2}{a_x^2 + \xi'} + \frac{y^2}{a_y^2 + \xi'} + \frac{z^2}{a_z^2 + \xi'} - 1 \right) \quad (\text{A.5})$$

and

$$\chi(\xi) \equiv a_x a_y a_z \int_{\xi}^{\infty} \frac{d\xi'}{R(\xi')}, \quad (\text{A.6})$$

where ξ is the positive square root of Eq. (A.1) as before. Both χ and Ω satisfy

$$\begin{aligned} \nabla^2 \Omega &= 0, \\ \nabla^2 \chi &= 0, \end{aligned} \quad (\text{A.7})$$

i.e., they are solution of Laplace's equation. Let us also introduce the elliptic integrals of the second kind ($v = x, y$ or z)

$$\gamma_v(\xi) \equiv a_x a_y a_z \int_{\xi}^{\infty} \frac{d\xi'}{(a_v^2 + \xi') R(\xi')}. \quad (\text{A.8})$$

γ_v satisfies the equations [14]

$$\nabla^2 \gamma_v + \frac{2}{v} \frac{\partial \gamma_v}{\partial v} = 0, \quad (\text{A.9})$$

where $v = x, y$ or z as before. We also derive expression for the derivatives of Ω . We find (notice that ξ depends on x)

$$\frac{\partial \Omega}{\partial x} = 2\pi \gamma_x x - \pi a_x a_y a_z \left(\frac{x^2}{a_x^2 + \xi} + \frac{y^2}{a_y^2 + \xi} + \frac{z^2}{a_z^2 + \xi} - 1 \right) \frac{1}{R(\xi)} \frac{d\xi}{dx} = 2\pi \gamma_x x, \quad (\text{A.10})$$

where we have used Eq. (A.1). In an identical fashion we obtain

$$\begin{aligned} \frac{\partial \Omega}{\partial y} &= 2\pi \gamma_y y, \\ \frac{\partial \Omega}{\partial z} &= 2\pi \gamma_z z. \end{aligned} \quad (\text{A.11})$$

We now define

$$Q \equiv \chi(\xi = 0)/2 = \frac{a_x a_y a_z}{2} \int_0^{\infty} \frac{d\xi'}{R(\xi')}, \quad (\text{A.12})$$

and the so called *depolarization factors*

$$n_v \equiv \gamma_v(\xi = 0)/2 = \frac{a_x a_y a_z}{2} \int_0^{\infty} \frac{d\xi'}{(a_v^2 + \xi') R(\xi')}. \quad (\text{A.13})$$

It is straightforward to show that the depolarization factors satisfy the sum rule:

$$n_x + n_y + n_z = 1. \quad (\text{A.14})$$

From this sum rule we directly obtain (by symmetry) the depolarization factors for a sphere: $n_x = n_y = n_z = 1/3$. It also follows from the definitions of the depolarization factors that

$$n_x < n_y < n_z \quad \text{if } a_x > a_y > a_z, \quad (\text{A.15})$$

i.e., the depolarization factor is smallest (largest) for the largest (shortest) axis.

APPENDIX B

Differential geometry

This appendix is an attempt to develop the necessary mathematical theory of curved surfaces in three dimensional space. The apparatus for dealing with curved surfaces is differential geometry and topology.

Consider a curve in three dimensional Euclidean space. A curve is fully characterized by one parameter, t , such as $t \rightarrow (x(t), y(t), z(t))$. In specifying a surface we need *two* parameters, u and v , to fully describe it

$$u, v \rightarrow \vec{x}(u, v) = (x(u, v), y(u, v), z(u, v)). \quad (\text{B.1})$$

We also require that the dependence on the parameters should be smooth. A surface is thus completely specified in a region of three dimensional Euclidean space by *two* parameters. We therefore expect that it is possible to treat any surface as a “two dimensional entity” without any reference to three dimensional space. It is the aim of this section to develop the mathematical tool (differential geometry) that allow such a treatment. In particular we describe the first and second fundamental forms which allow a complete description of the surface.

Let us consider the tangent plane at some point p , see Fig. B.1. The vectors $\partial\vec{x}/\partial u$ and $\partial\vec{x}/\partial v$ are parallel to the surface and hence span the tangent plane. The basis $\{\partial\vec{x}/\partial u, \partial\vec{x}/\partial v\}$ is called the *coordinate basis* in the neighbourhood of p . Many entities of interest involve the local tangent plane. For instance consider the element of length, ds^2 , in three dimensional Euclidean space:

$$ds^2 = d\vec{x} \cdot d\vec{x} = dx^2 + dy^2 + dz^2, \quad (\text{B.2})$$

where a dot denotes scalar multiplication. From the parametrization, Eq. (B.1), of a surface we see that (using the chain rule: $d\vec{x} = (\partial\vec{x}/\partial u)du + (\partial\vec{x}/\partial v)dv$ - expanding in the coordinate basis) the element of length between two infinitesimally close points is ($u^1 = u$ and $u^2 = v$)

$$ds^2 = \sum_{i,j} g_{ij} du^i du^j, \quad (\text{B.3})$$

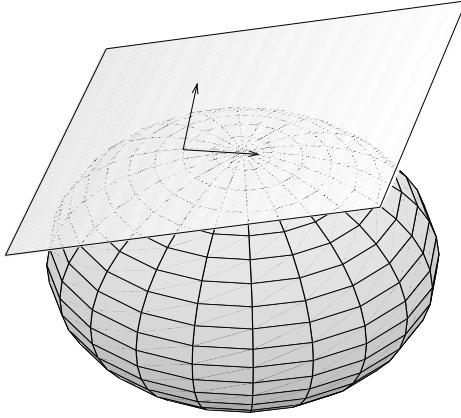


Figure B.1: The tangent plane at a point p on a sphere. The arrows indicate the tangent vectors $\partial\vec{x}/\partial u$ and $\partial\vec{x}/\partial v$.

where

$$g_{ij} = \frac{\partial\vec{x}}{\partial u^i} \cdot \frac{\partial\vec{x}}{\partial u^j}. \quad (\text{B.4})$$

Eq. (B.3) is called the *first fundamental form* and expresses the element of length in terms of u and v . The 2×2 tensor g_{ij} is called the metric tensor (note that g_{ij} is symmetric, *i.e.*, $g_{12} = g_{21}$). For the case of a *plane* surface with its normal parallel to the z-axis the length element is $ds^2 = dx^2 + dy^2$ and hence the metric tensor is

$$g_{ij} \equiv \eta_{ij} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (\text{B.5})$$

The above tensor is called the *flat* metric tensor. The inverse of the metric tensor is denoted g^{ij} and is hence a tensor that satisfies

$$\sum_j g^{ij} g_{jk} = \delta_k^i, \quad (\text{B.6})$$

where δ_k^i is the Kronecker delta. As an example consider the element of length for a cylindrical surface (in cylindrical coordinates): $ds^2 = dz^2 + \rho^2 d\phi^2$, where ρ (=constant) is the radius of the cylinder and ϕ is the angle of rotation around the z-axis. By simply making the reparametrization $z \rightarrow z, \rho\phi \rightarrow t$ the element of length becomes $ds^2 = dz^2 + dt^2$ and hence the metric tensor in this parametrization is simply the same as for a flat surface η_{ij} . We notice that the first fundamental form therefore does not completely characterize a surface. Two surfaces for which it is possible to find parametrizations such that their first fundamental forms are the same are said to be *isometric*. The cylinder is hence isometric to the plane (the cylinder can be “unrolled” into a plane).

The first fundamental form contains all necessary information for calculating metric properties such as arc length or area (but does not fully characterize the surface). Let us calculate the area element dS : the area of a small parallelogram on S is

given by $|\partial\vec{x}/\partial u \times \partial\vec{x}/\partial v|$. Using the mathematical identity

$$|\frac{\partial\vec{x}}{\partial u} \times \frac{\partial\vec{x}}{\partial v}|^2 + (\frac{\partial\vec{x}}{\partial u} \cdot \frac{\partial\vec{x}}{\partial v})^2 = |\frac{\partial\vec{x}}{\partial u}|^2 |\frac{\partial\vec{x}}{\partial v}|^2, \quad (\text{B.7})$$

we find the area element

$$dS \equiv |\frac{\partial\vec{x}}{\partial u} \times \frac{\partial\vec{x}}{\partial v}| dudv = \sqrt{g_{11}g_{22} - g_{12}^2} dudv = \sqrt{g} dudv, \quad (\text{B.8})$$

where $g \equiv \det g_{ij}$. The area element is hence given by the square root of the determinant of the metric tensor.

As we saw in the example with the cylinder the first fundamental form does not completely characterize a surface. To do this we must go beyond metric properties of the surface and look into also the *curvature* of the surface. Let $\vec{x}(u, v)$ be a parametrization of the surface in the neighbourhood of a point p . The distance from a point $q = \vec{x}(u, v)$ to the tangent plane at $p = \vec{x}(0, 0)$ is (see Fig. B.2)

$$s = [\vec{x}(u, v) - \vec{x}(0, 0)] \cdot \hat{N}(p), \quad (\text{B.9})$$

where $\hat{N}(p)$ is the normal to the tangent plane at p :

$$\hat{N} = (\frac{\partial\vec{x}}{\partial u} \times \frac{\partial\vec{x}}{\partial v}) / |\frac{\partial\vec{x}}{\partial u} \times \frac{\partial\vec{x}}{\partial v}|. \quad (\text{B.10})$$

Let us now Taylor expand around p according to:

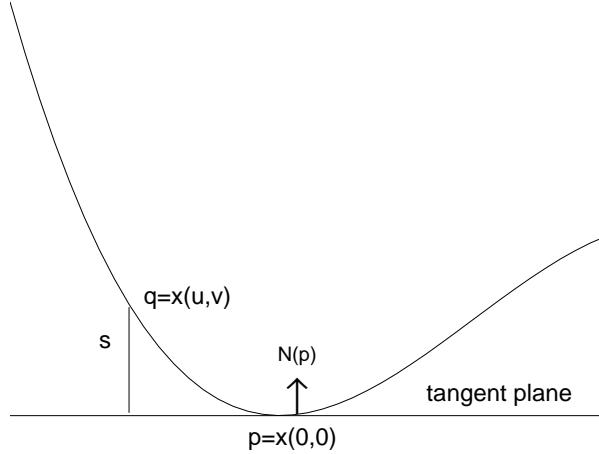


Figure B.2: A cut through a surface along the normal.

$$\vec{x}(u, v) = \vec{x}(0, 0) + \frac{\partial\vec{x}}{\partial u} du + \frac{\partial\vec{x}}{\partial v} dv + \frac{1}{2} [\frac{\partial^2\vec{x}}{\partial u^2} (du)^2 + 2 \frac{\partial^2\vec{x}}{\partial u \partial v} du dv + \frac{\partial^2\vec{x}}{\partial v^2} (dv)^2]. \quad (\text{B.11})$$

Inserting this expansion into Eq. (B.9) and using the fact that the vectors $\partial\vec{x}/\partial u$ and $\partial\vec{x}/\partial v$ lie in the tangent plane at p we find ($u^1 = u$ and $u^2 = v$)

$$s = \underbrace{\frac{1}{2} \sum_{i,j} h_{ij} du^i du^j}_{\Pi}, \quad (\text{B.12})$$

where

$$h_{ij} = \frac{\partial^2 \vec{x}}{\partial u^i \partial u^j} \cdot \hat{N}. \quad (\text{B.13})$$

Π is called the *second fundamental form* and measures curvature of a surface. In particular for a plane the normal distance to the tangent plane is everywhere zero and $\Pi \equiv 0$. The tensor h_{ij} is called the curvature tensor (note that h_{ij} is symmetric).

In principle there are infinitely many possible choices of basis vectors that span the tangent plane at some point p . We have so far used the coordinate basis which we introduced in connection to the first fundamental form. Let us now introduce a basis which is connected to curvature and hence the second fundamental form. The normal vector field \hat{N} introduced in Eq. (B.10) allow us to measure curvature along a curve on the surface; the normal \hat{N} along a curve on a plane is everywhere a constant, whereas for a curved surface, \hat{N} in general varies along the curve. Therefore the derivatives $\partial \hat{N}/\partial u$ and $\partial \hat{N}/\partial v$ are convenient measures of curvature since these entities yield zero for a plane. Furthermore the vectors $\partial \hat{N}/\partial u^i$ lie in the tangent plane at a point p , since from the normalization condition $\hat{N} \cdot \hat{N} = 1$ we obtain by differentiation $\hat{N} \cdot \partial \hat{N}/\partial u^i = 0$. The basis $\{\partial \hat{N}/\partial u, \partial \hat{N}/\partial v\}$ is thus an alternative basis to the coordinate basis which span the tangent space at p . Defining $h_i^j \equiv \sum_k g^{jk} h_{ik}$ it is straightforward to show that the above two bases are related according to [26]:

$$\frac{\partial \hat{N}}{\partial u^i} = - \sum_j h_i^j \frac{\partial \vec{x}}{\partial u^j}, \quad (\text{B.14})$$

i.e., related by the curvature tensor. The above relation is called the *Weingarten equations*.

Let us now proceed by introducing invariants related to curvature. The matrix h_i^j relates two different sets of local basis vectors and from elementary linear algebra we know the determinant and trace of such a matrix are invariants, i.e.,

$$K \equiv \det h_i^j = \det h_{ij} / \det g_{ij} \quad (\text{B.15})$$

and

$$H \equiv \frac{1}{2} \text{Tr} h_i^j = \frac{1}{2} \sum_i h_i^i = \frac{1}{2} \sum_{i,j} g^{ij} h_{ij} \quad (\text{B.16})$$

are invariant under a reparametrization. The entity K is called the Gaussian curvature and H is the mean curvature at the point p . Since h_i^j is a symmetric matrix it can always be diagonalized. Denote the corresponding eigenvalues (the so called *principal curvatures*) by k_1 and k_2 . We can then write the Gaussian and mean curvature according to

$$K = k_1 k_2 \quad (\text{B.17})$$

and

$$H = \frac{k_1 + k_2}{2}. \quad (\text{B.18})$$

The principal curvatures have simple geometrical interpretations: Let us imagine a curved surface, S , and let N be a plane which intersects S in such a way that the

normal in a point p is parallel to N . The intersection between N and S is then a curve. The normal curvature, k_n , in this point p is defined as the inverse radius of a circle which tangents this curve at p . k_n comes with a sign: the normal curvature is negative if the surface bends “away” from the normal of the surface and positive otherwise. Now imagine a rotation of the plane N around the normal of S at p . We get a continuous set of curves, all having a specific k_n . The principal curvatures, denoted k_1 and k_2 , are then the maximum and the minimum of this set of k_n . Note that when $K < 0$ the two curvatures k_1 and k_2 have different signs, this correspond to a saddle point. A remarkable property of the Gaussian curvature K is that, although we defined it entirely with the help of the second fundamental form, it can be shown that (Theorema Egregium) that it is entirely expressible in terms of the metric tensor (and derivatives thereof) [26]. The Gaussian curvature is therefore an intrinsic property of the two dimensional surface without reference to its embedding in three dimensional space. This observation provides the basis for Riemannian geometry [26, 58].

Topology is a way of characterizing surfaces according to which are continuously deformable into each other or not. Two surfaces, S_1 and S_2 , which are continuously deformable into each other are said to be *homeomorphic*, denoted $S_1 \simeq S_2$. For instance the surface of a cube is homeomorphic to that of a sphere. The sphere is however not homeomorphic to the torus (try to continuously deform a torus to a sphere. You will not succeed.). Topology thus describes surfaces according to which are continuously deformable into each other or not. Differential geometry, on the other hand, introduces different kind of *measures* on a surface, such as Gaussian and mean curvatures. A connection between topology and geometry is contained in *Gauss-Bonnet’s theorem* for compact surfaces, which states that the integral of the Gaussian curvature over a compact surface is a topological invariant,

$$\int_S K dS = 2\pi\chi(S). \quad (\text{B.19})$$

where $\chi(S)$ is the Euler characteristics of the surface. For a compact connected surface $\chi(S) = 2 - 2g$ where g is the number of holes in the surface. Observe that K is the Gaussian curvature and hence the LHS of Eq. (B.19) is a purely geometrical entity. The RHS is on the other hand defined within topology.

We have in this appendix shown that any quantity of interest (area, mean curvature, Gaussian curvature etc) for a surface can be obtained without “leaving” the surface; the first and second fundamental forms provide all the necessary information about the surface. We have also stated Gauss-Bonnet theorem which provides a connection between topology and differential geometry.

APPENDIX C

Molecular polarizabilities

In this appendix a general expression for the polarizability of a molecule is obtained.

Consider a molecule which, in the absence of any external fields, is characterized by a Hamiltonian H_0 and assume that H_0 has been diagonalized giving energy levels with energy E_k and eigenfunctions $\{|\Phi_k\rangle\}$. The molecular polarizability is given by Eq. (5.1), which we write:

$$\alpha^{\mu\nu}(\omega) = \frac{1}{4\pi\epsilon_0\hbar} \int_0^\infty dt e^{i\omega t} \left\{ \underbrace{\langle |\hat{d}^\mu(t)\hat{d}^\nu(0)| \rangle}_{I(t)} - \underbrace{\langle |\hat{d}^\nu(0)\hat{d}^\mu(t)| \rangle}_{II(t)} \right\}. \quad (\text{C.1})$$

Let us now evaluate $I(t)$ and $II(t)$. We have [using Eq. (5.3)]

$$\begin{aligned} I(t) &= \sum_k \rho_k \langle \Phi_k | \hat{d}^\mu(t) \hat{d}^\nu(0) | \Phi_k \rangle = \sum_{l,k} \rho_k \langle \Phi_k | e^{iH_0 t/\hbar} \hat{d}^\mu e^{-iH_0 t/\hbar} | \Phi_l \rangle \langle \Phi_l | \hat{d}^\nu | \Phi_k \rangle \\ &\quad \sum_{l,k} e^{-i\omega_{lk} t} \rho_k \langle \Phi_k | \hat{d}^\mu | \Phi_l \rangle \langle \Phi_l | \hat{d}^\nu | \Phi_k \rangle \end{aligned} \quad (\text{C.2})$$

where a parameter describing energy difference between levels: $\hbar\omega_{lk} = E_l - E_k$ has been defined and $\rho_k = \exp(-\beta E_k) / \sum_{k'} \exp(-\beta E_{k'})$ is the occupation probability of level k ($\sum_k \rho_k = 1$) in the absence of the external field. Similarly we obtain

$$II(t) = \sum_{l,k} e^{i\omega_{lk} t} \rho_k \langle \Phi_k | \hat{d}^\nu | \Phi_l \rangle \langle \Phi_l | \hat{d}^\mu | \Phi_k \rangle \quad (\text{C.3})$$

Inserting the above result into the expression for the polarizability Eq. (C.1) and carrying out the integration with respect to time, we find that the full expression for the molecular polarizability is

$$\alpha^{\mu\nu}(\omega) = \sum_{l,k} \Lambda_{lk}^{\mu\nu} \frac{\omega_{lk}^2}{\omega_{lk}^2 - \omega^2 - i\omega L}, \quad (\text{C.4})$$

where we taken the eigenfunctions to be real [so that $\langle \Phi_k | \hat{d}^\mu | \Phi_l \rangle = \langle \Phi_l | \hat{d}^\mu | \Phi_k \rangle$] for simplicity and defined

$$\Lambda_{lk}^{\mu\nu} = \rho_k \frac{\langle \Phi_k | \hat{d}^\mu | \Phi_l \rangle \langle \Phi_l | \hat{d}^\nu | \Phi_k \rangle}{2\pi\hbar\omega_{lk}\epsilon_0}. \quad (\text{C.5})$$

Damping was incorporated by the parameter L through the standard replacement, $\omega^2 \rightarrow \omega(\omega + iL)$. A transition can only occur if the frequency of the incoming electromagnetic field matches the energy difference between energy levels. The transition probability is determined by the square of the transition dipole matrix element. From the above relations the static polarizability, $\alpha_0^{\mu\nu}$ (corresponding to $\omega = 0$), is found to be $\alpha_0^{\mu\nu} = \sum_{l,k} \Lambda_{lk}^{\mu\nu}$.

APPENDIX D

Sum rules for molecular extinction cross sections

In this appendix we derive a sum rule for the extinction cross section for a single molecule.

Consider the extinction cross section, Eq. (5.4), for a single molecule. Start from the Kramer-Kronig relation, Eq. (5.5). By taking the limit of large ω , we find

$$-\frac{1}{\pi\omega^2} \int_{-\infty}^{\infty} \omega' Im[\alpha^{\mu\nu}(\omega')] d\omega' = Re[\alpha^{\mu\nu}(\omega)]|_{\omega \text{ large}}. \quad (\text{D.1})$$

We have used the fact that the imaginary part of the polarizability is odd to extend the integration to negative frequencies. By comparing with Eq. (5.4) the total integrated averaged extinction for a single molecule satisfies the sum rule:

$$\int \sigma(\omega)|_{\text{single mol.}} d\omega = -\frac{4\pi^2\omega^2}{3c} Re[\alpha^{\mu\mu}(\omega)]|_{\omega \text{ large}}. \quad (\text{D.2})$$

The above sum rule for the extinction is a general result. Let us now consider the molecular polarizability given by Eq. (C.4). The real part of the polarizability for large frequencies then becomes:

$$Re[\alpha^{\mu\nu}(\omega)]|_{\omega \text{ large}} = - \sum_{l,k} \Lambda_{lk}^{\mu\nu} \frac{\omega_{lk}^2}{\omega^2}. \quad (\text{D.3})$$

The *mean oscillator strength* between levels l and k , f_{lk} , is defined [59]:

$$f_{lk} \equiv \frac{2m\omega_{lk}}{3\hbar} \sum_{\mu} |\langle \Phi_k | x^{\mu} | \Phi_l \rangle|^2, \quad (\text{D.4})$$

where m is the mass the electron. The position operator is $x^{\mu} = \sum_{i=1}^n x_i^{\mu}$, with n being the number of electrons in the molecule and x_i^{μ} is the μ -component of the

position operator for electron i . For molecular Hamiltonians of the form $H_0 = \sum_{i=1}^n \hbar^2 \nabla_i^2 / 2m + V(\vec{x}_1, \dots, \vec{x}_n)$ (*i.e.*, no dependence on nuclear degrees of freedom) it can be shown that the mean oscillator strength satisfies the so called *Thomas-Reiche-Kuhn sum rule* [59, 60]

$$\sum_l f_{lk} = n. \quad (\text{D.5})$$

We proceed by assuming that the dipole operator is independent on nuclear degrees of freedom (Condon approximation) so that it can be written $\hat{d}^\mu = -ex^\mu$. Using the general expression for the integrated extinction, Eq. (D.2), together with Eqs. (D.3), (C.4), (C.5), (D.4) and (D.5) the averaged extinction cross section for a single molecule then becomes

$$\int \sigma(\omega)|_{\text{single mol.}} d\omega = \frac{\pi n e^2}{mc\epsilon_0}, \quad (\text{D.6})$$

i.e., the total integrated extinction is a constant independent on the exact nature of the electronic levels of the molecule. Note that the above integral is independent of \hbar and proportional to the number of electrons in the molecule. Interestingly, the result for the integrated molecular extinction cross section contained in Eq. (D.6) follows also from the “classical” polarizability given by Eq. (5.9).

The sum rules for the more general case, where the polarizability incorporates couplings to nuclear degrees of freedom is discussed by Hirschfelder *et al.* [59].